### Designing quantum phases in monolayer graphene

by

Pascal Nigge

B.Sc. Nanostructure Engineering, Julius Maximilian University of Würzburg,

2011

M.Sc. Nanostructure Engineering, Julius Maximilian University of Würzburg,

2014

### A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

### **Doctor of Philosophy**

in

# THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Physics)

The University of British Columbia (Vancouver)

October 2019

© Pascal Nigge, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the thesis entitled:

#### Designing quantum phases in monolayer graphene

submitted by **Pascal Nigge** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy** in **Physics**.

#### **Examining Committee:**

Andrea Damascelli, University of British Columbia (Physics and Astronomy) Supervisor

Douglas Andrew Bonn, University of British Columbia (Physics and Astronomy) Supervisory Committee Member

Gordon Walter Semenoff, University of British Columbia (Physics and Astronomy) Supervisory Committee Member

John Madden, University of British Columbia (Electrical and Computer Engineering)

University Examiner

Alireza Nojeh, University of British Columbia (Electrical and Computer Engineering)

University Examiner

Alexander Grüneis, University of Cologne (Physics) *External Examiner* 

#### **Additional Supervisory Committee Members:**

Joshua Folk, University of British Columbia (Physics and Astronomy) Supervisory Committee Member

### Abstract

The physics of quantum materials is at the heart of current condensed matter research. The interactions in these materials between electrons themselves, with other excitations, or external fields can lead to a number of macroscopic quantum phases like superconductivity, the quantum Hall effect, or density wave orders. But the experimental study of these materials is often hindered by complicated structural and chemical properties as well as by the involvement of toxic elements.

Graphene, on the other hand, is a purely two-dimensional material consisting of a simple honeycomb lattice of carbon atoms. Since it was discovered experimentally, graphene has become one of the most widely studied materials in a range of research fields and remains one of the most active areas of research today. However, even though graphene has proven to be a promising platform to study a plethora of phenomena, the material itself does not exhibit the effects of correlated electron physics.

In this thesis, we show two examples of how epitaxially grown large-scale graphene can be exploited as a platform to design quantum phases through interaction with a substrate and intercalation of atoms. Graphene under particular strain patterns exhibits pseudomagnetic fields. This means the Dirac electrons in the material behave as if they were under the influence of a magnetic field, even though no external field is applied. We are able to create large homogeneous pseudomagnetic fields using shallow nanoprisms in the substrate, which allows us to study the strain-induced quantum Hall effect in a momentum-resolved fashion using angle-resolved photoemission spectroscopy (ARPES).

In the second part, we show how the intercalation of gadolinium can be used to couple flat bands in graphene to ordering phenomena in gadolinium. Flat bands near the Fermi level are theorised to enhance electronic correlations, and in combination with novel ordering phenomena, play a key role in many quantum material families. Our ARPES and resonant energy-integrated X-ray scattering (REXS) measurements reveal a complex interplay between different quantum phases in the material, including pseudogaps and evidence for a density wave order.

## Lay Summary

Quantum materials are at the forefront of current research in physics and may hold the key for future technologies and applications. Some of the challenges in studying these materials are complicated crystal structures and toxic chemistry. Graphene, on the other hand, is a single atomic layer of carbon atoms arranged in a honeycomb lattice. Its unique mechanical, electronic, and optical properties have made it a highly sought after and well-studied material since its discovery in 2004. In this thesis, we present two examples how graphene can be used as a platform to study quantum material properties via tailored interactions with adatoms or substrates. The results can pave the way towards the on-demand design of quantum materials on a technologically relevant platform.

## Preface

Chapter 3. The results in this chapter are largely based on the publication "Room temperature strain-induced Landau levels in graphene on a wafer-scale platform" by P. Nigge et al. (2019). The work was a collaborative effort between the groups of A. Damascelli, S. A. Burke, D. A. Bonn and M. Franz at UBC and the group of U. Starke at the Max Planck Institute for Solid State research in Stuttgart. P. Nigge and A.C. Qu performed the angle-resolved photoemission spectroscopy (ARPES) experiments and analyzed the ARPES data. P. Nigge, A. C. Qu, E. Mårsell, and G. Tom performed the scanning tunnelling microscopy (STM) experiments and analyzed the STM data. É. Lantagne-Hurtubise and M. Franz provided the theoretical modelling, with input from C. Gutiérrez. S. Link and U. Starke grew the samples and performed the atomic force microscopy (AFM) experiment. P. Nigge, A.C. Qu, M. Zonno, M. Michiardi, M. Schneider, S. Zhdanovich, and G. Levy provided technical support and maintenance for the ARPES setup. A. Damascelli, M. Franz, S. A. Burke, D. A. Bonn, and C. Gutiérrez supervised the project. P. Nigge, A. C. Qu, É. Lantagne-Hurtubise, and C. Gutiérrez wrote the manuscript with input from all authors. A. Damascelli was responsible for the overall project direction, planning, and management.

Chapter 4. The results in this chapter are largely based on the publication "Correlated electron physics in gadolinium intercalated graphene" by P. Nigge et al. (2019). The work was a collaborative effort between the group of A. Damascelli at UBC and the groups of U. Starke and J. Smet at the Max Planck Institute for Solid State research in Stuttgart. P. Nigge and A. C. Qu performed the ARPES measurements with 21.2 eV photon energy. P. Nigge analyzed the ARPES measurements with 21.2 eV photon energy. S. Link performed and analyzed the ARPES measurements

ments at the I4 beamline at the MAX III synchrotron in Lund, Sweden. S. Link and U. Starke grew and characterized the samples. P. Nigge, A. C. Qu, F. Boschini, and R. J. Green performed the resonant energy-integrated X-ray scattering (REXS) measurements at the Canadian Light Source (CLS) in Saskatoon, Canada. P. Nigge and A. C. Qu analyzed the REXS data. R. J. Green performed the REXS theory calculations. P. Nigge, A. C. Qu, F. Boschini, M. Schneider, S. Zhdanovich, and G. Levy provided technical support and maintenance for the ARPES setup at the University of British Columbia. P. Nigge wrote the manuscript with input from all authors. A. Damascelli, U. Starke, and J. Smet supervised the project.

## **Table of Contents**

Ab	strac	tt.	iii			
La	y Sur	nmary	v			
Pro	Preface vi					
Ta	ble of	f Contents	iii			
Lis	List of Figures					
Gl	ossar	y	iii			
Ac	know	vledgments	XV			
1	Intr	oduction	1			
2	Met	hods	15			
	2.1	Angle-resolved photoemission spectroscopy	17			
	2.2	Scanning tunnelling microscopy	24			
	2.3	Resonant energy-integrated X-ray scattering	33			
	2.4	Low energy electron diffraction	38			
	2.5	Raman spectroscopy	41			
3	Stra	in-induced Landau levels in graphene	48			
4	Cor	related electron physics in gadolinium intercalated graphene '	76			

5	Conclusion and outlook	102
Bi	bliography	106
A	Publications	149
B	Conference contributions	152

## **List of Figures**

Figure 1.1	Structure of graphene	2
Figure 1.2	Electronic band structure of graphene	3
Figure 1.3	The quantum Hall effect in graphene	5
Figure 1.4	Epitaxial graphene on SiC	7
Figure 1.5	Photo of a graphene on SiC sample	8
Figure 1.6	Graphene as a versatile platform for quantum physics	9
Figure 1.7	Evidence for superconductivity in lithium decorated graphene	11
Figure 1.8	Unconventional superconductivity in twisted bilayer graphene	12
Figure 1.9	Model for Mott insulators	13
E 0 1		16
Figure 2.1	Comparison of experimental techniques	10
Figure 2.2	Electron mean free path in metals	18
Figure 2.3	Setup of an ARPES experiment	19
Figure 2.4	Energy diagram photoemission	23
Figure 2.5	Fermi edge on gold	24
Figure 2.6	ARPES on monolayer graphene	25
Figure 2.7	Fermi edge on monolayer graphene	25
Figure 2.8	Scanning tunneling microscopy setup and energy schematic .	26
Figure 2.9	Scanning tunneling microscopy modes	27
Figure 2.10	Scanning tunneling microscopy tip conditioning	29
Figure 2.11	Ag(111) surface state with STM	31
Figure 2.12	STM on epitaxially grown monolayer graphene on SiC $\ldots$	32
Figure 2.13	Resonant X-ray scattering process	36
Figure 2.14	Resonant X-ray scattering geometry	37

Figure 2.15	Low energy electron diffraction setup	39
Figure 2.16	Simulation of the low energy electron diffraction (LEED) pat-	
	tern for graphene on SiC	40
Figure 2.17	LEED pattern for monolayer graphene on SiC $\ldots$ .	41
Figure 2.18	Schematic of Raman spectroscopy process	43
Figure 2.19	Setup of a Raman spectroscopy experiment	44
Figure 2.20	Resonant Raman process in graphene	45
Figure 2.21	Raman spectroscopy of monolayer graphene on SiC	46
Figure 3.1	Identification of nanoprisms	49
Figure 3.2	AFM height distribution	51
Figure 3.3	Graphene layer coverage	51
Figure 3.4	Substrate-induced strain	52
Figure 3.5	Comparison of Fourier transforms for different graphene de-	
	formations	54
Figure 3.6	Momentum-resolved visualization of Landau levels	55
Figure 3.7	Fermi velocity and quasiparticle lifetime from ARPES	57
Figure 3.8	Fit of Landau levels for the exponent	58
Figure 3.9	Band structure of multilayer graphene	59
Figure 3.10	Model calculation of strain-induced Landau levels	60
Figure 3.11	Evolution of Landau levels with increasing uniform pseudo-	
	magnetic fields	63
Figure 3.12	Determination of the mass term	64
Figure 3.13	Sketch of pseudo-Landau levels with Semenoff mass	66
Figure 3.14	Calculation of pseudo-Landau levels with Semenoff mass	67
Figure 3.15	Model fit with constant mass term	67
Figure 3.16	Calculation for a uniform mass distribution	68
Figure 3.17	Measurement of the Raman spot size	69
Figure 3.18	Raman maps of the graphene 2D peak	71
Figure 3.19	Raman line spectrum <i>x</i> -direction	72
Figure 3.20	Raman line spectrum y-direction	73
Figure 3.21	Raman line spectra with fit	74
Figure 3.22	Comparison of experimental and model strain	75

Figure 4.1	Introduction to Gd-intercalated graphene	77
Figure 4.2	Angle-resolved photoemission spectroscopy (ARPES) on Gd-	
	intercalated graphene	79
Figure 4.3	Anisotropic mass enhancement	81
Figure 4.4	Ordering phenomena in Gd-intercalated graphene	84
Figure 4.5	Fitting of peaks in the parallel momentum plane	84
Figure 4.6	Theoretical X-ray absorption spectroscopy scattering factors .	86
Figure 4.7	Comparison of theoretical photon energy-dependent scattering	
	behaviours	87
Figure 4.8	Polarization dependence of REXS signal	87
Figure 4.9	Possible model of magnetic order in Gd-intercalated graphene	89
Figure 4.10	Band folding in Gd-intercalated graphene	91
Figure 4.11	Pseudogap anisotropy at room temperature	92
Figure 4.12	Pseudogap at the M point	92
Figure 4.13	Symmetrization of photoemission data	94
Figure 4.14	Fitting of energy distribution curves around ARPES kink feature	95
Figure 4.15	Fitting results of the energy distribution curves around the ARPES	
	kink feature	95
Figure 4.16	Simulation of coupling to a mode	96
Figure 4.17	Simulation of band folding in Gd-intercalated graphene	98
Figure 4.18	Results of simulation of band folding in Gd-intercalated graphene	99
Figure 4.19	Analysis of Lorentzian line fits to momentum distribution curves	100
Figure 4.20	Predicted phase diagram for highly-doped graphene	101
Figure 5.1	Combining twisting and strain in graphene flakes	104

## Glossary

2DEG two dimensional electron gas atomic force microscopy AFM ARPES angle-resolved photoemission spectroscopy Brillouin zone ΒZ CCD charge-coupled device CLS Canadian Light Source energy distribution curve EDC FS Fermi surface **FWHM** full width at half maximum Landau level LL low energy electron diffraction LEED LEEM low energy electron microscopy MDC momentum distribution curve MLG monolayer graphene quantum electrodynamics QED resonant energy-integrated X-ray scattering REXS

- **RIXS** resonant inelastic X-ray scattering
- **STM** scanning tunnelling microscopy
- **UHV** ultra high vacuum
- **VHS** Van Hove singularity
- WKB Wentzel-Kramers-Brillouin
- **XAS** X-ray absorption spectroscopy
- **XMCD** X-ray magnetic circular dichroism
- **XPS** X-ray photoelectron spectroscopy
- **XRD** X-ray diffraction
- **ZLG** zero layer graphene

## Acknowledgments

A PhD thesis in experimental physics is never just the work of a single person. Here I would like to acknowledge all the people who have helped to make this project possible.

First of all my supervisor Andrea Damascelli, who provided me with the opportunity to work on an exciting research project, gave me the academic freedom to pursue ideas and helped me navigate the sometimes rough waters of modern condensed matter research. My thesis committee and examiners for taking time out of their busy schedules to help evaluate the presented work. The research associates Giorgio Levy and Sergey Zhdanovich for always trying to keep the laboratory in smooth and operating conditions. A special thanks to our technicians Michael Schneider and Doug Wong, who always had an open ear and were always willing to lend a helping hand in acquiring, designing, assembling, commissioning, maintaining, and operating new and old equipment in the laboratory. The entire UBC ARPES group for support and input during the experimental efforts, especially Amy Qu for her time spent with the ARPES, LEED, STM, REXS, and Raman setups.

Ulrich Starke and Stefan Link from MPI Stuttgart for growing and characterizing the samples without which none of the presented work would have been possible. Marcel Franz and Étienne Lantagne-Hurtubise for their theory support and enlightening discussions during the pseudomagnetic field project. The groups of Sarah Burke and Doug Bonn for making physical, human, and temporal resources on their STM experiments available for our projects. Erik Mårsell and Miriam De-Jong for the preparation of the dogbone samples used for tip conditioning. Thank you to Brian de Alwis for providing and maintaining the LATEX template. And last but not least to my parents. Without their continued support and patience this thesis would not have been possible.

### **Chapter 1**

## Introduction

Graphene is a purely two-dimensional material. It consists of a single atomic layer of carbon atoms arranged in a honeycomb lattice. Due to graphene's remarkable mechanical, optical, and electronic properties, it is part of a highly active area of research in a number of fields in recent years. As a result, a range of excellent review articles have been published on the subject of graphene [1–5]. Hence, in this section only a brief overview summarizing the historical background and the most important properties, as they are relevant to the research of this thesis, are given.

The existence of free-standing two-dimensional crystals was already discussed over 80 years ago by Landau and Peierls. They argued that such structures could not exist because of divergent thermal fluctuations [6, 7]. Therefore, atomically thin layers were only known as part of heterostructures with lattice matched crystals [8, 9]. Nevertheless, the unusual electronic properties of graphene in the context of other carbon allotropes were noted early on by theorists [10–12]. Later it was realized that graphene could also be used as a platform for studying quantum electrodynamics (QED) [13–15]. This is due to the fact that charge carriers in graphene around the Dirac point behave as massless chiral Dirac fermions. This, in principle, allows one to probe relativistic QED phenomena in a condensed matter material at an effective speed of light of  $v_F \approx 1 \times 10^6$  m/s (300 times smaller than the speed of light in vacuum). Experimentally, the advent of graphene began with the groundbreaking discovery of Geim and Novoselov and the subsequent confir-



**Figure 1.1: Structure of graphene.** (a) The carbon honeycomb lattice of graphene can be described as two triangular lattices A (red) and B (blue). The unit cell vectors are denoted by  $\mathbf{a}_{1-2}$  and the three vectors connecting nearest neighbours by  $\delta_{1-3}$ . (b) Illustration of the overlap between the in-plane  $sp^2$  hybridized orbitals of adjacent carbon atoms. These form the so called  $\sigma$  bonds in graphene. (c) The out-of-plane  $p_z$  orbitals, in contrast, form the so called  $\pi$  bonds, that appear similar to the delocalized electron systems of aromatic molecules for example.

mation of the Dirac nature of the charge carriers in graphene [16–19]. Since then, an ever-growing number of research papers have been published and graphene still holds promise for a range of applications from flexible electronics to energy storage and biomedical applications [20–22].

The structure of graphene is illustrated in Figure 1.1a. The crystal can be described as two triangular lattices which together form the honeycomb structure. The carbon-carbon distance is  $a \approx 1.42$  Å and the lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(3,\sqrt{3})$$
 and  $\mathbf{a}_2 = \frac{a}{2}(3,-\sqrt{3}).$  (1.1)

The three nearest-neighbour vectors in real space are given by

$$\delta_1 = \frac{a}{2}(1,\sqrt{3}), \qquad \delta_2 = \frac{a}{2}(1,-\sqrt{3}) \qquad \text{and} \qquad \delta_3 = -a(1,0).$$
(1.2)

Carbon atoms have the electronic configuration  $[\text{He}]2s^22p^2$ . In graphene, two of the *p* orbitals and the *s* orbital  $sp^2$  hybridize and form three in-plane orbitals with an angle of  $120^\circ$  between them. Each of them overlaps with an in-plane orbital of a neighboring carbon atom. These are the so called  $\sigma$  bonds (see Figure 1.1b). The remaining out-of-plane  $p_z$  orbitals contain one electron per carbon atom and form



**Figure 1.2: Electronic band structure of graphene.** (a) Schematic of the Brillouin zone (BZ) of graphene with high symmetry points and reciprocal lattice vectors  $\mathbf{b}_{1-2}$  labelled. (b) Band structure of graphene as calculated using a tightbinding approach. For free standing graphene the bands are half filled, leading to a Fermi surface (FS) with six points at the corners of the Brillouin zone (BZ). (c) Linear dispersion around the K point forming a Dirac cone. (d) Energy contours of the graphene band dispersion. Starting from the Dirac point, electronic doping leads to a transition from a circular FS to a trigonally warped FS.

the so called  $\pi$  bonds (see Figure 1.1c). Similar to many aromatic molecules, the electrons in the  $\pi$  bonds are highly delocalized (compare for example benzene).

Many of the remarkable properties of graphene originate from the electronic band structure close to the Fermi level. The bands close to the Fermi level are dictated by the out of plane  $\pi$  bonds. The bonding and antibonding bands originating from the  $\sigma$  bonds lay further away from the Fermi energy. Graphene's Brillouin

zone (BZ) in reciprocal space is depicted in Figure 1.2a. Important high symmetry points in the hexagonal BZ around the  $\Gamma$  point are K and K' at the corners and M at the center along the edges. Their locations in momentum space as depicted in Figure 1.2a are as follows:

$$\mathbf{K} = (\frac{2\pi}{3\sqrt{3}a}, \frac{2\pi}{3a}), \qquad \mathbf{K}' = (\frac{4\pi}{3\sqrt{3}a}, 0) \qquad \text{and} \qquad \mathbf{M} = (\frac{\sqrt{3}\pi}{3a}, \frac{\pi}{3a}).$$
 (1.3)

The reciprocal lattice vectors are given by

$$\mathbf{b}_1 = (\frac{2\sqrt{3}\pi}{3a}, \frac{2\pi}{3a})$$
 and  $\mathbf{b}_2 = (0, \frac{4\pi}{3a}).$  (1.4)

The electronic band structure can be approximately calculated using a tight binding approach [10, 23]. Using the lattice constant  $a_0 = 2.46$  Å, the nearest neighbor hopping  $t ~(\approx 2.8 \text{ eV})$  (between different sublattices) and the next nearest neighbor hopping t' (between the same sublattices), the resulting dispersion is

$$E_{\pm} = \pm t \sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k}) \quad \text{with} \\ f(\mathbf{k}) = 2\cos(k_x a_0) + 4\cos(k_x \frac{a_0}{2})\cos(\sqrt{3}k_y \frac{a_0}{2}).$$
(1.5)

Here the "+" sign stands for the upper ( $\pi^*$ ) band and the "-" sign for the lower  $\pi$  band. Note, if t' = 0 is assumed as an approximation, the dispersion is particle-hole symmetric around zero energy. The resulting bands for that case are displayed in Figure 1.2b. The upper and lower bands meet in singular points at the corners of the BZ, forming the iconic linear dispersing Dirac cones (see Figure 1.2c). The Fermi velocity can be obtained by expanding the band structure around the K points, yielding  $v_F = \frac{3ta}{2\hbar} \approx 1 \times 10^6$  m/s [10]. At the M points the dispersions of two neighbouring Dirac cones merge, forming a highly anisotropic saddle point in the band structure. Looking at iso-energy contours as the energy is changed starting from the Fermi level, the circular electron pockets around the K and K' points begin to show trigonal warping along the high symmetry directions. Eventually the pockets merge at the M points and form a single hole pocket centered around the  $\Gamma$  point.

After the discovery of single-layer graphene, the quantum Hall effect played a crucial role in the confirmation of the chiral Dirac nature of the charge carriers in



**Figure 1.3:** The quantum Hall effect in graphene. (a) Quantum Hall effect as it would present itself in the longitudinal conductivity  $\sigma$  as a function of chemical potential for a two dimensional electron gas (2DEG). The Landau levels (LLs) have a linear succession with no peak at zero energy. (b) Quantum Hall effect for Dirac electrons in graphene. The LLs follow a square root sequence with a LL at zero energy. (c) For bilayer graphene the linear series recovers, but the LL at zero energy is still present. All LLs are broadened to reflect disorder and are inverted for hole carriers for clarity.

the material [17, 19]. The quantum Hall effect is a remarkable macroscopic phenomenon [24–26] which was first observed by K. v. Klitzing in 1980 [27]. It laid the ground work for the now very large community of topological order in condensed matter [28–30]. The effect is typically observed in clean two-dimensional materials under large magnetic fields and at cryogenic temperatures. Under the influence of the magnetic field, the charge carriers are forced onto quantized cyclotron orbits called Landau levels (LL). This leads to the famous plateaus in the Hall conductivity as the chemical potential is changed. This quantization  $(\frac{h}{e^2})$  only depends on natural constants and can thus be used as a precise standard reference for the electrical resistance [31, 32]. In normal two-dimensional electron gases (2DEGs) the quantization is linear in the LL index N and no level lies at zero energy (see Figure 1.3a). In contrast to that, LLs in graphene follow a  $\sqrt{N}$  behavior with a prominent signal at zero energy (see Figure 1.3b). This can serve as a hallmark of Dirac electrons in graphene for which the energetic position of the LLs can be described by [33–36]

$$E_N = \pm v_F \sqrt{2e\hbar BN}.$$
(1.6)

Here " $\pm$ " refers to hole- or electron-like charge carriers in the upper or lower cone of the dispersion,  $v_F$  is the Fermi velocity, and *B* is the magnitude of the perpendicular magnetic field. Because of the comparatively large energy spacings between the LLs even in moderate magnetic fields and the long lifetimes of the charge carriers between scattering events, the quantum Hall effect in graphene can even be observed in room temperature environments [37]. It thus marked the first macroscopic quantum phenomenon – outside the well-known areas of magnetism and semiconductor physics – to be present at nearly ambient conditions. For completeness the succession of LLs in bilayer graphene is depicted in Figure 1.3c. The usual linear dependence is recovered, but the state at zero energy still exists.

For any experimental effort, it is crucial to have access to clean and high quality samples. In the case of graphene, there are currently a number of approaches being carried out, all with their own advantages and disadvantages. They can in general be divided into two categories: top-down approaches in which three-dimensional graphite is exfoliated down to the two-dimensional graphene limit, or bottom-up approaches in which graphene is grown on substrates. The original discovery by the Manchester group relied on the top-down technique of mechanical exfoliation (also known as the Scotch tape method) [17, 38–40]. It produces high-quality samples, but only yields small quantities and is not very reproducible. Other top-down methods are based on the exfoliation of graphite in solution, which allows the production of graphene on industrial scales, but yields less high-quality samples [41–45]. On the bottom-up side, graphene can be directly synthesized from organic precursor molecules [46–50] or catalyzed to grow on substrates [51–56]. Producing large and uniform monolayers of graphene remains challenging for both approaches.

Epitaxially grown graphene on SiC is considered a promising route for the production of high-quality graphene on an insulating substrate on a wafer-scale size [57–59]. SiC is a large band gap ( $\approx 3 \text{ eV}$ ) semiconductor and exists in a number of different crystal structures. The graphene samples used for the research presented in this thesis were grown on 6H-SiC, which has a hexagonal lattice structure with a layered stacking order of ABCACB (see Figure 1.4a). The commercial wafers (see Fig. 1.5) are cleaned by hydrogen etching prior to the growth process. Graphene is then grown via the sublimation of silicon on the silicon-terminated surface of



**Figure 1.4: Epitaxial graphene on SiC.** (a) Schematic of the structure of the 6H-SiC substrate with its ABCACB stacking order. The top view (bottom) shows the three different layer-dependent registries for the Si atoms. (b) The first graphitic layer grown on the Si-terminated substrate saturates the Si dangling bonds and is thus not free-standing graphene. It is often called zero-layer graphene (ZLG) (top). A second carbon layer can be grown keeping the ZLG in place as a buffer. The top layer then acts as monolayer graphene (MLG) (middle). Alternatively, the Si bonds can be saturated through the intercalation of hydrogen also leading to a quasi free standing layer of graphene. (bottom). (c) Due to the lattice mismatch between the SiC substrate (yellow) and the graphene (blue) a reconstruction emerges, in which  $13 \times 13$  graphene cells fit  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  cells of the SiC to 0.1%.

the substrate at about 1500°C under an argon atmosphere of about 900 mbar. The first layer is the so called buffer layer (sometimes also called zero-layer graphene – ZLG). The buffer layer structurally already resembles graphene, but does not show a Dirac cone at the corners of the BZ. This is due to the dangling Si bonds at the surface. They bind to  $\frac{1}{3}$  of the carbon atoms in the buffer layer, thereby destroying the  $\pi$  bands of graphene [60]. To establish a quasi free standing monolayer of graphene, two approaches are possible: first, a second carbon layer can be grown leading to an electron-doped monolayer graphene sample which is decoupled from the substrate through the buffer layer. Alternatively, the dangling Si bonds can be saturated via the intercalation of hydrogen between the graphene and the substrate, which leads to a hole-doped monolayer graphene and the SiC substrate, a reconstruction emerges.  $13 \times 13$  graphene cells fit  $(6\sqrt{3} \times 6\sqrt{3})$ R30° cells of the SiC to 0.1%, which is illustrated in Figure 1.4c [59, 60]. One drawback of graphene on



Figure 1.5: Photo of a graphene on SiC sample. A typical graphene on SiC sample with a size of  $10 \text{ mm} \times 20 \text{ mm}$  is shown (red). The wafers (commercially bought from SiCrystal GmbH) are about  $350 \,\mu$ m thick and are doped with nitrogen atoms, but nevertheless become insulating below about 50 K. The samples are mounted using a copper paste (blue), which guarantees good thermal and electrical contact of the graphene. The specifics of the sample holder (yellow) depend on the experiment. Here shown is the sample holder for the X-ray scattering experiments. On both sides the shielding of the cryostat is visible (green), which prevents thermal radiation from heating up the sample.

SiC is the existence of terraces steps on the substrate due to slight misalignment of the wafer cuts from the ideal crystal orientation. This leads to small contributions of bi- and trilayer graphene during the growth process [57]. Epitaxially grown monolayers of graphene have already been used extensively in research, as they are compatible with a range of experimental techniques and offer the flexibility of, for example, adjusting the doping level and studying many-body physics phenomena through the intercalation or addition of suitable atoms [62–66].

Combining graphene's properties with the availability of a plethora of experimental data in a abroad range of research fields as well as high quality samples, graphene is positioned to be a unique candidate as a platform for the on-demand design of quantum phases. The theoretical idea of using graphene to simulate physics from different research fields was pointed out early by G. W. Semenoff in 1984 [13], but experimentally it took until 2004, when research groups around



**Figure 1.6: Graphene as a versatile platform for quantum physics.** Schematic illustrations of different tuning parameters and control knobs which can be applied to graphene to induced quantum phases on demand. (a) Atoms can be added on top of graphene or intercalated in between the graphene and the substrate. (b) Multiple graphene layers can be coupled and twisted with respect to each other. (c) Graphene layers can be strained or compressed. (d) Graphene nanoribbons can be synthesized, further reducing the dimensionality of the material. (e) Spin related properties and magnetism can be induced by adding magnetic moments. (f) Ultrafast light pulses allow the manipulation and creation of novel quantum phases.

K. S. Novoselov and A. K. Geim were able to isolate single layers of graphene and confirm the Dirac nature of their charge carriers [16–18]. Soon it was noted that for the exploitation of graphene's properties in optical or electrical applications like transistors, it would be necessary to open a band gap in the electronic structure. The quest to engineer such a gap became and still is the first showcase of how electronic properties could be designed starting with graphene as the platform. Until today a range of approaches to open a band gap have been proposed and experimentally demonstrated and the search still continues [67–72].

An overview of the tuning parameters and control knobs available for graphene is illustrated in Fig. 1.6. The first method is adding atoms to graphene (see Fig. 1.6a). This can happen as a decoration on top of graphene or as an intercalation between the graphene sheet and the supporting substrate. Depending on atomic species, deposition amounts and flux, substrate, as well as temperature, the arrangement and adsorption sites with respect to graphene can be varied. One particular example was the addition of alkali atoms to graphene. It was theoretically predicted that graphene decorated with a superlattice of lithium atoms can enhance the coupling between electrons and phonons in the system and hence lead to the emergence of superconductivity [73]. Experimentally, such an enhancement of the electron-phonon coupling was indeed observed in angle-resolved photoemission spectroscopy (ARPES) measurements after *in situ* deposition of different alkali atoms [62]. In 2015, it was again an ARPES effort that found evidence for a superconducting gap in the band structure of graphene, following the deposition of lithium atoms at cryogenic temperatures [66]. The main findings are summarized in Fig. 1.7. Upon deposition of the lithium atoms, an electronic doping is observed due to a transfer of electrons from lithium to graphene, shifting the Dirac point down to a binding energy of about 700 meV. Further, as long as the sample is kept at liquid helium temperatures during and after the deposition, the lithium atoms indeed appear to be ordering in the theoretically suggested superstructure. This is apparent in the Fermi surface (see Fig. 1.7b) by a back folding of the Dirac cones across the new Brillouin zone boundaries to the center of the zone. Additionally, the dispersion of the graphene bands shows prominent kink features near the Fermi level (see Fig. 1.7c). These deviations from the expected linear dispersion can be used to extract the electron-phonon coupling parameter  $\lambda$ . It was shown that an enhancement of the coupling between electrons and phonons could indeed be observed and that the primary contribution stems from lower energy vibrations in the material (see Fig. 1.7d). Finally, a temperature-dependent gap was observed after the deposition of lithium, suggesting a superconducting phase with a critical temperature of  $T_c \simeq 5.9 K$  (see Fig. 1.7e).

Another tuning parameter that has recently led to a frenzy of experimental and theoretical efforts is the twisting between two or more graphene layers (see Fig. 1.6b). At certain twist angles (so-called "magic angles") the induced Moiré



Figure 1.7: Evidence for superconductivity in lithium decorated graphene. (a) ARPES cut through the Dirac cone as indicated by the white line in (b). The deposition of lithium induces an electronic doping, shifting the Dirac point to a binding energy of about 700 meV. (b) Fermi surface of lithium-decorated graphene. Due to the superlattice of the lithium atoms on graphene, the size of the Brillouin zone changes (solid white - original and dashed white - new), leading to a folding of bands to the  $\Gamma$  point at the center of the Brillouin zone. (c) A close up ARPES cut of one of the Dirac cone branches reveals kink features - indicative of electronphonon coupling - near the Fermi level. (d) The electron-phonon coupling parameter  $\lambda$  extracted as a function of Li deposition time. The contribution of high-energy phonon modes (white circles) remains almost constant, while the electron-phonon coupling for lower-energy vibrational modes (black circles) increases significantly. (e) ARPES energy distribution curves (EDCs) at the point indicated by the white circle in (b) show a temperature-dependent gap opening between 15 K (red) and 3.5 K (blue). The data was symmetrized with respect to the Fermi energy. This figure is adapted from [66].



Figure 1.8: Unconventional superconductivity in twisted bilayer graphene. (a) Simulated band structure for twisted bilayer graphene at an angle of  $1.05^{\circ}$ . Flat bands emerge around the center of the Brillouin zone. (b) Current-voltage  $(V_{xx} - I)$ curves for a twisted bilayer graphene device at various temperatures with a carrier density of  $n = -1.44 \times 10^{12} cm^{-2}$ . The lowest temperatures show a plateau of vanishing resistivity with a critical current of about 50 nA. (c) Resistance versus temperature curves  $(R_{xx} - T)$  for different magnetic fields  $B_{\perp}$ . The region of zero resistance vanishes with increasing magnetic field. (d) Phase diagram of the resistance  $(R_{xx})$  in a twisted bilayer graphene device as a function of carrier density and temperature. Two superconducting domes are flanking a proposed Mott insulating phase, resembling the phase diagrams for other unconventional superconductors like the cuprates. This figure is adapted from [74].

pattern leads to the appearance of flat bands at the Fermi level (see Fig. 1.8a). Flat bands in general are associated with correlated electron behaviour as the screening of the charge carriers is greatly reduced and interactions between individual electrons become important. In a hand waiving picture, one can think of a situation where the charge carriers' effective mass is going to infinity and hence their ability to screen fluctuations is reduced.

Historically, the effects of electron correlations in solids were first observed in transition metal oxides. Band theory predicts a fully filled oxygen p-band (light grey in Fig, 1.9) and a partially filled transition metal d-band (dark grey and white in Fig, 1.9) in these materials, hence giving them metallic character. In contrast to this expectation many compounds showed insulating behaviour instead, indicating a band gap at the Fermi level [75]. Nevill Mott and Rudolf Peierls proposed a picture, based on the interactions between electrons, explaining these observations. On the one hand, when electrons are treated independently, the kinetic energy of



**Figure 1.9: Model for Mott insulators.** Two contrasting pictures for the density of states (DOS) around the Fermi level ( $E_F$ ) are depicted. (a) In the independent electron picture a band with width W is crossing the Fermi level. The partially filled band leads to metallic behaviour. (b) If correlations between electrons become important, the Coulomb repulsion energy U can open a gap at the Fermi level. The result is insulating behaviour even though band theory would predict a metal.

the charge carriers dominates and the hopping of electrons from atom to atom leads to an energy band of width W. Metallic behaviour is observed (compare Fig. 1.9a). On the other hand, the Coulomb repulsion energy U is included. Uindicates the cost of an electron hopping into an atomic orbital that already has an electron in it. If the Coulomb repulsion is sufficiently large compared to the kinetic energy, hopping to the next site is suppressed and the material becomes an insulator (compare Fig. 1.9b) [76, 77]. This picture later led to the development of the Hubbard model which is still of high interest today as it is thought to describe the essential physics of high-temperature superconductors [78, 79].

The importance of electronic correlations in graphene has been discussed extensively in theory [1, 80, 81] and indeed effects of many body interactions have been found experimentally, especially as the material is doped away from the Dirac point [64, 66, 82]. Experimental efforts in search for correlated electron behaviour in graphene culminated in recent findings showing the emergence of an unconventional superconducting phase in magic angle twisted bilayer graphene devices at temperatures below 1.7 K [74]. Transport measurements show a zero resistance state (see Fig. 1.8b) that is suppressed with the application of magnetic fields (see Fig. 1.8c). Mapping out the phase diagram of the resistance with the carrier density and the temperature as parameters (see Fig. 1.8d), reveals two superconducting domes adjacent to an unexpected insulating state [83]. The phase diagram shows intriguing similarities to the ones typically found in the high-temperature super-conductors such as the cuprates [84].

Another powerful control knob for the platform of graphene is strain or pressure to engineer the electronic band structure of graphene (see Fig. 1.6c). One example is the generation of pseudomagnetic fields under certain strain geometries [85]. The Dirac electrons in graphene behave as if they were in a magnetic field and can quantize into flat Landau levels, even though no external magnetic field has been applied. Pseudomagnetic fields were first observed in so called nanobubbles using scanning probe techniques and, depending on the magnitude of the strain, can reach several hundred tesla in strength [86]. The next parameter is a further reduction of dimensionality in graphene, leading to the formation of nanoribbons (see Fig. 1.6d). These can host interesting edge states depending on the edge geometry of the flake [67, 68, 87, 88]. Further, the prospect of adding spin-related properties to graphene has been studied extensively (see Fig. 1.6e). Magnetism can be introduced to graphene by adding atoms [89], proximity effects [90], or even defects [91]. Additionally, despite carbon being one of the lighter atoms in the periodic table with a small intrinsic spin-orbit coupling, it can be induced by the addition of Pb atoms to the carbon lattice of graphene [92, 93]. Finally, the exploitation of novel ultrafast pump-probe techniques can be a powerful tuning knob (see Fig. 1.6f). Dirac carriers can be studied out of equilibrium in the time domain [94] and experiments inducing ultrafast photocurrents in topologically insulating materials [95] should soon become possible in graphene as well.

This shows that graphene can be a versatile platform with a number of available tuning parameters to study the design of quantum phases. After introducing the important basic concepts of the experimental techniques in the next chapter, two examples of how specific control knobs in graphene can be used to study novel quantum phases will be presented in this thesis.

### Chapter 2

## Methods

In this chapter, the experimental techniques used during the course of the research will be briefly described. They can roughly be divided into three categories depending on whether they primarily provide information in real space, reciprocal space, or the BZ in momentum space (see Fig. 2.1). All of them have their own strengths and weaknesses in general and regarding the specific experiments with graphene on SiC in this thesis.

The experimental technique of STM is based on the precise scanning of an atomically sharp tip across the sample. If the distance between the tip and the sample is small enough ( $\sim$  fewÅ), charge carriers can tunnel from the tip into the material or vice versa depending on the applied voltage. STM thus can provide images with atomic resolution, while at the same time giving spectroscopic access to the local density of states by sweeping the bias voltage. Raman spectroscopy, on the other hand, is based on the inelastic scattering of monochromatic light. Photons from a laser source are focused onto the sample, which can be scanned laterally. The photons can couple to excitations in the material, giving rise to a characteristic shift in the energy of the outgoing photon. The reflected light is then analyzed in a spectrometer.

To study ordering phenomena in a material, scattering techniques are ideally suited. Also here different particles can be used as scattering probes. For LEED monochromatic electrons (in this thesis typically between 10 eV and 100 eV) are focused onto the sample. The diffracted electrons are then detected in reflection



**Figure 2.1: Comparison of experimental techniques.** (a) Scanning tunneling microscopy (STM) can provide spectroscopic information in real space with up to atomic resolution. Raman spectroscopy allows the measurement of excitations in a material, but the lateral resolution is limited to the size of the laser spot on the sample ( $\sim 1 \mu m$ ) (b) Scattering techniques like low-energy electron diffraction (LEED) or resonant energy-integrated X-ray scattering (REXS) provide direct access to ordering phenomena in reciprocal space. (c) Angle-resolved photoemission spectroscopy relies on the emission of electrons from the material. It is conceptualized best using the Brillouin zone (BZ) in momentum space.

on a phosphor screen. In REXS a similar principle is applied, but monochromatic X-ray photons instead of electrons are used. This experiment is carried out at synchrotron facilities which allows tuning of the photon energy (typically between 100 eV and 2000 eV for soft X-ray storage rings). While doing so, resonances for specific absorption edges can be selected. This enables chemical- and orbital-selective measurements with a high signal-to-noise ratio, allowing the detection of short-range ordering phenomena. As a plus, the additional degree of freedom of photon polarization can be used to distinguish between spin and charge excitations.

Finally, ARPES relies on the photoelectric effect. A monochromatic incoming photon emits a photoelectron, which carries information about its binding energy (kinetic energy of photoelectron) and crystal momentum (emission angle of photoelectron) inside the material. Analyzing both, ARPES allows the direct measurement of the spectral function in the BZ for charge carriers below the Fermi level. Over the years, many improvements and extensions to the "standard" ARPES experiments have become available, pushing for better energy and angular resolution, allowing for the detection of the photoelectron's spin, and implementing laser-based pump-probe setups with ultra short light pulses for measurements in the time domain.

### 2.1 Angle-resolved photoemission spectroscopy

ARPES is a powerful technique for the study of the electronic properties of quantum materials. It has broad applications in a range of scientific fields and has significantly contributed to our current understanding of the underlying principles in solid state physics. In this section, a brief overview of the historic and scientific background of the experimental method is given. For a more in-depth overview, several excellent books [96–101] and review articles [102, 103] are available. ARPES is based on the photoelectric effect, which was first explored in experiments by H. Hertz and W. Hallwachs in 1887 [104, 105]. The theoretical groundwork was laid in one of A. Einstein's famous publications in 1905 [106]. It paved the way to the underlying principle of photoemission as we know it today, in which the kinetic energy of the emitted electron  $E_{kin}$  is related to its binding energy in the material  $E_B$ , the energy of the incoming photon hv, and the work function of the material  $\phi$ .

$$E_{kin} = h\nu - \phi - |E_B| \tag{2.1}$$

Experimentally, this means that samples are exposed to monochromatic light and the emitted electrons are analyzed according to their kinetic energy. Photon sources routinely used for photoemission experiments are helium gas discharge lamps (He I: 21.2 eV and He II: 40.8 eV) and lasers in laboratory-based settings, or large-scale synchrotron facilities providing tunable photon energies in the soft X-ray regime. The resulting kinetic energies for the emitted electrons are often in a range with very short mean free paths (see Fig. 2.2). This means ARPES is a highly surface sensitive technique, ideally suited to monolayer samples like graphene. However, this also means that samples have to be clean on an atomic level and kept clean during the experiment. Hence, measurements and sample preparation have to be conducted under ultra high vacuum (UHV) conditions (pressure better than  $10^{-10}$  Torr).

For many quantum phenomena, not only is the energy of electrons near the Fermi level crucial, but also their dependence on momentum. Therefore, in addi-



**Figure 2.2: Electron mean free path in metals.** Electron mean free paths as a function of electron kinetic energy in various materials. Many follow the so called "universal curve" (red line), showing a minimum around 50 eV kinetic energy with a mean free path of only a few Å, corresponding to only a couple of atomic layers in most samples. Adapted from [107].

tion to the kinetic energy of the photoelectron, also the two emission angles (polar angle  $\theta$  and azimuthal angle  $\varphi$ ) have to be measured (see Fig. 2.3a). The most common electron analyzers for ARPES are hemispherical analyzers. Electrons emitted from the sample are focused onto the entrance slit and accelerated or decelerated to a preset pass energy in the lens column (see Fig. 2.3b). In the actual hemisphere, the electrons disperse according to their kinetic energy and one of the emission angles. Modern analyzers have two dimensional detectors usually consisting of a micro channel plate, a phosphor screen, and a charge-coupled device (CCD) camera. They can measure a range of kinetic energies and emission angles simultaneously.



**Figure 2.3: Setup of an ARPES experiment.** (a) Geometry of an ARPES experiment. An incoming photon (red) hits the sample and emits an electron (blue) under the polar angle  $\theta$  and azimuthal angle  $\varphi$ . (b) Schematic of a hemispherical electron analyzer. Photoelectrons emitted from the sample enter the lens column and are focused onto the entrance slit of the hemisphere. The electrons disperse according to their angle theta and kinetic energy  $E_{kin}$ , before hitting the two-dimensional detector. (a) adapted from [102].

ARPES takes advantage of the fact that the in-plane translational symmetry during the photoemission process is preserved. Hence, the parallel components of the momentum *inside* the material  $\mathbf{k}_{\parallel}$  can be directly related to the measured emission angles and therefore parallel components of the momentum of the photoelectron *outside* the material  $\mathbf{K}_{\parallel}$ :

$$k_x = K_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin\theta \cos\varphi \qquad (2.2)$$

$$k_y = K_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \theta \sin \varphi.$$
 (2.3)

Note here that the momentum carried by the photon can be neglected for typical energies used in photoemission experiments. For the perpendicular component of the momentum  $\mathbf{k}_{\perp}$  the situation is more complicated, as it is not conserved during the photoemission process. One can nevertheless determine the out-of-plane component, if the assumption of a nearly free electron as the final state is made.

The assumption is routinely made in photoemission experiments; however, it is expected to work well only in systems with simple free-electron-like Fermi surfaces and high-energy final states for which the influence of the crystal potential is small. Under this assumption  $\mathbf{k}_{\perp}$  can be written as

$$\mathbf{k}_{\perp} = \frac{1}{\hbar} \sqrt{2m(E_{kin}\cos^2\theta + V_0)}.$$
(2.4)

Here  $V_0$  is the so-called inner potential. It can be determined in a number of different ways: (i) setting  $V_0$  equal to the muffin tin potential from band structure calculations, (ii) using a  $V_0$  that optimizes the agreement between the measured and expected band structure, and (iii) experimentally by varying the photon energy and observing the periodicity in  $\mathbf{k}_{\perp}$  [102]. Note that for two-dimensional materials like graphene, the momentum component perpendicular to the sample is not properly defined, avoiding this complication altogether.

For a formal description of the photoemission process, it is instructive to start with Fermi's golden rule, which estimates the transition probability  $w_{fi}$  between an initial state  $\Psi_i$  with energy  $E_i$  and a final state  $\Psi_f$  with energy  $E_f$  for an incoming photon with energy hv:

$$w_{fi} = \frac{2\pi}{\hbar} \langle \Psi_f | H_{int} | \Psi_i \rangle^2 \, \delta(E_f - E_i - h\nu). \tag{2.5}$$

For a definition of the perturbation operator  $H_{int}$ , we can look at the interaction of an electron with mass *m* and the electromagnetic field **A**. Starting from the unperturbed Hamiltonian  $H_0 = \mathbf{p}^2/2m + eV(\mathbf{r})$ , this leads to the transformation  $\mathbf{p} \rightarrow \mathbf{p} - \frac{e}{c}\mathbf{A}$  for the momentum operator:

$$H = \frac{1}{2m} \left[ \mathbf{p} - \frac{e}{c} \mathbf{A} \right]^2 + eV(\mathbf{r})$$
  
=  $\frac{p^2}{2m} + \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{e^2}{2mc^2} A^2 + eV(\mathbf{r})$  (2.6)  
=  $H_0 + H_{int}$ .

The quadratic term in  $\mathbf{A}$  is usually neglected, as it only becomes relevant for extremely high photon intensities. Furthermore, if one assumes the electromagnetic field is constant over atomic distances, one can simplify the commutation relation
for **A** and **p**:

$$\left[\mathbf{p},\mathbf{A}\right] = -i\hbar\nabla\cdot\mathbf{A} = 0. \tag{2.7}$$

Note that the term  $\nabla \cdot \mathbf{A}$  can become important when effects like surface photoemission are taken into account [108–112]. The resulting  $H_{int}$  is then

$$H_{int} = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p}. \tag{2.8}$$

An additional simplification in the description of the photoemission process often used is the so-called sudden approximation. It states that the emitted photoelectron leaves the sample instantaneously and does not interact with the remaining (N-1)electron system left behind. This guarantees that the final state can be written as the product of the emitted electron and the (N-1) wave function. For low kinetic energy electrons, the time to leave the sample might become comparable to the response time of the system and the approximation breaks down. One can distinguish the two extreme cases. In the adiabatic regime the (N-1) system remains in its ground state and in photoemission a single symmetric peak is measured. On the other hand in the sudden regime, the (N-1) system is in an excited state and in photoemission additional peaks or tails are measured due to the overlap with several many-body states. [113–115]

When discussing photoemission experiments on correlated electron systems, the Green's function formalism can be a useful approach [116–121]. Here, the many body interactions can be expressed in terms of the complex self-energy  $\Sigma(\mathbf{k}, \boldsymbol{\omega}) = \Sigma'(\mathbf{k}, \boldsymbol{\omega}) + i\Sigma''(\mathbf{k}, \boldsymbol{\omega})$  of an electron with energy  $\boldsymbol{\omega}$  and momentum  $\mathbf{k}$ . The real and imaginary parts of the self-energy renormalize the energy and lifetime of the bare dispersion  $\varepsilon_{\mathbf{k}}$  of the electron. The Green's function as well as spectral function can both be expressed in terms of this self-energy:

$$G(\mathbf{k}, \boldsymbol{\omega}) = \frac{1}{\boldsymbol{\omega} - \varepsilon_{\mathbf{k}} - \Sigma(\mathbf{k}, \boldsymbol{\omega})}$$
(2.9)

and

$$A(\mathbf{k},\boldsymbol{\omega}) = -\frac{1}{\pi} \frac{\Sigma''(\mathbf{k},\boldsymbol{\omega})}{\left[\boldsymbol{\omega} - \boldsymbol{\varepsilon}_{\mathbf{k}} - \boldsymbol{\Sigma}'(\mathbf{k},\boldsymbol{\omega})\right]^2 + \left[\boldsymbol{\Sigma}''(\mathbf{k},\boldsymbol{\omega})\right]^2}.$$
 (2.10)

This implies that the spectral function as measured with ARPES can be directly related to the imaginary part of the Green's function  $(A(\mathbf{k}, \boldsymbol{\omega}) = -(\frac{1}{\pi})Im(G(\mathbf{k}, \boldsymbol{\omega})))$ . However, in reality the measured intensity depends on a number of factors and can be written as follows:

$$I(\mathbf{k}, \boldsymbol{\omega}) = I_0(\mathbf{k}, \boldsymbol{\nu}, \mathbf{A}) f(\boldsymbol{\omega}) A(\mathbf{k}, \boldsymbol{\omega}).$$
(2.11)

Here  $I_0(\mathbf{k}, \mathbf{v}, \mathbf{A})$  is proportional to the square of the one-electron matrix element and therefore depends on the momentum of the electron and the energy and polarization of the incoming photons [102]. Because ARPES removes electrons from the system, only the occupied density of states can be probed and we have to include the Fermi function  $f(\omega) = (exp(\omega/k_BT) + 1)^{-1}$ . In addition, the effects of a background signal and resolution broadening in momentum as well as in energy also have to be taken into account.

A schematic energy diagram of the photoemission process is illustrated in Fig. 2.4. The sample is electrically connected to the analyzer as well as to ground, so that emitted electrons can be replenished to avoid charge build-up and the Fermi levels in the sample and the analyzer are aligned. An incoming photon with the energy hv emits an electron with kinetic energy  $E'_{kin}$  depending on the electron's binding energy  $E_{bin}$  and the work function of the sample  $\phi_{sam}$ . The kinetic energy  $E_{kin}$  that is actually measured at the analyzer is different, as the work function of the analyzer  $\phi_{ana.}$  differs from that of the sample. As the work function of the analyzer is typically not known *a priori* or may change with time, reference measurements to determine the exact location of the Fermi level are needed. An example is shown in Fig. 2.5, where a polycrystalline gold sample was used, which can be prepared in situ in the UHV chamber. It shows the expected Fermi cut off which smears out with increasing temperature. The data can be fitted to a Fermi function after including an additional convolution with a Gaussian for the finite energy resolution. This way, the energetic position of the Fermi level can be established (around 16.85 eV kinetic energy in Fig. 2.5).

Now turning to a typical ARPES measurement on monolayer graphene on SiC, a Fermi surface and two cuts are depicted in Fig. 2.6. The samples were glued to the sample holder using a copper paste, guaranteeing good electrical and thermal



**Figure 2.4: Schematic energy diagram for photoemission.** The sample is electrically connected to the analyzer, so that the Fermi levels in the sample and the analyzer are aligned. An incoming photon with energy hv emits an electron with kinetic energy  $E'_{kin}$  depending on the electron's binding energy  $E_{bin}$  and the work function of the sample  $\phi_{sam}$ . The kinetic energy  $E_{kin}$  that is actually measured at the analyzer is different, as the work function of the analyzer  $\phi_{ana.}$  differs from that of the sample. Adapted from [122].

contact, and cleaned *in situ* in an oven at about 500°C over night. Due to charge transfer from the substrate to the graphene, monolayer samples on SiC show a significant electron doping. This leads to a shift of the Dirac point to about 450 meV binding energy. The Fermi surface already shows signs of trigonal warping, expected for these doping levels. One can look at the Fermi cut off by integrating in momentum over one of the linear branches of the Dirac cone, perpendicular to the Fermi surface (see Fig. 2.7). This way the resolution for different pass energy settings on the sample can be compared as long as the sample temperature is known. Note that these measurements can also be done on the gold calibration sample or any other metallic sample without strong spectroscopic features near the Fermi level. As expected, the energy resolution worsens with increasing pass energy, but the transmission of the analyzer is higher with increasing pass energy. Hence, a



**Figure 2.5: Fermi edge on gold.** Measured Fermi edge on a polycrystalline gold sample at two different temperatures. Data taken at 3.9 K is shown in blue, and 10.3 K in red. The data is fitted to a Fermi function using those temperatures and an additional convoluted Gaussian to account for the finite resolution of the experimental setup.

trade off between energy resolution and measurement time has to be made, keeping in mind factors like sample aging and availability of liquid helium.

### 2.2 Scanning tunnelling microscopy

Since its first implementation [123], STM has developed into a powerful technique that gives access to the local topography on an atomic scale as well as spectroscopy of the occupied and unoccupied density of states near the Fermi level. It relies on quantum mechanical tunnelling effects between an atomically sharp tip and the sample. A schematic setup for a STM experiment can be seen in Fig. 2.8a. Piezo scanners allow the precise control of the tip in the lateral directions as well as in the



**Figure 2.6: Angle-resolved photoemission on monolayer graphene.** (a) Fermi surface measured at one of the corners of the Brillouin zone (BZ). The Fermi surface shows signs of trigonal warping. (b) Cut along the  $k_x$  direction as indicated in (a). The Dirac point is at about 450 meV binding energy. (c) Similar cut as in (b), but along the  $k_y$  direction. The sample was held at a temperature of 7 K.



Figure 2.7: Fermi edge of monolayer graphene. The ARPES data for one linear branch of the Dirac cone was integrated in momentum perpendicular to the Fermi surface. Data was taken at 7 K. (a) Fermi edge measured with an analyzer pass energy (PE) of 1 eV. The edge was fitted to a Fermi function convolved with a Gaussian. The resulting energy resolution is  $\Delta = (0.9 \pm 0.2) \text{ meV}$ . (b) Fermi edge measured with an analyzer pass energy (PE) of 2 eV. The edge was fitted to a Fermi function convolved with a Gaussian. The resulting energy resolution is  $\Delta = (2.1 \pm 0.3) \text{ meV}$ . As expected, the energy resolution worsens with increasing pass energy.



**Figure 2.8: Scanning tunneling microscopy setup and energy schematic.** (a) A piezo scanner setup allows the precise positioning of the tip with respect to the sample. A bias voltage  $V_{bias}$  is applied between the sample and the tip. The resulting tunneling current is amplified and measured in a feedback loop. (b) The sample with work function  $\phi_{sample}$  and the tip with work function  $\phi_{tip}$  are at a distance d from each other. Due to the applied voltage, electrons can tunnel between tip and sample. Note that for useful spectroscopic information of the sample, the density of states of the tip has to be flat in the bias voltage range in question.

direction perpendicular to the sample. An applied bias voltage allows electrons to either tunnel into or out of the sample. The resulting current (typically nA or pA) is amplified and measured in a feedback loop. To obtain spectroscopic information about the density of states, the bias voltage can be varied. This technique always measures the convolution of the density of states of the sample with the density of states with tip. Therefore a tip material with a flat density of states around the Fermi level is mandated (see Fig. 2.8b). For the experiments shown in this thesis, a platinum-iridium tip cut from a wire was used. Note that in general STM measures the momentum-integrated density of states of the sample, but for certain materials the band dispersion can be indirectly accessed by analyzing quasi-particle interference patterns [124]. As a technique directly measuring the sample's surface, STM is a UHV experiment. Due to the strong dependence of the tunnelling signal on the tip's lateral position and distance from the sample, STM is highly susceptible to mechanical noise and thus has to be properly isolated from any sources of vibration.

Topographic images of the sample are usually taken in one of two modes of operation (see Fig. 2.9). In constant current mode, the height of the tip with respect



**Figure 2.9:** Scanning tunneling microscopy modes. (a) In constant current mode, the height of the tip is adjusted during the scan to keep the tunneling current constant. (b) In constant height mode, the vertical position of the tip is fixed and the tunneling current varies during the measurement.

to the sample is adjusted as it is scanned across the sample to keep the tunneling current constant. In constant height mode, the vertical position of the tip is fixed during the scan and the tunneling current varies. The constant height mode should be used carefully and only on flat samples, as the danger of crashing the tip into the sample is given.

For a brief introduction into the theory of STM, it is suitable to start with a simple picture of electrons tunneling through a potential barrier [125–127]. This causes a current that depends on the distance between the tip and the sample as well as the applied bias voltage. For a more in-depth treatment, several more involved theories of STM have been developed in the literature [128–131]. In the case of a negative bias voltage being applied to the sample with respect to the tip, electrons tend to flow from the sample to the tip. Using time dependent perturbation theory, the elastic current can be estimated by:

$$I_{sample \to tip} = -2e\frac{2\pi}{\hbar}|M|^2(\rho_s(\varepsilon) \cdot f(\varepsilon))(\rho_t(\varepsilon + eV) \cdot [1 - f(\varepsilon + eV)]). \quad (2.12)$$

Here  $\varepsilon$  is the energy with respect to the Fermi level of the sample, *e* is the electron charge, the factor of 2 arises from the spin degeneracy,  $|M|^2$  is the matrix element,  $\rho_s$  and  $\rho_t$  are the density of states of the sample and tip, respectively, and  $f(\varepsilon)$  is the Fermi function. Although most of the electrons will tunnel from the sample to

the tip in case of a negative bias voltage, some electrons will nevertheless tunnel from the tip to the sample. This contribution can be summarized as follows:

$$I_{tip\to sample} = -2e\frac{2\pi}{\hbar}|M|^2(\rho_t(\varepsilon + eV) \cdot f(\varepsilon + eV))(\rho_s(\varepsilon) \cdot [1 - f(\varepsilon)]).$$
(2.13)

The net tunneling current is then the difference between those two contributions after integrating over all energies:

$$I = -\frac{4\pi e}{\hbar} \int |M|^2 \rho_s(\varepsilon) \rho_t(\varepsilon + eV) \left\{ f(\varepsilon) [1 - f(\varepsilon + eV)] - [1 - f(\varepsilon)] f(\varepsilon + eV) \right\} d\varepsilon$$
(2.14)

This lengthy expression can simplified when keeping in mind that tunneling can only take place from occupied to unoccupied states. Whether a state is occupied or not is determined by the Fermi function, which at typical measurement temperatures of about 4.2 K ( $k_BT = 0.36 \text{ meV}$ ) can be well approximated by a step function (1 for energies below the Fermi level and 0 for energies above the Fermi level). Hence, we can approximate Eqn. 2.14 with

$$I \approx -\frac{4\pi e}{\hbar} \int_{-eV}^{0} |M|^2 \rho_s(\varepsilon) \rho_t(\varepsilon + eV) d\varepsilon.$$
(2.15)

As a second simplification, we can make use of the fact that we required the tip material to have a flat density of states around the Fermi level. Hence, the term  $\rho_t(\varepsilon + eV)$  can be assumed constant over the integral range:

$$I \approx -\frac{4\pi e}{\hbar} \rho_t(0) \int_{-eV}^0 |M|^2 \rho_s(\varepsilon) d\varepsilon.$$
(2.16)

Next, we make the assumption that the matrix element can also be treated as a constant. This is only true for limited energy ranges, when the exponentially decaying wave functions of the sample and the tip are independent and do not influence each other significantly [124, 125, 132]:

$$I \approx -\frac{4\pi e}{\hbar} \rho_t(0) |M|^2 \int_{-eV}^0 \rho_s(\varepsilon) d\varepsilon.$$
(2.17)

For an estimate of the matrix element, we can turn to our simple one-dimensional model of a wave function tunneling through a square potential barrier. In this case



**Figure 2.10: STM tip conditioning.** Topography images of terpyridine-phenylterpyridine (TPT) molecules on a Ag(111) surface. (a) Image taken with a "bad" tip with  $V_{bias} = +500 \text{ mV}$  and  $I_{tun.} = 10 \text{ pA}$ . The molecules look slightly blurry and replicas in the vertical direction are visible. This is indicative of a not perfectly sharp tip and more than one active tunneling junction. The Ag(111) surface shows the interference pattern of electron waves in the substrate scattering off the molecules. (b) Image taken with a "good" tip with  $V_{bias} = +7 \text{ mV}$  and  $I_{tun.} = 330 \text{ pA}$ . Molecules appear sharper and no replicas are visible. Note the different wavelength of the interference pattern due to the changed bias voltage. Both images were taken at a temperature of 4.2 K.

the Wentzel-Kramers-Brillouin (WKB) approximation yields  $|M|^2 = \exp(-2\gamma)$  for the tunneling probability with

$$\gamma = \frac{d}{\hbar} \sqrt{2m\beta}. \tag{2.18}$$

Here *d* is the distance between sample and tip (width of the barrier) and  $\beta$  depends on the work functions of the tip and the sample (height of the barrier). This exponential relationship between the tunnelling current and the distance ensures the extremely high spatial resolution of STM experiments. It also means that on flat samples the macroscopic shape of the tip is rather unimportant, as tunneling primarily happens from the outermost atom. The actual distance from the tip to the sample is not known and can change either due to the topography or due to a change in the density of states (defects, impurities, etc.). Calculations suggest a distance of several ångströms to be in a regime where vacuum tunnelling dominates over point contact phenomena [133]. From Eqn. 2.17 we see that STM measures the integrated density of states of the sample for the range of accessible bias voltages. For negative bias voltages, electrons tunnel from the sample to the tip and the occupied density of states of the sample are measured. For positive bias voltages, electrons tunnel from the tip to the sample and the unoccupied density of states of the sample are probed. To access the density of states, we have to look at the normalized derivative of the bias voltage dependent tunnelling current [134].

$$DOS = \frac{dI/dV}{\sqrt{C^2 + (I/V)^2}}$$
(2.19)

A small constant *C* is often added to avoid the singularity around 0 V. It should be noted that, just like in ARPES, STM does not measure the ground state, but an excited state as electrons are either added or removed from the material. Hence, effects like charging, Coulomb interactions, or screening can play an important role [135–137].

As we have learned, a well-conditioned tip is essential for STM measurements. This includes the structure (ideally sharp with a single atom at the tip) and the electronic properties (flat density of states around the Fermi energy). To accomplish this, a calibration sample with known structures and electronic properties is needed. In our case we use a Ag(111) surface which has been cleaned by cycles of ion sputtering and annealing. Next, some terpyridine-phenyl-terpyridine (TPT) molecules were deposited on it. Scanning over a region with molecules should yield sharp structures with no additional ghost replicas in any direction (compare Fig. 2.10). Replicas are an indication that the tip has multiple active tunnelling atoms that scan an area one after another. There are several ways to condition the tip in case improvements to the tip structure are deemed necessary: (i) for large changes, the tip can be rammed into the surface (typically several nanometers deep) and dragged around, (ii) for smaller changes, the tip can be poked into the surface (typically less than one nanometer deep) and the resulting protrusion can be scanned to get an idea of the tip geometry, and (iii) voltage pulses can be applied to the tip to remove material or adsorbates. In reality, the preparation of a "good" tip often requires a combination of all methods as well as an experienced eye, patience, and a bit of luck.



**Figure 2.11:** Ag(111) surface state with STM. (a) I(V) curve on a Ag(111) surface with a "bad" tip. In addition to the kink at -60 meV corresponding to the surface state, several additional features due to tip states are visible. (b) Normalized dI/dV curve of (a). The density of states is not flat, indicating a "bad" tip. (c) I(V) curve on a Ag(111) surface with a "good" tip. The surface state at -60 meV is the only clear feature. (d) Normalized dI/dV curve of (c). Apart from the expected step in the density of states due to the surface state, the tip does not induce any pronounced additional features.



**Figure 2.12:** STM on epitaxially grown monolayer graphene on SiC. (a) Overview topography image taken at  $V_{bias} = 30 \text{ mV}$  and  $I_{tun.} = 2 \text{ pA}$ . In addition to the honeycomb lattice of graphene, the  $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$  superlattice due to the lattice mismatch of graphene and the SiC substrate is visible. (b) Close up topography image taken at  $V_{bias} = 30 \text{ mV}$  and  $I_{tun.} = 2 \text{ pA}$ . The individual rings of the carbon lattice are clearly visible. The variation in tunneling current is probably induced by electronic or structural inhomogeneities in the underlying substrate or slight buckling of the graphene surface [140].

Besides the geometry of the tip, also its electronic properties have to be checked. The Ag(111) surface shows a well-known and pronounced surface state with a parabolic dispersion opening at -60 meV binding energy [138, 139]. This twodimensional electron gas at the surface leads to a step in the density of states. Other than that, the density of states of silver is expected to be flat around the Fermi energy. In the I(V) curve, the surface state should show up as a kink with a linear dependence on either side, which translates to a step function in the density of states after differentiation (compare Fig. 2.11). Any additional features indicate that the density of states of the tip is not flat. In that case, the same tip conditioning procedures as for the tip geometry can be applied. In general, a structurally "good" tip does not imply an electronically "good" tip or vice versa. Hence, after any tip alterations, both features should be checked.

After the tip is presumed suitable for experiments, the calibration sample can be switched with the actual monolayer graphene on SiC sample. A topographic overview image and a close-up view are shown in Fig. 2.12. They show the expected honeycomb lattice of graphene as well as the well-known  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  su-

per structure. The latter arises due to the lattice mismatch of the graphene and the underlying SiC substrate. Note here that tunneling spectroscopy with STM on graphene has the additional complication that direct tunneling between the tip and the graphene is not possible. This is due to the fact that the electrons in graphene reside near the K points at the corners of the BZ in momentum space and can not elastically tunnel. Inelastic tunneling is possible when taking for example phonons or substrate interactions into account [141–143].

#### 2.3 Resonant energy-integrated X-ray scattering

REXS is a powerful technique based on the scattering of photons (photon-in and photon-out). It is sensitive to the charge, orbital, spin, and lattice degrees of freedom, which has made REXS an increasingly popular choice for the study of intertwined ordering phenomena in a range of quantum materials [144]. The resonant nature of the technique allows the detection of weak and short-range phases. Among the great successes of REXS were the detection and characterization of the broken-symmetry charge density order in the cuprate family of high-temperature superconductors [145–153] and the orbital ordering in the manganites [154–156]. In the following section, a brief introduction into the theoretical background of REXS is given. For a more comprehensive review, several publications are available [157–161].

The interaction of an electromagnetic field with a solid can be described by an effective nonrelativistic coupling Hamiltonian  $H_{tot}$ :

$$H_{tot} = \sum_{j} \left\{ \frac{1}{2m} [\mathbf{p}_{j} - \frac{e}{c} \mathbf{A}(\mathbf{r}_{j}, t)]^{2} + V(\mathbf{r}_{j}, t) \right\} + \sum_{j \neq k} \frac{e^{2}}{|\mathbf{r}_{j} - \mathbf{r}_{k}|^{2}} + H_{EM}$$
$$= \underbrace{H_{el} + H_{EM}}_{H_{0}} + \underbrace{\frac{e}{mc} \sum_{j} \mathbf{A}(\mathbf{r}_{j}, t) \cdot \mathbf{p}_{j}}_{H_{int}^{lin}} + \underbrace{\frac{e^{2}}{2mc^{2}} \sum_{j} \mathbf{A}^{2}(\mathbf{r}_{j}, t)}_{H_{int}^{quad}}.$$
(2.20)

Here *m* is the fundamental mass of an electron, *e* is the charge of an electron,  $\mathbf{p}_j$  is the momentum of the *j*th electron,  $\mathbf{r}_j$  is the position of the *j*-th electron,  $\mathbf{A}(\mathbf{r}_j,t)$  represents the vector potential,  $V(\mathbf{r},t)$  is the lattice potential, and the term  $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|^2}$  is the Coulomb interaction term. Thus the noninteracting Hamiltonian  $H_0$  can be

split into an electronic part  $H_{el}$  and a part for the electromagnetic field  $H_{EM} = \sum_{\mathbf{q},v} \hbar \omega [a_v^{\dagger}(\mathbf{q}) a_v(\mathbf{q}) + 1/2]$  describing photons with wave vector  $\mathbf{q}$ , polarization v, and energy  $\hbar \omega$  being either created  $(a_v^{\dagger})$  or annihilated  $(a_v)$ . The interaction part of the Hamiltonian can be split into a part linear in the vector potential  $H_{int}^{lin}$  and a part quadratic in the vector potential  $H_{int}^{quad}$ . In general, we are interested in calculating the probability for a transition from an initial state  $|\Psi\rangle_i = |\Psi_{GS}\rangle_{el} \times |\phi_i\rangle_{EM}$  to a final state  $|\Psi\rangle_f = |\Psi_{GS}\rangle_{el} \times |\phi_f\rangle_{EM}$  with the photon states  $|\phi_i\rangle_{EM}$  and  $|\phi_f\rangle_{EM}$  and the electronic part  $|\Psi_{GS}\rangle_{el}$ , which we assume to be in the ground state. To calculate this transition probability  $\omega_{i\to f}$ , we can turn to the generalized Fermi's golden rule [162]:

$$\omega_{i \to f} = 2\pi |\langle \Psi_i | T | \Psi_f \rangle|^2 \delta(E_f - E_i).$$
(2.21)

Here the delta function guarantees the conservation of energy and the transfer matrix is defined as follows:

$$T = H_{int} + H_{int} \frac{1}{E_i - H_0 + i\eta} H_{int} + H_{int} \frac{1}{E_i - H_0 + i\eta} H_{int} \frac{1}{E_i - H_0 + i\eta} H_{int} + \dots$$
(2.22)

Before proceeding, we should note that for photon scattering techniques like REXS, we are looking for operator combinations in the interaction which annihilate a photon with wave vector  $\mathbf{q}$  and create a photon with wave vector  $\mathbf{q'}$   $(a(\mathbf{q})a^{\dagger}(\mathbf{q'}))$ . Hence, interaction terms in the transfer matrix which are quadratic in the vector potential are required, as  $\mathbf{A}(\mathbf{r},t) \propto \sum_{\mathbf{q},v} \boldsymbol{\varepsilon}_v \cdot [exp(i\mathbf{q} \cdot \mathbf{r} - i\omega t)a_v^{\dagger}(\mathbf{q}) + h.c.]$  ( $\boldsymbol{\varepsilon}_v$  is the polarization vector of polarization state v). If we now look at Eqn. 2.20 and Eqn. 2.22, we see that we get two contributions. The first one combines the quadratic interaction operator  $H_{int}^{quad}$  with the first term in Eqn. 2.22 and the second one combines the linear interaction operator  $H_{int}^{lin}$  with the second term in Eqn. 2.22.

$$\boldsymbol{\omega}_{i \to f}^{(1)} = 2\pi \left| \frac{e^2}{2mc^2} \left\langle \Psi_i \right| \sum_j \mathbf{A}^2(\mathbf{r}_j, t) \left| \Psi_f \right\rangle \right|^2$$
(2.23)

$$\omega_{i\to f}^{(2)} = 2\pi \left| \left(\frac{e}{mc}\right)^2 \sum_{M} \frac{\langle \Psi_i | \sum_j \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{p}_j | \Psi_M \rangle \langle \Psi_M | \sum_k \mathbf{A}(\mathbf{r}_k, t) \cdot \mathbf{p}_k | \Psi_f \rangle}{E_i - E_M + i\Gamma_M} \right|^2 (2.24)$$

Here the delta functions from Eqn. 2.21 are dropped for brevity and  $|\Psi_M\rangle$  describes a generic excited state of the solid interacting with the electromagnetic field with

energy  $E_M$  and lifetime  $\hbar/\Gamma_M$ . If we expand the square of the vector potential under the assumption of an elastic scattering process  $(\omega_{in} = \omega_{out}) \mathbf{A}^2(\mathbf{r}, t) \propto (\boldsymbol{\varepsilon}_{v_{in}}, \boldsymbol{\varepsilon}_{v_{out}}) \times exp(i(\mathbf{q}_{out} - \mathbf{q}_{in}) \cdot \mathbf{r}) \cdot a_{v_{out}}^{\dagger}(\mathbf{q}_{out}) a_{v_{in}}(\mathbf{q}_{in})$ , use the definitions of the initial state  $|\Psi_i\rangle$ and final state  $|\Psi_f\rangle$  from above, use the fact that  $E_i = E_{GS} + [n_{\mathbf{q}_{in}}\hbar\omega_{\mathbf{q}_{in}} + 1/2]$  and  $E_M = E_m + [(n_{\mathbf{q}_{in}} - 1)\hbar\omega_{\mathbf{q}_{in}} + 1/2]$ , and consider that  $a_{v_{out}}^{\dagger}(\mathbf{q}_{out})a_{v_{in}}(\mathbf{q}_{in}) |\phi_i\rangle_{EM} \propto |\phi_f\rangle_{EM}$ , we can rewrite Eqn. 2.23 and Eqn. 2.24 [144].

$$\boldsymbol{\omega}_{i \to f}^{(1)} = |\langle \boldsymbol{\psi}_{GS}| \sum_{j} exp(-i\mathbf{Q} \cdot \mathbf{r}_{j}) |\boldsymbol{\psi}_{GS}\rangle|^{2} \propto |\langle \boldsymbol{\psi}_{GS}| \,\boldsymbol{\rho}(\mathbf{Q}) |\boldsymbol{\psi}_{GS}\rangle|^{2}$$
(2.25)

$$\boldsymbol{\omega}_{i \to f}^{(2)} = \Big| \sum_{m} \sum_{j,k} \frac{\langle \boldsymbol{\psi}_{GS} | \boldsymbol{\varepsilon}_{\boldsymbol{v}_{out}} \mathbf{p}_{j} exp(i\mathbf{q}_{out} \cdot \mathbf{r}_{j}) | \boldsymbol{\psi}_{m} \rangle \langle \boldsymbol{\psi}_{m} | \boldsymbol{\varepsilon}_{\boldsymbol{v}_{in}} \mathbf{p}_{k} exp(-i\mathbf{q}_{in} \cdot \mathbf{r}_{k}) | \boldsymbol{\psi}_{GS} \rangle}{E_{GS} - E_{m} + \hbar \boldsymbol{\omega} + i\Gamma_{m}} \Big|^{2}$$
(2.26)

Here  $\rho(\mathbf{Q})$  is the Fourier transform of the electron density operator  $\rho(\mathbf{r}) = \sum_{i} \delta(\mathbf{r} - \mathbf{r})$  $\mathbf{r}_i$ ) and  $\mathbf{Q} = \mathbf{q}_{in} - \mathbf{q}_{out}$  is the momentum transfer between the scattered photon and the sample. It should be emphasized that we have gone from a description of the intermediate state including both the electronic and photonic part of the wave function  $|\Psi_M\rangle$  to a description of the intermediate state only involving the electronic part of the wave function  $|\Psi_m\rangle$  here.  $|\Psi_m\rangle$  is in general still an excited many-body state with a core hole. The first process in Eqn. 2.25 does not involve an intermediate state and is directly proportional to the square of the electronic density in the ground state. This leads to the conventional nonresonant X-ray diffraction (XRD) signal. Because it relies on the total number of electrons, it is typically more sensitive to atoms with higher atomic number and core electrons as they usually outnumber the valence electrons significantly. The second process in Eqn. 2.26 is associated with REXS. It can be understood more intuitively as a two-step process: First, an incoming photon promotes an electron into an excited state leaving a core hole behind. Second, a scattered photon is re-emitted and the core hole is filled again, leaving the sample in its ground state. The two processes are schematically illustrated in Fig. 2.13a. The advantage of REXS is now the resonant enhancement of the signal close to an absorption edge (see Fig. 2.13b). While the XRD signal is mostly independent of the photon energy, the REXS is peaked around the resonance and decays to zero away from it. By picking a specific absorption edge via tuning the photon energy, one can select certain chemical elements and orbitals. Further,



Figure 2.13: Schematic of resonant X-ray scattering process. (a) Comparison between nonresonant (left) and resonant (right) scattering process. The resonant scattering process can be described by an intermediate state  $|\Psi_m\rangle$  with a core hole connecting the ground states  $|\Psi_{GS}\rangle$ . (b) Effect of resonance enhancement close to an absorption edge. The nonresonant measurement (dashed blue) is mostly independent of the photon energy hv, while the resonant measurement (red) shows a peak of width  $\Gamma_{li}$  which decays to zero away from the resonance. Figure adapted from [144].

the signal is sensitive to spin excitations through the spin-orbit interaction of the core hole in the intermediate state. Experimentally, signal enhancements of more  $> 10^3$  have been found [163, 164], allowing the detection of weak and short-range ordering phenomena above the noise level, even if they are not accompanied by a lattice distortion.

If we now look at an actual realization of an REXS experiment, we first note that the technique requires a photon source with tunable photon energy in the X-ray regime. This means the use of synchrotron facilities is necessary. A number of beamlines dedicated to resonant X-ray scattering experiments are already available or under construction worldwide (ALS, APS, BESSY, CLS, DESY, Diamond, ESRF, NSLS-II, NSRRC, SLS, SOLEIL, Spring-8, SSRL) [144]. They can in general be divided into hard X-ray (>2.5 keV photon energy) and soft X-ray facilities (up to 2 keV photon energy). For the purposes of this thesis, we are looking at edges in the soft X-ray regime, which are available at the REXS endstation at the Canadian Light Source (CLS) [165]. In contrast to hard X-rays, soft X-rays add the additional complications of covering a smaller part of momentum space due to the smaller momentum of the photons and requiring the entire experiment to



Figure 2.14: Geometry of resonant X-ray scattering experiment. (a) The direction of the incoming photon  $(\mathbf{q}_{in}, hv_{in})$  is fixed to the beamline direction and the outgoing scattered photon  $(\mathbf{q}_{out}, hv_{out} \approx hv_{in})$  is detected. The sample can be rotated around various axes  $(\theta, \chi, \text{ and } \varphi)$  as well as moved laterally (x, y, and z). The direction of the outgoing photon is determined by the scattering angle  $\theta_{sc}$ . (b) Geometry showing the magnitude of the exchanged momentum Q between photon and sample. By projecting  $\mathbf{Q}$  onto the sample surface, the parallel  $(\mathbf{Q}_{\parallel})$  and perpendicular components  $(\mathbf{Q}_{\perp})$  of the transferred momentum can be calculated. Adapted from [144].

be in UHV due to the higher attenuation of photons with smaller photon energy. An illustration of the experimental setup is shown in Fig. 2.14. The direction of the incoming photon is fixed by the beamline, and the sample ( $\theta$ ) and the detector  $(2\theta = \theta_{sc})$  can be rotated individually. The sample can additionally be rotated in  $\chi$  and  $\varphi$  in a limited range as well as moved in all lateral directions x, y, and z for sample alignment. The sample stage can further be cooled with liquid helium and is equipped with heaters, allowing a continuous adjustment of the temperature. In our case, the photon detectors do not discriminate photon polarization or photon energy, so that the signal can be viewed as an energy integrated spectrum comprised of the elastic and inelastic part. In general, experimental schemes differentiating different energies of the scattered light are available (resonant inelastic X-ray scattering (RIXS)), but come at the cost of a reduced efficiency. Under the assumption of a nearly elastic scattering process ( $hv_{out} \approx hv_{in}$ ), the magnitude of

the transferred momentum can be expressed as  $Q = 2q_{in} \times \sin(\theta_{sc}/2)$  [144]. When the vector **Q** is projected onto the plane defining the sample surface, the parallel component **Q**<sub>||</sub> and perpendicular component **Q**<sub>⊥</sub> of the transferred momentum can be extracted (see Fig. 2.14b).

#### 2.4 Low energy electron diffraction

LEED is a useful technique for the characterization of surfaces based on the diffraction of electrons off the sample [166–169]. It relies on the groundbreaking hypothesis by Louis de Broglie that all particles can be associated with a wave like character [170]:

$$\lambda = \frac{h}{\sqrt{2mE_{kin}}}.$$
(2.27)

Here the wavelength  $\lambda$  depends on the mass of the electron *m* and the kinetic energy  $E_{kin}$ . *h* is the Planck constant. To obtain constructive interference between an incoming electron and a scattered electron the Laue condition has to be fulfilled [171]:

$$\mathbf{k} - \mathbf{k}_0 = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = \mathbf{G}_{hkl}.$$
 (2.28)

Here  $\mathbf{k}_0$  is the wave vector of the incident electron,  $\mathbf{k}$  is the wave vector of the diffracted electron,  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  are reciprocal lattice vectors, and *hkl* are a set of integer numbers. Note that the LEED process is elastic and therefore the magnitude of the electron wave vector remains unchanged ( $|\mathbf{k}| = |\mathbf{k}_0|$ ). For a two-dimensional material like graphene, the relationship in Eqn. 2.28 reduces to [168]:

$$\mathbf{k}^{\parallel} - \mathbf{k}_{0}^{\parallel} = h\mathbf{a}^{*} + k\mathbf{b}^{*} = \mathbf{G}_{hk}.$$
 (2.29)

Even though the first electron diffraction experiments were successfully performed early on [172, 173], it took until the 1960s to establish LEED as a tool in the analysis of surfaces [174–177]. This is mainly due to fact that LEED is a very surface-sensitive technique. Hence, atomically clean and flat surfaces are necessary, typically requiring UHV conditions and sample preparation. The surface sensitivity is directly related to the electron inelastic mean free path in a solid (compare with ARPES in Fig. 2.2) [107]. In the typical energy range (10 eV to 100 eV) the pen-



**Figure 2.15: Schematic setup of a low energy electron setup.** A monochromatic electron beam from an electron gun is collimated by a Wehnelt cap. The diffracted electrons pass through the suppressor grids before hitting a phosphor screen for detection. The sample is grounded.

etration depth is on the order of several Ångstroms, corresponding to a few unit cells of most materials. In general, LEED experiments can be performed in one of two ways: (i) qualitative analysis of the position and "sharpness" of the diffraction spots, and (ii) recording the intensities and profiles of individual spots as a function of the electron energy. The former is useful to determine the orientation, symmetry and general quality of a sample (we will stick to this approach in this thesis). The latter can give additional information about atomic positions, defects, terrace sizes, etc. on the surface, but requires a more comprehensive data analysis and theoretical modelling [178, 179].

A schematic illustration of a LEED experiment is shown in Fig. 2.15. An electron gun produces a monochromatic beam of electrons, which is collimated by a Wehnelt cap before hitting the electrically grounded sample. The scattered electrons pass through several suppressor grids and are then detected on a phosphor screen. The suppressor grids are supposed to repel inelastically scattered electrons with lower kinetic energy. Typical spot sizes of the electron beam on the sample are between 0.1 mm and 0.5 mm depending on the settings of the electron optics.

Before looking at an actual experimental LEED image of monolayer graphene on SiC, we can use the structural information available for the sample system to simulate the expected LEED pattern (see Fig. 2.16). The hexagonal structure of



**Figure 2.16:** Simulation of the LEED pattern for graphene on SiC. The hexagonal diffraction patterns of graphene (red) and the SiC substrate (blue) are rotated against each other by 30°. SiC has a slightly larger lattice constant than graphene in real space, leading to slightly smaller reciprocal lattice vectors in the LEED image. The lattice mismatch also leads to a  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  superstructure (green). Note that not all diffraction spots for the superstructure are shown for simplicity and easier comparison with the experimental LEED pattern (see Fig. 2.17).

graphene and the SiC substrate are rotated by  $30^{\circ}$  with respect to each other. The SiC has a slightly larger lattice constant than graphene in real space. In reciprocal space probed by LEED, the situation is reversed, so we expect the SiC diffraction spots to be slightly closer to the center of the image in comparison to the graphene diffraction spots. In addition, we have to keep the  $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$  superlattice between the graphene and the substrate in mind, which arises from the lattice mismatch. The comparatively large unit cell of the superstructure in real space leads to short reciprocal scattering vectors in the LEED image rotated by  $30^{\circ}$  form the graphene spots. Note that in Fig. 2.16 not all spots of the superstructure in the visible area are shown for simplicity and better comparison to the experimental data. Indeed the experimental LEED pattern of monolayer graphene on SiC shows the expected features (see Fig. 2.17). The diffraction spots of the SiC substrate



**Figure 2.17: LEED pattern for monolayer graphene on SiC.** Experimental LEED pattern obtained at 66 eV electron energy with the sample held at 6 K. The diffraction spots of the graphene are marked in red, the diffraction spots of the SiC substrate in blue, and the diffraction spots corresponding to the reconstructed superlattice between sample and substrate in green. The dark feature visible in the center of the image is due to the electron gun and electrical connections leading to it.

are considerably weaker compared to the graphene spots, as the former is buried beneath the graphene. Also note that only a limited number of superlattice spots are visible, in particular around the graphene spots. This could be due to additional interference effects and can change as the electron energy is modulated and higher-order diffraction spots come into the range of the detector. For the purposes of this thesis, we try to align the graphene sample in the depicted fashion in Fig. 2.17, to allow easy access to one of the corners of the BZ with the given photon energy in ARPES.

#### 2.5 Raman spectroscopy

Raman is a spectroscopic method used to study low-energy excitations in materials [180–182]. It is commonly applied in chemistry to identify molecules through

vibrational fingerprints or in solid state physics to study phonons or other collective excitations of a crystal [183–185]. Raman is based on the inelastic scattering of monochromatic light, which was first theorized in 1923 [186]. The effect was experimentally realized shortly after in 1928 by C. V. Raman and independently by G. Landsberg and L. Mandelstam [187–189]. The process of Raman spectroscopy is illustrated in Fig. 2.18. Starting from the electronic ground state, an incoming photon excites the material into a virtual state. Most of the time the decay returns it to the same vibrational level (Rayleigh scattering), meaning the emitted photon has the exact same energy as the incoming photon. Nevertheless, for a small number of photons the energy changes, as a vibrational mode in the material is either excited or absorbed by the photon. This is the Raman effect. If a vibrational mode in the material is excited, the energy of the outgoing photon is reduced by the energy of that mode (Stokes scattering). If a vibrational mode instead is deexcited, the emitted photon has an increased energy (anti-Stokes scattering). The ratio between Stokes and anti-Stokes scattering depends on the energy of the vibrational modes and the temperature. For typical phonon energies and temperatures, materials are mostly in the electronic and vibrational ground state, so that Stokes scattering dominates. Note that for known material parameters, the ratio between Stokes and anti-Stokes scattering can be used to determine the temperature of the sample [190-192].

The theory of Raman scattering can be illustrated by a simple model based on the polarizability of a material. For a more in-depth review a number of publications are available [193–195]. Excitations in a material (e.g. phonons) can be described by a periodic motion:

$$q = q_0 \cos(2\pi v_{vib}t). \tag{2.30}$$

Here *q* is the displacement,  $q_0$  the amplitude of the oscillation, and  $v_{vib}$  is the characteristic frequency of the oscillation. The electromagnetic field of an incoming photon induces a dipole moment *P* depending on the polarizability  $\alpha$  of the material:

$$P = \alpha E_0 \cos(2\pi v_0 t). \tag{2.31}$$



**Figure 2.18: Process of Raman spectroscopy.** (a) Both the electronic ground state (GS) and the excited state (ES) have a series of vibrational states associated with them. Typically the vibrations have a smaller energy scale then the difference between the electronic GS and ES. An incoming photon connects to a virtual state in the band gap. The emission of the scattered photon can either happen to the same vibrational state (Rayleigh scattering – black), to a state with higher vibrational energy (Stokes scattering – red), or to a state with lower vibrational energy (Anti-Stokes scattering – blue). (b) Energy shifts for the three different scattering processes. For Rayleigh scattering (black) no change in the photon energy is observed. For Stokes scattering (red) the energy of the emitted photon is lower, and for anti-Stokes scattering (blue) the energy of the emitted photon is higher. The elastically scattered component is much stronger than the two inelastic components. The intensity ratio between the Stokes and anti-Stokes peaks depends on the energies of the vibrations involved and the temperature.

Here  $E_0$  is the amplitude of the electromagnetic field and  $v_0$  is the energy-dependent frequency of the photon. For small amplitudes the polarizability can be expanded in terms of the displacement:

$$\alpha = \alpha_0 + q(\frac{\partial \alpha}{\partial t})_{q=0} + \dots$$
(2.32)



**Figure 2.19: Setup of a Raman spectroscopy experiment.** Monochromatic light from a laser is guided onto the sample. Optics of a microscope can be used to reduce the spot size of the beam on the sample and add lateral resolution to the experiment. The reflected light is analyzed according to its energy in a spectrometer with a grating and then detected. Adapted from [196].

Combining Eqn. 2.30, Eqn. 2.31, and Eqn. 2.32, we get a new expression for the induced dipole moment in the material:

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + q_0 \cos(2\pi v_{vib} t) E_0 \cos(2\pi v_0 t) (\frac{\partial \alpha}{\partial t})_{q=0}.$$
 (2.33)

The first term in Eqn. 2.33 describes the usual Rayleigh scattering process. The second term is the basis of Raman scattering. It can be slightly rewritten using one of the identities for trigonometric functions:

$$\frac{1}{2}q_0E_0(\frac{\partial\alpha}{\partial t})_{q=0}[\cos(2\pi\{v_0 - v_{vib}\}t) + \cos(2\pi\{v_0 + v_{vib}\}t)].$$
(2.34)

Here the first term describes a dipole with a decreased frequency (Stokes scattering) and the second term a dipole with an increased frequency (anti-Stokes scattering).

A typical experimental setup for Raman scattering is depicted in Fig. 2.19. As a source of intense monochromatic light, a laser is used. The light is guided through



**Figure 2.20: Resonant Raman process in graphene.** (a) Origin of the so called Raman G peak of graphene. The absorption of a photon generates an electron-hole pair. The recombination involves a  $\Gamma$ -point phonon with zero momentum. The energy difference between incoming and outgoing photon equals the energy of the phonon. (b) Origin of the so called Raman 2D peak of graphene. In addition to the resonant creation of the electron-hole pair, the process involves two *K*-point phonons that resonantly couple the K and K' valleys. In this case the energy difference between the incoming and outgoing photon equals the sum of the energies of the two phonons involved. In both (a) and (b) optical transitions are depicted as blue arrows and phonon transitions are depicted as orange arrows. Adapted from [197].

an optical setup onto the sample. Often a microscope is used to focus the light and reduce the spot size of the beam on the sample ( $\approx \mu m$  depending on the wavelength of the used light). This allows us to scan the sample with the photon beam and add lateral resolution to the experiment. The reflected light is guided through a spectrometer with a grating to discriminate different energies, then detected for read out.

Raman spectroscopy has been and still is a powerful tool in the field of graphene. The linear dispersing bands forming cones around the Dirac points allow for direct optical transitions and for the resonant creation of electron-hole pairs in a range of photon energies. The two dominant Raman features for monolayer graphene on SiC are the so called G and 2D peaks. The underlying processes for both are illustrated in Fig. 2.20. The G peak process involves the creation of an electron-hole pair through photon absorption and a single  $\Gamma$ -point phonon with zero momentum. The 2D peak process involves the creation of an electron-hole pair through photon and two *K*-point phonons which resonantly couple



**Figure 2.21: Raman spectroscopy of monolayer graphene on SiC.** Raman spectrum taken with a helium-neon laser (632.8 nm) with the sample at room temperature. (a) The low-energy part of the spectrum is dominated by sharp transitions corresponding to the SiC substrate. (b) At higher wave numbers, additional SiC peaks overlap with the graphene G peak (E2g stretching phonon mode at the  $\Gamma$  point). The G peak is indicated with a blue star slightly below  $1600 \text{ cm}^{-1}$ . The so-called graphene 2D peak appears due to an intervalley process involving two phonons. It can be used to determine the number of graphene layers and interactions with a substrate. (c) Close-up of the graphene 2D peak. Note the different intensity scales from (a) – (c).

the two valleys K and K' in graphene. In the first process the energy difference between the incoming and outgoing photon is equal to the energy of the single phonon, while in the second process the energy difference is equal to the sum of the energies of the two phonons involved [198-202]. In both cases the total momentum and energy of all particles must be conserved. At typical photon energies used for Raman experiments on graphene the momenta of the photons can be neglected and the optical transitions can be depicted as vertical transitions in the electronic band structure (compare Fig. 2.21). Raman spectroscopy can be used as a tool to determine the number of layers of graphene, analyze sample quality (defects, flake size, etc.), and to study low-energy excitations like phonons and their coupling to other degrees of freedom [197, 202–206]. A typical Raman spectrum of monolayer graphene epitaxially grown on a SiC substrate is shown in Fig. 2.21. The data was taken with light from a helium-neon laser (632.8 nm) and the sample at room temperature. At low energies, the spectrum is dominated by intense peaks corresponding to excitations in the SiC substrate. Around  $1600 \,\mathrm{cm}^{-1}$  the graphene G peak is visible, but also overlaps with signal from the substrate. By comparing our data with available Raman spectra for monolayer graphene on SiC form the literature we can identify the G peak (blue star in Fig. 2.21b) [207–210]. It arises from the E2g stretching phonon mode at the  $\Gamma$  point [203]. Around 2650 cm<sup>-1</sup>, the so-called graphene 2D peak originates from an intervalley scattering process involving two phonon modes [203]. It is sometimes also called  $G^*$  peak. The position and width of the 2D feature can be used to identify different numbers of graphene layers and interactions with different substrates [207, 211, 212]. Especially noteworthy here is the work by Lee et al. [213] which showed that for graphene on SiC the width of the Raman 2D peak is the fingerprint to differentiate between different numbers of graphene layers. They also showed that Raman features shift if graphene is transferred from SiC to another substrate, while the width of features remains unchanged and is intrinsic to the graphene. Finally, Mueller et al. [214] showed that by combining the analysis of the graphene G and 2D peaks it is possible to disentangle the effects from for example strain and doping in graphene. Unfortunately, this is not possible in our data due to the overlap of the G peak with features from the underlying SiC substrate.

## **Chapter 3**

# Strain-induced Landau levels in graphene

In the presence of strong magnetic fields, two-dimensional (2D) electron systems display highly degenerate quantized energy levels called Landau levels (LLs) [27]. When the Fermi energy is placed within the energy gap between these LLs, the system bulk is insulating and charge current is carried by gapless edge modes. This is the quantum Hall effect, belonging to the remarkable class of macroscopic quantum phenomena [215–218] and the first member of an ever-growing family of topological states [219, 220]. While angle-resolved photoemission spectroscopy (ARPES) has been a powerful tool to investigate numerous quantum phases of matter [84, 221, 222], the traditional quantum Hall states - and thus their momentumresolved structure - have remained inaccessible. Such observations are hindered by the fact that ARPES measurements are incompatible with the application of magnetic fields. Here, we circumvent this by using graphene's [1, 2, 17] peculiar property of exhibiting large pseudomagnetic fields under particular strain patterns [85] to visualize the momentum-space structure of electrons in the pseudo-quantum Hall regime. By measuring the unique energy spacing of the resulting pseudo-LLs with ARPES, we confirm the Dirac nature of the electrons in graphene and extract a pseudomagnetic field strength of B = 41 T. This momentum-resolved study of the quantum Hall phase up to room temperature is made possible by exploiting shallow triangular nanoprisms in the SiC substrates that generate large, uniform



**Figure 3.1: Identification of nanoprisms.** (a) Horizontal derivative AFM topography image of our monolayer graphene grown on a SiC substrate. Triangular nanoprisms are dispersed on the surface. Inset: AFM topography image of the same area. Substrate terrace steps are about 10nm in height. (b) Top: Close-up AFM topography of the area indicated by the black box in (a). Bottom: Line cut through the AFM data marked by the purple line in the close-up. (c) Overview STM topography image (200 nm × 200 nm,  $V_{sample} = 100 \text{ mV}$ ,  $I_{tun.} = 2 \text{ pA}$ ) showing a single nanoprism.

pseudomagnetic fields, arising from strain, confirmed by scanning tunnelling microscopy (STM) and model calculations. Our work demonstrates the feasibility of exploiting strain-induced quantum phases in 2D Dirac materials on a wafer-scale size, opening the field to a range of new applications.

Graphene was the first material in which a member of the striking class of macroscopic quantum phenomena [215–217, 223] – the quantum Hall effect (QHE) [27] – could be observed at room temperature, when subject to large magnetic fields [37]. In the quantum Hall state, charge carriers are forced into cyclotron orbits with quantized radii and energies known as LLs when subjected to the influence of a magnetic field. In order to observe this effect, certain conditions must be met: the magnetic field must be large enough that the resulting spacing between LLs is larger than the thermal energy ( $\Delta E_{LL} > k_BT$ ); the charge carrier lifetime between scattering events must be longer than the characteristic time of the cyclotron orbit ( $t_{\text{life}} > 1/\omega_c$ ); and the magnetic field must be uniform on length scales greater than the LL orbit. This typically mandates the need for cryogenic temperatures, clean materials, and large applied magnetic fields. Dirac fermions in graphene provide a way to lift these restrictions: Under certain strain patterns, graphene's electrons be-

have as if they were under the influence of large magnetic fields, without applying an actual field from outside the material [85, 86, 224, 225]. These so-called pseudomagnetic fields only couple to the relativistic electrons around the Dirac point and, under the QHE conditions above, lead to the formation of flat, quantized LLs. This has been successfully observed using a range of methods [86, 224, 225], but was so far restricted to small regions, which severely limits its applicability.

Here, we directly visualize the formation of flat LLs close to the Fermi energy induced by pseudomagnetic fields on wafer-scale semiconductor samples. By measuring the hallmark  $\sqrt{n}$  energy spacing and momentum dependence of the ensuing pseudo-LLs with angle-resolved photoemission spectroscopy (ARPES), and with the aid of model calculations, we confirm their quantum Hall nature and extract a pseudomagnetic field strength of B = 41 T. This is made possible by the presence of a distribution of triangular nanoprisms underneath the monolayer graphene in our samples based on the well-established platform of epitaxial graphene on SiC substrates [57, 61, 64, 226], as revealed by a combination of atomic force microscopy (AFM) and scanning tunneling microscopy (STM) measurements. STM experiments were performed at UBC under ultra-high vacuum conditions ( $< 5 \times 10^{-11}$  mbar) using a low-temperature scanning tunnelling microscope (Scienta Omicron) at liquid helium temperatures ( $\sim 4.2$  K). All images were acquired in constant-current mode using a cut platinum-iridium tip, which was conditioned by voltage pulsing and gentle indentation into a Ag(111) crystal. The samples were annealed at 550°C overnight with a final pressure of  $p = 3 \times 10^{-10}$  mbar *in situ* prior to the STM measurements. Graphene samples with a carbon buffer layer were epitaxially grown on commercial 6H-SiC substrates. The substrates were hydrogen-etched prior to the growth under argon atmosphere. Details are described by S. Forti and U. Starke [227]. AFM characterisation measurements were taken at the Max Planck Institute in Stuttgart.

Our topographic images of these samples (Fig. 3.1a inset) exhibit the wellknown terraces and step edges of graphene grown on 6H-SiC [57], which are due to a miscut of the wafers from the (0001) direction of up to 0.1°. A population of triangular nanoscale features are identified on the terraces of our samples (Fig. 3.1a), which are like those reported on similar substrates [228, 229]. These nanoprisms appear during the growth process of graphene on 6H-SiC and are controllable by



**Figure 3.2:** AFM height distribution. Height distribution for the AFM image in Fig. 3.1b (Top). Two Gaussians (red) can be fitted to the data to extract the depths of the nanoprisms. The integrated fraction curve is shown in yellow.



**Figure 3.3: Graphene layer coverage** (a) STM image taken across the edge of a nanoprism ( $V_{sample} = 30 \text{ mV}$ ,  $I_{tun.} = 10 \text{ pA}$ ). The graphene grows smoothly over the step without interruption. (b) AFM adhesion image taken in the same region as shown in Fig. 3.1a. The image shows no contrast between the nanoprisms and the surrounding terraces (black box), thus clearly indicating that the nanoprisms are covered by monolayer graphene.



**Figure 3.4:** Substrate-induced strain. (a) Schematic structure of 6H-SiC, showing its layered ABCACB stacking order with epitaxial graphene on top (yellow). Inside the nanoprism, a single layer *within* the unit cell is missing, exposing the graphene to a different substrate surface termination, as illustrated in the top view. The carbon buffer layer is not shown for clarity. (b) Atomically resolved STM images ( $10 \text{ nm} \times 10 \text{ nm}$ ,  $V_{sample} = 30 \text{ mV}$ ,  $I_{tun.} = 2 \text{ pA}$ ) inside (top) and outside (bottom) of the nanoprism. (c) Difference map of the two Fourier transformed (FT) images in (b) visualizing the strain pattern inside the nanoprism.

the argon flow in the chamber [229]. They cover between 5% and 10% of the terraces, which is supported by looking at the height distribution of the pixels in the AFM image in Fig. 3.1b (top). We can determine the depths of the nanoprisms as well as estimate the coverage of the nanoprisms on the sample (see Fig. 3.2). The difference in the position of the two fitted Gaussians leads to a depth of the nanoprisms of  $(2.7 \pm 0.7)$ Å. The integrated fraction curve indicates that about 5% to 10% of the total area is covered with nanoprisms. Further, the nanoprisms are completely covered by monolayer graphene, which is being demonstrated by our AFM adhesion images (see 3.3b). Adhesion images correspond to the force necessary to retract the tip from the sample. Adhesion is sensitive to the graphene coverage on the sample and can thus distinguish between zero-layer, monolayer, and bilayer graphene with sensitivity to grain boundaries [230, 231]. The AFM adhesion image in Fig. 3.3b (taken in the same region as in Fig. 3.1a) shows no contrast between the nanoprisms and the surrounding terraces, thus clearly indicating that the nanoprisms are covered by monolayer graphene.

The nanoprisms are equilateral triangles oriented in the same direction with a narrow size distribution around 300 nm side length. They are about  $(2.7 \pm 0.7)$  Å deep (Fig. 3.1b), which corresponds to a single missing SiC double layer or  $\frac{1}{6}$  of the 6H-SiC unit cell. This leads to a change in the registry between the silicon atoms in the top layer of the substrate and the graphene as illustrated in Fig. 3.4d. The strain created inside the nanoprisms cannot be relieved, because the nanostructures are continuously covered by monolayer graphene without additional grain boundaries as corroborated by our STM images across the edge (see Fig. 3.3a). The STM image shows how the graphene grows smoothly over the step without interruption. This assures that a possible strain inside the nanoprism can build up and is not relieved along grain boundaries. To obtain a more detailed view of the possible strain pattern, we perform additional detailed atomic resolution STM measurements. The images taken inside and outside the nanoprisms (Fig. 3.4e) show the expected  $(6\sqrt{3} \times 6\sqrt{3})$ R30° modulation with respect to SiC on top of the carbon honeycomb lattice [59]. However, taking the difference between the two Fourier transformed images (Fig. 3.4f) reveals a strain pattern inside the nanoprism, with a maximum observed strain of about  $3^{\circ}$ . While the strain pattern could not be determined for the entire triangle due to limitations during the STM measurements (i.e. large size of the nanoprisms and problems with the stability/cleanliness of the tip), Fig. 3.5 shows the differences of Fourier transforms for pristine graphene and graphene with various lattice deformations and might give some intuition for the experimentally observed strain pattern. Especially the shear strain in Fig. 3.5d shows some agreement with the experiment with one fixed axis and changes along the other two high symmetry directions (compare also Fig. 3.22).

In order to confirm if the induced strain pattern indeed leads to flat LLs close to the Fermi energy, we perform a series of high-resolution ARPES measurements. The experiments were performed at UBC in an ultra-high vacuum chamber equipped with a SPECS Phoibos 150 analyser with optimal resolutions of  $\Delta E = 6 \text{ meV}$  and  $\Delta k = 0.01 \text{ Å}$  in energy and momentum, respectively, at a base pressure of better than  $p = 7 \times 10^{-11}$  Torr. Photons with an energy of 21.2 eV were provided by a SPECS UVS300 monochromatized gas discharge lamp. Our homebuilt six-axis cryogenic manipulator allows for measurements between 300 K and 3.5 K. Additional datasets were taken at UBC with a second ARPES setup equipped with a



Figure 3.5: Comparison of Fourier transforms for different graphene deformations. The figure shows differences between Fourier transforms of pristine graphene and graphene with various lattice deformations. (a) Isotropic stretch of 3%. (b) Uniaxial stretch of 3% along the *y*-direction. (c) Rotation of  $3^{\circ}$ . (d) Shear strain of  $3^{\circ}$  in the *x*-direction.



Figure 3.6: Momentum-resolved visualization of LLs. (a) ARPES cut through the Dirac cone at the K point at 300 K. The data have been divided by the Fermi function and symmetrized to compensate for matrix element effects [232]. (b) Cut along the energy axis integrated around the K point in (a). (c) Second derivative of the data in (a) [233]. (d) Inverted second derivative of the data shown in (b) after smoothing. (a)-(d) Landau levels (LLs) are indicated by arrows. (e) Summary of LL data sets, with model fit according to Eqn. 3.1 shown in black; the 95% confidence interval of the fit is shown in grey. Different symbols indicate different samples and temperatures: sample A (6 K) [hexagons], sample B (6 K) [squares], sample B 2nd data set (6 K) [stars], sample B (300 K) [diamonds], sample C (6 K) [circles], and sample C 2nd data set (6K) [triangles]. The position of the Dirac point (DP) is indicated by the black arrow. Inset: Same data plotted versus  $\sqrt{n}$ , giving the expected linear behaviour for LLs in a Dirac material. (f) Sketch of various mechanisms which may lead to ARPES intensity inside the cone. Neither electron-phonon coupling nor contamination from bilayer graphene can explain the experimental findings.

Scienta R4000 analyser and a Scienta VUV5000 UV source with optimal resolutions of  $\Delta E = 1.5 \text{ meV}$  and  $\Delta k = 0.01 \text{ Å}^{-1}$  in energy and momentum, respectively, for 21.2 eV photons. The samples were annealed at 600°C for about 2h at  $p = 1 \times 10^{-9}$  Torr and then at 500°C for about 10h at  $p = 5 \times 10^{-10}$  Torr immediately before the ARPES measurements.

ARPES is a momentum- and energy-resolved technique that has proven to be a powerful tool in directly studying the electronic band structures of a vast variety of quantum phases of matter, from strongly-correlated electron systems and high-Tc superconductors [102] to topological insulators and semimetals [221, 222, 234]. Yet no study of quantum Hall states has been performed, since ARPES is strictly incompatible with the application of magnetic fields, as essential crystal momentum information carried by the photoemitted electrons would be lost through interaction with the field. However, this is different for pseudomagnetic fields, as they only interact with the Dirac electrons inside the material. We note that while a recently developed momentum-resolved technique compatible with magnetic fields has been reported [235], it necessarily requires sophisticated heterostructures, physically accessible fields, and is limited to a small sector of the Brillouin zone.

Our ARPES data, which – due to the ~1 mm spot size of the photon source – correspond to the spatial average over unstrained and strained regions of the sample, show the expected Dirac cone as well as new flat bands that gradually merge with the linear dispersion (Figs. 3.6a and 3.6c). The unequal energy spacing of these newly observed bands can be extracted from cuts along the energy direction at the K point (Fig. 3.6b) and their second derivative (Fig. 3.6d). The positions of the levels are directly read off the cuts along the energy direction without additional fitting routines. We estimate the accuracy of this procedure to determine the positions to about 20 meV. By plotting the positions of these bands (Fig. 3.6e), we observe the distinct  $\sqrt{n}$  energy spacing which is a hallmark of LLs for graphene's massless Dirac charge carriers [2], where *n* is the integer LL index. The spectrum of LLs in graphene is given by [1]

$$E_n = \operatorname{sgn}(n)\sqrt{2v_F^2\hbar eB \cdot |n|} + E_{DP}$$
(3.1)


**Figure 3.7: Fermi velocity and quasiparticle lifetime from ARPES.** (a) The linear dispersion of graphene (black circles) is fitted linearly (red line) to extract the Fermi velocity. (b) The extracted binding energy dependent line width (black circles) is fitted quadratically (red line) to illustrate the *decreasing* carrier lifetime at higher binding energies. The blue dashed line indicates a constant offset due to impurity scattering.

where  $v_F$  is the velocity of the electrons at the Fermi level,  $\hbar$  the reduced Planck constant, e the electron charge, B the magnitude of the (pseudo-)magnetic field, and  $E_{DP}$  the binding energy of the Dirac point. Using the ARPES dispersion map in Fig. 3.6a, the Fermi velocity is determined to be  $v_F = (9.50 \pm 0.08) \times 10^5$  m/s. The Fermi velocity can be directly extracted from the ARPES data. The momentum distribution curves at each binding energy are fitted using a Lorentzian with a constant background. The dispersion of the band can then be fitted linearly to determine the Fermi velocity (see Fig. 3.7a). Fitting our experimental data to Eq. (3.1) as done in Fig. 3.6e, we extract the magnitude of the pseudomagnetic field, which yields  $B = (41 \pm 2)$  T. Note, the uncertainty results from the fitting procedure and takes into account the spread of the Landau level positions between different samples and temperatures (compare Fig. 3.6e). Remarkably, this pseudomagnetic field value appears to be consistent between several samples from cryogenic temperatures (6K) up to room temperature. The model fit also consistently pinpoints the binding energy of the Dirac point to  $E_{DP} = (460 \pm 10)$  meV relative to the Fermi level, which gives us additional confidence in the  $\sqrt{n}$  dependence of our data points. The value agrees well with previous reports on this sample system [57, 236] and is attributed



**Figure 3.8: Fit of Landau levels for the exponent.** The positions of the Landau levels and the Dirac point (DP) are fitted to a function of the form  $f(x) = ax^b + c$  (dashed grey), where *b* is the exponent. For a  $\sqrt{n}$  behaviour b = 0.5 is expected. The position of the Dirac point with a binding energy of  $(0.45 \pm 0.02)$  eV is determined from Fig. 3.12b, where the uncertainty takes into account a possible slight variation of the position of the Dirac point between different samples. The fit results in a value for the exponent of  $b = (0.53 \pm 0.04)$ .

to charge transfer from the SiC substrate to the graphene layer. To gain even further confidence that the extracted Landau level positions and the position of the Dirac point follow a  $\sqrt{n}$  behaviour we fit a function of the form  $f(x) = ax^b + c$  to our data (see Fig. 3.8). The fit yields an exponent of  $b = (0.53 \pm 0.04)$ . Taking into account the error bars of the fit, this is compatible with a  $\sqrt{n}$  behaviour which would have an exponent of b = 0.5.

Additionally, the LLs are only resolved in the upper part of the Dirac cone, closer to the Fermi level. We attribute this effect to the increased scattering phase space as one moves away from the Fermi level, which reduces the scattering life-time of the carriers. The binding energy dependence of the lifetime of the carriers can also be directly extracted from the ARPES data. The width of the Lorentzians as a function of binding energy can be fitted quadratically with a constant offset. The



**Figure 3.9: Band structure of multilayer graphene.** (a) Band dispersions of graphene along high symmetry directions for monolayer (purple), bilayer (red), trilayer with ABA stacking (blue), trilayer with ABC stacking (blue dashed), quad-layer with ABAB stacking (green), quadlayer with ABAC stacking (green dashed), and quadlayer with ABCA stacking (green dash-dotted) calculated with a tight-binding model with parameters from [238]. (b) Same band structure as in (a), but as a close up around the K point. (c) Calculated bands overlaid on the experimental ARPES data.

linewidth is inversely proportional to the quasiparticle lifetime, thus showing how the latter *decreases* as one goes away from the Fermi level (see Fig. 3.7b). This is a manifestation of a simple Fermi liquid model. Electrons at the Fermi level have a certain lifetime between scattering events dictated by the concentration of impurities and defects. As one goes to higher binding energies, the phase space for electron-electron scattering increases  $\propto E_b^2$  and the lifetime decreases. We propose this as the reason why, experimentally, our LLs are only clearly resolved in the upper part of the cone closer to the Fermi level. When the scattering rate at some binding energy exceeds a critical value above which coherent circular orbits cannot be established, the LL quantization in the ARPES measurement disappears. We note that such asymmetric behaviour has been reported before in scanning probe measurements, and was attributed to a shorter vertical extension of wave functions at lower energies [86] as well as a reduced quasiparticle lifetime away from the Fermi level [237].

As for other alternative explanations of the data, we note that while previous ARPES studies of graphene on SiC have shown a rich variety of features [66, 239], the signature  $\sqrt{n}$  spacing of the new levels (Fig. 3.6e and inset) allows us to distin-



**Figure 3.10: Model calculation of strain-induced LLs.** (a) Top: Honeycomb lattice, with the two sublattices A (red) and B (yellow). The black arrows indicate the symmetry of the strain pattern. Bottom: Triangular flake with strain-induced pseudomagnetic field B = 41 T. The colour scale indicates the relative bond stretching. (b) Spectral function for the gapless case with Semenoff mass M = 0 meV. (c) Energy cut through the Dirac point (K) of the spectral function in (b). The dashed grey lines indicate the position of the Landau levels (LL) predicted by Eqn. 3.1.

guish the observed effect from other possibilities (Fig. 3.6f). For example, if spectral weight inside the Dirac cone arose from the coupling of electrons to phonons [66], it would be limited to characteristic vibrational energies. Similarly, contributions from bilayer and higher order graphene layers, which can appear in small quantities near step edges of the substrate during the growth process [239] (see also AFM adhesion image Fig. 3.3b), would lead to a manifold of bands, but would not reproduce the observed band structure [238, 240]. The calculated band dispersions for monolayer graphene, bilayer graphene, trilayer graphene, and quadlayer graphene with their different stacking possibilities are shown in Fig. 3.9. The parameters for the tight-binding model are based on the experimental findings of Ohta *et al.* [238]. Finally, a recent theoretical study shows that for certain defects in graphene a smearing out of the Dirac point can occur [241]. This would not explain the additional flat bands inside the Dirac cone and it should be noted that such defects were not observed during the STM measurements on our samples.

To gain deeper insights on the origin of the observed LLs, we model a region of graphene experiencing a uniform strain-induced pseudomagnetic field. We use the simplest such strain pattern, calculated by Guinea *et al.* [85], which exhibits the triangular symmetry of the underlying honeycomb lattice. Using a tight-binding approach, we directly simulate a finite-size strained region with open boundary conditions and armchair edges. In detail, we consider a minimal tight-binding model on the honeycomb lattice with nearest-neighbour hoppings and a sublattice-symmetry breaking Semenoff [13] mass term M:

$$H = -t \sum_{\langle \boldsymbol{r}, \boldsymbol{r}' \rangle} \left( c_A^{\dagger}(\boldsymbol{r}) c_B(\boldsymbol{r}') + \text{H.c.} \right) + M \left( \sum_{\boldsymbol{r}} c_A^{\dagger}(\boldsymbol{r}) c_A(\boldsymbol{r}) - \sum_{\boldsymbol{r}'} c_B^{\dagger}(\boldsymbol{r}') c_B(\boldsymbol{r}') \right)$$
(3.2)

where  $c_A^{\dagger}(\mathbf{r})$  ( $c_B^{\dagger}(\mathbf{r'})$ ) creates an electron in the  $p_z$  orbital at lattice site  $\mathbf{r}$  ( $\mathbf{r'}$ ) on the sublattice A (B) of the honeycomb lattice, t = 2.7 eV, and the nearest-neighbour distance is  $a_0 = 0.142 \text{ nm}$ . We neglect the electron spin, and thus consider effectively spinless fermions.

We construct a flake in the shape of an equilateral triangle of side length  $L \sim 56$  nm. The use of armchair edges ensures that we avoid the zero-energy edge modes appearing for zigzag edges [1]. We apply the simplest strain pattern respecting the triangular symmetry of the problem at hand, namely, the pattern introduced by Guinea *et al.* [85] which gives rise to a uniform (out-of-plane) pseudomagnetic field

$$\boldsymbol{B} = 4u_0 \frac{\hbar\beta}{ea_0} \hat{\boldsymbol{z}}$$
(3.3)

where  $\beta \approx 3.37$  in graphene[242], and the corresponding displacement field is given by

$$\mathbf{u}(r,\theta) = \begin{pmatrix} u_r \\ u_\theta \end{pmatrix} = \begin{pmatrix} u_0 r^2 \sin(3\theta) \\ u_0 r^2 \cos(3\theta) \end{pmatrix}.$$
 (3.4)

The hopping parameter renormalization induced by this displacement field is calculated using the simple prescription:

$$t \to t_{ij} = t \exp\left[-\frac{\beta}{a_0^2} \left(\varepsilon_{xx} x_{ij}^2 + \varepsilon_{yy} y_{ij}^2 + 2\varepsilon_{xy} x_{ij} y_{ij}\right)\right]$$
(3.5)

where  $(x_{ij}, y_{ij}) \equiv \mathbf{r}_i - \mathbf{r}_j$  is the vector joining the original (unstrained) sites *i* and *j*, and

$$\varepsilon_{ij} = \frac{1}{2} \left[ \partial_j u_i + \partial_i u_j \right] \tag{3.6}$$

is the strain tensor corresponding to the (in-plane) displacement field **u**. Outside the strained region (which we take as a triangle of slightly smaller length  $L_S \sim 48$  nm), we allow the strain tensor to relax:  $\boldsymbol{\varepsilon} \rightarrow e^{-\frac{r^2}{2\sigma^2}}\boldsymbol{\varepsilon}$ , where *r* is the perpendicular distance to the boundary of the strained region, and  $\sigma \sim 1$  nm. We define the length scale of the homogeneous magnetic field **B** to be the diameter of the largest inscribed circle in the triangle of side  $L_S$ :  $\lambda \equiv L_S/\sqrt{3} \sim 28$  nm. We stress here that our simulated flakes are much smaller than the experimentally observed triangular features of size  $\sim 300$  nm. The fact that we nevertheless reproduce the experimental features underlines how the number of observable LLs is limited by the length scale of the homogeneous pseudomagnetic field  $\lambda$ , rather than by the size *L* of the nanoprisms themselves. This length scale could be caused by the more complicated strain pattern present in the nanoprisms or be induced by disorder.

We then diagonalize the Hamiltonian (Eqn. 3.2) with hopping parameters given by Eqn. 3.5 to obtain the full set of eigenstates  $|n\rangle$  with energies  $E_n$ , and compute the momentum-resolved, retarded Green's function using the Lehman representation

$$G_{\alpha}^{R}(\boldsymbol{k},\boldsymbol{\omega}) = \sum_{n} \frac{|\langle n| c_{\alpha}^{\dagger}(\boldsymbol{k}) |0\rangle|^{2}}{\boldsymbol{\omega} - (E_{n} - E_{0}) - i\eta}$$
(3.7)

where  $\alpha = A, B$  is a sublattice (band) index, and  $\eta \sim 20$  meV is a small broadening parameter comparable to the experimental resolution. We then compute the one-particle spectral function,

$$A(\boldsymbol{k},\boldsymbol{\omega}) = -\frac{1}{\pi} \sum_{\alpha} \operatorname{Im} \left[ G_{\alpha}^{R}(\boldsymbol{\omega}, \boldsymbol{k}) \right]$$
(3.8)

which is proportional to the intensity measured in ARPES (modulo the Fermi-Dirac distribution and dipole matrix elements). We note that using a finite system introduces two main effects in the momentum-resolved spectral function: the appear-



Figure 3.11: Evolution of LLs with increasing uniform pseudomagnetic fields. Calculated spectral function in our triangular flake for fields B = 0, 41, 82 and 164 T (from left to right).

ance of a small finite-size gap at the Dirac points (in the absence of a magnetic field) and a momentum broadening of the bands (see Fig. 3.11a).

We find that the observed LL spectra can be well-reproduced by a triangular flake of side length L = 56 nm (Fig. 3.10a), subject to a uniform pseudomagnetic field B = 41 T over the entire flake (Fig. 3.10a). The maximal strain (or relative bond stretching) reaches around 3%, which is in good agreement with our STM measurements. The ARPES data can be simulated by calculating the energy and momentum-resolved spectral function  $A(\mathbf{k}, \boldsymbol{\omega})$  of this triangular flake, here shown in Fig. 3.10b and 3.10c. Our simulation clearly reproduces the main features of the ARPES data, namely levels that: (i) follow  $\sqrt{n}$  spacing in energy; (ii) are flat *inside* the Dirac cone and merge with the linearly dispersing bands; (iii) become less clearly resolved with increasing index n.

Features (ii) and (iii) can be understood by comparing the characteristic size of a Landau orbit  $\propto \sqrt{n} l_B$  (with the magnetic length  $l_B = \sqrt{\frac{\hbar}{eB}}$ ) to the length scale  $\lambda$ on which the pseudomagnetic field is uniform. For LLs to exist, an electron on a given Landau orbit must experience a uniform pseudomagnetic field [242], leading to the condition  $\sqrt{n} l_B \ll \lambda$ . Hence, for large fields *B* or large  $\lambda$ , flat bands are expected across the entire Brillouin zone, whereas Dirac cones are recovered in the opposite limit. In Fig. 3.11, we present the spectral function obtained for M = 0and increasing pseudomagnetic fields B = 0, 41, 82 and 164 T to highlight how



**Figure 3.12: Determination of the mass term.** (a) ARPES cut through the Dirac cone. Orange circles indicate the positions of the fitted Lorentzians. The red line and the dashed red line indicate linear fits through the orange circles for the upper and lower cone, respectively. The cut is symmetrized around the K point in the momentum direction to remove polarisation effects. (b) The same data as in (a), but fitted to a hyperbola instead. (c) Results for the gap size from the hyperbola fits for different ARPES slices along  $k_y$ . The curve shows the expected half-hyperbola and the gap size of ~0.25 eV is given by the minimum. Note, for graphene on SiC a range of mass terms is expected [226]. This means in an ARPES experiment we would average over areas with zero mass term and hence no gap and areas with a finite mass term and hence a finite gap. The fitting procedure outlined above thus only yields the largest gap in the observed area.

LLs evolve from a Dirac cone when B = 0 to completely flat bands when  $l_B \ll \lambda$ . This is analogous to keeping *B* fixed and increasing the size of the flake, but the latter method is strongly constrained by numerical resources. Here  $l_B = 4.0$ , 2.8 and 2.0 nm at B = 41, 82 and 164 T respectively, whereas  $\lambda \sim 30$  nm.

The bands observed in the ARPES data can thus be understood as LLs, where the orbit size is only somewhat smaller than  $\lambda$ : by comparing the experimental data and the model calculation, we estimate  $l_B \sim 4$  nm and  $\lambda \sim 30$  nm. Furthermore, since the size of Landau orbits grows as  $\sim \sqrt{|n|}$ , eventually it becomes comparable to  $\lambda$ , explaining why levels with higher index *n* are less clearly resolved.

However, our simple model (Figs. 3.10b and 3.10c) consistently exhibits a sharp zeroth LL (LL0), which is absent from the ARPES data. This discrepancy is surprising, since LL0 is known to be stable against inhomogeneities of the magnetic

field as well as against disorder, as long as the latter preserves the chiral symmetry of graphene [243]. Below, we provide a possible mechanism that broadens LLO without significantly affecting the higher LLs. It has been argued that graphene grown on SiC is subject to a sublattice-symmetry-breaking potential arising from the interaction with the substrate [226]. The minimal theoretical model describing this effect, which acts as a staggered potential between sublattices A and B, is the so-called Semenoff mass M [13]. Here we briefly discuss the effect of a Semenoff mass [13] M on pseudo-LLs and show that a *uniform* Semenoff mass cannot explain the observed spectrum. Starting from the linearly dispersing bands in the Dirac cone without any magnetic fields, a mass term opens a gap at the Dirac point. The size of the gap is equal to *twice* the size of the mass term M. Experimentally, it manifests in our ARPES cuts through the Dirac point by extending the linear dispersions of the lower and upper cones, for both sides with respect to the K point (Fig. 3.12a), in that these extrapolations do not meet in a single point, but are offset from each other. To accurately determine the size of the gap, we fit two Lorentzians with a constant background to momentum distribution curves in the upper and lower cones. The energy range of the fit is selected to avoid the prominent LLs. A hyperbola is then fitted to the bands (Fig. 3.12b) to determine top and bottom of the two bands, and in turn the gap size. The procedure is repeated for several cuts through the Dirac cone along the  $k_v$  direction. The results are summarised in Fig. 3.12c and the mass term is equal to half of the minimal gap size  $(\sim 0.25 \text{ eV})$ . This is comparable to the  $\sim 0.26 \text{ eV}$  gap observed in the same sample system by Zhou et al. [226].

Next, we describe the effects of a mass term on a Dirac dispersion including magnetic fields. In short, the mass term opens a gap at the Dirac point and shifts the LL spectrum for  $n \neq 0$  to [244]:

$$E_n = \operatorname{sgn}(n)\sqrt{2ev_F^2\hbar B \cdot |n| + M^2} + E_{DP}.$$
(3.9)

But note, that Eqn. 3.9 is not properly defined for n = 0 – to understand whether LLO is shifted to +M or -M (in valleys K and K'), we have to distinguish between real magnetic fields, which break time-reversal symmetry, and pseudomagnetic fields, which preserve time-reversal symmetry. For real magnetic fields [244], LLO



Figure 3.13: Sketch of pseudo-LLs with Semenoff mass. Depending on the sign of the mass term M, the zeroth LL (LL0) gets shifted to the upper or lower part of the cone. The spectrum is identical for valleys K and K', because pseudomagnetic fields preserve time-reversal symmetry. Higher LLs only get pushed away slightly from the Dirac point.

has opposite energy  $\pm M$  at *K* and *K'*. For pseudomagnetic fields, in order to preserve time-reversal symmetry, the spectrum must be identical in both valleys, and the energy of LL0 is determined by the sign of *M*, so for n = 0 we simply get  $E_{LL0} = E_{DP} \pm M$ . This is illustrated in Fig. 3.13 for different signs of the mass term, where LL0 either shifts to the top of the lower cone (M < 0) or the bottom of the upper cone (M > 0).

Our numerical simulations clearly show this behaviour (Fig. 3.14), but there is one additional caveat. The total pseudomagnetic flux must be vanishing in our flake by construction, as we require the strain to relax at the edges of the flake. This requirement generates a region near the boundaries of the strained area with a pseudomagnetic field of the reversed sign. This region hosts a LLO at an energy inverted with respect to the LLO coming from inside the strained area. This is visible in our calculations as weaker and more broadened (in momentum) levels, indicated by red arrows in Figs. 3.14b and 3.14c. Note that experimentally, a similar scenario is natural on our graphene on SiC samples as well. The strain inside the nanoprisms needs to relax away from the feature, thus creating an area with an inverted pseudomagnetic field.

To check if a *uniform* mass term of about the determined size can explain our findings, we fit the observed LLs to Eqn. 3.9 (see Fig. 3.15). While this model pro-



**Figure 3.14:** Calculation of pseudo-LLs with Semenoff mass. Calculated spectral function in our triangular flake with a uniform pseudomagnetic field B = 41 T and Semenoff masses M = 0, M = -135 meV, M = +135 meV, and averaged in the interval  $M \in [-135, 135]$  meV (from left to right). The positions of the LLs for the different cases are indicated, as well as the much weaker LL0 from the area surrounding the strained flake (red arrows in (b) and (c)).



Figure 3.15: Model fit with constant mass term. Fit of the observed LLs to Eqn. 3.9. Note the shifted indices for the LLs in this scenario. It places the Dirac point at a binding energy of 390 meV with M = 150 meV, compared to 450 meV obtained from the fit to Eqn. 3.1 without a mass term.



**Figure 3.16: Calculation for a uniform mass distribution.** (a) Spectral function averaged over a uniform distribution of Semenoff masses  $M \in [-135, 135]$  meV. (b) Energy cut through the Dirac point (K) of the spectral function in (a). The shaded grey area indicates the broadening of the LLs predicted by Eqns. 3.1 and 3.9.

duces a qualitatively good fit with M = 150 meV, it places the Dirac point at a binding energy of 390 meV, which is inconsistent with the experimental observations (compared to 450 meV obtained from the fit to Eqn. 3.1 without a mass term). This means, a *uniform* mass term M cannot explain the ARPES data.

Therefore, we postulate that the mass term M varies on a length scale much greater than the magnetic length  $l_B \sim 4$  nm, but smaller than the ARPES spot size (~1 mm). The variation can take place either from nanoprism to nanoprism, or within a given nanoprism, if it is tied to the length scale of the uniform pseudomagnetic field  $\lambda$ . In the former scenario, we can approximate the effect of the slowly-varying mass term M by averaging over the spectral function obtained with different fixed M (such as those shown in Figs. 3.14b and 3.14c). This is shown in Figs. 3.16d and 3.16e for a uniform distribution in the interval  $M \in [-135, 135]$  meV. As evident from Eqn. 3.9, the distribution of mass terms affects LLO most, while merely contributing an additional broadening to the higher levels. Note that, as observed experimentally, the variation of the mass term is not limited to the strained areas, but instead is a property of the whole sample; as a result, ARPES always picks up a spatial average of strained areas with LLs and unstrained



**Figure 3.17: Measurement of the Raman spot size.** (a) Image of the laser spot with the  $\times 50$  objective. (b) Line cut through the laser spot. A fit to a Gaussian profile (red) yields a FWHM of about  $6 \,\mu$ m. (c) Image of the laser spot with the  $\times 100$  objective. (d) Line cut through the laser spot. A fit to a Gaussian profile (red) yields a FWHM of about  $3 \,\mu$ m. The flat parts of the line cuts in (b) and (d) indicate a saturation of the detector at the center of the laser spot. These points were omitted for the purpose of the fits.

areas with the usual Dirac cone dispersion, both having the same distribution of mass terms and corresponding Dirac point gaps. This phenomenological model completely smears out LLO, while only slightly broadening the other levels (see Fig. 3.14d) and is in good agreement with the experimental data and may renew interest in the variation of the mass term in this sample system [226].

To support our idea of a mass term that varies on a length scale larger than the nanoprisms, we perform Raman spectroscopy measurements on our samples. The

measurements were taken at room temperature and in air on a HORIBA LabRAM system with a helium-neon laser (632.8 nm wavelength).

In previous experiments, it could be shown that a shift accompanied by a change in the width of the so-called graphene 2D feature indicates a change in the number of graphene layers, while a shift without a change in the width of graphene Raman features can indicate a modification of the interaction between graphene and the underlying substrate [213]. The lateral resolution of a Raman measurement is determined by the spot size of the laser beam on the sample. Images of the laser spots and an analysis of the profiles for our system for the  $\times 50$  and  $\times 100$  objectives are shown in Fig. 3.17. Lateral resolutions of 6  $\mu$ m and 3  $\mu$ m respectively could be determined from Gaussian fits. Using the  $\times 100$  objective, Raman maps of the graphene 2D peak were acquired (see Fig. 3.18). The 2D feature can be fitted with a Gaussian to extract its amplitude, position, and width. Step edges in the substrate with small contributions from bilayer graphene should show up as line features with a shift in the peak position as well as a change in the peak width. No features consistent with this are observed, indicating that the lateral resolution of the experiment is probably not good enough to resolve the step edges.

Additional measurements were taken as line measurements along the *x*-direction (see Fig. 3.19) as well as the *y*-direction (see Fig. 3.20), which allow us to cover larger lateral distances compared to the map measurements. Also here a Gaussian was used to fit the 2D peak in each spectrum to determine the peak position as well as the peak width. For the *y*-direction, no distinct features are visible. In contrast to that is the measurement along the *x*-direction. Here the peak position shows a periodic behavior, which is mostly independent of the peak width (see Fig. 3.19b and Fig. 3.19c).

The peak positions of the 2D feature along the x-direction can be fitted with a sine function, as done in Fig. 3.21b. This hints at the possibility that the interaction between the graphene layer and the SiC substrate is modulated with a period of about 20  $\mu$ m. If one makes the reasonable assumption that the mass term oscillates in accordance with the graphene-substrate interaction, this supports the idea of a varying mass term between individual nanoprisms. We note that our STM measurements are carried out on much smaller length scales compared to the observed modulation with Raman. Hence, it is not surprising to not see any evidence in this



Figure 3.18: Raman maps of the graphene 2D peak. Raman spectra were taken on a 20  $\mu$ m × 20  $\mu$ m grid (20 px × 20 px) with the ×100 objective. The graphene 2D peak was fitted to a Gaussian, which allows the extraction of the peak amplitude (a), peak position (b), and peak width (c).



**Figure 3.19: Raman line spectrum** *x***-direction.** (a) Raman line spectrum of the so-called graphene 2D feature along 60  $\mu$ m in the *x*-direction. Each spectrum was fitted with a Gaussian to extract the peak position (b) and peak width (c).

regard in those measurements. Currently we can only speculate about the underlying origin of the modulation. Typical length scales for superstructures between graphene and SiC are much shorter, but a relation to the step edges on the substrate (compare Fig. 3.1a), which have a spacing of several  $\mu$ m, seems possible.

Finally, we compare the strain model used in the calculations to the experimentally observed strain geometry, as far as possible (see Fig. 3.22). For that purpose we select an area in each of the three corners of the nanoprism and compare their



**Figure 3.20: Raman line spectrum** *y***-direction.** (a) Raman line spectrum of the graphene 2D feature along 60  $\mu$ m in the *y*-direction. Each spectrum was fitted with a Gaussian to extract the peak position (b) and peak width (c).

atomic lattice to an unstrained area outside the nanoprism. This is done using additional atomically resolved STM images and their Fourier transforms. Comparing the results to the theoretical results, we see that both agree well in terms of overall magnitude of the strain and the  $\frac{2\pi}{3}$  symmetry. While in the experiment the amplitude of the strain rotates as one goes from corner to corner, it is the phase of the strain with a constant amplitude in the calculations. This finding might motivate future theoretical studies in the area of pseudomagnetic fields.



Figure 3.21: Raman line spectra with fit. (a) Raman line spectra along the x direction around the graphene 2D peak. (b) The peak positions of the 2D peak (black points) are determined with a Gaussian fit of the individual spectra in (a). The peak positions can be fit with a sine function with a period of about  $20 \,\mu$ m (red).

In summary, this study provides the first demonstration of the room temperature strain-induced quantum Hall effect in graphene on a wafer-scale platform, as well as the first direct momentum-space visualization of graphene electrons in the strain-induced quantum Hall phase by ARPES, whereby the linear Dirac dispersion collapses into a ladder of quantized LLs. This opens a path for future momentumresolved studies of strain-induced, room temperature-stable topological phases in a range of materials including Dirac and Weyl semimetals [245-247], monolayer transition metal dichalcogenides [248], and even nodal superconductors [249, 250], all under large, potentially controllable pseudomagnetic fields. Importantly, these systems will feature time reversal invariant ground states - otherwise impossible with a true magnetic field - and may act as future building blocks for pseudospinor valleytronic-based technologies [251]. In light of the recently discovered unconventional superconductivity in "magic angle" twisted bilayer graphene [74, 83], strain-induced pseudomagnetic fields likewise raise the possibility of engineering exotic time reversal symmetric variants of correlated states including superconductivity in LLs [252] and fractional topological phases [253]. Our results lay the foun-



**Figure 3.22: Comparison of experimental and model strain.** (a) – (d) STM topography images with  $V_{sam.} = 30 mV$  and  $I_{tun.} = 2 pA$  taken at each corner of the nanoprism and outside. The Fourier transform of each image is shown as an inset. (e) Schematic showing the position of the measurements with respect to the nanoprism. (f) – (h) Difference of the Fourier transforms between the strained areas inside the triangle (top, bottom and side) and the unstrained areas outside. (i) – (k) Difference of the Fourier transforms between the triangle (top, bottom and side) and the unstrained areas inside the triangle (top, bottom and side) and the strained areas inside the triangle (top, bottom and side) and unstrained graphene for the model calculation.

dations for bottom-up strain-engineering of novel macroscopic quantum phases at room temperature and at the technologically relevant wafer-scale.

## **Chapter 4**

## **Correlated electron physics in gadolinium intercalated graphene**

Quantum materials include several classes of materials in which the interaction between electrons leads to a complex phase diagram. They feature phenomena like unconventional superconductivity, pseudogaps, or density wave orders. Unravelling the origin and interplay of these quantum phases represents one of the great challenges in physics today and is key in predicting the future design of quantum materials and their translation from fundamental research to applications. In light of the recent discovery of a Mott insulating phase and unconventional superconductivity in so called "magic angle" graphene, we investigate the novel, tailor-made, and wafer-scale sized quantum material based on ultra-highly doped graphene coupled to an ordered monolayer of gadolinium. We demonstrate correlation-induced flat bands, a temperature-dependent pseudogap, and signatures of a density wave order up to room temperature.

The physics of correlated electrons remains at the forefront of formidable challenges in science and describes materials in which the interaction between electrons cannot be treated as an averaged background. Materials in the field typically feature a complex phase diagram as a function of electronic doping, mechanical pressure, magnetic field, and temperature, displaying remarkable phenomena like unconventional superconductivity, a pseudogap phase, antiferromagnetism, or density wave orders (see Fig. 4.1a). Prominent examples include the cuprates [84]



Figure 4.1: Introduction to Gd-intercalated graphene. (a) Schematic exemplary phase diagrams of prominent correlated electron physics material classes as a function of doping (cuprates and iron-based) or pressure (organic compounds and heavy fermions). All show a complex interplay between different quantum phases such as superconductivity (SC), charge order (CO), pseudogaps (PG), spin-Peierls (SP) phases, or antiferromagnetic order (AF). Adapted from [254]. (b) Electronic band structure of graphene. The linearly dispersing Dirac cones touch at the corners of the Brillouin zone (BZ), while the saddle point halfway between neighboring corners along the BZ edge lead to a Van Hove singularity (VHS). High symmetry points of the hexagonal BZ are indicated. (c) Illustration of the structure of Gd-intercalated graphene. The Gd atoms (orange) sit between the topmost Si atoms of the substrate (red) and the graphene monolayer (grey). The size of the unit cell increases from  $(13 \times 13)$  units of graphene (blue) to  $(13\sqrt{3} \times 13\sqrt{3})$ R30° units of graphene (yellow) for the whole sample system of substrate, Gd atoms, and graphene. (c) is adapted from the dissertation of S. Link, one of our collaborators on this project at MPI Stuttgart [255].

and iron-based [256] superconductors, organic superconductors [257], and heavy fermion compounds [258]. Understanding the manifold of quantum phases and their interplay is often complicated by equally complex chemical and structural properties. Hence, a search for new platforms for correlated electron physics is mandated. Graphene, a two-dimensional honeycomb layer of carbon atoms, is one of the most widely studied materials over the past 15 years [1, 2] and has recently emerged as a prime candidate after the reported discovery of a Mott insulating phase [83] and unconventional superconductivity [74] in bilayer graphene. It was proposed that when the two graphene layers are twisted with respect to each other by the so called "magic angle", flat bands close to the Fermi level lead to the en-

hancement of electronic correlations. An alternative approach to realize flat bands in graphene is large electronic doping up to the M point, where the Dirac dispersions of two neighbouring K points meet (see Fig. 4.1b).

Exploiting this route, we investigate a new material based on intercalated epitaxial graphene on SiC [57]. The samples were grown on commercial 6H-SiC wafers. The substrates were hydrogen-etched prior to the growth under argon atmosphere. Details are described by S. Forti and U. Starke [227]. Gadolinium is deposited from an electron-beam evaporator while the samples are held at  $600^{\circ}$ C. The samples are subsequently flashed to  $1000^{\circ}$ C to complete the intercalation process. Samples are characterized by low energy electron beam diffraction (LEED), low energy electron microscopy (LEEM), and X-ray photoelectron spectroscopy (XPS) (for details see dissertation of S. Link, one of our collaborators on this project at MPI Stuttgart [255]). For ex-situ experiments, the samples are capped with a thin bismuth layer to prevent oxidation. The cap can be removed by annealing the samples in ultra-high vacuum (UHV). Using gadolinium as an ordered intercalant, we are able to induce the required doping levels. A single layer of Gd atoms arranged in a triangular lattice sits between the topmost Si atoms of the SiC(0001) substrate below and the monolayer graphene on top. The structure leads to an enlarged unit cell, covering  $(13\sqrt{3} \times 13\sqrt{3})R30^{\circ}$  graphene unit cells, as determined from LEED measurements [255] and illustrated in Fig. 4.1c. LEED images allow the determination of the sample quality, orientation, and atomic structure.

Angle-resolved photoemission spectroscopy (ARPES) has proven to be a powerful tool for the study of novel quantum materials and their intertwined phase diagrams [102, 103]. We use ARPES to directly visualize the electronic band structure of our material close to the Fermi level. Experiments with He I photons (21.2 eV) were performed at UBC in a ultra-high vacuum chamber equipped with a SPECS Phoibos 150 analyzer with optimal resolutions of  $\Delta E = 6$  meV and  $\Delta k = 0.01 \text{ Å}^{-1}$  in energy and momentum, respectively, at a base pressure of better than  $p = 7 \times 10^{-11}$  Torr. Photons were provided by a SPECS UVS300 monochromatized gas discharge lamp. Our homebuilt six-axis cryogenic manipulator allows for measurements between 300 K and 3.5 K. The samples were annealed at  $600^{\circ}$ C for about 2 h at  $p = 1 \times 10^{-9}$  Torr and then at 500°C for about 10 h at  $p = 5 \times 10^{-10}$  Torr immediately before the ARPES measurements. Experimental



Figure 4.2: Electronic structure measured with angle-resolved photoemission spectroscopy (ARPES). (a) Symmetrized Fermi surface (FS) measured with He I photons (21.2 eV). (b) ARPES cut through the Dirac point as indicated by the yellow line. The Dirac point is shifted to a binding energy of about -1.6 eV due to the electron doping of the intercalated Gd atoms. (c) ARPES cut along the KMK direction as indicated by the yellow line. Around the M point the experiment reveals are remarkably flat dispersion, not expected by a nearest-neighbour tight-binding calculation (green), where the band position was shifted down in energy to reflect highly doped pristine monolayer graphene. (d) Schematic illustration of the FS evolution for graphene as a function increased electron doping. Starting with two circular electron pockets centered at the corners of the Brillouin zone (BZ) (top), increased doping leads to trigonal warping (middle). Further doping induces a Lifshitz transition of the FS topology to a single hole pocket centered around the center of the BZ (bottom). Panels (b) - (d) were adapted from the dissertation of S. Link, one of our collaborators for this project in the group of U. Starke at MPI Stuttgart [255].

data shown in Figs. 4.2b+c were acquired at the I4 beamline at the MAX III synchrotron facility in Lund, Sweden (for details on these measurements see [255]).

Looking at the Fermi surface (FS) for graphene with increasing electron doping, one expects two circular electron pockets centered on the K points of the Brillouin zone (BZ) which show triangular warping as the electron density increases. Finally, at the Lifshitz transition, the two pockets merge and the FS topology changes to a single hole pocket centered on the  $\Gamma$  point of the BZ. This is illustrated in Fig. 4.2d. The ARPES data show, that it is possible to reach the required doping levels in monolayer graphene through the intercalation of gadolinium (Figs. 4.2a–c). The FS shows the expected triangular warping and merging of the two electron pockets.

Note that for He I photons (21.2 eV) (Fig. 4.2a) the spectral weight at the M point is suppressed because of matrix element effects. The temperature dependent data taken at the M point in Fig. 4.12 shows that there is indeed spectral weight at this point and the two electron pockets are merging and are starting to form a single hole pocket. In addition, data taken by our collaborators at MPI Stuttgart [255] at a synchrotron facility with variable photon energy (Fig. 4.2c) show more clearly that the dispersions from neighbouring K points are touching. The Dirac point is shifted down to a binding energy of about 1.7 eV (Fig. 4.2b). Around the M point, the measurements reveal a flat band at the Fermi level, strongly renormalized from the calculated dispersion for highly doped pristine graphene (Fig. 4.2c). Such a behaviour has been observed before in graphene samples doped with calcium and potassium and was attributed to the proximity of the Van Hove singularity to the Fermi level in combination with many-body interactions [65]. More recently this was also reported for graphene samples on iridium substrates doped with caesium [259]. Here the importance of band folding and hybridization in the system was stressed.

Compared to the tight-binding calculation, quadratic fits show an enhancement of the effective mass of the charge carriers by about a factor of 30 ( $m_{KMK}^* \approx 24 m_0$ ) along the KMK direction, while perpendicular to that along the  $\Gamma M\Gamma$  direction, the effective mass remains almost unchanged  $(m^*_{\Gamma M \Gamma} \approx 0.2 m_0)$  (see Fig. 4.3). To determine the effective mass of charge carriers around the M point, the band dispersion as measured by ARPES can be used (compare Fig. 4.2c). Energy distribution curves (EDCs) are fitted to extract the position of the band along both the KMK and the  $\Gamma M \Gamma$  directions. To allow the comparison between the two high symmetry directions, the "replica" band, which resides about 0.25 eV below the Fermi level, was used. The bands are then fitted to a quadratic function, which gives access to the curvature of the bands and thus the effective carrier mass via the relation  $m_{eff} = \hbar^2 / \left| \frac{\partial^2 E}{\partial t^2} \right|$  (see Fig. 4.3). This yields an effective mass for the hole-like carriers along KMK of  $(24.2 \pm 1.1) m_0$  and an effective mass for the electron-like carriers along  $\Gamma M \Gamma$  of  $(0.20 \pm 0.02) m_0$ . Note that we are comparing the absolute values of the effective masses. Because of the curvature of the bands for electrons and holes one expects a positive value for the effective mass of electrons and a negative value for the effective mass of holes. The errors are determined from the



**Figure 4.3:** Analysis of the effective mass of the charge carriers. (a) Band dispersion along the KMK direction around the M point (indicated by the green line in the schematic Brillouin zone) as determined from fits to energy distribution curves (EDCs). The data points are fitted to a quadratic function (red) to extract the effective band mass. (b) Band dispersion along the  $\Gamma M\Gamma$  direction around the M point (indicated by the green line in the schematic Brillouin zone) as determined from fits to EDCs. The data points are fitted to a quadratic function (red) to extract the effective band mass. The "replica" band about 0.25 eV below the Fermi level (compare Fig. 4.2c above) was used for the analysis to allow the comparison between both high symmetry directions.

uncertainties of the quadratic fit to the band dispersion. These values can be compared to the tight-binding model for pristine graphene. The next-nearest neighbour model predicts carrier masses of  $0.24 m_0$  along  $\Gamma M\Gamma$  and  $0.73 m_0$  along KMK. Hence, a mass enhancement of roughly a factor of 30 is experimentally observed along KMK, while along  $\Gamma M\Gamma$  the effective mass remains mostly unchanged compared to the theoretical prediction. This creates a highly anisotropic picture with heavy hole-like carriers along KMK and comparatively light electron-like carriers along  $\Gamma M\Gamma$ .

The area of the Fermi surface  $(A_{FS})$  can be set in relation to the area of the Brillouin zone  $(A_{BZ})$  to obtain information about the number of charge carriers per unit cell  $(N_{uc})$  using the equation  $N_{uc} = 2 \cdot \frac{A_{FS}}{A_{BZ}}$ . The factor of two arises from the spin degeneracy of the bands in graphene. We are using the area of the graphene Brillouin zone as reference, so that the resulting number of electrons is calculated per graphene unit cell. Luttinger's theorem [260] thereby guarantees that the area of the Fermi surface is conserved even under the influence of the many-body interactions present in the sample systems. We extract the carrier density in the system to  $(5.1\pm2.0) \times 10^{14} \text{ cm}^{-2}$ . This number is also supported by transport measurements by our collaborators in the groups of U. Starke and J. Smet at MPI Stuttgart who measured the Hall resistance of the samples as a function of magnetic field. This corresponds to a doping of  $0.8\pm0.2$  electrons per Gd atom, agreeing well with the expectation that two electrons per Gd atom are needed to saturate the dangling Si bonds of the substrate to establish a quasi-freestanding monolayer of graphene [60].

Hence, gadolinium is in the Gd<sup>3+</sup> configuration, leaving the half-filled *f*-orbitals as the only open shell. In combination with the well-known Coulomb repulsion of the *f*-electrons in gadolinium leading to a split of the *f*-bands [261, 262], this naturally explains the lack of Gd states in the ARPES data around the Fermi energy. The described picture is supported by synchrotron photoemission measurements by our collaborators in the group of U. Starke at MPI Stuttgart [255]. Their experiment allows the identification of the Gd lower Hubbard *f*-states through a highly photon energy-dependent photoemission cross-section [263]. The data show spectral weight around the expected 9 eV binding energy, which exhibits a strong resonance enhancement across a Gd absorption edge (Gd  $N_5$  edge around 150 eV) [255].

After describing the electronic structure of the material, we now turn to the possible ordering phenomena of the intercalated gadolinium atoms. Resonant energyintegrated X-ray scattering (REXS) has been an invaluable tool in elucidating emerging ordering phenomena in a range of materials with high sensitivity and chemical selectivity [144, 161]. Our experiments were performed at the resonant soft X-ray scattering (RSXS) endstation of the REIXS beamline of the Canadian Light Source in Saskatoon. The photon energy can be changed from 100 eV to 2500 eV with an energy resolution  $E/\Delta E > 5000$ . The endstation is equipped with a 10-motion ultra-high vacuum diffractometer and a closed-cycle cryostat for variable sample temperatures from 22 K to 380 K. The pressure during experiments is better than  $p = 5 \times 10^{-10}$  Torr. Samples were annealed *in situ* to about 500°C for 8 h immediately before the experiments. Samples were aligned using a SiC substrate Bragg diffraction spot *in situ* and low energy electron diffraction (LEED) measurements during sample growth. Despite our material only containing a single atomic layer



Figure 4.4: Ordering phenomena revealed by resonant energy integrated Xray scattering (REXS). (a) Photon energy-dependent X-ray absorption at the Gadolinium  $M_{4/5}$  edge. Both transitions  $(3d_{5/2} \text{ and } 3d_{3/2})$  are clearly visible, despite the material incorporating only a single layer of Gd atoms. (b) Momentumresolved measurements along the graphene direction on resonance (red) and off resonance (blue and green) reveal a Gd ordering vector around 0.07  $\text{\AA}^{-1}$  (red star). The inset shows the same data with the background removed. The photon energies for the three scans are indicated by red, green, and blue circles respectively in panel (a). (c) Temperature-dependent measurements of the Gd ordering vector show a strong stability against thermal fluctuations. (d) REXS intensity as a function of in-plane momentum resonant to the Gd  $M_5$  edge. The data has been interpolated and symmetrized based on 41 slices taken in a range of about  $120^{\circ}$ . (e) Resonance map across the Gd  $M_5$  edge for two prominent features along the negative  $k_x$  direction. A strong resonance enhancement for both peaks is evident. (f) Comparison of the experimental resonance behavior of the peak indicated by the white box in panel (e) after background subtraction (black) to the expected behavior for a small periodic modulation of the Gd lattice positions (red).



**Figure 4.5: Fitting of peaks in the parallel momentum plane.** Ordering vectors extracted from the in-plane momentum REXS map in Fig. 4.4d. Each measured slice from the REXS experiment is fitted to a background and Gaussian peaks. From there, the peak positions, intensities, and widths can be read out. Peak intensities are represented by the size of the circles and different colours correspond to the peak widths.

of Gd, we can clearly identify the resonant  $M_{4/5}$  edge around 1200 eV photon energy (Fig. 4.4a). Along the graphene direction, e.g. the direction along which the structural graphene Bragg peak would be expected at higher momentum, we resolve an ordering peak resonant to the Gd edge (Fig. 4.4b). This feature is surprisingly stable up to 380 K (see Fig. 4.4c). The coherence length of the phase can be estimated by computing the inverse half width at half maximum of the peak [151] and comes out to  $(72.5 \pm 2.6)$  Å. To obtain a full picture of momentum space - as far as it is accessible with the given photon energy at the gadolinium resonance – we rotate the sample in small increments to measure slices along different directions in the parallel momentum plane. The results are summarized in 4.4d. We are able to reveal a number of ordering phases, which mostly follow the expected  $60^{\circ}$  or  $120^{\circ}$  symmetry. After a background subtraction, the features can be fitted with Gaussians to extract their position, width, and intensity. The results are summarized in Fig. 4.5. We note that the photon energy at the Gd  $M_{4/5}$  edge limits us to about  $1 \text{ Å}^{-1}$  in momentum space. The experiment is therefore more suitable for longer wavelength orders, which in turn appear at small momenta in scattering experiments. For comparison the  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  superstructure observed with LEED [255] corresponds to a scattering vector length of  $1.7 \text{ Å}^{-1}$  and is thus not detectable in our X-ray scattering experiments.

To gain insight into the origin of the observed ordering vectors, we measure detailed resonance maps across the gadolinium M<sub>5</sub> edge (see Fig. 4.4e). The extracted photon energy-dependent resonant scattering behaviour can then be compared to calculated scattering factors based on parameters from the X-ray absorption spectroscopy data. For a theoretical description of the resonance behavior of the observed REXS features, we use the software package Quanty [264–266]. It allows modelling of the 3*d* to 4*f* transition at the Gd  $M_{4/5}$  edge including all relevant spin-orbit and multipole Coulomb interactions. In a first step, the model parameters are optimized to match the results of the X-ray absorption spectroscopy (XAS) data (see Fig. 4.6a). Using these parameters, the full complex isotropic ( $f^0$ ) and magnetic ( $f^1$ ) scattering factors can be calculated (see Fig. 4.6b). Note that the imaginary part of  $f^0$  is the XAS signal. In a final step, the scattering factors are used to compute the energy-dependent resonant scattering for different ordering phenomena (see Fig. 4.7). We compare magnetic ordering ( $I(E_{in}) \propto |f^1(E_{in})|^2$ ),



Figure 4.6: Theoretical description of the X-ray absorption spectroscopy (XAS) signal at the Gd  $M_{4/5}$  edge. (a) The parameters of the model (red) are optimized to match the experimental data (black). (b) Using the parameters from (a), the real (black) and imaginary (red) parts of the isotropic ( $f^0$ ) and magnetic ( $f^1$ ) scattering factors can be calculated.

charge ordering  $(I(E_{in}) \propto |f^0(E_{in} - \Delta E) - f^0(E_{in} + \Delta E)|^2)$ , and a small periodic modulation of the lattice  $(I(E_{in}) \propto |f^0(E_{in})|^2)$  [267]. The experimental data clearly agrees best with the lattice modulation (see Fig. 4.4f and Fig. 4.7). We note that the emergence of density wave orders is usually accompanied by such a modulation [268–270] and that the charge response might be covered by the lattice response of *f*-electrons close to the atomic core. Hence, we observe signatures of density wave type orders in the material.

Further evidence for the possibility of density wave order comes from the polarization dependence of the resonant signal (see Fig. 4.8). The signal is strong



Figure 4.7: Energy-dependent resonant scattering at the gadolinium  $M_5$  edge for different ordering phenomena based on the complex scattering factors from Fig. 4.6. (a) Comparison of experimental data (black) to theory based on magnetic ordering (red). (b) Comparison of experimental data (black) to theory based on charge ordering (red). (c) Comparison of experimental data (black) to theory based on a small periodic lattice modulation (red).



**Figure 4.8: Polarization dependence of REXS signal.** The observed peaks resonant to the Gd edge show a strong dependence on the incident photon polarization. The light comes in at a grazing angle of  $15^{\circ}$ , so that the linear vertically polarized photons (red) are mostly oriented in the sample plane, while the linear horizontally polarized photons (blue) are mostly oriented out of the sample plane.

for incident photons with a polarization alignment in the sample plane, while it is mostly suppressed for photons with a polarization aligned out of the sample plane. This is similar to what has been observed for density wave phases in the cuprate superconductors [271]. We note that up to now we were only able to analyze the resonance behaviour and hence the scattering origin of the single peak shown above. One could argue that the similar temperature dependence of peaks hints at the same scattering origin, but a more extensive analysis in future experiments seems mandated.

Next, we briefly discuss the magnetic properties of Gd-intercalated graphene. Applying Hund's rules to the  $Gd^{3+}$  configuration leads to a  ${}^8S_{7/2}$  ground state with zero orbital momentum and a 7/2-spin magnetic moment. Our collaborators at MPI Stuttgart have measured the magnetization of the gadolinium intercalated graphene samples to look into the possibility of an ordering of the magnetic moments [255]. The material shows no magnetization at zero magnetic field, excluding a simple ferromagnetic picture. Note that bulk gadolinium enters a ferromagnetic phase around room temperature [272]. For large magnetic fields the magnetization per atom approaches  $7 \mu_B$ , consistent with the Gd<sup>3+</sup> picture. Further, the magnetization is positive for positive magnetic fields and negative for negative magnetic fields, which indicates that the material is not dominated by diamagnetic interactions. For an ideal paramagnet, the magnetization is expected to follow the Brillouin function instead. The experimental magnetization – measured at a temperature of 2K – does not follow the Brillouin function at 2 K. This could indicate that an interaction between the Gd magnetic moments is present, hindering the atomic moments from aligning in the external magnetic field. But it should be noted that an ordered phase might have a short coherence length with fluctuating character. We also note that an identical magnetization curve was measured for two different angles of incidence for the X-ray magnetic circular dichroism (XMCD) measurements [255]. Finally, we have to keep in mind that the gadolinium atoms sit on a triangular lattice (compare Fig. 4.1c), and thus a highly degenerate magnetic ground state due to frustration of the spin moments has to be considered.

One possibility to resolve the frustration of a triangular lattice is a Heisenbergtype spin ordering. Instead of two distinct spin orientations (up and down) in a simple antiferromagnetic order, this model incorporates three different spin orien-



**Figure 4.9:** Possible model of antiferromagnetic order in Gd-intercalated graphene. (a) Heisenberg-type ordering with three different spin orientations (blue, red, and yellow) of the Gd unit cell including graphene and the SiC substrate. The original unit cell is indicated in dashed yellow, the unit cell with the additional magnetic order in dashed purple. (b) Possibility for the alignment of each Gd magnetic moment within a unit cell. The in-plane orientation of the spins is colour-coded and shown here for a spin-up cell (red) as shown in (a). (c) The vortex-like structure leads to a finite out-of-plane spin component. The simplest possibility for this component is shown here with positive out-of-plane spin in red and negative out-of-plane spin in blue.

tations (each 120° offset from the next one). Applying the Heisenberg model to the unit cells of Gd-intercalated graphene is illustrated in Fig. 4.9a. Here the large unit cells are ordered in the 120° pattern instead of individual atoms. One possibility for the alignment of the Gd spins within a cell is depicted in Fig. 4.9)b for the in-plane component and in Fig. 4.9)c for the out-of-plane component. The pattern resembles the vortex-like structure of skyrmions, which have been predicted and observed in other condensed matter systems [273–278]. We stress that the shown model is only one possibility of a magnetic order on a triangular lattice and the detailed spin configuration of the Gd moments is presently not known. Finally, looking at the momentum distribution of some peaks in Fig. 4.4d and Fig. 4.5, a large radial extension in the parallel momentum plane is observed. A similar behaviour with a glass-like state has recently been discussed in terms of an antiferromagnetic phase transition in a cuprate superconductor sample system [279].

The next question is, which quantum phases can be induced as a result of a possible coupling between the flat-band electrons in graphene and the ordering phenomena of the intercalated Gd atoms? A natural starting point is the crossings between the original FS and the reconstructed FS due to the Gd order. This is illustrated for the tight-binding-based band dispersion for highly-doped pristine graphene in Fig. 4.10a. Note, for simplicity we are limiting ourselves here to the case of next nearest neighbour hopping terms in graphene. For a complete description of the band structure additional terms can be considered, e.g. next nearest neighbour hopping terms in graphene or terms describing the interaction with the gadolinium atoms and the substrate. For this purpose we only consider the ordering vector with longest coherence length (see Figs. 4.4b+c), as we expect this feature to have the most pronounced impact on the band dispersion as measured with photoemission. The ordering vector is short compared to the size of the graphene BZ, but it is apparent that the crossings appear along the  $\Gamma K$  high-symmetry directions (see Fig. 4.10a). Looking at the symmetrized ARPES energy distribution curves along this direction (Fig. 4.10b), we observe a temperature dependent gap. The symmetrization of the data facilitates the visualization of gap features, as it removes the effects of the temperature dependent Fermi cut-off (see Fig. 4.13). The spectral intensity does not vanish completely inside the gap and no sharp quasi-particle peaks are visible. Hence, the feature is best described as a pseudogap. The mo-



**Figure 4.10: Band folding in Gd-intercalated graphene.** (a) Band folding for graphene and the ordering vector with the longest coherence length as detected by our REXS measurements. Tight-binding calculated Fermi surface (FS) for highly-doped pristine graphene in red and folded bands in dashed blue. The bands cross along the  $\Gamma$ K direction as indicated by the arrows. The inset shows a close up look of the  $\Gamma$ K direction. (b) ARPES measurements along the  $\Gamma$ K direction as a function of temperature. The symmetrized energy dispersion curves reveal as pseudogap stable up to room temperature. (c) FS with overlaid prominent scattering vectors as shown in Fig. 4.4d in red, green, blue, and yellow, respectively. The red arrows connect non-equivalent points on the FS from the M point to the  $\Gamma$ K direction.



**Figure 4.11: Pseudogap anisotropy at room temperature.** In agreement with the prediction from the band folding, the pseudogap is mostly centered around the  $\Gamma K$  direction. The data was taken at 300 K with measurements between the  $\Gamma M$  and  $\Gamma K$  directions (indicated by the red area in the schematic BZ in the corner). The data was then symmetrized.



**Figure 4.12: Pseudogap at the M point.** Symmetrized ARPES energy distribution curves (EDCs) at the M point show no pseudogap at 300 K. At lower temperatures, a pseudogap also opens up here.
mentum distribution of the gap is shown in Fig. 4.11. The largest pseudogaps are found around the  $\Gamma$ K direction, as expected from the simple band folding model. This hints at a situation where the potential induced by the gadolinium ordering is not strong enough to induce measurable spectral weight on the folded bands, but nevertheless a finite coupling leads to the opening of a hybridization gap at the crossing points with the original bands, which is then observable in photoemission. The data was taken at 300 K. Going to lower temperatures, the picture changes and we observe a pseudogap at the M point as well (see Fig. 4.12). This is not unexpected, as our model is based only on the scattering vector with the longest coherence length and hence presumably the greatest impact on the electronic dispersion. When the temperature is reduced, the coupling to other scattering vectors (compare Fig. 4.4) cannot be ignored and the band folding model becomes appreciably more complicated with band crossings at various points of the Brillouin zone.

Next, we superimpose the prominent scattering vectors found in our REXS data on the FS of our material as determined with ARPES (Fig. 4.10c). The majority of the vectors (yellow, green, blue) connect equivalent points on the FS, but one vector along the SiC direction (red) connects the dispersion along  $\Gamma K$  and the M point of two neighboring BZs. This could be connected to the suppression of spectral weight around the M point in the photoemission data. We note here that none of the vectors satisfies a nesting condition of the FS, a property that has been discussed extensively for various materials [280–283].

Lastly, we want to look more closely at the prominent kink feature around 250 meV binding energy in the ARPES measurements that connects to a "replica" band along the KMK direction (see Figs. 4.2b+c). A close up ARPES data set taken roughly along the KMK direction is shown in Fig. 4.14a. The data clearly shows the anticrossing of two branches in the electronic dispersion. The energy distribution curves (EDCs) can be fitted with two peaks to gain more insight (see Fig. 4.14). The results are summarized in Fig. 4.15. Looking at the peak positions, we can identify the two branches of the dispersion that asymptotically approach a binding energy value of about 230 meV on either side of the crossing (see Fig. 4.15a). The widths and areas of the two peaks show a similar complementary behaviour for the upper and lower branches and indicate a shift of spectral weight from one branch to the other across the kink as observed in the ARPES measurements (see



**Figure 4.13: Symmetrization of photoemission data.** An energy dispersion curve measured with photoemission on polycrystalline gold at a temperature of about 10 K is shown (red circles). Photoemission only measures occupied states, hence a Fermi cut-off is visible. For the shown data the Fermi level lies at about 16.85 eV kinetic energy. A Fermi function is fitted to the data around the cut-off for illustration (blue). For symmetrization the data are first mirrored with respect to the Fermi energy (red triangles for the data and grey line for the Fermi fit) and then the original data and the mirrored data are added (solid red diamonds for the data and black line for the Fermi functions). The sum of the two Fermi functions is just a flat line and polycrystalline gold is a simple metal and thus does not show any gap features at the Fermi level.

Figs. 4.15b+c). Now the questions is: what is the underlying physics causing the apparent anticrossing? The two obvious candidates are coupling to a bosonic mode (e.g. a phonon mode) and the band folding discussed above.

First, we look at the possibility of an interaction between a phonon mode and the electronic dispersion of graphene. Kink features in graphene have already been discussed extensively in terms of electron-phonon coupling in the past and the optical phonon mode around 250 meV is known to couple strongly to the electrons in various graphene sample systems [62, 66, 284, 285]. Also the effects of so-



**Figure 4.14: Fitting of energy distribution curves (EDCs) around ARPES kink feature.** (a) Close up ARPES map of the kink feature along the KMK direction (compare 4.2b and 4.2c). The Fermi level is indicated by the dashed white line. (b) EDCs extracted from (a) are fitted to two peaks and a background (red lines). The range of the fits is indicated by the length of the red lines and excludes the Fermi cut-off. A clear anticrossing is observed.



**Figure 4.15: Fitting results of the energy distribution curves (EDCs) around the ARPES kink feature.** (a) Position of the two Gaussian peaks for different EDCs. The lower branch is shown in red and the upper branch in black. Both branches asymptotically approach a binding energy value of about 230 meV (dashed blue line) for higher or lower momenta away from the kink respectively. (b) Widths of the two peaks around the kink feature, with the upper branch in black and the lower branch in red. (c) The areas of the two peaks around the kink feature show a shift of spectral weight from one branch to the other across the anticrossing. The upper branch is shown in black and the lower branch in red.



**Figure 4.16: Simulation of coupling to a mode.** (a)–(c) Simulation of the crossing of two modes. The linear dispersion (red) could, for example, be the electronic dispersion of graphene. The flat mode (red) could stand for an optical phonon mode of graphene. (a) No coupling between the modes. (b) Coupling of 0.02 eV between the two modes. (c) Coupling of 0.05 eV between the two modes. (c)–(f) Same dispersions as in (a)–(c), but with a Gaussian broadening to indicate a finite lifetime of the modes and resolution effects. (g)–(i) Same dispersions and coupling constants, but projected only on the linear dispersing (electronic) mode. This could represent a simple model for a possible ARPES measurement.

called "replica" bands in ARPES due to strong electron-phonon coupling have been observed, especially in SrTiO<sub>3</sub> based structures [286, 287], while they were controversial in highly-doped graphene samples [65, 288]. To simulate the effect of a coupling between electrons and phonons, we employ a simple model with a linearly dispersing band representing the electrons and a flat band representing an optical phonon mode (see Fig. 4.16). If we now increase the coupling between the two modes by adjusting the off-diagonal elements in the Hamiltonian, we observe two effects. Firstly, with increasing coupling, an increasing gap at the point of crossing

between the two bands is observed (see Figs. 4.16a–c). Secondly, with increasing coupling, there is an increased intermixing between the phonon and electron character of the system around the crossing point. Since ARPES is only sensitive to the electronic part of the spectrum, we can project the eigenvectors of the system onto the electronic character only, to obtain a better representation of a possible ARPES measurement (see Figs. 4.16g–i). We see that for the right choice of coupling strength, we can indeed simulate the expected kink feature (Fig. 4.16h). It should be noted that especially for larger couplings, our simple model breaks down and more sophisticated calculations have to be conducted [289, 290]. They lead to the appearance of higher harmonics for the phonon excitations, which have also been observed experimentally [287]. Our ARPES data on Gd-intercalated graphene shows no signs of such multi-phonon excitations.

As a second possibility, we look at the band folding as an origin of the replica band and anticrossing in the ARPES data. We start with the band structure for pristine graphene from a tight binding model (Fig. 4.17a). An iso-energy contour can be selected that resembles the Fermi surface of Gd-intercalated graphene, justifying the choice of a band structure based on pristine graphene as a starting point (Fig. 4.17b). Now we apply the band folding based on the REXS data as already described above (compare Fig. 4.10a), leading to a total of seven modes in the system (the original band plus six scattered bands). Due to the comparatively short scattering vector and hence close proximity of all bands, a finite coupling leads to a strong intermixing of the original band dispersion onto all modes. This is illustrated in Figs. 4.17c–i. The results of the band folding for both high-symmetry directions KMK and K $\Gamma$ K are shown in Figs. 4.18a+b without coupling and in Figs. 4.18c+d with a coupling of 30 meV. The folding model can indeed produce a "replica" band around the M point as well as shift spectral weight between different modes as observed with ARPES (see Fig. 4.18c).

Between the high-symmetry points K, M, and  $\Gamma$  the dispersions of all modes run basically in parallel and are hard to distinguish for finite couplings. In an attempt to find signatures of the modes, we conduct a linewidth analysis of momentum distribution curves (MDCs) along the  $\Gamma$ K direction (see Fig. 4.19). Fitting the MDCs to a single Lorentzian reveals additional spectral weight on either side of the "main" band (see Fig. 4.19a). This offset is systematic and and present along



Figure 4.17: Simulation of band folding in Gd-intercalated graphene. (a) Isoenergy contours from a tight-binding model for pristine graphene. (b) A contour is selected that most closely represents the doping level (Fermi surface) in Gdintercalated graphene. (c)–(i) The bands are folded according to the measured REXS scattering vector (see 4.4c and 4.10a) with a six-fold symmetry. For a finite coupling (here 0.03 eV) the character of the original band gets mixed with the folded bands. The amount of character of the graphene dispersion is shown as color plots for the original band (c) and the folded bands (d)–(i), indicating a strong intermixing even for moderate couplings.



**Figure 4.18:** Results of simulation of band folding in Gd-intercalated graphene. (a) Original band dispersion for pristine graphene from a tight-binding model along the KMK direction (red) and folded bands (blue) without coupling. (b) Original band dispersion for pristine graphene from a tight-binding model along the K $\Gamma$ K direction (red) and folded bands (blue) without coupling. (c) Same dispersion as in (a), but with a finite coupling of 0.03 eV and a Gaussian broadening. (d) Same dispersion as in (b), but with a finite coupling of 0.03 eV and a Gaussian broadening.

the whole analysis window (see Fig. 4.19b). Fitting the MDCs to three Lorentzian peaks (see Fig. 4.19c) captures the additional spectral weight. Thus, this could be taken as further evidence for the band folding model. It should be noted that the folding model also leads to a splitting of the bands around the K points (see Figs. 4.18c+d). This is not visible in the ARPES measurements, possibly due to the large binding energy of the Dirac point and hence energetic distance to the Fermi level.



**Figure 4.19:** Analysis of Lorentzian line fits to momentum distribution curves (MDCs). (a) Exemplary MDC fitted to a constant background and a single Lorentzian (green). The fit underestimates the dispersion on either side of the peak. (b) Difference of the experimental MDCs along the  $\Gamma$ K direction and fits with a single Lorentzian peak. The fit systematically deviates from the experimental data. (c) When the MDCs are fitted to three instead of one Lorentzian, the additional spectral weight on either side of the main peak is captured, indicating the possibility of additional bands dispersing parallel to the original one as predicted by the band folding simulation.

In summary, we found good arguments for either possibility for the kink feature and "replica" band observed in the ARPES data. While a definite distinction cannot be made at this point, it may be worth putting forward the idea of a feedback between both mechanisms. This way, the energy scale set by the phonon mode – coupling to the electronic degrees of freedom – would make the system susceptible and would feed back to ordering phenomena and their scattering vectors.

Concluding, we have investigated a novel quantum material playground combining flat bands in graphene coupled to an ordered lattice of intercalated gadolinium atoms. We observe an interplay of quantum phases at temperatures above 300 K in a purely two-dimensional and wafer-scale material. Our results strongly hint at an intimate relationship between the observation of a pseudogap in photoemission and ordering phenomena detected by resonant X-ray scattering, shedding new light on the vastly important field of correlated electron systems outside the scope of Mott physics. We expect the material system to play an important role in the study of highly-doped graphene, which has already been extensively discussed theoretically in terms of spin and charge density wave orders as well as unconventional superconductivity in proximity to the Van Hove singularity [81, 291, 292]



**Figure 4.20: Predicted phase diagram for highly-doped graphene.** Predicted phase diagram of highly-doped graphene as calculated by the authors of [291]. Around the Van Hove singularity, a competition between unconventional superconductivity and a spin-density wave order is expected as function of electronic doping.

(see Fig. 4.20). Comparing the experimental findings on gadolinium intercalated graphene so far with the proposed phase diagram for highly-doped graphene it appears that we can indeed reach the required doping levels to reach the Van Hove singularity at the M point of the dispersion in graphene. In the phase diagram, this would put us in a regime where a spin density wave should be the dominating order parameter (yellow region in Fig. 4.20). We find evidence for density wave orders in our X-ray scattering experiments, but it should be noted that the calculations were done for pristine graphene and especially the X-ray scattering technique is most sensitive to the gadolinium atoms. Nevertheless, combing all the experimental evidence it might be fruitful to think about future experiments that allow the tuning of the chemical potential around the Van Hove singularity to search for possible superconducting regions in the phase diagram. This could for example be attempted by the deposition of additional atoms or by back gating the samples. We also want to stress the prospect of adding magnetic interactions to the growing field of flat bands in graphene.

## Chapter 5

## **Conclusion and outlook**

We have shown that monolayer graphene can provide a two-dimensional platform for the design and investigation of novel and emergent quantum phases. The sample systems are chemically simple, clean, and non-toxic. The presented examples in this thesis display quantum phenomena on a wafer-scale platform up to room temperature, which can facilitate the future exploitation of the observed effects in devices and applications.

In the first example, we utilize heteroepitaxial strain between graphene and the supporting SiC substrate to induce pseudomagnetic fields. These fields are unique for linearly dispersing Dirac electrons and arise only for certain strain geometries. The homogeneity of the pseudomagnetic field allows us to observe the pseudoquantum Hall effect with its Landau level quantization using angle-resolved photoemission spectroscopy (ARPES). Additionally, the peculiar behavior of the zeroth Landau level gives us new insight into the sublattice symmetry breaking Semenoff mass term in the graphene on SiC sample system.

In the second example, we show that through the intercalation of gadolinium atoms between the SiC substrate and the monolayer graphene, we can achieve the ultra-high doping levels required to reach the Van Hove singularity at the M point of the dispersion. Here a transition of the Fermi surface topology from two electron pockets to a single hole pocket takes place and a strong renormalization from the expected band structure due to electronic correlations is observed. The temperature- and momentum-dependent pseudogap detected with ARPES can be connected to ordering phenomena as determined by resonant energy-integrated Xray scattering (REXS). The possibility of adding magnetic properties to the field of flat bands in graphene is discussed.

Looking ahead to future potential experimental and theoretical research directions using graphene as a versatile design platform with a range of available control parameters, a number of possibilities appear feasible. A more tunable approach for the creation of different strain patterns (magnitude as well as geometry), either through optimization of the growth process or top-down techniques, would enable further studies in the area of pseudomagnetic fields. On top of that, strain has also been discussed in terms of an enhancement of electron-phonon coupling and possible resulting superconductivity [293–295]. For the gadolinium-intercalated graphene samples, a further study of the phononic interactions with the observed ordering phenomena and a possible connection to the magnetic properties of the sample system would be beneficial. Here, theoretical efforts are hindered by the computational cost of the large unit cell, but resonant inelastic X-ray scattering (RIXS) experiments could help elucidate the situation. In contrast to its energyintegrated counter part REXS, RIXS also analyzes the energy of the outgoing photon and – in combination with a new generation of high-resolution spectrometers - can distinguish magnetic and lattice excitations and possibly their interactions in the sample [296–300]. It could also be feasible to directly image the spin texture of the sample using spin-polarized tips in scanning probe techniques [301–303].

Going beyond the scope of this thesis, the twist angle between different graphene layers as a control parameter has recently received a lot of attention, following the experimental discovery of correlated electron phases and unconventional superconductivity at so-called "magic" angles [74, 83, 304]. Additionally, at a twist angle of 30° between two graphene layers, the physics of quasicrystals without translational periodicity can be studied [305, 306]. Also, combining the twist angle with other control parameters appears to be a promising direction. Using hydrostatic pressure to change the coupling between two twisted layers can tune the superconducting transition without the need for tedious, precise alignment of the graphene flakes [304]. Twisting can also be combined with the strain-induced pseudomagnetic fields discussed in this thesis. When graphene is rotated with respect to black phosphorus, the resulting Moiré pattern leads to strain that induces pseu-



Figure 5.1: Combining twisting and strain in graphene flakes. (a) Schematic of the measurement set-up showing the STM tip. G and BP represent monolayer graphene and the multilayer black phosphorus flake respectively, SiO<sub>2</sub> is 300 nmthick silicon dioxide, Si is highly-doped silicon and A is the tunnelling current. The graphene is grounded via a Au electrode. A back-gate voltage  $V_g$  is applied through the doped Si electrode. (b) Sketch of graphene on BP showing the emergence of Moiré patterns. The rotation angle  $\theta$  is defined as the angle between the BP zigzag direction and the nearest graphene zigzag direction. (c) dI/dV spectra taken on samples with different twist angles between graphene and black phosphorus. A series of Landau level peaks are visible for all samples with the first Landau level labeled by grey circles. (d) The peak positions are plotted versus  $sgn(N)\sqrt{|N|}$  to show the expected linear behaviour for Landau levels. The slope of the curves and hence the strength of the pseudomagnetic field varies with the twist angle. (e) The strength of the pseudomagnetic field  $(B_S)$  is plotted as a function of the twist angle  $\theta$  between graphene and black phosphorus, showing the tunability of the approach. The figure was adapted from [224].

domagnetic fields in graphene [224]. Depending on the twist angle, the magnitude of the strain and hence the strength of the pseudomagnetic field can be tuned (see Fig. 5.1). Unfortunately, all of these sample systems are currently limited to small graphene flakes and device geometries. This makes it difficult for conventional ARPES with large spot sizes of the incident light to directly measure the electronic band structure. Fortunately, new developments in the ARPES community, based either on synchrotron radiation and focusing zone plates or laser-based systems in which optical setups can be used to reduce the spot size on the sample, can add an additional layer of lateral control to the technique of ARPES [307–309]. These advances could also benefit experiments on graphene nanoribbons. They further add dimensionality as a control knob in graphene and introduce the prospect of tailoring edge states with interesting magnetic and topological properties [67, 68, 87, 88]. Finally, ultra-fast pump-probe setups in combination with ARPES experiments are becoming more widely available. They can be used to study the dynamics of carriers in materials on very short time scales [94, 310, 311], generate and manipulate ultra-fast currents [312, 313], induce or enhance quantum phenomena like superconductivity [314–316], and access new physics like so-called time crystals, limited strictly to non-equilibrium conditions [317]. Exciting times still lie ahead for the platform of graphene and beyond.

## **Bibliography**

- [1] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. The electronic properties of graphene. *Reviews of Modern Physics*, 81(1):109–162, Jan. 2009. doi:10.1103/RevModPhys.81.109. URL https://link.aps.org/doi/10.1103/RevModPhys.81.109. → pages 1, 13, 48, 56, 61, 77
- [2] A. K. Geim and K. S. Novoselov. The rise of graphene. *Nature materials*, 6 (3):183–191, 2007. URL
   http://www.nature.com/nmat/journal/v6/n3/abs/nmat1849.html. → pages 48, 56, 77
- [3] M. J. Allen, V. C. Tung, and R. B. Kaner. Honeycomb Carbon: A Review of Graphene. *Chemical Reviews*, 110(1):132–145, Jan. 2010. ISSN 0009-2665. doi:10.1021/cr900070d. URL https://doi.org/10.1021/cr900070d.
- [4] A. K. Geim. Graphene: Status and Prospects. *Science*, 324(5934): 1530–1534, June 2009. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1158877. URL http://www.sciencemag.org/content/324/5934/1530.
- [5] Y. Barlas, K. Yang, and A. H. MacDonald. Quantum Hall effects in graphene-based two-dimensional electron systems. *Nanotechnology*, 23(5): 052001, 2012. ISSN 0957-4484. doi:10.1088/0957-4484/23/5/052001. URL http://stacks.iop.org/0957-4484/23/i=5/a=052001. → page 1
- [6] R. Peierls. Quelques proprits typiques des corps solides. Annales de l'institut Henri Poincar, 5(3):177–222, 1935. URL http://www.numdam.org/item/?id=AIHP\_1935\_5\_3\_177\_0. → page 1
- [7] L. D. Landau. Zur Theorie der phasenumwandlungen II. *Phys. Z.* Sowjetunion, 11(545):26–35, 1937.  $\rightarrow$  page 1

- [8] J. A. Venables and G. D. T. Spiller. Nucleation and growth of thin films. In Surface Mobilities on Solid Materials, pages 341–404. Springer, 1983. → page 1
- [9] J. W. Evans, P. A. Thiel, and M. C. Bartelt. Morphological evolution during epitaxial thin film growth: Formation of 2d islands and 3d mounds. *Surface Science Reports*, 61(1-2):1–128, 2006. → page 1
- [10] P. R. Wallace. The band theory of graphite. *Physical Review*, 71(9):622, 1947.  $\rightarrow$  pages 1, 4
- [11] J. W. McClure. Diamagnetism of Graphite. *Physical Review*, 104(3): 666–671, Nov. 1956. doi:10.1103/PhysRev.104.666. URL https://link.aps.org/doi/10.1103/PhysRev.104.666.
- [12] J. C. Slonczewski and P. R. Weiss. Band structure of graphite. *Physical Review*, 109(2):272, 1958.  $\rightarrow$  page 1
- [13] G. W. Semenoff. Condensed-Matter Simulation of a Three-Dimensional Anomaly. *Physical Review Letters*, 53(26):2449–2452, Dec. 1984. doi:10.1103/PhysRevLett.53.2449. URL https://link.aps.org/doi/10.1103/PhysRevLett.53.2449. → pages 1, 8, 61, 65
- [14] E. Fradkin. Critical behavior of disordered degenerate semiconductors. II. Spectrum and transport properties in mean-field theory. *Physical review B*, 33(5):3263, 1986.
- [15] F. D. M. Haldane. Model for a quantum Hall effect without Landau levels: Condensed-matter realization of the" parity anomaly". *Physical Review Letters*, 61(18):2015, 1988.  $\rightarrow$  page 1
- [16] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306(5696):666–669, Oct. 2004. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1102896. URL http://science.sciencemag.org/content/306/5696/666. → pages 2, 9
- [17] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America*, 102 (30):10451–10453, July 2005. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.0502848102. URL http://www.pnas.org/content/102/30/10451. → pages 5, 6, 48

- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438(7065):197, Nov. 2005. ISSN 1476-4687. doi:10.1038/nature04233. URL https://www.nature.com/articles/nature04233. → page 9
- [19] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature*, 438 (7065):201–204, Nov. 2005. ISSN 1476-4687. doi:10.1038/nature04235. URL https://www.nature.com/articles/nature04235. → pages 2, 5
- [20] K. Kostarelos and K. S. Novoselov. Graphene devices for life. *Nature Nanotechnology*, 9:744–745, Oct. 2014. ISSN 1748-3395.
   doi:10.1038/nnano.2014.224. URL https://www.nature.com/articles/nnano.2014.224. → page 2
- J.-H. Ahn and B. H. Hong. Graphene for displays that bend. *Nature Nanotechnology*, 9:737–738, Oct. 2014. ISSN 1748-3395. doi:10.1038/nnano.2014.226. URL https://www.nature.com/articles/nnano.2014.226.
- [23] S. Reich, J. Maultzsch, C. Thomsen, and P. Ordejn. Tight-binding description of graphene. *Physical Review B*, 66(3):035412, July 2002. doi:10.1103/PhysRevB.66.035412. URL https://link.aps.org/doi/10.1103/PhysRevB.66.035412. → page 4
- [24] R. B. Laughlin. Quantized Hall conductivity in two dimensions. *Physical Review B*, 23(10):5632–5633, May 1981. doi:10.1103/PhysRevB.23.5632.
   URL https://link.aps.org/doi/10.1103/PhysRevB.23.5632. → page 5
- [25] D. C. Tsui, H. L. Stormer, and A. C. Gossard. Two-Dimensional Magnetotransport in the Extreme Quantum Limit. *Physical Review Letters*, 48(22):1559–1562, May 1982. doi:10.1103/PhysRevLett.48.1559. URL https://link.aps.org/doi/10.1103/PhysRevLett.48.1559.
- [26] R. B. Laughlin. Anomalous Quantum Hall Effect: An Incompressible Quantum Fluid with Fractionally Charged Excitations. *Physical Review Letters*, 50(18):1395–1398, May 1983. doi:10.1103/PhysRevLett.50.1395. URL https://link.aps.org/doi/10.1103/PhysRevLett.50.1395. → page 5

- [27] K. v. Klitzing, G. Dorda, and M. Pepper. New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance. *Physical Review Letters*, 45(6):494–497, Aug. 1980. doi:10.1103/PhysRevLett.45.494. URL https://link.aps.org/doi/10.1103/PhysRevLett.45.494. → pages 5, 48, 49
- [28] S. M. Girvin and A. H. MacDonald. Off-diagonal long-range order, oblique confinement, and the fractional quantum Hall effect. *Physical Review Letters*, 58(12):1252–1255, Mar. 1987. doi:10.1103/PhysRevLett.58.1252. URL https://link.aps.org/doi/10.1103/PhysRevLett.58.1252. → page 5
- [29] X. G. Wen and Q. Niu. Ground-state degeneracy of the fractional quantum Hall states in the presence of a random potential and on high-genus Riemann surfaces. *Physical Review B*, 41(13):9377–9396, May 1990. doi:10.1103/PhysRevB.41.9377. URL https://link.aps.org/doi/10.1103/PhysRevB.41.9377.
- [30] X.-G. Wen. Topological orders and edge excitations in fractional quantum Hall states. Advances in Physics, 44(5):405–473, Oct. 1995. ISSN 0001-8732. doi:10.1080/00018739500101566. URL https://doi.org/10.1080/00018739500101566. → page 5
- [31] B. Jeckelmann and B. Jeanneret. The quantum Hall effect as an electrical resistance standard. *Reports on Progress in Physics*, 64(12):1603, 2001. ISSN 0034-4885. doi:10.1088/0034-4885/64/12/201. URL http://stacks.iop.org/0034-4885/64/i=12/a=201. → page 5
- [32] R. E. Prange and S. M. Girvin. *The Quantum Hall Effect*. Springer Science & Business Media, Dec. 2012. ISBN 978-1-4612-3350-3.
   Google-Books-ID: mxrSBwAAQBAJ. → page 5
- [33] E. V. Gorbar, V. P. Gusynin, V. A. Miransky, and I. A. Shovkovy. Magnetic field driven metal-insulator phase transition in planar systems. *Physical Review B*, 66(4):045108, 2002. → page 5
- [34] Y. Zheng and T. Ando. Hall conductivity of a two-dimensional graphite system. *Physical Review B*, 65(24):245420, June 2002.
   doi:10.1103/PhysRevB.65.245420. URL https://link.aps.org/doi/10.1103/PhysRevB.65.245420.
- [35] V. P. Gusynin and S. G. Sharapov. Unconventional Integer Quantum Hall Effect in Graphene. *Physical Review Letters*, 95(14):146801, Sept. 2005.

doi:10.1103/PhysRevLett.95.146801. URL https://link.aps.org/doi/10.1103/PhysRevLett.95.146801.

- [36] N. M. R. Peres, F. Guinea, and A. H. Castro Neto. Electronic properties of disordered two-dimensional carbon. *Physical Review B*, 73(12):125411, Mar. 2006. doi:10.1103/PhysRevB.73.125411. URL https://link.aps.org/doi/10.1103/PhysRevB.73.125411. → page 5
- [37] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim. Room-Temperature Quantum Hall Effect in Graphene. *Science*, 315(5817): 1379–1379, Mar. 2007. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1137201. URL http://science.sciencemag.org/content/315/5817/1379. → pages 6, 49
- [38] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth. The structure of suspended graphene sheets. *Nature*, 446 (7131):60–63, Mar. 2007. ISSN 1476-4687. doi:10.1038/nature05545. URL https://www.nature.com/articles/nature05545. → page 6
- [39] K. I. Bolotin, K. J. Sikes, J. Hone, H. L. Stormer, and P. Kim. Temperature-Dependent Transport in Suspended Graphene. *Physical Review Letters*, 101(9):096802, Aug. 2008. doi:10.1103/PhysRevLett.101.096802. URL https://link.aps.org/doi/10.1103/PhysRevLett.101.096802.
- [40] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer. Ultrahigh electron mobility in suspended graphene. *Solid State Communications*, 146(9):351–355, June 2008. ISSN 0038-1098. doi:10.1016/j.ssc.2008.02.024. URL http://www.sciencedirect.com/science/article/pii/S0038109808001178. → page 6
- [41] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff. Graphene-based composite materials. *Nature*, 442(7100):282–286, July 2006. ISSN 0028-0836. doi:10.1038/nature04969. URL http://www.nature.com/nature/journal/v442/n7100/full/nature04969.html. → page 6
- [42] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, and R. S. Ruoff. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of

exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *Journal of Materials Chemistry*, 16(2):155–158, Dec. 2006. ISSN 1364-5501. doi:10.1039/B512799H. URL https://pubs.rsc.org/en/content/articlelanding/2006/jm/b512799h.

- [43] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 45 (7):1558–1565, June 2007. ISSN 0008-6223. doi:10.1016/j.carbon.2007.02.034. URL http://www.sciencedirect.com/science/article/pii/S0008622307000917.
- [44] D. Li, M. B. Mller, S. Gilje, R. B. Kaner, and G. G. Wallace. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology*, 3(2): 101–105, Feb. 2008. ISSN 1748-3395. doi:10.1038/nnano.2007.451. URL https://www.nature.com/articles/nnano.2007.451.
- [45] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, and J. N. Coleman. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology*, 3(9): 563–568, Sept. 2008. ISSN 1748-3387. doi:10.1038/nnano.2008.215. URL

http://www.nature.com/nnano/journal/v3/n9/abs/nnano.2008.215.html.  $\rightarrow$  page 6

- [46] M. Mueller, C. Kuebel, and K. Muellen. Giant Polycyclic Aromatic Hydrocarbons. *Chemistry A European Journal*, 4(11):2099–2109, 1998. ISSN 1521-3765. doi:10.1002/(SICI)1521-3765(19981102)4:11(2099:: AID-CHEM2099)3.0.CO;2-T. URL https://onlinelibrary.wiley.com/doi/abs/ 10.1002/%28SICI%291521-3765%2819981102%294%3A11%3C2099% 3A%3AAID-CHEM2099%3E3.0.CO%3B2-T. → page 6
- [47] N. Tyutyulkov, G. Madjarova, F. Dietz, and K. Mllen. Is 2-D Graphite an Ultimate Large Hydrocarbon? 1. Energy Spectra of Giant Polycyclic Aromatic Hydrocarbons. *The Journal of Physical Chemistry B*, 102(50): 10183–10189, Dec. 1998. ISSN 1520-6106. doi:10.1021/jp982651b. URL https://doi.org/10.1021/jp982651b.
- [48] X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Rder, and K. Mllen. Two-Dimensional Graphene Nanoribbons. *Journal of the American*

*Chemical Society*, 130(13):4216–4217, Apr. 2008. ISSN 0002-7863. doi:10.1021/ja710234t. URL https://doi.org/10.1021/ja710234t.

- [49] J. Wu, W. Pisula, and K. Mllen. Graphenes as Potential Material for Electronics. *Chemical Reviews*, 107(3):718–747, Mar. 2007. ISSN 0009-2665. doi:10.1021/cr068010r. URL https://doi.org/10.1021/cr068010r.
- [50] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer. Ultrathin Epitaxial Graphite: 2d Electron Gas Properties and a Route toward Graphene-based Nanoelectronics. *The Journal of Physical Chemistry B*, 108(52):19912–19916, Dec. 2004. ISSN 1520-6106. doi:10.1021/jp040650f. URL https://doi.org/10.1021/jp040650f. → page 6
- [51] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. d. Heer. Electronic Confinement and Coherence in Patterned Epitaxial Graphene. *Science*, 312(5777):1191–1196, May 2006. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1125925. URL http://science.sciencemag.org/content/312/5777/1191. → page 6
- [52] W. A. de Heer, C. Berger, X. Wu, P. N. First, E. H. Conrad, X. Li, T. Li, M. Sprinkle, J. Hass, M. L. Sadowski, M. Potemski, and G. Martinez. Epitaxial graphene. *Solid State Communications*, 143(1):92–100, July 2007. ISSN 0038-1098. doi:10.1016/j.ssc.2007.04.023. URL http://www.sciencedirect.com/science/article/pii/S0038109807002980.
- [53] J. Hass, W. A. d. Heer, and E. H. Conrad. The growth and morphology of epitaxial multilayer graphene. *Journal of Physics: Condensed Matter*, 20 (32):323202, 2008. ISSN 0953-8984.
  doi:10.1088/0953-8984/20/32/323202. URL http://stacks.iop.org/0953-8984/20/i=32/a=323202.
- [54] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong\*. Layer Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Letters*, 9(8):3087–3087, Aug. 2009. ISSN 1530-6984. doi:10.1021/nl901829a. URL https://doi.org/10.1021/nl901829a.
- [55] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Hong. Large-scale pattern growth of

graphene films for stretchable transparent electrodes. *nature*, 457(7230): 706, 2009. URL http:

//search.proquest.com/openview/c6c597356b919152c5186de1154a673e/ 1?pq-origsite=gscholar&cbl=40569.

- [56] P. W. Sutter, J.-I. Flege, and E. A. Sutter. Epitaxial graphene on ruthenium. *Nature Materials*, 7(5):406–411, May 2008. ISSN 1476-4660. doi:10.1038/nmat2166. URL https://www.nature.com/articles/nmat2166. → page 6
- [57] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Roehrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and T. Seyller. Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Materials*, 8(3):203, Mar. 2009. ISSN 1476-4660. doi:10.1038/nmat2382. URL https://www.nature.com/articles/nmat2382. → pages 6, 8, 50, 57, 78
- [58] S. Das Sarma, A. K. Geim, P. Kim, and A. H. MacDonald. Foreword. *Solid State Communications*, 143(1):1–2, July 2007. ISSN 0038-1098.
   doi:10.1016/j.ssc.2007.04.030. URL http://www.sciencedirect.com/science/article/pii/S0038109807003158.
- [59] C. Riedl, C. Coletti, and U. Starke. Structural and electronic properties of epitaxial graphene on SiC (0 0 0 1): a review of growth, characterization, transfer doping and hydrogen intercalation. *Journal of Physics D: Applied Physics*, 43(37):374009, 2010. URL http://iopscience.iop.org/article/10.1088/0022-3727/43/37/374009/meta. → pages 6, 7, 53
- [60] S. Forti, K. V. Emtsev, C. Coletti, A. A. Zakharov, C. Riedl, and U. Starke. Large-area homogeneous quasifree standing epitaxial graphene on SiC(0001): Electronic and structural characterization. *Physical Review B*, 84(12):125449, Sept. 2011. doi:10.1103/PhysRevB.84.125449. URL https://link.aps.org/doi/10.1103/PhysRevB.84.125449. → pages 7, 82
- [61] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke. Quasi-Free-Standing Epitaxial Graphene on SiC Obtained by Hydrogen Intercalation. *Physical Review Letters*, 103(24):246804, Dec. 2009. doi:10.1103/PhysRevLett.103.246804. URL https://link.aps.org/doi/10.1103/PhysRevLett.103.246804. → pages 7, 50

- [62] A. V. Fedorov, N. I. Verbitskiy, D. Haberer, C. Struzzi, L. Petaccia, D. Usachov, O. Y. Vilkov, D. V. Vyalikh, J. Fink, M. Knupfer, B. Buechner, and A. Grueneis. Observation of a universal donor-dependent vibrational mode in graphene. *Nature Communications*, 5, Feb. 2014. doi:10.1038/ncomms4257. URL http://www.nature.com/ncomms/2014/140206/ncomms4257/full/ncomms4257.html. → pages 8, 10, 94
- [63] D. A. Siegel, C.-H. Park, C. Hwang, J. Deslippe, A. V. Fedorov, S. G. Louie, and A. Lanzara. Many-body interactions in quasi-freestanding graphene. *Proceedings of the National Academy of Sciences*, 108(28): 11365–11369, July 2011. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.1100242108. URL https://www.pnas.org/content/108/28/11365.
- [64] A. Bostwick, F. Speck, T. Seyller, K. Horn, M. Polini, R. Asgari, A. H. MacDonald, and E. Rotenberg. Observation of Plasmarons in Quasi-Freestanding Doped Graphene. *Science*, 328(5981):999–1002, May 2010. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1186489. URL http://science.sciencemag.org/content/328/5981/999. → pages 13, 50
- [65] J. L. McChesney, A. Bostwick, T. Ohta, T. Seyller, K. Horn, J. Gonzlez, and E. Rotenberg. Extended van Hove Singularity and Superconducting Instability in Doped Graphene. *Physical Review Letters*, 104(13):136803, Apr. 2010. doi:10.1103/PhysRevLett.104.136803. URL https://link.aps.org/doi/10.1103/PhysRevLett.104.136803. → pages 80, 96
- [66] B. M. Ludbrook, G. Levy, P. Nigge, M. Zonno, M. Schneider, D. J. Dvorak, C. N. Veenstra, S. Zhdanovich, D. Wong, P. Dosanjh, C. Strasser, A. Stoehr, S. Forti, C. R. Ast, U. Starke, and A. Damascelli. Evidence for superconductivity in Li-decorated monolayer graphene. *Proceedings of the National Academy of Sciences*, 112(38):11795–11799, Sept. 2015. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.1510435112. URL http://www.pnas.org/content/112/38/11795. → pages 8, 10, 11, 13, 59, 60, 94
- [67] Y.-W. Son, M. L. Cohen, and S. G. Louie. Energy Gaps in Graphene Nanoribbons. *Physical Review Letters*, 97(21):216803, Nov. 2006. doi:10.1103/PhysRevLett.97.216803. URL https://link.aps.org/doi/10.1103/PhysRevLett.97.216803. → pages 9, 14, 105

- [68] M. Y. Han, B. zyilmaz, Y. Zhang, and P. Kim. Energy Band-Gap Engineering of Graphene Nanoribbons. *Physical Review Letters*, 98(20): 206805, May 2007. doi:10.1103/PhysRevLett.98.206805. URL https://link.aps.org/doi/10.1103/PhysRevLett.98.206805. → pages 14, 105
- [69] G. Giovannetti, P. A. Khomyakov, G. Brocks, P. J. Kelly, and J. van den Brink. Substrate-induced band gap in graphene on hexagonal boron nitride: Ab initio density functional calculations. *Physical Review B*, 76(7):073103, Aug. 2007. doi:10.1103/PhysRevB.76.073103. URL https://link.aps.org/doi/10.1103/PhysRevB.76.073103.
- Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, and Z. X. Shen. Uniaxial Strain on Graphene: Raman Spectroscopy Study and Band-Gap Opening. *ACS Nano*, 2(11):2301–2305, Nov. 2008. ISSN 1936-0851. doi:10.1021/nn800459e. URL https://doi.org/10.1021/nn800459e.
- [71] F. Xia, D. B. Farmer, Y.-m. Lin, and P. Avouris. Graphene Field-Effect Transistors with High On/Off Current Ratio and Large Transport Band Gap at Room Temperature. *Nano Letters*, 10(2):715–718, Feb. 2010. ISSN 1530-6984. doi:10.1021/nl9039636. URL https://doi.org/10.1021/nl9039636.
- [72] X. Xu, C. Liu, Z. Sun, T. Cao, Z. Zhang, E. Wang, Z. Liu, and K. Liu. Interfacial engineering in graphene bandgap. *Chemical Society Reviews*, 47 (9):3059–3099, May 2018. ISSN 1460-4744. doi:10.1039/C7CS00836H. URL https://pubs.rsc.org/en/content/articlelanding/2018/cs/c7cs00836h. → page 9
- [73] G. Profeta, M. Calandra, and F. Mauri. Phonon-mediated superconductivity in graphene by lithium deposition. *Nature Physics*, 8(2):131–134, Feb. 2012. ISSN 1745-2473. doi:10.1038/nphys2181. URL http://www.nature.com/nphys/journal/v8/n2/full/nphys2181.html.  $\rightarrow$  page 10
- [74] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero. Unconventional superconductivity in magic-angle graphene superlattices. *Nature*, 556(7699):43–50, Apr. 2018. ISSN 1476-4687. doi:10.1038/nature26160. URL https://www.nature.com/articles/nature26160. → pages 12, 13, 74, 77, 103
- [75] J. H. d. Boer and E. J. W. Verwey. Semi-conductors with partially and with completely filled3d-lattice bands. *Proceedings of the Physical Society*, 49

(4S):59–71, Aug. 1937. ISSN 0959-5309. doi:10.1088/0959-5309/49/4S/307. URL https://iopscience.iop.org/article/10.1088/0959-5309/49/4S/307.  $\rightarrow$  page 12

- [76] N. F. Mott and R. Peierls. Discussion of the paper by de Boer and Verwey. *Proceedings of the Physical Society*, 49(4S):72–73, Aug. 1937. ISSN 0959-5309. doi:10.1088/0959-5309/49/4S/308. URL https://iopscience.iop.org/article/10.1088/0959-5309/49/4S/308.  $\rightarrow$  page 13
- [77] N. F. Mott. The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals. *Proceedings of the Physical Society.* Section A, 62(7):416–422, July 1949. ISSN 0370-1298. doi:10.1088/0370-1298/62/7/303. URL https://iopscience.iop.org/article/10.1088/0370-1298/62/7/303. → page 13
- [78] J. Hubbard. Electron Correlations in Narrow Energy Bands. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 276(1365):238–257, Nov. 1963. ISSN 1364-5021, 1471-2946. doi:10.1098/rspa.1963.0204. URL http://rspa.royalsocietypublishing.org/content/276/1365/238. → page 13
- [79] E. Dagotto. Correlated electrons in high-temperature superconductors. *Reviews of Modern Physics*, 66(3):763–840, July 1994. doi:10.1103/RevModPhys.66.763. URL https://link.aps.org/doi/10.1103/RevModPhys.66.763. → page 13
- [80] V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, and A. H. Castro Neto. Electron-Electron Interactions in Graphene: Current Status and Perspectives. *Reviews of Modern Physics*, 84(3):1067–1125, July 2012. doi:10.1103/RevModPhys.84.1067. URL https://link.aps.org/doi/10.1103/RevModPhys.84.1067. → page 13
- [81] A. M. Black-Schaffer and C. Honerkamp. Chiral d-wave superconductivity in doped graphene. *Journal of Physics: Condensed Matter*, 26(42):423201, Sept. 2014. ISSN 0953-8984. doi:10.1088/0953-8984/26/42/423201. URL https://iopscience.iop.org/article/10.1088/0953-8984/26/42/423201/meta. → pages 13, 100
- [82] S. Ulstrup, M. Schler, M. Bianchi, F. Fromm, C. Raidel, T. Seyller, T. Wehling, and P. Hofmann. Manifestation of nonlocal electron-electron

interaction in graphene. *Physical Review B*, 94(8):081403, 2016. URL https://journals.aps.org/prb/abstract/10.1103/PhysRevB.94.081403.  $\rightarrow$  page 13

- [83] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, R. C. Ashoori, and P. Jarillo-Herrero. Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature*, 556(7699):80–84, Apr. 2018. ISSN 1476-4687. doi:10.1038/nature26154. URL https://www.nature.com/articles/nature26154. → pages 14, 74, 77, 103
- [84] A. Damascelli, Z. Hussain, and Z.-X. Shen. Angle-resolved photoemission studies of the cuprate superconductors. *Reviews of modern physics*, 75(2): 473, 2003. URL https://journals.aps.org/rmp/abstract/10.1103/RevModPhys.75.473. → pages 14, 48, 76
- [85] F. Guinea, M. I. Katsnelson, and A. K. Geim. Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering. *Nature Physics*, 6 (1):30, Jan. 2010. ISSN 1745-2481. doi:10.1038/nphys1420. URL https://www.nature.com/articles/nphys1420. → pages 14, 48, 50, 61
- [86] N. Levy, S. A. Burke, K. L. Meaker, M. Panlasigui, A. Zettl, F. Guinea, A. H. C. Neto, and M. F. Crommie. Strain-Induced PseudoMagnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles. *Science*, 329(5991): 544–547, July 2010. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1191700. URL http://science.sciencemag.org/content/329/5991/544. → pages 14, 50, 59
- [87] Y.-W. Son, M. L. Cohen, and S. G. Louie. Half-metallic graphene nanoribbons. *Nature*, 444(7117):347, Nov. 2006. ISSN 1476-4687. doi:10.1038/nature05180. URL https://www.nature.com/articles/nature05180. → pages 14, 105
- [88] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Mllen, and R. Fasel. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature*, 466(7305):470–473, July 2010. ISSN 1476-4687. doi:10.1038/nature09211. URL https://www.nature.com/articles/nature09211. → pages 14, 105
- [89] H. Gonzalez-Herrero, J. M. Gomez-Rodriguez, P. Mallet, M. Moaied, J. J. Palacios, C. Salgado, M. M. Ugeda, J.-Y. Veuillen, F. Yndurain, and

I. Brihuega. Atomic-scale control of graphene magnetism by using hydrogen atoms. *Science*, 352(6284):437–441, Apr. 2016. ISSN 0036-8075, 1095-9203. doi:10.1126/science.aad8038. URL https://science.sciencemag.org/content/352/6284/437.  $\rightarrow$  page 14

- [90] Z. Wang, C. Tang, R. Sachs, Y. Barlas, and J. Shi. Proximity-Induced Ferromagnetism in Graphene Revealed by the Anomalous Hall Effect. *Physical Review Letters*, 114(1):016603, Jan. 2015. doi:10.1103/PhysRevLett.114.016603. URL https://link.aps.org/doi/10.1103/PhysRevLett.114.016603. → page 14
- [91] O. V. Yazyev and L. Helm. Defect-induced magnetism in graphene. *Physical Review B*, 75(12):125408, Mar. 2007. doi:10.1103/PhysRevB.75.125408. URL https://link.aps.org/doi/10.1103/PhysRevB.75.125408. → page 14
- [92] F. Calleja, H. Ochoa, M. Garnica, S. Barja, J. J. Navarro, A. Black, M. M. Otrokov, E. V. Chulkov, A. Arnau, A. L. Vazquez de Parga, F. Guinea, and R. Miranda. Spatial variation of a giant spinorbit effect induces electron confinement in graphene on Pb islands. *Nature Physics*, 11(1):43–47, Jan. 2015. ISSN 1745-2481. doi:10.1038/nphys3173. URL https://www.nature.com/articles/nphys3173. → page 14
- [93] I. I. Klimovskikh, M. M. Otrokov, V. Y. Voroshnin, D. Sostina, L. Petaccia, G. Di Santo, S. Thakur, E. V. Chulkov, and A. M. Shikin. Spin-Orbit Coupling Induced Gap in Graphene on Pt(111) with Intercalated Pb Monolayer. ACS Nano, 11(1):368–374, Jan. 2017. ISSN 1936-0851. doi:10.1021/acsnano.6b05982. URL https://doi.org/10.1021/acsnano.6b05982. → page 14
- [94] I. Gierz, J. C. Petersen, M. Mitrano, C. Cacho, I. C. E. Turcu, E. Springate, A. Stoehr, A. Koehler, U. Starke, and A. Cavalleri. Snapshots of non-equilibrium Dirac carrier distributions in graphene. *Nature Materials*, 12(12):1119–1124, Dec. 2013. ISSN 1476-4660. doi:10.1038/nmat3757. URL https://www.nature.com/articles/nmat3757. → pages 14, 105
- [95] L. Braun, G. Mussler, A. Hruban, M. Konczykowski, T. Schumann, M. Wolf, M. Muenzenberg, L. Perfetti, and T. Kampfrath. Ultrafast photocurrents at the surface of the three-dimensional topological insulator Bi2se3. *Nature Communications*, 7:13259, Oct. 2016. ISSN 2041-1723. doi:10.1038/ncomms13259. URL https://www.nature.com/articles/ncomms13259. → page 14

- [96] M. Cardona and L. Ley. Photoemission in solids I: General principles, volume 26 of Topics in Applied Physics. Springer-Verlag, 1978. → page 17
- [97] S. Huefner. Photoelectron Spectroscopy: Principles and Applications. Springer Science & Business Media, Apr. 2003. ISBN 978-3-540-41802-3.
- [98] S. Huefner. Very high resolution photoelectron spectroscopy, volume 715. Springer, 2007. URL https://books.google.ca/books?hl=en&lr=&id=Jd1tCQAAQBAJ&oi=fnd& pg=PR14&dq=photoemission+spectroscopy+very+high+resolution+ huefner&ots=DKxrCJExty&sig=pNoi\_-MhQGMIxw0MXOvoIGKYoLE.
- [99] B. Feuerbacher, B. Fitton, and R. F. Willis. *Photoemission and the electronic properties of surfaces*. John Wiley & Sons, 1978.
- [100] S. D. Kevan. *Angle-resolved photoemission: theory and current applications*, volume 74. Elsevier, 1992.
- [101] W. Schattke and M. A. Van Hove. Solid-state photoemission and related methods: theory and experiment. John Wiley & Sons, 2008. → page 17
- [102] A. Damascelli. Probing the Electronic Structure of Complex Systems by ARPES. *Physica Scripta*, 2004(T109):61, Jan. 2004. ISSN 1402-4896. doi:10.1238/Physica.Topical.109a00061. URL http://iopscience.iop.org/1402-4896/2004/T109/005. → pages 17, 19, 20, 22, 56, 78
- [103] F. Reinert and S. Huefner. Photoemission spectroscopyfrom early days to recent applications. *New Journal of Physics*, 7(1):97, Apr. 2005. ISSN 1367-2630. doi:10.1088/1367-2630/7/1/097. URL http://iopscience.iop.org/1367-2630/7/1/097. → pages 17, 78
- [104] H. Hertz. Ueber einen Einfluss des ultravioletten Lichtes auf die electrische Entladung. Annalen der Physik, 267(8):983–1000, Jan. 1887. ISSN 1521-3889. doi:10.1002/andp.18872670827. URL http://onlinelibrary.wiley.com/doi/10.1002/andp.18872670827/abstract.  $\rightarrow$  page 17
- [105] W. Hallwachs. Ueber den Einfluss des Lichtes auf electrostatisch geladene Koerper. Annalen der Physik, 269(2):301–312, Jan. 1888. ISSN 1521-3889. doi:10.1002/andp.18882690206. URL http://onlinelibrary.wiley.com/doi/10.1002/andp.18882690206/abstract. → page 17

- [106] A. Einstein. ber einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. Annalen der Physik, 322(6): 132–148, Jan. 1905. ISSN 1521-3889. doi:10.1002/andp.19053220607. URL http://onlinelibrary.wiley.com/doi/10.1002/andp.19053220607/abstract. → page 17
- [107] M. P. Seah and W. A. Dench. Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surface and Interface Analysis*, 1(1):2–11, Feb. 1979. ISSN 1096-9918. doi:10.1002/sia.740010103. URL http://onlinelibrary.wiley.com/doi/10.1002/sia.740010103/abstract. → pages 18, 38
- [108] T. Miller, W. E. McMahon, and T.-C. Chiang. Interference between bulk and surface photoemission transitions in Ag (111). *Physical review letters*, 77(6):1167, 1996.  $\rightarrow$  page 21
- [109] E. D. Hansen, T. Miller, and T.-C. Chiang. Surface photoemission in Ag (100). *Physical Review B*, 55(3):1871, 1997.
- [110] E. D. Hansen, T. Miller, and T.-C. Chiang. Observation of photoemission line widths narrower than the inverse lifetime. *Physical review letters*, 80 (8):1766, 1998.
- [111] T. Michalke, A. Gerlach, K. Berge, R. Matzdorf, and A. Goldmann. Interference of direct transitions and surface emission in ARPES studied by changing the light incidence angle. *Physical Review B*, 62(15):10544, 2000.
- [112] F. Pforte, T. Michalke, A. Gerlach, A. Goldmann, and R. Matzdorf. Strong contributions from surface electromagnetic fields to angle-resolved photoemission intensities of copper. *Physical Review B*, 63(11):115405, 2001. → page 21
- [113] S. Doniach and M. Sunjic. Many-electron singularity in X-ray photoemission and X-ray line spectra from metals. *Journal of Physics C: Solid State Physics*, 3(2):285–291, Feb. 1970. ISSN 0022-3719. doi:10.1088/0022-3719/3/2/010. URL https://iopscience.iop.org/article/10.1088/0022-3719/3/2/010. → page 21
- [114] G. D. Mahan. Many-Body Effects on X-Ray Spectra of Metals. In H. Ehrenreich, F. Seitz, and D. Turnbull, editors, *Solid State Physics*,

volume 29, pages 75–138. Academic Press, Jan. 1974. doi:10.1016/S0081-1947(08)60424-5. URL http://www.sciencedirect.com/science/article/pii/S0081194708604245.

- [115] J. W. Gadzuk and M. Sunjic. Excitation energy dependence of core-level x-ray-photoemission-spectra line shapes in metals. *Physical Review B*, 12 (2):524, 1975. → page 21
- [116] A. Abrikosov. Quantum field theoretical methods in statistical physics. Pergamon Press, 1965. → page 21
- [117] L. Hedin and S. Lundqvist. Solid State Physics vol 23 ed F Seitz. D Turnbull and H Ehrenreich (New York: Academic) p, 1, 1969.
- [118] A. L. Fetter and J. D. Walecka. *Quantum theory of many-particle systems*. Courier Corporation, 2012.
- [119] G. D. Mahan. Many-particle physics. Springer Science & Business Media, 2013.
- [120] E. N. Economou. *Green's functions in quantum physics*, volume 3. Springer, 1983.
- [121] G. Rickayzen. Green's functions and condensed matter. Courier Corporation, 2013. → page 21
- [122] Cepheiden. Photoelektronenspektroskopie, Jan. 2018. URL https://de.wikipedia.org/w/index.php?title=Photoelektronenspektroskopie& oldid=172559826. Page Version ID: 172559826. → page 23
- [123] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel. Surface studies by scanning tunneling microscopy. *Physical review letters*, 49(1):57, 1982. → page 24
- [124] J. E. Hoffman. A Search for Alternative Electronic Order in the High Temperature Superconductor BSCCO by Scanning Tunneling Microscopy. PhD Thesis, School University of California, Berkeley, 2003. → pages 26, 28
- [125] J. Bardeen. Tunnelling from a many-particle point of view. *Physical Review Letters*, 6(2):57, 1961. → pages 27, 28
- [126] J. Tersoff and D. R. Hamann. Theory and application for the scanning tunneling microscope. *Physical review letters*, 50(25):1998, 1983.

- [127] J. Tersoff and D. R. Hamann. Theory of the scanning tunneling microscope. *Physical Review B*, 31(2):805, 1985. → page 27
- [128] J. Pendry, A. B. Pretre, B., B. C. H. Krutzen, and B. C. H. Krutzen. Theory of the scanning tunnelling microscope. *Journal of Physics: Condensed Matter*, 3(24):4313, 1991. → page 27
- [129] M. Tsukada, K. Kobayashi, N. Isshiki, and H. Kageshima. First-principles theory of scanning tunneling microscopy. *Surface Science Reports*, 13(8): 267–304, 1991.
- [130] W. A. Hofer, A. S. Foster, and A. L. Shluger. Theories of scanning probe microscopes at the atomic scale. *Reviews of Modern Physics*, 75(4):1287, 2003.
- [131] H. J. Zandvliet and A. van Houselt. Scanning tunneling spectroscopy. Annual Review of Analytical Chemistry, 2:37–55, 2009. → page 27
- [132] M. H. Cohen, L. M. Falicov, and J. C. Phillips. Superconductive tunneling. *Physical Review Letters*, 8(8):316, 1962. → page 28
- [133] N. D. Lang. Resistance of a one-atom contact in the scanning tunneling microscope. *Physical Review B*, 36(15):8173, 1987. → page 29
- [134] J. A. Stroscio, R. M. Feenstra, and A. P. Fein. Electronic structure of the Si (111) 2x1 surface by scanning-tunneling microscopy. *Physical review letters*, 57(20):2579, 1986. → page 30
- [135] J. Repp, G. Meyer, F. E. Olsson, and M. Persson. Controlling the charge state of individual gold adatoms. *Science*, 305(5683):493–495, 2004. → page 30
- [136] L. Jdira, P. Liljeroth, E. Stoffels, D. Vanmaekelbergh, and S. Speller. Size-dependent single-particle energy levels and interparticle Coulomb interactions in CdSe quantum dots measured by scanning tunneling spectroscopy. *Physical Review B*, 73(11):115305, Mar. 2006. doi:10.1103/PhysRevB.73.115305. URL https://link.aps.org/doi/10.1103/PhysRevB.73.115305.
- [137] K. A. Cochrane, A. Schiffrin, T. S. Roussy, M. Capsoni, and S. A. Burke. Pronounced polarization-induced energy level shifts at boundaries of organic semiconductor nanostructures. *Nature Communications*, 6:8312, Oct. 2015. ISSN 2041-1723. doi:10.1038/ncomms9312. URL https://www.nature.com/articles/ncomms9312. → page 30

- [138] G. Nicolay, F. Reinert, S. Huefner, and P. Blaha. Spin-orbit splitting of the L-gap surface state on Au(111) and Ag(111). *Physical Review B*, 65(3): 033407, Dec. 2001. doi:10.1103/PhysRevB.65.033407. URL https://link.aps.org/doi/10.1103/PhysRevB.65.033407. → page 32
- [139] F. Reinert, G. Nicolay, S. Schmidt, D. Ehm, and S. Huefner. Direct measurements of the L-gap surface states on the (111) face of noble metals by photoelectron spectroscopy. *Physical Review B*, 63(11):115415, Mar. 2001. doi:10.1103/PhysRevB.63.115415. URL https://link.aps.org/doi/10.1103/PhysRevB.63.115415. → page 32
- [140] Y. Murata, T. Mashoff, M. Takamura, S. Tanabe, H. Hibino, F. Beltram, and S. Heun. Correlation between morphology and transport properties of quasi-free-standing monolayer graphene. *Applied Physics Letters*, 105(22): 221604, Dec. 2014. ISSN 0003-6951. doi:10.1063/1.4902988. URL https://aip.scitation.org/doi/10.1063/1.4902988. → page 32
- [141] Y. Zhang, V. W. Brar, F. Wang, C. Girit, Y. Yayon, M. Panlasigui, A. Zettl, and M. F. Crommie. Giant phonon-induced conductance in scanning tunnelling spectroscopy of gate-tunable graphene. *Nature Physics*, 4(8): 627–630, Aug. 2008. ISSN 1745-2481. doi:10.1038/nphys1022. URL https://www.nature.com/articles/nphys1022. → page 33
- [142] T. O. Wehling, I. Grigorenko, A. I. Lichtenstein, and A. V. Balatsky. Phonon-Mediated Tunneling into Graphene. *Physical Review Letters*, 101 (21):216803, Nov. 2008. doi:10.1103/PhysRevLett.101.216803. URL https://link.aps.org/doi/10.1103/PhysRevLett.101.216803.
- [143] Y. Zhang, V. W. Brar, C. Girit, A. Zettl, and M. F. Crommie. Origin of spatial charge inhomogeneity in graphene. *Nature Physics*, 5(10):722–726, Oct. 2009. ISSN 1745-2481. doi:10.1038/nphys1365. URL https://www.nature.com/articles/nphys1365. → page 33
- [144] R. Comin and A. Damascelli. Resonant X-Ray Scattering Studies of Charge Order in Cuprates. Annual Review of Condensed Matter Physics, 7 (1):369–405, 2016. doi:10.1146/annurev-conmatphys-031115-011401. URL https://doi.org/10.1146/annurev-conmatphys-031115-011401. → pages 33, 35, 36, 37, 38, 82
- [145] G. Ghiringhelli, M. L. Tacon, M. Minola, S. Blanco-Canosa, C. Mazzoli, N. B. Brookes, G. M. D. Luca, A. Frano, D. G. Hawthorn, F. He, T. Loew, M. M. Sala, D. C. Peets, M. Salluzzo, E. Schierle, R. Sutarto, G. A.

Sawatzky, E. Weschke, B. Keimer, and L. Braicovich. Long-Range Incommensurate Charge Fluctuations in (Y,Nd)Ba2cu3o6+x. *Science*, 337 (6096):821–825, Aug. 2012. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1223532. URL http://science.sciencemag.org/content/337/6096/821.  $\rightarrow$  page 33

- [146] A. J. Achkar, R. Sutarto, X. Mao, F. He, A. Frano, S. Blanco-Canosa, M. Le Tacon, G. Ghiringhelli, L. Braicovich, M. Minola, M. Moretti Sala, C. Mazzoli, R. Liang, D. A. Bonn, W. N. Hardy, B. Keimer, G. A. Sawatzky, and D. G. Hawthorn. Distinct Charge Orders in the Planes and Chains of Ortho-III-Ordered YBa2cu3o6+delta Superconductors Identified by Resonant Elastic X-ray Scattering. *Physical Review Letters*, 109(16): 167001, Oct. 2012. doi:10.1103/PhysRevLett.109.167001. URL https://link.aps.org/doi/10.1103/PhysRevLett.109.167001.
- [147] J. Chang, E. Blackburn, A. T. Holmes, N. B. Christensen, J. Larsen, J. Mesot, R. Liang, D. A. Bonn, W. N. Hardy, A. Watenphul, M. v. Zimmermann, E. M. Forgan, and S. M. Hayden. Direct observation of competition between superconductivity and charge density wave order in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.67</sub>. *Nature Physics*, 8(12):871–876, Dec. 2012. ISSN 1745-2481. doi:10.1038/nphys2456. URL https://www.nature.com/articles/nphys2456.
- [148] R. Comin, A. Frano, M. M. Yee, Y. Yoshida, H. Eisaki, E. Schierle,
  E. Weschke, R. Sutarto, F. He, A. Soumyanarayanan, Y. He, M. L. Tacon,
  I. S. Elfimov, J. E. Hoffman, G. A. Sawatzky, B. Keimer, and
  A. Damascelli. Charge Order Driven by Fermi-Arc Instability in
  Bi2sr2-xLaxCuO6+delta. *Science*, 343(6169):390–392, Jan. 2014. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1242996. URL
  http://science.sciencemag.org/content/343/6169/390.
- [149] M. Le Tacon, A. Bosak, S. M. Souliou, G. Dellea, T. Loew, R. Heid, K.-P. Bohnen, G. Ghiringhelli, M. Krisch, and B. Keimer. Inelastic X-ray scattering in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> reveals giant phonon anomalies and elastic central peak due to charge-density-wave formation. *Nature Physics*, 10(1): 52–58, Jan. 2014. ISSN 1745-2481. doi:10.1038/nphys2805. URL https://www.nature.com/articles/nphys2805.
- [150] E. H. d. S. Neto, R. Comin, F. He, R. Sutarto, Y. Jiang, R. L. Greene, G. A. Sawatzky, and A. Damascelli. Charge ordering in the electron-doped superconductor Nd2xCexCuO4. *Science*, 347(6219):282–285, Jan. 2015.

ISSN 0036-8075, 1095-9203. doi:10.1126/science.1256441. URL http://science.sciencemag.org/content/347/6219/282.

- [151] R. Comin, R. Sutarto, E. H. d. S. Neto, L. Chauviere, R. Liang, W. N. Hardy, D. A. Bonn, F. He, G. A. Sawatzky, and A. Damascelli. Broken translational and rotational symmetry via charge stripe order in underdoped YBa2cu3o6+y. *Science*, 347(6228):1335–1339, Mar. 2015. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1258399. URL http://science.sciencemag.org/content/347/6228/1335. → page 85
- [152] R. Comin, R. Sutarto, F. He, E. H. da Silva Neto, L. Chauviere, A. Frao, R. Liang, W. N. Hardy, D. A. Bonn, Y. Yoshida, H. Eisaki, A. J. Achkar, D. G. Hawthorn, B. Keimer, G. A. Sawatzky, and A. Damascelli. Symmetry of charge order in cuprates. *Nature Materials*, 14(8):796–800, Aug. 2015. ISSN 1476-4660. doi:10.1038/nmat4295. URL https://www.nature.com/articles/nmat4295.
- [153] E. H. d. S. Neto, B. Yu, M. Minola, R. Sutarto, E. Schierle, F. Boschini, M. Zonno, M. Bluschke, J. Higgins, Y. Li, G. Yu, E. Weschke, F. He, M. L. Tacon, R. L. Greene, M. Greven, G. A. Sawatzky, B. Keimer, and A. Damascelli. Doping-dependent charge order correlations in electron-doped cuprates. *Science Advances*, 2(8):e1600782, Aug. 2016. ISSN 2375-2548. doi:10.1126/sciadv.1600782. URL http://advances.sciencemag.org/content/2/8/e1600782. → page 33
- [154] S. B. Wilkins, P. D. Spencer, P. D. Hatton, S. P. Collins, M. D. Roper, D. Prabhakaran, and A. T. Boothroyd. Direct Observation of Orbital Ordering in La0.5sr1.5mno4 Using Soft X-ray Diffraction. *Physical Review Letters*, 91(16):167205, Oct. 2003.
  doi:10.1103/PhysRevLett.91.167205. URL https://link.aps.org/doi/10.1103/PhysRevLett.91.167205. → page 33
- [155] S. S. Dhesi, A. Mirone, C. De Nada, P. Ohresser, P. Bencok, N. B. Brookes, P. Reutler, A. Revcolevschi, A. Tagliaferri, O. Toulemonde, and G. van der Laan. Unraveling Orbital Ordering in La0.5sr1.5mno4. *Physical Review Letters*, 92(5):056403, Feb. 2004. doi:10.1103/PhysRevLett.92.056403. URL https://link.aps.org/doi/10.1103/PhysRevLett.92.056403.
- [156] K. J. Thomas, J. P. Hill, S. Grenier, Y.-J. Kim, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D. F. McMorrow, G. Sawatzky, and M. van Veenendaal. Soft X-Ray Resonant Diffraction Study of Magnetic and Orbital Correlations in a Manganite Near Half Doping. *Physical*

*Review Letters*, 92(23):237204, June 2004. doi:10.1103/PhysRevLett.92.237204. URL https://link.aps.org/doi/10.1103/PhysRevLett.92.237204.  $\rightarrow$  page 33

- [157] M. Blume. Magnetic scattering of x rays (invited). Journal of Applied Physics, 57(8):3615–3618, Apr. 1985. ISSN 0021-8979. doi:10.1063/1.335023. URL https://aip.scitation.org/doi/10.1063/1.335023. → page 33
- [158] G. Materlik and C. J. Sparks. *Resonant anomalous X-ray scattering: theory and applications*. North-Holland, Aug. 1994. ISBN 978-0-444-82025-9. Google-Books-ID: YNHvAAAAMAAJ.
- P. Carra and B. T. Thole. Anisotropic x-ray anomalous diffraction and forbidden reflections. *Reviews of Modern Physics*, 66(4):1509–1515, Oct. 1994. doi:10.1103/RevModPhys.66.1509. URL https://link.aps.org/doi/10.1103/RevModPhys.66.1509.
- S. D. Matteo. Resonant x-ray diffraction: multipole interpretation. *Journal of Physics D: Applied Physics*, 45(16):163001, Mar. 2012. ISSN 0022-3727. doi:10.1088/0022-3727/45/16/163001. URL https://iopscience.iop.org/article/10.1088/0022-3727/45/16/163001/meta.
- [161] J. Fink, E. Schierle, E. Weschke, and J. Geck. Resonant elastic soft x-ray scattering. *Reports on Progress in Physics*, 76(5):056502, Apr. 2013. ISSN 0034-4885. doi:10.1088/0034-4885/76/5/056502. URL https://iopscience.iop.org/article/10.1088/0034-4885/76/5/056502/meta. → pages 33, 82
- [162] H. Bruus and K. Flensberg. Many-body quantum theory in condensed matter physics: an introduction. Oxford university press, 2004. → page 34
- [163] P. Abbamonte, L. Venema, A. Rusydi, G. A. Sawatzky, G. Logvenov, and I. Bozovic. A Structural Probe of the Doped Holes in Cuprate Superconductors. *Science*, 297(5581):581–584, July 2002. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1070903. URL http://science.sciencemag.org/content/297/5581/581. → page 36
- [164] P. Abbamonte, A. Rusydi, S. Smadici, G. D. Gu, G. A. Sawatzky, and D. L. Feng. Spatially modulated 'Mottness' in La(2-x)Ba(x)CuO4. *Nature Physics*, 1(3):155–158, Dec. 2005. ISSN 1745-2481. doi:10.1038/nphys178. URL https://www.nature.com/articles/nphys178. → page 36

- [165] D. G. Hawthorn, F. He, L. Venema, H. Davis, A. J. Achkar, J. Zhang, R. Sutarto, H. Wadati, A. Radi, T. Wilson, G. Wright, K. M. Shen, J. Geck, H. Zhang, V. Novk, and G. A. Sawatzky. An in-vacuum diffractometer for resonant elastic soft x-ray scattering. *Review of Scientific Instruments*, 82 (7):073104, July 2011. ISSN 0034-6748. doi:10.1063/1.3607438. URL https://aip.scitation.org/doi/10.1063/1.3607438. → page 36
- [166] M. A. v. Hove and S. Y. Tong. Surface Crystallography by LEED: Theory, Computation and Structural Results. Springer Science & Business Media, Dec. 2012. ISBN 978-3-642-67195-1. Google-Books-ID: qC\_vCAAAQBAJ. → page 38
- [167] K. Oura, V. G. Lifshits, A. A. Saranin, A. V. Zotov, and M. Katayama. Surface Science: An Introduction. Springer Science & Business Media, Mar. 2013. ISBN 978-3-662-05179-5. Google-Books-ID: aeznCAAAQBAJ.
- [168] M. A. VanHove, W. H. Weinberg, and C.-M. Chan. Low-Energy Electron Diffraction: Experiment, Theory and Surface Structure Determination.
   Springer Science & Business Media, Dec. 2012. ISBN 978-3-642-82721-1.
   Google-Books-ID: bWLyCAAAQBAJ. → page 38
- [169] J. B. Pendry. Low-Energy Electron Diffraction. In V. Bortolani, N. H. March, and M. P. Tosi, editors, *Interaction of Atoms and Molecules with Solid Surfaces*, Physics of Solids and Liquids, pages 201–211. Springer US, Boston, MA, 1990. ISBN 978-1-4684-8777-0. doi:10.1007/978-1-4684-8777-0\_7. URL https://doi.org/10.1007/978-1-4684-8777-0\_7. → page 38
- [170] R. M. Eisberg and R. Resnick. Quantum physics of atoms, molecules, solids, nuclei, and particles. Wiley, 1985. ISBN 978-0-471-87373-0.
   Google-Books-ID: mv5QAAAAMAAJ. → page 38
- [171] C. Kittel, P. McEuen, and P. McEuen. Introduction to solid state physics, volume 8. Wiley New York, 1996. → page 38
- [172] G. P. Thomson and A. Reid. Diffraction of Cathode Rays by a Thin Film. *Nature*, 119(3007):890, June 1927. ISSN 1476-4687. doi:10.1038/119890a0. URL https://www.nature.com/articles/119890a0.  $\rightarrow$  page 38
- [173] C. J. Davisson and L. H. Germer. Reflection of Electrons by a Crystal of Nickel. *Proceedings of the National Academy of Sciences*, 14(4):317–322,

Apr. 1928. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.14.4.317. URL https://www.pnas.org/content/14/4/317.  $\rightarrow$  page 38

- [174] E. J. Scheibner, L. H. Germer, and C. D. Hartman. Apparatus for Direct Observation of LowEnergy Electron Diffraction Patterns. *Review of Scientific Instruments*, 31(2):112–114, Feb. 1960. ISSN 0034-6748. doi:10.1063/1.1716903. URL https://aip.scitation.org/doi/10.1063/1.1716903. → page 38
- [175] L. H. Germer and C. D. Hartman. Improved Low Energy Electron Diffraction Apparatus. *Review of Scientific Instruments*, 31(7):784–784, July 1960. ISSN 0034-6748. doi:10.1063/1.1717051. URL https://aip.scitation.org/doi/10.1063/1.1717051.
- [176] J. J. Lander, J. Morrison, and F. Unterwald. Improved Design and Method of Operation of Low Energy Electron Diffraction Equipment. *Review of Scientific Instruments*, 33(7):782–783, July 1962. ISSN 0034-6748. doi:10.1063/1.1717975. URL https://aip.scitation.org/doi/10.1063/1.1717975.
- [177] G. Ertl. Untersuchung von oberflchenreaktionen mittels beugung langsamer elektronen (LEED): I. Wechselwirkung von O2 und N20 mit (110)-, (111)- und (100)-Kupfer-Oberflchen. Surface Science, 6(2): 208–232, Feb. 1967. ISSN 0039-6028. doi:10.1016/0039-6028(67)90005-2. URL http://www.sciencedirect.com/science/article/pii/0039602867900052. → page 38
- [178] E. G. McRae. Self-consistent multiple-scattering approach to the interpretation of low-energy electron diffraction. *Surface Science*, 8(1): 14–34, July 1967. ISSN 0039-6028. doi:10.1016/0039-6028(67)90071-4. URL http://www.sciencedirect.com/science/article/pii/0039602867900714. → page 39
- [179] J. B. Pendry. Reliability factors for LEED calculations. Journal of Physics C: Solid State Physics, 13(5):937–944, Feb. 1980. ISSN 0022-3719. doi:10.1088/0022-3719/13/5/024. URL https://iopscience.iop.org/article/10.1088/0022-3719/13/5/024/meta. → page 39
- [180] J. R. Ferraro. Introductory Raman Spectroscopy. Elsevier, Jan. 2003. ISBN 978-0-08-050912-9. → page 41
- [181] D. A. Long and D. A. Long. *Raman spectroscopy*, volume 276. McGraw-Hill New York, 1977.
- [182] N. Colthup. Introduction to Infrared and Raman Spectroscopy. Elsevier, Dec. 2012. ISBN 978-0-323-16160-2. → page 41
- [183] R. L. McCreery. Raman Spectroscopy for Chemical Analysis. John Wiley & Sons, Feb. 2005. ISBN 978-0-471-23187-5. Google-Books-ID: qY4MI0Zln1YC. → page 42
- [184] A. Ferrari, J. Robertson, S. Reich, and C. Thomsen. Raman spectroscopy of graphite. *Philosophical Transactions of the Royal Society of London*. *Series A: Mathematical, Physical and Engineering Sciences*, 362(1824): 2271–2288, Nov. 2004. doi:10.1098/rsta.2004.1454. URL https://royalsocietypublishing.org/doi/abs/10.1098/rsta.2004.1454.
- [185] K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, and M. S. Feld. Ultrasensitive chemical analysis by Raman spectroscopy. *Chemical reviews*, 99(10):2957–2976, 1999. → page 42
- [186] A. Smekal. Zur Quantentheorie der Dispersion. *Naturwissenschaften*, 11 (43):873–875, Oct. 1923. ISSN 1432-1904. doi:10.1007/BF01576902. URL https://doi.org/10.1007/BF01576902. → page 42
- [187] C. V. Raman. A new radiation [Reproduced from Indian J. Phys., 1928, 2, 387398]. *Current Science*, 74(4):382–386, 1998. ISSN 0011-3891. URL https://www.jstor.org/stable/24101519. → page 42
- [188] G. S. Landsherg and L. I. Mandelstam. New phenomenon in scattering of light (preliminary report). *Journal of the Russian Physico-Chemical Society, Physics Section*, 60:335, 1928.
- [189] G. Landsberg and L. Mandelstam. ber die Lichtzerstreuung in Kristallen. *Zeitschrift fr Physik*, 50(11):769–780, Nov. 1928. ISSN 0044-3328. doi:10.1007/BF01339412. URL https://doi.org/10.1007/BF01339412.  $\rightarrow$  page 42
- [190] J. P. Dakin, D. J. Pratt, G. W. Bibby, and J. N. Ross. Distributed optical fibre Raman temperature sensor using a semiconductor light source and detector. *Electronics Letters*, 21(13):569–570, June 1985. ISSN 0013-5194. doi:10.1049/el:19850402. → page 42

- [191] J. B. Cui, K. Amtmann, J. Ristein, and L. Ley. Noncontact temperature measurements of diamond by Raman scattering spectroscopy. *Journal of Applied Physics*, 83(12):7929–7933, May 1998. ISSN 0021-8979. doi:10.1063/1.367972. URL https://aip.scitation.org/doi/abs/10.1063/1.367972.
- [192] I. Calizo, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau. Temperature dependence of the Raman spectra of graphene and graphene multilayers. *Nano letters*, 7(9):2645–2649, 2007. → page 42
- [193] H. A. Szymanski. Raman Spectroscopy: Theory and Practice. Springer Science & Business Media, Dec. 2012. ISBN 978-1-4684-3024-0.
   Google-Books-ID: VX\_rBwAAQBAJ. → page 42
- B. S. Shastry and B. I. Shraiman. Theory of Raman scattering in Mott-Hubbard systems. *Physical Review Letters*, 65(8):1068–1071, Aug. 1990. doi:10.1103/PhysRevLett.65.1068. URL https://link.aps.org/doi/10.1103/PhysRevLett.65.1068.
- [195] G. Keresztury. Raman Spectroscopy: Theory. In *Handbook of Vibrational Spectroscopy*. American Cancer Society, 2006. ISBN 978-0-470-02732-5. doi:10.1002/0470027320.s0109. URL https://onlinelibrary.wiley.com/doi/abs/10.1002/0470027320.s0109.  $\rightarrow$  page 42
- [196] sree. Raman spectroscopy, Oct. 2016. URL http://way2science.com/raman-spectroscopy-2/. → page 44
- [197] L. M. Malard, M. A. Pimenta, G. Dresselhaus, and M. S. Dresselhaus. Raman spectroscopy in graphene. *Physics Reports*, 473(5):51–87, Apr. 2009. ISSN 0370-1573. doi:10.1016/j.physrep.2009.02.003. URL http://www.sciencedirect.com/science/article/pii/S0370157309000520. → pages 45, 47
- [198] S. Reich and C. Thomsen. Raman Spectroscopy of Graphite. *Philosophical Transactions: Mathematical, Physical and Engineering Sciences*, 362 (1824):2271–2288, 2004. ISSN 1364-503X. URL https://www.jstor.org/stable/4488952. → page 47
- [199] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and others. Raman spectrum of graphene and graphene layers. *Physical review letters*, 97(18):

187401, 2006. URL https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.97.187401.

- [200] R. Narula and S. Reich. Double resonant Raman spectra in graphene and graphite: A two-dimensional explanation of the Raman amplitude. *Physical Review B*, 78(16):165422, Oct. 2008. doi:10.1103/PhysRevB.78.165422. URL https://link.aps.org/doi/10.1103/PhysRevB.78.165422.
- [201] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, and M. S. Dresselhaus. Raman spectroscopy of graphene and carbon nanotubes. *Advances in Physics*, 60(3):413–550, June 2011. ISSN 0001-8732. doi:10.1080/00018732.2011.582251. URL https://doi.org/10.1080/00018732.2011.582251.
- [202] A. C. Ferrari and D. M. Basko. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature Nanotechnology*, 8(4): 235–246, Apr. 2013. ISSN 1748-3395. doi:10.1038/nnano.2013.46. URL https://www.nature.com/articles/nnano.2013.46. → page 47
- [203] A. C. Ferrari. Raman spectroscopy of graphene and graphite: Disorder, electronphonon coupling, doping and nonadiabatic effects. *Solid State Communications*, 143(1):47–57, July 2007. ISSN 0038-1098. doi:10.1016/j.ssc.2007.03.052. URL http://www.sciencedirect.com/science/article/pii/S0038109807002967. → page 47
- [204] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, and R. Saito. Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy, Jan. 2010. URL https://pubs.acs.org/doi/abs/10.1021/nl904286r.
- [205] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz. Spatially resolved Raman spectroscopy of single-and few-layer graphene. *Nano letters*, 7(2):238–242, 2007.
- [206] L. G. Canado, A. Jorio, E. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, and A. C. Ferrari. Quantifying defects in graphene via Raman spectroscopy at different excitation energies. *Nano letters*, 11(8):3190–3196, 2011. → page 47
- [207] J. Roehrl, M. Hundhausen, K. V. Emtsev, T. Seyller, R. Graupner, and L. Ley. Raman spectra of epitaxial graphene on SiC(0001). *Applied Physics Letters*, 92(20):201918, May 2008. ISSN 0003-6951.

doi:10.1063/1.2929746. URL https://aip.scitation.org/doi/abs/10.1063/1.2929746.  $\rightarrow$  page 47

- [208] D. Rouchon, L. Becerra, O. Renault, K. Kaja, D. Mariolle, and N. Chevalier. Raman Spectra and Imaging of Graphene Layers Grown by SiC Sublimation. *AIP Conference Proceedings*, 1267(1):445–446, Aug. 2010. ISSN 0094-243X. doi:10.1063/1.3482607. URL https://aip.scitation.org/doi/10.1063/1.3482607.
- [209] F. Fromm, M. H. O. Jr, A. Molina-Snchez, M. Hundhausen, J. M. J. Lopes, H. Riechert, L. Wirtz, and T. Seyller. Contribution of the buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001). *New Journal of Physics*, 15(4):043031, 2013. ISSN 1367-2630. doi:10.1088/1367-2630/15/4/043031. URL http://stacks.iop.org/1367-2630/15/i=4/a=043031.
- [210] X. Qin, X. Chen, F. Zhang, L. Xiao, X. Xie, X. Yang, X. Xu, X. Hu, and P. Yu. Polarized Raman Scattering of Epitaxial Graphene Prepared by Thermal Decomposition of SiC. *ECS Journal of Solid State Science and Technology*, 7(3):M35–M40, Jan. 2018. ISSN 2162-8769, 2162-8777. doi:10.1149/2.0231803jss. URL http://jss.ecsdl.org/content/7/3/M35. → page 47
- [211] Z. H. Ni, W. Chen, X. F. Fan, J. L. Kuo, T. Yu, A. T. S. Wee, and Z. X. Shen. Raman spectroscopy of epitaxial graphene on a SiC substrate. *Physical Review B*, 77(11):115416, Mar. 2008. doi:10.1103/PhysRevB.77.115416. URL https://link.aps.org/doi/10.1103/PhysRevB.77.115416. → page 47
- [212] Z. Ni, Y. Wang, T. Yu, and Z. Shen. Raman spectroscopy and imaging of graphene. *Nano Research*, 1(4):273–291, Oct. 2008. ISSN 1998-0000. doi:10.1007/s12274-008-8036-1. URL https://doi.org/10.1007/s12274-008-8036-1. → page 47
- [213] D. S. Lee, C. Riedl, B. Krauss, K. von Klitzing, U. Starke, and J. H. Smet. Raman spectra of epitaxial graphene on SiC and of epitaxial graphene transferred to SiO2. *Nano letters*, 8(12):4320–4325, 2008. → pages 47, 70
- [214] N. S. Mueller, S. Heeg, M. P. Alvarez, P. Kusch, S. Wasserroth, N. Clark, F. Schedin, J. Parthenios, K. Papagelis, C. Galiotis, M. Kalbac, A. Vijayaraghavan, U. Huebner, R. Gorbachev, O. Frank, and S. Reich. Evaluating arbitrary strain configurations and doping in graphene with

Raman spectroscopy. 2D Materials, 5(1):015016, Nov. 2017. ISSN 2053-1583. doi:10.1088/2053-1583/aa90b3. URL https://iopscience.iop.org/article/10.1088/2053-1583/aa90b3.  $\rightarrow$  page 47

- [215] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell. Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor. *Science*, 269(5221):198–201, July 1995. ISSN 0036-8075, 1095-9203. doi:10.1126/science.269.5221.198. URL http://science.sciencemag.org/content/269/5221/198. → pages 48, 49
- [216] D. D. Osheroff, R. C. Richardson, and D. M. Lee. Evidence for a New Phase of Solid He3. *Physical Review Letters*, 28(14):885–888, Apr. 1972. doi:10.1103/PhysRevLett.28.885. URL https://link.aps.org/doi/10.1103/PhysRevLett.28.885.
- [217] R. Willett, J. P. Eisenstein, H. L. Stoermer, D. C. Tsui, A. C. Gossard, and J. H. English. Observation of an even-denominator quantum number in the fractional quantum Hall effect. *Physical Review Letters*, 59(15): 1776–1779, Oct. 1987. doi:10.1103/PhysRevLett.59.1776. URL https://link.aps.org/doi/10.1103/PhysRevLett.59.1776. → page 49
- [218] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. Microscopic Theory of Superconductivity. *Physical Review*, 106(1):162–164, Apr. 1957. doi:10.1103/PhysRev.106.162. URL https://link.aps.org/doi/10.1103/PhysRev.106.162. → page 48
- [219] M. Z. Hasan and C. L. Kane. Colloquium: Topological insulators. *Reviews of Modern Physics*, 82(4):3045–3067, Nov. 2010.
   doi:10.1103/RevModPhys.82.3045. URL https://link.aps.org/doi/10.1103/RevModPhys.82.3045. → page 48
- [220] X.-L. Qi and S.-C. Zhang. Topological insulators and superconductors. *Reviews of Modern Physics*, 83(4):1057–1110, Oct. 2011. doi:10.1103/RevModPhys.83.1057. URL https://link.aps.org/doi/10.1103/RevModPhys.83.1057. → page 48
- [221] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan. A topological Dirac insulator in a quantum spin Hall phase. *Nature*, 452 (7190):970–974, Apr. 2008. ISSN 1476-4687. doi:10.1038/nature06843. URL https://www.nature.com/articles/nature06843. → pages 48, 56
- [222] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain,

and Z.-X. Shen. Experimental Realization of a Three-Dimensional Topological Insulator, Bi2te3. *Science*, 325(5937):178–181, July 2009. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1173034. URL http://science.sciencemag.org/content/325/5937/178.  $\rightarrow$  pages 48, 56

- [223] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. Theory of Superconductivity. *Physical Review*, 108(5):1175–1204, 1957. doi:10.1103/PhysRev.108.1175. URL http://link.aps.org/doi/10.1103/PhysRev.108.1175. → page 49
- [224] Y. Liu, J. N. B. Rodrigues, Y. Z. Luo, L. Li, A. Carvalho, M. Yang,
  E. Laksono, J. Lu, Y. Bao, H. Xu, S. J. R. Tan, Z. Qiu, C. H. Sow, Y. P.
  Feng, A. H. C. Neto, S. Adam, J. Lu, and K. P. Loh. Tailoring sample-wide pseudo-magnetic fields on a grapheneblack phosphorus heterostructure. *Nature Nanotechnology*, 13(9):828, Sept. 2018. ISSN 1748-3395. doi:10.1038/s41565-018-0178-z. URL
  https://www.nature.com/articles/s41565-018-0178-z. → pages 50, 104, 105
- [225] M. C. Rechtsman, J. M. Zeuner, A. Tuennermann, S. Nolte, M. Segev, and A. Szameit. Strain-induced pseudomagnetic field and photonic Landau levels in dielectric structures. *Nature Photonics*, 7(2):153–158, Feb. 2013. ISSN 1749-4893. doi:10.1038/nphoton.2012.302. URL https://www.nature.com/articles/nphoton.2012.302. → page 50
- [226] S. Y. Zhou, G.-H. Gweon, A. V. Fedorov, P. N. First, W. A. d. Heer, D.-H. Lee, F. Guinea, A. H. C. Neto, and A. Lanzara. Substrate-induced bandgap opening in epitaxial graphene. *Nature Materials*, 6(10):770, Oct. 2007. ISSN 1476-4660. doi:10.1038/nmat2003. URL https://www.nature.com/articles/nmat2003. → pages 50, 64, 65, 69
- [227] S. Forti and U. Starke. Epitaxial graphene on SiC: from carrier density engineering to quasi-free standing graphene by atomic intercalation. *Journal of Physics D: Applied Physics*, 47(9):094013, Mar. 2014. ISSN 0022-3727. doi:10.1088/0022-3727/47/9/094013. URL http://iopscience.iop.org/0022-3727/47/9/094013. → pages 50, 78
- [228] M. L. Bolen, S. E. Harrison, L. B. Biedermann, and M. A. Capano. Graphene formation mechanisms on 4h-SiC(0001). *Physical Review B*, 80 (11):115433, Sept. 2009. doi:10.1103/PhysRevB.80.115433. URL https://link.aps.org/doi/10.1103/PhysRevB.80.115433. → page 50

- [229] D. M. Pakdehi, K. Pierz, S. Wundrack, J. Aprojanz, T. T. N. Nguyen, T. Dziomba, F. Hohls, A. Bakin, R. Stosch, C. Tegenkamp, F. J. Ahlers, and H. W. Schumacher. Homogeneous Large-area Quasi-freestanding Monolayer and Bilayer Graphene on SiC. arXiv:1811.04998 [cond-mat], Nov. 2018. URL http://arxiv.org/abs/1811.04998. arXiv: 1811.04998. → pages 50, 52
- [230] K. V. Emtsev, F. Speck, T. Seyller, L. Ley, and J. D. Riley. Interaction, growth, and ordering of epitaxial graphene on SiC{0001} surfaces: A comparative photoelectron spectroscopy study. *Physical Review B*, 77(15): 155303, Apr. 2008. doi:10.1103/PhysRevB.77.155303. URL http://link.aps.org/doi/10.1103/PhysRevB.77.155303. → page 52
- [231] C. Virojanadara, M. Syvjarvi, R. Yakimova, L. I. Johansson, A. A. Zakharov, and T. Balasubramanian. Homogeneous large-area graphene layer growth on 6h-SiC(0001). *Physical Review B*, 78(24):245403, Dec. 2008. doi:10.1103/PhysRevB.78.245403. URL https://link.aps.org/doi/10.1103/PhysRevB.78.245403. → page 52
- [232] E. L. Shirley, L. J. Terminello, A. Santoni, and F. J. Himpsel.
   Brillouin-zone-selection effects in graphite photoelectron angular distributions. *Physical Review B*, 51(19):13614–13622, May 1995. doi:10.1103/PhysRevB.51.13614. URL
   https://link.aps.org/doi/10.1103/PhysRevB.51.13614. → page 55
- [233] P. Zhang, P. Richard, T. Qian, Y.-M. Xu, X. Dai, and H. Ding. A precise method for visualizing dispersive features in image plots. *Review of Scientific Instruments*, 82(4):043712, Apr. 2011. ISSN 0034-6748. doi:10.1063/1.3585113. URL http://aip.scitation.org/doi/abs/10.1063/1.3585113. → page 55
- [234] B. Q. Lv, N. Xu, H. M. Weng, J. Z. Ma, P. Richard, X. C. Huang, L. X. Zhao, G. F. Chen, C. E. Matt, F. Bisti, V. N. Strocov, J. Mesot, Z. Fang, X. Dai, T. Qian, M. Shi, and H. Ding. Observation of Weyl nodes in TaAs. *Nature Physics*, 11(9):724–727, Sept. 2015. ISSN 1745-2481. doi:10.1038/nphys3426. URL https://www.nature.com/articles/nphys3426. → page 56
- [235] J. Jang, H. M. Yoo, L. N. Pfeiffer, K. W. West, K. W. Baldwin, and R. C. Ashoori. Full momentum- and energy-resolved spectral function of a 2d electronic system. *Science*, 358(6365):901–906, Nov. 2017. ISSN

0036-8075, 1095-9203. doi:10.1126/science.aam7073. URL http://science.sciencemag.org/content/358/6365/901.  $\rightarrow$  page 56

- [236] A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg. Quasiparticle dynamics in graphene. *Nature Physics*, 3(1):36–40, Jan. 2007. ISSN 1745-2473. doi:10.1038/nphys477. URL http://www.nature.com/nphys/journal/v3/n1/full/nphys477.html. → page 57
- [237] Y. J. Song, A. F. Otte, Y. Kuk, Y. Hu, D. B. Torrance, P. N. First, W. A. de Heer, H. Min, S. Adam, M. D. Stiles, A. H. MacDonald, and J. A. Stroscio. High-resolution tunnelling spectroscopy of a graphene quartet. *Nature*, 467(7312):185–189, Sept. 2010. ISSN 1476-4687. doi:10.1038/nature09330. URL https://www.nature.com/articles/nature09330. → page 59
- [238] T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, and
  E. Rotenberg. Interlayer Interaction and Electronic Screening in Multilayer
  Graphene Investigated with Angle-Resolved Photoemission Spectroscopy. *Physical Review Letters*, 98(20):206802, May 2007.
  doi:10.1103/PhysRevLett.98.206802. URL
  https://link.aps.org/doi/10.1103/PhysRevLett.98.206802. → pages 59, 60
- [239] T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg. Controlling the Electronic Structure of Bilayer Graphene. *Science*, 313(5789):951–954, Aug. 2006. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1130681. URL http://science.sciencemag.org/content/313/5789/951. → pages 59, 60
- [240] D. Marchenko, D. V. Evtushinsky, E. Golias, A. Varykhalov, T. Seyller, and O. Rader. Extremely flat band in bilayer graphene. *Science Advances*, 4 (11):eaau0059, Nov. 2018. ISSN 2375-2548. doi:10.1126/sciadv.aau0059. URL http://advances.sciencemag.org/content/4/11/eaau0059. → page 60
- [241] P. Kot, J. Parnell, S. Habibian, C. Straer, P. M. Ostrovsky, and C. R. Ast. Band dispersion of graphene with structural defects. arXiv:1811.00087 [cond-mat], Oct. 2018. URL http://arxiv.org/abs/1811.00087. arXiv: 1811.00087. → page 60
- [242] M. Settnes, S. R. Power, and A.-P. Jauho. Pseudomagnetic fields and triaxial strain in graphene. *Physical Review B*, 93(3):035456, Jan. 2016. doi:10.1103/PhysRevB.93.035456. URL https://link.aps.org/doi/10.1103/PhysRevB.93.035456. → pages 61, 63

- [243] Y. Aharonov and A. Casher. Ground state of a spin-onehalf charged particle in a two-dimensional magnetic field. *Physical Review A*, 19(6): 2461–2462, June 1979. doi:10.1103/PhysRevA.19.2461. URL https://link.aps.org/doi/10.1103/PhysRevA.19.2461. → page 65
- [244] B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori. Massive Dirac Fermions and Hofstadter Butterfly in a van der Waals Heterostructure. *Science*, 340 (6139):1427–1430, June 2013. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1237240. URL http://science.sciencemag.org/content/340/6139/1427. → page 65
- [245] D. Pikulin, A. Chen, and M. Franz. Chiral Anomaly from Strain-Induced Gauge Fields in Dirac and Weyl Semimetals. *Physical Review X*, 6(4): 041021, Oct. 2016. doi:10.1103/PhysRevX.6.041021. URL https://link.aps.org/doi/10.1103/PhysRevX.6.041021. → page 74
- [246] A. Cortijo, Y. Ferreirs, K. Landsteiner, and M. A. Vozmediano. Elastic Gauge Fields in Weyl Semimetals. *Physical Review Letters*, 115(17): 177202, Oct. 2015. doi:10.1103/PhysRevLett.115.177202. URL https://link.aps.org/doi/10.1103/PhysRevLett.115.177202.
- [247] T. Liu, D. I. Pikulin, and M. Franz. Quantum oscillations without magnetic field. *Physical Review B*, 95(4):041201, Jan. 2017.
   doi:10.1103/PhysRevB.95.041201. URL https://link.aps.org/doi/10.1103/PhysRevB.95.041201. → page 74
- [248] H. Rostami, R. Roldn, E. Cappelluti, R. Asgari, and F. Guinea. Theory of strain in single-layer transition metal dichalcogenides. *Physical Review B*, 92(19):195402, Nov. 2015. doi:10.1103/PhysRevB.92.195402. URL https://link.aps.org/doi/10.1103/PhysRevB.92.195402. → page 74
- [249] G. Massarelli, G. Wachtel, J. Y. T. Wei, and A. Paramekanti.
  Pseudo-Landau levels of Bogoliubov quasiparticles in strained nodal superconductors. *Physical Review B*, 96(22):224516, Dec. 2017. doi:10.1103/PhysRevB.96.224516. URL
  https://link.aps.org/doi/10.1103/PhysRevB.96.224516. → page 74
- [250] E. M. Nica and M. Franz. Landau levels from neutral Bogoliubov particles in two-dimensional nodal superconductors under strain and doping gradients. *Physical Review B*, 97(2):024520, Jan. 2018.

doi:10.1103/PhysRevB.97.024520. URL https://link.aps.org/doi/10.1103/PhysRevB.97.024520.  $\rightarrow$  page 74

- [251] T. Low and F. Guinea. Strain-Induced Pseudomagnetic Field for Novel Graphene Electronics. *Nano Letters*, 10(9):3551–3554, Sept. 2010. ISSN 1530-6984. doi:10.1021/nl1018063. URL https://doi.org/10.1021/nl1018063. → page 74
- [252] B. Uchoa and Y. Barlas. Superconducting States in Pseudo-Landau-Levels of Strained Graphene. *Physical Review Letters*, 111(4):046604, July 2013. doi:10.1103/PhysRevLett.111.046604. URL https://link.aps.org/doi/10.1103/PhysRevLett.111.046604. → page 74
- [253] P. Ghaemi, J. Cayssol, D. N. Sheng, and A. Vishwanath. Fractional Topological Phases and Broken Time-Reversal Symmetry in Strained Graphene. *Physical Review Letters*, 108(26):266801, June 2012. doi:10.1103/PhysRevLett.108.266801. URL https://link.aps.org/doi/10.1103/PhysRevLett.108.266801. → page 74
- [254] Z. F. Weng, M. Smidman, L. Jiao, X. Lu, and H. Q. Yuan. Multiple quantum phase transitions and superconductivity in Ce-based heavy fermions. *Reports on Progress in Physics*, 79(9):094503, 2016. ISSN 0034-4885. doi:10.1088/0034-4885/79/9/094503. URL http://stacks.iop.org/0034-4885/79/i=9/a=094503. → page 77
- [255] S. Link. Intercalation of Graphene on SiC(0001): Ultra-high Doping Levels and New 2D materials. PhD thesis, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, 2018. URL https://opus4.kobv.de/opus4-fau/frontdoor/index/index/docld/9766. → pages 77, 78, 79, 80, 82, 85, 88
- [256] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono. Iron-Based Layered Superconductor La[O(1-x)F(x)]FeAs (x = 0.05-0.12) with Tc = 26 K. *Journal of the American Chemical Society*, 130(11):3296–3297, Mar. 2008. ISSN 0002-7863. doi:10.1021/ja800073m. URL https://doi.org/10.1021/ja800073m. → page 77
- [257] T. Ishiguro, K. Yamaji, and G. Saito. Organic Superconductors. Springer Science & Business Media, Dec. 2012. ISBN 978-3-642-58262-2.
   Google-Books-ID: ViPwCAAAQBAJ. → page 77
- [258] N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich. Magnetically mediated

superconductivity in heavy fermion compounds. *Nature*, 394(6688):39–43, July 1998. ISSN 1476-4687. doi:10.1038/27838. URL https://www.nature.com/articles/27838.  $\rightarrow$  page 77

- [259] N. Ehlen, M. Hell, G. Marini, E. H. Hasdeo, R. Saito, G. Di Santo,
  L. Petaccia, G. Profeta, and A. Grueneis. Origin of the flat band in heavily
  Cs doped graphene. *arXiv:1903.09038 [cond-mat]*, Mar. 2019. URL
  http://arxiv.org/abs/1903.09038. arXiv: 1903.09038. → page 80
- [260] J. M. Luttinger and J. C. Ward. Ground-state energy of a many-fermion system. II. *Physical Review*, 118(5):1417, 1960. URL https://journals.aps.org/pr/abstract/10.1103/PhysRev.118.1417. → page 81
- [261] W. Lenth, F. Lutz, J. Barth, G. Kalkoffen, and C. Kunz. Giant Resonance Enhancement of the 4 f, 5 p, and 5 s States in the Photoemission Spectra of Rare-Earth Compounds. *Physical Review Letters*, 41(17):1185, 1978. URL https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.41.1185. → page 82
- [262] J. K. Lang, Y. Baer, and P. A. Cox. Study of the 4f and valence band density of states in rare-earth metals. II. Experiment and results. *Journal of Physics F: Metal Physics*, 11(1):121, 1981. ISSN 0305-4608. doi:10.1088/0305-4608/11/1/015. URL http://stacks.iop.org/0305-4608/11/i=1/a=015. → page 82
- [263] V. I. Grebennikov, T. V. Kuznetsova, and A. G. Kuchin. Resonant photoemission spectroscopy study of the d and f states in GdNi5 xCux intermetallics. *Bulletin of the Russian Academy of Sciences: Physics*, 79 (1):134–138, Jan. 2015. ISSN 1934-9432. doi:10.3103/S1062873815010141. URL https://doi.org/10.3103/S1062873815010141. → page 82
- [264] M. W. Haverkort, M. Zwierzycki, and O. K. Andersen. Multiplet ligand-field theory using Wannier orbitals. *Physical Review B*, 85(16): 165113, Apr. 2012. doi:10.1103/PhysRevB.85.165113. URL https://link.aps.org/doi/10.1103/PhysRevB.85.165113. → page 85
- [265] M. W. Haverkort, G. Sangiovanni, P. Hansmann, A. Toschi, Y. Lu, and S. Macke. Bands, resonances, edge singularities and excitons in core level spectroscopy investigated within the dynamical mean-field theory. *EPL* (*Europhysics Letters*), 108(5):57004, Dec. 2014. ISSN 0295-5075.

doi:10.1209/0295-5075/108/57004. URL https://iopscience.iop.org/article/10.1209/0295-5075/108/57004/meta.

- [266] Y. Lu, M. Hoeppner, O. Gunnarsson, and M. W. Haverkort. Efficient real-frequency solver for dynamical mean-field theory. *Physical Review B*, 90(8):085102, Aug. 2014. doi:10.1103/PhysRevB.90.085102. URL https://link.aps.org/doi/10.1103/PhysRevB.90.085102. → page 85
- [267] A. J. Achkar, F. He, R. Sutarto, J. Geck, H. Zhang, Y.-J. Kim, and D. G. Hawthorn. Resonant X-Ray Scattering Measurements of a Spatial Modulation of the Cu \$3d\$ and O \$2p\$ Energies in Stripe-Ordered Cuprate Superconductors. *Physical Review Letters*, 110(1):017001, Jan. 2013. doi:10.1103/PhysRevLett.110.017001. URL https://link.aps.org/doi/10.1103/PhysRevLett.110.017001. → page 86
- [268] G. Gruener. The dynamics of charge-density waves. *Reviews of Modern Physics*, 60(4):1129–1181, Oct. 1988. doi:10.1103/RevModPhys.60.1129. URL https://link.aps.org/doi/10.1103/RevModPhys.60.1129. → page 86
- [269] P. Monceau. Electronic crystals: an experimental overview. Advances in Physics, 61(4):325–581, Aug. 2012. ISSN 0001-8732.
   doi:10.1080/00018732.2012.719674. URL https://doi.org/10.1080/00018732.2012.719674.
- [270] B. H. Savitzky, I. E. Baggari, A. S. Admasu, J. Kim, S.-W. Cheong, R. Hovden, and L. F. Kourkoutis. Bending and breaking of stripes in a charge ordered manganite. *Nature Communications*, 8(1):1883, Dec. 2017. ISSN 2041-1723. doi:10.1038/s41467-017-02156-1. URL https://www.nature.com/articles/s41467-017-02156-1. → page 86
- [271] M. Bluschke, A. Frano, E. Schierle, D. Putzky, F. Ghorbani, R. Ortiz, H. Suzuki, G. Christiani, G. Logvenov, E. Weschke, R. J. Birgeneau, E. H. d. S. Neto, M. Minola, S. Blanco-Canosa, and B. Keimer. Stabilization of three-dimensional charge order in YBa 2 Cu 3 O 6+x via epitaxial growth. *Nature Communications*, 9(1):2978, July 2018. ISSN 2041-1723. doi:10.1038/s41467-018-05434-8. URL https://www.nature.com/articles/s41467-018-05434-8. → page 88
- [272] C. Rau and S. Eichner. Evidence for ferromagnetic order at gadolinium surfaces above the bulk Curie temperature. *Physical Review B*, 34(9): 6347–6350, Nov. 1986. doi:10.1103/PhysRevB.34.6347. URL https://link.aps.org/doi/10.1103/PhysRevB.34.6347. → page 88

- [273] A. N. Bogdanov and U. K. Rler. Chiral Symmetry Breaking in Magnetic Thin Films and Multilayers. *Physical Review Letters*, 87(3):037203, June 2001. doi:10.1103/PhysRevLett.87.037203. URL https://link.aps.org/doi/10.1103/PhysRevLett.87.037203. → page 90
- [274] U. K. Roessler, A. N. Bogdanov, and C. Pfleiderer. Spontaneous skyrmion ground states in magnetic metals. *Nature*, 442(7104):797, Aug. 2006.
   ISSN 1476-4687. doi:10.1038/nature05056. URL https://www.nature.com/articles/nature05056.
- [275] S. Muehlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, and P. Bni. Skyrmion Lattice in a Chiral Magnet. *Science*, 323 (5916):915–919, Feb. 2009. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1166767. URL https://science.sciencemag.org/content/323/5916/915.
- [276] N. Romming, C. Hanneken, M. Menzel, J. E. Bickel, B. Wolter, K. v. Bergmann, A. Kubetzka, and R. Wiesendanger. Writing and Deleting Single Magnetic Skyrmions. *Science*, 341(6146):636–639, Aug. 2013. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1240573. URL https://science.sciencemag.org/content/341/6146/636.
- [277] B. Dupe, M. Hoffmann, C. Paillard, and S. Heinze. Tailoring magnetic skyrmions in ultra-thin transition metal films. *Nature Communications*, 5: 4030, June 2014. ISSN 2041-1723. doi:10.1038/ncomms5030. URL https://www.nature.com/articles/ncomms5030.
- [278] P.-J. Hsu, A. Kubetzka, A. Finco, N. Romming, K. von Bergmann, and R. Wiesendanger. Electric-field-driven switching of individual magnetic skyrmions. *Nature Nanotechnology*, 12(2):123–126, Feb. 2017. ISSN 1748-3395. doi:10.1038/nnano.2016.234. URL https://www.nature.com/articles/nnano.2016.234. → page 90
- [279] M. Kang, J. Pelliciari, A. Frano, N. Breznay, E. Schierle, E. Weschke, R. Sutarto, F. He, P. Shafer, E. Arenholz, M. Chen, K. Zhang, A. Ruiz, Z. Hao, S. Lewin, J. Analytis, Y. Krockenberger, H. Yamamoto, T. Das, and R. Comin. Evolution of charge order topology across a magnetic phase transition in cuprate superconductors. *Nature Physics*, 15(4):335, Apr. 2019. ISSN 1745-2481. doi:10.1038/s41567-018-0401-8. URL https://www.nature.com/articles/s41567-018-0401-8. → page 90
- [280] D. S. Dessau, Z.-X. Shen, D. M. King, D. S. Marshall, L. W. Lombardo, P. H. Dickinson, A. G. Loeser, J. DiCarlo, C.-H. Park, A. Kapitulnik, and

W. E. Spicer. Key features in the measured band structure of Bi2sr2cacu2o8+: Flat bands at EF and Fermi surface nesting. *Physical Review Letters*, 71(17):2781–2784, Oct. 1993. doi:10.1103/PhysRevLett.71.2781. URL https://link.aps.org/doi/10.1103/PhysRevLett.71.2781.  $\rightarrow$  page 93

- M. D. Johannes, I. I. Mazin, and C. A. Howells. Fermi-surface nesting and the origin of the charge-density wave in NbSe2. *Physical Review B*, 73(20): 205102, May 2006. doi:10.1103/PhysRevB.73.205102. URL https://link.aps.org/doi/10.1103/PhysRevB.73.205102.
- [282] E. Hassinger, G. Knebel, K. Izawa, P. Lejay, B. Salce, and J. Flouquet. Temperature-pressure phase diagram of URu2si2 from resistivity measurements and ac calorimetry: Hidden order and Fermi-surface nesting. *Physical Review B*, 77(11):115117, Mar. 2008. doi:10.1103/PhysRevB.77.115117. URL https://link.aps.org/doi/10.1103/PhysRevB.77.115117.
- [283] K. Terashima, Y. Sekiba, J. H. Bowen, K. Nakayama, T. Kawahara, T. Sato, P. Richard, Y.-M. Xu, L. J. Li, G. H. Cao, Z.-A. Xu, H. Ding, and T. Takahashi. Fermi surface nesting induced strong pairing in iron-based superconductors. *Proceedings of the National Academy of Sciences*, 106 (18):7330–7333, May 2009. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.0900469106. URL http://www.pnas.org/content/106/18/7330. → page 93
- [284] F. Mazzola, J. W. Wells, R. Yakimova, S. Ulstrup, J. A. Miwa, R. Balog, M. Bianchi, M. Leandersson, J. Adell, P. Hofmann, and T. Balasubramanian. Kinks in the sigma Band of Graphene Induced by Electron-Phonon Coupling. *Physical Review Letters*, 111(21):216806, Nov. 2013. doi:10.1103/PhysRevLett.111.216806. URL https://link.aps.org/doi/10.1103/PhysRevLett.111.216806. → page 94
- [285] D. Haberer, L. Petaccia, A. V. Fedorov, C. S. Praveen, S. Fabris, S. Piccinin, O. Vilkov, D. V. Vyalikh, A. Preobrajenski, N. I. Verbitskiy, H. Shiozawa, J. Fink, M. Knupfer, B. Buechner, and A. Grueneis. Anisotropic Eliashberg function and electron-phonon coupling in doped graphene. *Physical Review B*, 88(8):081401, Aug. 2013. doi:10.1103/PhysRevB.88.081401. URL https://link.aps.org/doi/10.1103/PhysRevB.88.081401. → page 94
- [286] C. Cancellieri, A. S. Mishchenko, U. Aschauer, A. Filippetti, C. Faber, O. S. Barii, V. A. Rogalev, T. Schmitt, N. Nagaosa, and V. N. Strocov.

Polaronic metal state at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface. *Nature Communications*, 7:10386, Jan. 2016. ISSN 2041-1723. doi:10.1038/ncomms10386. URL https://www.nature.com/articles/ncomms10386.  $\rightarrow$  page 96

- [287] Z. Wang, S. McKeown Walker, A. Tamai, Y. Wang, Z. Ristic, F. Y. Bruno, A. de la Torre, S. Ricc, N. C. Plumb, M. Shi, P. Hlawenka, J. Snchez-Barriga, A. Varykhalov, T. K. Kim, M. Hoesch, P. D. C. King, W. Meevasana, U. Diebold, J. Mesot, B. Moritz, T. P. Devereaux, M. Radovic, and F. Baumberger. Tailoring the nature and strength of electronphonon interactions in the SrTiO<sub>3</sub>(001) 2d electron liquid. *Nature Materials*, 15(8):835–839, Aug. 2016. ISSN 1476-4660. doi:10.1038/nmat4623. URL https://www.nature.com/articles/nmat4623. → pages 96, 97
- [288] M. Calandra and F. Mauri. Electronic structure of heavily doped graphene: The role of foreign atom states. *Physical Review B*, 76(16):161406, Oct. 2007. doi:10.1103/PhysRevB.76.161406. URL https://link.aps.org/doi/10.1103/PhysRevB.76.161406. → page 96
- [289] C. N. Veenstra, G. L. Goodvin, M. Berciu, and A. Damascelli. Elusive electron-phonon coupling in quantitative analyses of the spectral function. *Physical Review B*, 82(1):012504, July 2010. doi:10.1103/PhysRevB.82.012504. URL http://link.aps.org/doi/10.1103/PhysRevB.82.012504. → page 97
- [290] C. N. Veenstra, G. L. Goodvin, M. Berciu, and A. Damascelli. Spectral function tour of electron-phonon coupling outside the Migdal limit. *Physical Review B*, 84(8):085126, Aug. 2011. doi:10.1103/PhysRevB.84.085126. URL http://link.aps.org/doi/10.1103/PhysRevB.84.085126. → page 97
- [291] M. L. Kiesel, C. Platt, W. Hanke, D. A. Abanin, and R. Thomale. Competing many-body instabilities and unconventional superconductivity in graphene. *Physical Review B*, 86(2):020507, 2012. URL https://journals.aps.org/prb/abstract/10.1103/PhysRevB.86.020507. → pages 100, 101
- [292] R. Nandkishore, L. S. Levitov, and A. V. Chubukov. Chiral superconductivity from repulsive interactions in doped graphene. *Nature Physics*, 8(2):158–163, Feb. 2012. ISSN 1745-2473. doi:10.1038/nphys2208. URL

http://www.nature.com/nphys/journal/v8/n2/full/nphys2208.html.  $\rightarrow$  page 100

- [293] J. Pesic, R. Gajic, K. Hingerl, and M. Belic. Strain-enhanced superconductivity in Li-doped graphene. *EPL (Europhysics Letters)*, 108 (6):67005, Dec. 2014. ISSN 0295-5075. doi:10.1209/0295-5075/108/67005. URL https://iopscience.iop.org/article/10.1209/0295-5075/108/67005/meta. → page 103
- [294] G. Gui, J. Li, and J. Zhong. Band structure engineering of graphene by strain: First-principles calculations. *Physical Review B*, 78(7):075435, Aug. 2008. doi:10.1103/PhysRevB.78.075435. URL https://link.aps.org/doi/10.1103/PhysRevB.78.075435.
- [295] C. Si, Z. Sun, and F. Liu. Strain engineering of graphene: a review. *Nanoscale*, 8(6):3207–3217, 2016. doi:10.1039/C5NR07755A. URL https://pubs.rsc.org/en/content/articlelanding/2016/nr/c5nr07755a.  $\rightarrow$ page 103
- [296] M. Beye, F. Hennies, M. Deppe, E. Suljoti, M. Nagasono, W. Wurth, and A. Fhlisch. Dynamics of Electron-Phonon Scattering: Crystal- and Angular-Momentum Transfer Probed by Resonant Inelastic X-Ray Scattering. *Physical Review Letters*, 103(23):237401, Dec. 2009. doi:10.1103/PhysRevLett.103.237401. URL https://link.aps.org/doi/10.1103/PhysRevLett.103.237401. → page 103
- [297] H. Yavas, M. v. Veenendaal, J. v. d. Brink, L. J. P. Ament, A. Alatas, B. M. Leu, M.-O. Apostu, N. Wizent, G. Behr, W. Sturhahn, H. Sinn, and E. E. Alp. Observation of phonons with resonant inelastic x-ray scattering. *Journal of Physics: Condensed Matter*, 22(48):485601, Nov. 2010. ISSN 0953-8984. doi:10.1088/0953-8984/22/48/485601. URL https://iopscience.iop.org/article/10.1088/0953-8984/22/48/485601/meta.
- [298] Y. Y. Peng, M. Hashimoto, M. M. Sala, A. Amorese, N. B. Brookes, G. Dellea, W.-S. Lee, M. Minola, T. Schmitt, Y. Yoshida, K.-J. Zhou, H. Eisaki, T. P. Devereaux, Z.-X. Shen, L. Braicovich, and G. Ghiringhelli. Magnetic excitations and phonons simultaneously studied by resonant inelastic x-ray scattering in optimally doped Bi1.5pb0.55sr1.6la0.4cuo6+delta. *Physical Review B*, 92(6):064517, Aug. 2015. doi:10.1103/PhysRevB.92.064517. URL https://link.aps.org/doi/10.1103/PhysRevB.92.064517.

- [299] S. Moser, S. Fatale, P. Krueger, H. Berger, P. Bugnon, A. Magrez, H. Niwa, J. Miyawaki, Y. Harada, and M. Grioni. Electron-Phonon Coupling in the Bulk of Anatase TiO2 Measured by Resonant Inelastic X-Ray Spectroscopy. *Physical Review Letters*, 115(9):096404, Aug. 2015. doi:10.1103/PhysRevLett.115.096404. URL https://link.aps.org/doi/10.1103/PhysRevLett.115.096404.
- [300] T. Devereaux, A. Shvaika, K. Wu, K. Wohlfeld, C. Jia, Y. Wang, B. Moritz, L. Chaix, W.-S. Lee, Z.-X. Shen, G. Ghiringhelli, and L. Braicovich. Directly Characterizing the Relative Strength and Momentum Dependence of Electron-Phonon Coupling Using Resonant Inelastic X-Ray Scattering. *Physical Review X*, 6(4):041019, Oct. 2016. doi:10.1103/PhysRevX.6.041019. URL https://link.aps.org/doi/10.1103/PhysRevX.6.041019. → page 103
- [301] R. Wiesendanger, H.-J. Guentherodt, G. Guentherodt, R. J. Gambino, and R. Ruf. Observation of vacuum tunneling of spin-polarized electrons with the scanning tunneling microscope. *Physical Review Letters*, 65(2): 247–250, July 1990. doi:10.1103/PhysRevLett.65.247. URL https://link.aps.org/doi/10.1103/PhysRevLett.65.247. → page 103
- [302] D. Wortmann, S. Heinze, P. Kurz, G. Bihlmayer, and S. Bluegel. Resolving Complex Atomic-Scale Spin Structures by Spin-Polarized Scanning Tunneling Microscopy. *Physical Review Letters*, 86(18):4132–4135, Apr. 2001. doi:10.1103/PhysRevLett.86.4132. URL https://link.aps.org/doi/10.1103/PhysRevLett.86.4132.
- [303] A. Kubetzka, M. Bode, O. Pietzsch, and R. Wiesendanger. Spin-Polarized Scanning Tunneling Microscopy with Antiferromagnetic Probe Tips. *Physical Review Letters*, 88(5):057201, Jan. 2002. doi:10.1103/PhysRevLett.88.057201. URL https://link.aps.org/doi/10.1103/PhysRevLett.88.057201. → page 103
- [304] M. Yankowitz, S. Chen, H. Polshyn, Y. Zhang, K. Watanabe, T. Taniguchi, D. Graf, A. F. Young, and C. R. Dean. Tuning superconductivity in twisted bilayer graphene. *Science*, 363(6431):1059–1064, Mar. 2019. ISSN 0036-8075, 1095-9203. doi:10.1126/science.aav1910. URL https://science.sciencemag.org/content/363/6431/1059. → page 103
- [305] S. J. Ahn, P. Moon, T.-H. Kim, H.-W. Kim, H.-C. Shin, E. H. Kim, H. W. Cha, S.-J. Kahng, P. Kim, M. Koshino, Y.-W. Son, C.-W. Yang, and J. R. Ahn. Dirac electrons in a dodecagonal graphene quasicrystal. *Science*, 361

(6404):782–786, Aug. 2018. ISSN 0036-8075, 1095-9203. doi:10.1126/science.aar8412. URL https://science.sciencemag.org/content/361/6404/782.  $\rightarrow$  page 103

- [306] W. Yao, E. Wang, C. Bao, Y. Zhang, K. Zhang, K. Bao, C. K. Chan, C. Chen, J. Avila, M. C. Asensio, J. Zhu, and S. Zhou. Quasicrystalline 30 twisted bilayer graphene as an incommensurate superlattice with strong interlayer coupling. *Proceedings of the National Academy of Sciences*, 115 (27):6928–6933, July 2018. ISSN 0027-8424, 1091-6490. doi:10.1073/pnas.1720865115. URL https://www.pnas.org/content/115/27/6928. → page 103
- [307] F. Joucken, E. A. Quezada-Lpez, J. Avila, C. Chen, J. L. Davenport, H. Chen, K. Watanabe, T. Taniguchi, M. C. Asensio, and J. Velasco. Nanospot angle-resolved photoemission study of Bernal-stacked bilayer graphene on hexagonal boron nitride: Band structure and local variation of lattice alignment. *Physical Review B*, 99(16):161406, Apr. 2019. doi:10.1103/PhysRevB.99.161406. URL https://link.aps.org/doi/10.1103/PhysRevB.99.161406. → page 105
- [308] P. V. Nguyen, N. C. Teutsch, N. P. Wilson, J. Kahn, X. Xia, V. Kandyba, A. Barinov, G. Constantinescu, N. D. M. Hine, X. Xu, D. H. Cobden, and N. R. Wilson. Visualizing electrostatic gating effects in two-dimensional heterostructures. *arXiv:1904.07301 [cond-mat]*, Apr. 2019. URL http://arxiv.org/abs/1904.07301. arXiv: 1904.07301.
- [309] F. Joucken, J. Avila, Z. Ge, E. A. Quezada-Lopez, H. Yi, R. Le Goff,
  E. Baudin, J. L. Davenport, K. Watanabe, T. Taniguchi, M. C. Asensio, and
  J. Velasco. Visualizing the Effect of an Electrostatic Gate with
  Angle-Resolved Photoemission Spectroscopy. *Nano Letters*, 19(4):
  2682–2687, Apr. 2019. ISSN 1530-6984.
  doi:10.1021/acs.nanolett.9b00649. URL
  https://doi.org/10.1021/acs.nanolett.9b00649. → page 105
- [310] I. Gierz, F. Calegari, S. Aeschlimann, M. Chavez Cervantes, C. Cacho, R. Chapman, E. Springate, S. Link, U. Starke, C. Ast, and A. Cavalleri. Tracking Primary Thermalization Events in Graphene with Photoemission at Extreme Time Scales. *Physical Review Letters*, 115(8):086803, Aug. 2015. doi:10.1103/PhysRevLett.115.086803. URL https://link.aps.org/doi/10.1103/PhysRevLett.115.086803. → page 105

- [311] I. Gierz, M. Mitrano, J. C. Petersen, C. Cacho, I. C. E. Turcu, E. Springate, A. Stoehr, A. Koehler, U. Starke, and A. Cavalleri. Population inversion in monolayer and bilayer graphene. *Journal of Physics: Condensed Matter*, 27(16):164204, Apr. 2015. ISSN 0953-8984.
  doi:10.1088/0953-8984/27/16/164204. URL https://iopscience.iop.org/article/10.1088/0953-8984/27/16/164204/meta. → page 105
- [312] D. Sun, G. Aivazian, A. M. Jones, J. S. Ross, W. Yao, D. Cobden, and X. Xu. Ultrafast hot-carrier-dominated photocurrent in graphene. *Nature Nanotechnology*, 7(2):114–118, Feb. 2012. ISSN 1748-3395. doi:10.1038/nnano.2011.243. URL https://www.nature.com/articles/nnano.2011.243. → page 105
- [313] C. Kastl, C. Karnetzky, H. Karl, and A. W. Holleitner. Ultrafast helicity control of surface currents in topological insulators with near-unity fidelity. *Nature Communications*, 6:6617, Mar. 2015. ISSN 2041-1723. doi:10.1038/ncomms7617. URL https://www.nature.com/articles/ncomms7617. → page 105
- [314] D. Fausti, R. I. Tobey, N. Dean, S. Kaiser, A. Dienst, M. C. Hoffmann, S. Pyon, T. Takayama, H. Takagi, and A. Cavalleri. Light-Induced Superconductivity in a Stripe-Ordered Cuprate. *Science*, 331(6014): 189–191, Jan. 2011. ISSN 0036-8075, 1095-9203. doi:10.1126/science.1197294. URL https://science.sciencemag.org/content/331/6014/189. → page 105
- [315] T. Kampfrath, L. Perfetti, F. Schapper, C. Frischkorn, and M. Wolf. Strongly Coupled Optical Phonons in the Ultrafast Dynamics of the Electronic Energy and Current Relaxation in Graphite. *Physical Review Letters*, 95(18):187403, Oct. 2005. doi:10.1103/PhysRevLett.95.187403. URL https://link.aps.org/doi/10.1103/PhysRevLett.95.187403.
- [316] M. Mitrano, A. Cantaluppi, D. Nicoletti, S. Kaiser, A. Perucchi, S. Lupi,
  P. Di Pietro, D. Pontiroli, M. Ricc, S. R. Clark, D. Jaksch, and A. Cavalleri.
  Possible light-induced superconductivity in K<sub>3</sub>C<sub>60</sub> at high temperature. *Nature*, 530(7591):461–464, Feb. 2016. ISSN 1476-4687.
  doi:10.1038/nature16522. URL
  https://www.nature.com/articles/nature16522. → page 105
- [317] J. Zhang, P. W. Hess, A. Kyprianidis, P. Becker, A. Lee, J. Smith, G. Pagano, I.-D. Potirniche, A. C. Potter, A. Vishwanath, N. Y. Yao, and

C. Monroe. Observation of a discrete time crystal. *Nature*, 543(7644): 217–220, Mar. 2017. ISSN 1476-4687. doi:10.1038/nature21413. URL https://www.nature.com/articles/nature21413.  $\rightarrow$  page 105

## Appendix A

## **Publications**

During the course of this PhD thesis I was involved in a number of research projects. Some of these projects have resulted in peer reviewed publications, which are listed here.

• Room temperature strain-induced Landau levels in graphene on a waferscale platform.

**P. Nigge**, A. C. Qu, É. Lantagne-Hurtubise, E. Mårsell, S. Link, G. Tom, M. Zonno, M. Michiardi, M. Schneider, S. Zhdanovich, G. Levy, U. Starke, C. Gutiérrez, D. Bonn, S. A. Burke, M. Franz, and A. Damascelli *submitted*, *arXiv:1902.00514* [cond-mat.mtrl-sci]

• Correlated electron physics in gadolinium intercalated graphene.

**P. Nigge**, A. C. Qu, S. Link, F. Boschini, J. Geurs, M. Schneider, S. Zhdanovich, G. Levy, J. Smet, R. J. Green, U. Starke, and A. Damascelli *in preparation* 

• Bandgap opening in graphene by selective symmetry breaking.

A. C. Qu, **P. Nigge**, C. Gutiérrez, S. Link, G. Levy, M. Michiardi, M. Schneider, S. Zhdanovich, U. Starke, and A. Damascelli

in preparation

• Evidence for superconductivity in Li-decorated monolayer graphene.

B. M. Ludbrook, G. Levy, P. Nigge, M. Zonno, M. Schneider, D. J. Dvorak,C. N. Veenstra, S. Zhdanovich, D. Wong, P. Dosanjh, C. Straßer, A. Stöhr,S. Forti, C. R. Ast, U. Starke, and A. Damascelli

*Proceedings of the National Academy of Sciences.* 2015 Sep 22;112(38): 11795-9.

• Collapse of superconductivity in cuprates via ultrafast quenching of phase coherence.

F. Boschini, E. H. da Silva Neto, E. Razzoli, M. Zonno, S. Peli, R. P. Day,
M. Michiardi, M. Schneider, B. Zwartsenberg, P. Nigge, R. D. Zhong, J.
Schneeloch, G. D. Gu, S. Zhdanovich, A. K. Mills, G. Levy, D. J. Jones, C.
Giannetti, and A. Damascelli

Nature materials. 2018 May;17(5):416.

• Vanishing of the pseudogap in electron-doped cuprates via quenching of the spin-correlation length.

F. Boschini, M. Zonno, E. Razzoli, R. P. Day, M. Michiardi, B. Zwartsenberg, **P. Nigge**, M. Schneider, E. H. da Silva Neto, A. Erb, S. Zhdanovich, A. K. Mills, G. Levy, C. Giannetti, D. J. Jones, and A. Damascelli

submitted, arXiv:1812.07583 [cond-mat.str-el]

Additional publications based on work before the Phd:

• Tropospheric chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with weak organic acids.

A. Laskin, R. C. Moffet, M. K. Gilles, J. D. Fast, R. A. Zaveri, B. Wang, **P. Nigge**, and J. Shutthanandan

Journal of Geophysical Research: Atmospheres. 2012 Aug 16;117(D15).

• An environmental sample chamber for reliable scanning transmission x-ray microscopy measurements under water vapor.

S. T. Kelly, **P. Nigge**, S. Prakash, A. Laskin, B. Wang, T. Tyliszczak, S. R. Leone, and M. K. Gilles

Review of Scientific Instruments. 2013 Jul 30;84(7):073708.

• Adsorption geometry and electronic structure of iron phthalocyanine on Ag surfaces: A LEED and photoelectron momentum mapping study.

V. Feyer, M. Graus, **P. Nigge**, M. Wießner, R. G. Acres, C. Wiemann, C. M. Schneider, A.Schöll, and F. Reinert

Surface science. 2014 Mar 1;621:64-8.

• The geometric and electronic structure of TCNQ and TCNQ+Mn on Ag (001) and Cu (001) surfaces.

V. Feyer, M. Graus, **P. Nigge**, G. Zamborlini, R. G. Acres, A. Schöll, F. Reinert, and C. M. Schneider

*Journal of electron spectroscopy and related phenomena. 2015 Oct 1;204: 125-31.* 

• Three-dimensional tomographic imaging of molecular orbitals by photoelectron momentum microscopy.

M. Graus, C. Metzger, M. Grimm, P. Nigge, V. Feyer, A. Schöll, and F. Reinert

The European Physical Journal B. 2019 Apr 1;92(4):80.

## **Appendix B**

## **Conference contributions**

During the course of this PhD thesis I was fortunate to present our work during a number of international research conferences and meetings, which are listed below in chronological order.

- Graphene and related materials: Properties and Applications (GM), May 2016, invited talk (*Adatom-induced superconductivity in monolayer graphene*), Paestum, Italy
- Spectroscopies in novel superconductors (SNS), June 2016, talk + poster (*Adatom-induced superconductivity in monolayer graphene*), Ludwigsburg, Germany
- Center for quantum materials meeting (MPI-QMI-UT), December 2016, talk (*Adatom-induced superconductivity in monolayer graphene*), Tokyo, Japan
- Canadian-American-Mexican Graduate student physics conference (CAM), August 2017, talk (*Adatom-induced superconductivity in monolayer graphene*), Washington D.C., USA
- Superconductivity in atomically thin materials and heterostructures (Super-Thin), November 2017, invited talk (*From evidence of superconductivity towards correlated electron physics in monolayer graphene*), Lugano, Switzerland

- Center for quantum materials meeting (MPI-QMI-UT), December 2017, talk (*Correlated electron physics in graphene*), Stuttgart, Germany
- Center for quantum materials winterschool (MPI-QMI-UT), February 2018, poster (*Momentum-resolved landau quantization via strain-induced pseudo-magnetic fields in graphene*), Tokyo, Japan
- Center for quantum materials meeting (MPI-QMI-UT), December 2018, talk (*Designing quantum phases in monolayer graphene – Momentum-resolved Landau levels in strained graphene*), Tokyo, Japan
- International winterschool on electronic properties of novel materials (IWE-PNM), March 2019, poster (*Direct observation of momentum-resolved Landau levels in strained single-layer graphene*), Kirchberg, Austria
- Canadian graduate quantum conference (CGQC), June 2019, poster (Momentum-resolved Landau quantization via strain-induced pseudomagnetic fields in graphene), Sherbrooke, Canada
- Properties, Fabrication and Applications of Nano-Materials and Nano-Devices (Nano-M&D), June 2019, invited talk (declined), Paestum, Italy
- Gordon Research Conference New materials and structures in topological and correlated systems (GRC), June 2019, poster (*Momentum-resolved Landau quantization via strain-induced pseudomagnetic fields in graphene*), Hongkong, China