Electron-Phonon Mediated Superconductivity Probed by ARPES: from MgB$_2$ to Lithium-Decorated Graphene

by

Bartholomew Mears Ludbrook

B.Sc. Hons., Victoria University of Wellington, 2007
B.A., Victoria University of Wellington, 2007
M.Sc., Victoria University of Wellington, 2009

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)

November 2014

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Abstract

This thesis traces a path from conventional superconductivity in a bulk material to the introduction of superconductivity and other novel phenomena in graphene.

Magnesium diboride is a conventional superconductor, where the pairing is mediated by the electron-phonon coupling. ARPES (angle resolved photoemission spectroscopy) is shown to be an excellent probe to quantitatively study the momentum dependence of the electron-phonon coupling, demonstrating the origin of the distribution of superconducting gap sizes previously observed with other experimental techniques.

Next, we exploit our understanding of the electron-phonon coupling to study how it can be tuned in a low dimensional system. It is shown that the electron-phonon coupling in graphene can be strongly enhanced by the deposition of alkali adatoms. High resolution, low temperature ARPES measurements provide the first experimental evidence of superconductivity in this two-dimensional system, showing a temperature dependent pairing gap, and an estimated $T_c$ of $\sim 6$ K.

Finally, we present a study of another graphene-adatom system expected to show novel physics. Thallium on graphene has been predicted to enhance the spin-orbit coupling, leading to a robust topological insulator state. From ARPES measurements characterizing this system, we disentangle the long-range and short-range scattering contributions and show that thallium atoms act as surprisingly strong short-range scatterers. Our results are consistent with theoretical predictions for this system, indicating it is a good place to search for a two-dimensional topological insulator.
Preface

Experimental physics is a highly collaborative endeavour and the work presented here could not have been done without the help and input of numerous individuals. Collaborations including sample growth, theoretical support, and complementary experimental techniques, have all benefited this project immensely. This thesis consists of three projects where I have been the primary researcher. Each will produce a publication on which I am lead author. Here I will detail the various contributions from myself, and others, to each of the projects.

In all cases, the contributions of the UBC-ARPES group must be recognized for the work done to maintain a world-class system that made the experimental work possible. Under the supervision of A. Damascelli, I have contributed significantly, as have G. Levy, C.N. Veenstra, D. Wong, P. Dosanjh, and M. Schneider. The code used for visualizing and analyzing data has been written primarily by G. Levy and C.N. Veenstra.

For the work on MgB$_2$ in Chapter 3 samples were grown by N. Zhigadlo at ETH Zurich. The time-resolved spectroscopy and subsequent analysis was done by S. dal Conte, C. Gianetti and G. Cerullo at the Universita Cattolica del Sacro Cuore in Italy. I conducted the ARPES measurements, along with all of the analysis and interpretation of data. The code used for the self-energy analysis was written by C.N. Veenstra. The code for the extraction of the Eliashberg function was a mix of code written by J. Shi (and made available online) and myself. I performed density functional theory and other electronic structure calculations with help from Z. Zhu. I wrote the manuscript [1] with input from C. Giannetti, S. dal Conte, and A. Damascelli. A. Damascelli supervised and provided guidance on all aspects
of the measurements and analysis.

For the project of lithium on graphene in Chapter 4, graphene samples were provided by A. Stohr, S. Forti, and U. Starke at MPI-Stuttgart. The code used for the self-energy analysis was written by C.N. Veenstra. The code for the extraction of the Eliashberg function was a mix of code written by J. Shi (and made available online) and myself. I designed and assembled the UHV chamber used to prepare the graphene samples. I performed the ARPES and analysis on Li-graphene with assistance from G. Levy. Measurements on niobium were done by D. Dvorak and S. Zdhanovich. A. Damascelli supervised and provided guidance on all aspects of the measurements and analysis, and I wrote the manuscript [2] resulting from this work with input and editing from A. Damascelli and G. Levy.

The thallium on graphene project presented in Chapter 5 involved significant collaboration. The project was initiated by C. Ast and C. Strasser, and samples were provided by U. Starke and S. Forti from MPI-Stuttgart. C. Strasser and I carried out preliminary measurements. I conducted the bulk of the experimental work presented here and in the resulting manuscript. Scanning tunnelling microscopy was done by S. Burke and A. MacDonald with assistance from a summer student under my supervision, K. Chow, and input from me. The scattering theory work was done by T. Wehling. The manuscript resulting from this work [3] was written by C. Strasser and C. Ast, with input from A. Damascelli and me.

Over the course of my PhD, I have contributed to numerous other projects in ways ranging from technical assistance to experimental assistance. These contributions are not described in this thesis, but the resulting publications are listed in Appendix A.
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List of Symbols and Acronyms

$\Sigma''$ imaginary part of the electronic self-energy

$\Sigma'$ real part of the electronic self-energy

$\alpha^2 F(\omega)$ Eliashberg function

$\delta$ Short-range scattering potential

$\epsilon$ dielectric constant

$\epsilon_{km}^b$ electronic bare-band dispersion

$\lambda$ electron-phonon coupling parameter

MBE molecular beam epitaxy

k electron momentum

ARPES angle resolved photoemission spectroscopy

BCS Bardeen-Cooper-Schreiffer

CP cold phonons

$E_D$ Dirac point

$E_F$ Fermi energy

EPC electron-phonon coupling
List of Symbols and Acronyms

**FS**  Fermi surface

**FWHM**  full-width at half-maximum

**GIC**  graphite intercalated compound

**HWHM**  half-width at half-maximum

**KK**  Kramers-Kronig

**KKBF**  Kramers-Kronig bare-band fitting

**MDC**  momentum distribution curve

**MEM**  maximum-entropy method

**MgB$_2$**  magnesium diboride

**Nb**  niobium

**SCP**  strongly-coupled phonons

**STM**  scanning tunnelling microscopy

**$T_c$**  superconducting transition temperature

**Tl**  thallium

**UBC**  University of British Columbia
Acknowledgements

I would like to acknowledge and thank all of those who have contributed to this project over the years, beginning with the UBC ARPES lab, whose members work tirelessly to maintain a cantankerous, but ultimately state-of-the-art system. Giorgio Levy leads this effort, with assistance from Eduardo da Silva Neto, Michael Schneider, and past members Riccardo Comin, Christian Veenstra, Jason Zhu, and Ryan Wicks. Thanks also to the technical staff Pinder Dosanjh and Doug Wong, who build, fix, and advise, when we are in trouble.

This project benefited enormously from all of the collaborators who contributed directly, or helped frame this work in a wider context. Thank you, Carola Strasser and Christian Ast, for a valuable collaboration on the graphene projects. Thank you, Stefano dal Conte and Claudio Giannetti, for the time-resolved measurements on MgB$_2$. Thank you, Roberta Relabora, Jun Fuji, Piero Torelli, Ivana Vobornik, and Giancarlo Panaccione, the APE beamline scientists in Trieste, for the assistance with a project that does not appear here, but was immensely enjoyable to work on. Thank you, Andrew MacDonald and Sarah Burke, for the STM measurements on graphene. Thank you, Ali Khademi and Josh Folk, for the frequent discussions and ongoing collaboration on transport in graphene.

Thanks also to Mona Berciu, Doug Bonn, Ilya Elfmov, Marcel Franz, Steve Plotkin, and George Sawatzky, for the discussions, advice, and feedback over the course of my PhD, and on this thesis.

Finally, thank you to my supervisor, Andrea Damascelli, for the guidance and encouragement. Thank you for the hard work that you put in, that motivates us to work hard.
For Fiona Jean Hodge,
thank you for the distractions.
Chapter 1

Introduction

One of the major goals of condensed matter physics is the description of electrons in a solid. In the simplest case, the properties of the electron are determined by the periodic potential of the crystal lattice. In reality, electrons interact with each other, with the vibrations of the lattice, and with a host of other possible excitations. The description of this system of interacting particles defines the many-body problem; understanding this behaviour in complex systems is arguably the most formidable challenge in condensed matter physics. But as great as the challenge is, the rewards are greater. Emergent from the soup of particles and interactions, phenomena such as superconductivity demonstrate the wealth of new physics, and new technology, waiting to be unlocked.

Improvements in experimental probes have allowed ever more insight into the complex electronic structure of correlated materials. ARPES, the primary technique used in this thesis, can access the low energy electronic excitations resolved in both energy and momentum. As a result, ARPES can measure signatures of interactions in complex systems that are not accessible to other techniques. However, the interpretation of ARPES data remains challenging in such systems, partly because general descriptions of the electronic phenomena arising from many-body physics are still very limited.

A useful strategy for tackling problems in physics is to start from the simplest solvable description, and add in the interesting complexity little by little. A similar approach works in the experimental investigation of complex interacting systems. By studying systems that are dominated by one type of interaction, theory can make accurate predictions and experiments can be reliably interpreted. An example of this is MgB$_2$ where superconductivity at
39 K is induced by the interaction between electrons and the vibrations of the lattice; other interactions can be ignored. In Chapter 3, we present new measurements on this conventional superconductor, providing new insights into its phonon-mediated superconductivity. As a next step, in Chapter 4, we show how the electron-phonon coupling can in fact be tuned in monolayer graphene through the deposition of lithium adatoms. We present evidence that suggests, for the first time, the presence of superconductivity in this two-dimensional carbon crystal. Finally, in Chapter 5, we explore another way of tuning the properties of graphene based on a prediction of a topological insulator phase stabilized through heavy adatom deposition. We present a thorough characterization of TI adatoms on graphene, concluding that this is a promising system to observe the predicted effect.

1.1 MgB$_2$: a multi-gap superconductor

The mechanism that allows electrons to overcome their Coulomb repulsion and form superconducting pairs in conventional superconductivity is the coupling between electrons and phonons. This interaction is described by the so-called ‘glue function’ or Eliashberg function which is akin to the spectrum of phonon excitations weighted by the strength of the coupling with the electronic states. The strength of this interaction is given by the dimensionless electron-phonon coupling constant, $\lambda$, which enters into the determination of the superconducting transition temperature, $T_c$.

The experimental determination of the Eliashberg function is of paramount importance, because it identifies the phonon modes that are coupling to the electronic states, and are therefore directly involved in the superconducting pairing mechanism. There are a number of experimental probes that can access the Eliashberg function, including electron-tunnelling which gave the first example of this in lead (Pb) [4]. However, most techniques probe the momentum-integrated Eliashberg function, related to the average EPC over the entire Fermi surface. Sophisticated calculations, including details of both
1.1. \textit{MgB}_2: a multi-gap superconductor

the electronic and phononic structure, can now provide a fully momentum-resolved view of the electron-phonon coupling, showing that in many cases, certain parts of the Fermi surface are more strongly coupled than others. This calls for an experimental probe that can do the same. ARPES provides the momentum resolved electronic structure, and in Chapter 2 it is shown that this leads to the experimental determination of the momentum-resolved Eliashberg functions and electron-phonon coupling strength. The Eliashberg function is the link between experiment and theory for the electron-phonon coupling in conventional superconductors.

Superconductivity in MgB$_2$ at 39 K was discovered in 2001 [5] and was quickly understood in terms of electron-phonon mediated conventional superconductivity, albeit with a remarkably high $T_c$. When experiments started to show some unexpected results relating to the size of the superconducting gap, it was proposed that this material might be the first known example of a multi-gap superconductor, whereby the Fermi surfaces of different orbital character couple to different phonon modes with different strength, leading to Fermi surface dependent superconducting gaps. This was confirmed by ARPES [6], an ideal probe for disentangling the superconductivity of distinct Fermi surfaces.

With better samples, and better experiments, the picture became even more complex, but also more interesting. Electron tunnelling spectroscopy measurements of the superconducting gap showed that not only are there two distinct gaps, but that there is a distribution of gaps on each Fermi surface [7]. In Chapter 3 we present the highest quality ARPES measurements ever performed on this material, where the electron-phonon coupling is clearly manifest in the kinks in the dispersion. It is shown that the anisotropy of the electron-phonon coupling around the Fermi surface explains the distribution of gaps seen in recent experiments [7], and theory [8–12].
1.2. Superconductivity in lithium-decorated graphene

Based on a solid understanding of electron-phonon mediated superconductivity, one can begin to explore how these properties can be manipulated or introduced in a system. Tailoring new bulk materials by combining particular elements into a specific crystal structure is one approach, but it faces many (often insurmountable) challenges from the restrictions of chemistry. Working with low dimensional systems, on the other hand, the properties of the entire system can be tuned by modifications to the surface. Graphene, a perfect two dimensional crystal of carbon atoms, is an ideal place to start.

Graphene is host to a wide array of spectacular phenomena \cite{13, 14}, making it of interest for both fundamental and applied research. Superconductivity is arguably the most important property that has not been observed in monolayer graphene. This is not for lack of theoretical and experimental effort \cite{15-21}, and a recent theoretical work has suggested a way to make graphene superconducting through the adsorption of lithium adatoms \cite{17}. The proposed superconductivity is electron-phonon mediated, as in MgB$_2$. In fact, the phenomenology of superconductivity in Li-graphene should be very similar to that of MgB$_2$, barring its two-gap nature.

While not observed in pure bulk graphite, superconductivity occurs in certain GICs (graphite intercalated compounds) with $T_c$ of up to 11.5 K in the case of CaC$_6$ \cite{22, 23}. The origin of superconductivity in these materials has been identified in the enhancement of electron-phonon coupling induced by the intercalant layers \cite{24, 25}. The observation of a superconducting gap on the graphitic $\pi^*$ bands in bulk CaC$_6$ \cite{26} suggests that realizing superconductivity in monolayer graphene might be a real possibility.

Although the Li-based GIC – bulk LiC$_6$ – is not known to be superconducting, Li decorated graphene emerges as a particularly interesting case with a predicted superconducting $T_c$ of up to 8.1 K \cite{17}. The proposed mechanism for this enhancement of $T_c$ is the removal of the confining potential of
1.3. Graphene: a robust topological insulator?

the graphite C \(_6\) layers, which changes both the occupancy of the Li 2s band (or the ionization of the Li) and its position with respect to the graphene layer, ultimately leading to an increase of the electron-phonon coupling from \(\lambda = 0.33\) to 0.61 in going from bulk to monolayer LiC\(_6\). Based on similar considerations, it has also been argued that the LiC\(_6\) monolayer should exhibit the largest value for both \(\lambda\) and thus \(T_c\), among all alkali-metal-C\(_6\) superlattices [17].

In Chapter 4 we demonstrate how the electron-phonon coupling in a single layer of graphene can be strongly enhanced by the presence of lithium deposited at low temperature. We provide the first evidence for the presence of a temperature-dependent pairing gap on part of the graphene-derived \(\pi^*\) Fermi surface. The detailed evolution of the density of states at the gap edge, as well as the phenomenology analogous to the one of known superconductors such as niobium, indicate that the pairing gap observed at 3.5 K in graphene is associated with superconductivity. Based on the BCS (Bardeen-Cooper-Schreffer) gap equation, \(2\Delta = 3.5 k_b T_c\), the measured gap of \(\Delta = 0.9\text{meV}\) suggests that Li-decorated graphene is superconducting with \(T_c \simeq 5.9\text{K}\), remarkably close to the value of 8.1 K found in density-functional theory calculations [17].

1.3 Graphene: a robust topological insulator?

Tailoring the properties of low-dimensional systems in general, and graphene in particular, opens immense possibilities for both fundamental and applied research. A natural progression from our study of Li-graphene is to use similar methods and techniques to explore what other novel physics graphene can host. In the relatively new field of topological insulators, the topology of the electronic wavefunction can be tailored by controlling which symmetries are respected in a sample, leading to topologically protected surface or edge states. Thallium adatoms on graphene have been predicted to open a signif-
icant spin-orbit gap at the Dirac point, transforming graphene into a robust
topological insulator [27].

Graphene was the first material predicted to be a topological insulator,
where it was claimed that a gap would open at the Dirac point of the elec-
tronic structure, while gapless, spin-polarized edge modes persist at the sam-
ple boundaries [28]. The origin of this gap is the spin-orbit coupling, which is
generally proportional to the atomic mass, and hence is very weak for carbon:
calculations have estimated the size of the gap to be on the order of $\mu eV$, or
$\sim 0.01 K$ [29, 30]. Proposals to enhance the size of the gap focus on enhancing
the spin-orbit coupling experienced by the low-energy electronic excitations
in graphene. A particularly interesting proposal, from an experimental point
of view, aims to achieve this through the adsorption of heavy adatoms [27].

There are several criteria that a heavy adatom must meet in order to be
considered a candidate. First, the adsorption site should be the hollow site,
at the centre of the graphene hexagon. This allows the adatom to mediate
the second-neighbor hopping without breaking the sublattice symmetry. The
adatoms must be non-magnetic so as not to break time-reversal symmetry,
which implies the complete charge transfer of any unpaired electrons. And
finally, the adatom should interact strongly with the graphene $\pi$ electrons.
Extensive density functional theory and tight binding calculations identified
indium and thallium as the best options, and they were shown to open spin-
orbit gaps of up to 6 and 20 meV respectively, many orders of magnitude
larger than the intrinsic gap of graphene.

The theoretical prediction of a large spin-orbit gap the Dirac point of
thallium decorated graphene motivated our experiments. In Chapter[5] we
present a comprehensive phenomenology of thallium adatoms on the mono-
layer graphene surface, highlighting where our results agree with theoretical
predictions for this system. In particular, a detailed study of the scattering
mechanisms in this system reveals the important contribution of short-range
scattering, indicating the graphene electrons do ‘feel’ the Tl atoms. Whether
this leads to the predicted gap remains to be seen.
1.4 Outline

Chapter 2 begins with a description of [ARPES](#), the experimental technique used in all of the projects presented in this thesis. This is followed by a discussion of what ARPES can tell us, beyond the simple band structure of a material. In particular, it is shown how the electron-phonon interaction, important for conventional superconductivity, can be quantitatively analyzed from ARPES spectra. These techniques are applied to MgB$_2$ in Chapter 3, where we gain new insight into this multi-gap superconductor. In Chapter 4 we provide the first ever evidence for superconductivity in graphene, showing how lithium deposited at low temperature stabilizes this state via the same mechanism as in MgB$_2$. In Chapter 5 we explore another way to modify the properties of graphene, with the aim of creating a 2D topological insulator. We describe how thallium adatoms interact with the graphene monolayers, and show that this system is a good place to look for the quantum spin hall state.

This thesis demonstrates the power of the ARPES technique for understanding the origins of superconductivity in both 3D and 2D systems, and for characterizing new low-dimensional systems. This is also a thesis about materials. It is about how novel materials can be made and measured, all in ultra-high vacuum, and at temperatures a few degrees above absolute zero. And while these conditions are not conducive to the imminent development of ground-breaking new technology, hopefully the work presented in this thesis will contribute in some way to bringing future materials and technologies to fruition.
Chapter 2

ARPES: Experiment & Analysis

ARPES measures the energy and momentum of the occupied electronic states in a solid. The highest occupied states form a surface in momentum space at constant energy, known as the Fermi surface, which defines many of the electronic, thermal, and optical properties of the solid. ARPES is one of very few probes that can directly measure the Fermi surface, and hence it is a powerful tool in determining the electronic structure of materials. ARPES is also sensitive to the signatures of an interacting system via the kinks and other anomalies that appear in the electronic dispersion, making it an important technique for understanding the origin of complex many-body phenomena. This chapter introduces the experimental technique, and outlines what it can tell us about interactions. This is followed by a sketch of the theoretical framework for performing a quantitative analysis of the electron-phonon coupling, and an explanation of how this relates to the superconducting properties of a material.

2.1 Introduction to ARPES

ARPES traces its origins to the photoelectric effect first explained by Albert Einstein in 1905, the year now referred to as the annus mirabilis. The realization that light was quantized explained why light incident on a conducting material leads to the emission of electrons only when the energy of the light, $h\nu$, is above a certain threshold, regardless of the intensity. The
kinetic energy ($E_{\text{kin}}$) of the outgoing electron is given by

$$E_{\text{kin}} = h\nu - \phi - |E_b|, \quad (2.1)$$

and hence from the measured kinetic energy, the binding energy of the electron in the solid $E_b$ can be determined. The work function $\phi$ is a material dependent quantity that defines the minimum energy required for an electron to escape the solid.

The photoemitted electron has wavevector or momentum $\mathbf{K} = \mathbf{p}/\hbar$ with magnitude $K = \sqrt{2mE_{\text{kin}}}/\hbar$. The angle at which the electron is photoemitted is related to its momentum by:

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

$$K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin(\theta) \sin(\varphi)}, \quad (2.3)$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \cos(\theta)}, \quad (2.4)$$

where the polar ($\theta$) and azimuthal ($\varphi$) emission angles are defined by the experimental geometry shown in Fig. 2.1.

Given the components of the electrons momentum in vacuum, we would like to find the crystal momentum $\mathbf{k}$ of the electron in the solid. Due to the translational symmetry in the x-y plane, the components of $\mathbf{K}$ parallel to the sample surface are conserved across the sample-vacuum interface, giving

$$\mathbf{K}_\parallel = \mathbf{k}_\parallel = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin(\theta)}, \quad (2.5)$$

where $\mathbf{k}_\parallel$ is the crystal momentum of the electron. The momentum of the incoming photon is much smaller than the electron momentum, and can be ignored.

There is no such symmetry in the direction perpendicular to the surface, and so the perpendicular component of the momentum is not conserved. Rather,

$$\mathbf{k}_\perp = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \theta + V_0)}, \quad (2.6)$$
2.1. Introduction to ARPES

Figure 2.1: **Geometry of a typical ARPES measurement.** The absorption of photons with energy $h\nu$ leads to the photoemission of electrons with energy $E_{kin}$. The positions of the photon source and the analyzer are fixed. Rotating the sample about the x and y axes defines which emission angles will be detected. From Ref. [31]
2.1. Introduction to ARPES

Figure 2.2: The 3D dataset produced by the UBC ARPES system. ARPES measurement of Sr$_2$RuO$_4$ showing how the spectral function can be cut at a constant energy or momentum. The Fermi surface is the constant energy cut at $E=0$, while the band dispersion along several high symmetry directions in the Brillouin zone are seen in the side panels. From Ref. [32].

where $V_0$ depends on details of the band structure and the work function. While these details can be determined experimentally or from calculations, the more common approach is to compare the experimental Fermi surface with calculated ones for different values of $k_{\perp}$.

The typical ARPES experiment measures the kinetic energy and the emission angles of a photoelectron relative to the sample plane. This is all the information necessary to build up a picture of the 3-dimensional $k_x, k_y, E$ space, and the occupied electronic states within, as shown for the perovskite material Sr$_2$RuO$_4$ in Fig. 2.2.
2.1. Introduction to ARPES

Figure 2.3: The ‘universal’ inelastic mean-free-path curve. The inelastic mean-free-path, or escape depth, of photoelectrons shows a minima for kinetic energies between 20 and 50 eV. ARPES using photon sources in this range are particularly sensitive to the electronic structure from sample surface, which is not always the same as in the bulk. From Ref. [31]

2.1.1 The UBC system

Many systems studied with ARPES are layered or 2D materials and as such possess a natural cleavage plane. Measuring involves cleaving a single crystal sample in vacuum, exposing a clean, well ordered face. For the many systems that cannot simply be cleaved in vacuum, it is necessary to be able to prepare clean and atomically flat surfaces. To this end, I designed and built a preparation chamber where samples could undergo cycles of sputtering and annealing, and where deposition of adatoms or thin films could be done at temperatures between 300 K and 1200 K, and in ultra-high vacuum. The addition of these capabilities opened up new avenues of research including the preparation of atomically flat metal single crystal samples, graphene, MBE-grown topological insulator samples, and niobium thin-film growth.

In the case of metallic single crystals, sputtering involves the bombardment of the sample with energized (100-3000 eV) ionized argon particles.
2.1. Introduction to ARPES

Figure 2.4: **Diagram of an ARPES electron analyzer.** A voltage applied between the hemispheres selects the kinetic energy that will hit the centre of the detector, and the range of kinetic energies that will be detected. From Ref. [33]

The Ar$^+$ ions hit the sample surface, imparting enough energy to remove adsorbed atoms and sample material. Sputtering leads to significant surface roughness. Annealing involves heating the sample, typically to the point where the mobility of the surface atoms is significantly increased, allowing the surface to reconstruct. In the case of graphene samples, annealing simply removes any surface contaminants due to the transportation of the sample in air, leaving a pristine single crystal surface. Samples are transferred directly from the preparation chamber to the ARPES chamber without breaking vacuum, and thus preserving the clean surface for measurements.

The other key components of a state-of-the-art ARPES system are the photon source, the electron analyzer, and the cryogenic sample manipulator. The UBC ARPES chamber uses a gas discharge lamp$^1$ to provide a monochromatized source of photons. Helium gas is typically used, giving a primary excitation line at HeI=21.2 eV, and a less intense line at 41.8 eV, which lie in the ultra violet spectrum. At these photon energies, the kinetic energy of the photoelectrons corresponds to the minimum of the inelastic

$^1$SPECS UV300
mean free path for excited electrons in solids. Put another way, ARPES at these photon energies is extremely surface sensitive, as shown in Fig. 2.3. This can be a blessing or a curse, depending on the experimental aims, and should be kept in mind when interpreting results.

The electron analyzer consists of two concentric hemispheres where a radial voltage may be applied. Photoelectrons with kinetic energy $E_{\text{kin}} \pm \delta$ are directed onto a detector where $\delta$ can be set between several hundred meV, and several eV. Photoelectrons with energy $E_k$ hit the centre of the detector, and different kinetic energies are resolved along one axis of the 2D detector [Fig. 2.4]. The other axis of the detector resolves the angle of the photoelectron ($\theta$), and in this way, the detector collects a 2D image of energy vs. momentum.

The energy and momentum resolution are in principle determined by the parameters of the analyzer, but in reality are also affected by stray magnetic fields and electronic noise at the experiment chamber. The latter two are reduced as much as possible by shielding the photoemitted electron path from magnetic fields, and by eliminating any loops to the electronic ground, which can pick up noise by induction from stray magnetic fields. In the best conditions, the angular resolution has been determined to be $0.3^\circ$. The energy resolution is determined by fitting the Fermi edge of a polycrystalline gold sample with a Fermi-Dirac distribution function convoluted with a Gaussian whose width corresponds to the resolution:

$$I_{f dk}(\omega) = [f(\omega, T) (a + b \omega)] \otimes R_\omega.$$ (2.7)

This is shown in Fig. 2.5 for two temperatures. Resolution values of $\sim 5$ meV are typical for the high resolution measurements presented in this thesis.

Samples are mounted on a 6-axis cryogenic manipulator that allows the sample temperature to be controlled between 300 and 3.5 K, with an accuracy of $\pm 0.1$ K. The analyzer and lamp are fixed in position, and so by changing the angle of the sample with respect to the analyzer, different emission angles are sampled, and the 2D Fermi surface may be mapped out, as shown in
Figure 2.5: **Measuring the experimental energy resolution.** Fitting the Fermi edge of a polycrystalline gold sample at a known temperature with Eq. 2.7 allows one to determine the energy resolution, as shown here for two temperatures. The thermal smearing of the Fermi-Dirac distribution is shown between 3.5 K and 15 K. The resolution is found to be 5 ± 0.5 meV at both temperatures.
2.2 The spectral function

ARPES probes the imaginary part of the single-particle Green’s function propagator describing an interacting system, a quantity known as the spectral function:

\[ A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \epsilon^b_k - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}. \]  

(2.8)

Here, \( \epsilon^b_k \) is the bare-band of the non-interacting system, and \( \Sigma(k, \omega) = \Sigma'(k, \omega) + i \Sigma''(k, \omega) \) is the complex electron self-energy describing the interactions. In a non-interacting system, \( \Sigma(k, \omega) = 0 \), and the spectral function consists of a single pole at each \( k \) along the bare-band \( \epsilon^b_k \). In an interacting system, the form of the self-energy determines how the spectral function is modified: the real part relates to the renormalization of the electron energy, affecting the observed dispersion of the band, while the imaginary part relates to the lifetime, and the broadening of the spectral function.

2.3 Self-energy analysis

Accessing the self-energy is an increasingly important goal of ARPES measurements, as it provides the link between experiment and theory. In the case where the self-energy is weakly momentum dependent, it is convenient to analyze the spectral function in terms of constant energy cuts, or MDCs at \( \omega = \tilde{\omega} \) [see Fig. 2.6]. As long as \( \epsilon^b_k \) can be linearized about the MDC peak maximum at \( k = k_m \), the MDC will have a Lorentzian lineshape [34]. Using the Taylor expansion of the bare-band about the MDC peak maximum \( k = k_m \) (i.e. \( \epsilon^b_k = \epsilon^b_{k_m} + v^b_{k_m} (k - k_m) + ... \) ignoring higher order terms, and realizing that \( \tilde{\omega} = \Sigma'_\omega + \epsilon^b_{k_m} \), Eq. 2.8 can be rewritten as

\[ A_{\tilde{\omega}}(k) \approx \frac{A_0}{\pi} \frac{\Delta k_m}{(k - k_m)^2 + (\Delta k_m)^2}. \]  

(2.9)
2.3. Self-energy analysis

Figure 2.6: Illustration of the spectral function and self-energy. (a) Strong electron-phonon coupling modifies the spectral function, and the extracted MDC dispersion (orange) differs from the known bare-band by the real part of the self-energy (green). (b) The Lorentzian lineshape of the MDC at $\tilde{\omega}$ with peak maximum at $k_m$ and HWHM $\Delta k_m$. From Ref. [33]
2.3. Self-energy analysis

This is recognizable as the form of a Lorentzian with [HWHM] Δkₘ and weight A₀ given by

\[ Δkₘ = -Σ''/v_k^b, \]

\[ A₀ = 1/v_k^b = \int A_{\tilde{\omega}}(k)dk. \]  (2.10)

The Lorentzian fits at ω = \tilde{\omega}, having peak maximum kₘ, determine all the quantities required to calculate the self-energy, provided the bare-band is known:

\[ Σ' = \tilde{\omega} - ϵ_k^b, \]

\[ Σ'' = -Δkₘv_k^b. \]  (2.11)

Of course, the bare-band is never really known *a priori*. It can, however, be found from experimental data through a self consistent, iterative procedure that simultaneously determines the real and imaginary parts of the self-energy, and the bare-band [34]. This routine relies on the fact that Σ'(ω) and Σ''(ω) are determined independently (although both depending on the bare-band), but each must be consistent with the KK (Kramers-Kronig) transform of the other⁡ (this method is known as Kramers-Kronig bare-band fitting, or KKBF). Starting with a guess for the parameters of the second order polynomial bare-band, the self-energies are determined from Σ'MDC = \tilde{\omega} - ϵ_k^b and Σ''MDC = -Δkₘv_k^b, and compared with their KK transforms:

\[ Σ'_{KK}(\omega) = \frac{1}{\pi} \text{PV} \int_{-\infty}^{\infty} \frac{Σ''_{MDC}(x)}{x - \omega} dx, \]

\[ Σ''_{KK}(\omega) = -\frac{1}{\pi} \text{PV} \int_{-\infty}^{\infty} \frac{Σ'_{MDC}(x)}{x - \omega} dx, \]  (2.12)

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²This is simply a result of the general theorem that the real and imaginary parts of an analytic complex function are KK related.
2.4 Signatures of bosons in ARPES

where PV denotes the Cauchy principle value. The bare-band is varied until \( \Sigma'_{MDC}(\omega) \) (\( \Sigma''_{MDC}(\omega) \)) is self-consistent with \( \Sigma'_{KK}(\omega) \) (\( \Sigma''_{KK}(\omega) \)).

The methods presented here are valid for a weakly momentum-dependent self-energy, and will fail when the self-energy is strongly momentum dependent. It is difficult to know, in a real system, what amounts to ‘strong’ momentum dependence. One clue is a non-Lorentzian MDC lineshape, however, a Lorentzian lineshape does not guarantee weak momentum dependence [34, 35]. The failure of the KKBF (Kramers-Kronig bare-band fitting) routine is a fairly good indicator, but again, simulations have shown that in certain cases it is possible to have self-consistent \( \Sigma_{MDC} \) and \( \Sigma_{KK} \) that do not give the true self-energy [36]. There is an alternative method of calculating \( \Sigma'' \) without any knowledge of the bare-band, and that has been shown to be immune to strong local momentum dependence of the self-energy. From Eqns. 2.10 and 2.11 we see that

\[
\Sigma''_{\text{Ratio}} = -\Delta k_m / A_0 ,
\]

which can be calculated directly from the parameters of the MDC fits. This quantity can act as a consistency check on the self-energy analysis as any spurious k-dependent effects appearing in the self-energy calculated in the KKBF routine would lead to deviations between \( \Sigma''_{\text{Ratio}} \) and \( \Sigma''_{MDC} \). The agreement of these two quantities can be used as an indicator of the reliability of the self-energy determined from real materials, which often show some momentum dependence.

2.4 Signatures of bosons in ARPES

The self-energy describes how a bare particle is ‘dressed’ by its interactions with electrons and bosons. The composite of the bare particle and its relevant interactions is known as a quasiparticle, and both its energy and lifetime are renormalized with respect to those of the bare particle. These renormalizations introduce features in the spectral function that are measured with
2.4. Signatures of bosons in ARPES

ARPES. For the systems studied in this thesis, the relevant bosons are the quantized lattice vibrations known as phonons. In the following, we discuss the electron-phonon coupling, and demonstrate how ARPES measurements access details of this interaction that is so important for conventional superconductivity.

2.4.1 Electron-phonon coupling

Certain interactions in a solid introduce an attractive potential between electrons, allowing them to overcome their Coulomb repulsion and form composite bosons known as Cooper pairs. The condensate of these new bosons is the superconducting state. An early successful description of superconductivity, BCS theory, treated the pairing interaction of two electrons at the Fermi energy with opposite spin and momentum by a constant potential, without reference to its origin.

In conventional superconductors, it is the exchange of phonons that mediates the pairing interaction. The link between BCS theory and the theory of electron-phonon coupling in metals is credited to Eliashberg, and the theory bears his name [37, 38]. The central quantity is the bosonic spectrum, Eliashberg function, or simply $\alpha^2 F(\omega)$, which is described below. This function defines the properties of this class of superconductors.

The electron-phonon interaction involves the scattering of an electron of momentum $k$ to a state with momentum $k'$ via a phonon of momentum $q = k' - k$, with probability given by the electron-phonon coupling matrix elements $g(k, k', v)$ ($v$ is the phonon mode index). The Eliashberg function is found by summing over the ways to scatter an electron from $\epsilon_k$ to $\epsilon_{k'}$ weighted by their probability:

$$\alpha^2 F_k(\omega) = \sum_{k',v} |g(k, k', v)|^2 \delta(\omega - \omega_{v,q}) \delta(\epsilon_k - \epsilon_{k'}) .$$  \hspace{1cm} (2.14)

Here the first delta function relates to the phonon energy, while the second is the electron energy within the quasi-elastic approximation [56]. This func-
2.4. Signatures of bosons in ARPES

...tion is akin to the phonon density of states weighted by the strength of the coupling to electrons, although is it not simply a product of the two as the name misleadingly suggests. This is a very important quantity that defines the electron-phonon coupling in a system. The dimensionless momentum-resolved electron-phonon coupling constant is given by:

\[ \lambda_k = 2 \int_0^\omega d\omega' \frac{\alpha^2 F_k(\omega')}{\omega'} , \]  

(2.15)

These quantities are given here in their momentum-resolved form to provide grounds for comparison with ARPES, which measures the momentum-resolved electronic structure. The momentum-integrated quantities are retrieved by summing over all pairs of \( \mathbf{k}, \mathbf{k}' \) in Eq. 2.14, or by averaging \( \lambda_k \) over the Fermi surface.

The Eliashberg function is related to the real and imaginary parts of the self energy via the integral relations

\[ \Sigma_k'(\omega) = \int_{-\infty}^\infty dv \int_0^\omega d\omega' \alpha^2 F_k(\omega') \frac{2\omega'}{v^2 - \omega'^2} f(v + \omega) , \]  

(2.16)

\[ |\Sigma_k''(\omega)| = \pi \hbar \int_0^\infty d\omega' \alpha^2 F_k(\omega')[1 - f(\omega - \omega') + 2n(\omega') + f(\omega + \omega')] , \]  

(2.17)

where \( f(\omega) \) and \( n(\omega') \) are the Fermi-Dirac and Bose-Einstein distribution functions for the electrons and phonons respectively.

2.4.2 Extracting \( \alpha^2 F(\omega) \) from ARPES data

Given the self-energy determined from ARPES measurements, the challenge is to pull out the momentum resolved \( \alpha^2 F_k(\omega) \) function. The simplest approach is to perform an integral inversion by minimising

\[ \chi^2 = \sum_i \frac{[D_i - \Sigma_k'(\epsilon_i)]^2}{\sigma_i^2} \]  

(2.18)

against \( \alpha^2 F_k(\omega) \), where \( D_i \) are the data, \( \sigma_i \) is the error, and \( \Sigma_k' \) is defined by Eq. 2.16. However, this tends to fail due to the noise in the data. There need
2.4. Signatures of bosons in ARPES

to be some constraints imposed on the form of $\alpha^2 F_k(\omega)$. Next, we discuss two ways to achieve this.

**Maximum entropy method**

The MEM (maximum-entropy method) is an integral inversion procedure to extract the Eliashberg function from ARPES data originally presented in Ref. [39], and used in the analysis of numerous systems since [40]. Instead of the direct inversion of Eq. 2.18, this method minimizes the functional

$$L = \frac{\chi^2}{2} - aS,$$

(2.19)

where $\chi^2$ is defined as above, and $S$ is the generalized Shannon-Jaynes entropy:

$$S = \int_0^\infty d\omega [\alpha^2 F(\omega) - m(\omega) - \alpha^2 F(\omega) ln \frac{\alpha^2 F(\omega)}{m(\omega)}].$$

(2.20)

Here, $m(\omega)$ is a ‘best guess’ at the form of the Eliashberg function, and the entropy term will be maximized for $m(\omega) = \alpha^2 F_k(\omega)$. The parameter $a$ in Eq. 2.19 is a multiplier that determines how much importance to place on the entropy term, and hence the constraint function on the Eliashberg function.

**Self consistent method**

An alternative method uses the experimentally determined imaginary part of the self-energy as a constraint on the inversion procedure. This is achieved by fitting the real and imaginary parts of the self-energy simultaneously, with the same Eliashberg function. This amounts to minimising

$$\chi^2 = \sum_i \frac{[D_i - \Sigma'_k(\epsilon_i)]^2}{\sigma_i^2} + \sum_j \frac{[D_j - \Sigma''_k(\epsilon_j)]^2}{\sigma_j^2},$$

(2.21)

where $D_i$ and $D_j$ are the data for the real and imaginary parts of the self energy respectively, and $\Sigma'_k$ and $\Sigma''_k$ are defined in Eqs. 2.16 and 2.17. A
2.5. From electron-phonon coupling to superconductivity

Further constraint is involved by taking $\alpha^2 F_k(\omega)$ to be a sum of Lorentzians whose peak position, width, and area can vary.

The merits of the two methods are discussed where they are applied in chapters 3 and 4, but the main point is that they both work, in the sense that they both provide reasonable $\alpha^2 F_k(\omega)$ functions with spectral weight at the same frequencies. Values of $\lambda_k$ agree, although the values from the self-consistent method are consistently 10-20% larger, probably reflecting the approximation of the Eliashberg function.

2.5 From electron-phonon coupling to superconductivity

Strong-coupling Eliashberg theory is very successful at describing the superconducting properties of conventional superconductors based on the details of the electron-phonon coupling. Some of the relationships relevant to ARPES measurements are outlined below.

The critical temperature, below which the superconducting state can persist, is related to $\lambda$ through the Allen-Dynes formula:

$$k_B T_c = \frac{\hbar \omega_{ln}}{1.2} \exp \left[ - \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right], \quad (2.22)$$

where $\omega_{ln}$ is the logarithmic average phonon frequency defined as,

$$\omega_{ln} = \exp \left[ \frac{2}{\lambda} \int_0^{\infty} \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln \omega \right], \quad (2.23)$$

and $\mu^*$ is the dimensionless Coulomb potential, typically on the order of 0.1.

The other key parameter of the superconducting state of relevance to ARPES is the superconducting gap, which opens below $T_c$. This gap appears as a suppression of spectral weight in the single-particle density of states at the Fermi level. Its physical origin is the energy required to break a Cooper pair. BCS theory gives a universal relationship between the transition
2.5. From electron-phonon coupling to superconductivity

Figure 2.7: Example of the Dynes function. The Dynes function (Eq. 2.25) describes a linear density of states with a BCS-like gapped Fermi surface, and includes a phenomenological pair-breaking term $\Gamma$ that broadens the features. Simulations are plotted here for $\Gamma = 0, 0.1$, and $0.2$ times the gap, $\Delta = 1.4 \text{ meV}$.

The gap in the single particle density of states as measured by a spectroscopic probe such as photoemission or electron tunnelling is described by the Dynes function [41],

$$D(\omega) = \text{Re} \left[ \frac{\omega - i \Gamma}{[(\omega - i \Gamma)^2 - \Delta^2]^{1/2}} \right],$$

where $\Gamma$ is a phenomenological pair-breaking term that broadens the edge of the gap. This function is plotted with a gap value $\Delta = 1.4 \text{ meV}$ and various values of $\Gamma$ in Fig. 2.7.

To summarize, the ability of ARPES to measure both the $k$-resolved superconducting gap, and the signatures of the phonon (or more generally, bo-
2.5. From electron-phonon coupling to superconductivity

... coupling is one of the reasons this technique is so important for the study of the high-\(T_c\) cuprate superconductors, where the magnitude (and phase) of the gap varies strongly over the Fermi surface. In those materials, the origin of the coupling, and hence the gap, is poorly understood. In the next two chapters of this thesis we use ARPES to understand the anisotropic electron-phonon coupling in the conventional multi-gap superconductor MgB\(_2\), and then to demonstrate how superconductivity can be created in graphene.
Chapter 3

Anisotropic Electron-Phonon Coupling in the Multi-Gap Superconductor MgB$_2$

Certain interactions in a solid introduce an attractive potential between electrons, allowing them to overcome their Coulomb repulsion and form Cooper pairs. The condensate of these new bosons is the superconducting state. The origin of this attractive potential is the question at the heart of research into high-temperature superconductivity. *Conventional* superconductors, on the other hand, are well understood, and it is the electron-phonon coupling that mediates the pairing interaction.

As discussed in Chapter 2, the electron-phonon interaction involves the scattering of electrons from momentum $\mathbf{k}$ to $\mathbf{k}'$ by a phonon with momentum $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. This is described by the Eliashberg function, $\alpha^2 F(\omega)$. Momentum resolved techniques such as ARPES access a momentum resolved quantity $\alpha^2 F_k(\omega)$ which includes the phonon mediated interactions between one point $\mathbf{k}$ on a Fermi surface and all other points $\mathbf{k}'$ on all Fermi surfaces. On the other hand, optical measurements provide the function $\alpha^2 F(\omega)$ which involves a momentum average over the entire Brillouin zone.

We study the conventional multi-gap superconductor MgB$_2$ with two complementary techniques: ARPES and time-resolved optical spectroscopy. With ARPES, we study the strength of the electron-phonon coupling to different parts of the Fermi surface, demonstrating a strong anisotropy. Next, we use a novel time-resolved optical spectroscopy technique that discriminates between strongly and weakly coupled phonons based on the relaxation...
3.1 Introduction

MgB\textsubscript{2} consists of graphene-like boron planes separated by a magnesium layer [Fig. 3.1(a)]. The electronic structure near the Fermi level is entirely determined by the boron orbitals. In the honeycomb structure, the boron 2s, 2p\textsubscript{x} and 2p\textsubscript{y} orbitals form \textit{sp\textsuperscript{2}} hybrids. The direct overlap of these along the B-B bond direction forms three covalent \textit{σ} bands, two of which cross the Fermi level. The 2p\textsubscript{z} orbitals form two \textit{π} bands, both of which cross the Fermi level. The Mg donates two electrons to the boron planes, and the Mg\textsuperscript{2+} ion interacts strongly with the B p\textsubscript{z} orbitals, pulling the \textit{π} bands down in energy [43]. The \textit{σ} bands, being formed from in-plane orbitals, are essentially two-dimensional. They have very little k\textsubscript{z} dispersion, and form two concentric tube-like Fermi surfaces about Γ\textsubscript{A} in the 3D Brillouin zone in Fig. 3.1(b). The \textit{π} bands on the other hand, are very strongly dispersing along k\textsubscript{z}, forming the network of Fermi surfaces near the zone boundary. The electronic band structure, calculated by density functional theory, is shown in Figs. 3.1(d-f) for the high symmetry cuts through the Brillouin zone shown in Fig. 3.1(c). The character of the orbital is represented by the width of the bands, showing that the \textit{σ} bands consist of the B p\textsubscript{x} and p\textsubscript{y} orbitals, while the \textit{π} bands are of p\textsubscript{z} character.

The superconducting properties of MgB\textsubscript{2} were discovered in 2001 [5] and with its relatively high \textit{T}\textsubscript{c} of 39 K, there was immense interest in the mechanism behind its superconductivity. MgB\textsubscript{2} was quickly established as a conventional superconductor, where the pairing mechanism is mediated by the electron-phonon interaction [44], but with a twist. Early experiments indicated that MgB\textsubscript{2} might have two distinct superconducting energy gaps.
3.1. Introduction

Figure 3.1: MgB$_2$ atomic and electronic structure. (a) The structure of MgB$_2$ consists of graphene-like hexagonal boron planes separated by Mg layers. (b) The Fermi surface is defined by the B orbitals, leading to two tubular $\sigma$ sheets around the $\Gamma$ point, and two $\pi$ surfaces out near the zone boundary [from Ref. [42] ]. A guide to the hexagonal Brillouin zone and the labels of the high symmetry points is shown in (c). Density functional theory calculated band structure shows the dispersion of the boron derived $\sigma$ and $\pi$ bands which cross $E_F$. The width of the bands is proportional to the boron $p_x$, $p_y$, $p_z$ orbital character in (d), (e), (f) respectively.
Calculations based on strong-coupling Eliashberg theory supported this [8, 9] and ARPES measurements shortly thereafter confirmed it with measurements of a 3 meV gap on the $\pi$ band, and a 7 meV gap on the $\sigma$ band [6].

It was recently shown experimentally that even the two gap picture is not quite the full story. Tunnelling data shows a distribution of gaps about the values expected for each Fermi surface [7]. This was in fact predicted by calculations using a fully anisotropic Eliashberg model [9, 11, 12], where the anisotropy originates in the electron-phonon coupling. However, this momentum dependence of the electron-phonon coupling has never been observed.

In the following section, we use ARPES to examine the momentum-resolved electron-phonon coupling. We show that the coupling at the $\sigma$ band Fermi surfaces is significantly larger than the Fermi surface averaged value measured by other techniques, which explains the large superconducting gap. Furthermore, the electron-phonon coupling is stronger on the inner band, and anisotropic in momentum on the outer band, in agreement with theory, and explaining the observed distribution of superconducting gaps.

High-quality single crystals of MgB$_2$ were grown using a cubic anvil technique. The details of the crystal growth and extensive characterization are given in Ref. [50]. Optical measurements were done on polished samples at 300 K. For ARPES, samples were oriented with Laue diffraction, then cleaved in vacuum to expose a clean surface. Measurements were done at 10 K, and in vacuum better than $4 \times 10^{-11}$ Torr. Energy and angular resolution were set to 15 meV and 0.01 Å$^{-1}$, respectively.

### 3.2 ARPES on MgB$_2$

There are few reports of ARPES measurements on MgB$_2$ [6, 49, 51, 52], and the quality of the data has been limited by the quality of the cleaved sample surface. MgB$_2$ single crystals are typically on the order of 0.5 - 1 mm$^2$ with a thickness less than 0.3 mm, which provides a technical challenge to preparing
3.2. ARPES on MgB$_2$

the samples for measurement. A further problem is that, despite the layered boron planes, there is strong electronic bonding along the c-axis, and samples do not cleave easily. The cleaved sample surface is typically multi-faceted and rough. The disorder scatters the outgoing photoelectrons, which leads to a poorly defined $k_{\|}$, and hence poorly momentum resolved bands. The measurements presented here were obtained by careful sample preparation, and by cleaving many samples in order to increase the statistical likelihood of obtaining a clean, flat surface.

The high quality ARPES data reported here reveal a number of features not observed in previous studies [6, 51]. The Fermi surface measured with p-polarised light in Fig. 3.2(a) shows the two hole-like $\sigma$ sheets around the $\Gamma$ point, and one of the $\pi$ sheets out towards the zone boundary. There is a strong intensity modulation of the $\sigma$ bands around the Fermi surface due to the interplay between the $p_x$, $p_y$ orbital symmetries and the polarization of the incoming light [53]. Switching between $s$ and $p$ polarized light selects the inner or outer $\sigma$ band, as shown in Figs. 3.2(c) and (d) for the dispersion along $\Gamma$-K (the red dashed line in Fig. 3.2(a)). The two $\sigma$ band Fermi surfaces have been colourized artificially based on these polarization dependent dispersions which clearly show two bands.
Figure 3.2: **ARPES measurements showing the Fermi surface and band dispersion of MgB$_2$**

(a) The Fermi surface of MgB$_2$ showing the inner (red) and outer (blue) $\sigma$ bands, and the $\pi$ band (black) crossing near the zone boundary. Panel (b) shows the $\sigma$ bands in more detail on the left, and the $k_z$ integrated calculated Fermi surface on the right. The band dispersions measured along $\Gamma$K (red dashed line in panel (a)) are shown in panel (c), along with the calculated dispersions (blue) which have been rigidly shifted by -140 meV to get agreement at $E_F$. (d) Outer $\sigma$ band dispersion measured with s polarized light, which suppresses the intensity of the inner band.
3.2. ARPES on MgB$_2$

While the perpendicular component of the electron momentum is not conserved, it is well defined, as discussed in Chapter 2. $k_z$ is determined by the photon energy, as well as unknown, material specific quantities such as the inner potential $V_0$. A comparison of the experimental Fermi surface with calculated ones for different values of $k_z$ shown in Fig. 3.3 indicates that our measurements are cutting the 3D Fermi surface [see Fig. 3.1(b)] at approximately $k_z=0$.

The electronic dispersion of the $\sigma$ bands is calculated with density functional theory at $k_z=0$, and is compared to the experimental dispersions in Figs. 3.2(c) and (d). The calculations are rigidly shifted in energy by -140 meV to get the correct Fermi level crossing (i.e. agreement at $E=0$) but otherwise the agreement is good. We note that a similar shift was needed to match calculated band structure to bulk sensitive de Haas-van Alphen measurements [54], which measures the Fermi contour areas. This implies there remains some tweaking of the band structure parameters to be done, but also that the discrepancy observed is not due to a surface effect. The Fermi contour areas (which are proportional to the number of electrons in the band) for the light and heavy holes are found to be 0.06 and 0.125 ± 0.01 Å$^{-2}$, or approximately 3.5 and 7.5 % of the Brillouin zone, again, in agreement with the bulk sensitive de Haas-van Alphen measurements for $k_z=0$ [54]. This shows that despite its surface sensitivity, ARPES is in fact measuring the bulk electronic structure of this material. The good agreement between the shifted band structure and the ARPES dispersions also indicates that electron-electron interactions are not likely to be important in MgB$_2$, as these often cause strong deviations between density functional theory and measured dispersions [51].

The $\sigma$ band dispersions measured along $\Gamma K$ (red line in Fig. 3.2(a)) shown in Figs. 3.2(c) and (d) show striking ‘kinks’ at around 70 meV binding energy. These renormalizations are signatures of the strong electron-phonon coupling. Next, we show how a detailed analysis of the ARPES spectra yields unique insight on the EPC, and how it relates to superconductivity in MgB$_2$. 
3.2. ARPES on MgB

Figure 3.3: **Determination of k_z.** The Fermi surface measured by ARPES can be compared with calculated Fermi surfaces for different values of k_z. The central \(\sigma\) bands show little k_z dispersion due to their 2D nature. The \(\pi\) bands, on the other hand, vary strongly with k_z throughout the Brillouin zone. Comparison between the data and calculation shows that for this photon energy (21.2 eV) we are measuring at approximately k_z=0. Here, k_z is given in units of \(2\pi/c\).

Band dispersions were measured along the two high symmetry directions \(\Gamma K\) and \(\Gamma M\), providing four datasets for analysis corresponding to the inner band (labelled \(\sigma_1\)) along \(\Gamma K\), and the outer band (\(\sigma_2\)) along \(\Gamma K, \Gamma M,\) and \(\Gamma M'\) (where the prime indicates a different M point). Measurements of the \(\pi\) band dispersion did not show any signs of strong renormalization, but this is likely due to the strong k_z dispersion which broadens features in the ARPES spectral function \[55\].

The intensity profiles at constant energy, known as momentum distribution curves or MDCs, are fitted with a Lorentzian and a constant background, as described in Chapter\[2\]. This generates the peak maximum (\(k_m\)) and peak width (\(\Delta k_m\)) at energy \(\omega_m\). These parameters are related to the real and imaginary parts of the self-energy as follows,

\[
\Sigma' = \omega_m - \epsilon_{km}^b, \\
\Sigma'' = -\Delta k_m v_{km}^b, \tag{3.1}
\]

where \(\epsilon_{km}^b\) is the energy of the bare band at \(k_m\) and \(v_{km}^b\) is its velocity. We use a self-consistent fitting procedure to extract the self energy and bare-band together without any *a priori* knowledge of the bare-band. The Kramers-Kronig relation between the experimentally determined real and imaginary
3.2. ARPES on MgB$_2$

Figure 3.4: Kramers-Kronig bare-band fitting to determine the self-energy. MDC dispersions are plotted on top of the raw data in (a) and (d). The momentum space cut in (a) is along ΓK, while in (d) it is along MΓM. The real and imaginary parts of the self-energy are plotted in black in (b,c,e,f), while the KK transforms are shown in red. The imaginary part of the self energy calculated from the spectral weight, $\Sigma''_{ratio}$ is shown in dashed green, and its good agreement with the MDC width $\Sigma''(\omega)$ is a confirmation that the KKBF analysis can be applied (see text).
3.2. ARPES on MgB$_2$

parts of the self-energy is the self-consistency criteria [34, 36]. Figures 3.4 (a) and (d) show the MDC dispersion overlayed on the raw data, where the ‘kinks’ are clear signatures of coupling with phonon modes.

The real and imaginary parts of the self-energy (black) and their Kramers-Kronig transforms (red) are determined from Eq. 3.1 and the KKBF procedure (described in further detail in Chapter 2), and plotted in Figs. 3.4(b,c,e,f). In each case there is a one-to-one correspondence between the peak in $\Sigma'$ and the step in $\Sigma''$ at an energy of $\sim 70$ meV. While $\Sigma'$ describes the renormalization of the band, $\Sigma''$ is related to the inverse lifetime. The step in $\Sigma''$ implies an additional scattering channel opens at that energy, reducing the lifetime of the quasiparticles, causing the increase in the measured MDC linewidth.

The self energy is related to the bosonic spectrum by [56]

$$
\Sigma'_k(\omega) = \int_{-\infty}^{\infty} dv \int_0^{\infty} d\omega' \alpha^2 F_k(\omega') \frac{2\omega'}{v^2 - \omega'^2} f(v + \omega), \quad (3.2)
$$

where $f(\omega)$ is the Fermi distribution function. The momentum resolved $\alpha^2 F_k(\omega)$ function is extracted from the self-energy by an integral inversion procedure described in detail in Chapter 2. Briefly, the real part of the self energy is calculated from a trial $\alpha^2 F_k(\omega)$, and compared to the experimentally determined one. $\alpha^2 F_k(\omega)$ is varied, subject to a constraint function, until the generated self energy fits the experimental one, and hence the bare-band plus self-energy agrees with the MDC dispersion. We use the self-energy extracted from the self consistent fitting procedure and a histogram model based on the equilibrium optics (Fig.3.7(a)) for the constraint function.

The key results of the electron-phonon coupling analysis are summarized in Fig.3.5. We observe a strong anisotropy of the electron-phonon coupling strength between the two $\sigma$ bands, and along different momentum directions. The MDC dispersions, all showing the strong kink at $\sim 70$ meV, are plotted in orange in Fig.3.5(a-c) along with the bare-band (gray) determined by the KKBF procedure described above. The MEM fitting to the real part of the self-energy [data in black, fit in red in Figs.3.5(d,e,f)] determines the $\alpha^2 F(\omega)$ shown in the lower panels. The success of the fit is also seen in the MDC.
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Figure 3.5: **Extraction of $\alpha^2 F_k(\omega)$ in MgB$_2$.** (a-c) MDC dispersions (orange) for the three unique momentum cuts measured with ARPES. The bare-band determined from the KKBF is shown in gray. The real part of the self energy (black) is fitted with Eq. 3.2 and the MEM procedure described in the text. The successful fits (red) correspond to the Eliashberg functions in panels (j,k,l). Further confirmation of the fitting can be seen in the MDC dispersion calculated from the MEM fit in panels (a,b,c). The imaginary part of the self-energy determined from the KK transform of the fit to the real part is shown in (g,h,i). The Eliashberg functions, plotted in colour in (j,k,l), are used to calculate $\lambda$, shown as the black line in (j,k,l).
3.2. ARPES on MgB$_2$

<table>
<thead>
<tr>
<th>Band</th>
<th>Direction</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_1$</td>
<td>ΓK</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>ΓK</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>$\sigma_2'$</td>
<td>ΓM</td>
<td>1.25 ± 0.1</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>ΓM'</td>
<td>1.15 ± 0.1</td>
</tr>
<tr>
<td>$\sigma_{av}$</td>
<td>All</td>
<td>1.25 ± 0.2</td>
</tr>
</tbody>
</table>

Table 3.1: Summary of $\lambda_k$ for MgB$_2$.

dispersion calculated from the $\alpha^2 F_k(\omega)$ [i.e. $\epsilon_k = \epsilon^b_k + \Sigma'$, black line in panels (a,b,c)]. The imaginary part of the self-energy is calculated from the KK transform of the fit to $\Sigma'$, and in each case agrees with the experimental one in Fig. 3.4.

The momentum resolved electron-phonon coupling strength, sometimes referred to as the mass-enhancement parameter, in the Eliashberg formalism is given by:

$$\lambda_k = 2 \int_0^\omega d\omega' \frac{\alpha^2 F_k(\omega')}{\omega'}, \quad (3.3)$$

and is plotted in Figs 3.5(j,k,l), showing how $\lambda_k$ is calculated from the energy weighted integral of the $\alpha^2 F_k(\omega)$ function (black lines). The inner $\sigma$ band has a larger mass-enhancement parameter along ΓK (1.6 ± 0.1) than the outer band does along either of the high symmetry directions (1.0 ± 0.1 along ΓK, and 1.2 ± 0.1 along ΓM ). These results are summarized in Table 3.1 and visually in Fig. 3.6.

The agreement with fully anisotropic Eliashberg calculations for the values of the k-resolved electron-phonon coupling on the $\sigma$ bands is very good. In particular we make the comparison with the results of Ref. [12] in Fig. 3.6, who used a denser k-mesh than earlier calculations, and is therefore better resolved. However, other theoretical studies find a similarly anisotropic result [9, 11].

Taking the values of $\lambda_k$ presented here, we can weight them by the Fermi contour areas (where $\sigma_2$ is over twice the size of $\sigma_1$) to get an approximate $\sigma$
band average coupling of $\lambda_\sigma = 1.25\pm0.2$. This number can be compared with values of 1.0 to 1.2 which are often reported from calculations and experiment [54, 57].

As an interesting aside, a common approach to extracting the electron-phonon coupling (or the mass-enhancement factor) from ARPES data is to look at the ratio of the bare-band slope to the renormalized band velocity and equate this to $(1 + \lambda)$. However, exceedingly large values are often reported, and the validity of this approach has recently been questioned [34, 36]. Indeed, from the measurements presented here, we would find values of $\lambda_k$ between 1.7 and 2.7, almost a factor of two larger than predicted. This provides some experimental evidence supporting the conclusions of Refs. [34, 36], showing the need for a complete self-energy analysis in order to access information on the electron-phonon coupling from ARPES data.
3.2. ARPES on MgB$_2$

Figure 3.6: **Momentum resolved $\lambda_k$**. The summary of experimental data in (a) compares very well with fully anisotropic Eliashberg calculations in (b) (from Ref. [12]). Note that in the experimental data, the points along $\Gamma K$ were measured at one point, and are repeated here based on the symmetry of the Fermi surface. The point along $\Gamma M$ was measured along two directions and found to be the same.
3.3 Time-resolved optics

In order to further understand the strong coupling measured on the electronic $\sigma$ bands, we use a novel time-resolved optical spectroscopy to study the electron-phonon coupling. This technique is bulk sensitive, and momentum-integrated, and therefore provides complimentary information to the momentum-resolved, surface sensitive ARPES measurements.

We begin by determining the momentum integrated, or Fermi surface averaged, Eliashberg function from equilibrium (as opposed to time-resolved) optical reflectivity. Reflectivity data shown in Fig. 3.7(a) from Ref. [59] is fit within the extended Drude model, which describes the infra-red response of metals with strong electron-phonon coupling [60]. While the details of the model will not be discussed here, the Drude-like response depends on the electron-phonon coupling, and the details of the latter are recovered from fitting the optical reflectivity. The extracted $\alpha^2 F(\omega)$ is shown inset in Fig. 3.7(a) and is dominated by a peak at 70 meV. The electron-phonon coupling strength is determined to be $\lambda = 1.1 \pm 0.1$, which agrees with several other bulk sensitive probes [54], but is larger than the average value found in theory [57].

The great advantage of a time-resolved optical technique lies in its ability to single out different bosonic modes involved in the coupling with quasiparticles on the basis of the decay time of their characteristic relaxation dynamics [61]. In a pump-probe experiment, the system is ‘pumped’ into an excited state by an initial laser pulse, and then ‘probed’ after some delay time. The earliest dynamics after photoexcitation is phenomenologically described by treating electrons and phonons as two interacting systems both characterized at each delay time $\tau$ by their own temperature [62]. In layered materials like graphite and the cuprates the excited electrons exchange their excess energy through two decay channels: they thermalize with a fraction of SCP (strongly-coupled phonons) on a fast time scale ($< 1$ ps) and, on a slower time scale, with the complementary fraction of less interacting lattice
3.3. Time-resolved optics

![Image of a graph with various annotations]

Figure 3.7: **Time-resolved optics measurements on MgB$_2$.** (a) Equilibrium reflectivity measured with spectroscopic ellipsometry (red line) and extended Drude model fit to the data (black line). The fit determines the momentum-integrated Eliashberg function, shown as the histogram inset. The calculated phonon density of states from Ref. [58] is shown in red for comparison in arbitrary units. (b) Sketch of a pump-probe experiment: after laser excitation the hot electrons thermalize with a fraction of SCP on a time scale of 100 fs and after 1 ps with the rest of the lattice (cold phonons). The trace is the temporal trace at probe energy of 1 eV. The black line is the 3TM fit to the data (explained in text).
3.3. Time-resolved optics

Here, the transient variation of reflectivity $\delta R/R$ is measured with unprecedented temporal resolution ($\sim 15\,\text{fs}$) over a broad spectral region between 1100 and 1600 nm. The MgB$_2$ transient response is reported in Fig. 3.7(b) measured with a photon energy of 1 eV. It has previously been shown that the relative variation of the reflectivity in the infra-red region far from the plasma frequency of 6 eV can be explained as a broadening of the Drude peak due to the change in the electronic temperature through the increase of the temperature of the bosonic modes strongly coupled to the hot electrons [61]. For that reason we fit the $\delta R/R(t)$ trace within the three temperature model used to interpret time resolved ARPES and reflectivity data [61, 62]. The key elements of this model are that the rate of energy transfer from the hot electrons to the strongly coupled phonons depends on the number of such phonon modes (or the phonon density of states), and the strength of the coupling. These two quantities are related to parameters determined in the fitting procedure: the fraction of total phonon modes that are strongly coupled, and the SCP contribution to the total $\alpha^2 F(\omega)$ (and hence also $\lambda$). According to the fit, plotted in black in Fig. 3.7(b) the SCP modes correspond to a small fraction $f = 0.15-0.22$ of the total lattice modes, but contributes a coupling strength $\lambda_{SCP} = 0.53 - 0.75$.

By comparing $\alpha^2 F(\omega)$ and the phonon density of states in Fig. 3.7(a), it is seen that the SCP modes must relate to the peak around 70 meV, as it is the only part of the spectrum where such a small fraction of the phonon modes can contribute such a large coupling strength. This energy corresponds to the boron-boron bond stretching modes with $E_{2g}$ symmetry [58]. These modes change the orbital overlap of the $p_x, p_y$ electronic states which form the electronic bands at the Fermi level. This leads to the very clear, strong signature of the electron-phonon coupling in the electronic spectral function measured in ARPES.
3.4 Conclusion

We have presented a direct experimental evidence of the anisotropy of the electron-phonon coupling in MgB$_2$. Time resolved reflectivity directly identifies the strongly coupled phonons responsible for the large $T_c$ in MgB$_2$, while ARPES measures the momentum-resolved coupling via the electronic excitations. Not only does the coupling vary between the $\pi$ and $\sigma$ bands, but there is a strong anisotropy between the $\sigma$ bands, and even along different high-symmetry directions on same sheet. These results are the first direct evidence of the detailed anisotropy of the electron-phonon coupling in MgB$_2$. This anisotropy is the root cause of the distribution of superconducting gaps measured by electron tunnelling [7]. It is also an essential ingredient in the accurate calculation of the superconducting properties of this material [8, 9] (i.e. calculations that do not include the anisotropy fail to determine the correct $T_c$).

MgB$_2$ is often considered to be at the limit of what the electron-phonon coupling can achieve in terms of superconductivity. Despite much effort, $T_c$ has not been increased. So while MgB$_2$ might be considered a dead-end for applications, it certainly serves as a test-bed for our understanding of the electron-phonon coupling, and phonon-mediated superconductivity. Many of the features observed in this system, including multi-gap superconductivity, and the phonon induced band renormalizations, are observed in the novel iron-based superconductors [63]. For the methods used here to be successfully applied to more complex systems, it is essential to demonstrate their reliability on a well understood system such as MgB$_2$. 


Chapter 4

Superconductivity in Lithium-Decorated Graphene

Monolayer graphene exhibits many spectacular electronic properties [13, 14], with superconductivity being arguably the most notable exception despite intense theoretical and experimental efforts [15–21]. To overcome this limitation, it was theoretically proposed that superconductivity might be induced by enhancing the electron-phonon coupling through the decoration of graphene with an alkali adatom superlattice [17]. While experiments have indeed demonstrated an adatom-induced enhancement of the electron-phonon coupling [16, 20, 64], superconductivity has never been observed. Using angle-resolved photoemission spectroscopy (ARPES) we show that lithium deposited on graphene at low temperature strongly modifies the phonon density of states, leading to an enhancement of the electron-phonon coupling by a factor of 3, or $\lambda \simeq 0.58$. On part of the graphene-derived $\pi^*$-band Fermi surface, we then observe the opening of a $\Delta \simeq 0.9 \text{meV}$ temperature-dependent pairing gap. This suggests, for the first time, that Li-decorated monolayer graphene is superconducting at 3.5 K.

4.1 Introduction

Graphene is a two dimensional crystal of carbon in a honeycomb structure [Fig.4.1(a)]. The lattice is held together by strong, fully occupied $\sigma$ bonds, while the electronic structure is completely determined by the carbon $p_z$ orbitals, which form the conical $\pi$ bands at the $\mathbf{K}$ points of the Brillouin zone, shown in Fig.4.1(b) and (c). In freestanding graphene, the $\pi$ bands are half
4.1. Introduction

filled, putting the crossing of the bands at the Fermi level. The relationship between the energy of the band and the momentum (the dispersion) around the crossing point is linear, and formally equivalent to the solution of the 2D massless Dirac equation [65]. The crossing point is therefore known as the Dirac point, \( E_D \). Many of the unique and fascinating properties of graphene follow from this unusual electronic structure [13, 14, 66], but it is the 2D nature of this material that makes it so tunable. Adatoms on the surface have been used to control the carrier density [67–71], but also different interactions (electron-electron or electron-phonon) [16, 72, 73], and metal-insulator transitions [74, 75] to name a few examples. In the following we are interested in how adatoms can induce superconductivity in monolayer graphene.

Superconductivity occurs in certain bulk graphite intercalated compounds (GICs) with \( T_c \) of up to 11.5 K in the case of CaC\(_6\), and 6.5 K for YbC\(_6\) [22, 23]. KC\(_8\) and RbC\(_8\) both show superconductivity below 2 K [76]. Superconductivity in these materials is well described by DFT calculations, and is understood to be conventional, driven by the electron-phonon coupling (EPC) [24, 25, 77]. The intercalant atoms sit in the centre of the hexagons (the hollow sites) between graphite layers, forming an ordered \( \sqrt{3} \times \sqrt{3} R30^\circ \) (CaC\(_6\), YbC\(_6\)) or \( 2 \times 2 \) (KC\(_8\), RbC\(_8\)) structure. There is a charge transfer from the intercalant atoms to the graphite, leading to electron doping of the \( \pi^* \) bands.

There is some evidence to suggest that the electron doping alone is the origin of superconductivity in the graphite planes, and that the intercalant atom’s sole role is to provide extra charge carriers [78–80]. The prevailing view, however, is that the intercalant atoms alter both the electronic and the phononic structure of the material, leading to an enhanced EPC, and superconductivity [24, 25, 76]. There is a correlation between the GICs that are superconducting, and the presence of a partially occupied intercalant derived band at the Brillouin zone centre [76], arising due to the incomplete ionization of the intercalants outer shell electron(s). DFT calculations show that the intercalant layers introduce low-energy, in-plane phonon modes that
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Figure 4.1: **Graphene structure and band structure.** (a) The honeycomb structure of graphene with the primitive unit cell and lattice vectors shown in cyan. (c) The electronic structure consists of cone-like bands at each corner of the hexagonal Brillouin zone in (b). Lithium on graphene is expected to form a $\sqrt{3} \times \sqrt{3} R30^\circ$ superlattice, where the new unit cell (shown in green) is three times larger than that of pristine graphene, and rotated by $30^\circ$.

---

...can couple strongly to the intercalant electronic states at the Fermi level [24, 25]. While theory is clear on the importance of the intercalant electronic states, the recent observation of the superconducting gap on the graphitic $\pi^*$ band in bulk CaC$_6$ shows that the carbon derived bands are also involved [26]. This suggests that superconductivity in 2D monolayer graphene is a real possibility.

Recent DFT based calculations have suggested that superconductivity can be induced in graphene through the ordered adsorption of certain alkali metals [see Fig.4.1(d)] [17]. Although the lithium GIC, LiC$_6$, is not known to be superconducting, Li decorated graphene emerges as a particularly interesting case, with a superconducting transition temperature calculated to be $\sim$8 K. The proposed mechanism for this enhancement of $T_c$ is the removal of the confining potential of the graphite layers, which shifts the Li band down to the Fermi level where it becomes partially occupied. The presence
of these states at $E_F$ enables a strong coupling with new lithium in-plane phonon modes ($\text{Li}_{x,y}$), and with out of plane carbon modes ($C_z$) that was previously forbidden by symmetry. To understand this last point, note that the electron-phonon perturbation operator for the $C_z$ modes is odd with respect to the $z$ axis \[81\], and can only couple electronic states with opposite parity. The graphene $\pi^*$ bands have universally odd $z$-parity, and therefore intraband coupling via the $C_z$ mode is forbidden. On the other hand, the Li 2s band has even $z$-parity, enabling interband coupling with the $\pi^*$ bands.

This picture was partially validated by ARPES measurements of Cs, Rb, K, Na, Li, and Ca deposited on graphene, with the observation of an adatom-dependent vibrational mode across the series \[20\]. The presence of the alkali adatoms introduces a low-energy ($\leq 100\text{meV}$) phonon mode to the system, and/or enhances the coupling to the out-of-plane carbon vibrations. However, the strength of the EPC was still too low to lead to superconductivity. In this chapter, we present an ARPES study of lithium deposited on monolayer graphene at low temperature. We observe evidence of the Li 2s band, and a strong enhancement of the EPC, in line with recent theoretical predictions. High-resolution, low temperature ARPES measurements show evidence of a partially gapped Fermi surface, indicative of superconductivity.

Epitaxial graphene monolayers with a carbon buffer layer were grown under argon atmosphere on hydrogen-annealed 6H-SiC(0001) substrates, as described in Ref. \[82\]. The carbon buffer layer passivates the dangling bonds at the SiC surface, enabling the formation of the decoupled graphene monolayer. The samples were annealed at 500 °C and $8 \times 10^{-10}$ Torr for 1 hour, immediately prior to the ARPES measurements. Lithium adatoms were deposited from a commercial SAES alkali metal source, with the graphene samples held at 8 K. Bulk Nb polycrystalline samples, with $T_c = 9.2$ K, were fractured in the ARPES chamber to expose a clean surface prior to the experiments. The ARPES measurements were performed with s-polarized 21.2 eV photons on an ARPES spectrometer equipped with a SPECS Phoibos 150 hemispherical analyzer, a SPECS UVS300 monochromatized gas discharge...
4.2. Lithium adatoms on graphene and the effects of sample temperature

lamp, and a 6-axes cryogenic manipulator that allows controlling the sample temperature between 300 and 3.5 K, with an accuracy ±0.1 K. Band and Fermi surface mapping, as well as the study of electron-phonon coupling, were performed at 8 K with energy and angular resolution set to 15 meV and 0.01 Å⁻¹, respectively. For the measurements of the superconducting gaps, energy and angular resolution were set to 6 meV and 0.01 Å⁻¹, while the sample temperature was varied between 3.5 and 15 K. During the ARPES measurement the chamber pressure was better than 4×10⁻¹¹ Torr.

4.2 Lithium adatoms on graphene and the effects of sample temperature

ARPES measurements of the electronic structure of pristine and Li-decorated graphene at 8 K, characterized by the distinctive Dirac cones at the corners of the hexagonal Brillouin zone, are shown in Fig. 4.2(a-d): Li adatoms electron-dope the graphene sheet via charge-transfer doping, leading to a shift of the Dirac point to higher binding energies. As evidenced by the evolution of the graphene sheet carrier density in Fig. 4.2(h), this trend begins to saturate after several minutes of Li deposition; concomitantly, we observe the emergence of new spectral weight at the Brillouin zone centre [see the comparison of the Γ-point ARPES dispersion for pristine and 10 minute Li-decorated graphene in Fig. 4.2(e,f)].

The spectral weight at Γ is likely to be a superposition of a superstructure-induced folding, and the Li 2s band, but these are difficult to disentangle as they occur in the same energy and momentum region. The lithium is predicted to form an ordered $\sqrt{3}\times\sqrt{3} R 30^\circ$ superlattice [shown in Fig. 4.1(d)]. The new periodic potential would create a new Brillouin zone, backfolding the band structure along the zone boundaries. The expected reconstructed Brillouin zone is shown as the dashed white hexagon in Fig. 4.2(g), and the graphene $\pi$ bands would be backfolded to Γ. In support of this, we note that the shape of the new feature shown in Fig. 4.2(f) is reminiscent of the
4.2. Lithium adatoms on graphene and the effects of sample temperature

Figure 4.2: Charge-transfer doping of graphene by lithium adatoms. (a) Dirac-cone dispersion measured by ARPES at 8 K on pristine graphene and (b,c,d) after 3, 6 and 10-minute Li evaporation respectively. The measurements were taken along the K-point momentum cut indicated by the thick white line in the Fermi surface plot in (g). The Dirac point, already located below $E_F$ on pristine graphene due to the charge-transfer from the SiC substrate (a), further shifts to higher energies with Li evaporation (b-d); the presence of a single well-defined Dirac cone indicates a macroscopically uniform Li-induced doping. While no bands are present at the $\Gamma$-point on pristine graphene (e), new spectral weight is detected on 10-minute Li-decorated graphene in (f) and (g), indicating a possible $\sqrt{3} \times \sqrt{3} R 30^\circ$ backfolding of the electronic structure induced by Li ordering, and the Li $2s$ band. As illustrated in the 8 K sheet carrier density plot versus Li deposition time in (h), which accounts for the filling of the $\pi^*$ unfolded Fermi surface, the spectral weight at $\Gamma$ is achieved for charge densities $n_{2D} \gtrsim 9 \times 10^{13} \text{cm}^{-2}$ (but completely disappears if the sample temperature is raised above $\sim 40 K$; see Fig. 4.3).
4.2. Lithium adatoms on graphene and the effects of sample temperature

Dirac cone, and that this form of reconstruction has been observed for bulk LiC$_6$ as well as intercalated bilayer C$_6$LiC$_6$ [83, 84]. On the other hand, the Li 2s band is expected to form as a parabolic, free electron-like band at Γ. Here, we note that the symmetry of the Fermi surface shown in Fig. 4.2(g) is circular, and not hexagonally warped as one would expect for the folded bands. Additionally, the area of the Γ Fermi contour is larger than that of the π band Fermi contour, as predicted for the parabolic band [17].

At the saturation of doping, we find a sheet charge-carrier density $n_{2D} \approx 9 \times 10^{13}$ cm$^{-2}$. Assuming Li forms an ordered LiC$_6$ structure [Fig. 4.1(d)] after 4 minutes evaporation (i.e. one Li per three unit cells), this corresponds to a charge transfer to the graphene $\pi^*$ bands of $0.14 \pm 0.02$ electrons per Li adatom. This is significantly lower than what is reported in Li-intercalated compounds, where the Li is found to be completely ionized [85]. The latter is an important point, since the incomplete ionization of the Li 2s electrons is necessary in order to form a Li band at the Γ point, which in turn has been identified as a key element in the enhancement of the electron-phonon coupling [17, 25, 76].

After lithium deposition, for temperatures between 3.5 K and 20 K, the Li adatoms appear stable on the graphene surface. Fermi contours measured at 7 K, 13 K, and 17 K shown in Figs. 4.4(a1-a3) exhibit no change in area within the bounds of uncertainty, as seen in the $k_y$-integrated MDCs in Fig. 4.4(b). Increasing the temperature above 20 K leads to a progressive reduction of the charge transfer doping, seen in the shift of the Dirac point in the raw data in Fig. 4.3(a) and in the extracted carrier density in Fig. 4.4(c). A significant broadening of the $\pi^*$ bands with increasing temperature is also apparent, signifying increasing surface disorder. At 50 K there is a sudden disappearance of the Γ spectral weight [Fig. 4.3(b)], and it does not reappear upon subsequent cooling.

The strong, irreversible temperature dependence of the doping, the temperature induced disorder, and the disappearance of the spectral weight are all in stark contrast with behaviour seen in Li-intercalated bulk graphite and
4.2. Lithium adatoms on graphene and the effects of sample temperature

Figure 4.3: Temperature dependence of the band dispersion in Li-Graphene. (a1-a5) ARPES measurements through the Dirac point at \( \overline{K} \) showing a reduction in the n-type doping as the temperature is increased. A significant broadening of the bands can also be seen, particularly above 50 K, which is an indication of surface disorder. (b1-b5) ARPES measurements at \( \Gamma \) showing the complete disappearance of the backfolded bands at 50 K.
Figure 4.4: **Evolution of the charge density with temperature.** Measuring the Fermi surface of a Li-doped sample as a function of temperature (a1-a3) while warming up shows that the carrier density remains constant up to \( \sim 20 \) K. The \( k_y \)-integrated MDCs in (b) emphasize this point, showing no change in the area of the Fermi contour in this temperature range. Combining this data with the temperature dependence in Fig. 4.3(a), we show the temperature dependence of the graphene \( \pi^* \) band carrier density between 7 K and 100 K. At temperatures below \( \sim 20 \) K the doping is stable. Above \( \sim 20 \) K, however, there is a reduction of \( n \) with increasing temperature, with the sheet carrier density returning to the starting value of clean graphene \( (1 \times 10^{13} \text{ cm}^{-2}) \) at around 100 K.

Bilayer graphene [85, 86] where the Li intercalates easily at room temperature, and the doping is stable between 30 K and 300 K. This suggests that the lithium resides on the graphene surface, as opposed to intercalating between the graphene and substrate.

The evidence so far indicates the lithium forms an ordered layer on the
4.3 Enhancement of the electron-phonon coupling

graphene surface, and the Li 2s band is partially occupied, only for lithium deposited on graphene at low temperature. The ordering disappears at 50 K. This is an important point that distinguishes this work from previous studies, and explains why we succeed in observing an enhancement of the electron-phonon coupling. While the doping-saturation regime was already reached in previous in-situ alkali-deposition studies [20], the spectral weight at Γ was not observed presumably because the sample temperatures of ∼ 50 K were too high.

4.3 Enhancement of the electron-phonon coupling

Here, we perform a detailed analysis of the electron-phonon coupling in the graphene π∗ band as a function of lithium coverage. The lithium layer is predicted to modify the phononic structure, which in turn modifies the electronic structure via the electron-phonon coupling (EPC). These renormalizations of the electron energy and lifetime are described by the real and imaginary parts of the self-energy respectively. In an actual ARPES measurement, as presented below, these features would appear as ‘kinks’ in the dispersion, where the band velocity changes abruptly, or as steps in the MDC linewidth at the energy of the strongly coupled phonon.

Measurements were performed along the cut shown by the white line in Fig.4.6(e) for three different lithium deposition times: 3 minutes, 6 minutes and 10 minutes. The electron-phonon coupling analysis discussed below cannot be performed on the clean, undoped sample due to the proximity of the Dirac point to the Fermi level, which makes it difficult to follow the MDC dispersion. At 3 minutes, the doping is not saturated, and the spectral weight at Γ is not yet apparent. Depositions of 6 and 10 minutes are both in the saturated doping regime, and the spectral weight at Γ is present. This cut was chosen because it intersects the K point, giving the full dispersion from the Fermi energy to the Dirac point. The MDCs are fitted with
a Lorentzian plus linear background to determine the peak maximum $k_m$ and $\Delta k_m$, and the KKBF routine was used to self-consistently determine the bare-band and self-energies [see Chapter 2 for more details]. The results of this process are summarized in Fig. 4.3. The MEM was used to fit the real part of the self-energy, and extract the Eliashberg function for the different Li coverages, and finally the k-resolved electron-phonon coupling parameter was calculated from \[ \lambda_k = 2 \int d\omega \alpha^2 F_k(\omega)/\omega. \] These results are summarized in Fig. 4.6.

Graphene doped with alkali adatoms always shows a strong kink in the $\pi^*$ band dispersion at a binding energy of about 160 meV [20, 64]. This is true for the Li-decorated samples at all coverages studied here, as seen in the raw data in Fig. 4.2(a-d). This high-energy feature is even better visualized in the extracted momentum-distribution curve (MDC) dispersions [Fig. 4.3(a-c) and Fig. 4.6(b-d)]. This structure stems from the coupling to carbon in-plane ($C_{xy}$) phonons [17, 25] of $E_{2g}$ symmetry which, despite the apparent strength, contribute little to the overall coupling parameter due to their high energy (note that $\omega$ appears as a weighting factor in the integral calculation of $\lambda$). The contribution to $\lambda_k$ from these high-energy modes between 100 and 200 meV can be isolated by integrating over $\alpha^2 F_k(\omega)$ in that energy range. We find $\lambda_{k,HE} = 0.14 \pm 0.05$, and it remains approximately constant for all Li coverages studied here, as illustrated by the white symbols in Fig. 4.6(i).
4.3. Enhancement of the electron-phonon coupling

Figure 4.5: **Self-consistent self-energy analysis.** MDC dispersions, determined by fitting the ARPES data with Eqn. 2.9, are plotted in orange in (a-c) and are used to extract the self-energy using the self-consistent Kramers-Kronig procedure described. The bare-band [gray in (a-c)] corresponds to the real and imaginary parts of the self-energy calculated from Eqn. 2.10 plotted in orange in panels (d-f). The correct bare-band is identified by the good agreement between the real and imaginary parts of the self-energy, and their KK transforms (blue).
4.3. Enhancement of the electron-phonon coupling

Figure 4.6: **Analysis of electron-phonon coupling in Li-decorated graphene.** (a) Dirac dispersion from 3-minute Li-decorated graphene, along the $k$-space cut indicated in the Fermi surface plot in (e), exhibiting kink anomalies due to electron-phonon coupling (white line: MDC dispersion). (b-d) MDC dispersion and bare-band obtained from the self-consistent Kramers-Kronig bare-band fitting (KKBF) routine [34, 36], for several Li coverages (see Chapter 2); the real part of the self-energy $\Sigma'$ is shown in the side panels (orange: $\Sigma'$ from KKBF routine analysis; black: $\Sigma'$ corresponding to the Eliashberg function presented below). (f-h) Eliashberg function $\alpha^2 F(\omega)$ from the integral inversion of $\Sigma'(\omega)$ [39], and electron-phonon coupling constant $\lambda_k = 2 \int d\omega \alpha^2 F(\omega) / \omega$, where the colour shading represents the strength of the total EPC. In (h) the theoretical result from Ref. [17] for a LiC$_6$ monolayer are also shown (gray shading). (i) Experimentally-determined contribution to the total (black symbols) electron-phonon coupling from phonon modes in the energy range 100 - 250 meV (blue shading, white symbols) and 0-100 meV (orange shading); the coupling of low-energy modes strongly increases with Li coverage.
4.3. Enhancement of the electron-phonon coupling

The effects of lithium become more significant in the modifications to the low-energy part of the dispersion, below ~100 meV. With 10 minutes of Li deposition [Fig. 4.6(d)], an additional kink is clearly visible at around 30 meV binding energy, along with the associated peak in the real part of the self-energy $\Sigma'$. These changes occur with increasing Li coverage, which can be seen in the progressive enhancement of both MDC-dispersion kink and $\Sigma'$ peaks in Fig. 4.6(b-d). The lack of any appreciable variation in carrier density between the 6 and 10 minute Li depositions [Fig. 4.2(h)] suggests it is really the increase in the number of Li atoms – and thus perhaps in the degree of order within the Li layer – that is driving these changes.

The extracted Eliashberg functions in Fig. 4.6(f-h) tell the same story: at high Li coverage, spectral weight in the Eliashberg functions appears at energies below 60 meV, indicating the presence of phonon modes coupling strongly to the graphene electronic excitations. It is these low energy contributions to $\alpha^2 F_k(\omega)$ that lead to the large values of $\lambda_k$, as seen in the energy-resolved $\lambda_k(\omega)$ plotted as the solid line in Figs. 4.6(f-h).

In order to understand the origin of these new modes, we can look to existing calculations for this system and similar ones such as CaC$_6$ [17, 25]. There is a strong consensus that the alkali in-plane (Li$_{xy}$) vibrational modes lie between 10 and 40 meV, while the carbon out-of-plane (C$_z$) modes are around 50-80 meV. Comparison with the experimental Eliashberg functions in Figs. 4.6(f-h) leads to the conclusion that the Li$_{xy}$ modes are involved, while it is less clear if the C$_z$ modes are also important.

As for the total electron-phonon coupling $\lambda_k$ for each coverage, represented by the black symbols in Fig. 4.6(i), we note that our values measured on the $\pi^*$-band Fermi surface at an intermediate location between $\Gamma K$ and $K M$ directions [Fig. 4.6(e)] provide an effective estimate for the momentum-averaged coupling strength. We state this based on observations of anisotropic electron-phonon coupling around the $\pi^*$-band Fermi surface in both decorated graphene [20] and intercalated graphite [79]. In those cases, the maximum and minimum values of $\lambda$ were measured along $\Gamma K$ and $K M$.
and the value measured at the intermediate Fermi crossing corresponds approximately to the momentum-averaged coupling strength along the \( \pi^* \)-band Fermi surface.

Remarkably, the value \( \lambda_k = 0.58 \pm 0.05 \) observed at the highest Li coverage [Fig. 4.6(i)] is approaching \( \lambda = 0.61 \) predicted for monolayer LiC\(_6\) [17]; close agreement is also found for experimental and calculated energy-resolved \( \lambda_k(\omega) \) in Fig. 4.6(h), with most of the electron-phonon coupling enhancement coming from the low-energy phonon modes. Finally, \( \lambda_k \simeq 0.58 \) achieved here on 10 minute Li-decorated graphene is much larger than the momentum-averaged results previously reported for both Li and Ca deposition (\( \lambda \simeq 0.22 \) and 0.28 respectively [20]), and is even comparable to \( \lambda \simeq 0.58 \) observed for bulk CaC\(_6\) [79].

We note that this enhancement is critically dependent on the presence of the spectral weight at \( \Gamma \), and disappears when the latter is disordered by increasing temperature. The enhancement of the EPC with increasing Li coverage can be reversed by increasing the temperature above 50 K, the point at which the spectral weight at \( \Gamma \) vanishes. The EPC was studied on a Li-decorated sample (10 min) annealed at 60 K, and is compared to the analysis pre-annealing in Fig. 4.7. We see the near total disappearance of the low-energy renormalizations of the band. The self-energy is dominated by a peak around -180 meV, and the coupling is determined to be 0.13 \( \pm \) 0.05, close to the value of the low-coverage sample. While we assign this effect to the disappearance of the \( \Gamma \) bands, it must also be noted that the charge carrier density is reduced from \( 1 \times 10^{14} \) to \( 5 \times 10^{13} \) cm\(^{-2} \) after annealing at 60 K. It is possible that the doping plays a role in the modification of the electron-phonon coupling, but it is not possible to disentangle the two effects as the saturation of doping is associated with the appearance of the spectral weight at \( \Gamma \).

As a consistency check on the analysis and extraction of the EPC strength, we have done a parallel analysis using a simplified model of \( \alpha^2 F_k(\omega) \) consisting of four Lorentzians whose position, width, and area can be varied in
4.3. Enhancement of the electron-phonon coupling

![Graph showing enhancement of electron-phonon coupling](image)

**Figure 4.7**: Reversible enhancement of the electron-phonon coupling. The MDC dispersion (orange) and real part of the self energy (orange, right-hand panel) for the 10-minute Li sample in (a) show the strong kink at around 30 meV. (b) After annealing to 60 K for several minutes, the low energy feature is no longer apparent. (c) The Eliashberg functions corresponding to the fits to the self energy (black) in (a) and (b) are shown in light orange and light blue respectively. The absence of the low energy feature results in a severely diminished $\lambda_k$, shown as the solid lines in (c).

In order to simultaneously fit the real and imaginary parts of the self-energy, the $\alpha^2 F_k(\omega)$ found with this method is in good agreement with that found by the MEM, with the main peaks at the same energies. The resulting $\lambda = 0.55 \pm 0.05$ is slightly larger than the value from the MEM ($0.46 \pm 0.05$), an effect that has been previously observed when comparing these analysis methods in other materials.\(^{[40]}\) While the MEM is sensitive to the noise of the data, the agreement of these two methods implies they both capture the underlying structure of $\alpha^2 F_k(\omega)$.

For an electron-phonon coupling parameter on the order of $\lambda_k \sim 0.6$, the expected superconducting transition temperature can be calculated with the Allen-Dynes formula\(^{[3]}\) to be $\sim 8$ K. With this in mind, the next section describes the direct measurement of a signature of superconductivity in Li-graphene.

\(^{[3]}\)The Coulomb parameter is set to $\mu^* = 0.115$, \[Eq. 2.22\] based on what is known of CaC$_6$, and following Ref. \[17\]
4.3. Enhancement of the electron-phonon coupling

Figure 4.8: Comparison of two methods for determining $\alpha^2 F_k(\omega)$ and $\lambda_k$. The real and imaginary parts of the self-energy for the 6-minute Li-decorated sample are shown in orange in (a) and (b). The maximum-entropy method is used to fit $\Sigma'$ in black in (a1), and its Kramers-Kronig transform is shown in blue in (a2). The Eliashberg function and electron-phonon coupling constant $\lambda_k$ are shown in (c). An alternate method for extracting $\alpha^2 F_k(\omega)$ by simultaneously fitting the real and imaginary parts of the self-energy with equal weighting is shown in (b). The Eliashberg function, which consists of four Lorentzians whose position and size is varied to achieve a good fit, is shown in (d), along with $\lambda_k$. 
4.4 Spectroscopic gap: evidence of superconductivity

Next we use high-resolution, low-temperature ARPES to search for the opening of a temperature-dependent pairing gap along the $\pi^*$-band Fermi surface, as a direct spectroscopic signature of the realization of a superconducting state in monolayer LiC$_6$. To increase our experimental sensitivity, as illustrated in Fig.4.9(a) and following the approach introduced for FeAs [87] and cuprate [88] superconductors, we perform an analysis of ARPES energy distribution curves (EDC) integrated in $dk$ along a one-dimensional momentum-space cut perpendicular to the Fermi surface. This provides the added benefit that the integrated EDCs can be modelled in terms of a simple Dynes gap function [41] multiplied by a linear density of states and the Fermi-Dirac distribution function, all convolved with a Gaussian resolution function:

$$I_{f_{dk}}(\omega) = [f(\omega, T) (a + b \omega) \left| \text{Re} \frac{\omega - i\Gamma}{\sqrt{(\omega - i\Gamma)^2 - \Delta^2}} \right|] \otimes R_\omega, \quad (4.1)$$

where the parameters $a$ and $b$ describe the linear density of states, $\Delta$ is the size of the superconducting gap, and $\Gamma$ is a phenomenological scattering term.

As shown in Fig.4.9(a) and especially 4.9(b) for data from the k-space location indicated by the white circle in Fig.4.6(e), a temperature dependence characteristic of the opening of a gap can be observed near $E_F$: at variance with the case of Au spectra crossing precisely at $E_F$ according to the Fermi-Dirac distribution function [Fig.4.10(a)], the leading edge mid-point of the Li-graphene spectra moves away from $E_F$ in cooling from 15 to 3.5 K. When fit to Eq.4.1, this returns a gap value $\Delta = 0.9 \pm 0.2$ meV at 3.5 K (with $\Gamma \simeq 0.09$ meV). Given its small value compared to the experimental resolution, the gap opening is best visualized in the symmetrized data in Fig.4.9(c), which minimizes the effects of the Fermi function, and in the density of states in Fig.4.9(d) when the effect of the 6 meV energy resolution
on the fitting function is simply removed (owing to the integration of the ARPES intensity in $dk$, this analysis is unaffected by momentum resolution [87]).
Figure 4.9: **Spectroscopic observation of a pairing gap in Li-decorated graphene.** (a) Dirac dispersion from 10-minute Li-decorated graphene measured at 15 and 3.5 K, at the k-space location indicated by the white circle in Fig. 4.6(e); the temperature dependence is here evaluated for EDCs integrated in the 0.1 Å⁻¹ momentum region about \( k_F \) shown by the white box (bottom), with the only changes occurring near \( E_F \) (top). A closer look at the near-\( E_F \) region in (b) shows the crossing point of the Li-graphene spectra is shifted away from \( E_F \) (cyan dashed line), due to the pull-back of the leading edge at 3.5 K. A fit to the Dynes gap equation yields a gap \( \Delta \simeq 0.9 \text{ meV} \) at 3.5 K (and 0 meV at 15 K). The superconducting gap opening is best visualized in the symmetrized data in (c), i.e. by taking \( I(\omega) + I(-\omega) \) which minimizes the effects of the Fermi function even in the case of finite energy and momentum resolutions [89, 90], and in the density of state plot in (d) where the effect of the 6 meV resolution on the fitting function is simply removed [blue and red symbols in (c) represent the smoothed data, while the light shading gives the root-mean-square deviation of the raw data].
Figure 4.10: Reference pairing gap in polycrystalline niobium. (a) The Fermi edge measured on polycrystalline gold shows the crossing point of the two temperature curves at $E=0$, and no change in the position of the leading edge with temperature, as expected for a normal metal. This is in contrast to niobium, a known superconductor with $T_c \sim 9 \, K$, where the leading edge of the EDC in (b) shifts at low temperature. A Dynes fit to the Fermi edge yields a gap $\Delta \simeq 1.4 \, meV$ at 3.5 K (and 0 meV at 15 K). The symmetrized data are shown in (c) where the temperature dependent gap is more obvious. The same symmetrized fit is shown in blue in (d), and is compared to a simulation with the 6 meV energy resolution set to 0.
The spectroscopic gap appears to be anisotropic: it is either absent or vanishingly small along the KM direction. High-resolution measurements performed at the high symmetry point along KM do not show a gap (Fig. 4.11). The EDC of the Li-G at this point on the Fermi surface has its crossing point at 0, and the shape of the edge is the same as a reference measurement on polycrystalline gold. The slight difference in the slope of the edge crossing zero is attributed to a small difference in the experimental resolution between the two measurements. The gap is either closed or too small to measure with the resolution of this study. Either way, it demonstrates an anisotropy of the gap. This is perhaps not so surprising as bulk CaC$_6$ is thought to have an anisotropic superconducting gap.[91–93]

![Figure 4.11: Absence of a gap along KM.](image)

The detection of a temperature-dependent anisotropic gap with a leading-edge profile described by the Dynes function – with its asymmetry about $E_F$ and associated transfer of spectral weight to just below the gap edge – suggests the gap is a superconducting pairing gap. The phenomenology would be in fact very different in the case of a Coulomb gap, i.e. the depression in
density of states at $E_F$ due to the combination of disorder with long-range Coulomb interactions [94]. In addition to being isotropic in momentum, this would lead to a rigid shift of the spectra leading edge, as observed in the emergence of the small nodal gap – and thus of a fully gaped excitation spectrum – in deeply underdoped cuprates [95]. Similarly, the observed gap is inconsistent with a charge density wave origin, since the gap is tied to the Fermi energy as opposed to a particular wavevector (the latter might occur at the M points, when graphene is doped all the way to the Van Hove singularities resulting in a highly-nested hexagonal Fermi surface [18], or at the $\overline{K}$ points in the case of a $\sqrt{3} \times \sqrt{3}R30^\circ$ reconstruction leading to a Dirac-point gap).

To further explore the nature of the gap observed on Li-decorated graphene (and also demonstrate our ability to resolve a gap of the order of 1 meV), in Fig.4.10(b-d) we show as a benchmark comparison analogous results from a bulk, polycrystalline niobium sample – a known BCS superconductor with $T_c \approx 9.2K$ and gap $\Delta \approx 1.4$ meV. The edge shift [Fig.4.10(b)] and the dip in the symmetrized spectra [Fig.4.10(c)] are more pronounced than in the Li-graphene case, owing to the larger gap, but the behaviour is qualitatively very similar. The Dynes fit of the integrated EDCs Fermi edge determines the gap to be $\Delta = 1.4 \pm 0.2$ meV (with $\Gamma \approx 0.14$ meV), in excellent agreement with the reported values [38].

It has been shown that in a 2 dimensional superconductor, there will be a thermodynamic instability relating to the unbinding of vortex-anti-vortex pairs above some critical temperature [96]. This is known as a Kosterlitz-Thouless transition, and if $T_{KT} \leq T_c$ then superconductivity will be suppressed. Estimates of $T_{KT}$ rely on parameters such as the superfluid density which are not known for this system. However, a phenomenological relationship between the sheet resistance and $T_{KT}/T_c$ has been demonstrated [97], showing that quite large sheet resistances are needed to reduce $T_{KT}$ below $T_c$ (on the order of kΩ). Li-graphene is heavily doped, with a typical sheet resistance below 1 kΩ [98], and so the possibility of a KT transition can
reasonably be set aside at this stage.

4.5 Conclusion

The electron-phonon coupling and its relation to superconductivity is well enough understood that plausible predictions about new superconducting materials can be made from theory. Such a prediction was made for Li-decorated graphene, and we present the experimental evidence to support this. It is only through low-temperature sample preparation in an ultra-clean, ultra-high vacuum environment, that lithium leads to a strong enhancement of the electron-phonon coupling, as measured by ARPES on the graphene $\pi^*$ band Fermi surface.

Taken together, our ARPES study of Li-decorated monolayer graphene provides the first evidence for the presence of a temperature-dependent pairing gap on part of the graphene-derived $\pi^*$ Fermi surface. The detailed evolution of the density of states at the gap edge, as well as the phenomenology analogous to the one of known superconductors such as Nb – as well as CaC$_6$ and NbSe$_2$, which also show a similarly anisotropic gap around the K point [91–93, 99, 100] – indicate that the pairing gap observed at 3.5 K in graphene is associated with superconductivity. Based on the BCS gap equation, $\Delta = 3.5 \, k_b T_c$, this suggests that Li-decorated graphene might be superconducting with $T_c \approx 5.9$ K, remarkably close to the value of 8.1 K found in density-functional theory calculations [17].
Many interesting properties of graphene can be tuned by the appropriate introduction of impurities. This concerns not just charge-transfer doping through adatoms or molecules to tune the position of the Dirac point with respect to the Fermi level [67–71], but also different interactions (electron-electron or electron-phonon) [16, 72, 73], metal-insulator transitions [74, 75] and the emergence of superconductivity [2, 15, 17, 18, 21]. It has also been proposed that graphene could be tuned to become a 2D topological insulator [27, 101, 102].

Graphene was originally predicted to be a 2D topological insulator [28] however the spin-orbit coupling resulting from carbon’s small atomic number [103] is too weak to produce any experimentally observable, or technologically useful, effects. The path to making graphene into a robust topological insulator is through opening a gap at the crossing of the $\pi$ bands at the corners of the hexagonal Brillouin zone, and in order to do this, the spin-orbit coupling must be enhanced. Following an exhaustive search using electronic structure calculations, thallium was identified as an element that when deposited on monolayer graphene, could enhance the spin-orbit coupling, and open a gap at the Dirac point on the order of tens of meV, several orders of magnitude larger than in intrinsic graphene [27]. In addition to being heavy, thallium met several other criteria. Firstly, the atoms sit at the hollow sites, in the middle of the carbon hexagons, where they can most effectively mediate the second-neighbour hopping that gives rise to the spin-orbit term in the Kane-Mele model [28]. Secondly, the adatom must have no magnetic moment so as not to break time-reversal symmetry. The calculations indicate that the sole unpaired $6p$ electron is fully ionized (ie. it is transferred to the graphene
sheets), leading to electron doping of the $\pi$ bands.

Using ARPES, we studied the system of thallium adatoms on graphene, characterizing the modifications to the electronic structure, and the role of temperature. Many of the predictions from the theoretical work were found to be correct, and this information will stimulate future studies of Tl on graphene with ARPES and other experimental techniques, and is presented in Section 5.1. Studying the evolution of the linewidth at the Fermi level with increasing Tl coverage revealed details of the scattering mechanisms at play in this system. In Section 5.2 it is shown that short-range $\delta$-like scattering due to the adatoms is significant in this system, despite the expectation that Coulomb scattering would dominate. Interestingly, this too lends support to one of the predictions from theory that implies Tl is a very good candidate for realizing a topological insulator from graphene.

5.1 Preparation of Tl adatoms on graphene

Epitaxial graphene monolayers with a buffer layer were grown under argon atmosphere on hydrogen annealed 6H-SiC(0001) at MPI-FKF in Stuttgart [82]. ARPES and scanning tunneling microscopy (STM) measurements were performed at UBC. The ARPES experiments used linearly-polarized photons with an energy of 40.8 eV and an ARPES spectrometer equipped with a SPECS Phoibos 150 hemispherical analyzer and UVS300 monochromatized gas discharge lamp. Energy and angular resolution were set to 15 meV and 0.3°. The graphene samples were slightly post-annealed after insertion into ultra-high vacuum, and right before Tl deposition in the ARPES chamber. It has been calculated that thallium is one of the most mobile atoms on the graphene surface [104]. Therefore, Tl atoms were evaporated from an electron beam evaporator on a cold sample to avoid surface diffusion (at 4.5K for STM (scanning tunnelling microscopy) and 8K for ARPES). All subsequent measurements were also done in the same temperature range. During measurements the samples were kept at a pressure better than $7 \times$
5.1. Preparation of Tl adatoms on graphene

STM measurements demonstrate that, at very low temperatures and concentrations, thallium atoms are present as immobile monomers on the surface [see Fig. 5.1]. The topographic image shows a thallium covered graphene monolayer for a coverage of 0.2%. Even at this low coverage, a small fraction of adsorbed thallium appears to be in dimer or trimer form, although the vast majority appear to be thallium monomers. This has also been confirmed by Tl deposition on a clean Au(111) surface [Fig.5.1(a)] using the same parameters and yielding the same number density. It is difficult to find regions where both the thallium adatom and the graphene lattice can be visualized simultaneously. This is due to electronic inhomogeneities in the substrate and buffer layer. Thallium on more uniform graphene patches appears to sit on the hollow site, in agreement with predictions from density functional theory (DFT) calculations [27, 104], although the large apparent size of the thallium adatoms makes a more conclusive assignment difficult, and graphene’s inherent electronic inhomogeneity make an identification of the adsorption

Figure 5.1: Calibration of thallium deposition. STM images of Tl adatoms deposited from and electron-beam evaporator on Au(111) [panel (a)], and graphene/SiC [(b) and (c)]. Tl atoms are imaged as the bright spots in (a), and as the orange/gold spots in (b) and (c). Samples were held at 4.5 K during deposition and measurement, and the adatoms showed no signs of diffusion, and were predominantly isolated, single atoms. The coverage shown here corresponds to 2 minutes evaporation and 0.2% of a monolayer.
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Site difficult, thallium on more uniform graphene patches appears to sit on the hollow site, in agreement with predictions from density functional theory (DFT) calculations [27, 104]. As the precise coverage is important for the subsequent quantitative analysis of the ARPES data, the STM results were also used for the precise flux calibration of the Tl evaporator.
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Figure 5.2: Dispersion of the graphene $\pi$ bands with increasing Tl coverage. Raw ARPES data measured the the $\overline{K}$ point of the Brillouin zone shows how the electronic structure is modified with increasing Tl coverage from left to right. The numbers along the top indicate the coverage of Tl as a percentage of a monolayer, where a monolayer would correspond to one Tl atom per carbon atom. There is some doping of the $\pi$ bands due to charge transfer from the Tl adatoms, but only up to 1%. With increasing coverage beyond this, the trend reverses, and the Dirac point can be seen to shift back towards the Fermi level. The MDC width increases with increasing coverage.
Figure 5.2 shows the experimental band structure of an epitaxial graphene monolayer near the K-point, measured in the geometry shown in Fig. 5.3(a). The concentration $x$ of thallium atoms on the surface is given in percent of a graphene monolayer, i.e. the number of thallium atoms per carbon atom. The left-hand side data set is from the pristine graphene monolayer, exhibiting an initial n-type doping due to the intrinsic charge transfer from the SiC substrate [82]. Upon thallium deposition, there is a charge transfer from the thallium atom to the graphene sheet: electron doping increases so that the Dirac point shifts to higher binding energies, away from the Fermi level. For concentrations higher than $\sim 1\%$, the trend is reversed, and the Dirac point shifts back towards the Fermi level. We ascribe this to the onset of pairing and clustering of atoms, which reduces the efficiency of charge transfer doping. For this reason, in the scattering analysis in Section 5.2, we concentrate on the dilute limit below 1\%, where clustering effects can be neglected. The strong broadening of the ARPES line width at the higher coverages makes it very difficult to determine whether there is a spectroscopic gap appearing at the Dirac point. Theory predicts that there should be a spin-orbit coupling induced gap of 20 meV at 6 \% coverage [27], but this would be unobservable with the level of broadening seen.

The shift of the Dirac point to higher binding energies upon thallium deposition illustrated in Fig. 5.2 corresponds to an increase of the Fermi contour area. The corresponding evolution of Fermi wave vector $k_F$, as well as charge carrier density $n$ and energy shift are shown in Fig. 5.3 (b), (c), and (d) respectively. Below a coverage of 1\%, all three parameters are increasing monotonically. The energy shift reflects the increase in occupation due to the donation of electrons by the thallium atoms. A simple model employing graphene’s linear band dispersion is used to estimate the charge transfer per thallium atom from the energy of the Dirac point ($E_D$):

$$E_D = \sqrt{\pi} \hbar \nu_F \sqrt{N_0 + N_e},$$ (5.1)

where $\nu_F$ is the band velocity near the Fermi level, $N_0$ is the number of electrons in the clean graphene, and $N_e$ is the number of electrons donated...
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Figure 5.3: **Charge transfer doping from Tl atoms.** ARPES measurements were performed at the K point of the Brillouin zone, shown with the blue line in (a). MDCs at the Fermi level show the evolution of the Fermi wavevector in (b). The charge density in (c), calculated from the FS contour area, increases linearly with coverage until about 1%, where the trend reverses. A similar trend is seen in (d), where the energy shift of the Dirac point is shown. A simple model relating $\Delta E_D$, the coverage, and the number of electrons donated per Tl is shown in green, indicating that the Tl donates one electron per atom.

by the adatoms (proportional to the number of adatoms times the number of electrons per adatom). The best fit is found for 1.0 ± 0.1 electrons donated per thallium atom to the graphene layer, shown in green in Fig. 5.3(d). This confirms one of the results from DFT calculations for thallium adatoms on graphene [27], implying the Tl atoms donate their sole unpaired 6$p$ electron to the graphene, and therefore have no magnetic moment.

While the Tl atoms are immobile below 8 K in the topographic images [Fig. 5.1], we observe that the thallium atoms are extremely mobile on the graphene surface at higher temperatures (cf. Ref. [104]). This is illustrated in the temperature dependence of the 2D carrier density $n$ in Fig. 5.4 for a Tl coverage of 0.6%. Above 15 K, a rapid decrease in doping efficiency can be observed, which we attribute to the clustering of the mobile Tl atoms, indicating that Tl is only very weakly bonded to the graphene. Comparing the temperature dependence of the doping and linewidth with that of potassium on graphene is instructive. Both show a decrease in $n$ back towards the
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Figure 5.4: Temperature dependence of thallium on graphene. Panels (a) and (b) compare the temperature dependence of the doping from thallium and potassium atoms between 8 K and 100 K. In both cases there is a reduction in the carrier concentration as the temperature is increased. The MDC linewidth measured at the Fermi level shows a clear difference for the two adatoms. The linewidth increases with temperature in the case of thallium (c), but decreases for potassium (d). In all figures, the black data point represents the clean graphene, while the black arrow shows how the quantity changes following the low temperature deposition of 0.6% Tl or 1.5% K.
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initial value of graphene/SiC, but the MDC linewidth of Tl/MLG increases with temperature, while that of K/MLG decreases. This is consistent with a picture where potassium is re-evaporated with increasing temperature, and the graphene reverts to its pristine state. The opposite behaviour of Tl on graphene indicates that it is not leaving the surface, but rather, forming clusters that make the surface more inhomogeneous and leading to the observed broadening of the linewidth in Fig.5.4(c).

Figure 5.5: **Annealing Tl on graphene.** (a) ARPES spectrum of clean monolayer graphene. (b) ARPES from a Tl-deposited and annealed sample, showing the Dirac point shifting towards the Fermi level, opposite to what is seen for low temperature deposition. Subsequent deposition and annealing cycles (c,d) continue to push the system towards charge-neutrality, where the Dirac point is at the Fermi level, and the carrier density is zero.

Annealing the Tl-decorated graphene to 700°C for 30 minutes reduces the carrier density to zero, bringing the Dirac point to the Fermi level, shown in Fig.5.5. Fig.5.6 shows the charge carrier density after annealing, as a function of coverage. The reduction in doping observed with increasing coverage (blue data points) tends to approach the values of the clean graphene, shown as a dotted line in Fig.5.6. The further reduction past this value for the annealed samples implies the Tl is interfering with the charge transfer from the SiC substrate, perhaps by intercalating between the graphene and substrate. This behaviour has been seen with gold atoms [105], and with oxygen [106] on a similar system and so is perhaps not surprising. It is an
5.1. Preparation of Tl adatoms on graphene

Figure 5.6: **Annealing Tl on graphene.** The carrier concentration for low temperature deposited Tl is shown in blue. Depositing Tl at low temperature followed by annealing at 700°C leads to a large reduction in the carrier concentration, plotted in gold.

interesting prospect, however, due to the theoretical interest in studying how Tl adatoms can modify the electronic structure of graphene.

To summarize the characterization of Tl on graphene, we have shown that isolated monomers exist only up to \( \sim 1\% \) concentration, and are only stable as such below 15 K. There is evidence that Tl intercalates between the graphene and substrate at high temperatures, bringing the Dirac point to the Fermi level. The Tl adatoms are fully ionized, as predicted, and therefore act as long-range charged impurity scatterers at the graphene surface. In the next section, we examine the scattering more closely, and show that the Tl atoms also act as strong short-range scatterers.
5.2 Long-range vs. short-range scattering

Adatoms on graphene tend to reduce the quasiparticle lifetime by introducing long-range (Coulomb) scattering and/or short-range (δ-potential) scattering \[107\]. This depends on how the impurity modifies the electronic structure through its interaction with the graphene layer, i.e. donating charge to the graphene layer and acting as a charged impurity, or being attached in some way to the graphene layer. This ranges from weakly-attached physisorption \[108\] to the formation of a covalent bond as in the example of hydrogen, which sp³-hybridizes the carbon bond severely affecting the graphene electronic structure \[74\]. While it is generally agreed upon that the charge carrier mobility \(\mu\) is inversely proportional to the density of charged impurities \(n_{\text{imp}}\), resulting in an increase of the scattering rate upon doping, other reports claim an increase of the quasiparticle lifetime upon doping with charged impurities \[109\]. Such behaviour critically depends on screening, which is determined through the dielectric constant \(\epsilon\) of the system.

Although Coulomb scattering is often assumed to be the dominant scattering mechanism in graphene, short-range scattering can become appreciable if dielectric screening is highly effective in reducing Coulomb scattering relative to short range scattering, or if there are impurity states close to the Fermi level giving rise to a particularly strong scattering potential. Therefore, in real systems, it is not necessarily \textit{a priori} clear which scattering mechanism is dominant. Here, we use the experimental spectral function measured by angle-resolved photoemission spectroscopy (ARPES) on thallium-doped epitaxial graphene to observe the scattering behaviour induced by the thallium adatoms, and disentangle Coulomb (long-range) from δ-like (short-range) scattering contributions.

At a constant low temperature, linewidth broadening at the Fermi level from interactions (i.e., electron-electron, electron-phonon, electron-plasmon) can be regarded as a small, constant contribution. In a Fermi liquid, linewidth broadening at the Fermi level due to interactions vanishes as \(T^2\) when the temperature goes to zero. Consequently, the spectral linewidth at the Fermi
level reflects predominantly defect and disorder contributions. Both long range and short-range scattering mechanisms can be described by an analytic expression for the self-energy in the dilute limit. Fitting the self-energy to the experimental data allows us to extract the fundamental parameters of the scattering mechanisms at play in the graphene layers.

The line widths carrying the scattering information are taken from the full-width at half maximum (FWHM) of momentum distribution curves (MDCs) at the Fermi level; these are shown for a selection of thallium coverages in Fig. 5.7(a). The MDCs were fitted with a Voigt function – a convolution of a Gaussian and Lorentzian – which represents the intrinsic Lorentzian line-shape of the spectral function convolved with a Gaussian function due to the experimental resolution. The width of the Gaussian resolution function was set to match the experimental momentum resolution $0.016 \, \text{Å}^{-1}$, while the extracted Lorentzian FWHM (full-width at half-maximum) can be related to the scattering, or lifetime.

The linewidth increases monotonically with increasing thallium coverage shown in Fig. 5.7(b) due to scattering from the randomly adsorbed thallium atoms. We analyze data up to $x = 0.5\%$ in order to avoid effects of clustering that we have shown to appear around 1\%. We assume that the linewidth which we measure for the clean sample comes from initial disorder, defects and residual interactions, and does not change with Tl coverage. In order to unravel the contributions from the thallium-induced disorder to the linewidth broadening and thus the corresponding contribution to graphene’s electrodynamics, we discuss two scattering mechanisms in more detail.

The first mechanism is due to scattering from charged impurities, which has a long-range effect due to the screened Coulomb potential. Since thallium donates one electron per atom to the graphene sheet, it can be treated as a long-range Coulomb scatterer. The linewidth broadening, which can be directly modelled by the imaginary part of the self-energy, has the following
5.2. Long-range vs. short-range scattering

simplified expression:

$$\Sigma''_{\text{long}} = \alpha^2 n_{\text{imp}} v_F \pi I(2\alpha)/k_F, \quad (5.2)$$

where $\alpha$ is the effective fine-structure constant, $I(2\alpha)$ is a function defined in Ref. [110], $v_F$ is the Fermi velocity, $n_{\text{imp}}$ is the impurity density (which relates to the thallium concentration $x$ via $n_{\text{imp}} = 2x/A$ where $A$ is the area of the graphene unit cell), and $k_F = \sqrt{\pi(\nu n_{\text{imp}} + \nu_0)}$ is the Fermi momentum with $\nu$ being the number of electrons donated per impurity atom, and $\nu_0$ the charge density in graphene before thallium deposition.
5.2. Long-range vs. short-range scattering

Figure 5.7: Analysis of the ARPES linewidth. (a) The MDC linewidth is fitted with a Voigt lineshape, which consists of a Lorentzian peak convoluted with a Gaussian accounting for the experimental resolution. The linewidth as a function of Tl coverage is shown in blue in (b). Modelling using various values of the parameters $\delta$ and $\epsilon$ are also shown.
5.2. Long-range vs. short-range scattering

The only free parameter in Eq. 5.2 is the effective fine structure constant of graphene; all other parameters can be determined from the experiment. The effective fine structure constant depends on the dielectric constant $\epsilon$ through $\alpha = 2.2/\epsilon$. The dielectric constant in turn is determined by the underlying substrate; the smaller its value, the stronger the long-range scattering contribution to the linewidth broadening. From the analysis of plasmaron signatures in epitaxial graphene on a buffer layer on SiC(0001) [111], the dielectric constant has been determined to be $\epsilon = 22 \pm 8$. The long range scattering calculated from Eq. 5.2 using this value of $\epsilon$ is shown in Fig. 5.7(b) in red, and clearly does not fit the measured linewidth evolution with thallium coverage. Recent calculations, however, point towards an overestimate of the dielectric constant [112], suggesting that the actual value is likely smaller. Indeed, by analyzing the band velocity renormalization in epitaxial graphene, a reduced value $\epsilon = 7.26 \pm 0.02$ was found [113]. The linewidth broadening from long-range scattering for this value of the dielectric constant is shown as a yellow line in Fig. 5.7(b), and again, it only accounts for part of the experimental linewidth broadening. One must go to values of $\epsilon$ far from those reported in the literature in order to adequately describe the data in Fig. 5.7(b). Therefore, another mechanism is likely to contribute to the experimental linewidth.

A second prominent scattering mechanism that arises in the presence of disorder is short-range scattering from an effective $\delta$-potential. This approach does not distinguish between inter- and intra-valley scattering in graphene, but it does capture the general strength of short-range scattering. Short range scattering is appreciable when adatoms have states close to the Fermi level, thereby inducing a sizeable scattering potential [114, 115]. Its effect on the linewidth broadening can be modelled by the self-energy within the Wolff-Clogston-model [116, 117]. We adopt a self-consistent implementation in the dilute limit within the coherent potential approximation, whereby the varying potentials of a random distribution of adatoms is replaced by an ordered lattice of effective potentials [118]:
5.2. Long-range vs. short-range scattering

Figure 5.8: **Calculations of the short range scattering.** The real and imaginary parts of the lattice Green’s function are shown in (a) in blue and green respectively. (b) The imaginary part of the self-energy for the short-range scattering model described by Eq. 5.3 with parameters $\delta = -5 \text{ eV}$ and $x = 1\%$. The inset shows the dependence of $\text{Im}\Sigma_{\text{short}}$ on $\delta$ at an energy of 0.5 eV relative to the Dirac point, which corresponds to near $E_F$ in the measurements.
5.2. Long-range vs. short-range scattering

\[ \Sigma''_{\text{short}}(\omega) = x \delta \text{Im} \left( 1 + \frac{\delta G^0(\omega - \Sigma(\omega))}{1 - \delta G^0(\omega - \Sigma(\omega))} \right) \]  

(5.3)

where \( G^0(\omega) \) is the lattice Green’s function of the unperturbed graphene lattice [119] and \( \delta \) is the scattering potential. As the thallium concentration \( x \) as well as the lattice Green’s function are known [the latter is here shown in Fig. 5.8(a)], the only free parameter in the short-range scattering model is the scattering potential parameter \( \delta \).

The overall behaviour of the imaginary part of the short-range scattering self-energy for graphene is shown in Fig. 5.8(b). Its rather strong energy dependence is due to the special energy dependence of the graphene lattice Green’s function [Fig. 5.8(b)] in conjunction with that of the scattering potential itself. The dependence on the scattering potential \( \delta \) at an energy \( \omega = 0.5 \text{ eV} \), thus in the vicinity of the experimentally relevant energies, is shown in the inset of Fig. 4(b). For \( \delta \to \pm \infty \), which can be interpreted as a missing atom in the lattice, the imaginary part approaches the same finite value. For small values of \( \delta \), the imaginary part of the self-energy varies more rapidly, although it remains bounded, and exhibits a maximum value for \( \delta \approx -5 \text{ eV} \).

To evaluate the combined effect of both scattering processes, we calculate the linewidth from a theoretical spectral function generated by including the long and short-range scattering self-energies from Eqs. 5.2 and 5.3 in the single particle Green’s function of graphene. Using the most accurate experimental determination of \( \epsilon \) from Ref. [113], \( \delta \) remains as the only fitting parameter. The model agrees well with the experimental data for \( \epsilon = 7.26 \) and \( \delta = -3.2 \pm 1 \text{ eV} \) shown as the green shading in Fig. 5.7(b). As it turns out, the contributions from short-range and long-range scattering have comparable magnitudes.

When comparing the value here obtained for \( \delta \) with available calculations in the literature [27], we have to keep in mind that our short-range scattering model does not distinguish between different angular momentum channels, but rather attributes equal scattering amplitude to all scattering
channels. Nevertheless, we can obtain a ballpark estimate for $\delta$ from the formula $\delta = \frac{t_{ad}^2}{|\Delta E|}$, where $t_{ad}$ is the hopping to the Tl adatom and $\Delta E$ is the energy difference between the unperturbed (free) Tl adatom states and the Fermi level [114, 115]. From the parameters reported in Ref. [27], we can estimate a theoretical value $\delta_{th}$ ranging from -1 to -4 eV. Therefore our results suggest that short range scattering in this system lies on the larger side of the theoretically predicted range.

Similar effects of enhanced scattering due to impurities have been observed in a number of transport experiments [107, 120, 121], in agreement with our findings. There, the main scattering indicator is the carrier mobility, which decreases linearly with increasing impurity density. By contrast, a decreasing photoemission linewidth upon potassium doping has been reported by Siegel et al. [73]. We attribute this variance to the different doping regime, and correspondingly different intrinsic screening, that were probed in the experiments. Carrier scattering mechanisms in graphene (including charge impurities, resonant scatterers, and ripples) have been strongly debated [120, 122], and predominance of one or the other mechanism is largely sample dependent. For graphene subjected to charged impurities, e.g. alkali adatoms, long-range scattering is typically expected to be much more effective in charge carrier scattering than short range scattering [121, 123, 124]. Thallium adatoms on graphene, having an impurity charge of +1, might be expected to behave in a similar fashion. We showed, however, that this is a system where both mechanisms have nearly equal contributions due to the proximity of thallium impurity states to the Fermi level. More generally, this implies that it cannot be a priori assumed what scattering mechanism will dominate in any given impurity-graphene system.

5.3 Conclusion

In summary, we have quantitatively shown that Tl adatoms on a monolayer of epitaxial graphene grown on a buffer layer on SiC(0001) have a large effect on
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the quasiparticle scattering rate. The Tl adatoms introduce disorder and act on the graphene electronic structure both as Coulomb long-range scatterers as well as short-range scatterers with a $\delta$-like potential. By modelling the self-energy for both scattering mechanisms, we are able to extract a strong short-range scattering potential $\delta = -3.2 \pm 1$ eV. Thus, short-range scattering can contribute to a sizeable increase of the scattering rate, even in the case of charged impurities where long-range Coulomb scattering is usually expected to dominate. These findings, and the ability to predict and/or account for conflating scattering mechanisms, will have important implications in the development of novel impurity-graphene-based electronics.

Our study of this system was motivated by the prediction that Tl adatoms could tune the topology of the wavefunction in graphene. While our data is unable to confirm this, we verify that some of the necessary conditions for this are met in this system, including showing that isolated adatoms exist at low temperature and low coverage, and the complete ionization of the Tl $6p$ electron. The strong $\delta$ scattering is also an indication that the theory work is on the right track, implying a significant hopping term between the adatom and the graphene. This is an essential ingredient for the spin-orbit coupling of a heavy adatom to rub off on the graphene and create the predicted topological insulator.
Chapter 6

Conclusions

This thesis brings together three projects, employing angle-resolved photoemission spectroscopy to quantitatively understand interactions in a well characterised many-body system, and then to study similar interactions in new systems.

Combining the ability of ARPES to measure the momentum-resolved electronic structure and advanced data analysis techniques based on the self-energy, we can access the momentum-resolved electron-phonon coupling, which is a crucial quantity for the description of superconductivity. Similar approaches have been used on simple metals with great success, but its application to materials such as the high $T_c$ cuprate superconductors is hindered by the unknown, but complex nature of the bosonic excitations. We study MgB$_2$, a well characterized conventional multi-gap superconductor, and unequivocally demonstrate the anisotropy of the electron-phonon coupling that leads to the high $T_c$ of 39 K.

The electronic states formed from the in-plane boron orbitals couple very strongly to phonon modes centred around 70 meV. One of these bands shows an electron-phonon coupling strength approximately twice as large as the expected average value from calculations. The coupling measured on the other band is also larger than the expected average, and its magnitude varies around the Fermi surface. These results are entirely consistent with calculations, and explain a number of recent measurements of the anisotropic superconducting gap.

Next, we use sample preparation techniques in ultra-high vacuum, and at low temperature, to modify graphene in such a way that it demonstrates phonon mediated superconductivity. We do this by depositing lithium adatoms,
which form new electronic and phononic states that are available to partic-
icate in the electron-phonon coupling. Using the techniques established on
MgB$_2$, we demonstrate a large enhancement of the electron-phonon coupling
up to $\lambda \sim 0.6$.

High-resolution, low-temperature ARPES measurements then provide di-
rect evidence for the presence of a temperature-dependent pairing gap on part
of the graphene-derived $\pi^*$ Fermi surface. The detailed evolution of the den-
sity of states at the gap edge, as well as the phenomenology analogous to
the one of known superconductors such as Nb, indicates that the pairing gap
observed at $3.5$ K in graphene is associated with superconductivity. Based on
the BCS gap equation, $\Delta = \frac{3}{5} k_B T_c$, this suggests that Li-decorated graphene
might be superconducting with $T_c \sim 5.9$ K, remarkably close to the value of
8.1 K predicted from density-functional theory calculations.

The third project also involves the modification of graphene with adatoms,
and in that sense, is a natural progression from the second. Motivated by the
prediction that thallium adatoms could transform graphene into a topologi-
cal insulator, we performed a detailed characterization of this system. Using
ARPES supported by STM measurements, we show that isolated adatoms
exist at low temperature and low coverage, and that the Tl $6p$ electron is
completely ionized. These are both considered necessary conditions for the
appearance of the topological insulator state.

From a detailed analysis and modelling of the ARPES linewidth at the
Fermi level, we quantitatively show that Tl has a large effect on the quasi-
particle scattering rate. The adatoms introduce disorder and act on the
graphene electronic structure both as Coulomb long-range scatterers as well
as short-range scatterers with a $\delta$-like potential. This strong $\delta$ scattering
is another indication that the theory work is on the right track, implying a
significant hopping term between the adatom and the graphene. This is an
essential ingredient for the spin-orbit coupling of a heavy adatom to rub off
on the graphene and create the predicted topological insulator.

To reiterate from the introduction, this thesis demonstrates the power of
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the ARPES technique for understanding the origins of superconductivity in both 3D and 2D systems, and for characterizing new low-dimensional systems. This is also a thesis about materials. It is about how novel materials can be made and measured, all in ultra-high vacuum, and at temperatures a few degrees above absolute zero. And while these conditions are not conducive to the imminent development of ground-breaking new technology, hopefully the work presented in this thesis will contribute in some way to bringing future materials and technologies to fruition.
Bibliography


Bibliography


[78] Pan, Z.-H. *et al.* Electronic Structure of Superconducting KC₆ and Nonsuperconducting LiC₆ Graphite Intercalation Compounds: Ev-


Bibliography


Appendix A

Additional Publications

Over the course of my PhD, I have contributed to numerous other projects in ways ranging from technical assistance to experimental assistance. These contributions are not described in this thesis, but the resulting publications are listed below.


Appendix A. Additional Publications


