Optical Detection of Paramagnetic and Cyclotron Resonance in Semiconductors

By

IAN J. M. BOOTH

B.Sc., M.Sc., Lakehead University, 1980

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE STUDIES
(Department of Physics)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
March 1985
© Ian Jeremy M. Booth, 1985
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.
ABSTRACT

Optical Detection of Magnetic Resonance (ODMR) has been used to observe both paramagnetic and diamagnetic resonance of photo-excited electrons and holes in GaP, ZnTe and AgBr. Paramagnetic resonance of conduction electrons in GaP has been studied and the microwave frequency and power dependence of the effect analysed. The maximum signal strength was observed to produce approximately 1% change in luminescence at 1.6 K. The g value deduced from the resonance was 2.000 ± 0.005. The resonance was homogeneously broadened giving the electron lifetime as approximately 4 nanoseconds.

Paramagnetic resonance of electrons and holes has also been detected in AgBr.

The background signals present in ODMR experiments have been investigated and are shown to be caused by diamagnetic or cyclotron resonance heating of photoexcited carriers. Measurements at microwave frequencies of 9.2 and 36.3 GHz have been made on GaP, ZnTe and AgBr, and cyclotron resonance of electrons and holes observed. The effective masses of light and heavy holes in GaP were found to be 0.154 ± 0.01 and 0.626 ± 0.06 respectively while the electron effective mass was 0.36 ± 0.10. The electron scattering time was shorter than that for holes by a factor of approximately three, most likely due to scattering by isoelectronic nitrogen impurities. Resonances were observed in ZnTe at effective mass values of 0.30 ± 0.20 and 0.76 ± 0.20
corresponding to electrons and heavy holes. In both GaP and ZnTe resonances due to electrons and holes appeared in different luminescence bands indicating the sensitivity of different recombination centres to heating of either carrier type. Cyclotron resonance of electrons and holes was also observed in AgBr and showed the effects of conduction and valence band non-parabolicity. A feature in the electron resonance indicated enhanced trapping of electrons with certain energies by emission of one or more LO phonons.
# TABLE OF CONTENTS

Abstract.

Chapter 1. Introduction.  
1.1 Historical.  
1.2 Paramagnetic Resonances.  
1.3 Advantages of ODMR.  
1.4 Cyclotron Resonance.  
1.5 Overview of the thesis.  

Chapter 2. Apparatus and Experimental Techniques.  
2.1 Apparatus.  
2.2 Experimental Procedures.  
2.3 Commentary.  

Chapter 3. Gallium Phosphide and Zinc Telluride.  
3.1 Introduction.  
3.2 Exciton formation and luminescence in GaP.  
3.3 Other work on GaP.  
3.4 Results.  
3.5 Discussion.  
3.6 Cyclotron Resonance.  
3.7 ODMR in ZnTe.  
3.8 Other Materials.  
3.9 Summary.  

Chapter 4. Silver Bromide.  
4.1 AgBr.  
4.2 ODMR in AgBr.  
4.3 Results.  
4.4 Discussion.  
4.5 Summary.  

Chapter 5. Conclusions and Suggestions for Further Work.  
5.1 Gallium Phosphide.  
5.2 Zinc Telluride.  
5.3 Silver Bromide.  
5.4 Curve fitting.  
5.5 Comments and Suggestions for Further Work.  

Appendix A. Curve Fitting.  
Statistical Analysis.  

Bibliography.
LIST OF TABLES

Table 3.1. Microwave induced luminescence changes. 41
Table 3.2. GaP Cyclotron Resonance results. 68
Table A.1. Gaussian L.S. coefficients. 113
Table A.2. Lorentzian L.S. coefficients. 113
Table A.3. Revised Gaussian L.S. coefficients. 117
Table A.4. Revised Lorentzian L.S. coefficients. 117
Table A.5. Correlation coefficients and confidence limits. 119
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.1</td>
<td>Basic ODMR experiment.</td>
</tr>
<tr>
<td>Fig. 1.2</td>
<td>Luminescence processes.</td>
</tr>
<tr>
<td>Fig. 2.1</td>
<td>Apparatus.</td>
</tr>
<tr>
<td>Fig. 3.1</td>
<td>GaP bandstructure.</td>
</tr>
<tr>
<td>Fig. 3.2</td>
<td>GaP-N and GaP-Bi luminescence.</td>
</tr>
<tr>
<td>Fig. 3.3</td>
<td>Exciton states in GaP.</td>
</tr>
<tr>
<td>Fig. 3.4</td>
<td>ODMR in GaP-N.</td>
</tr>
<tr>
<td>Fig. 3.5</td>
<td>ODMR in GaP-S.</td>
</tr>
<tr>
<td>Fig. 3.6</td>
<td>ODMR in GaP-Bi.</td>
</tr>
<tr>
<td>Fig. 3.7</td>
<td>ODMR microwave power dependence.</td>
</tr>
<tr>
<td>Fig. 3.8</td>
<td>GaP-N Zeeman spectrum.</td>
</tr>
<tr>
<td>Fig. 3.9</td>
<td>ODMR signal at 36.3 GHz.</td>
</tr>
<tr>
<td>Fig. 3.10</td>
<td>GaP cyclotron resonance.</td>
</tr>
<tr>
<td>Fig. 3.11</td>
<td>GaP-N cyclotron resonance.</td>
</tr>
<tr>
<td>Fig. 3.12</td>
<td>GaP-S cyclotron resonance.</td>
</tr>
<tr>
<td>Fig. 3.13</td>
<td>GaP-Bi cyclotron resonance.</td>
</tr>
<tr>
<td>Fig. 3.14</td>
<td>Cyclotron resonance at 36.3 GHz.</td>
</tr>
<tr>
<td>Fig. 3.15</td>
<td>ZnTe luminescence.</td>
</tr>
<tr>
<td>Fig. 3.16</td>
<td>ZnTe ODMR at 5220 A.U.</td>
</tr>
<tr>
<td>Fig. 3.17</td>
<td>ZnTe ODMR at 5290 A.U.</td>
</tr>
<tr>
<td>Fig. 4.1</td>
<td>AgBr bandstructure.</td>
</tr>
<tr>
<td>Fig. 4.2</td>
<td>AgBr luminescence.</td>
</tr>
<tr>
<td>Fig. 4.3</td>
<td>ODMR in AgBr.</td>
</tr>
<tr>
<td>Fig. 4.4</td>
<td>ODMR in AgBr.</td>
</tr>
<tr>
<td>Fig. 4.5</td>
<td>Cyclotron resonance in AgBr.</td>
</tr>
<tr>
<td>Fig. 4.6</td>
<td>Low power cyclotron resonance signal.</td>
</tr>
</tbody>
</table>
Fig. 4.7 Power dependent cyclotron resonance signal. 92
Fig. A.1 The Nelder-Mead minimization procedure. 112
Fig. A.2 The convergence process. 114
Fig. A.3 Gaussian and Lorentzian fits to data. 116
Fig. A.4 Fits from IA5. 121
ACKNOWLEDGEMENTS

It gives me much pleasure to thank my research supervisor, Dr. C. F. Schwerdtfeger, for his advice and instruction.

The help given by Dr. R. Barrie and Dr. J. Eldridge in criticizing this thesis and improving its presentation is gratefully acknowledged.

Thanks are also due to Dr. W. Czaja for his helpful criticism of our publications. Our appreciation is due to Dr. J. Merz and Dr. W. Czaja for donating samples of Zinc Telluride and Silver Bromide.

The assistance of my parents in the analysis of data, which was invaluable, is greatly appreciated.

Finally thanks are due to NSERC for the award of a post-graduate Scholarship and to the University of British Columbia for a Teaching Assistantship, and to NSERC Grant # 67/2228 for supporting part of the work.
Chapter 1. INTRODUCTION

1.1 Historical.

Precession of the spin of an electron was first observed by P. Zeeman in 1896 after theoretical predictions by Sir Joseph Larmor. When a magnetic field is applied parallel to the spin axis of the electron, precession occurs about the field direction with a frequency given by:

\[ \omega = g \mu_e B / \hbar \]

where \( B \) is the magnetic field, \( \mu_e \) the magnetic moment of the electron, \( g \) the Landé factor (=2.0023 for free space), and \( \hbar \) is Planck's constant.

Quantum mechanically this means that the energy levels of the electron in a magnetic field will be separated by amounts \( \hbar \omega \) and, for the electron, there will be two levels corresponding to spins parallel and anti-parallel to the magnetic field.

Transitions between the two spin states can be induced by electromagnetic fields of frequency \( \omega \), and these transitions correspond to absorption or to induced emission.
of a photon. This is known as paramagnetic resonance. The change in the electron spin in such a transition is unity since the spin changes from +1/2 to -1/2 and a photon of spin 1 is absorbed or emitted. Thus the transition conserves both energy and angular momentum.

The transition is caused by the interactions of the electron magnetic field with the magnetic component of the electromagnetic field which must be perpendicular to the applied magnetic field.

Electrons at a finite temperature in a magnetic field will tend to redistribute their spin energies in such a way as to produce a Boltzmann distribution of energy differences. Thus, when an electromagnetic field is applied at resonance, a net absorption of energy will occur as electrons move from the lower to the higher energy state, and this absorption can be measured in a variety of ways. This is the basis of electron paramagnetic resonance (EPR) studies which have been used to determine magnetic resonance frequencies of electrons in semiconductors.

In a typical EPR experiment the material under investigation is placed in a magnetic field in a microwave cavity. The microwave frequency is fixed at the resonant frequency of the cavity, and the magnetic field is swept. At resonance the increased absorption of the microwave power by the sample changes the Q factor of the cavity. This causes
an observable change in the microwave power reflected from
the cavity.

In 1952 Brossel and Bitter (1) investigated
paramagnetic resonance of electrons in mercury vapour with
the atoms in an excited state. The excitation was produced
by irradiation with intense light of appropriate wavelength.
Electrons in the excited state normally decay to their
ground state emitting photons whose polarization depends on
their spin prior to the decay process. The application of a
paramagnetic resonance signal changed the relative
populations of the spin states of the electrons and thus the
polarization of the emitted light; this change was detected.

The first observation in a solid material was that of
Geschwind et al. (2) who measured luminescence changes from
Cr impurities in Al₂O₃. Since then many other substances
have been studied and resonances have been observed (3-10).

In a magnetic field charged particles participate in
another type of phenomenon known as cyclotron resonance. A
charged particle, moving at right angles to a magnetic
field, experiences a force $e \mathbf{v} \times \mathbf{B}$ where $e$ is the electron
charge, and $\mathbf{B}$ the magnetic field. This results in circular
motion about the magnetic field direction at angular
frequency $eB/m$, where $m$ is the electron mass. These orbits
are quantized so that an infinite series of levels exist
separated by energy $\hbar \omega$. Transitions between these levels can be induced by an electromagnetic field because of the interaction of the electric component of this field with the electron. The absorption of energy from the applied field can be measured in the same way as that described for EPR.

The effect was first observed in gaseous plasmas by Lax et al. in 1950 (11). It was later seen in the semiconductor Ge by Dresselhaus et al. in 1953 (12) and has since been observed in other solid materials.

Detection of cyclotron resonance by its effects on luminescence has only recently been reported by Romestain and Weisbuch (13) in CdTe and by Baranov et al. in Ge (14).

It is to be noted that the effects of cyclotron resonance have been observed in ODMR experiments as background signals underlying the desired paramagnetic resonance signals (7,15-17).

A Typical Experiment.

The essential elements of an ODMR experiment are shown in Fig.1.1. The material on which the measurements are to be taken is generally cooled to the liquid helium temperature range, since paramagnetic resonances and the luminescence processes used to observe them are strongly affected by temperature. The sample may be doped with
Fig. 11

Basic ODMR Experiment

Chopped Microwaves

Variable Magnetic Field

Filter to Remove Laser Beam

Excitation Beam

Modulated Luminescence

Sample

Data Collection

Detector

Lock-in Det.
impurities to produce particular types of recombination centres. Free carriers are generated by an excitation source, usually a laser although arc lamps, electron beams or x-rays are sometimes used. The carriers recombine in various ways, the most common luminescent processes being the decay of electrons, either free or bound to an impurity centre, and donor-acceptor pair recombination. At high enough excitation levels, bound multi-exciton complexes at impurity centres and electron-hole drops may be observed.

A magnetic field is generated either by a conventional electromagnet or by a superconducting magnet. Magnetic resonances are excited by a microwave field which is generally held at a fixed frequency while the magnetic field sweeps through the resonances. Resonance heating of the carriers or their spins affects the recombination processes and results in observable changes in the luminescence either in total intensity, polarization, or wavelength, which is monitored after appropriate filtering. The microwaves are chopped to produce an a.c. signal which is measured by a lock-in detector or similar device.

1.2 Paramagnetic Resonances.

The most common application of ODMR to date has been in the detection of paramagnetic resonances of carriers, free or bound. A number of techniques have been developed to enhance the sensitivity of the basic ODMR experiment.
The effects of electron paramagnetic resonance may be illustrated by the simple examples shown in Fig. 1.2. Fig. 1.2(a) shows a typical donor-acceptor pair system with allowed recombinations of a spin 1/2 electron and a spin 3/2 hole.

Allowed transitions are ones in which the spin of the electron system changes by unity or zero during the decay, compensating for the spin of the photon emitted. On average half of the donor-acceptor pairs populated will have spin states that allow optical transitions, the other half will decay by non-radiative processes. The EPR transitions shown between the the electron spin states will cause pairs with optically disallowed transitions to become allowed, and vice versa. Since pairs with optically allowed transitions will recombine faster than those without, the net effect of the resonance signal will be to increase luminescence at the expense of non-radiative decays.

The spin states of the electrons and holes are split in the magnetic field and an EPR transition between electron spin states can cause a spin-forbidden recombination to become allowed. In the absence of the EPR resonance only electron-hole pairs with the appropriate spins can recombine, thus the resonance increases the luminescence.

An exciton is a bound system of an electron and a hole,
b) Exciton levels formed by spin 1/2 electrons and spin 3/2 holes. Transitions involving a change of 0 or ±1 in $M_j$ are allowed while those causing a change of ±2 are forbidden as shown.
somewhat similar to a hydrogen atom. Fig. 1.2(b) shows the exciton states formed from spin 1/2 electrons and spin 3/2 holes. An example of such a system is GaP which will be considered in Chapter 3. The exciton states formed depend on the populations of the initial electron and hole spin states. In particular the $|2, +2\rangle$ exciton states, with dipole forbidden optical decays, are more likely to form when the electron spins are heated thus reducing the luminescence. In theory a change in luminescence of 50% could be observed at absolute zero for a saturation epr signal. These points are discussed in more detail in Chapter 3.

In practice changes of the order of 1% are to be expected. A similar argument can be applied in the case of hole paramagnetic resonance. A number of processes are present in a practical experiment which reduce the size of the observed signal. Obviously the sample is not at absolute zero so that the carrier spins will not be completely polarized. In addition the carrier spin temperature may be higher than the sample temperature depending on the spin lattice relaxation time and free carrier lifetimes. Once excitons are formed thermalization may occur within the exciton levels 'washing out' the effects of the resonance if it only affected the carriers while free. A maximum change in luminescence should be produced by saturating the paramagnetic resonance, but if this is inhomogeneously broadened, i.e. different parts of the crystal have slightly different resonant frequencies, only a small packet of spins
can be saturated at one time.

In some cases the factors just mentioned may be overcome or used to advantage to enhance signal detectability.

Conduction electron spin resonance (CESR) is widely used to measure the g value of free electrons (6,10,18). Instead of relying on thermalization or spin selective recombination to produce a polarization in spins, electrons are produced in a particular spin state by using circularly polarized light for excitation. The recombination radiation emitted parallel to the applied magnetic field will be circularly polarized provided the electrons 'remember' their initial spins, and a magnetic resonance signal will show up as a decrease in this polarization. In order to generate spin polarized electrons, the excitation light must be applied parallel to the magnetic field (since a transverse magnetic field rapidly depolarizes them), and should be resonant with the band gap. The method works best in systems where the recombination time of the electrons is less than their spin thermalization time.

In a conventional ODMR experiment where spin population differences are not produced by the excitation light, circular polarization is sometimes visible in the luminescence, and a considerable enhancement can be seen in
an ODMR signal by monitoring only one polarization. In some cases equal and opposite signals are seen by looking at oppositely polarized components of the luminescence, thus the paramagnetic resonance does not change the total intensity of the luminescence significantly but only its polarization, and an experiment that monitored total intensity would not give a signal (17,19). Since different circular polarizations within an emission line correspond to the recombination of excitons with different spin components, this will exhibit Zeeman splitting in a magnetic field. Thus similar enhancements in ODMR signals may be obtained by observing single Zeeman components. In general the Zeeman components will only be distinct at higher magnetic fields corresponding to microwave frequencies in the region of 30 GHz or above.

An ODMR signal corresponds to the change in relative spin populations of electrons or holes as the magnetic resonance excitation is turned on or off. A saturation resonance signal would equalize the spins (i.e. depolarize them completely) and give the greatest signal. In many cases the paramagnetic resonance is inhomogeneously broadened so that the microwave excitation can only affect a fraction of the total spins at any time as it sweeps through the resonance, and thus a saturation signal cannot be realized. A method sometimes used to overcome this is to modulate the field, (usually the applied magnetic field although the microwave frequency could be modulated instead)
over a small range at a frequency higher than the spin relaxation time, allowing more particles to participate in the resonance at any time, and thereby increasing the ODMR signal (7,15,20,21).

In luminescence spectra having contributions from several recombination centres or processes it is often desirable to identify which components exhibit a particular ODMR signal. This can be done by setting the magnetic field at resonance and sweeping through the spectrum with a monochromator, measuring the ODMR signal and comparing this 'ODMR spectrum' with the actual optical spectrum. This method can be complicated by the fact that luminescence bands not showing the ODMR signal may still have broad background signals caused by luminescence changes due to microwave dielectric or carrier heating. By doing a second scan with the magnetic field off resonance and subtracting, the true spectral dependence of the ODMR signal may be obtained, but in situations where several resonances are present, or signal-to-noise ratios are poor, it is often better to do a series of magnetic field scans at different wavelengths corresponding to salient features in the optical spectrum (such as strong emission peaks from different centres) to deduce the spectral dependence.
1.3 Advantages of ODMR.

ODMR looks at resonances visible, at least in principle, with conventional microwave absorption EPR techniques. Depending on the system being considered, ODMR may have several advantages. Observation of an EPR signal requires the absorption of a measurable amount of microwave power by a weak magnetic dipole transition and subsequent dissipation of this power via spin relaxation. In particular, at low temperature the EPR signal tends to saturate and become unobservable unless very low microwave power levels are used, and this gives a poor signal to noise ratio. As ODMR carriers are photo-generated, this obviates the necessity for doping (except for suitable recombination centres). The weak magnetic dipole transitions excited by the EPR signal cause macroscopic changes in the optical transition probability, and effectively amplify the EPR signal. Furthermore a saturation of the spins by the microwave excitation results in a maximum ODMR signal (although it may also broaden it) and so is not a problem as in conventional EPR. In addition to giving better signals in appropriate circumstances, ODMR serves as a tool to study luminescence processes as well as paramagnetic resonances.

ODMR signals from free carriers can indicate how recombination at a particular centre is affected by the spins of the recombining particles, and ODMR of particles
trapped at luminescence centres gives information directly about the nature and symmetry of the centres.

1.4 Cyclotron Resonance

Conventional detection of cyclotron resonance in semiconductors involves measuring the absorption of microwaves by free carriers in a magnetic field (22). The carriers may be thermally or optically generated, or may come from donor or acceptor impurities. Cyclotron resonance measurements give information on the effective mass of electrons and holes, and their mobility. Measurement of cyclotron resonance is in some ways analogous to that of paramagnetic resonance, however the cyclotron resonance is excited by the electric field component of the microwaves rather than by the magnetic component as in EPR, and it tends to be much stronger and more readily observable.

Several factors limit the usefulness of the technique, however. The scattering time of the free carriers determines the width of the cyclotron signal in most cases, and is generally much shorter than the spin relaxation time which governs the width of EPR lines. The condition for obtaining a distinct resonance is \( \omega_c \tau \approx 1 \), \( \omega_c \) being the cyclotron frequency and \( \tau \) the scattering time of the carriers. In many cases this precludes the observation of cyclotron resonance at reasonable microwave frequencies and
magnetic field strengths. Doping with donor or acceptor impurities also tends to reduce carrier mobility, and cyclotron resonance measurements are generally made on samples of high purity. Saturation of the resonance is not a problem as in EPR, but application of excessive microwave power may heat the carriers and change their scattering probability causing asymmetry in the resonance. If the conduction or valence band in question is significantly non-parabolic, this will also result in a change in the apparent effective mass.

Optical detection of cyclotron resonance has been reported only recently in GaAs and CdTe (13) and in Ge (14). The resonances of electrons and holes in GaAs and CdTe were observed by monitoring changes in luminescent intensity and lineshape induced by carrier heating. In Ge the resonant heating produces observable decreases in electron-hole drop luminescence. The measurements are in many ways analogous to ODMR experiments although they tend to rely on observing changes in total intensity rather than looking at changes in polarization as is often done in ODMR.

Optical detection of cyclotron resonance offers few direct advantages over the more commonly used technique of measuring microwave cyclotron absorption by photo-generated carriers, since this absorption is readily observable being much stronger than in EPR signals. However, by using optical
detection, information may be obtained about trapping and luminescence processes and their sensitivity to carrier temperature.

1.5 Overview of the thesis

Chapter 2 describes the experimental procedure and the apparatus used, and discusses the relative merits of the digital photon counting technique used in part of the work and those of lock-in detection.

Chapter 3 reviews previous work on paramagnetic and cyclotron resonances in GaP and ZnTe and presents the results of our investigation of these materials.

In GaP paramagnetic resonance of electrons was observed in luminescence from Bi and S impurities; this had not been reported in the literature previously and supports the work of Cavenett on ODMR from N centre luminescence. The expected change in luminescence caused by the resonance was calculated and good agreement was found with the experimentally observed signal. By using two microwave frequencies it was determined that the resonances were homogeneously broadened, and a carrier lifetime of approximately 4 nanoseconds was deduced from the widths of the resonances, a result not previously reported.

Cyclotron resonance of electrons and light and heavy
holes was observed to cause a decrease in luminescence from N, S and Bi centres. Although the effective mass values determined from these measurements were not significantly more accurate than those already published, different centres were shown to be sensitive to cyclotron heating of electrons or holes depending on the trapping process involved, a phenomenon not previously seen.

A calculation of the effect based on the theoretical trapping cross-section of the N impurity showed good agreement with the experimental results.

Cyclotron resonance of electrons and holes was also observed in various luminescence bands from ZnTe, however interpretation of the results was difficult because of uncertainty in the impurity content of the crystal.

Chapter 4 details our investigation of AgBr. Paramagnetic resonances observed using ODMR were shown to resemble substantially those of other researchers. Cyclotron resonance was also observed in the luminescence from isoelectronic iodine centres and showed some interesting features not seen in conventional cyclotron resonance experiments on this material. In particular an enhancement of luminescence shown in part of the electron resonance line indicated an increased trapping probability for electrons with certain energies due to interaction with optical phonons. The effective masses of hot electrons calculated
from the results agreed substantially with theoretical predictions.

Chapter 5 contains our conclusions and some suggestions for further work.

An appendix describes a new method for non-linear curve fitting which was devised in connection with the extraction of data from the rather noisy signals produced in our experiments. This is compared with another method which has been proposed recently and is shown to be less susceptible to convergence to false minima.
Chapter 2. Apparatus and Experimental Techniques.

2.1 Apparatus

A block diagram of the equipment used in the ODMR experiments is shown in Fig. 2.1. The liquid helium Dewar used in the initial work differed from the one shown in being smaller and containing no superconducting magnet. The magnetic field was originally supplied by a Varian electromagnet. Due to the bulk of this device luminescence could be viewed only in a direction at right angles to the magnetic field (out of the same window used for the excitation beam in fact) rather than parallel to the magnetic field as shown for the superconducting magnet Dewar. Both Dewars had an outer jacket to contain the liquid nitrogen pre-coolant. Helium, once transferred, could be allowed to boil off into a return line, at approximately atmospheric pressure, or be pumped out, thus cooling the liquid to below its lambda point (2.2 degrees K.). The vapour pressure of the helium could be measured by means of a mercury manometer attached to the Dewar. Both inner Dewars (containing the helium) were constructed from Pyrex glass to allow optical measurements and to reduce heat conduction up the walls. Quartz windows were provided in the outer metal casing of the Dewars. The Dewar vacuum was maintained continuously by a pumping system consisting of a diffusion pump and a roughing pump. The vacuum was better than 10⁻⁴ torr.
Apparatus showing 9.2 GHz microwaves and superconducting magnet.
Both Dewars, when filled, would retain liquid helium for between two and three hours depending on the power dissipation of the microwaves and the light being used, and whether the helium was being pumped to a lower temperature.

The electro-magnet used in the initial measurements produced fields of up to 15 kilogauss, its power supply could be computer controlled either to set a particular field strength, or to produce a field which was swept between preassigned limits. The field was calibrated using the EPR resonance of diphenylpicryl hydrazyl (DPPH) at $g=2.0037$ which was observed by conventional microwave absorption.

The superconducting magnet used in later experiments provided fields up to 50 kilogauss. A detailed description of this device has been given by O. Ziemilis (23).

The power supply for this magnet could be driven either by the computer or by a sweep box. The magnet was also provided with a 'persistent switch' which allowed the power supply to be turned off once the desired field was reached. This could eliminate heating from the current leads in the Dewar; however, since our experiments always involved sweeping the magnetic field, this facility was not used.

Optical excitation of the sample was produced by a
Spectra Physics 185 argon ion laser which generated 1/2 Watt of power at 4880 A.U. and could be tuned to other wavelengths in the range 4580 A.U. to 5145 A.U. The ultraviolet excitation required for the studies of AgBr was provided by a Spectra Physics 285 helium-cadmium laser operating at 3250 A.U. or by a PEK 500 Watt mercury arc lamp.

A narrow band of luminescence from the sample was selected by a Spex monochromator and detected by a Hamamatsu R928 photomultiplier tube which had a good response in the range of interest. The output of the photomultiplier fed a pulse shaping electronic circuit as a preliminary to photon counting.

Microwave excitation was available at 9.2 and 36.3 GHz. At 9.2 GHz approximately 10 Watts of power was provided by a Hughes model 1177 travelling wave tube amplifier driven by a reflex klystron. The output of the klystron was fed to the amplifier through a diode switch which allowed the microwaves to be modulated (chopped) by a square wave from a pulse generator, the on and off times being equal.

The sample was mounted on a non-conducting (teflon or quartz) rod in the centre of a TE102 cavity coupled to the waveguide by a small hole and a moveable teflon plug to allow impedance matching.
The microwave power reflected from the cavity was detected in one arm of a 'magic Tee' and this signal was used to tune the klystron to resonance with the cavity and to adjust the impedance match. Automatic tuning of the klystron to the cavity was not used because the frequency drift was not large enough to cause problems, especially in view of the large widths of the resonances observed. The chopping would also tend to interfere with the automatic tuner.

Optical access to the cavity was provided by circular holes in the sides and slots in the bottom plate. These were so placed as to interfere as little as possible with the current flow associated with the TE102 mode. Q factors of around 2000 were obtained, the exact value varying with the particular sample under investigation.

At 36.3 GHz a Varian reflex klystron provided up to 800 milliWatts of power. Chopping was achieved by modulating the reflector voltage with a square wave which switched the klystron on and off one of its modes.

The sample was mounted in the open end of a waveguide with no cavity resonator. This provided good optical access although it reduced the available microwave field strength. A resonator, when properly tuned to the source, should amplify the microwave power density by a factor
approximately equal to the resonant Q value. There were two reasons for not using a resonator: first, because adequate optical access would be difficult to provide, especially for the collection of luminescence which requires holes in the bottom of the resonator; and second, because the size of some of the samples used would have made them difficult to accommodate in the system. The net effect would have been to reduce the Q factor of a resonator to such an extent that it was not deemed worthwhile using one.

It should be noted that paramagnetic resonances are excited by the magnetic component of the microwave field, while cyclotron resonances respond to the electric field component. The TE102 cavity used at 9.2 GHz has a node in the electric field at its centre, and a maximum magnetic field, thus it was necessary to displace the samples from the centre of the cavity in cyclotron resonance measurements. At 36.3 GHz no such problems existed since no cavity was used. We believe that this simple method for producing a variable field has not been described before. It was critical in determining the existence of the cyclotron resonances discussed in chapters 3 and 4.

Changes in detected luminescence, synchronous with the microwave chopping, were detected using either a lock-in detector or an up-down counter. The latter device consisted of a digital electronic counter which could be switched to
count positively or negatively at the microwave chopping frequency. Thus optical counts generated with the microwave source switched on were subtracted from those produced with the microwaves off. Since the on/off times were equal, any microwave-induced change in the luminescence showed up as a net positive or negative count. It was found necessary to suppress incoming pulses for a few microseconds each time the counter was switched to prevent transient pulse errors.

Data were collected with a NovaII minicomputer which could sweep either the magnetic field or the spectrometer in a series of steps over the desired range, pausing at each step to record the output of the lock-in detector or the up-down counter. If the photoluminescence spectrum was required, the computer could record the output of the photomultiplier system directly by using an analog to digital converter.

The number of steps in a scan, and the time spent in collecting data at each step, were set by the operator.

2.2 Experimental Procedures.

In most ODMR experiments the change in luminescence caused by the microwave resonance was less than 1% so that obtaining adequate signal to noise ratios was often a problem. As an illustration: for an ODMR signal causing a 0.1% change in luminescence with a photon count rate of one
million per second, and a data collection time of one second per step, the ODMR signal would give an output of 1000 counts. This was equal to the statistical fluctuation in the one million photon count so that the signal to noise ratio was unity. Since the statistical fluctuations increase as the square root of the total count, and the signal increases linearly, it would be necessary to spend 100 seconds per step to obtain a signal to noise ratio of 10. A typical scan contained 50 steps and took about 1.5 hours. Since low frequency effects such as drift in the count rate and microwave frequency become significant over such times, data were generally acquired with a step time of 5 seconds and the computer was programmed to repeat the scan as many times as desired and to average the results. Low frequency noise was thus filtered out.

Efforts were made to extend the available running time by reducing the heat loss from the Dewars, since the signal to noise ratio of weak signals could be improved by longer data collection times. Because the liquid helium was usually pumped to below the lambda point to reduce bubbling, it was not possible to transfer more helium without interrupting the experiment. When more helium was transferred into an already cold Dewar, the optical windows often became contaminated with air which generally leaked in and froze on to the inner surfaces of the flask. Baffles and insulation were used to reduce heat leaks caused by conduction through
the helium gas and by radiation from the top of the Dewar.

The maximum running times obtained were limited by heat conduction down the Dewar walls, waveguide, and in the case of the superconducting magnet Dewar, the magnet support rods and current leads. This heat conduction was calculated to be approximately 5 Watts for the superconducting magnet and would be sufficient to boil off 10 litres of liquid helium (a typical amount used in a run) in approximately two hours due to the low latent heat of vapourization of helium.

The heat generated by the 9.2 GHz microwaves at full power was approximately 2.5 Watts allowing for losses in the waveguide system and the 50% duty cycle due to chopping. The maximum laser power was less than one half Watt. Thus the length of runs was even more severely limited in some experiments.

Since the up-down counter was used interchangeably with the lock-in detector, a comparison of the two devices is in order. The up-down counter reduces statistical fluctuations in the photon counts by summing a large number of them as the signal gathering time is increased. The lock-in detector monitors an analog signal which is proportional to the optical count rate, and this will have the same statistical fluctuations. The lock-in detector reduces these with the low-pass filter after detection has occurred and, for longer data collection times, the time constant of this filter can
be increased thus reducing the noise. In our apparatus the computer was programmed to read the lock-in output twenty times per step and to average the results. This produced the same effect as a longer time constant without smearing the signal from step to step. Thus, in principle, the signal/noise performances of the two systems should be approximately the same.

The lock-in detector has the advantage of being phase sensitive so that if the luminescence changes are delayed with respect to the microwave signal this can be compensated for by adjusting the phase angle on the lock-in. The same effect could be achieved with an up-down counter by shifting the up-down switching pulses with respect to the microwave switching signal, but this would require additional electronics. Lock-in detectors could operate in the 100 kHz range if it were desired to study ODMR signals at such frequencies: for example in the examination of spin lattice relaxation times; while digital up-down counters could not readily be switched as rapidly without causing unacceptable counting errors. The up-down counter could operate at very low switching speeds, however. In our work switching frequencies from 20 to 5000 Hz were used, most experiments being done at 500 Hz. The quality of data obtained from the lock-in detector and from the up-down counter was found to be about the same. The main advantage of the up-down counter was that it gave a numerical value for the ODMR signal.
which, by comparison with the observed optical count rate, indicated the magnitude of the signal as a percentage change in luminescence.

2.3 Commentary.

It should be noted that a delay of approximately 6 months was introduced into the experiments by building work required to install the superconducting magnet. Operation of the system was also slowed down by the nature of the computing system. The input was via punched paper tape and an old fashioned teleprinter. Thus, to input the operating system required about 20 minutes if all went smoothly. In many cases, however, a system fault in the last stages of input made a re-run necessary.

A teleprinter is not a satisfactory substitute for the terminal input used on even the least expensive of modern home computers.
Chapter 3. Gallium Phosphide and Zinc Telluride.

3.1. Introduction

Gallium phosphide is a III-V semi-conductor with a cubic lattice. The band structure is shown in Fig. 3.1. The valence band is twofold degenerate at the Γ point k=0, the heavy hole band having approximately eight times the density of states of the light hole band. The third hole band is split off by the spin orbit interaction and has its maximum 0.127 eV below the other two (24).

The conduction band has three equivalent minima lying along the [1,0,0] directions at the X points (25). The conduction band minimum at the Γ point lies above the minima at the X points by 0.5 eV as shown, thus the minimum band gap of interest in most electronic and luminescence measurements is indirect.

The conduction and valence bands are approximately spherical at the Γ point with effective masses 0.13 (26) for the electrons and 0.67 and 0.17 for the heavy and light holes (27) respectively, all values are in units of mass of the free electron. The X point minima are anisotropic with longitudinal and transverse effective mass parameters $m_{\parallel} = 1.5$ and $m_{\perp} = 0.18$ (28).

The g value of electrons bound to neutral donors has been measured to be $1.9976 \pm 0.0008$ by EPR experiments (29),
FIG. 3.1 GAP BANDSTRUCTURE

Direct band gap

Indirect band gap

2.878 EV

2.339 EV

0.127 EV

Valence bands

Γ X
and a value of $1.996 \pm 0.002$ was determined for photoexcited electrons using ODMR (30). The $g$ value of holes has been estimated from Zeeman measurements of excitons bound at nitrogen impurities to be $0.99 \pm 0.06$ (31).

3.2. Exciton formation and luminescence in GaP

Optical recombination of photo-excited electrons and holes occurs largely at defects and impurity sites. An important class of recombination centres are isoelectronic impurities which form localized states of excitons in the band gap. Nitrogen and bismuth form such centres in GaP being isoelectronic with phosphorous. Nitrogen in particular is generally present as a residual impurity in GaP in concentrations of the order of one part in a million. Exciton recombination can also occur at neutral donors such as sulphur, selenium and tellurium which substitute for phosphorous as donors in GaP (29). The efficiency of optical recombination at neutral donors is much lower than at isoelectronic centres due to the high probability of Auger recombination, with the donor electron taking the energy of the exciton and becoming ionized (32).

Donor-acceptor pair (DAP) recombination is another important process in materials with a high density of donors and acceptors, in which electrons and holes trapped at donor and acceptor impurities recombine radiatively, the recombination energy depending on the donor-acceptor
separation. A modification of this process has been observed in GaP in which donor bound electrons recombine with holes trapped at isoelectronic bismuth centres (33). In our measurements, however, donor-acceptor pair recombination was not significant.

Excitons may form at isoelectronic recombination centres by two methods. An electron and hole may form an exciton while free and the exciton become trapped at an impurity, or the impurity may bind one particle first after which the second becomes trapped in the Coulomb field of the first particle (30). In GaP the isoelectronic impurity bismuth has been shown to bind a hole with an energy of approximately 40 meV by DAP luminescence measurements (33) as well as by the observation of donor-like electron excited states at bismuth centres (34) and by analysis of the phonon assisted recombination of bound excitons (35).

The nitrogen centre is thought to be an electron trap although the binding energy of approximately 8 meV deduced from radiative decay time measurements (36) has made this more difficult to prove. Analysis of the phonon assisted recombination of nitrogen bound excitons supports this interpretation (37) as does a comparison of electronegativity differences between nitrogen, bismuth, and the phosphorous atoms which they replace (38).
The free exciton in GaP has a binding energy of 10 meV (39), and on the isoelectronic impurities nitrogen and bismuth the total binding energies are 21 meV and 107 meV respectively (36). Luminescence is primarily observed from trapped excitons. The luminescence spectrum observed from nitrogen and bismuth centres differs markedly as shown in Fig. 3.2. The nitrogen luminescence spectrum is dominated by the so called A and B line no-phonon transitions. The A and B lines are caused by excitons with total angular momenta $J$ of 1 and 2 respectively, formed by the antiparallel or parallel alignment of a spin 1/2 electron with a spin 3/2 hole. The phonon assisted transition of A and B excitons are relatively weak due to the small binding energy of the electron to the nitrogen atom (40). At lower energy a third line, generally referred to as the C line results from the recombination of excitons at neutral sulphur donor impurities.

The bismuth center luminescence is dominated by phonon assisted transitions. At low temperature the A line is not seen due to thermalization with the B line which in this case lies 2.7 meV lower in energy. The B line, no-phonon transition, is seen only weakly since the decay of the $J=2$ exciton is forbidden and can only occur by mixing with the A line states in the presence of a magnetic field, crystal strains, or with the assistance of phonons. The fact that a no-phonon transition can be seen at all in an indirect gap semiconductor is due to the fact that, being localized at an
The A and B lines due to N and the C line caused by S impurities are shown.

The B exciton no phonon line and numerous phonon replicas are seen.
impurity, the electron or hole wave-function is spread out in k space and a finite probability of a direct transition exists.

The bulk of the luminescence from the bismuth centre is contained in the broad band of phonon assisted transitions, the various peaks correspond to combinations of different types of phonons and have been identified by Dean and his co-workers (33). The greater strength of the phonon replicas in the Bi spectrum as compared to the N spectrum is due to the stronger binding of the hole to the Bi atom, which results in stronger coupling to the phonon modes.

The exciton states formed at isoelectronic impurities in GaP have been described by Cavenett (30) in explaining the effect of electron paramagnetic resonance on photoluminescence. The exciton states formed from spin 1/2 electrons and spin 3/2 holes are shown in Fig 3.3 with their expected splitting in a magnetic field. The zero field splitting shown for the B line has been observed in luminescence from bismuth (41) and in multi-exciton complexes with N centres (42) but is unobservable for single excitons bound to nitrogen atoms. The splitting has been attributed to the crystal field which is expected to be felt more strongly at the bismuth impurity which is repulsive to the electron in an exciton (41). However Morgan (43) has shown that such splitting can be caused by coupling of the
The exciton states formed by a spin 1/2 electron and a spin 3/2 hole are shown with their composition, splitting in a magnetic field, and optical transitions.
exciton to phonon modes with \( \Gamma_3 \) and \( \Gamma_5 \) symmetries. Coupling to the \( \Gamma_3 \) mode (corresponding to strain along the \([1,0,0]\) axis) tends to raise the triplet while coupling to the \( \Gamma_5 \) mode (\([1,1,1]\) axis) raises the doublet. As already mentioned, the \( J=2 \) excitons can only decay by mixing with the \( J=1 \) states, thus the \( |2,2> \) and \( |2,-2> \) excitons having no corresponding \( A \) states to mix with have dipole forbidden transitions and do not contribute luminescence to the B line. In a magnetic field the various Zeeman components are expected to be circularly polarized as shown, \( \sigma \) representing right and left circular polarization for luminescence emitted parallel to the magnetic field while \( \pi \) represents linear polarization in luminescence emitted at right angles to the field.

To calculate the expected change in luminescence from the A and B lines with the application of an electron paramagnetic resonance signal, the relative rates of formation of the various exciton states are calculated assuming a thermal distribution of electron and hole spin states \( (n_1 - n_6) \) before exciton formation, also assuming that the probability of a particular exciton forming is proportional to the populations of electrons and holes with the appropriate spin states.

The exciton state spin wave functions shown in Fig.3.3 must be multiplied by their complex conjugates to give the
probabilities, thus the coefficients of the various electron 
and hole spin states that make up the exciton levels are 
squared. For example, the relative number of $|1,1\rangle$ excitons 
formed would be:

$$ P_{11} = n_1.n_4 /4 + 3.n_2.n_3 /4 $$

Taking the total number of electrons or holes to be:

$$ n = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 $$

the values of $n_1 - n_6$ may be calculated assuming a thermal 
distribution:

$$ n_1 = n.e^{-\alpha_e} / (1 + e^{-\alpha_e}) $$

$$ n_2 = n / (1 + e^{-\alpha_e}) $$

$$ n_3 = n.e^{-3\alpha_h} / (1 + e^{-\alpha_h} + e^{-2\alpha_h} + e^{-3\alpha_h}) $$

$$ n_4 = n.e^{-2\alpha_h} / (1 + e^{-\alpha_h} + e^{-2\alpha_h} + e^{-3\alpha_h}) $$

where:

$$ \alpha_e = g_e\beta H / kT $$

$$ \alpha_h = g_h\beta H / kT $$

$g_e$ and $g_h$ being the electron and hole $g$ values, $H$ the 
magnetic field, $\beta$ the Bohr magnetron and $kT$ the thermal 
energy.

When an EPR signal is applied, the populations of the
electron spin states are equalized assuming a saturation signal. Therefore:

\[ n_1 = n_2 = n/2 \]

The relative formation rates of the various exciton states have been calculated using this procedure as shown in Table 3.1. The electron and hole g values are taken to be 2 and 1, respectively for temperatures of 1.6 and 4 degrees K and a magnetic field strength of 3.4 kiloGauss. The change in intensity with the application of microwaves indicated by \( P^u \) is shown for each state and the total change in intensity for the A and B lines is also calculated. Several points are worth noting. The A and B lines are both expected to decrease in intensity at the EPR resonance as more excitons are formed in the non-radiative \( |2,2> \) state; the change in the A line is greater than that in the B line, and the effect decreases rapidly with increasing temperature. It can also be seen that the changes in individual exciton states are larger than in the total luminescence, and can be either positive or negative so that if the change in one Zeeman component of the A or B line is monitored using high resolution spectroscopy or a circular polarization filter the ODMR signal observed can be either positive or negative depending upon which component is used, and should be larger than the ODMR signal shown by the entire (A or B) line.
TABLE 3.1

MICROWAVE INDUCED LUMINESCENCE CHANGES

<table>
<thead>
<tr>
<th></th>
<th>1.6 K</th>
<th>4 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P11</td>
<td>0.5212</td>
<td>0.5077</td>
</tr>
<tr>
<td>Pu1</td>
<td>0.4834</td>
<td>0.4931</td>
</tr>
<tr>
<td>P10</td>
<td>0.4087</td>
<td>0.4599</td>
</tr>
<tr>
<td>Pu0</td>
<td>0.4047</td>
<td>0.4591</td>
</tr>
<tr>
<td>P1-1</td>
<td>0.3170</td>
<td>0.4158</td>
</tr>
<tr>
<td>Pu1-1</td>
<td>0.3384</td>
<td>0.4275</td>
</tr>
<tr>
<td>P22</td>
<td>0.4291</td>
<td>0.4715</td>
</tr>
<tr>
<td>Pu2</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>P21</td>
<td>0.4217</td>
<td>0.4661</td>
</tr>
<tr>
<td>Pu21</td>
<td>0.4501</td>
<td>0.4792</td>
</tr>
<tr>
<td>P20</td>
<td>0.4087</td>
<td>0.4599</td>
</tr>
<tr>
<td>Pu20</td>
<td>0.4047</td>
<td>0.4591</td>
</tr>
<tr>
<td>P2-1</td>
<td>0.3917</td>
<td>0.4529</td>
</tr>
<tr>
<td>Pu2-1</td>
<td>0.3633</td>
<td>0.4399</td>
</tr>
<tr>
<td>P2-2</td>
<td>0.3720</td>
<td>0.4453</td>
</tr>
<tr>
<td>Pu2-2</td>
<td>0.3258</td>
<td>0.4213</td>
</tr>
</tbody>
</table>

A line change 1.636% 0.267%
B line change 0.327% 0.051%

The numbers in this table represent the relative populations of the various exciton states with and without a resonance signal. They are not normalized.
A number of processes may reduce the experimentally observed ODMR signals below the levels predicted by the theory. Non-saturation of the electron spins by the microwave signal, either due to inadequate microwave power or to inhomogeneous broadening of the electron resonance, would reduce the effect seen in all exciton states. Thermalization between the different Zeeman components would diminish the larger ODMR signals expected in individual Zeeman lines and the signals from the entire A or B lines would be reduced as well. Thermalization between the A and B line states would equalize the size of the ODMR signal seen in either line, increasing the B and decreasing the A signal. Incomplete thermalization of the electron spins before exciton formation would reduce the observed effect which depends on thermally induced spin polarization of the electron population.

3.3 Other work on GaP

Title and his co-workers have observed paramagnetic resonance of electrons at neutral donor impurities S, Se and Te in GaP (29,44). They obtained a g value of 1.9976 ± 0.0008 which they predict should be approximately the same as the g value of an electron in the conduction band. Cavenett (30) has measured the conduction electron g value directly using ODMR measurements of luminescence from the N centre, obtaining the value g=1.996 ± 0.002. The signal
observed by Cavenett was smaller than predicted theoretically, representing only a 0.1% change in luminescence, no dependence of the ODMR signal on polarization was found, and the B line appears to have given as strong a signal as the A line in contrast to the theoretical predictions. ODMR signals in luminescence from Cu doped GaP have also been observed (45) and are attributed to microwave induced transitions between exciton states at defects which involve pairs of Cu atoms.

3.4 Results

ODMR signals in luminescence from N, S and Bi centres in GaP were measured and are shown in Figs. 3.4 to 3.6 (46). The g values derived for the three luminescence centres agree to within the experimental error giving a value $g = 1.9993 \pm 0.005$ which is also isotropic. Attempts were made to observe resonances of holes or to observe resonances between exciton states; these were, however, unsuccessful.

Some effort was made to analyse the observed resonances in more detail. The N and S centres were both present in the same sample as residual impurities. Different samples were used to measure the Bi center luminescence, and these had a fairly heavy and somewhat inhomogeneous doping of Bi. The ODMR signals from the Bi samples were observed to be weaker than those from the purer samples used for the N and S measurements.
The electron ODMR signal seen as a 1% change in the N luminescence.
The ODMR signal from the S luminescence
FIG. 3.6 ODMR IN GAP-BI

The ODMR signal seen as a 0.1% change in the Bi luminescence
The microwave power dependence of the ODMR signal strength from the N luminescence was measured and the results are shown in Fig.3.7. The fit shown by the solid line is calculated on the basis of a two level system at the sample temperature (1.6 degrees K) being saturated by a radio frequency field. The experimental points were obtained by scanning the resonance at a series of microwave power settings, the scatter being primarily due to drift in the optical system and sample temperature between scans. The results indicate that saturation of the resonance was achieved at the maximum microwave power levels, giving an ODMR signal that represented approximately a 1% change in luminescence. Similar measurements on the Bi luminescence ODMR signal, although hampered by the poor signal to noise ratio, indicated that this resonance was also saturated.

The relative ODMR signal strength from the A and B lines of the N luminescence was measured by selecting the A or B line with the spectrometer and scanning the resonance. Both lines were found to give the same ODMR signal strength. The Bi centre luminescence was also observed to show the ODMR signal equally in the zero phonon line and the phonon replicas.

Attempts were made to observe the predicted enhancement of the ODMR signal by selecting particular Zeeman components using a circular polarization analyser, taking the
FIG. 3.7  ODMR MICROWAVE POWER DEPENDENCE

The N luminescence ODMR signal strength as a function of microwave power. The resonance is seen to be saturated at maximum power.
luminescence parallel to the magnetic field. No change in the ODMR signal could be seen for either right or left circular polarization.

This prompted an investigation of the Zeeman splitting of the A and B lines; a typical spectrum is shown in Fig. 3.8. with the exciton states responsible for the various lines shown. Circular polarization is expected in the $<2,+1|$ and $<1,+1|$ lines and should result in their extinction when a circular analyzer of the appropriate polarization is placed in the optical system. This was done and no variation in the Zeeman spectrum was seen for either polarization. Thus a significant circular polarization of the Zeeman components was not being produced even at the high magnetic fields used. (A polarization of a few percent may have existed but would have been too small to be seen by the method just described).

ODMR measurements of individual components could not be made since the splittings could not be resolved at the magnetic field strength used in the ODMR experiment.

Temperature dependent measurements of the ODMR signals were rather limited since the samples were immersed in liquid helium, generally pumped to below the lambda point to eliminate bubbling. By focussing the laser excitation onto a small area of the sample and increasing the power...
The spectrum of the N centre luminescence at a magnetic field of 25 k Gauss showing the different exciton components.
significant heating could be produced. For the GaP-N sample the ratio of the A and B line luminescence provides a rough thermometer since at low temperatures thermalization favours the B line.

Comparing the ODMR results for low and high level laser excitation, the ODMR signal strength was observed to drop by a factor of approximately 2 at high laser power which apparently heated the luminescing region of the sample to roughly 2 degrees K.

In the Bi doped sample high laser power densities were observed to bring up a series of new lines in the luminescence spectrum including one at 5555A.U. just above the B line. Obviously these were the A line and its phonon replicas which are not seen at all at low temperature due to the greater splitting between the A and B lines. No ODMR signals could be detected in the new lines; presumably the increased temperature made the effect unmeasurable.

The results mentioned so far were obtained from measurements at 9.2 GHz microwave frequency. A measurement of the ODMR signal was also made at 36.3 GHz for the N centre luminescence with results shown in Fig. 3.9. The signal was considerably weaker than at 9.2 GHz despite the fact that according to theory, the ODMR effect should get stronger at higher magnetic fields. This was presumably due to the lower available microwave power level and absence of
FIG. 3.9 ODMR SIGNAL AT 36.3 GHz

ODMR signal from the N luminescence at high frequency
a resonant cavity (the 9.2 GHz cavity amplified the power level at the sample by a factor of the order of 1000).

By comparing the widths of the resonances at 9.2 and 36.3 GHz it can be seen that the resonance retained approximately the same width in field i.e. became relatively narrower in frequency indicating that the line width is due to homogeneous broadening.

3.5 Discussion

Our observations of ODMR of electrons in GaP suggest the following remarks. The fact that the signal was observed for several luminescences including N which acts as an electron trap and Bi which is a hole trap shows that the effect is due to resonance of electrons in the conduction band, at least in the case of Bi. Cavenett (30) has suggested that for the N centre the electron trapped at the N centre before capturing a hole is affected by the resonance. If this is so, it must have the same g value and spin relaxation time as the free electrons to within the accuracy of the experiments. Measurements at 36.3GHz indicated that the resonance was homogeneously broadened, giving the spin relaxation time as approximately 4 nanoseconds from the line widths. Whether this represents the spin-lattice relaxation time or the electron lifetime before trapping a hole, which is known to be shorter than the exciton decay time (36), is not clear. The linewidth
observed by Cavenett (30) was comparable to our results. The linewidths observed by Title (29) using conventional EPR at 77 degrees K were appreciably smaller than ours (by as much as a factor of 4) although the linewidths increased with impurity concentration. Since the EPR results would not be subject to lifetime broadening due to recombination, and since our samples were of higher purity than Title's doped material, it is reasonable to conclude that the lifetime determined from our results represents the electron lifetime against hole capture.

An attempt was also made to determine the line broadening mechanism by analysing the resonance line shapes. The results are given in Appendix A for several sets of data from the N centre luminescence. However, it could not be conclusively shown whether the data were better fitted by a Gaussian or by a Lorentzian line profile.

The strength of the ODMR signal seen from the N centre luminescence was observed to be equal for the A and B line, representing approximately a 1% change in luminescence at resonance which is larger than the predicted signal for the B line but smaller than for the A line. This is presumably due to thermalization between A and B line states which is known to be rapid (36), and would result in the ODMR induced changes in the two lines being averaged. Thus the observed signal is the same as that which would be obtained
by monitoring the A and B lines combined. Agreement with theory is then quite good, and the experimentally observed signal approximates the maximum predicted theoretically.

The ODMR signal observed in the Bi luminescence was considerably weaker than that of the N centre signal. The Bi luminescence at 1.6 degrees K derives entirely from the B line but the ODMR signal should still be the average of the A and B line signals since the A excitons are still formed but thermalize into B excitons due to the larger splitting. The reason for the weaker signal is probably the longer recombination time for excitons at Bi centres (reportedly a factor of 30 greater than for N (36)) which would allow more thermalization within the B exciton states, thus weakening the signal.

Our inability to observe enhancement of the ODMR signals by detecting circularly polarized components of the luminescence was explained by the absence of circular polarization in the Zeeman components of the A and B lines even at high magnetic fields. Zeeman studies of the N, S and Bi centres in GaP reported in the literature (31,41) have not described the observation of polarization in the Zeeman components, although there is no statement that polarization was looked for and not found. Cavenett (30) reports having looked for polarization dependence of the ODMR signal from the N centre with negative results. Why polarization has not been seen is not clear but may be due to crystal strains or
defects.

The B line optical decay occurs through mixing with the A line states by strains or an applied magnetic field. In our experiments it was observed that the B line intensity was not significantly affected by the magnetic fields used, indicating that crystal defects were predominantly responsible for the mixing of the exciton levels. Since observation of magnetic circular polarization depends on alignment of the excitons with the magnetic field, the presence of random defects interacting strongly with the excitons will disorient them and reduce the circular polarization of the emitted luminescence. Such effects would also broaden the Zeeman lines and an investigation along these lines might resolve the question.

Another negative result was the failure to observe resonances either of holes or between exciton states. Inter-exciton resonances are expected at $g=0.75$ and $g=1.25$ for the A and B excitons respectively (8). Cavenett (30) reports seeing a very weak resonance at $g=1.35$ corresponding to the B line, but we were unable to detect this signal, presumably due to inadequate sensitivity. The A line is even more difficult to observe since it causes a redistribution within the A line states all of which have allowed optical transitions, thus no net change in luminescence occurs. The resonance would manifest itself as a change in the A line
luminescence polarization but, as just mentioned, this cannot be seen.

Resonance of holes should manifest itself as a decrease in luminescence as for the electron resonance, however the effect would be smaller because of the lower hole $g$ value. A calculation of the A line for a temperature of 1.6 degrees K predicts a change in luminescence of 1.6 %. Although, in principle, a change of this magnitude should be visible, the signal would be weakened by inhomogeneous broadening of the hole resonance from crystal defects. This is due to the much larger effect of the crystal lattice on the hole $g$ value than on the electron $g$ value through spin-orbit coupling (29).

The number of effects observed or not observed that can be attributed to crystal defects suggests that ODMR studies on carefully prepared samples of higher quality than those available to us should be interesting. Alternatively, the effect of externally applied strains on ODMR and luminescence could be studied.

Finally the temperature dependence observed for the ODMR signal in GaP - N agreed approximately with theory, a factor of 2 decrease in the signal for heating to 2 degrees K being somewhat greater than expected. However, the estimation of temperature from the A to B line ratio was of limited accuracy because of the unequal heating of different
3.6 Cyclotron Resonance

ODMR experiments on GaP-N often showed non-resonant background signals, apparently microwave heating induced changes in luminescence. In some broad scans, looking for other resonances, this background was observed to be magnetic field dependent. It was therefore decided to investigate it. Fig 3.10 shows the result of a broad ODMR sweep, the background falls off to near zero at high field. The electron ODMR signal shows up on the high side of this large signal. The background signal represents a decrease in luminescence of several percent with the application of microwaves. The appearance of the signal suggests a very broad cyclotron resonance which is expected if microwave heating of photo-excited carriers is responsible. To test this hypothesis a sample was moved into a region of the microwave cavity where the electric field was stronger, the signal was observed to increase as expected for cyclotron resonance. The microwave power dependence was measured and it was observed that the signal increased linearly with the microwave power. All parts of the N luminescence were seen to be affected equally by the resonance.

Luminescence from S centres was observed and a
ODMR signal from the N luminescence over a wide range of magnetic fields
different signal was seen. Figs. 3.11 and 3.12 show the signals observed in N and S luminescence with fits for the cyclotron resonance equation:

\[
P_A \propto \frac{1 + \omega_C^2 \tau^2 + \omega^2 \tau^2}{(1 + \omega_C^2 \tau^2 - \omega^2 \tau^2)^2 + 4\omega^2 \tau^2} \times \frac{N e^2 \tau}{m^*}
\]

where \(P_A\) is the power absorbed from the microwave field, \(\omega\) is the microwave frequency, \(\omega_C\) the cyclotron frequency given by:

\[
\omega_C = eH/m^*
\]

e being the electronic charge, \(H\) the magnetic field, \(m^*\) the carrier effective mass, and \(\tau\) the carrier scattering time. Inhomogeneous broadening will result if \(\omega\) or \(m^*\) are energy dependent as is likely at higher carrier temperatures due to phonon scattering.

The curve fitting procedure used is described in Appendix A. It will be seen that the S luminescence gives a signal suggesting a resonance at higher field than for the N luminescence. Assuming that the signals are caused by cyclotron resonance, the effective mass values indicated are 0.89 ± 0.25 for the S and 0.36 ± 0.1 for the N. The quoted error bounds were obtained by varying the fit parameters and comparing the residuals to see how much change in the effective mass parameter was needed appreciably to worsen the fit. Several sets of data were obtained for each centre, and the variation in the results for these was also used to
ODMR signal from the N luminescence showing electron cyclotron resonance
FIG. 3.12 GAP-S CYCLOTRON RESONANCE

ODMR signal from the S luminescence showing hole cyclotron resonance
help arrive at the values given above. The values of $\omega_T$ for the two centres were of the order of 0.9 for the S and 0.3 for the N centre, the low $\omega_T$ for the N resonance accounts for the large error in the effective mass.

The effective masses deduced from the two resonances suggest electrons and heavy holes. It was hypothesized that trapping at luminescence centres was reduced by cyclotron heating of the free carriers, and that heating of the carrier type trapped first would have the greatest effect on the luminescence from that centre. N binds an electron weakly and a neutral S donor should capture a hole first before another electron.

Attempts were made to observe cyclotron resonance in GaP-Bi with the results shown in Fig 3.13. The resonance appears to be caused by heavy holes as suggested by the fact that Bi is a hole trap, but the value of $\omega_T$ is too low to be sure due to increased impurity scattering in the doped crystals.

Since the electron and light and heavy hole resonances should all be present to some extent in the luminescence but could not be resolved because of the low values of $\omega_T$, measurements were made at 36.3 GHz with the results shown in Fig. 3.14. The signal to noise ratio was poorer because of the low microwave power and absence of a cavity, but it can
ODMR signal from the Bi centre showing a very broad resonance attributed to holes.
FIG. 3.14 CYCLOTRON RESONANCE AT 36.3 GHZ

ODMR signal from N luminescence showing light and heavy hole resonances
be seen that the resonances are better resolved. It was found that the N and S luminescence gave similar resonances at the higher frequency, two resonances were seen which lead to effective mass values of \(0.154 \pm 0.015\) and \(0.626 \pm 0.03\). These correspond to the light and heavy holes. The difference in intensities between the two resonances is to be expected since the light hole band has a lower density of states than the heavy hole band. The electron resonance was not resolved but the fits calculated for the light and heavy holes indicated the presence of the electron signal as an underlying effect. A 'baseline slope' parameter was used in fitting the light and heavy hole peaks which were each fitted individually. The baseline slopes were included to take account of field dependent signals present underneath the resonance being fitted (such as the tail of other resonances), which would not be accounted for by the cyclotron resonance formula. The baseline slopes calculated for the light and heavy hole resonances differed markedly, indicating another underlying signal.

The peak of the electron resonance would have been at the valley between the hole peaks, but because of the electron's lower \(\omega_t\) value and splitting of the electron resonance due to the anisotropic effective mass, it was not resolved.

Cyclotron resonance measurements by Schwerdtfeger (27) using microwave absorption of photo-excited carriers at
35GHz gave signals similar to those shown in Fig. 3.14; the electron resonance was not seen except as a possible 'filling in' of the valley between the hole resonances.

The GaP-Bi samples were also run at 36.3GHz but the resonance thought to be due to holes was still too broad to give a useful value of effective mass.

The results of our measurements of cyclotron resonance in GaP are shown in Table 3.2 which gives the effective mass and $\omega_1$ values determined from 9.2GHz and 36.3GHz and the range of values given in the literature. Our results show an apparent discrepancy between the 9.2GHz and 36.3GHz effective mass values of the heavy holes. The 9.2GHz value determined from the S luminescence signal is probably too high because of unresolved light hole and electron contributions to the signal which would tend to distort the fit.

We next consider the mechanism by which cyclotron heating of carriers reduces the luminescence from a recombination centre. Since the entire luminescence was observed to be affected equally, the effect must be due to a reduction in the trapping probability of heated carriers at the centre, or else to impact ionization of carriers already trapped before they can recombine.
TABLE 3.2
GaP CYCLOTRON RESONANCE RESULTS

<table>
<thead>
<tr>
<th></th>
<th>9.2 GHz</th>
<th>36.3 GHz</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e^*$</td>
<td>0.36±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{th}^*$</td>
<td>0.89±0.25</td>
<td>0.626±0.03</td>
<td>0.52(A)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.67+.04(B)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.88(C)</td>
</tr>
<tr>
<td>$\omega_\tau$</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{th}$</td>
<td>0.8</td>
<td>2.6</td>
<td>0.16(A)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.17+.01(B)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.132(C)</td>
</tr>
</tbody>
</table>

A. Bandstructure calculations (78)
B. Cyclotron resonance (27)
C. Bandstructure measurements (78)
The expected heating of electrons at the maximum microwave power levels used was estimated taking the scattering time to be given by the electron resonance $\omega_1$ values at 9.2 GHz. The maximum microwave electric field strength inside the sample was calculated to be of the order of 100 V/Cm giving an average electron heating of approximately 0.5 meV. Since the N centre binds an electron with an energy of 8 meV, and the binding energy at S and Bi centres is even larger, the possibility of impact ionization by microwave heated electrons can be ruled out.

Experimental evidence for the energy dependence of the trapping probability of carriers in GaP has been obtained by Dean (47) in excitation spectrum measurements. His work showed increased luminescence from the isoelectronic centres N and Bi when the photo-excited carriers were generated near to the band edges using resonant excitation, and when carriers could thermalize rapidly to the bottom of the band by phonon emission.

A theoretical analysis of trapping cross sections of electrons at ionized impurities in semiconductors has been made by M.Lax (77). He shows that the trapping cross section should increase with decreasing temperature as electrons can be trapped into increasingly large orbits about the impurities. Lax also calculates the trapping cross section for neutral impurities and finds a $1/T$ dependence.
Trapping of an electron at a neutral isoelectronic N impurity in GaP is more complicated since the shallow bound state for this centre will produce strong resonant trapping and scattering effects (38). A calculation of the pseudopotential for the N impurity in GaP by Faulkner (79) shows a deep narrow potential well. Faulkner has calculated the scattering and trapping cross sections for this potential for electrons and finds an energy dependence of the form:

$$\frac{1}{E_i + E_e}$$

$E_i$ is the binding energy of the electron on the N atom, and $E_e$ the electron kinetic energy prior to trapping. In our measurements the maximum heating expected from the microwaves was 0.5 meV and the thermal energy of the electrons at 1.6 degrees K only 0.13 meV while $E_i$ for the N centre is 8 meV, thus the trapping cross section should decrease approximately linearly with increasing microwave power. This was observed. The decrease in luminescence expected for the maximum microwave heating is estimated to be 5.8 %, in good agreement with the observed signals which represent an approximately 5 % decrease in intensity.

It may be questioned whether trapping cross sections calculated for plane wave electrons are applicable to electrons in cyclotron orbits, for example, an electron in a cyclotron orbit about an impurity might have an increased
trapping probability. The pseudopotentials at isoelectronic impurities are short range effects, that calculated by Faulkner for N in GaP is negligible beyond two lattice spacings or about 10 A.U. The cyclotron orbit radius of electrons in the lowest Landau level for the resonance magnetic field strength is approximately 100 A.U., so the isoelectronic trap should not be able to 'see' the difference between the cyclotron orbit and a plane wave electron.

3.7 ODMR in ZnTe

Samples of zinc telluride were obtained from J. Merz at Bell Laboratories. These were doped with isoelectronic oxygen, one sample containing the isotope O_{18}. Residual impurities such as phosphorous, which forms a shallow acceptor level when substituting for Te, were also present.

Zinc telluride has a direct band gap of 2.38 eV (48), the valence band maximum being degenerate. The effective masses of light and heavy holes in ZnTe have been measured by Stradling (49) using cyclotron resonance absorption measurements of thermally excited holes at a microwave frequency of 1556 Hz. The effective masses were:
the heavy hole band being non-spherical. The electron effective mass has been estimated at between 0.12 and 0.22 from magneto-optical studies of luminescence from shallow acceptors and donors (50, 51).

ODMR measurements on ZnTe have been made by Killoran, Cavenett and Dean (14) who observed the effects of electron paramagnetic resonance as a change in the polarization of donor-acceptor pair luminescence in P-doped ZnTe. The g value obtained was +0.401 and was attributed to resonance of electrons on unidentified shallow donors, possibly Al atoms substituting for Zn. Large background signals were also reported and were dependent on the magnetic field, the wavelength and the polarization of the luminescence being measured.

The luminescence spectrum of our ZnTe sample is shown in Fig. 3.15. The near band gap luminescence has a sharp peak at 5220 A.U. This is commonly seen in ZnTe and is attributed to exciton recombination at a number of shallow acceptors including P substituting for Te, and Li and Cu substituting for Zn (14). Other lines correspond to
ZnTe luminescence spectrum showing near band gap luminescence and the deeper 0 isoelectronic centre spectrum.
recombination at acceptors and donors. The luminescence spectrum of the oxygen centres shows the expected series of phonon replicas already observed for this isoelectronic impurity (52).

Attempts were made to observe the electron resonance in various parts of the luminescence, both by monitoring the total intensity and by using a circular polarization analyser. No signal was seen anywhere in the vicinity of the expected value of $g=0.401$. Magnetic field dependent background signals were seen in all parts of the luminescence, however, and these were investigated using 9.2GHz microwaves with the results shown in Figs. 3.16 and 3.17. Two distinct lineshapes were observed depending upon which part of the luminescence was monitored.

The 5220 A.U. line and the oxygen centre luminescence both gave resonances which suggested an effective mass of the order of 0.3, while the 5290 A.U. peak gave a resonance with an effective mass value of approximately 0.8. An unusual feature of these resonances is that they represent an increase in the luminescence at resonance rather than a decrease of the type seen in most of the other cyclotron resonance results.

Measurements were also made at 36.3GHz but no useful results were obtained but the low power level made the
ODMR signal showing an increase in luminescence caused by electron cyclotron resonance.
FIG. 3.17 ZnTe ODMR AT 5290 Å

Hole resonance in 5290 A.U. luminescence
signal too weak to observe.

The effective mass values deduced from the 9.2 GHz resonances were: \(0.8 \pm 0.2\) and \(0.3 \pm 0.2\) having \(\omega\tau\) values of the order of 0.9 and 0.2 respectively. These values suggest heavy holes and electrons, or possibly light holes. In view of the difference in the \(\omega\tau\) values for the two resonances, the low effective mass signal was probably caused by electrons rather than by the light holes which were observed by Stradling to have approximately the same \(\omega\tau\) value as the heavy holes.

The fact that the effect of the resonances was to increase luminescence suggests that there are non-radiative decay processes which compete for electrons and holes, and which are inhibited by microwave carrier heating. However, different resonances are observed in different luminescence bands which contradicts this hypothesis since, if non-radiative processes are inhibited, all the luminescence should increase in proportion and the observed resonance should be the same in all bands.

Another possibility is that the observed luminescence bands correspond to exciton recombination at ionized acceptors and donors. Evidence has been obtained from Zeeman measurements that the 5220 A.U. luminescence originates from ionized acceptors (51). Ionized impurities will tend to be
neutralized by photo-generated electrons and holes (13) and cyclotron heating is expected to reduce the rate at which ionized atoms are neutralized either by reducing the trapping probability as was observed in GaP, or by impact ionization of neutralized atoms. Thus the number of ionized centres available for luminescence would be increased, although the exciton trapping rate might be reduced by the heating. It should be pointed out that optical recombination of excitons at neutral donors and acceptors is also expected but will be much less efficient due to the non-radiative Auger recombination process already discussed for GaP. It follows that an increase in the number of ionized centres should result in an increase in luminescence.

Our inability to observe the electron paramagnetic resonance was probably due to the absence of appropriate donor impurities needed to produce the donor-acceptor pair luminescence reported by Killoran et al (14) which was not visible in our sample.

3.8 Other Materials.

ODMR measurements were made on samples of CdS and CdIn₂S₄ and magnetic field dependence background signals were observed. The \( \omega_T \) values of these resonances were too low to give any measure of carrier effective mass, it was not even possible to determine whether the resonances were due
to electrons or holes. It was evident that, to obtain useful results, cyclotron ODMR experiments need to be done with high purity materials and at high microwave frequencies. This is generally true for conventional cyclotron resonance work.

3.9 Summary

ODMR measurements were used to observe the effect of paramagnetic resonance of electrons on luminescence from N, S, and Bi impurities in GaP. ODMR signals had not been previously reported from S and Bi luminescence and our results confirm the interpretation that the signal seen for N impurities is due to resonance of photo-excited conduction band electrons. A calculation was made of the expected luminescence change as a result of the resonance and was found to agree very well with the observed signal strength when the rapid thermalization between the A and B lines was taken into account. The temperature dependence of the effect was measured over a limited range by laser heating of the sample and the decrease in signal predicted theoretically was observed. The resonance was shown to be homogeneously broadened giving a lifetime of 4 nano seconds. By considering the results of conventional EPR on GaP it was inferred that this lifetime was the electron-hole capture time. Circular polarization effects were absent from the luminescence, this was attributed to the effects of crystal defects on excitons which were shown to be considerable. Our
inability to see paramagnetic hole resonance effects was also thought to be due to crystal defects causing homogeneous broadening of the hole signal.

Cyclotron resonance of electrons and holes was observed by ODMR, the first such measurement in this material. The sensitivity of different luminescence bands to electron or hole resonance was shown to be determined by the trapping processes for the corresponding impurities, the carrier type trapped first by a neutral impurity had the greatest effect when heated. The magnitude and temperature dependence of the effect was measured and compared with theoretical predictions for the trapping cross section of the N impurity and good agreement was found. Accurate values of light and heavy hole effective masses were obtained by measurements at 36.3 GHz and agreed with the results of conventional cyclotron resonance experiments. The electron resonance could not be resolved properly at 36.3 GHz, presumably due to the anisotropic electron effective mass and shorter scattering time, probably caused by resonance scattering from N impurities.

ODMR studies of ZnTe showed electron and hole cyclotron resonances and, as in GaP, different luminescence bands gave signals corresponding to electrons or holes. Unlike the GaP results, the ZnTe luminescence was increased by the cyclotron resonances. It was hypothesized that ionized
impurity centres were responsible for most of the near band gap luminescence, an assumption supported by Zeeman measurements reported in the literature, and that cyclotron heating increased the number of ionized impurities. Recombination at neutral centres could be reduced correspondingly but such recombinations would be less efficient optically due to non-radiative Auger processes. The increase in luminescence observed for the isoelectronic oxygen centre luminescence presumably represented a net increase in the free carrier population caused by reduced trapping at other centres. If our interpretation of the results is correct, this technique could provide a valuable tool for identifying luminescence bands in ZnTe as originating from ionized or neutral acceptors or donors, especially in cases where other techniques, such as Zeeman spectroscopy, do not work (e.g. due to unresolvable splittings).

Attempts to observe the electron paramagnetic resonance in ZnTe by ODMR were unsuccessful due to a lack of appropriate donors to produce the donor-acceptor luminescence band in which the effect manifests itself.
Silver bromide is a highly polar material with an indirect band gap of 2.69 eV (53). The bandstructure is shown in Fig. 4.1 and is, in some respects, the inverse of that in GaP. The conduction band minimum is centred at the $\Gamma$ point and is approximately spherical, while the four valence band maxima lie at the X points and are elliptical, giving a hole an anisotropic effective mass (54). Both conduction and valence bands are appreciably non-parabolic due to the strong electron-phonon coupling to be described later.

Several pure crystals of AgBr were obtained from W. Czaja, EPF, Lausanne, Switzerland. These included one crystal with identified crystal axes. The crystals, though not intentionally doped, contained some residual impurities. The main impurity was iodine which, being chemically similar to bromine, is generally present in undoped AgBr in concentrations of the order of one part per million.

4.2 ODMR in AgBr.

The luminescence spectrum of AgBr contains two principal features. A weak zero phonon line and a series of multi-phonon replicas from exciton recombination on isoelectronic iodine centres forms a broad band which peaks
\[ \varepsilon = 0.15 \text{eV} \]
\[ \delta = 0.58 \text{eV} \]
at approximately 4900 A.U. as shown in Fig.4.2. At lower energy a broad featureless continuum peaks at around 5700 A.U. This latter band is thought to arise from electron-hole recombination at interstitial silver atoms or multi-atom silver specks (55,56), and is enhanced either by exposing the crystal to light or by stresses induced in thermal cycling to liquid helium temperatures. It can be reduced by annealing the sample at 200 degrees C for 24 hours and cooling to room temperature slowly (53,57).

ODMR measurements on AgBr have been reported previously, first by Hayes, Owen and Walker (58), and by Marchetti and his co-workers (56,59). Hayes et al observed a single resonance at g=1.8 in the 5700 A.U. luminescence band using a microwave frequency of approximately 20 GHz. Marchetti (56), using 10 Watts of microwave power at 35 GHz, has observed a series of resonances in the same luminescence band at g values of 1.49, 1.75, 1.81 and 2.08 all apparently isotropic. He attributed the g=1.49 and g=2.08 values to free electron, and to hole paramagnetic resonances respectively. He assigned the two intermediate resonances to electrons trapped on the defect or centre responsible for the 5700 A.U. luminescence. This interpretation was verified by comparing the effects on signals from samples doped with various carrier trapping impurities. Marchetti and Burberry (59) have also studied ODMR signals from iodine centre luminescence using AgBr crystals doped with various levels of iodine. At intermediate doping levels (of the order of
FIG. 4.2 A G B R LUMINESCENCE

Iodine centre luminescence

Defect site luminescence

Slit Width x 10

INTENSITY (arb. units)

WAVELENGTH Å
100 ppm) a single broad resonance at about \( g=5.65 \) was observed. They attributed this to transitions within the angular momentum states of the iodine bound exciton.

4.3 Results.

The results of our measurements (75) on the 5700 A.U. luminescence band, at 9.2 and 36.3 GHz are shown in Figs. 4.3 and 4.4. At 9.2 GHz two resonances were seen at \( g=2.07 \pm 0.02 \) and \( g=1.81 \pm 0.02 \) and were isotropic to within the experimental errors. In some of the data a third peak was visible merged with the large signal at \( g=1.81 \) and on the high field, low \( g \) value, side. At 36.3 GHz only one resonance was seen at \( g=1.708 \pm 0.01 \) which was also isotropic.

The 4900 A.U. iodine emission band yielded a very different ODMR spectrum. No trace of any of the relatively sharp EPR lines seen from the 5700 A.U. band was detected using either 9.2 or 36.3 GHz microwave stimulation. Instead, two broader resonances were observed as shown in Fig. 4.5. These we attribute to cyclotron resonance of electrons and holes. This is supported by the striking similarity of these results to those obtained by direct detection of cyclotron resonance reported by other workers (60-65). However, there are differences which will be discussed later.
FIG. 4.3 ODMR IN AGBR

ODMR of 5700 A.U. band showing electron and hole resonances.
FIG. 4.4 ODMR IN AgBr

Electron resonance at high frequency

36.3 GHz

$g = 1.71$
FIG. 4.5 CYCLOTRON RESONANCE IN AGBR

Cyclotron resonance of electrons and holes in I luminescence

\[ m^* = 0.29 \]

\[ m^* = 1.1 \]

36.3 GHz

\[ \Delta I \]

MAGNETIC FIELD kG

0 10 20
Unlike the EPR resonances, which caused increased emission, the signals represent a decrease in luminescence at resonance. The lower resonance, attributed to electron cyclotron resonance, was isotropic. The higher resonance was broadened in certain directions but the width of the resonance, and the poor signal to noise ratio, made it impossible to determine whether this was caused by the unresolved splitting of the line which is expected for a hole cyclotron resonance in this material.

At 9.2 GHz, where more microwave power was available, the power dependence of the cyclotron resonances was studied with the results shown in Figs. 4.6 and 4.7. At low power levels the electron and hole resonances both appear to be homogeneously broadened lines giving approximately the same effective mass values as the 36.3 GHz results. As the microwave power level was increased the hole resonance strengthened and broadened, while the electron resonance changed sign (i.e. luminescence increased at resonance) and broadened. The spectral dependence of the ODMR signals was checked by scanning the iodine spectrum with the magnetic field set at the peak of the electron and hole resonances. The ODMR 'spectra' so obtained resembled the photoluminescence spectrum.

It should be noted that the ODMR signals from the electron and hole resonances sit on a large non-resonant background signal presumably caused by dielectric heating.
FIG. 4.6 LOW POWER CYCLOTRON RESONANCE SIGNAL

Electron cyclotron resonance at low frequency showing homogeneous line shape

$m^* = 0.308$

9.2 GHz

$\Delta I$

MAGNETIC FIELD kG

0 1.5 3.0
FIG. 4.7 POWER DEPENDENT CYCLOTRON RESONANCE SIGNAL

Electron and hole resonances as a function of microwave power

- **I** Full Power
- **II** - 10 dB
- **III** - 20 dB
- **IV** - 30 dB

**MAGNETIC FIELD** (kG)

0 10

**9.2 GHz**

- $m^* = 2.1$
- $m^* = 1.4$
- $m^* = 1.6$
- $m^* = 0.26$
Also no trace of the cyclotron resonances or background is seen in the 5700 A.U. luminescence band.

4.4 Discussion.

Our ODMR results from the 5700 A.U. band agree substantially with those of Hayes et al and Marchetti, the 9.2 GHz data showing the hole resonance at \( g = 2.07 \) and the two trapped electron resonances merged with the \( g = 1.81 \) resonance stronger. At 36.3 GHz only the \( g = 1.7 \) resonance is seen, indicating that the \( g = 1.81 \) signal becomes relatively weaker at higher field. This agrees with Marchetti's observation that this resonance decreases in intensity at lower temperature (4.2 degrees K to 1.7 degrees K) since in both cases the splitting of spin states in the magnetic field increases with respect to the thermal energy. Our failure to observe the other lines at high frequency may be attributed to the low microwave power available. The fact that the \( g = 1.81 \) and \( g = 1.7 \) resonances are almost completely merged at lower frequency indicates that the lines are at least in part homogeneously broadened. Failure to observe EPR lines in the iodine centre luminescence is probably due to the fact that, being an isoelectronic centre, the exciton decay times are longer which allows greater thermalization of spins before recombination.

Cyclotron resonance of electrons in AgBr has been observed by several researchers using conventional microwave
absorption techniques and photo generated carriers. The first measurement was made by Ascarelli and Brown (60) who observed an asymmetric and strongly temperature dependent signal which indicated an effective mass of 0.27.

Baxter and Ascarelli (61), and Tamura and Masumi (62,63,64) have studied the temperature dependence of this resonance in more detail by changing the lattice temperature and increasing the carrier temperature using high microwave fields. Tamura and Masumi observed an increase in effective mass of up to 15% with high levels of microwave excitation, which they compared with the theoretical predictions of Lee, Low and Pines (LLP) (66) and Larsen (67). Hodby and co-workers (65) have observed an increase in apparent electron effective mass of approximately 5% at very high microwave frequencies and magnetic field strengths at which the first excited cyclotron level is approximately 20% of the LO phonon energy. They monitored the cyclotron resonance by measuring changes in sample photoconductivity.

Cyclotron resonance of holes has been seen only by Tamara and Masumi (54) who used microwave absorption at 34 GHz. They observed a resonance at $m^*=0.99$ for a magnetic field parallel to the [1,0,0] direction. This resonance split into two lines when the field was applied along other axes.
Both electron and hole effective masses in AgBr are strongly energy dependent due to non-parabolicity of the electron and valence bands. This is due to the strong coupling between carriers and LO phonons ($\alpha_e = 1.6$, $\alpha_h = 2.8$) (54). $\alpha$ is the constant for coupling of electrons and holes to the longitudinal optical phonon mode and is defined as:

$$\alpha = \frac{e^2}{\hbar} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right) \left( \frac{m_b}{2\hbar\omega_{LO}} \right)^{1/2}$$

where $\varepsilon_s$ and $\varepsilon_\infty$ are the low and high frequency lattice dielectric constants, $\hbar\omega_{LO}$ the energy of a longitudinal optical phonon, and $m_b$ the band mass of the electron which is the effective mass in the absence of the electron-phonon interaction.

The lattice relaxation energy in the presence of an electron is approximately equal to $\alpha\omega_{LO}\hbar$, and for values of alpha greater than 6 the electron becomes trapped in the potential well so produced (65).

A theoretical analysis of the polaron-electron effective mass in strongly polar materials by Lee, Low and Pines (66), is carried only to the first order; it predicts the increase in effective mass caused by electron-phonon interaction without calculating the energy dependence. The work of Larsen (67), however, indicates a strongly energy dependent mass. In particular, when the electron approaches the LO phonon energy of 17.2 meV the electron mass should
increase rapidly to reach a value approximately 40% greater than that for a cold electron for a coupling of $\alpha = 1.6$.

Our results with optically detected resonance agree in some respects with those obtained by conventional methods. The splitting of the hole resonance seen by Tamura and Masumi (54) was not resolved in our work, due to homogeneous line broadening and, at 36.3 GHz, by poor signal to noise ratio. Splitting should be apparent with the applied magnetic field along the [1,1,1] direction which was the orientation used in many of our experiments. The shift in hole resonance to higher effective mass at high microwave power levels was to be expected from the non parabolic nature of the valence band.

The asymmetry of the electron cyclotron resonance showed unusual features. In conventional electron resonance experiments the electron signal usually displays a tail on the high level field side due to hot electrons with greater effective mass. Our results at 36.3 GHz showed an inverted tail: the main peak appeared as a decrease in luminescence while the tail showed an increase. Thus microwave heating of cold electrons reduced their recombination rate at iodine centres, presumably by reducing their trapping probability, while heating of hot electrons increased their recombination rate. For the low microwave powers used, the heating is small compared to the carrier temperature so that the effect can not be ascribed to an increase in the hot electron
population at the expense of cold electrons due to microwave heating.

A possible explanation is that hot electrons can drop quickly onto traps with the emission of one or more LO phonons. Such effects have been observed in other materials. Malm and Haering (68) measured the dependence of photoluminescent intensity from recombination centres in CdS as a function of excitation wavelength and showed that recombination is enhanced when electrons can drop to a bound state with the emission of an integral number of LO phonons. Dean (47) has observed the same process in excitation spectra of GaP for both N and Bi luminescence centres. A similar effect has recently been observed in excitation spectra of AgBr doped with various impurities (76). In the present case, resonant heating of an electron near the LO phonon energy would increase its probability of making a rapid transition to a bound state at an iodine impurity. It should be noted that the isoelectronic iodine centre traps a hole first, then an electron is attracted to the charged centre and enters one of a set of hydrogen-like orbits (69). Thus there will be a band of energies just below the LO phonon energy from which electrons can make a phonon assisted transition to a bound state. The theory of polaron mass presented by Larsen (67) predicts a rapid increase in effective mass as the electron reaches the LO phonon energy, due to the strong electron-phonon interaction. For a
coupling of $\alpha=1.6$ the theory predicts an increase of about 40% in effective mass over that for a cold electron, although the accuracy of the theory is questionable in this range. The negative tail of the electron resonance in our data shows general agreement with this theory, the peak of this feature appeared in fields between 20% and 50% higher than the main electron signal. The tail was inhomogeneously broadened due to rapid variation in electron effective mass near the LO phonon energy.

At 9.2 GHz the electron resonance showed no appreciable asymmetry, homogeneous broadening having become dominant. At sufficiently high levels of microwave power the signal inverted and broadened. This indicates that the electrons had been heated to near the LO phonon energy so that the negative tail of the resonance was stronger than the low energy electron peak. The broadening of the signal was caused by increased scattering of the hot electrons by acoustic and optical phonons (64).

An attempt was made to estimate the heating expected from the microwaves. The rms electric field strength in the microwave cavity in the vicinity of the sample at maximum excitation was calculated to be 180 V/Cm. Approximating the sample by an ellipsoid gave the field strength inside the sample as 90 V/Cm (70). The electron scattering time was calculated from the $\omega T$ value of the low power electron resonance at 9.2 GHz, giving the average energy acquired by
an electron between scatterings as approximately 28 meV. This figure is obviously an overestimate since scattering increases due to emission of acoustic and optical phonons as the electrons are heated, but it indicates that heating of the free electrons of the order of one LO phonon energy does occur at the highest levels of microwave excitation.

4.5 Summary

Cyclotron resonance of electrons and holes in AgBr has been studied using ODMR. Our work has shown that recombination at iodine isoelectronic impurities is affected by cyclotron heating of electrons and holes as well as by microwave dielectric heating. All parts of the iodine bound exciton luminescence were shown to be equally affected indicating that the effects were caused by changes in the trapping rate of electrons and holes at the centres rather than by changes in the exciton decay processes. Cyclotron heating of holes and cold electrons reduced their recombination at iodine centres, while heating of electrons near the LO phonon energy increased their trapping rate. This is explained by the enhanced trapping of a hot electron by the emission of an LO phonon. Measurements at lower microwave frequency with sufficient power to heat the bulk of the electrons to approximately the LO phonon energy showed considerable enhancement of the luminescence at resonance, substantiating this explanation.
This technique provided a means of measuring the effective mass of hot electrons near the LO phonon energy directly. A comparison of the effective mass of the hot electrons determined by their cyclotron resonance with that predicted by theory gives reasonable agreement.

Cyclotron resonance of holes was also observed but the expected splitting could not be resolved due to the width of the resonance and insufficient microwave power at high frequency.

The ODMR results obtained from the 5700 A.U. luminescence band confirm those of Hayes et al and Marchetti (58,56). The absence of cyclotron resonance effects in this luminescence indicates that trapping at the centres responsible is much less sensitive to cyclotron heating of carriers. The nature of these centres is not completely understood, although they appear to involve some type of defect. The paramagnetic resonances of electrons bound to the trapping centre were shown to be homogeneously broadened.

It is worth noting that although optical detection of cyclotron resonance has been reported in very few materials, such resonances may have been observed but not recognized. The resonance reported by Marchetti and Burberry (59) in the luminescence of iodine doped AgBr at $g=5.65$, and attributed
to a transition between states of the iodine bound exciton, was almost certainly the electron cyclotron resonance signal. The greater width of their resonance compared to those reported here, and its lack of strong asymmetry, is presumably due to the higher level of iodine doping and consequent increase in impurity scattering.
Chapter 5. Conclusions and Suggestions for further work.

5.0 Introduction.

Sections 5.1 to 5.4 contain brief statements which define the new results which are reported in the body of this thesis. Section 5.5 contains some suggestions for further work.

5.1 Gallium Phosphide.

1) ODMR signals from Bi and S impurities have been observed, they confirm that the N signal corresponds to conduction electron resonance. The signals were shown to be saturated and homogeneously broadened indicating a lifetime of approximately 4 nano seconds.

2) The maximum signal expected was calculated and found to give good agreement with the experimental results. The comparison showed that there is rapid thermalization between the A and B lines. The temperature dependence of the signal was measured over a limited range and was found to decrease with temperature as predicted.

3) Polarization effects expected in the ODMR signal were not observed. This was shown to be due to a lack of circular polarization and confirmed by Zeeman
measurements. The hole paramagnetic resonance signal was also absent. Both effects were attributed to crystal strains and defects.

4) Cyclotron resonance of electrons and holes was observed by ODMR. Luminescence centres were shown to be most sensitive to cyclotron heating of the carrier type first trapped by the neutral centre. The microwave power dependence of the effect was measured and showed good agreement with theory for the N centre. Qualitative agreement was also obtained for the S centre. Measurements at 36.3 GHz gave accurate values for light and heavy hole effective masses, these agreed with cyclotron resonance results obtained by other workers.

5.2 Zinc Telluride.

1) ODMR measurements on ZnTe revealed cyclotron resonances of electrons and holes. As in GaP different resonances were observed in different luminescence bands. Unlike GaP, the resonances caused an increase in luminescence. This was attributed to an increase in the number of ionized impurities as a result of carrier heating which resulted in more efficient luminescence. The signal to noise ratio at 36.3 GHz was too low to allow useful results to be obtained for this frequency.
2) The electron paramagnetic resonance signal was not seen. This was explained by the absence of donor-acceptor pair luminescence bands from our samples due to a lack of appropriate impurities. No paramagnetic resonance signal could be seen in any of the bound exciton luminescence.

5.3 Silver Bromide.

1) Paramagnetic resonances of holes and trapped electrons were observed and the electron resonance was shown to be homogeneously broadened. Other results agreed with those already reported in the literature.

2) Cyclotron resonance of electrons and holes was observed by ODMR in the iodine bound exciton luminescence. The resonances caused a decrease in luminescence, but a tail on the electron resonance corresponding to hot electrons showed increased luminescence. Experiments at 9.2 GHz with adequate microwave power to heat the electron population showed that hot electrons did, in fact, enhance the luminescence from the iodine centre. The heating effects were calculated to be of the order of the LO phonon energy and the effect was explained by the increased trapping rate for those electrons able to drop to a bound state with the emission of an LO
phonon. The effective mass of hot electrons was estimated from the cyclotron resonance results and found to agree with the theoretical predictions to within the experimental error.

3) The poor signal to noise ratio at 36.3 GHz prevented a more accurate comparison with theory. The hole resonance was observed to broaden and shift to higher effective mass as expected at high microwave power levels, but the hole resonances could not be resolved properly to permit a more detailed analysis.

5.4 Curve fitting.

1) An original method of non-linear curve fitting was developed to allow the best fits of theoretical profiles to noisy data to be made. This was compared to the other available methods and was found to converge rapidly and to be relatively insensitive to false minima.

2) The method was applied to our data in an attempt to use statistical criteria in discriminating between various mechanisms.
5.5 Comments and Suggestions for Further Work.

1) It has been shown that the background signals often present in ODMR experiments are caused by microwave heating and, in particular, cyclotron heating of free carriers. In some cases cyclotron resonances may have been observed in ODMR experiments and mistaken for EPR signals, as was mentioned in the case of AgBr. Since cyclotron heating is caused by the microwave electric field and EPR by the magnetic component the two processes can be distinguished by placing the sample at the nodes of a microwave resonator. Some convenient means of moving the sample in the resonator during an experiment, and without disturbing the field in the resonator, is desirable and should be developed.

2) The use of ODMR to observe cyclotron resonance is subject to the same limitations as conventional cyclotron resonance measurements due to short carrier scattering times in many materials and consequently broad resonances. The effective mass values reported in this thesis were comparable with those determined by conventional cyclotron experiments. The main advantage in using ODMR is that information may be gained about trapping and luminescence processes which are affected by the resonances. The results reported here showed both reductions and increases in trapping at impurities as a result of cyclotron heating, in some cases
allowing theoretical predictions to be tested.

3) One of the factors limiting the usefulness of ODMR is the quality of the signals that can be obtained. In cases where the resonance produces only a small change in luminescence, or where the luminescence itself is weak, the statistical noise in the luminescence may obscure the desired signals. In some cases this may be remedied by using high microwave power levels or stronger excitation sources, but this is not always possible technically. Signal averaging as described in this thesis can be used to improve the signal to noise ratio as much as is desired if sufficient time is spent in collecting data. In our experiments, the running time of the Dewars imposed a limit on the time that could be spent on such data collection because, as explained in Chapter 2, refilling the Dewar during a run posed generally insurmountable difficulties. Some efficient means of filling a Dewar with liquid helium even while being pumped on seems desirable. The alternative, of constructing a Dewar which has a longer running time, might produce some improvement but hardly the factor of 10 or so which is needed.

4) The results of ODMR studies on GaP showed several negative results which were attributed to crystal defects. Measurements on high quality, strain free,
crystals would therefore be of interest. Alternatively, the effects of strains on observed effects could be studied by artificially stressing the crystals. The absence of polarization reported here was only approximate, circular polarization of a few percent may have existed and been undetectable. A more sensitive measurement of the magnetic circular polarization of the Zeeman components of excitons in GaP could allow a more definite analysis of the depolarizing effects in GaP.

The predicted polarization dependent ODMR signals in GaP-N luminescence should be observable in the Zeeman components of the exciton lines. To separate these spectroscopically in an ODMR experiment would require microwave frequencies of the order of 70 GHz.

An interesting feature of the ODMR cyclotron resonance results was the difference in the signals observed at 9.2 and 36.3 GHz from the N luminescence, a broad electron signal being dominant at 9.2 GHz while the hole resonances were more apparent at 36.3 GHz. Measurements at an intermediate frequency such as 20GHz should help to show whether the electron signal disappears due to unresolved splitting as we suggest.

5) The ZnTe results indicate a means of distinguishing ionized or neutral donor or acceptor recombination centres by the resonances shown in their luminescence. A test of our interpretation of these resonances could
be made by using a ZnTe sample doped with an acceptor or donor with known luminescence properties. Better resolution of the observed cyclotron resonances could be obtained if sufficient microwave power was available at higher frequencies such as 36.3 GHz.

6) The electron cyclotron resonance in AgBr showed an interesting enhancement of trapping for hot electrons. A higher microwave power level at 36.3 GHz where the asymmetry of this resonance is visible would allow the effects of significant microwave heating to be studied as was done at 9.2 GHz. Better signal to noise ratios could also be obtained which would allow a better comparison to be made with the theory. Resolving the splitting of the hole resonances should be possible and similar effects might be visible in them. A study of other polar materials such as AgCl and KBr using this technique is also indicated.
APPENDIX 1. Curve Fitting.

To determine which of the two hypotheses regarding signal output profile was correct, it was necessary to find least-squares fits for the expressions:

\[ y(i) = A + E \cdot i + B \cdot \exp(-D(C-i)^2) \]  
\[ y(i) = A + E \cdot i + \frac{(1+C^2D^2+i^2D^2)(1+C^2D^2)(B-A)}{(1-C^2D^2+i^2D^2)} + 4C^2D^2 \]

It is to be noted that the terms \( A + E \cdot i \) are included because the base signal output is known to have a positive slope for increasing frequency.

The author has previously described a method for fitting the plain Lorentzian curve to experimental data (71). However, recently (72) it has been suggested that the method of Nelder and Meade (73), in somewhat modified form, is superior to other methods.

The Nelder and Meade procedure had been tested already in connection with our previous work and had been found to converge slowly and to be difficult to start. It was thus thought worth testing the proposed new variant.

Unfortunately the printed version of the new procedure was written in a non-standard version of the PASCAL language and was incomprehensible. A new version was therefore written in BASIC to run on the computer available with the
In essence, for two variables, the procedure is as follows: suppose that the contours $R=0.1$, $R=0.05$ etc. in Figure A.1 represent equal values of the residuals of the trial function and the experimental data for:

$$R = (y(x_1,x_2) - y_{obs}(x_1,x_2))^2$$

Any threenon-collinear initial points are taken in the $(x_1,x_2)$ space, $a_1,a_2$ and $a_3$ say. Naturally, the closer these are to the actual minimum the more rapidly will the process converge. The algorithm then proceeds as follows:

1) Evaluate the residuals at $a_1,a_2,a_3$.
2) Suppose that $a_i$ has the largest residual. Then (in N dimensions) evaluate the residual at a new point $a_i'$ which is anti-symmetric with respect to $a_i$ through the point which is the centroid of the remaining points.
3) If the residual at $a_i'$ is smaller than that at $a_i$ but not smaller than the least residual at one of the remaining points, $a_i'$ replaces $a_i$ and the process is repeated.
4) If the residual at $a_i'$ is less than any other residual, another new point $a_i''$ is defined at double the distance from the centroid. If the residual at this point is again the lowest, $a_i''$ is accepted, otherwise $a_i'$ is accepted. The process then repeats.
5) If $a_i'$ has a higher residual than $a_i$, a new point $a_i'''$ is tested, where $a_i'''$ is half way between $a_i'$ and the centroid. If the residual is now less than that at $a_i$ the new point is accepted. If not, all points except the one with the lowest residual are moved half way towards the centroid and the process repeats.

Fig. A.1.
FIG. A1

THE NELDER-MEAD MINIMIZATION PROCEDURE

The three starting points $a_1$ to $a_3$ are shown on a contour map with the three new trial points marked by *
A graphic illustration of the way in which the process works is given in Figure A.2.

The new method was applied to the data sets derived from our experiments. Convergence from a plausible trial input (derived by inspecting the data and roughly evaluating base-slope and height, peak position height and width) was fairly slow (c.a. 20 minutes) in BASIC. The FORTRAN version was faster (c.a. 2 minutes). Results for 5 data sets are shown in Tables A.1 and A.2.

<table>
<thead>
<tr>
<th>Data Set #</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5489.36</td>
<td>4638.04</td>
<td>1015.07</td>
<td>1874.05</td>
</tr>
<tr>
<td>B</td>
<td>11082.3</td>
<td>11991.2</td>
<td>5075.37</td>
<td>10622.52</td>
</tr>
<tr>
<td>C</td>
<td>19.0711</td>
<td>20.2828</td>
<td>18.2713</td>
<td>23.8522</td>
</tr>
<tr>
<td>D</td>
<td>.222158</td>
<td>.239845</td>
<td>.249994</td>
<td>.108304</td>
</tr>
<tr>
<td>E</td>
<td>.348464</td>
<td>-.099438</td>
<td>.195465</td>
<td>.021466</td>
</tr>
<tr>
<td>Residual</td>
<td>6.039E6</td>
<td>1.279E7</td>
<td>5.339E6</td>
<td>3.893E7</td>
</tr>
</tbody>
</table>

Table A.1. Gaussian L.S. coefficients.

<table>
<thead>
<tr>
<th>Data Set #</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>251.655</td>
<td>254.673</td>
<td>-319.256</td>
<td>223.065</td>
</tr>
<tr>
<td>B</td>
<td>3012.29</td>
<td>3031.71</td>
<td>179.129</td>
<td>2175.93</td>
</tr>
<tr>
<td>C</td>
<td>18.7898</td>
<td>20.1411</td>
<td>18.0421</td>
<td>23.6111</td>
</tr>
<tr>
<td>D</td>
<td>.159806</td>
<td>.148402</td>
<td>.264559</td>
<td>.143477</td>
</tr>
<tr>
<td>E</td>
<td>-56.8243</td>
<td>-6.47207</td>
<td>-27.6918</td>
<td>-21.7666</td>
</tr>
<tr>
<td>Residual</td>
<td>5.294E7</td>
<td>7.583E7</td>
<td>8.980E6</td>
<td>4.511E7</td>
</tr>
</tbody>
</table>

Table A.2. Lorentzian L.S. coefficients.

In terms of the residuals it is clear that the Gaussian curve provides the best fit to the data. However, inspection
Four successive steps in the minimization process starting from points $a_1$, $a_2$ and $a_3$ are shown.
of the plots of calculated and observed data points suggested that the Lorentzian fit might have converged to a false minimum. A typical example is shown in Figure A.3, where it is seen that the Lorentzian appears to underestimate the data at the lower end.

A number of further runs were made with different starting conditions in the hope that alternative, and better, parameters would be obtained. These were unavailing.

It was next decided to try our own method (71). In essence this takes each of the trial parameters in turn and seeks the value of that parameter which gives the least residual. After cycling through the variables the process is repeated from the start until no further change occurs. The determination of the best variable values is achieved by quadratic interpolation using:

\[ x(i+1) = x(i) + dx(fm - fp)/(2fm - 4f0 + 2fp) \]

where:

\[ fm = f(xi - dx) \]
\[ f0 = f(xi) \]
\[ fp = f(xi + dx) \]

Since it is assumed that the residuals are quadratic functions of position this may lead to divergence when the condition is not satisfied. To avoid this, the programme is
A comparison of two possible line shapes fitted to the ODMR signal from GaP-N showing the deviation of the Lorentzian fit at low field.
so arranged as to take as the next value of \( x_i \) that member of \( x(i+1) \), \( x_i - dx \), \( x_i \), or \( x_i + dx \) which gives the least residual.

The results derived from the operation of this programme, using as starting values those given in Tables A.1. and A.2. are shown in tables A.3. and A.4.

<table>
<thead>
<tr>
<th>Data Set #</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5630.67</td>
<td>4379.02</td>
<td>1019.99</td>
<td>1662.56</td>
</tr>
<tr>
<td>A</td>
<td>11229.3</td>
<td>11960.6</td>
<td>5054.56</td>
<td>10428.8</td>
</tr>
<tr>
<td>B</td>
<td>19.0879</td>
<td>20.2518</td>
<td>18.2207</td>
<td>23.6277</td>
</tr>
<tr>
<td>C</td>
<td>.222943</td>
<td>.241384</td>
<td>.258487</td>
<td>.111812</td>
</tr>
<tr>
<td>D</td>
<td>-8.78307</td>
<td>15.0888</td>
<td>4.72859</td>
<td>19.1017</td>
</tr>
<tr>
<td>E</td>
<td>5.668E6</td>
<td>1.195E7</td>
<td>5.123E6</td>
<td>3.558E7</td>
</tr>
<tr>
<td>Residual</td>
<td>4379.02</td>
<td>11960.6</td>
<td>5054.56</td>
<td>10428.8</td>
</tr>
<tr>
<td></td>
<td>20.2518</td>
<td>18.2207</td>
<td>23.6277</td>
<td>.111812</td>
</tr>
<tr>
<td></td>
<td>.241384</td>
<td>.258487</td>
<td>.111812</td>
<td>19.1017</td>
</tr>
<tr>
<td></td>
<td>15.0888</td>
<td>4.72859</td>
<td>19.1017</td>
<td>3.558E7</td>
</tr>
<tr>
<td></td>
<td>5.668E6</td>
<td>1.195E7</td>
<td>5.123E6</td>
<td>3.558E7</td>
</tr>
</tbody>
</table>

Table A.3. Revised Gaussian L.S. coefficients.

<table>
<thead>
<tr>
<th>Data Set #</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4295.33</td>
<td>3015.40</td>
<td>497.539</td>
<td>-1562.43</td>
</tr>
<tr>
<td>A</td>
<td>5181.97</td>
<td>3796.65</td>
<td>804.270</td>
<td>1298.64</td>
</tr>
<tr>
<td>B</td>
<td>19.0892</td>
<td>20.0000</td>
<td>18.1076</td>
<td>23.4852</td>
</tr>
<tr>
<td>C</td>
<td>.279086</td>
<td>.290409</td>
<td>.334848</td>
<td>.121133</td>
</tr>
<tr>
<td>D</td>
<td>3.40091</td>
<td>-19.4032</td>
<td>-8.86383</td>
<td>-44.7434</td>
</tr>
<tr>
<td>E</td>
<td>4.856E6</td>
<td>1.650E7</td>
<td>5.801E7</td>
<td>3.826E7</td>
</tr>
<tr>
<td>Residual</td>
<td>497.539</td>
<td>804.270</td>
<td>1298.64</td>
<td>.121133</td>
</tr>
<tr>
<td></td>
<td>18.1076</td>
<td>23.4852</td>
<td>.121133</td>
<td>-44.7434</td>
</tr>
<tr>
<td></td>
<td>.279086</td>
<td>.290409</td>
<td>.334848</td>
<td>3.826E7</td>
</tr>
<tr>
<td></td>
<td>3.40091</td>
<td>-19.4032</td>
<td>-8.86383</td>
<td>3.826E7</td>
</tr>
</tbody>
</table>

Table A.4. Revised Lorentzian L.S. coefficients.

It is evident that the IA5 and IA6 Lorentzian coefficients have changed completely. Also it will be seen that whilst the residuals for IA6 to IA8 still show that the Gaussian version is superior, the difference is not so great as before. In addition, for IA5, the Lorentzian now gives a
lower residual although by a very small amount.

STATISTICAL ANALYSIS

The standard Chi-square test for goodness of fit is not applicable to data of the type involved in our experiments since they do not involve frequencies. It was therefore decided to compute the correlation coefficients, defined by:

\[ r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \]

A.3.

where the \( x_i \) are calculated values and the \( y_i \) are the observed values. In practice A.3. is used in the form:

\[ r = \frac{\sum x_i y_i - (\sum x_i)(\sum y_i)/N}{\sqrt{\left( \sum x_i^2 - (\sum x_i)^2/N \right) \left( \sum y_i^2 - (\sum y_i)^2/N \right)}} \]

This reduction is satisfactory so long as \( r \) is not so small that cancellation results in loss of accuracy.

The 95% confidence limits on \( r \) can be derived using Fisher's transformation (74) to normal form:

\[ z = \log((1+r)/(1-r))/2 \]

The results are shown in Table A.5.
<table>
<thead>
<tr>
<th>Gaussian</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper 95%</td>
<td>.996</td>
<td>.992</td>
<td>.981</td>
<td>.980</td>
</tr>
<tr>
<td>r</td>
<td>.994</td>
<td>.989</td>
<td>.973</td>
<td>.973</td>
</tr>
<tr>
<td>Lower 95%</td>
<td>.992</td>
<td>.984</td>
<td>.961</td>
<td>.964</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lorentzian</th>
<th>IA5</th>
<th>IA6</th>
<th>IA7</th>
<th>IA8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper 95%</td>
<td>.997</td>
<td>.992</td>
<td>.984</td>
<td>.984</td>
</tr>
<tr>
<td>r</td>
<td>.995</td>
<td>.985</td>
<td>.969</td>
<td>.971</td>
</tr>
<tr>
<td>Lower 95%</td>
<td>.993</td>
<td>.970</td>
<td>.939</td>
<td>.949</td>
</tr>
</tbody>
</table>

Table A.5. Correlation coefficients and conf. limits.

It is clear that in the cases of IA5-IA8 the Gaussian curve gives superior correlation, although the difference is small. The difference for IA5 is in the reverse sense, however the difference is so small that the result is not significant. This conclusion is supported by the values of the hypothesis test statistic (74):

\[ H_0 = \frac{(z_1 - z_0)}{\sigma_{z_1} - z_0} \]

where \( \sigma_{z_1} - z_0 = \sqrt{\frac{1}{N-3} + \frac{1}{N-3}} \)

The values are:

| IA5 | .316 |
| IA6 | .661 |
| IA7 | .256 |
| IA8 | .175 |

which supports the assertion that the Gaussian and Lorentzian fits are not significantly different at the 95%
level which is accepted as the least for which this statistic is valid.

In addition it may be remarked that the base-line slope for IA5 is negative for both Gaussian and Lorentzian fits. This is contrary to established fact and is probably due to the wide dispersion of the data points at the high frequency end of the curve as shown in Figure A.4.
Another set of GaP-N ODMR data fitted by Gaussian and Lorentzian line shapes.
Bibliography

4. Cavenett, B.C., J. Luminescence 18/19, 846 (1979)


25. Dean, P.J., J. Luminescence 7, 51 (1973)


29. Title, R.S., Phys. Rev. 154, 668 (1967)


38. Czaja, W., Festkorperprobleme 11, 65 (1971)


40. Dean, P.J., J. Luminescence 1/2, 398 (1970)


52. Merz, J.L., Phys. Rev. 176, 961 (1968)
64. Tamura, H., Solid State Comm. 10, 297 (1972)
74. Fisher, R.A., METRON 1, 3 (1921)
77. Lax, M., Phys. Rev. 119, 1502 (1960)
78. Czaja, W., Phys. d. kondensierten Materie. 12, 226 (1971)
79. Faulkener, R.A., Phys. Rev. 175, 991 (1968)
PUBLICATIONS


I. Booth "Non-equilibrium effect in electromagnetic resonators". Speculation in Science and Technology (Accepted 1984)


S. Fong, W. Keeler, and I. Booth "Pressure dependent Hall effect measurements in InSb", 1979 Congress of the CAP