HIGH RESOLUTION LASER SPECTROSCOPIC STUDIES OF DEFECTS AND IMPURITIES IN CRYSTALLINE SOLIDS

By

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DECLARATION

The contents of this thesis are my own work, except where indicated. The work was conducted while I was a full time graduate student at the Australian National University. This thesis has never been submitted to another university or similar institution.

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June 1989
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ABSTRACT

This thesis is an account of studies of impurities and defects in crystalline solids using high resolution laser spectroscopy. Though conventional spectroscopic techniques such as absorption and emission investigations provide introductory data for some of the studies, the thesis relies on recently developed techniques, which utilise high resolution tunable dye lasers to excite electronic transitions in solids, such as spectral holeburning and Raman heterodyne detection. Chapter one provides an introduction to these techniques as well as an overview of the theory underlying the nature of electronic transitions in solids.

Chapter two is a study of magnesium related uranium-oxygen complexes in lithium fluoride and utilises a pulsed laser to carry out polarised selective excitation and emission experiments. Group theoretical methods are applied to the resulting electronic and vibrational spectra to establish the structure and symmetry of the centres.

The substitutional uranium centre in strontium and barium tungstate is the subject of a high resolution holeburning investigation, detailed in chapter three. This represents the first observation of persistent spectral holeburning in an actinide doped crystal. High resolution Zeeman holeburning studies show the centre to be of lower symmetry than previous workers had concluded and line profile studies have determined the mechanism to be photophysical, involving a reorientation of the uranium ion between two sites.

Two photon persistent holeburning is observed in a samarium centre in calcium sulphate and this is described in chapter four. Transient holes are also burnt in the zero phonon lines of two samarium centres and these are interpreted in terms of optical pumping amongst nuclear hyperfine ground state levels and excited state absorption.

The depth of a transient hole burnt in the N-V centre in diamond is found to exhibit sudden changes for particular magnetic field strengths and orientations.
This effect is described in chapter five and is explained as being due to enhanced ground state spin-spin cross relaxation between optically active centres and other defect centres. This occurs when ground state splittings in the two spin reservoirs are resonant and causes the effect of optical pumping to be reduced. A dip in transmission is also observed when the magnetic field is close to a \( <111> \) crystal direction, at the level anticrossing field. This is interpreted as being due to a reduction in optical pumping caused by state mixing.

In chapter six, the N-V diamond centre is used to observe electron paramagnetic resonance using the Raman heterodyne technique for the first time. Signals are observed up to the instrumental limit of 1 GHz and radio frequency power broadening effects are observed. Transient electron spin effects such as nutation, spin echoes and free induction decay are also observed for the first time using Raman heterodyne detection.
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CHAPTER ONE

AN INTRODUCTION TO THE THEORY AND TECHNIQUES OF HIGH RESOLUTION LASER SPECTROSCOPY

1A PREFACE

The names of Newton and Einstein are synonymous with the greatest of breakthroughs in classical and modern physics. The field of laser spectroscopy is no exception. As early as the seventeenth century, Newton could be said to have undertaken the first spectroscopic study when he split sunlight into its component colours using a prism. A quarter of a millennium later, Einstein laid down the principles of spontaneous and stimulated emission, the theoretical cornerstones on which laser operation is based. It was only forty years later that Maiman achieved lasing action for the first time and, in the thirty years since then, laser engineering has advanced to the stage that commercially available models can produce indefinite beams of tunable, coherent radiation with linewidths of as little as 1 MHz.

It is conceivable that Newton could have split the visible spectrum to produce a light source capable of being tuned to one of, say, a hundred components. Advances over the following three hundred years produced monochromators which could do ten thousand times better. Commercially
available dye lasers, such as those used in this study, can split the visible spectrum into a thousand times more components and specially stabilised lasers, built in laboratory conditions, can resolve many orders of magnitude more, though these are rarely tunable, and, as such, are of little use to the spectroscopist.

Not only do such lasers have significantly narrower bandwidth than previous spectroscopic tools but they can produce a much stronger beam at a greatly improved efficiency. To produce 50 mW of light with a 1 MHz linewidth, a monochromator would require an input white light power of greater than ten million watts, an unfeasible demand. The dye lasers used in this study may produce such an output when pumped by a 5 W argon ion laser.

The spectroscopist does not merely capitalise on the laser engineer, however. The contributions spectroscopists have made and continue to make to laser advancement are, in themselves, substantial. Technological improvements in laboratory hardware have opened up an enormous field of spectroscopic study. The invention of the laser and its advancement have certainly not only allowed the spectroscopist to add further significant figures to existing results but it has allowed new techniques to investigate previously inaccessible phenomena.

This thesis details five studies of crystalline solids which would have been technologically impossible fifteen years ago. Each utilises a range of lasers to optically excite electronic transitions within the solid. The analysis of excitation and emission and the effect of further perturbations have allowed, through the principles of quantum mechanics and group theory, the structure of and dynamic processes within the solids to be determined.

In this study, high resolution techniques will be referred to as methods for which the experimental resolution is less than the inhomogeneous linewidths of the electronic transitions in the solid. Low resolution techniques are generally limited by monochromator slit widths which generally broaden features such that only inhomogeneous linewidths may be resolved though, in this study, these methods still employ sophisticated equipment such as pulsed dye lasers.
In chapter two, a study of magnesium related uranium-oxygen complexes in lithium fluoride is described. Though the main part of this study is not strictly high resolution, it is included as an example of a low resolution spectroscopic study which is invariably carried out to categorise materials such that worthwhile high resolution techniques may be applied in a logical sequence. In this case, high-resolution techniques fail to reveal any new information though the low resolution polarisation data reveals much that was unknown about the centres.

A similar pulsed laser categorical study confirms earlier workers' results for uranium doped strontium and barium tungstate in chapter three. High resolution studies show that persistent holes can be burnt in the zero phonon lines. Magnetic fields are applied to the crystal and the resulting hole splittings are used to correct earlier workers' conclusions about the position of the uranium ion within the crystal structure. The holeburning mechanism is, in itself, of interest and, in this case, a reversion to low resolution techniques provides the data to model the effect.

Chapter four demonstrates two further high resolution holeburning techniques. Samarium centres in calcium sulphate are shown to exhibit transient spectral holeburning effects and one centre is shown to exhibit two photon spectral holeburning, a property which makes the material a candidate for high density information storage. Once again the holeburning mechanisms are of interest and reveal information about processes within the solid.

High resolution transient holeburning is used as a meter to gauge the rate of dynamic processes within a diamond in chapter five. This technique is simple but is a new method for investigating interactions between different sets of centres in solids and may be applicable to studies of other systems. In the case studied here, of the N-V centre, the nature of the ground state is determined, clarifying previous contradictory reports about the centre.

A second new effect is observed in the N-V centre in diamond. This is Raman heterodyne detection of electron paramagnetic resonance. This is a non-linear, coherent beating effect which relies on a high resolution laser beam to
excite optical transitions within the solid as well as a radio frequency field to excite transitions in the split ground state. Chapter six details the success of this technique and of the same detection method to observe spin transient effects.

The remaining two sections of this chapter deal with an introduction to the theory of electronic interactions in solids, which result in laser spectroscopy being such an invaluable investigative tool and a general description of the techniques of laser spectroscopy used to investigate these interactions.

1B ELECTRONIC INTERACTIONS IN SOLIDS

1B(i) Determination of energy levels in atoms

Crystalline solids are a regular arrangement of atoms in a three dimensional structure. Consequently, to determine the energy levels of a crystalline solid, it is instructive to first consider the energy levels of an atom, before introducing the effects of the crystal field.

The Hamiltonian for an atom containing more than a few electrons is complex and solutions to Schrödinger’s equation may only be found through a succession of approximations. The electrostatic component of the Hamiltonian, for an atom having i electrons and Z protons may be written as,

\[
H = \sum_i \left( \frac{\hbar^2}{8\pi^2m} \Delta_i - \frac{1}{4\pi\varepsilon_0} \frac{Z\varepsilon^2}{r_i} + \sum_{j<i} \frac{1}{4\pi\varepsilon_0} \frac{\varepsilon^2}{r_{ij}} \right) \tag{1.1}
\]

where \(m\) and \(\varepsilon\) are the electronic mass and charge respectively, \(r_i\) is the distance between the point nucleus and the \(i\)th electron and \(r_{ij}\) is the distance between the \(i\)th and \(j\)th electrons. The three terms in the expression represent the electronic kinetic energy, the electron-nuclear potential energy and electron-electron potential
These electrostatic interactions are the dominant terms in all atomic Hamiltonians and their solution gives rise to a large range of energy level gaps, which includes gaps which may be excited optically, that is, those of tens of thousands of wavenumbers. Even such a simple expression is difficult to solve due to the complexity of the third term. It is the outer, less tightly bound electrons which give rise to the optical phenomena observed in this study. Approximations are required, therefore, to simulate the shielding effect of the inner electrons on the outer electrons. The second and third terms may then be considered as a single potential due to the nucleus and inner electrons acting on the outer electrons.

Additional interactions are weaker and may be considered as perturbations of the electrostatic Hamiltonian. Many of these perturbations are due to interactions between the electron spin magnetic moment and magnetic fields which are produced by atomic processes.

The largest of these is spin-orbit coupling which makes a contribution to the Hamiltonian of hundreds of wavenumbers. It can be shown (Cagnac and Peyroula 1975) that this interaction energy is given by,

$$\Delta E = \frac{\hbar^2}{8\pi^2 m^2 c^2} \left[ \frac{1}{r} \frac{\partial W}{\partial r} \right] l.s \quad (1.2)$$

where $W$ is the electrostatic potential energy and $l$ and $s$ are the electron's orbital and spin angular momentum respectively. Where the atom has several electrons, the situation is, once again, greatly complicated. Assumptions as to the method of coupling between angular momenta produce different values for the Hamiltonian. Here, techniques such as laser spectroscopy become particularly useful to understand the form of the coupling. The fine structure of an optical transition may be investigated, whether or not the exact nature of the Hamiltonian is known, to reveal information about the spin-orbit coupling from the order of the
splitting and its magnitude. Such an effect may be observed in the emission spectrum of CaSO$_4$:Sm$^{2+}$ (see section 4A(ii), Danby et al 1988) though no reference is made to the Hamiltonian in this study as the spin-orbit coupling in Sm$^{2+}$ is well understood.

Having accounted for the spin-orbit interaction and its appearance spectroscopically, as fine structure, the hyperfine structure may be considered. This term in the Hamiltonian is due to the interaction of the nuclear magnetic moment, $I$, with the magnetic field due to the atomic state's total electronic spin magnetic moment, $J$. It has the form,

$$\Delta E = A I J \quad (1.3)$$

where $A$ is the hyperfine coupling tensor. Once again, laser spectroscopy is an appropriate tool with which to investigate this term. Nuclear effects are small, typically less than one wavenumber and high resolution lasers are appropriate to study them. In chapter five, the hyperfine structure of the P1 colour centre in diamond is observed and in chapter six, the hyperfine structure of the N-V colour centre in diamond is observed. These interactions have been explained previously but a knowledge of the nature of this effect has allowed an explanation of two radically different processes in the N-V centre. Similarly, in chapter four, a knowledge of the hyperfine splitting in CaSO$_4$:Sm allows an explanation of transient spectral holeburning in terms of optical pumping (see section 1C(iv)). The nature of the hyperfine interaction is such that a nucleus with nuclear spin, $I$, is split into $2I+1$ degenerate levels. This degeneracy may be lifted by a perturbation. The N-V centre, for instance, has a triplet spin ground state and, therefore, as the total angular momentum, $L$, is zero, the states, when split by a magnetic field (see section 1B(iii)), are characterised by $m_L = m_S = 0$ or $\pm 1$. The $S=\pm 1$ states are split into three components by the hyperfine interaction. The $S=0$ state remains a singlet as there can be no coupling between a nuclear magnetic moment and a
state having no angular momentum and, therefore, no associated magnetic field.

Other nuclear interactions such as superhyperfine and quadrupole terms may add to the Hamiltonian and the solution of Schrödinger’s may be complicated by taking into account relativistic effects. These effects are not directly encountered in this study.

The complexity of the Hamiltonian has been briefly illustrated. It is clear that a solution of the complete Schrödinger equation is rarely possible, especially in solids for which a further term will be added to the Hamiltonian in the next section. Optical spectroscopy investigates only a portion of the range of eigenvalues. The experimental results of this study are sufficient to draw conclusions as to the general nature of all wavefunctions, however, through the knowledge obtained about the optically allowed transitions and centre symmetries.

1B(ii) Determination of energy levels in impurity ions and colour centres in solids

The principles which apply to the calculation of the energy levels of free atoms also apply to impurity ions in solids and to colour centres. In the case of an impurity ion, the Hamiltonian is identical to that of an atom with the addition of a term to account for the influence of the crystal field. Colour centres are physically different from impurity ions in that they are composed of one or more electrons localised close to a defect. They may be regarded as being bound to the positively charged centre and have a spectrum of energy levels analogous to impurity ion centres. This spectrum usually consists of energy level separations in the visible range, thus colouring the solid, as for the N-V centre which colours diamond rose.

The effect of the crystal field on a free ion is to reduce its symmetry from isotropic to that of the site. The Hamiltonian must transform as the totally symmetric representation, that is, the energy eigenvalues, \( \langle \psi | H | \psi \rangle \), must be unchanged by a group operation corresponding to the point symmetry of the ion. Every ion must
be positioned at a site described by one of the thirty-two point groups. The properties and symmetry of the groups are well understood and documented (for instance, Koster et al. 1963) and application of this information to laser spectroscopic data provides a powerful tool with which to determine the nature of the centre, its symmetry and the form of its wavefunctions.

The application of group theory to the quantum mechanics associated with optically excited centres is thus essentially concerned with the symmetry properties of the Hamiltonian and the degeneracy of the energy levels. Indeed, all degeneracy in a system is due to symmetry, excepting accidental degeneracy. Again, the exact Hamiltonian need not be known for substantial conclusions to be reached about the solid under investigation.

Consider the spin triplet ground state of the N-V centre, for instance (see chapters 5 and 6). If the centre could, notionally, be isolated in an isotropic environment, the three spin levels would be degenerate. In diamond, however, only the \( |+\rangle \) and \( |-\rangle \) levels are degenerate, split from the \( |0\rangle \) level by 2.88 GHz. This simple observation immediately rules out the centre symmetry from being many of the point groups of lowest symmetry, for which degenerate levels may not exist, and the five cubic point groups whose crystal field would not split a triply degenerate spin system. To determine the exact symmetry of the centre, further observations are required to which similarly simple group theoretical considerations may be applied.

Laser spectroscopy relies on the absorption of a photon by a centre and its subsequent relaxation through spontaneous emission or some other process. Excitation is stimulated by the electric or magnetic component of the laser field but transitions between all energy levels are not allowed. For a given system, the transition probability for two states, \( \psi_1 \) and \( \psi_2 \), stimulated by an operator, \( O \), is proportional to \( \left| \langle \psi_1 | O | \psi_2 \rangle \right|^2 \) (Corney 1977). If this is equal to zero then the transition is forbidden.

Typically, magnetic and electric dipole operators produce different sets of
allowed transitions. These sets may be obtained through the application of group theory. Except for the case of accidental degeneracies which are not concerned with symmetry considerations, each energy level corresponds to a single irreducible representation of the group. Furthermore, operators may be expressed in terms of the irreducible representations of the group. It can be shown (Leech and Newman 1969) that the transition probability is only non-zero if the direct product of the initial and final energy level representations and that corresponding to the operator contain the totally symmetric irreducible representation, $\Gamma_1$. This statement is often referred to as the fundamental selection rule and has its physical basis in that any observable phenomenon, such as photon absorption, must be unaffected by symmetry operations which leave the centre unperturbed. Group theoretical tables contain information on irreducible representations and the bases of electric and dipole operators. Application of these selection rules to spectroscopic data is a quick and easy way of interpreting data (see chapter 2).

That electric and magnetic dipole allowed transitions form different sets is apparent from the form of the operators. The electric dipole term in the Hamiltonian is given by $e \mathbf{r} \cdot \mathbf{E}$ where $\mathbf{E}$ is the electric vector of the laser field. The magnetic dipole term in the Hamiltonian is given by, $\mu \mathbf{H}$, where $\mathbf{H}$ is the magnetic vector of the laser field and the magnetic dipole operator is given by,

$$\mu = \frac{e}{mc}(L+2S) \quad (1.4)$$

The electric dipole operator is radial and the magnetic dipole operator is axial thus causing the corresponding irreducible representations to be different and two sets of selection rules result. Furthermore, it can be shown through a consideration of the relative magnitudes of the electric and magnetic vectors in electromagnetic fields and their influence on the Hamiltonian (Loudon 1973), that, in the case of a transition allowed due to both electric and magnetic dipole stimulation, the electric dipole transition will be stronger by a factor of $2\varepsilon_0 \hbar c/e^2$, the fine structure constant
(about 137). This complicates spectroscopic analysis when an electric dipole is expected to be forbidden. The states need only be slightly admixed for the forbidden electric dipole transition to become stronger than the allowed magnetic dipole transition.

Excitation and relaxation processes in solids also take place via phonon processes. Once again, the analysis of spectra in which excitation and emission processes are coupled to phonons may be interpreted using group theory. Molecular vibrations, relating to only the centre itself, may be calculated and labelled and applied to the situation in which the molecule is held in a solid. These vibrations are constrained by the nature of the centre and hence an analysis of the spectra reveals information about the symmetry and structure of the solid. This is illustrated by the information gleaned about the \( C_{4v} \) magnesium related centre in lithium fluoride (see section 2C(ii)).

1B(iii) The Effect of Magnetic Fields on Energy Levels in Solids

In the same way that the crystal electric field perturbs the isotropic Hamiltonian, an externally applied magnetic field may further perturb the Hamiltonian of a centre within a solid. The effect of such a perturbation may be calculated through a direct solution of the total Schrödinger equation but this has already been shown to be a complex process. A more realistic approach is to combine experimentally known data with group theoretical techniques.

Where a system of several interacting energy levels occurs, a matrix technique simplifies the algebra. Consider a three level system for which the unperturbed energy levels are known. Schrödinger's equation may be written as,

\[
\begin{bmatrix}
\psi_1 \\
\psi_2 \\
\psi_3
\end{bmatrix}
= \begin{bmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 & 0 \\
0 & 0 & \varepsilon_3
\end{bmatrix}
\begin{bmatrix}
\psi_1 \\
\psi_2 \\
\psi_3
\end{bmatrix}
\]

(1.5)
where $\psi_i$ are the unperturbed Hamiltonian's eigenfunctions and $\varepsilon_i$ are the corresponding energy eigenvalues.

A Zeeman perturbation adds matrix elements of the form $\langle \psi_i | \mu \cdot H | \psi_j \rangle$ to both sides of the equation. Group theory allows each matrix element to be determined using the fundamental selection rule (see previous section) and tables of Clebsch-Gordan coefficients. Diagonalisation of the new energy matrix yields the new energy eigenvalues.

Consider two examples. Firstly, the application of a magnetic field along the z-axis of the N-V centre (see chapters 5 and 6). This perturbation has $\Gamma_2$ irreducible representation in $C_{3v}$ symmetry. It is known that the ground state is a spin triplet consisting of a singlet and a doublet, and the components of the irreducible representations are $\Gamma_2$, $\Gamma_3^+$ and $\Gamma_3^-$ respectively. Clebsch-Gordan coupling coefficients are given in standard group theoretical tables (for instance, Koster et al 1963) and show that only two matrix elements are non-zero, resulting in a new energy matrix,

$$
\begin{pmatrix}
|+\rangle & |0\rangle & |-\rangle \\
\Gamma_3^+ & \Gamma_2 & \Gamma_3^- \\
\end{pmatrix}
$$

$$
\begin{pmatrix}
\langle+| & \Gamma_3^- & D/3 + \mu \cdot H \\
\langle0| & \Gamma_2 & 0 \\
\langle-| & \Gamma_3^+ & 0 \\
\end{pmatrix}
$$

where $D$ is equal to 2.88 GHz, the singlet-doublet zero-field splitting (zero of energy is arbitrary). The matrix is diagonal and substitution yields a linear splitting of the $|+\rangle$ and $|-\rangle$ levels, a linear Zeeman effect, and no change to the $|0\rangle$ spin level. High resolution, non-linear techniques are ideal to confirm these conclusions (see chapter 6).

A second example is the uranium impurity ion centre in strontium tungstate (see chapter 3). Three excited energy levels, with experimentally determined $\Gamma_2$, $\Gamma_1$
and $\Gamma_2$ irreducible representations respectively, are spaced by 16 and 160 cm$^{-1}$. The centre has $C_2$ symmetry and a field is applied along the local $z$-axis ($\Gamma_1$ perturbation). Defining the lowest excited state to be the energy zero, the perturbed matrix is,

\[
\begin{pmatrix}
\Gamma_2 & 0 & \mu \cdot H \\
0 & \Gamma_1 & 0 \\
\mu \cdot H & 0 & \Gamma_2
\end{pmatrix}
\]

On axis terms are zero due to a further symmetry consideration, that of time reversal. Diagonalisation, given that $\mu \cdot H <<< 160$ cm$^{-1}$, gives final energy eigenvalues of $-(\mu \cdot H)^2/(160 \text{cm}^{-1})$, 16 cm$^{-1}$ and 160 cm$^{-1}$ + $(\mu \cdot H)^2/(160 \text{cm}^{-1})$. The splitting of the outer energy levels is quadratic but, at experimentally obtainable magnetic fields, much smaller than typical linear Zeeman effect splittings. Only high resolution techniques are able to resolve such shifts.

Note that $\mu$ may be evaluated from theoretical considerations or experimental considerations derived from spectroscopic data and is often expressed in terms of $g$, the Landé $g$-factor which accounts for terms in $L$ and $S$, and $\mu_B$, the Bohr magneton.

**1B(iv) Lifetimes and linewidths of transitions between energy levels in solids**

It has been shown (Corney 1977) that the transition probability for two states, $\psi_1$ and $\psi_2$, induced by an operator, $O$, is proportional to $|\langle \psi_1 | O | \psi_2 \rangle|^2$. The process of relaxation to the original state through spontaneous emission is proportional to this excitation probability (Corney 1977) and a phenomenological decay time is assumed. It is sufficient to say, therefore, that the spontaneous
emission decay time is short for transitions that have large excitation (or stimulated emission) probabilities and vice versa.

It is often the case, however, that the lifetime of a state may be shortened by phonon emission. Consider the usual case of a centre having several closely separated (10 - 1000 cm\(^{-1}\)) excited states and an energy separation between the ground state and lowest excited state corresponding to an optical photon. At helium temperatures, excitation, to all but the lowest of excited states, would result in rapid phonon spontaneous emission and relaxation of the centre to the lowest excited state with a time constant of, typically, around \(10^{-10}\) seconds. The lowest excited state is not able to emit single phonons to relax to the ground state as the density of states for phonons is zero at such high frequencies. Multiphonon spontaneous emission may occur but, as many phonons must be emitted spontaneously, this is much less likely and the lifetime rises to, typically, \(10^{-4}\) seconds. This is known as a metastable state.

Possible phonon modes may be calculated from group theoretical considerations of the lattice and, therefore, vary between solids. Consequently, the effect of phonons on a metastable lifetime is hard to determine. The lifetime of the optically excited state in the diamond N-V colour centre (see chapters 5 and 6) is 13 ns (Reddy 1989). The transition probability is known to be high and the lifetime may be concluded to be little affected by multiphonon emission. In the uranium centre in strontium tungstate (see chapter 3), however, the lifetime of the lowest excited state is 20 \(\mu\)s. The transition has a lower probability, resulting in a longer lifetime, but this may now be reduced by multiphonon emission which reduces the excited state population thus quenching the photon emission. Higher excited states of the strontium tungstate uranium centre have much shorter lifetimes due to spontaneous emission of one or only a few phonons of low energy, for which the density of states is high, and evidenced by their broader homogeneous linewidths.

The homogeneous linewidth is the broadening of a transition within any single centre and is constant for all similar centres. The homogeneous linewidth,
\( \Gamma_h \), of a transition is related to the optical dephasing time, \( T_2' \), of the system by, \( \Gamma_h = 1/\pi T_2' \), where \( T_2' \) is given by,

\[
\frac{1}{T_2'} = \frac{1}{2T_1} + \frac{1}{T_2^\phi}
\]  

(1.8)

where \( T_1 \) is the state lifetime as given by considerations already discussed above and \( T_2^\phi \) is the dephasing time due to interactions which cause the wavefunction of the excited state to dephase but not decay to another state (Macfarlane et al 1983). Typical of such processes are interactions with nuclear and electron spins.

Metastable homogeneous linewidths are typically less than 1 MHz whilst excited states immediately higher in energy may be homogeneously broadened to many GHz. This is the case for the uranium centre in strontium tungstate (see section 3C(i)).

The energy levels in a solid are influenced by the crystal field (see section 1B(ii)). As most crystals are formed at temperatures greater than room temperature, there will be a distribution in the exact crystal field for each similar centre. Consequently, the energy levels will be slightly different for each centre though the homogeneous broadening for all will be equal. The strain is normally distributed and, the transition will appear to have a Gaussian lineshape with an inhomogeneous linewidth, \( \Gamma_i \), of, typically, many GHz. For metastable levels, this will be composed of many overlapping homogeneous transitions (figure 1.1) though homogeneous broadening may dominate for some higher excited states which results in Lorentzian lineshapes.

Traditionally, only inhomogeneous lineshapes have been within the range of the resolution of spectroscopic instrumentation. Hyperfine structure could rarely be resolved and little could be said about dynamic processes within solids. The advent of the high resolution laser has allowed the homogeneous linewidth to be accessible and, consequently, investigations to be made on a range of previously
Figure 1.1 The Gaussian line profile of an electronic transition in a solid. The transition for each individual centre has a Lorentzian lineshape with linewidth, $\Gamma_h$. Each centre experiences a slightly different crystal field due to lattice imperfections which cause the transition frequencies to vary. The overall lineshape is composed of the sum of individual centres and is thus inhomogeneously broadened to a linewidth, $\Gamma_i$. (*line drawing from Macfarlane and Shelby 1987*)
inaccessible processes. The following section describes the techniques used to do this.

1C TECHNIQUES IN HIGH RESOLUTION LASER SPECTROSCOPY

1C(i) Selective excitation and emission

The absorption, excitation and emission spectra of solids at low temperatures consist of a series of sharp lines, at frequencies corresponding to electronic transitions, and bands, at frequencies corresponding to phonon assisted transitions. Such spectra may be obtained using traditional techniques using white light sources and monochromators. Much information may be gleaned through interpretation of these spectra and, though high resolution lasers may now probe within inhomogeneously broadened transitions to examine homogeneous effects, such investigations are still invaluable as a preliminary step to a high resolution study.

Pulsed tunable dye lasers now make this technique a simpler task when combined with boxcar integrator analysis. The principles of this method are illustrated in figure 1.2. The laser produces a pulse of light which is incident upon the crystal. The emission from the crystal is dispersed by the monochromator and detected by the photomultiplier. To avoid laser scatter from being detected, the potential to the first dynode is turned on shortly after the laser pulse has finished. The signal from the photomultiplier is processed by the boxcar integrator. The period of integration is chosen to be long but no greater than a few lifetimes of the excited states being investigated to prevent background light from comprising a significant component of the signal. Alternatively, a very short period of integration may be chosen and the delay between the laser pulse and integration may be varied. The decay of the boxcar signal yields the excited state lifetime.
Figure 1.2 (a) Schematic diagram for selective excitation (laser frequency is fixed and monochromator is scanned) and selective emission (monochromator is fixed and laser frequency is scanned). (b) Schematic timing diagram. For selective excitation and emission $t_2$ is large as illustrated. For lifetime measurements $t_2$ is small and $t_1$ is varied.
A typical characterisation proceeds through three stages. Firstly, the monochromator is set to detect emission at all frequencies and the laser frequency is scanned. The resulting spectrum shows all excitations in the frequency range chosen.

The laser may now be tuned to a feature of the zero order excitation spectrum. The monochromator is then scanned so that an emission spectrum is obtained. This process is known as selective excitation. Zero phonon lines of the same centre will give similar emission spectra and the features of the zero order spectrum may be separated into sets belonging to different centres.

These individual excitation spectra may be isolated by using selective emission. Here, the monochromator is set to detect emission at a given frequency and the laser frequency is scanned.

More sophisticated techniques may be applied using these general principles once this process is complete. Chapter 2 illustrates how interfering spectra may be isolated and how repetitions of the same technique using different exciting and detecting polarisations gives further information on the nature of the centre, its energy levels and the transitions between energy levels.

1C(ii) Fluorescence line narrowing

The pulsed laser is regarded as being a low resolution instrument for spectroscopic categorisation of materials as described in the previous section. The linewidth of the pulsed laser used in this investigation (see section 2B) was only 10 GHz, however. Though this resolution is rarely useful in investigating homogeneous linewidths, it is narrower than the inhomogeneous linewidth of many zero phonon lines and may, therefore, be used as a high resolution tool. One such application is fluorescence line narrowing.

Fluorescence line narrowing (Denisov and Kizel 1967, Szabo 1970) relies on exciting only part of the inhomogeneous line with a pulse of laser radiation. The
time evolution of the resulting fluorescence may then be studied using techniques similar to those described for lifetime measurements in the preceding section. The boxcar integrator is set to various delays whilst the monochromator is scanned over the resonant inhomogeneous line. The variation in spectra with time delay reveals information on excited state processes, such as interactions between centres experiencing slightly different crystal potential and with hyperfine levels.

This technique is useful to resolve features of lines which may be obscured by inhomogeneous broadening. For instance, in the uranium centre in barium tungstate, the two lowest energy levels may not be resolved due to strain broadening. By exciting a small part of the higher energy level, the fluorescence of only a small portion of the centres could be detected. As both energy levels were similarly affected by their specific crystal field environment, the fluorescence from each level is similarly narrowed and could be resolved (see section 3A(ii)).

Fluorescence line narrowing is still limited by the resolution of the monochromator but is useful to resolve features obscured by inhomogeneous broadening but accessible by fluorescence dispersion apparatus.

1C(ii) Persistent spectral holeburning

Detection of fluorescence line narrowing, in ruby (Szabo 1970), was the first demonstration that the inhomogeneous linewidth of transitions in solids could be penetrated. The advent of high resolution tunable dye lasers has enabled homogeneous linewidths to be studied in many solids and, for those solids in which persistent spectral holeburning occurs, such homogeneous linewidth studies become a simpler task.

Persistent spectral holeburning refers to an optical process in which centres are excited but fail to relax to their original ground state during a period greater than the excited state lifetime. Subsequent irradiation of these altered centres at the original laser frequency is no longer resonant, the centre may not be
excited and, therefore, no emission may be detected. If the laser is held at a constant frequency for a long enough period, it is possible to alter sufficient centres to substantially reduce the absorption and, therefore, the excitation signal strength. That part of the inhomogeneous lineshape with anomalously low absorption is known as a spectral hole.

For a transition homogeneously broadened over a greater frequency than the laser linewidth, the width of the spectral hole is, ideally, twice the homogeneous linewidth. The laser interacts with a spectral range equal to one homogeneous width thus removing these centres from the absorption line. When the laser frequency is then scanned to record the new lineshape, the probe beam also interacts with centres having a spectral range equal to one homogeneous width thus producing a spectral hole with a width double the homogeneous width (figure 1.3). Other broadening mechanisms may prevent this relationship from being exact and, in the case that the homogeneous linewidth of the transition is narrower than the laser linewidth, the hole width may be limited by laser jitter.

Persistent spectral holeburning was first observed in organic solids (Gorokhovskii et al 1974, Kharlamov et al 1974) and has since been shown to occur in a host of other materials. Comprehensive reviews of the work in this field already exist (Moerner 1988).

The mechanism for such holeburning effects may be divided into two categories. Photochemical holeburning refers to a photoinduced change in the chemical composition of the centre. Most commonly this refers to ionisation of an impurity ion but other mechanisms include bond breaking, bond reorientation, known as tautomerisation, and bond changing, known as isomerisation.

Photophysical holeburning occurs when a centre reorients itself with respect to its local environment. This is shown to be the case for the uranium centre in strontium tungstate in this study (see chapter 3).

Both of these mechanisms may produce unstable new centres. The energy required to induce the change is equal to one visible photon. It is uncommon,
High resolution lasers are capable of exciting a single, or a very few, homogeneous lines, within an inhomogeneously broadened envelope. The non-resonant emission from the resulting electronic decay may be detected, using a filter or spectrometer, by a photomultiplier. By steadily varying the laser frequency, the excitation line shape of the inhomogeneously broadened energy level may be obtained.

Under certain circumstances continued excitation at a particular frequency causes a chemical or physical change to the structure of the centre which is being excited. This causes a lack of absorption in the line profile at this frequency. This lack of absorption is known as a SPECTRAL HOLE.

The high resolution laser causes a small section of the inhomogeneous line, over which it may be scanned, to appear to have a constant absorption and, therefore, excitation signal. When a section of line containing a spectral hole is scanned, the total emission varies as shown.

Figure 1.3 Persistent spectral holeburning.
therefore, for a centre to be completely ionised or radically altered physically and
the stabilisation energy, the energy difference in ground states before and after
holeburning, is frequently much less than the energy of the photon which induces
the change. Consequently, many photoinduced changes are reversible and almost
all are reversed by thermal cycling above helium temperatures. Even at helium
temperatures such holes have a finite lifetime caused by thermal reversal of the
holeburning process.

Selective two photon persistent holeburning is an exception. Here a high
resolution laser selectively excites centres in a solid. A second beam interacts with
the excited centres and causes a photochemical or photophysical change.
Subsequent investigation of the zero phonon line, using only the high resolution
laser, reveals a persistent spectral hole, ideally broadened to twice the
homogeneous width of the transition. The second beam need not, therefore, be
high resolution and is likely to be effective at a different frequency to the high
resolution beam (figure 1.4).

This effect has been demonstrated in several centres including
BaFCl:Sm²⁺ (Macfarlane et al 1986, Macfarlane 1987). The product of this
photochemical holeburning mechanism arises after the centre has absorbed two
photons and may be expected to be relatively stable. It has been shown that
thermal cycling to room temperature does not remove the spectral hole. In this
case, the electron is truly ionised whereas most single photon mechanisms are
thought to merely involve the removal of the electron to a nearby trap. Two photon
spectral holeburning has been demonstrated in CaSO₄:Sm²⁺ in this study (see
chapter 4).

Two photon persistent spectral holeburning has been suggested as a third
dimension to compact disc style digital memories (Castro et al 1978). In this
system, digital information is stored as a 'hole' or 'no hole' to represent '1' and '0'
throughout the spectral range of a zero phonon line. Two photon holeburning is
particularly appropriate for this application due to the lack of degradation caused
Figure 1.4 Two photon persistent holeburning. Only those centres excited by the initial high resolution laser may be excited by the second laser. Subsequent investigation with the high resolution laser reveals a spectral hole at the original high resolution laser frequency.
by reading the information from the crystal. Information may only be written to the crystal when the gating beam is introduced. These advantages are also applicable to the use of this effect to produce optical filters where the material is 'burnt' to allow only required frequencies to be passed.

1C(iv) Transient holeburning

Holeburning which decays with the lifetime of the resonant excited state is less useful than persistent spectral holeburning for both application and experimental reasons. Clearly, applications with a lifetime of a few milliseconds or less are impractical and this time period is often too short to take experimental data.

Such phenomena may reveal useful information about the dynamic processes within the solid, however. Simple measurements, such as hole depth, may enable an explanation of the holeburning mechanism to be made. Transient holeburning mechanisms are generally very different from persistent holeburning mechanisms in that they involve a redistribution of the state populations rather than a change in the eigenstates themselves.

The simplest mechanism for transient holeburning is saturation holeburning. When a high resolution dye laser, resonant with part of a zero phonon line, excites centres to an excited state, the ground state population becomes depleted. Though an increase in laser power results in an increase in emission, it also results in further depletion of the ground state. Introduction of a second, weaker probe beam reveals a spectral hole in the zero phonon line corresponding to the static laser frequency and which becomes deeper with increased static laser power. The hole may not exceed a depth of 50 %, however. In this limit, stimulated emission from the excited state becomes equal to excitation of the ground state, these transition probabilities being equal.

Transient holes may also be formed when the ground state population is
redistributed to higher excited states. This process involves absorption of a second photon from the resonant excited state and is believed to be responsible for transient holeburning effects in CaSO₄:Sm²⁺ (see chapter 4).

Optical pumping consists of a process by which the ground state is depopulated through a redistribution of the population to other ground state levels such as fine structure or hyperfine states. Figure 1.5 illustrates the process through which optical pumping produces optical holes. A centre is excited from one ground state level and relaxes to an alternate ground state level. Subsequent laser irradiation at the initial frequency may no longer excite a transition and a spectral hole is burnt. The depth of the hole is determined by the rate at which the centres relax back to their original state such that excitation and subsequent emission may take place. This relaxation is typically rapid due to small ground state splittings and may take place through spin flips or spontaneous phonon emission, for instance. Introduction of a second laser as a scanning probe is often used to investigate the hole and antihole structure which reveals information on the ground state splittings (for instance, Reddy et al 1989). In this study, the transient hole depth induced by a high resolution laser is used to monitor various spin-spin cross-relaxation processes in the N-V centre in diamond (see chapter 5) as a function of magnetic field.

1C(v) Perturbation spectroscopy

The field of perturbation spectroscopy is an enormous one. The effect of a magnetic field on the Hamiltonian of a centre has already been considered (see section 1B(iii)). Electric fields and uniaxial stress perturb the Hamiltonian in analogous ways to magnetic fields though these techniques are not used in this thesis.

Since the inception of optical spectroscopy of solids, the effect of perturbations on spectra has played a critical part in the study of structure.
Figure 1.5 Optical pumping.
(a) The centre is excited from one ground state
(b) Relaxation is to a different ground state
(c) The centre is no longer resonant with the exciting laser beam and the resulting lack of absorption causes a spectral hole.
(d) Relaxation between ground states through phonon processes, spin flip-flops etc. returns the centre to its original ground state. The depth of the spectral hole is thus dependent on the average speed of this process.
Traditional techniques were limited by the resolution of light dispersion equipment such that only gross effects such as linear Zeeman splittings of inhomogeneously broadened levels could be detected.

The high resolution laser now allows interactions within a fraction of an inhomogeneous linewidth to be studied. The inhomogeneous widths of the zero phonon lines of the excited states of the uranium centre in strontium tungstate (see chapter 3) are several hundred GHz but, by 'marking' a subset of identical centres through holeburning, quadratic Zeeman shifts of less than 10 MHz may be detected. Through a study of these interactions, conclusions regarding the centre symmetry are drawn.

The linear Zeeman effect may also be utilised at low magnetic fields with the aid of high resolution lasers. In chapter 5, high resolution lasers are utilised to study spin-spin cross-relaxation in the N-V centre in diamond. The rate at which cross-relaxation occurs may be measured in terms of transient hole depth. By applying a steadily varying magnetic field perturbation, the transient hole depth is seen to vary, from which conclusions may be drawn about the nature of the holeburning process, the N-V centre's interaction with a magnetic field and the presence of other colour centres in the diamond crystal.

1C(vi) Other techniques in high resolution laser spectroscopy

Magnetic perturbations were used to split spin ground state levels in radio frequency resonance experiments (Zavoisky 1945, Bloch et al 1946) long before the first laser was operated. Using these techniques, electron paramagnetic resonance and nuclear magnetic resonance, much information was gathered about the ground states of centres in solids and several previously undiscovered phenomena were observed. These include nutation (Torrey 1949), free induction decay (Hahn¹ 1950) and spin echoes (Hahn² 1950). These effects are caused by transient changes induced in the populations of split ground state levels by a radio
frequency field.

The high resolution laser has allowed the optical analogues of all these effects to be observed by coupling a ground state level to an excited state using a frequency switchable laser or a switchable perturbation which causes the laser to be resonant and then non-resonant with a transition (Brewer and Shoemaker 1971, 1972).

More recently, a novel, coherent Raman effect has allowed the detection of nuclear magnetic resonance using both laser and radio frequency fields (Wong et al 1983). Coherence is created between the split ground state levels by the radio frequency field and between excited and ground states by the laser field. This induces a coherence between the two non-resonant levels. The resulting field beats with the laser field to produce a modulation of the laser beam at the frequency corresponding to the ground state splitting.

This study presents an account of the use of Raman heterodyne detection to observe electron paramagnetic resonance for the first time (see chapter 6). This effect is observed in the spin triplet ground state of the N-V centre in diamond (see chapter 5). This method is preferable to conventional techniques as both magnetic field and radio frequency may be varied continuously whilst the electron paramagnetic resonance signal is continuously displayed on a screen.

Tunable high frequency modulation of light is technologically useful and further development of this technique may result in the development of amplitude modulation equipment for optical communications.
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CHAPTER TWO

SELECTIVE EXCITATION AND EMISSION STUDIES OF MAGNESIUM RELATED URANIUM-OXYGEN COMPLEXES IN LITHIUM FLUORIDE

2A INTRODUCTION

It has long been known that crystals of lithium fluoride doped with uranium and grown in an oxygen atmosphere give a green fluorescence that is attributed to hexavalent uranium (Slattery 1929, Runciman 1956). Although several centres are involved, giving rise to complex spectra, there is commonly a dominant centre with a sharp emission line at 18941 cm\(^{-1}\) (527.8 nm) for which the emission and excitation have been extensively studied (Srinivasan et al 1985, Runciman et al 1986 and references therein). This centre has \(C_{4v}\) symmetry and is considered to be associated with a \(\text{UO}_5\text{F}\) group (Feofilov 1959), where five of the six nearest neighbour F\(^{-}\) ions have been replaced by O\(^{2-}\) ions.

When magnesium is added to the crystal growing melt, the resultant crystals give, additionally, a blue emission (Runciman and Wong 1979). This is attributed to the formation of centres where all the nearest neighbour fluorines are replaced with O\(^{2-}\) ions and a Mg\(^{2+}\) ion replaces a Li\(^{+}\) ion for charge neutrality. The Mg\(^{2+}\) may substitute for Li\(^{+}\) at different crystallographic Li\(^{+}\) sites resulting in centres with varying symmetries. Calculations have been
made of the relative formation energies of the tetragonal and orthorhombic magnesium centres (Runciman et al 1984, 1985).

Mg$^{2+}$ along a $\langle 110 \rangle$ direction can give a centre with orthorhombic symmetry and is considered to be associated with the dominant absorption and emission at 482.87 and 486.68 nm respectively (Runciman and Wong 1979). Mg$^{2+}$ along a $\langle 100 \rangle$ axis would give rise to a tetragonal centre and is considered as that which gives rise to the absorption and emission lines at 476.48 and 482.66 nm respectively. In this chapter the polarised excitation and emission spectra associated with the orthorhombic and tetragonal centres are used to deduce the symmetry of the electronic states involved, which are then compared with those for previously reported U$^{6+}$ systems. Such comparisons reveal how the variation of centre symmetry affects the splitting of levels and the selection rules for transitions between levels, information which is necessary for a satisfactory determination of the electronic wavefunctions. Excitation and emission for a third Mg$^{2+}$ centre closely related to the orthorhombic centre are also presented.

2B EXPERIMENTAL DETAILS

Crystals of LiF were pulled from the melt in an atmosphere of 50 Torr of oxygen using the Czochralski method. The concentration of uranium (as U$_3$O$_8$) in the melt was 0.1% and, for the crystals described here, 1.0% molar of MgF$_2$ was also incorporated. Crystals with cubic faces of size 4 x 4 x 3 mm were cleaved from the boule.

A pulsed tunable dye laser, Molelectron DL II, with a 10 GHz linewidth, was used for the selective emission and excitation. The dye laser was pumped with a Molelectron nitrogen laser. The Ar$^+$ line of a Spectra-Physics 171 laser at 476.5 nm coincides with the sharp absorption line of one of the centres and was used for
Figure 2.1 Definition of axes with respect to the laboratory frame.
excitation in this case.

For the polarisation measurements the laser was directed along the x direction and the emission detected at right angles along the y axis, with the z axis vertical in both cases (figure 2.1). The polarisation directions of the incident and emitted radiation are denoted within square brackets, for example \([y,x]\). The crystals were mounted such that the faces were along the xyz directions and were cooled to 10 K by a flow of helium gas.

**2C RESULTS AND DISCUSSION**

**2C(i) Determination of centres present in LiF:U,Mg**

In order to determine which magnesium related centres were present within the LiF:U crystal, the non-selective excitation spectrum, in which the pulsed laser frequency is scanned whilst detecting all emission, was recorded (figure 2.2). There are several excitation lines in the 460-500 nm range but selective excitation revealed that most of these are associated with three centres denoted by G, L and L'. Each centre has a sharp emission line at 482.6 nm (G₁), 486.6 nm (L₁) and 492.6 nm (L'₁) and a corresponding strong absorption line at 476.5 nm (G₂), 482.8 nm (L₂) and 486.9 nm (L'₃).

**2C(ii) Selective excitation and emission of the G centre**

The emission at 482.6 nm has been reported previously (Kaplyanskii and Moskvin 1963, Runciman and Wong 1979). By monitoring this emission and scanning the excitation frequency it was shown that the centre responsible for this emission gives a strong absorption at 476.5 nm and at high temperature also emits at this wavelength. It has been concluded from uniaxial stress measurements that
Figure 2.2 The excitation of the LiF:U,Mg crystal, between 460 and 505 nm, monitoring all the emission (zero order). The wavelengths of the three principal absorption lines associated with the three magnesium related centres are indicated.
these emission lines are associated with transitions at a centre of tetragonal ($C_{4v}$) symmetry (Kaplyanskii and Moskvin 1963). Both transitions are polarised along the axis of the centre with the higher energy transition being electric dipole and the lower energy transition magnetic dipole. Exciting the 476.5 nm absorption line and detecting the 482.6 nm emission line gives a strong signal in $[z,x]$ polarisation but a weak signal in all other polarisations (figure 2.3). This is consistent with an $A_1\rightarrow A_1$ (electric dipole) transition in absorption and an $A_2\rightarrow A_1$ (magnetic dipole) transition in emission for a site of $C_{4v}$ symmetry as assigned previously (Kaplyanskii and Moskvin 1963). In excitation all the vibrational features in fig 2.3 are polarised in the same way and can be concluded to be associated with $A_1$ vibrations.

The 476.5 nm Ar$^+$ line coincides with the $A_1\rightarrow A_1$ zero phonon line and is used to obtain the emission associated with the G centre in figure 2.4. The excitation, however, lies in the vibronic absorption band associated with the L centre and consequently related features appear in the emission spectrum. These features can be subtracted to obtain the emission spectrum of the G centre. Furthermore, with knowledge of the selection rules for a $C_{4v}$ centre, (table 1 in Srinivasan et al 1985, reproduced as table 2.1 here) the polarised emission spectra for the two polarisations of excitation can be utilised to calculate the side bands associated with $A_1$ and E modes of vibration. By digitising the spectra in figure 2.4 and subtracting $[y,z]$ from $[z,x]$, both $A_2\rightarrow E$ modes and features due to the L centre are eliminated to produce the $A_2\rightarrow A_1$ magnetic dipole spectrum. The features due to the L centre may then be isolated by reducing the excitation wavelength slightly thus preventing excitation of the G centre whilst continuing to excite the L centre via the vibronic excitation band. Subtraction of this spectrum from the $[y,z]$ spectrum in figure 2.4 produces the spectrum of $A_2\rightarrow E$ modes only. Both are shown in figure 2.5.
Figure 2.3 The low temperature polarised excitation spectrum of the magnesium related C$_{4v}$ centre. The emission is detected at 482.6 nm. The crystal with (001) faces was used and the x,y,z laboratory axes were parallel to the crystallographic [100], [010] and [001] directions.
Figure 2.4 The polarised emission spectra of the G centre in LiF:U,Mg, exciting with the 476.5 nm Ar+ laser line. The crosses denote features associated with the L centre. The side band in the [z,x] polarisation direction includes contributions from $A_1$ and E vibrational modes, whereas the [y,z] polarisation is associated with E vibrational modes only.
Figure 2.5 The vibrational side band associated with $A_1$ modes (upper curve) and $E$ modes (lower curve), corresponding to the emission shown in figure 2.4. The contribution due to depolarisation of the emission and due to L centre emission has been eliminated.
TABLE 2.1 Selection rules for A2→Γ emission with A1→A1 electric dipole excitation in C4v symmetry.

<table>
<thead>
<tr>
<th>Electric dipole induced</th>
<th>Magnetic dipole induced</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2→A2</td>
<td>A2→E</td>
</tr>
<tr>
<td>[z,z]</td>
<td>1</td>
</tr>
<tr>
<td>[z,x]</td>
<td>0</td>
</tr>
<tr>
<td>[y,z]</td>
<td>0</td>
</tr>
<tr>
<td>[y,x]</td>
<td>0</td>
</tr>
</tbody>
</table>

The high frequency features in the side bands are of most interest. They lie above the frequency of the lattice modes of the crystal at greater than 500 cm⁻¹ and will be associated with the stretching motion of the U-O bonds. In a UO₆ group distorted to C4v symmetry there will be three modes of A₁ symmetry and one with E symmetry, and this is in accordance with what is observed here. Figure 2.5 shows three sharp A₁ features shifted from the zero phonon line by 812, 737 and 685 cm⁻¹ and one weak E feature at 717 cm⁻¹. It is noted that there is one A₁ vibrational feature more than that associated with the UO₅F group (Srinivasan et al. 1985) providing substantial evidence for the correct identification of both of these centres.

Appendix 2C(ii) - U-O stretching vibrations of a UO₆ molecule distorted to C₄v symmetry.

To determine the symmetry displacements of the UO₆ molecule, each atom is considered to be a point mass. Associated with each point mass are a set of local coordinates which, for convenience are chosen as shown in figure 2.6. Due to the influence of a magnesium ion along the [001] direction, the oxygen atoms denoted by subscript 5 and 6 are inequivalent and the molecule has C₄v symmetry.

The character table for the C₄v group (table 2.2) shows the eight symmetry operations of the group (in five classes) and the five irreducible representations.
Figure 2.6 The local axes, as chosen for the UO$_6$ molecule. All $x$ and $y$ axes are in the horizontal plane. All $z$ axes are in the vertical plane. Axis sets 1 to 6 correspond to oxygen ion sites. Axis set 7 corresponds to the uranium ion site.
The molecule has seven constituent atoms and therefore 21 degrees of freedom. It follows that there will be 21 symmetry displacements, each of which will correspond to one of the four one-dimensional irreducible representations of the group or, in pairs, to the single two-dimensional irreducible representation.

**TABLE 2.2 C₄ᵥ group character table.**

<table>
<thead>
<tr>
<th>irreducible representation</th>
<th>E</th>
<th>2C₄</th>
<th>C₄²</th>
<th>2σᵥ</th>
<th>2σ₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁ (Γ₁)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂ (Γ₂)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁ (Γ₃)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂ (Γ₄)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>E (Γ₅)</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

To find the sum of the characters of the normal modes it is necessary to perform each class of operation on the molecule and observe the effect on the local coordinate systems. Each axis which remains unmoved in direction and space contributes 1 to the total character, χᵣ, of the class of operation performed. An axis which remains fixed in space but is rotated through an angle, φ, contributes \( \cos \phi \) to \( \chiᵣ \). Each total character is the sum of characters due to the individual atoms. The total character table is shown in table 2.3.

**TABLE 2.3 Total character table for C₄ᵥ operations on a UO₆ molecule.**

<table>
<thead>
<tr>
<th>symmetry operation</th>
<th>E</th>
<th>2C₄</th>
<th>C₄²</th>
<th>2σᵥ</th>
<th>2σ₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chiᵣ )</td>
<td>21</td>
<td>3</td>
<td>-3</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

The total character table represents the linear combination of characters of
the irreducible representations of the normal modes. The total representation for $C_{4v}$ reduces to, $5A_1 + A_2 + 2B_1 + B_2 + 6E$.

To determine the physical form of the vibrations it is first necessary to determine the form of each symmetry displacement in terms of the symmetry coordinates. The transformation table (table 2.4) enables suitable representations to be obtained by inspection. For instance \{x_1 \, x_2 \, x_3 \, x_4\} is a suitable representation as all operations of the set transform the set coordinates within the representation.

**TABLE 2.4** Local axis transformation table for $C_{4v}$ group operations on a UO$_6$ molecule.

<table>
<thead>
<tr>
<th>group operation</th>
<th>E</th>
<th>$C_4$</th>
<th>$C_4^3$</th>
<th>$C_4^2$</th>
<th>$\sigma_v^{(1)}$</th>
<th>$\sigma_v^{(2)}$</th>
<th>$\sigma_d^{(1)}$</th>
<th>$\sigma_d^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>$x_2$</td>
<td>$x_4$</td>
<td>$x_3$</td>
<td>$-x_1$</td>
<td>$-x_3$</td>
<td>$-x_4$</td>
<td>$-x_2$</td>
<td></td>
</tr>
<tr>
<td>$x_2$</td>
<td>$x_3$</td>
<td>$x_1$</td>
<td>$x_4$</td>
<td>$-x_4$</td>
<td>$-x_2$</td>
<td>$-x_3$</td>
<td>$-x_1$</td>
<td></td>
</tr>
<tr>
<td>$x_3$</td>
<td>$x_4$</td>
<td>$x_2$</td>
<td>$x_1$</td>
<td>$-x_3$</td>
<td>$-x_1$</td>
<td>$-x_2$</td>
<td>$-x_4$</td>
<td></td>
</tr>
<tr>
<td>$x_4$</td>
<td>$x_1$</td>
<td>$x_3$</td>
<td>$x_2$</td>
<td>$-x_2$</td>
<td>$-x_4$</td>
<td>$-x_1$</td>
<td>$-x_3$</td>
<td></td>
</tr>
<tr>
<td>$y_1$</td>
<td>$y_2$</td>
<td>$y_4$</td>
<td>$y_3$</td>
<td>$y_1$</td>
<td>$y_3$</td>
<td>$y_4$</td>
<td>$y_2$</td>
<td></td>
</tr>
<tr>
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<td>$y_3$</td>
<td>$y_1$</td>
<td>$y_4$</td>
<td>$y_4$</td>
<td>$y_2$</td>
<td>$y_3$</td>
<td>$y_1$</td>
<td></td>
</tr>
<tr>
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<td>$y_4$</td>
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<td>$y_1$</td>
<td>$y_3$</td>
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</tr>
<tr>
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<td>$y_3$</td>
<td>$y_2$</td>
<td>$y_2$</td>
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<td></td>
</tr>
<tr>
<td>$z_1$</td>
<td>$z_2$</td>
<td>$z_4$</td>
<td>$z_3$</td>
<td>$z_1$</td>
<td>$z_3$</td>
<td>$z_2$</td>
<td>$z_4$</td>
<td></td>
</tr>
<tr>
<td>$z_2$</td>
<td>$z_3$</td>
<td>$z_1$</td>
<td>$z_4$</td>
<td>$z_4$</td>
<td>$z_2$</td>
<td>$z_3$</td>
<td>$z_1$</td>
<td></td>
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<tr>
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<td>$z_4$</td>
<td>$z_2$</td>
<td>$z_1$</td>
<td>$z_3$</td>
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<td>$z_2$</td>
<td>$z_4$</td>
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<tr>
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<td>$z_3$</td>
<td>$z_2$</td>
<td>$z_2$</td>
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<td>$z_1$</td>
<td>$z_3$</td>
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<tr>
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<td>$-x_5$</td>
<td>$x_5$</td>
<td>$-x_5$</td>
<td>$y_5$</td>
<td>$y_5$</td>
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<tr>
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<td>$-x_5$</td>
<td>$x_5$</td>
<td>$-y_5$</td>
<td>$y_5$</td>
<td>$y_5$</td>
<td>$-x_5$</td>
<td>$x_5$</td>
<td></td>
</tr>
<tr>
<td>$x_6$</td>
<td>$y_6$</td>
<td>$-y_6$</td>
<td>$-x_6$</td>
<td>$x_6$</td>
<td>$-x_6$</td>
<td>$y_6$</td>
<td>$y_6$</td>
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<tr>
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<td>$-x_6$</td>
<td>$x_6$</td>
<td>$-y_6$</td>
<td>$y_6$</td>
<td>$y_6$</td>
<td>$-x_6$</td>
<td>$x_6$</td>
<td></td>
</tr>
<tr>
<td>$x_7$</td>
<td>$y_7$</td>
<td>$-y_7$</td>
<td>$-x_7$</td>
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<td>$-x_7$</td>
<td>$y_7$</td>
<td>$y_7$</td>
<td></td>
</tr>
<tr>
<td>$y_7$</td>
<td>$-x_7$</td>
<td>$x_7$</td>
<td>$-y_7$</td>
<td>$y_7$</td>
<td>$y_7$</td>
<td>$-x_7$</td>
<td>$x_7$</td>
<td></td>
</tr>
<tr>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td>$z_5$</td>
<td></td>
</tr>
<tr>
<td>$z_6$</td>
<td>$z_6$</td>
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<td>$z_6$</td>
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<td>$z_6$</td>
<td>$z_6$</td>
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</tr>
<tr>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td>$z_7$</td>
<td></td>
</tr>
</tbody>
</table>
The new character table for each representation (table 2.5) allows the modes corresponding to each representation to be determined through a process analogous to that which was performed to determine the total number of each vibrational mode.

**TABLE 2.5** Character table for reducible representations for C\(_{4v}\) operations on a UO\(_6\) molecule.

<table>
<thead>
<tr>
<th>Basis</th>
<th>E</th>
<th>2C(_4)</th>
<th>C(_{4v})</th>
<th>2(\sigma_v)</th>
<th>2(\sigma_d)</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>{x_1x_2x_3x_4}</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>A(_2) + B(_2) + E</td>
</tr>
<tr>
<td>{y_1y_2y_3y_4}</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>A(_1) + B(_1) + E</td>
</tr>
<tr>
<td>{z_1z_2z_3z_4}</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>A(_1) + B(_1) + E</td>
</tr>
<tr>
<td>{x_5y_5}</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>E</td>
</tr>
<tr>
<td>{x_6y_6}</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>E</td>
</tr>
<tr>
<td>{x_7y_7}</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>E</td>
</tr>
<tr>
<td>{z_5}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>A(_1)</td>
</tr>
<tr>
<td>{z_6}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>A(_1)</td>
</tr>
<tr>
<td>{z_7}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>A(_1)</td>
</tr>
</tbody>
</table>

Projection operators corresponding to each irreducible representation may then be applied to each representation to determine the form of the symmetry displacements. The form of the projection operator (neglecting normalisation factors) for a given irreducible representation operating on a coordinate, \(c\), is,

\[
\sum_{\text{all group operators}} \chi_i c' 
\]

where \(\chi_i\) is the character of the group operator (table 2.3) and \(c'\) is the transformed coordinate after the operation (table 2.4). For instance, consider the projection
operator corresponding to $A_2$ operating on $x_1$,

$$\begin{align*}
P^{(A_2)} x_1 &= 1.x_1 + 1.(x_2 + x_4) + 1.x_3 + (-1).(-x_1.x_3) + (-1).(-x_4.x_2) = (\text{a constant}).(x_1 + x_2 + x_3 + x_4)
\end{align*}$$

which corresponds to a rotation about the $C_4$ axis.

It is only necessary to operate on one coordinate of the reducible representation as, for instance,

$$\begin{align*}
P^{(A_2)} x_1 = P^{(A_2)} x_2 = P^{(A_2)} x_3 = P^{(A_2)} x_4.
\end{align*}$$

For two-dimensional representations, two linearly independent symmetry displacements exist, therefore at least two coordinates must be operated upon. The symmetry displacements for all $A_1$ and $E$ modes are illustrated in figures 2.7 and 2.8, respectively.

To determine the normal modes of vibration it is necessary to add spring and stiffness constants to the molecular bonds. For the purpose of this study it is sufficient to determine the number of $A_1$ and $E$ stretching modes which can be achieved intuitively by taking linear combinations of symmetry displacements. Three linearly independent $U$-$O$ stretching modes can be produced from the $A_1$ symmetry displacements (figure 2.9). The two remaining modes do not involve $U$-$O$ stretches and consist of the three axial atoms moving resonantly whilst the remaining four atoms move either in phase, to produce a pure translation (i.e. a vibration of the whole molecule within the crystal structure), or out of phase, which involves only a change of $U$-$O$ bond angle. Such vibrations are likely to occur at lower frequencies due to the stiffness constant being much smaller than the spring constant.

Only one (doubly degenerate) $U$-$O$ stretching mode can be produced from the $E$ symmetry displacements (figure 2.9). This is a linear combination of
Figure 2.7 The A₁ symmetry displacements for a UO₆ molecule with Cᵥ symmetry. Displacements of ions are described by vectors expressed in terms of local axes.
Figure 2.8 The $E$ symmetry displacements for a $\text{UO}_6$ molecule with $C_4v$ symmetry. The two components are indicated by thick and (thin) arrows. Displacements of ions are described by vectors expressed in terms of local axes.
Figure 2.9 The U-O stretching modes of a UO$_6$ molecule with C$_{4v}$ symmetry.
symmetry displacements labelled $y_2$-y4 and $x_7$ in figure 2.8. All other E modes involve only rotations or bond angle variations.

The $B_1$ mode with reducible representation \{$y_1$ $y_2$ $y_3$ $y_4$\} also involves U-O stretches (figure 2.9) but this mode is not detected using our present spectroscopic technique.

If the symmetry of the cubic UO$_6$ group is changed by replacing an oxygen atom with a fluorine atom, the symmetry displacements remain identical to those calculated for the distorted UO$_6$ above. The spring constant for the U-F bond is likely to be very different to that for the U-O bond due to differences in the mass of the ions and the covalency of the bonds. As a result, it is likely that one of the resulting normal modes involving stretching along the C$_4$ axis will be dominated by the U-O spring constant whilst the other will be dominated by the U-F spring constant. Consequently, only two $A_1$ modes and one with E symmetry will be observed for the UO$_5$F molecule in the same region as the U-O stretching modes of the UO$_6$ molecule. This is confirmed experimentally as noted in the main body of the text.

2C(iii) Selective excitation and emission of the L centre.

In the magnesium doped crystals studied, the centres giving the most intense emission have sharp zero phonon lines at 486.6 and 492.6 nm (figure 2.10). They are associated with two different centres but each has three lines in its excitation spectrum (figure 2.11). These associated centres are denoted as L and L'. The emission due to the L' centre is considerably weaker than the L centre, therefore the polarisation study is restricted to the L centre.

The L centre has been observed previously (Srinivasan 1982) and is considered to be a magnesium related centre with C$_{2v}$ symmetry. The transition giving rise to the absorption and emission at 486.6 nm can be shown to be magnetic dipole in origin by both exciting and detecting at this wavelength. For
Figure 2.10 The emission of the magnesium (C$_{2v}$) L centre and the related L' centre (broken curve). The excitation wavelength was 482.8 nm for the full curve and 486.9 nm for the broken curve.
Figure 2.11 The excitation spectrum associated with the (C\textsubscript{2v}) L centre with the emission being detected at 486.6 nm (full curve). The positions of the three principal lines associated with the L' centre are also indicated (broken curve) for which emission was detected at 492.6 nm.
detection at right angles the signal is strongest when the magnetic vector is vertical in both excitation and emission, \([y,x]\) polarisation, indicating an axial magnetic dipole transition between \(A_1\) and \(A_2\) or \(B_1\) states (see appendix 2C(iii)). The emission in the other three combinations of polarisation directions is weaker although not quite by the factor of two predicted for such a transition. This is commonly experienced for laser selective excitation. The polarisation ratios are less than those predicted from group theoretical analysis but this is attributed to scatter of the excitation and emission radiations rather than to a departure from \(C_{2v}\) symmetry. Such small perturbations would be unlikely to have a preferred direction within the crystal and would therefore not account for a change in polarisation ratios. The polarisation of the zero phonon line at 486.6 nm, however, is not consistent with a transition between states of any alternative symmetry.

The lowest excited state in many other \(U^{6+}\) centres has been shown to have \(A_2\) symmetry and it is, therefore, more likely that this is the case here. Most notably, the lowest excited state in the G centre has been ascribed as being an \(A_2\) state (see section 2C(ii)). The L and G centres may both be regarded as distorted cubic \(UO_6\) centres in that the centre symmetries are reduced from \(O_h\) to \(C_{4v}\) and \(C_{2v}\) respectively by distorting the cubic centre with a magnesium ion along a \(\langle 100\rangle\) direction or a \(\langle 110\rangle\) direction respectively. Compatibility tables (Koster et al 1963) show that all irreducible representations of \(O_h\) symmetry which, when distorted to \(C_{4v}\) symmetry produce \(A_2\) states, also produce \(A_2\) states when distorted to \(C_{2v}\) symmetry. The emission line is therefore assigned to a magnetic dipole \(A_2 \rightarrow A_1\) transition and the predicted polarisations for excitation, monitoring this emission line, are given in table 2.6.
TABLE 2.6 Selection rules for $A_1 \rightarrow \Gamma$ excitation while monitoring $A_2 \rightarrow A_1$ magnetic dipole emission in $C_{2v}$ symmetry (see appendix 2C(iii)).

<table>
<thead>
<tr>
<th>Polarisation</th>
<th>$A_1 \rightarrow A_1$</th>
<th>$A_1 \rightarrow B_1$</th>
<th>$A_1 \rightarrow B_2$</th>
<th>$A_1 \rightarrow A_2$</th>
<th>$A_1 \rightarrow B_1$</th>
<th>$A_1 \rightarrow B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[z,z]$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$[y,z]$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$[y,x]$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$[z,x]$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

N.B. $A_1 \rightarrow A_2$ (electric dipole induced) and $A_1 \rightarrow A_1$ (magnetic dipole induced) are forbidden transitions.

For equal numbers of all the crystallographically equivalent $C_{2v}$ centres with their $z_i$ and $y_i$ axes along (110) directions (figure 2.12) it is not possible to distinguish between transitions polarised along the local $z_i$ and $y_i$ axes. For this reason, $A_1 \rightarrow A_1$ and $A_1 \rightarrow B_2$ electric dipole transitions cannot be distinguished using the present measurements, nor can $A_1 \rightarrow A_2$ and $A_1 \rightarrow B_1$ magnetic dipole transitions be distinguished.

From the polarisation data shown in figure 2.13, the first three excited electronic states can be seen to have $A_2$, $B_1$ and $A_1$ (or $B_2$) symmetry. The polarisation of the vibronic band seen in excitation (polarisation data not shown) involves $A_1$ modes including the local mode peak at 465.9 nm coupled to the strong electronic transition at 482.8 nm.

Polarisation of the emission (figure 2.14) can be analysed in a similar way and the selection rules for exciting the $A_1 \rightarrow A_1$ transition at 482.8 nm are given in table 2.7. The local mode is again seen to gain its intensity from the electronic transition at 486.6 nm. The rest of the side band, however, is electric dipole in origin involving a distribution of $A_2$ (or $B_1$) vibrations. The electronic transitions are summarised in figure 2.15 and the vibronic transitions in figure 2.16.
Figure 2.12 The orientation of the axes of the $C_{2v}$ centre with respect to the cubic axis.
Figure 2.13 The polarised excitation spectra of the magnesium $C_{2v}$ centre in the region of the three lowest energy transitions (see figure 2.11, emission detected at 486.6 nm).
Figure 2.14 The polarised emission of the magnesium $C_{2v}$ centre exciting at 482.8 nm.
Figure 2.15 The electronic energy levels and transitions of hexavalent uranium-oxygen centres. As noted in the text, for the C$_{2v}$ symmetry experiments cannot conclusively distinguish between A$_1$ and B$_2$ or between A$_2$ and B$_1$. 
Figure 2.16 The vibronic transitions observed in emission and absorption.
TABLE 2.7 Selection rules for \( A_2 \rightarrow \Gamma \) emission with \( A_1 \rightarrow A_1 \) electric dipole excitation in \( C_{2v} \) symmetry (see appendix 2C(iii)).

<table>
<thead>
<tr>
<th>Electric dipole induced</th>
<th>Magnetic dipole induced</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_2 \rightarrow A_2 )</td>
<td>( A_2 \rightarrow A_1 )</td>
</tr>
<tr>
<td>( A_2 \rightarrow B_1 )</td>
<td>( A_2 \rightarrow B_1 )</td>
</tr>
<tr>
<td>( A_2 \rightarrow B_2 )</td>
<td>( A_2 \rightarrow B_2 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>polarisation</th>
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<th>( [y,z] )</th>
<th>( [y,x] )</th>
<th>( [z,x] )</th>
<th>( [z,z] )</th>
<th>( [y,z] )</th>
<th>( [y,x] )</th>
<th>( [z,x] )</th>
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</thead>
<tbody>
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<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>( y )</td>
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<td>2</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

N.B. \( A_2 \rightarrow A_1 \) (electric dipole induced) and \( A_2 \rightarrow A_2 \) (magnetic dipole induced) are forbidden transitions.

Appendix 2C(iii) - Relative intensities of transitions in a \( C_{2v} \) centre.

The fundamental selection rule states that there is only a finite transition probability between two states, \( \psi_1 \) and \( \psi_2 \), coupled by an operator, \( O \), if the matrix element, \( \langle \psi_1 | O | \psi_2 \rangle \) contains the identity representation, \( \Gamma_1 \) (see section 1B(ii)). The ground state of all \( U^6^+ \) centres has \( \Gamma_1 (A_1) \) irreducible representation as the ion has a closed shell configuration (assuming the bonding is entirely ionic which may not be strictly true in all cases but all such centres reported to date have \( A_1 \) ground states). In excitation, therefore, only transitions from \( A_1 \) need to be considered. All emission occurs as a result of a transition from the lowest excited state (figure 2.10).

To determine the symmetry of the lowest excited state, it is necessary to consider the strength of emission in the resonant case for different polarisations of input and output radiation. The strength of the emission detected is dependent upon the number of centres excited within the solid and whether each centre emits radiation in the polarisation monitored. There are 12 possible \( (110) \) orientations for the magnesium ion within the crystal (figure 2.17) and each is considered to be equally common. By adding the number of centres which may absorb and emit radiation for each case, the relative intensities may be found. The resultant data is
Figure 2.17 The twelve [110] directions in the LiF lattice relative to the substitutional UO$_6$ centre. Each [110] direction defines the $z$ axis for magnesium ions which may substitute to form $C_{2v}$ centres in these positions. The laboratory frame axes are also indicated.
shown in table 2.8.

**TABLE 2.8** Selection rules for $A_1 \rightarrow \Gamma$ excitation with $\Gamma \rightarrow A_1$ emission in $C_{2v}$ symmetry.

<table>
<thead>
<tr>
<th>Electric dipole induced</th>
<th>Magnetic dipole induced</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Excite</strong></td>
<td><strong>Emit</strong></td>
</tr>
<tr>
<td>$A_1 \rightarrow A_1$</td>
<td>$A_1 \rightarrow A_1$</td>
</tr>
<tr>
<td>$A_1 \rightarrow B_1$</td>
<td>$B_1 \rightarrow A_1$</td>
</tr>
<tr>
<td>$A_1 \rightarrow B_2$</td>
<td>$B_2 \rightarrow A_1$</td>
</tr>
<tr>
<td>$A_2 \rightarrow A_1$</td>
<td>$A_1 \rightarrow B_1$</td>
</tr>
<tr>
<td>$A_1 \rightarrow B_1$</td>
<td>$A_1 \rightarrow B_2$</td>
</tr>
<tr>
<td>$A_1 \rightarrow B_2$</td>
<td>$A_1 \rightarrow B_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basis</th>
<th>$[z,z]$</th>
<th>$[y,z]$</th>
<th>$[y,x]$</th>
<th>$[z,x]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[z,z]$</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$[y,z]$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$[y,x]$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$[z,x]$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

N.B. $A_2 \leftrightarrow A_1$ (electric dipole induced) and $A_1 \leftrightarrow A_1$ (magnetic dipole induced) are forbidden transitions.

**TABLE 2.9** $C_{2v}$ group character table.

<table>
<thead>
<tr>
<th>Symmetry operation</th>
<th>irreducible representation</th>
<th>E</th>
<th>$2C_4$</th>
<th>$C_4^2$</th>
<th>$2\sigma_v$</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$ ($\Gamma_1$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
</tr>
<tr>
<td>$B_1$ ($\Gamma_2$)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$Y$ or $x$</td>
</tr>
<tr>
<td>$A_2$ ($\Gamma_3$)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$Z$</td>
</tr>
<tr>
<td>$B_2$ ($\Gamma_4$)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>$X$ or $y$</td>
</tr>
</tbody>
</table>

N.B. Electric dipole bases in lower case, magnetic dipole bases in upper case.

Consider the first column of table 2.8. For the $A_1 \rightarrow A_1$ transition to be allowed, the irreducible representation of the coupling operator must be $\Gamma_1$ (as $\Gamma_1 \times \Gamma_1 \times \Gamma_1 = \Gamma_1$). This is the case for the $z$ basis in $C_{2v}$ (see table 2.9) and therefore light polarised along any of the $z_i$ (local) axes may excite an $A_1 \rightarrow A_1$ transition, which will decay, polarised along the $z_i$ axes. In figure 2.17, the $z_i$ axes of centres 5 to 8 and 9 to 12 lie at 45° to the $z$ crystallographic direction and each may be
excited. The $z_i$ axes of centres 1 to 4 are perpendicular to the $z$ crystallographic direction and therefore may not be excited by $z$-polarised light. If emission is detected in the $z$-polarisation the same centres may be detected as were excited and therefore 8 of the 12 centres are detected. In the $x$-polarisation the emission from centres 5 to 8 is not detected as these $z_i$ axes are perpendicular to the crystallographic $x$-axis and therefore only four of the 12 centres are detected, giving a two to one ratio for the $[z,z]$ to $[z,x]$ orientations.

All data in tables 2.6, 2.7 and 2.8 are calculated in this way, normalisation being attained by multiplication by $1/2 \cos^2 45^\circ$ for excitation at $45^\circ$ to the local axis and multiplication by $1/2 \cos^2 45^\circ$ for emission at $45^\circ$ to the detection polarisation. Ratios of emission strengths may not be compared between columns however, as the transition probabilities are not equal for different transitions. This is most clearly illustrated in the comparison of the strength of an electric and magnetic dipole induced transition (see section 1B(ii)).

Table 2.8 illustrates that, as the $[y,x]$ orientation gives strongest emission for resonant excitation at 486.6 nm (experimental data not shown), in a ratio of the order of two to one relative to all other orientations, the transition must be magnetic dipole induced and the lowest excited energy level must have $A_2$ or $B_1$ symmetry.

Similar conclusions about the other electronic transitions may now be drawn using tables 2.6 and 2.7, which assume that emission is always from an $A_2$ state and, when detected selectively at 486.6 nm, is a magnetic dipole transition. In the latter case, the transition is $\Gamma_3 \rightarrow \Gamma_1$ and hence, to be allowed, the magnetic dipole operator must also have $\Gamma_3$ irreducible representation $(\Gamma_3 \times \Gamma_3 \times \Gamma_1 = \Gamma_1)$. Consequently, the magnetic vector of the emission is polarised along the $z_i$ axes.

2C(iv) Spectral holeburning in uranium doped lithium fluoride

Investigations with high resolution dye lasers showed that persistent spectral holes could not be burnt in the zero phonon lines of the G or L centres or
the UO$_5$F centre. This null result adds further weight to conclusions as to the structure of the centres. The lack of persistent holeburning indicates the stability of the centres, typical of fully charge compensated impurity ion centres.

**2D CONCLUSION**

The relative energies and symmetry assignments of the electronic energy levels for the two centres analysed above are summarised in figure 2.15. These are compared with two other uranium-oxygen centres which have been analysed previously, UO$_5$F in LiF (Srinivasan et al 1985) and UO$_4$ in KMgG$_3$ (Manson et al 1984). In all cases the emission is associated with a magnetic dipole transition polarised along the axis of the centre. Thus in all cases the lowest lying excited state has the transformation properties of a rotational vector directed along the local axis, R$_z$ (using the notation of Wilson et al 1955). In higher symmetry (cubic) the three components R$_x$, R$_y$, R$_z$ of such a vector would be degenerate but there is no evidence of states with R$_x$ transformation properties adjacent to the lowest excited state and R$_x$ states are only observed in the L centre. Thus in both the magnesium related centres there must be substantial distortions from a cubic crystal field owing to the presence of the charge compensating Mg$^{2+}$ ions.

In three of the cases, for the UO$_5$F, the UO$_6$Mg (C$_{4v}$) and for the UO$_4$ centres, there are four equivalent oxygens lying in a plane perpendicular to the fourfold axis and, should the electronic wavefunction giving rise to the first excited state be associated with orbits in this plane, it is easy to see how a similarity between these three systems could arise. This is indeed thought to be the situation for UO$_5$F at least, as Runciman et al (1986) have obtained a satisfactory account of the first excited states using an electronic wavefunction of the central uranium ion and the four equatorial oxygens. The UO$_6$Mg (C$_{2v}$) emission could not be
explained, at least so simply, in the same way and it will undoubtedly require more sophisticated calculation to establish if there is a common explanation.

A distortion with pronounced direction can always introduce significant odd-parity crystal-field terms and leads to mixing of even and odd parity wavefunctions and transitions that are polarised parallel (or perpendicular) to the distortion. It therefore seems reasonable that, for all the systems without inversion symmetry, the strongest transition is associated with electric dipole transitions polarised along the principal axis of the centre. In each case, $C_{4v}$ and $C_{2v}$, this corresponds to the observed $A_1 \rightarrow A_1$ transition.
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The study presented in this chapter has been presented in different form in The
Journal of Physics C: Solid State Physics, Volume 20, pages 3993-4003. The
published paper contains contradictions in local axis definition between diagrams
and text and, consequently, some of the tables presented here have been
amended.
CHAPTER THREE

PERSISTENT SPECTRAL HOLEBURNING IN URANIUM DOPED TUNGSTATES

3A. INTRODUCTION

3A(i) Spectroscopy of uranium doped tungstates and molybdates

The spectroscopy of uranium doped tungstates and molybdates has attracted little attention relative to the study of uranium doped sodium and lithium fluoride. Only one uranium related centre forms in tungstate crystals and this makes spectral analysis simple. This study is the first high resolution investigation of the system and reveals much that was previously inaccessible using low resolution techniques. Persistent optical holes have been burnt in the zero phonon spectral lines of ionic solids doped with transition metal ions (Jessop et al 1980, Macfarlane and Vial 1986, Macfarlane and Lenth 1986) and lanthanide ions (Macfarlane and Shelby 1987) but this study represents the first observation of spectral holeburning in actinide ion doped crystals.

The absorption and emission of uranium doped barium and strontium tungstates and molybdates has revealed three excited electronic energy levels (Morozov et al 1972), which were ascribed to a tetrahedral UO$_4^{2-}$ complex. The centre was expected to have $S_4$ symmetry, the U$^{6+}$ ion substituting directly into the
Figure 3.1 The UO₄ substitutional site in the tungstate ion. The uranium ion substitutes directly for the tungsten ion at a site of $S_4$ symmetry.
scheelite lattice for a W\(^{6+}\) ion or Mo\(^{6+}\) ion (figure 3.1). Further investigations (t'Lam and Blasse 1980) drew the same conclusions and attributed the small splitting between two of the levels to the influence of the non-cubic crystal field component at the uranium site though no calculations were attempted. In these studies it was established that there was little difference between the tungstates and equivalent molybdates and this study is restricted to only the tungstates. More significant differences occur when the anion is changed from strontium or barium to calcium. The spectral bands of uranium doped calcium tungstate were structureless making these compounds unsuitable for spectral holeburning investigations.

3A(ii) Laser spectroscopy of uranium doped tungstates

Pulsed laser selective excitation investigations confirmed the existence of three excited electronic energy levels. For uranium doped strontium tungstate these give rise to zero phonon lines at 652.1 nm (\(\alpha\)), 658.4 nm (\(\beta\)) and 659.1 nm (\(\gamma\)) (figure 3.2), whilst for uranium doped barium tungstate the equivalent zero phonon lines occur at 647.6 nm, 654.4 nm and 654.6 nm (figure 3.3). Selective emission investigations showed these zero-phonon lines to belong to the same centre and that only one emitting centre is present. Strain broadening of the zero phonon lines and the weakness of the \(\gamma\) absorption caused the \(\beta\) and \(\gamma\) levels to be indistinguishable in barium tungstate using selective excitation, though the existence of two separate levels was confirmed using fluorescence line narrowing (figure 3.4).

The \(\alpha\) and \(\gamma\) zero phonon lines are strongly \(\sigma\) (\(E \perp c\)) polarised and the \(\beta\) lines are \(\pi\) (\(E \parallel c\)) polarised in absorption though scattered light causes this polarisation to be less pronounced in excitation. In the more heavily doped strontium tungstate samples the inhomogeneous broadening was larger for all three zero phonon lines, causing the \(\beta\) and \(\gamma\) lines to overlap.
Figure 3.2 Excitation spectrum of SrWO₄:U at 10K measured in σ polarisation. The β zero phonon transition is π polarised but is seen here due to scattering of light within the crystal.

Emission detected using filter shown in Fig. 3.5 to exclude laser irradiation.
Figure 3.3 Excitation spectrum of BaWO₄:U at 10K measured in σ polarisation. The β and γ zero phonon lines cannot be resolved using this technique but both are expected to contribute to the zero phonon line at 654.5 nm due to light scattering within the crystal.
Figure 3.4 Fluorescence line narrowing spectrum for BaWO$_4$:U at 10 K. Laser excitation was resonant with emission from the $\beta$ level, shown.
3B. EXPERIMENTAL DETAILS

Crystals were pulled from the melt in an argon atmosphere using the Czochralski method. Crystals of the order of 2 mm x 4 mm x 3 mm were cut from the boule and oriented using Laue back reflection x-ray diffraction. Microprobe techniques determined the uranium concentrations to be 200 ppm for the strontium tungstate samples used in all experiments except the low resolution holeburning. The sample used for this latter technique had a uranium concentration of 500 ppm. The barium tungstate crystals had an estimated concentration of 100 ppm of uranium.

The selective excitation and emission spectroscopy was performed using a Molectron DLII tunable dye laser pumped by a Molectron pulsed nitrogen laser. The crystal was mounted in a flow tube and cooled to 10K. The temperature could be controlled by varying the helium flow rate and monitored by measuring the voltage drop across a carbon resistor (270 $\Omega$ at room temperature) mounted next to the crystal. The emission was detected by a gated photomultiplier after being dispersed by a monochromator. The photomultiplier signal was processed by a boxcar averager. For lifetime measurements the boxcar sampling period delay could be scanned and the emission plotted as a function of the time between excitation and emission. As only one centré emits in this region of the spectrum, all or any part of the emission could be detected in order to determine the excitation spectrum. Likewise, the fluorescence spectrum could be determined by pumping at any wavelength within the excitation spectrum.

For holeburning experiments the emission passing through a Corion LG-697 long wavelength pass filter was detected perpendicular to the laser beam. The filter eliminates the detection of scattered laser light but allows the detection of emission in the low energy part of the band (figure 3.5).

High resolution holeburning experiments were performed using a Coherent 699-21 ring dye laser with a linewidth of 1 MHz pumped by a
Figure 3.5  Emission spectrum of SrW$_2$O$_4$:U at 10K measured in $\sigma$ polarisation. The dashed curve indicates the transmission of the filter used for recording excitation spectra.
Spectra-Physics 171 argon ion laser. The crystals were in helium exchange gas at 5 K and mounted on a rod which allowed for rotation of the sample in the coils of a superconducting magnet.

Low resolution holeburning experiments were performed using a Spectra-Physics 375 dye laser with a linewidth of 30 GHz pumped by a Spectra-Physics 171 argon ion laser. The crystal was again mounted in a flow tube and cooled to 10 K. To give the required accuracy in the measurement of the line profile the beam was split into three components (figure 3.6). Ninety percent of the beam power was directed onto the crystal during holeburning and was blocked whilst recording the line profile. Six percent of the beam power was directed onto the same part of the crystal and was used as the excitation source whilst recording data. The remaining four percent was used to monitor power fluctuations. The photomultiplier signal was divided by this signal to provide a normalised emission signal. The total power output from the dye laser was 200mW.

Absorption measurements were made in the same helium flow tube arrangement by detecting the light, generated by a tungsten light source and transmitted by the crystal, using a monochromator and photomultiplier.

3C. RESULTS AND DISCUSSION

3C(i). Persistent holeburning in uranium doped tungstates

In strontium tungstate, holes, with lifetimes greater than several hours, could be burnt in all three zero phonon lines. At 5 K, holes burnt in the lowest energy level (γ) were limited in width by laser jitter and it can be concluded that the homogeneous linewidth of the transition is less than 1 MHz. Holes burnt in the β line had a width of 20 MHz and hence the homogeneous linewidth is 10 MHz (see section 1C(iii)). This homogeneous linewidth will be established through direct
Figure 3.6 Experimental apparatus for spectral holeburning.
phonon emission to the $\gamma$ level (see section 1B(iv)) as there is little evidence of emission from the $\beta$ level.

Holeburning in the $\alpha$ line could only be detected in the strongly doped sample where the inhomogeneous linewidth was found to be 1300 GHz. The holes had a width of 400 GHz and hence the homogeneous linewidth is 200 GHz, again determined by direct phonon emission to lower levels. The weakly doped sample did not exhibit holeburning in the $\alpha$ level as the inhomogeneous linewidth in this sample was only 500 GHz.

Figure 3.7 shows the line profiles of the $\beta$ and $\gamma$ lines in the highly doped samples after a hole has been burnt in the centre of the $\beta$ line with the low resolution dye laser. As a result a hole has also been burnt in the centre of the $\gamma$ line with similar depth and width indicating that the strain which causes the inhomogeneous broadening does not alter the separation between energy levels. Due to the overlapping of the inhomogeneous lines, a hole is also burnt directly in the high energy tail of the $\gamma$ line coincident with the central hole in the $\beta$ line. The corresponding hole in the high energy tail of the $\beta$ line, although weak, can be observed.

Due to the weakness of the $\gamma$ absorption, holeburning in the barium tungstate crystals was restricted to the $\beta$ zero phonon line. These holes were laser linewidth limited as the close proximity of the $\beta$ and $\gamma$ lines (5 cm$^{-1}$) limits hole broadening through direct phonon emission from the $\beta$ level to the $\gamma$ level.

3C(ii) Zeeman effect and site symmetry

Holes burnt with the high resolution dye laser in the $\beta$ and $\gamma$ lines were found to be displaced quadratically in a magnetic field. When the field is applied perpendicular to the c-axis of the crystal as well as being displaced, the hole splits and upon rotating the crystal about the c-axis the hole splitting was found to vary. The maximum splitting occurs when the field is $30^\circ \pm 5^\circ$ from a (100) direction and
Figure 3.7 Optical holeburning in a concentrated SrW04:U crystal at 10K measured in π polarisation. The α zero phonon transition is σ polarised but is seen here due to scattering of light within the crystal. The hole has been burned at 658.3 nm and causes burning in the β line at this frequency and a side hole in the γ line at 659.0 nm. A hole is also burnt in the component of the γ line at 658.3 nm and gives a side hole in β at shorter wavelength, 657.7 nm.
after successive 90° rotations whereas the holes merge at 45° to maxima (figure 3.8). When the field was out of the a-b plane (figure 3.9) there was a splitting into two lines. However when the field was applied along the c-axis a shift, but no splitting, was observed. Table 3.1 summarises the size of these hole shifts.

**TABLE 3.1** Quadratic Zeeman shifts as determined by spectral holeburning experiments.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero phonon line</td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Energy ($\gamma=0$)</td>
<td>161</td>
<td>16</td>
</tr>
<tr>
<td>H ALONG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X LOCAL AXIS</td>
<td>-</td>
<td>+110</td>
</tr>
<tr>
<td>Y LOCAL AXIS</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Z LOCAL AXIS</td>
<td>-</td>
<td>-20</td>
</tr>
</tbody>
</table>

All Zeeman shifts are quadratic, indicating that the symmetry is sufficiently low that all degeneracy has been lifted. In addition, the splitting indicates that there are two crystallographically equivalent but magnetically inequivalent centres within the solid. SrWO$_4$ has a scheelite lattice structure (no. 88, C$_{4h}^6$ in Schönflies notation) and the uranium ion may occupy a position of S$_4$, C$_2$, S$_2$ or C$_1$ symmetry (Henry and Lonsdale 1969). The uranium ions presumably substitute for the tungsten ions which are in sites of S$_4$ symmetry but cannot remain precisely at the substitutional site as the S$_4$ group still has a two fold degenerate irreducible representation.

S$_2$ and C$_1$ may also be ruled out as possible site symmetries for the uranium centre. The sites of S$_2$ symmetry have inversion symmetry and so electric dipole transitions are not allowed. However, it has been shown (Morozov et al 1972) that the zero phonon transitions are electric dipole in nature. If the uranium ions substituted into C$_1$ sites, our axial and transverse magnetic field results could
Figure 3.8 The position and splitting of a hole in the $\gamma$ line in SrW$_{24}$:U as affected by the magnetic field direction in the (001) plane. The hole has been burned at zero field at the frequency indicated. An external magnetic field of 1.5 T is then applied and the holeburning spectra measured. 0° corresponds to the position of maximum splitting (at 30° to [100]).
Figure 3.9 Quadratic Zeeman shifts of spectral holes in the γ and β zero-phonon line in SrWO$_4$:U. The magnetic field is perpendicular to the c-axis of the crystal at 30° to [100], the direction of maximum splitting.
be explained. However for a general field direction, at an angle other than 0° or 90° to the c-axis, there would be four inequivalent sites. This would cause the hole to split into four components, which was not observed. The elimination of S$_2$ and C$_1$ site symmetries suggest that the uranium ion is at a site of C$_2$ symmetry.

The splitting pattern indicates that the two sets of magnetically inequivalent centres are oriented perpendicular to each other and the most probable explanation is for the uranium ion to be displaced up or down the c-axis from the central site (figure 3.10). Some relaxation of the oxygen may also be involved. The displacement lowers the symmetry from S$_4$ to C$_2$ and there are two such centres with their principal axes (local z-axes) aligned with the S$_4$ principal axis but with their local x and y axes orthogonal. This can be seen by considering the nearest neighbour oxygens. As the oxygen ions are arranged approximately tetrahedrally in the lattice, with the displaced uranium ion lying closer to one pair of oxygen ions, there would then exist two perpendicularly oriented sets of centres. Furthermore, the axis joining the pair of oxygen ions in the tungstate lattice lie at an angle of 29° and -61° to the (100) direction. These angles coincide, within the limits of experimental uncertainty, with the magnetic field angle required to give a maximum splitting (the angles are the same but the signs could not be determined with the equipment available). Thus it would seem clear that a magnetic field aligned directly along (or perpendicular to) one of the oxygen pairs gives the maximum quadratic Zeeman displacement. This is defined as the local x axis. When the field is along the x axis of one C$_2$ centre it will be along the local y axis of the other C$_2$ centre and gives a significantly smaller shift, if any. When the field is applied along the c-axis of the crystal it is along the local z axis of both centres. They are then magnetically equivalent and hole shifts will be equal, with no resultant splitting.

There are only two irreducible representations, $\Gamma_1$ or $\Gamma_2$, in the C$_2$ group. The ground state of hexavalent uranium has a closed electron shell and hence will transform as the symmetric $\Gamma_1$ irreducible representation. The $\alpha$ and $\gamma$ lines are
Figure 3.10 The C\textsubscript{2} substitutional sites in the scheelite structure. W represents the S\textsubscript{4} site in the perfect crystal. If the tungsten ion is replaced by a uranium ion then the equilibrium position can be at U' or U'', both with C\textsubscript{2} symmetry but not necessarily with the same ground state energy, as schematically illustrated below.
completely polarised perpendicular to the c-axis (σ spectrum) in absorption. Electric dipole excitation perpendicular to the c-axis transforms as $\Gamma_2$ irreducible representation in $C_2$ symmetry and therefore the $\alpha$ and $\gamma$ levels must be associated with an excited $\Gamma_2$ state ($\Gamma_1 \times \Gamma_2 \times \Gamma_2 = \Gamma_1$), thus satisfying the fundamental selection rule, see section 1B(ii)). The $\beta$ line is polarised along the c-axis in absorption ($\pi$ spectrum). Electric dipole excitation along the c-axis transforms as $\Gamma_1$ irreducible representation in $C_2$ symmetry and therefore the $\beta$ level must be associated with an excited $\Gamma_1$ state ($\Gamma_1 \times \Gamma_1 \times \Gamma_1 = \Gamma_1$).

An energy level experiences a quadratic Zeeman shift when there is an interaction between it and another level. As the UO$_4^{2-}$ centre is entirely non-degenerate, the necessary off-diagonal Zeeman matrix elements are only non-zero if the cross product of the two states and magnetic field irreducible representations is the symmetry representation (see section 1B(ii)). In $C_2$ symmetry the two possibilities are,

$$\Gamma_1 \times \Gamma_1 \times \Gamma_1 = \Gamma_1$$  \hspace{1cm} (3.1a)

and

$$\Gamma_1 \times \Gamma_2 \times \Gamma_2 = \Gamma_1$$  \hspace{1cm} (3.1b)

A magnetic field along the crystal c-axis and hence the local z-axis transforms as a $\Gamma_1$ irreducible representation and can therefore cause levels with like irreducible representations to interact. A magnetic field perpendicular to the c-axis transforms as a $\Gamma_2$ irreducible representation and can cause states belonging to different irreducible representations to interact.

The $\alpha$ and $\gamma$ zero phonon lines associated with $\Gamma_2$ states should therefore interact when a magnetic field is applied along the c-axis. No movement of the $\alpha$ level can be measured as the homogenous linewidth is too broad but the proposed interaction is consistent with the observation that holes burned in the $\gamma$ line shifted to lower energy with $H\parallel z$. The same field, however, also causes holes
in the β line in both BaWO₄:U and SrWO₄:U to be displaced to lower energy. The β line is associated with a Γ₁ level and, therefore, there must be a further Γ₁ level at higher energies. It has been suggested (t Lam and Blasse 1979) that there is a fourth electronic level 927 cm⁻¹ above the β level in SrWO₄:U. It is not clear how this was distinguished from the vibronic sideband of the α zero phonon line, but would appear to be too high in energy to explain the observed Zeeman shifts of the β level as an effective g-value of around 4 would be required to account for such interactions (see overleaf). The more likely location of the relevant Γ₁ level (δ) is adjacent to the α level lying just within the vibronic band. Absorption and selective laser excitation and emission techniques have failed to distinguish the zero phonon line from the vibronic band.

The perpendicular field will give interactions between unlike symmetry states. Therefore there will be interactions between the δ level and the α and γ levels and between the β level and the α and γ levels. The size of the individual interactions cannot be uniquely deduced from present measurements as holes burnt in both the α and γ levels are shifted by two indistinguishable interactions simultaneously. Interactions between close lying levels are likely to be dominant and this is certainly true for one direction, the local x axis, where there is a large repulsion (~120 MHzT⁻² in SrWO₄) of β and γ levels (figure 3.9). For the orthogonal centre, where the field is along the local y axis, the β level shifts are zero for both SrWO₄ and BaWO₄ though the γ level is shifted (figure 3.9). This is taken as an indication that the β↔γ interaction is small and that the γ level is being repelled by the δ level. For SrWO₄ the size of these interactions are summarised in figure 3.11. Note that in figure 3.9 the effect of applying a magnetic field along both the local x axis and the local y axis is observed because, although the magnetically inequivalent centres are oriented perpendicular to each other in the a-b plane of the crystal, the x-axis may be oriented in the b direction or the c direction depending on whether the displacement of the uranium ion is positive or negative.

For two levels separated by an energy, ε, interacting through an
Figure 3.11 Summary of quadratic Zeeman interactions in SrW04:U in units of MHzT$^{-2}$. The experimental shifts of the $\beta$ and $\gamma$ lines are given adjacent to the levels. The strengths of the various interactions are given beside the arrow although when more than one interaction with a given level is involved the magnitude of the separate interactions cannot be uniquely determined.
off-diagonal Zeeman interaction \((g_{\text{eff}}\mu_B H)\) the repulsion of levels is given by,

\[
\Delta E = g_{\text{eff}}^2 \mu_B^2 H^2 / k \quad (3.2)
\]

Therefore, the strengths of the above interactions can be characterised by the size of the effective g-value. For the \(\beta \leftrightarrow \gamma\) interaction this gives for \(H||x\) values of \(g_{\text{eff}} = 0.4\) and \(g_{\text{eff}} = 1.6\) for SrWO\(_4\) and BaWO\(_4\) respectively. Interactions for \(H||z\) give values of \(g_{\text{eff}} = 1.5\) and \(2.0\) respectively.

**3C(iii). The holeburning mechanism**

To determine the holeburning mechanism further experimental observations have to be considered.

(a) Holes burnt in the \(\beta\) and \(\gamma\) lines using the low resolution dye laser in the dilute sample were found to be filled by irradiation at the wavelength of the \(\alpha\) zero-phonon line using the same laser power for a similar period of time as was used to burn the hole.

(b) In the concentrated sample, holes burnt in the \(\beta\) and \(\gamma\) lines using the low resolution dye laser revealed that the overall distributions of the resultant inhomogeneous lines had been shifted to a lower frequency and the line had been broadened (figure 3.12). The area under the lines remains constant to within the limits of accuracy of our experiment.

(c) In the concentrated sample, the overall distribution of the line profiles of the \(\beta\) and \(\gamma\) zero phonon lines could be shifted to higher and lower frequency by burning holes in the lower and higher frequency sides of the \(\alpha\) zero phonon line respectively (figure 3.13). Again, the area under the lines remains constant to within the limits of accuracy of our experiment.

(d) Allowing the crystal to rise to a temperature of greater than 50K and then recooling to 10K or lower returned the line profile to its original shape and
Figure 3.12 Excitation of the β and γ lines in the concentrated crystal at 10K, recorded in σ polarisation. The solid line is that obtained upon cooling the crystal from room temperature. A second trace (short dash) gives the spectrum after holeburning at 658.4 nm. As well as the holes at the burn frequency and the associated one in the β line, note that the antiholes are predominantly at lower energy. This gives an apparent broadening of the zero phonon line towards lower energy. The long dashed curve gives the spectrum after pumping the α zero phonon line. This causes removal of holes and a displacement of both β and γ zero phonon lines to lower energy.
Figure 3.13 The $\beta$ and $\gamma$ line profiles as affected by spectral holeburning in the $\alpha$ zero phonon line in SrWO$_4$:U. The upper trace shows the line profile upon cooling to 10 K. The second trace shows the line profile after holeburning on the high energy wing of the $\alpha$ zero phonon line. The third shows the line profile after subsequent holeburning on the low energy side of the $\alpha$ zero phonon line. The lower trace shows the line profile after cycling the temperature to 100 K.
position, irrespective of sample and the preceding holeburning cycle (figure 3.13).

Figure 3.10 shows that for each site there are two equivalent positions for the uranium ion, displaced either positively, U', or negatively, U", along the c-axis from the substitutional site. In an ideal crystal the sites will be isoenergetic with a potential barrier between the two sites. In a real crystal the two sites are likely to be experiencing a different potential due to defects in the crystal structure which cause the inhomogeneity of the zero phonon lines (see section 1B(iv)). The crystal will therefore have an ensemble of centres each having two alternative ground state sites, U' and U", with varying gaps between their ground state energies, schematically illustrated in figure 3.14.

The constant area under the excitation line profile, (b) and (c), suggests that the number of centres before and after holeburning remains constant. This suggests a photophysical holeburning mechanism in which laser excitation may produce a distortion of the centre, causing the electronic transition energy to be changed slightly but not to change the centre's electronic structure fundamentally as would be the case for photochemical holeburning (see section 1C(iii)).

It is proposed, therefore, that holeburning occurs when the centre is excited from the ground state to the excited state and relaxes back to the electronic ground state, but the location of the uranium ion is changed during the process. Once in the new site there is insufficient thermal energy for the ion to return to the original site. The hole is created because the frequency of the electronic transition to the excited state will now be different. All transitions at the laser (burn) frequency could become completely removed by this pumping cycle resulting in very deep holes. This is the case for the β and γ lines into which holes approaching 100% in depth can be burnt by irradiating with 100 mW for 30 s using the high resolution laser (table 3.2). However when the low resolution laser was used a hole of only 70% depth could be burnt in the β and γ lines and this is attributed to a sizeable fraction of the centres having their alternative resonant frequencies within the 30 GHz linewidth of the laser. Similarly, the α line shows only shallow holeburning (table 3.2)
Figure 3.14 Schematic illustration of potential energy wells for the position of the substitutional uranium ions. In each centre there are two sites, $U'$ and $U''$, as indicated in figure 3.10. With random internal lattice strain the relative depth of the two wells can be varied. The population within the wells attained with slow cooling is indicated by the black dots.
because there will only be a small number of the centres for which the shift in frequency is larger than the homogeneous linewidth.

**TABLE 3.2** Maximum hole depth attainable in SrWO₄:U samples using high and low resolution lasers.

<table>
<thead>
<tr>
<th>Doping concentration</th>
<th>200ppm</th>
<th>500ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1MHz</td>
<td>30GHz</td>
</tr>
<tr>
<td>Laser resolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero phonon line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>-</td>
<td>20%</td>
</tr>
<tr>
<td>β</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>γ</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
</tr>
</tbody>
</table>

The changes in the zero phonon line shape which occur upon optical excitation or thermal cycling, (b), (c) and (d), can also be understood if the frequency of the anti-hole is considered in more detail. There is a distribution in the energies of the U' and U" sites and when the crystal is first cooled the lower potential energy position will be favoured. Holes were burnt at 5 K before increasing the temperature to 30 K for several minutes and then returning it to 5 K with no significant loss of hole depth. This suggests that little thermal reorientation takes place below 30 K and this would prevent a Maxwell-Boltzmann distribution characteristic of lower temperatures from occurring. If then there is some correlation between the ground state energy and the corresponding absorption frequency, as can occur when the strain has less effect on the excited state energies (figure 3.14), the observed zero phonon line will have a dominant contribution from higher frequencies. Slow cooling therefore will give a zero phonon line biased to higher energies.

A different distribution of centres will be attained when optical excitation causes reorientation of the uranium ion and this will result in a different zero phonon line profile. The centres may be excited with equal probability by pumping
evenly over the width of a zero phonon line or pumping within the homogeneously broadened vibronic band for long periods. The population of the various potential wells will then become evenly distributed as the uranium ion falls back to its alternate sites and is unable to reorient thermally. The associated zero phonon line will correspondingly have a more even contribution from all wells and hence be at lower frequency than that attained by slow cooling. If, therefore, a sample for which a hole has been burned in the \( \gamma \) or \( \beta \) zero phonon line is subsequently irradiated at the frequency of the \( \alpha \) zero phonon line, with its much larger homogeneous width (as described in (a)) a wide range of centres will be excited. This irradiation will result in a zero phonon lineshape close to that described for broad band pumping. This has the effect of eliminating the holes and displacing the line further to lower energies (figure 3.12). Similarly the \( \beta \) and \( \gamma \) zero phonon line profiles may be manipulated by pumping on only the high or low frequency sides of the \( \alpha \) zero phonon line. Due to the large homogeneous width of the \( \alpha \) zero phonon line, broad holes result from optical illumination at this frequency (figure 3.15). These broad holes appear in the \( \beta \) and \( \gamma \) zero phonon line profiles as large shifts in the average optical transition energy (figure 3.13).

The effect of narrow band pumping or holeburning is to depopulate centres with absorption at the laser frequency regardless as to whether the absorption is associated with a high or low energy potential well. The absorption is not lost but merely shifted to the frequency of the complementary uranium location. Starting with a sample which has been slowly cooled where the uranium ions are predominantly in their lower energy site, holeburning will have the effect of displacing them to their high energy sites. The associated new absorption will in general be displaced to lower energy. This is seen in figure 3.12 where holeburning within the \( \beta \) zero phonon line decreases absorption at the burn frequency but increases the absorption at lower energy, longer wavelength.

Holeburning in the \( \alpha \) zero phonon line is analogous. Figure 3.15 shows the profile of the concentrated SrW0\(_4\) sample before and after burning a hole for 15
Figure 3.15 The α zero phonon line in the concentrated SrW\textsubscript{0.4}U sample at 10K measured in σ polarisation. The solid line gives the spectra obtained upon slow cooling whereas the dashed curve gives that attained after holeburning at 652.0 nm using 180 mW for 15 minutes.
minutes with a 180 mW laser beam. A shallow broad hole is visible but in addition the overall line profile has been shifted to lower energies. Broad band excitation or thermal cycling after holeburning will erase the hole and restore the zero phonon lineshape as discussed in the previous paragraph.

In all of the above cases the overall absorption or excitation intensities integrated over the zero phonon line remain constant. This is the important characteristic to establish the holeburning mechanism as photophysical rather than photochemical.

3C(iv) Holeburning efficiency

Much of the interest in spectral holeburning concerns the search for a material suitable for optical data storage (Castro et al 1978) in which both frequency and spatial domains are used for storing logical '1's and '0's as 'holes' or 'no holes' (see section 1C(iii)). An important parameter for deciding what sort of materials may be suitable for optical data storage is holeburning efficiency. This is defined as being the probability that a photoinduced change will occur when a centre absorbs a photon. A high holeburning efficiency would result in a reduced 'write' time but would increase the erasure of data during reading.

In terms of \([dT(t)/dt]_{t=0}\), the initial holeburning rate in terms of transmission, \(T_0\), the initial sample transmission, \(I\), the laser intensity, \(h\), Planck's constant (6.6 x 10^{-34} Js), \(\nu\), the laser frequency, \(R\), the total reflection loss and \(s\), the absorption cross section, it can be shown (Moerner et al 1984) that the holeburning efficiency, \(\eta\), is given by,

\[
\eta = \frac{[dT(t)/dt]_{t=0}}{sT_0(I/h\nu)(1-T_0-R)}
\]  

(3.3)

\([dT(t)/dt]_{t=0}\) was found to be 0.1 s^{-1} (figure 3.16) when burning in the \(\gamma\) zero phonon
Figure 3.16 Holeburning rate for the $\gamma$ line in SrWO$_4$:U at 10K. The trace shows emission as a function of time as a hole is burnt, starting from an unburnt section of the zero phonon line at t=0. The straight line approximates the t=0 holeburning rate.
line of SrWO$_4$:U with $T_0 = 0.96$, using a laser beam with $I = 10^5$ Wm$^{-2}$ and $\nu = 4.5 \times 10^{14}$ Hz. The value of $R$ is taken to be negligible. The absorption cross section, $s$, is equal to the ratio of the absorption coefficient of the centre at the laser frequency to the density of centres within one homogeneous linewidth of the laser frequency, $N_\nu$. For high initial sample transmission, the laser frequency absorption coefficient is simply the ratio of the crystal absorption to crystal length, $L$, that is, $(1-T_0)/L$. For a hole limited by laser linewidth, $\Delta \nu_{\text{laser}}$, the proportion of centres within one homogeneous linewidth of the laser is $\Delta \nu_{\text{laser}} / \Delta \nu_{\text{inhom}}$ (for holes burnt near to the line centre) where $\Delta \nu_{\text{inhom}}$ is the inhomogeneous linewidth of the zero phonon line.

If $P$ is the proportion of tungsten ions replaced by uranium ions, $\rho$ is the density of SrWO$_4$ (6200 kgm$^{-3}$), $N_A$ is Avogadro's number ($6 \times 10^{23}$) and $M$ is the molecular mass of SrWO$_4$ (0.34 kg) then $N_\nu$ is given by,

$$N_\nu = \frac{\Delta \nu_{\text{laser}}}{\Delta \nu_{\text{inhom}}} \cdot \frac{P \rho N_A}{M} \quad (3.4)$$

Substituting our data for a SrWO$_4$ crystal with $L = 2$ mm, $\Delta \nu_{\text{inhom}} = 10^{11}$ Hz and $P = 2 \times 10^{-4}$ gives a holeburning efficiency of the order of $10^{-4}$. This holeburning efficiency is thought to be too low to be of any technological interest (Moerner and Levenson 1985).

The low quantum efficiency provides evidence that a substantial, though possibly reduced, potential barrier between the two possible uranium ion sites in the centre also exists in the excited electronic state. This is concluded from the fact that for every ten thousand times the transition is excited the uranium ion, during its 20 $\mu$s lifetime in the excited state, moves only once to its alternate site to produce an optical hole. Had there been no such barrier to reorientation the holeburning efficiency would be 0.5 corresponding to relaxation to either equilibrium site with equal probability. It is further possible that the reorientation does not occur in the excited state at all but rather in the ground state during the relaxation cycle. For
example, there is radiative decay to vibrational levels up to 800 cm\(^{-1}\) above the ground state and in these states there will be enough energy to cross the potential barrier. Evidence for this is the fact that when the sample is heated to 50K, weakly populating such vibrational levels, spectral holes are eliminated.

\section*{3D Conclusion}

Spectral holes have been burnt in SrWO\(_4\):U and BaWO\(_4\):U which has allowed techniques of high resolution spectroscopy to be used to determine the site symmetry of the centre. Quadratic Zeeman shifts of the narrow spectral holes have shown that the substitution of U\(^{6+}\) ions is distorted in one of two crystallographically equivalent directions along the c-axis. This reduces the centre symmetry from \(S_4\) (tetragonal) to \(C_2\) (monoclinic). The \(\alpha\), \(\beta\) and \(\gamma\) zero phonon lines are assigned to states which transform as \(\Gamma_2\), \(\Gamma_1\) and \(\Gamma_2\) irreducible representations respectively and a further \(\Gamma_1\) state lies at higher energies.

The magnitudes of the g-values obtained from the Zeeman effect investigations are as high as 2.0. This is higher than for degenerate first excited states of U\(^{6+}\) in uranyl (Denning \textit{et al} 1976) and in an octahedral environment (Runciman \textit{et al} 1985) which indicates that with the large spin-orbit parameter there is a significant orbital contribution in determination of the Zeeman interaction.

Although there has been significant progress towards understanding the electron configurations involved in the excited states of hexavalent uranium in uranyl ions (Denning \textit{et al} 1979), in molecules such as UF\(_6\) (Hay 1979) and in complexes such as UO\(_5\)F (Runciman \textit{et al} 1985), so far there has been no work dealing with the tetrahedral unit. Analogous to the linear and octahedral environments it is expected that the excited states will be formed from the transfer of an electron from a nearest neighbour oxygen to an f-electron orbit on the
uranium. This results in a large number of possible electron-hole states and assumptions concerning the relative energies of the $a_1$, $t_1$ and $t_2$ f-electron orbits and the $\sigma$ and $\pi$ ligand orbitals are desirable. Consideration must first be given to the magnitude of the distortions lowering the symmetry from $T_d$ to $S_4$ and $C_2$. In this regard the near degeneracy of the $\beta$ and $\gamma$ levels (16 cm$^{-1}$ separation in SrWO$_4$ and 5 cm$^{-1}$ in BaWO$_4$) is taken to be significant. The Zeeman perturbation which has the largest effect on their separation is that of field at right angles to the crystal c-axis implying an approximate higher symmetry system with a principal axis in the a-b plane. The uranium ion could, for example, lie between two oxygen ions with the other two oxygen ions being at a somewhat larger distance giving a perturbed linear molecule. This is reasonably consistent with the Zeeman data, particularly as it was shown that it was a field along the oxygen-oxygen axis, the axis of the perturbed linear molecule, that gave the maximum Zeeman effect. However, none of the other spectroscopic characteristics of the system, such as emission wavelength, g-values or features at many multiples of the symmetric mode frequency ($\nu = 730$ cm$^{-1}$, Morozov et al 1971), are in any way like that of a uranyl ion. Thus the origin of the approximate symmetry in the a-b plane is not clear and the exact geometry of the centre must therefore still be in some doubt.

It has been pointed out (Blasse 1987) that the emission maximum of the U$^{6+}$ luminescence in oxides shifts gradually from green to red as the uranium coordination changes gradually from six to four. The uranium centre in strontium and barium tungstate emits at a longer wavelength than for any other uranium doped oxide. Furthermore, the emitting zero phonon line in these compounds lies 15 nm higher in wavelength than in uranium doped calcium tungstate which would be expected to have very similar spectroscopic properties. This trend to higher emission wavelength with decreasing coordination is therefore confirmed as the uranium ion in the strontium and barium compounds is thought to be no longer symmetrically placed between the four oxygen ions. The different spectroscopic properties of uranium doped calcium tungstate are attributed to uranium ions
substituting directly for tungsten ions, without experiencing a distortion, giving a coordination for the uranium ion of four.

The holeburning mechanism has been shown to be photophysical arising from the reorientation of the uranium between the two distorted sites. This situation is very similar to the two level system that has been well utilised to explain holeburning in glassy systems (Hayes et al. 1988). The major difference is that the two level description of glasses as first proposed by Anderson et al. (1972) and Phillips (1972) is an approximation for the many degrees of freedom present in a glass whereas here there are strictly only two ground states possible for each substitutional site. A better analogy might be that of ReO₄ molecules in alkali halides where the ion can substitute in two different orientations (Sievers et al. 1985). The holeburning efficiency of 10⁻⁴ is too low for these materials to be of practical use for digital information storage.
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The study presented in this chapter has been published in different form in The Journal of Physics: Condensed Matter Physics, Volume 1, pages 1339-1352. (1989)
CHAPTER FOUR

TRANSIENT AND TWO PHOTON PERSISTENT SPECTRAL HOLEBURNING IN SAMARIIUM DOPED CALCIUM SULPHATE

4A INTRODUCTION

4A(i) General spectroscopy of CaSO₄:Sm³⁺

Spectra of lanthanide doped crystals have proved to be of great interest for many decades due to the sharp zero phonon lines corresponding to $4f^n \rightarrow 4f^n$ transitions. The classical spectroscopy of these materials has been summarised in many books and reviews (Wybourne 1965, Dieke 1968, Hufner 1978, Kaplyanskii and Macfarlane 1987) and, indeed, a review of high resolution spectroscopy of rare earth ions in solids has been published (Macfarlane and Shelby 1987). This study presents new, high resolution studies of a material not covered by previous investigations.

The general spectroscopy of CaSO₄:Sm³⁺ had been completed upon the start of this study (Danby et al 1988). Figure 4.1 shows the non-selective excitation spectrum of the crystal, in which the pulsed laser frequency is scanned and all emission is detected. Selective excitation spectra were also recorded while monitoring the individual emission lines. This revealed the presence of three crystallographically distinct Sm³⁺ centres, the principal excitation lines of which
Figure 4.1 Excitation spectrum of CaSO$_4$:Sm at 10 K detecting all emissions. The groups of lines were found to be associated with three distinct Sm$^{3+}$ centres denoted A, B and C. (from Danby et al 1988)
have been labelled as either A, B or C in figure 4.1. Selective excitation of these zero phonon lines revealed the emission spectra shown in figure 4.2. Some of the weak lines evident in figure 4.1 did not appear to be correlated with the emission lines of these three centres, suggesting that further centres may also be present.

4A(ii) Conversion of Sm$^{3+}$ centres to Sm$^{2+}$ centres in CaSO$_4$

The emission spectrum of the CaSO$_4$:Sm$^{3+}$ sample following x-irradiation to an exposure level of 10$^3$ Ckg$^{-1}$ reveals a series of new lines between 680 and 740 nm (figure 4.3). These lines are ascribed to the $^5$D$_0 \rightarrow ^7$F$_0$, $^7$F$_1$ and $^7$F$_2$ transitions of a Sm$^{2+}$ centre (Danby et al. 1988). A reduction of 20 to 30 percent in the relative magnitude of the Sm$^{3+}$ A centre suggested that only this centre is converted to a Sm$^{2+}$ centre during x-irradiation. Comparisons with previous work on CaSO$_4$:Eu$^{3+}$ (Danby 1983) suggests that the A centre is formed when a Sm$^{3+}$ ion replaces a Ca$^{2+}$ ion substitutionally at a centre of C$_{2v}$ symmetry. The lack of local charge compensation would then be likely to make conversion of Sm$^{3+}$ to Sm$^{2+}$ more energetically favourable than for a locally charge compensated centre.

Studies of the conversion between Sm centres under ultraviolet illumination have also been conducted (Calvert and Danby 1984, Danby et al. 1988). The Sm$^{3+} \rightarrow$Sm$^{2+}$ process was found to be strongly temperature dependent as had been reported previously for the related material, CaSO$_4$:Eu$^{3+}$ (Danby 1988) in which the mechanism was found to rely on thermally induced population transfer between the upper states of the europium-oxygen complex. Within this model, the pathway for photochemical conversion is essentially closed for temperatures below 50 K and, indeed, for CaSO$_4$:Sm$^{3+}$ very little conversion was found to take place at 10 K.

By contrast, only five minutes ultraviolet illumination of previously x-irradiated CaSO$_4$:Sm$^{3+}$ at 10 K was found to produce a 95 percent decrease in the overall Sm$^{2+}$ emission level and this was accompanied by a corresponding
Figure 4.2 Emission of the three centres, A, B and C. The A trace is obtained by excitation at 562.7 nm which is resonant with the highest energy emission line. The B trace excitation is at 563.2 nm and the C trace excitation at 561.8 nm. (from Danby et al 1988)
Figure 4.3 Emission of the Sm$^{2+}$ centre in CaSO$_4$ at 10 K. The excitation wavelength is at 689.2 nm. (from Danby et al 1988), corresponding to the $^5D_0 - ^7F_0$ transition.
increase in the Sm$^{3+}$ A centre emission. This response suggested that photochemical and perhaps gated holeburning via conversion of Sm$^{2+}$ to Sm$^{3+}$ centres may be possible in CaSO$_4$:Sm and this was the major objective of the study presented here. Investigations of transient holeburning in the Sm$^{3+}$ A centre and the Sm$^{2+}$ centre to which it was converted were also carried out.

4B EXPERIMENTAL DETAILS

The single crystal samples of CaSO$_4$:Sm used for this work were grown by slow evaporation from concentrated H$_2$SO$_4$ using a technique which has been fully described elsewhere (Calvert and Danby 1984). All studies of the Sm$^{3+}$ centres in CaSO$_4$ were performed using the "as grown" material with a nominal concentration of 0.05% Sm$^{3+}$. The studies of Sm$^{2+}$ centres were performed by first reducing a quantity of the Sm$^{3+}$ dopant ions to Sm$^{2+}$ by x-irradiating the sample to an exposure level of 10$^3$ Ckg$^{-1}$ using a Co x-ray tube operating at 40 kV.

The high resolution holeburning measurements were performed using a Coherent 599-21 standing wave dye laser with a linewidth of 2 MHz. A dye solution of 10$^{-2}$ M Exciton LD688 dye in a 4 to 1 mixture of butyl alcohol and glycerol (Beber and Szabo 1984) was used for the Sm$^{2+}$ measurements at 690 nm and a 10$^{-2}$ M solution of Exciton Rhodamine 560 dye in ethylene glycol was used for the Sm$^{3+}$ measurements at 560 nm. A measure of the absorption was obtained by monitoring the emission intensity at 725 nm due to the $^5$D$_0$→$^7$F$_2$ transition for Sm$^{2+}$ and at 600 nm due to the $^4$G$_{5/2}$→$^6$H$_{7/2}$ transition for Sm$^{3+}$. A Spectra Physics model 171 Argon ion laser operating in multiline mode was used as the gating source for the photon gated holeburning experiments. This was focussed to provide optical power densities of 20 Wcm$^{-2}$ in the visible (principally 488 nm and 514 nm) and 2 Wcm$^{-2}$ in the ultraviolet (330 - 360 nm). For these measurements
the samples were maintained at 2 K by immersion in superfluid liquid helium.

**4C RESULTS AND DISCUSSION**

**4C(i) Optical holeburning in CaSO$_4$:Sm$^{3+}$**

A high resolution study of the dominant A centre line at 562.7 nm was performed using the unfocussed beam from the standing wave dye laser described above (power density 2.5 W cm$^{-2}$). This revealed that the line had an inhomogeneous width of approximately 8 GHz and exhibited no apparent burning while the laser frequency was scanned across the line at sweep rates of 8 GHz s$^{-1}$ or greater. When the laser scan was stopped within the line however, the emission intensity dropped rapidly by approximately 30% of its unburned value. Decreasing the laser power density using neutral density filters was found to decrease the proportional hole depth but increasing the power density by focussing the beam produced no increase in hole depth beyond 30%. This suggests that the hole burning is associated with $^{147}$Sm (I=7/2) and $^{149}$Sm (I=7/2) isotopes, which are 30% naturally abundant and the only naturally occurring Sm isotopes with non-zero nuclear spin. As the centre is an odd electron system there will be a Kramers degeneracy (Abragam and Bleaney 1986) which may be lifted by the influence of a nuclear spin. For the isotopes with a nuclear spin of I = 7/2 this will lead to the presence of eight hyperfine levels and holeburning can arise through a laser induced redistribution of the population among these levels (see section 1C(iv), figure 1.5). There is no equivalent holeburning mechanism for the 70% of Sm isotopes without nuclear spins.

No long lived holes were detected when sweeping the laser 100 ms after the burning process nor could any gated permanent holes be produced by introducing a second photon frequency in the ultraviolet. Evidence of ultraviolet
induced photochemical changes in CaSO₄:Sm has been reported (Calvert and Danby 1984). This previous study was conducted at room temperature, however, and it is not surprising that at low temperatures valence changes are not observed as photochemical change in the related material, CaSO₄:Eu³⁺, also shows strong temperature dependence (Danby 1988).

4C(ii) Optical holeburning in CaSO₄:Sm²⁺

The ⁵D₀ → ⁷F₀ transition of the single Sm²⁺ centre lies at 689.2 nm and a high resolution dye laser study determined the inhomogeneous width to be 5 GHz. By stopping the laser scan when the frequency is within the inhomogeneous line of the transition a hole was burned to a depth of 90% of the original absorption strength using a laser power of 1 W cm⁻². The hole was short lived and the hole spectrum could not be measured with a single laser beam. The spectrum could be measured, however, using two laser beams. The two beams were generated by driving an acousto-optic modulator at two adjacent radio frequencies. One beam was fixed in frequency and gave rise to deep holes and hence only weak emission. The second beam was swept in frequency and used to read the hole generated by the first. This second beam was weaker than the burn beam but because there was no associated burning the emission level was high and the spectrum was readily detectable using the excitation technique. A single sharp hole with no antihole was observed. The holewidth was 4 MHz, set by laser jitter. With focusing, the hole depth increased marginally whereas a reduction in intensity reduced the hole depth.

The hole depth is a measure of the fraction of centres held in levels other than the ground state. One of these levels will be the excited state, but since inversion cannot be achieved (see section 1C(iv)), the observed hole depths of 90% cannot be explained by saturation holeburning, that is population in the excited state. Levels intermediate between the ground and excited states could not
explain the large hole depth as additional reservoirs of population should be long lived to give deep holes. This means that the holes themselves would be long lived but this is not the case. Measurement of fast recovery of the hole in absorption was not successful but excitation measurements give a value limited by the excited lifetime (figure 4.4), implying a recovery rate faster than 10 ms.

The population reservoir may, however, be at a level higher in energy than the resonant excited state. The absorption of the \(^5\)D\(_0\) state in cubic lattices, SrF\(_2\) and SrCl\(_2\), has been studied previously (Payne et al 1988). It was found that considerable excited state absorption occurs to several higher excited states. The reduction of symmetry to \(C_{2v}\) in the CaSO\(_4\) host lattice causes further electronic transition probabilities to become non-zero and it would therefore appear likely that excited state absorption takes place. Some of the hole depth may therefore be attributed to centres which absorb two or more photons thus creating populations in higher electronic states. These states generally have lifetimes many orders of magnitude smaller than that of the \(^5\)D\(_0\) state and so it is unlikely that this population could account for a hole depth of 90% unless the relaxation process occurs through a different route to absorption. A search for high energy emission revealed nothing at wavelengths less than 689 nm and so it is unlikely that the higher excited states relax directly back to the ground state. The precise mechanism producing the very deep holes remains to be determined.

Permanent holeburning was achieved when a second illumination source was introduced. This provides further evidence of excited state absorption. With a 20 Wcm\(^{-2}\) Ar\(^+\) visible laser beam, a 7% deep long lived hole was obtained after 15 minutes exposure (figure 4.5). Faster burning was achieved with ultraviolet irradiation. For a 2 Wcm\(^{-2}\) beam at 351-363 nm a 7% permanent hole was attained after 5 minutes irradiation although at these wavelengths the ultraviolet beam alone causes some non-selective photochemical change. Although the gating wavelengths may not be optimum, these rates are still very slow and totally unrealistic for digital memory device application (Castro et al 1978). The slow rate
Figure 4.4 The CaSO$_4$:Sm$^{2+}$ transient hole lifetime measured by changes in the emission level between strongly and weakly absorbing parts of the zero phonon line after acousto-optically switching the laser frequency for pulses of 60 ms (upper trace), 17 ms, 6 ms and 3 ms (lower trace).
Figure 4.5 Gated optical hole burned in the 689.2 nm zero phonon line of CaSO₄:Sm²⁺ using the Ar⁺ laser lines at 488 and 514 nm for the gating light. The strength of the signal, detected in excitation, is expressed as a percentage of the absorption in the centre of the zero phonon line.
is accentuated by the short lived holeburning effect which causes a large reduction in the number of optically active centres during irradiation.

The widths of the permanent holes are 200 MHz, much larger than that of the short lived holes. These holes are the result of burning for several minutes and could acquire some width from the long term laser drift though this effect could only account for an increase in width of less than 10 MHz. Rather, the increased width is indicative of a different mechanism such as there being a valence change associated with the permanent hole, whereas there is no such change for the short lived hole. The redistribution of charge in the crystal can then change the effective fields at the crystal sites and account for the much broader holes. Similar effects were observed in the gated holeburning of LiGaO₃:Co²⁺ (Macfarlane et al 1986). The Sm³⁺→Sm²⁺ valence change in BaFCl gave hole widths which were observed to be concentration dependent (Winnacker et al 1985). For a concentration of 0.05% Sm²⁺, the widths were found to be 200MHz, similar to those observed here for CaSO₄:Sm.

**4D CONCLUSION**

It has been argued that CaSO₄:Sm has promising characteristics for gated holeburning both for Sm³⁺→Sm²⁺ using the resonant transition in the green and for Sm²⁺→Sm³⁺ for a transition in the red. The latter has been demonstrated and thus CaSO₄:Sm is a further example where a Sm²⁺ transition exhibits gated holeburning (Macfarlane 1988). There is no technological promise for the material as burning rates were exceedingly slow, requiring several minutes of two laser irradiation to produce measurable permanent holes.

Interesting short lived holeburning effects were observed for both ions. For the ⁴H⁵/₂ → ⁶G⁵/₂ Sm³⁺ transition at 562 nm the holeburning is due to redistribution
of population in the nuclear levels in each of the 15% abundant $^{147}$Sm and $^{149}$Sm isotopes. A similar effect could not account for the very deep holes produced in the $^5D_0 \rightarrow ^7D_0$ transition of Sm$^{2+}$ at 689.2 nm and the holeburning process in this case remains to be explained though a redistribution of the population to higher excited levels is thought to be involved in the mechanism.
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This study has been presented in altered form in The Journal of Luminescence, Volume 42, pages 83-88 though I did not contribute to the work on the conventional spectroscopy of the samarium centres included in the introduction to this chapter.
CHAPTER FIVE

TRANSIENT SPECTRAL HOLE BLEACHING THROUGH CROSS RELAXATION AND LEVEL ANTICROSSING IN THE DIAMOND N-V COLOUR CENTRE

5A INTRODUCTION

5A(i) The N-V centre

Much interest has been shown in the N-V colour centre since first being reported (Du Preez 1965) though contrasting interpretations have been put forward to explain the phenomena associated with it. The data and analysis presented here and in the next chapter seek to clarify the nature of the centre and its interactions.

The N-V centre is created in Ib diamonds after radiation damage and annealing at temperatures over 900 K and is considered to arise from substitutional nitrogen accompanied by a vacancy at a nearest carbon site (Davies and Hamer 1976). Consequently the centres are aligned along the (111) axes of the diamond and have trigonal (C\textsubscript{3v}) symmetry.

The centre gives rise to a broad, strongly absorbing (100% for white light absorption for the sample used in this study) zero phonon line at 638 nm associated with an A→E transition. The excited state is known to have a lifetime of only 13 ns (Reddy 1989) and it had been thought that the levels involved in the optical transition were spin singlets. Electron paramagnetic resonance (EPR)
studies of a triplet state observed during optical pumping were thought to correspond to an intermediate metastable triplet level (figure 5.1) (Loubser and van Wyk 1977). This conclusion was based on enhancement of the EPR signals upon illumination with light at 638 nm. Subsequent work has suggested the existence of a metastable level 75.6 cm\(^{-1}\) above the ground state (Nisida \textit{et al} 1989) though there is no evidence to suggest that this level is involved in the excitation and relaxation process. Figure 5.2 shows a room temperature EPR signal from the diamond used in this study, recorded without illumination. The presence of the signal despite dark conditions suggests that the triplet may, in fact, be the ground state. The enhanced EPR signals previously reported could then be interpreted as arising from optical pumping and this is substantiated by the appearance of part of the EPR signal in emission (figure 5.1). Two laser holeburning measurements have confirmed the triplet to be the ground state and hence the optical transition involved is \(^3A\rightarrow^3E\) (Reddy \textit{et al} 1987). This is substantiated by spin coherence measurements (van Oort \textit{et al} 1988) and Raman heterodyne detection techniques (see chapter 6). Further evidence for a triplet ground state is provided by the present data and interpretation is, therefore, in terms of a \(^3A\rightarrow^3E\) transition.

The Zeeman Hamiltonian for the spin \(S=1\) levels of the N-V ground state (neglecting hyperfine effects) may therefore be written as,

\[
H = \mu_B (H \cdot g \cdot S) + D [S_z^2 - S(S+1)/3] \tag{5.1}
\]

where \(|D| = 2.88\) GHz gives the zero field ground state splitting. The sign of \(D\) has not been determined but is irrelevant for the purposes of this discussion. The \(g\)-value is isotropic with a value of 2.01 (Loubser and van Wyk 1977, 1978). The energy matrix for a centre with its axis at an angle \(\theta\) to the field is given on page 121 (\(|x\), \(|y\), \(|z\) basis).
Figure 5.1 The EPR of the optically illuminated N-V centre, aligned along a \( \langle 111 \rangle \) direction, shown in dispersion. Zero magnetic field corresponds to 3300 Gauss. (line drawing from Loubser and van Wyk 1977)
Figure 5.2 EPR of the N-V centre with the magnetic field along [111] and without optical illumination, shown in dispersion. Zero magnetic field corresponds to 12500 Gauss. Slight misalignment of the field is indicated by the non-degeneracy of the signals due to the three sets of unaligned N-V centres.
\[
\begin{bmatrix}
\frac{1}{3}D & -ik \cos \theta & 0 \\
-ik \cos \theta & \frac{1}{3}D & -ik \sin \theta \\
0 & ik \sin \theta & \frac{2}{3}D
\end{bmatrix}
\]  (5.2)

where \( k = g \mu_B H \). In general there are four orientations (the centres related by inversion are indistinguishable in a magnetic field) of the trigonal centre in the cubic crystal (figure 5.3), the [111] and [11-1] directions defined as being parallel to the centre 1 and centre 2 principal axes respectively. In the (110) plane of rotation indicated, defining the direction of the field, \( \theta \), with respect to centre 1, the orientation of the axis of centre 2 to the field is \( \theta - 70.5^\circ \) and to centres 3 and 4, \( \cos^{-1}(\cos(\theta - 54.7^\circ)/\sqrt{3}) \). The energy levels of any given field orientation can be obtained by diagonalising the energy matrix (5.2) with the appropriate values for \( \theta \) and \( k \).

5A(ii) Holeburning in the N-V centre

Long lived spectral holes have been reported in the 638 nm zero phonon line with time constants of 40 s, 500 s and several hours (Harley et al 1984, Nisida et al 1989). The investigation presented here is concerned with short lived optical holes, however. Transient spectral holes burnt in the 638 nm zero phonon line of the N-V centre arise from optical pumping between levels of the spin triplet ground state (Reddy et al 1987) and have a lifetime of 2 ms (Reddy 1989, Runciman et al 1989). This optical pumping during the process of excitation and relaxation is confirmed by the asymmetry of the transient holeburning spectrum. The enhancement of EPR signals due to optical illumination (Loubser and van Wyk 1977, Nisida et al 1989) is therefore confirmed as being due to the optical pumping. During continuous illumination, the depth of the hole depends on the balance between the optical pumping and the spin relaxation within the triplet levels (see section 1C(iv)). In zero magnetic field this corresponds to optical
Figure 5.3 Orientation of trigonal axes. The experimental traces are taken as the magnetic field is varied in the (T10) plane, shaded.
pumping between the spin singlet and spin doublet levels or, in the presence of a field, between all three levels of the triplet.

5A(iii) Cross relaxation in the N-V centre

The dynamic system which determines the depth of the hole during optical illumination may be represented by a system of heat reservoirs (Veeman et al 1975). For the N-V centre, irradiated at 638 nm, six heat reservoirs may interact by means of cross relaxation or otherwise. They are (with reference to figure 5.4);

O₁: A set of N-V centres aligned along a particular crystallographic direction, with the optical transition from any ground state resonant with the laser.

O₂: A set of N-V centres aligned along a different crystallographic direction to the centres in O₁, also having a resonant optical transition with the exciting laser. Note that there are four centre orientations (figure 5.3) but all interactions may be explained by considering only two of these, whereby sets O₁ and O₂ may correspond to different centre orientations for different experimental conditions.

I₁: The set of N-V centres aligned in the same crystallographic direction as set O₁ but with no transition resonant with the laser. Due to the sharpness of the laser linewidth relative to the inhomogeneous linewidth of the optical transition, this set is substantially larger than O₁. Sets O₁ and I₁ compose a total set of similarly oriented N-V centres, NV₁. The total set, NV₁, may be considered for interactions where this reservoir provides a centre with an appropriately split triplet ground state such that spin flip-flops with an optically pumped reservoir may take place. The NV₁ reservoir is considered not to be optically pumped though subset O₁ is resonant with the laser.

I₂: The set of N-V centres aligned in the same crystallographic direction as set O₂ but with no transition resonant with the laser. Set NV₂ is the sum of sets O₂ and I₂, analogous to set NV₁.

S: An entirely different ground state spin system.
Figure 5.4 The heat reservoirs (as discussed in the text) for the diamond sample during optical illumination at 638 nm.
L: The lattice.

In addition, the optical pumping cycle is represented by a 'refrigerator' which attempts to maintain both optically active triplet spin systems' temperatures at that determined by the pumping cycle alone. Under most conditions, the optical hole depth is determined by the strength of the optical pumping and the rate at which the optically pumped centres may relax either via spin-lattice relaxation or spin-spin relaxation with the reservoirs of optically inactive centres which are already in equilibrium with the lattice. These interactions are indicated in figure 5.4 by thick lines. Other heat reservoirs exist within the diamond but these are ignored for the sake of clarity, at this stage.

It is common for spin-spin cross relaxation, involving energy conserving spin 'flip-flops' of neighbouring centres to be a faster process than spin-lattice relaxation (Abragam and Bleaney 1970). Spin-spin cross relaxation requires resonant conditions to be significant however. This is always the case for sets of triplet centres oriented in the same crystallographic direction. However, there are other situations, at particular field strengths and orientations, for which there is accidental coincidence between ground state splittings of the probed centre and those of the other type of centre or the inequivalent orientation of the N-V centre. The coincidence brings the two separate ensembles of centres into resonance thus greatly increasing the significance of that particular cross relaxation interaction. Since the relaxation of the combined system is always faster than that of the separate ensemble of centres, the result of any matching of energy separations is a reduction in the significance of the 'refrigerating' optical pumping and hence a reduction in optical hole depth, that is, hole bleaching.

The additional cross relaxation interactions which may occur are marked on figure 5.4 by thinner lines and may be divided into three categories;

(1) Reduction of the hole depth occurs when the separation of the energy levels of the N-V centre matches those of an entirely different colour centre in the diamond. In the crystal used here, this is the paramagnetic P1 centre.
(2) There is an enhanced spin-spin interaction between magnetically equivalent N-V centres when the magnetic field is tuned so that, within each of these centres, the levels are equally spaced.

(3) A reduction of the hole depth occurs when there is a matching between the splittings of orientationally inequivalent N-V centres.

Analogous effects have been observed for holeburning in LaF₃:Pr³⁺, where population reservoirs are stored in nuclear hyperfine levels (Otto et al. 1986). Sweeping the strength of the magnetic field causes transient changes in the hole depth at values of the magnetic field where the Zeeman splittings of the Pr³⁺ hyperfine levels match that of the fluorine nuclear spin system. In the present case, the population reservoirs are in the electron spin levels and our optical study presents an illustration of the effect of various spin-spin cross relaxation interactions on these reservoirs.

5A(iv) The P₁ centre

The P₁ centre involves a single substitutional nitrogen site with S=1/2 electron spin ground state (Smith et al. 1959, Cook and Whiffen 1966, Loubser and du Preez 1965). The P₁ centre exhibits a static Jahn-Teller distortion from T₄ to C₃ᵥ symmetry and the EPR is that of a trigonal centre with a predominant hyperfine interaction with the nitrogen (I = 1) nuclear spin. The spin Hamiltonian for the P₁ centre is given by

\[ H = \mu_B (\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}) + S \cdot A \cdot I \]  

(5.3)

\( g \) is isotropic with a value of 2.024 and the hyperfine coupling parameters have values of \( A_\parallel = 0.114 \text{ GHz} \) and \( A_\perp = 0.081 \text{ GHz} \) (Smith et al. 1959). The hyperfine axis is determined by the C-N axis and consequently the P₁ centre has four possible crystallographic orientations identical to the crystallographic orientations
of the N-V centre.

5A(v) Level anticrossing

A further situation which may give rise to a change in the hole depth is when one of the splittings within the triplet approaches zero. When the magnetic field is along an N-V centre main axis, the |+⟩ and |0⟩ spin levels should cross at 1020 Gauss. Any small deviation of the magnetic field from the [111] direction or the strain perturbations at the N-V centre will mix the spin states and the latter will not, therefore, cross in practice. This situation is more commonly referred to as level anticrossing. The holeburning signal and its width will be associated with the resultant admixture of the |+⟩ and |0⟩ spin states in the anticrossing region.

5B EXPERIMENTAL DETAILS

The diamond crystal was a 1 mm cube with (100), (110) and (110) faces. The diamond was located in helium exchange gas within the bore of a superconducting magnet and could be rotated about the light direction which was at right angles to the field direction. The temperature was approximately 10 K. For a given orientation of the crystal, the transmission of a narrow-band (1 MHz) laser at the peak of the zero phonon line, at 638 nm, was measured as the field was swept at 5 Gauss/second from 0 to 1500 Gauss. The laser output power was 50 mW but best results were achieved by decreasing the power incident on the diamond to less than 1 mW to decrease the transient hole depth thus causing the small changes in hole depth due to cross relaxation effects to be emphasised. In terms of the thermodynamic model (see section 5A(iii)) this corresponds to decreasing the strength of the 'refrigerating' optical pumping to allow the effects of
spin-spin cross relaxation to be more easily detected.

A set of coils wound parallel to the field provided field modulation of a few Gauss and enabled a simultaneous measurement of the derivative of the transmission. The modulation was applied at 5 Hz and the signal was detected with an Ithaco Dynatrac 391A lock-in amplifier, set to a 12.5 ms time constant. The sweeps were repeated for various field orientations. No signal averaging was required for this series of measurements. Low field scans (0 to 150 Gauss) were signal averaged up to 20 times, however.

5C RESULTS AND DISCUSSION

5C(i) Cross relaxation between N-V centres and P1 centres

The splitting of the ±1/2 spin levels in the P1 centre is given by equation 5.3. Because of the isotropic g-value this splitting will be equal to $g \mu_B H$ for all orientations of magnetic field and cross relaxation may occur when the N-V ground state $|0\rangle \leftrightarrow |+\rangle$ splitting derived from the energy matrix (equation 5.2) is equal to this. For a magnetic field along the axis of an N-V centre (say centre 1 in figure 5.3) this will occur when $g \mu_B H = D/2$ and hence at a field strength of 511 Gauss. This is illustrated in figure 5.5. The resonant conditions are seen to coincide with a reduction in transmission of the diamond. This is interpreted as being due to a reduction in hole depth caused by an increase in spin-spin cross relaxation between the optically active triplet system heat reservoir, $O_1$, and the P1 spin system heat reservoir, $S$. This increase in spin-spin cross relaxation decreases the overall spin-spin relaxation time and hence decreases the effect of optical pumping. Upon rotating the field direction from the [111] direction to the [110] direction (angle $\theta$) the $|0\rangle$ and $|+\rangle$ levels approach at a slower rate and an increase in the required field strength to 770 Gauss results. This is shown from the solid line
Figure 5.5(a) Transmission of diamond crystal at 638 nm measured as a function of magnetic field strength in \( \sigma (E||[111]) \) polarization with \( H||[111] \). The crystal temperature was 10 K.

(b) Zeeman splitting for centres with \( H||[111] \). The three centres are (i) \( S = 1/2 \) system, (ii) an N-V centre with field along the main axis and (iii) an N-V centre with a field at an angle of 70.5° to the principal axis.

The vertical lines indicate the origin of the holeburning features and the arrows indicate the transitions involved in the cross relaxation. The long dashed line indicates a spin forbidden transition.
Figure 5.6(a) Differential of transmission of diamond crystal at 638 nm as a function of magnetic field for field orientations between H\{111\} and H\{110\}. (b) Cross relaxation signals as a function of field orientation and field strength. The experimental values from (a) are indicated by triangles and calculated values are given by the solid and dashed lines. The solid line is the variation predicted for N-V\leftrightarrow P1 cross relaxation and the dashed lines those predicted for N-V\leftrightarrow N-V cross relaxation.
(calculated crossing field) and the adjacent triangles (experimental results) in figure 5.6(b). Within the same range of field orientations, the axis of centre 2 is at a larger angle to the field and consequently gives signals at higher fields. These signals correspond to cross relaxation between spin systems O₂ and S. As the angle to centre 1 is increased, the angle to centre 2 decreases until the field bisects the centre axes when it is along [110]. Hence two lines merge at the [110] magnetic field orientation (figure 5.6). The close fit between the calculated crossing points of the N-V and P1 centre splittings and the experimental features suggest that the mechanism, involving enhanced cross relaxation between spin reservoirs, is correct.

Further evidence which confirms the nature of the cross relaxation is the nitrogen hyperfine interaction which gives rise to structure on each of the above N-V↔P1 cross relaxation features and this is discussed for H||[111]. The P1 centres and the N-V centres are both aligned along the (111) axes and hence the field will also be along the axis of one P1 orientation. The hyperfine interaction shifts the aligned mᵢ = ±1 states by an energy of 0.114 GHz and, as the splittings within the P1 and N-V system are changing with the field strength in opposite sense, decreasing and increasing respectively, the hyperfine levels give coincidences at ±19 Gauss from the mᵢ = 0 field value. At the same time the magnetic field is at an angle of 70.5° to the axis of the other P1 centre orientations. For these, the effective hyperfine coupling parameter is,

\[
\sqrt{(A_{||}^2 \cos^2 70.5° + A_\perp^2 \sin^2 70.5°)}
\]

and hence there are another two lines separated by ±15 Gauss. Therefore, the inclusion of the hyperfine interaction within the P1 centre accounts for the five line pattern observed for H||[111] (figure 5.7(a)). The ratio of the line sizes should be in proportion to the ratio of the number of centres giving rise to each line. All four orientations of P1 centre contribute to the central feature but only the aligned
Figure 5.7 Actual (a) and modelled (b) illustrations of the holeburning features associated with the P1 hyperfine structure for H∥[111]. The model accounts for the theoretical separations and relative sizes of features. The scale is calibrated in Gauss relative to a zero which corresponds to 510 Gauss.
centre orientation contributes to the outer pair of features. The three remaining centre orientations are all at 70.5° to the field and therefore contribute to the remaining features. As there are an equal number of centres aligned in all four directions the expected ratio, from the central feature outwards, is 4:3:1. Figure 5.7(b) shows a model for the line shape based on this ratio and the calculated splittings of the lines, whilst figure 5.7(a) shows the experimental trace. The measured central line is larger than expected, suggesting there may also be cross relaxation with other $S=1/2$, $g=2$ centres in the diamond.

When the field is rotated in the (110) plane, one of the three hyperfine axes of the P1 centres not aligned along [111] is no longer at the same angle to the field. A seven line pattern in the size ratio 4:2:1:1 is expected but this is never resolved. Also, for magnetic fields at an angle to the N-V centre main axis, the triplet splittings are not a linear function of field strength. This results in the hyperfine features being displaced asymmetrically about the central line and the effect of this can be seen best in traces close to the [110] field orientation (figure 5.6). At [110], the field is at the same angle to two pairs of P1 centres and a five line pattern in the size ratio 4:2:2 is expected though this is hard to confirm due to a slight misalignment of the field causing the signals due to N-V centres 1 and 2 (figure 5.3) to interfere.

5C(ii) **Cross relaxation between magnetically equivalent N-V centres**

Cross relaxation between an optically active N-V centre and any other magnetically equivalent N-V centre may occur at all field strengths and orientations but may be enhanced under certain circumstances. In this situation, the three N-V ground state energy levels are equally spaced and mutual spin flip-flops can take place with adjacent centres occupying either of the alternate triplet states rather than just one. There is, therefore, a greater likelihood of cross relaxation between reservoirs $O_1$ and $NV_1$ (the $NV_1$ reservoir consists of the sum of $O_1$ and $I_1$
reservoirs) and between reservoirs $O_2$ and NV$_2$ (figure 5.4) resulting in a faster relaxation rate for the optically active centres. This yields a reduced hole depth.

An analytical expression can be obtained for the field strength required to give equally spaced levels from the energy matrix (equation 5.2). The eigenvalues, $\lambda$, are obtained by solving the determinant equation,

$$\lambda^3 + \left(\frac{-1}{3}D^2 - k^2\right)\lambda + \left[\frac{2}{27}D^3 - \frac{1}{3}Dk^2(3\cos^2 \theta - 1)\right] = 0 \quad (5.5)$$

The standard solutions to such a cubic equation leads to the three energy separations (for instance, Stevenson 1984),

$$v_i = 2\sqrt{3} \left(\frac{3k^2 + D^2}{9}\right)^{1/2} \sin\left(\frac{\alpha}{3} + \Delta\right) \quad \Delta = \frac{\pi}{3}, \frac{2\pi}{3}, \pi \quad (5.6)$$

where

$$\cos \alpha = \frac{9Dk^2 - 27Dk^2 \cos^2 \theta + 2D^3}{2\left(3k^2 + D^2\right)} \quad (5.7)$$

When $\alpha = \pi/2$, the magnitude of two energy separations are equal and the third is double the first two, which is the situation for three equally spaced levels. Hence to have equally spaced levels,

$$9Dk^2 - 27Dk^2 \cos^2 \theta + 2D^3 = 0 \quad (5.8)$$
Solving for the field strength gives,

\[ H = \frac{D}{g\mu_B} \frac{1}{3} \left( \frac{2}{3\cos^2 \theta - 1} \right)^{1/2} \]  \hspace{1cm} (5.9)

When \( \cos \theta \) is less than \( 1/\sqrt{3} \) the solution for \( H \) becomes imaginary. This corresponds to the angle being greater than 54.7° where the levels are unequally spaced for all field values. This is always the case for centres 3 and 4 (figure 5.3) when the field is being rotated in the (110) plane.

It can be seen that the smallest field that will give equally spaced levels is \( D/3g\mu_B \), when the field is along the trigonal axis of the centre. In this case, diagonalisation of the energy matrix (equation 5.2) shows that the eigenfunctions of the electronic states are the basis functions. Consequently, the cross relaxation required is \( |+\rangle \leftrightarrow |-\rangle \) with \( |0\rangle \leftrightarrow |+\rangle \), pure spin states, and although energy can be conserved the angular momentum cannot, thus the transition is forbidden. For a field at an angle to the trigonal axis the field strength required to give equally spaced levels is larger, as given by equation 5.9. The eigenstates are mixtures of the \( |+\rangle \), \( |-\rangle \) and \( |0\rangle \) basis functions, implying poorer spin quantisation. Energy and angular momentum may now both be conserved and the mutual spin flips become allowed. Hence the \( 1\leftrightarrow 1 \) feature associated with centre 1, which is forbidden for \( H||[111] \), becomes progressively stronger as the angle is increased (figure 5.3).

Centre 2 makes an angle greater than 54.7° to the field when it is close to the [111] direction and no signals are observed. However, at angles close to \( H||[110] \), centre 2 makes an angle of 35.3° to the field and cross relaxation features are observed. For \( H||[110] \), centres 1 and 2 are both at the same angle to the field and the \( 2\leftrightarrow 2 \) feature coincides with the \( 1\leftrightarrow 1 \) signal (figure 5.6).
5C(iii) Cross relaxation between magnetically inequivalent N-V centres

Two magnetically inequivalent centres may interact through cross relaxation when there is a common ground state splitting. This corresponds to cross relaxation between reservoirs $O_1$ and $NV_2$ or between reservoirs $O_2$ and $NV_1$ (figure 5.4), resulting in a faster relaxation rate for the optically active centres and a reduction in hole depth.

From equation 5.6, the three energy separations for each centre are given by,

$$C \sin \left( \frac{\alpha_1}{3} + \frac{\pi}{3} \right), C \sin \left( \frac{\alpha_1}{3} + \frac{2\pi}{3} \right), C \sin \left( \frac{\alpha_1}{3} + \pi \right)$$

and

$$C \sin \left( \frac{\alpha_2}{3} + \frac{\pi}{3} \right), C \sin \left( \frac{\alpha_2}{3} + \frac{2\pi}{3} \right), C \sin \left( \frac{\alpha_2}{3} + \pi \right)$$

(5.10)

(5.11)

where $\alpha_1, \alpha_2$ are given by equation 5.7, with $\theta = \theta_1, \theta_2$, respectively, for each centre and $C$ is a constant for a given field. As cross relaxation is dependant only on resonance between splittings, the sign of each term is irrelevant. Ignoring sign, if there is one common value between these two sets then the sets are equal (see appendix 5C(iii)). This implies that, for two inequivalently oriented centres, the three resonances coincide at the same magnetic field strength. It is, therefore, sufficient to establish one such coincidence and the field at which this occurs can be calculated using the analytical solutions (equation 5.6) or by numerical diagonalisation of the energy matrices (equation 5.2). Our calculations were performed on a computer using the latter technique.

When the magnetic field is along the [110] direction, centre 1 is aligned at the same angle to the field as centre 2 (figure 5.3) and hence the $1\leftrightarrow2$ cross relaxation should occur at the same field value as that for $1\leftrightarrow1$ (or $2\leftrightarrow2$), previously established. Away from the [110] direction, there are three separate
signals, the central one being associated with that between inequivalent centres 1 and 2. Following the signal with angle, it is seen to merge with that from the $1\leftrightarrow 3$ ($1\leftrightarrow 4$) cross relaxation when the field is along the [111] direction, where centres 2, 3 and 4 are all aligned at the same angle to the field. The $1\leftrightarrow 3$ and $1\leftrightarrow 4$ signals should coincide throughout, so long as the field is in the (110) plane. The observed splitting away from the $H||[111]$ direction is due to a slight misorientation of the field. Allowing for this misorientation the calculated field values make excellent agreement with the observed position for the sharp decrease in the depth of the spectral hole (figure 5.6) and the conclusion is that these dips are indeed due to cross relaxation effects.

Appendix 5C(iii) - Proof that if sets (5.10) and (5.11) have a common value then the sets are equivalent.

(i) If $\alpha_1$ were equal to $\alpha_2$, the sets would be equal for all field values. This may occur when $\theta_1$ is equal to $\theta_2$ (equation 5.7) which is the case for magnetically equivalent centres but cannot be the case for magnetically inequivalent centres.

(ii) Suppose the common value in sets occurs when,

$$\sin\left(\frac{\alpha_1}{3} + \frac{\pi}{3}\right) = \sin\left(\frac{\alpha_2}{3} + \frac{2\pi}{3}\right)$$

Then, taking inverse sine and equating,

$$\alpha_1 = \alpha_2 + \pi$$

By substituting for $\alpha_1$ in the second and third terms of set (5.10), the third and first terms of set (5.11) are generated respectively,

$$\sin\left(\frac{\alpha_1}{3} + \frac{2\pi}{3}\right) = \sin\left(\frac{\alpha_2}{3} + \pi\right) \quad \text{and,} \quad \sin\left(\frac{\alpha_1}{3} + \pi\right) = -\sin\left(\frac{\alpha_2}{3} + \frac{\pi}{3}\right)$$
Hence all three splittings are resonant at the same field value for this case (as only the magnitude of the splitting is relevant).

(iii) The only other possibility for resonance between members of the sets occurs when,

\[ \sin\left(\frac{\alpha_1}{3} + \frac{\pi}{3}\right) = \sin\left(\frac{\alpha_2}{3} + \pi\right) \]

By an entirely analogous process to (ii) it can be shown that both sets have three members of common magnitude and it has, therefore, been shown that, for any two centres, for any crystal alignment, all three splitting resonances will occur at the same field.

5C(iv) N-V centre level anticrossing

The broader feature (half-width ~ 20 Gauss) at 1020 Gauss, which occurs when the magnetic field is along the [111] direction, is associated with the level anticrossing of the |+\rangle and |0\rangle levels.

Reduced hole depth can result if the levels approach each other to within the homogeneous width of the optical transitions and, as a result, the |+\rangle and |0\rangle states can no longer provide separate population reservoirs. This mechanism is ruled out, however, by the large increase in the width of the level anticrossing absorption dip as the field is rotated from the N-V centre main axis (figure 5.8). By diagonalising the energy matrix (equation 5.2), it can be shown that an on-axis field will cause the |+\rangle and |0\rangle triplet levels to be more closely separated than an off-axis field at field values close to level anticrossing. Therefore, if the hole bleaching was due to the approach of the triplet levels to within the optical homogeneous width, the on-axis level anticrossing dip would be broader than for the off-axis case.
Figure 5.8 The transmission of the diamond crystal at 638 nm indicating the broadening of the level anticrossing dip as magnetic field misalignment (indicated) is increased. 'LAC' corresponds to 1020 Gauss and the total scan is 630 Gauss.
The increase in the width of the level anticrossing dip with increasing angle suggests that the hole bleaching mechanism is associated with triplet level state mixing which occurs over increasing magnetic field ranges as the field is rotated from the N-V centre main axis. A reduction of the hole depth near level anticrossing could imply that the state mixing gives rise to an increased spin flip-flop rate in the ground state but a subsequent investigation (van Oort and Glasbeek 1989) has shown that there is no change in the spin-spin relaxation time.

The hole depth may also be influenced by the optical pumping rate itself, however. Optical pumping usually occurs through relaxation to a preferred spin quantised ground state but, close to level anticrossing, the spin states become mixed and a reduction in the optical pumping rate may result. The level anticrossing dip appears to become shallower as field misalignment is increased which would not be expected as the $|0\rangle$ and $|+\rangle$ states of the aligned set of centres become the symmetric and antisymmetric admixtures at the level anticrossing field for all misalignments. The hole depth adjacent to the level anticrossing dip is not equal for different misalignments, however, as it is determined by the cross relaxation rate of equivalent spin flip-flops in equivalently oriented centres and each set of ground state triplet levels are mixed differently for different crystal orientations. As there are four centre orientations, a change in field angle causes a complex response in hole depth. The small size of the crystal made rotation impossible without a change in the incident conditions with a resulting change in output power, compounded by varying persistent holeburning effects. Qualitatively, however, greater variations in transmission, both gradual and sudden (for the specific values previously discussed), were observed when the field was close to the [111] direction. This is interpreted as being due to good spin quantisation resulting in strong optical pumping for the aligned centre. The decrease in the level anticrossing transmission dip with increased misalignment is, therefore, attributed to a masking of the dip due to weak optical pumping away from level anticrossing. It is concluded, therefore, that the level anticrossing dip in transmission is not due
Figure 5.9 Transmission of diamond crystal at 638 nm measured as a function of magnetic field strength in $\sigma (E||[111])$ polarization with $H||[111]$, signal averaged over 20 sweeps.
to an increase in spin dynamics but, rather, that it is due to a reduction in optical pumping between ground state levels caused by state mixing.

5C(v) Low field results

A similar effect to the level anticrossing hole bleaching could be expected at zero field as the $|\pm\rangle$ and $|\mp\rangle$ energy levels are degenerate for all centre orientations. A sharp (~10 Gauss) decrease in the hole depth near zero field has been observed (figures 5.5 and 5.9). A subsequent investigation (van Oort and Glasbeek 1989) has shown that the ground state spin-spin relaxation time increases from 2 ms to 4 ms in a magnetic field suggesting that the effect arises from an increased spin-spin cross relaxation rather than by a process similar to that which occurs near level anticrossing. This is analogous to other cross relaxation features but, in this case, occurs between all four sets of magnetically inequivalent N-V centres, upon the ground state splitting resonance, at 2.88 GHz, being established. The feature has an increased width attributed to the decreased rate at which the levels approach. In addition, there is a gradual increase in the hole depth (figure 5.5) which probably reflects the change in absorbance of the $^3A$ ground level as a function of magnetic field. Further investigations are necessary to establish the correct origin of the gradual change.

Several other less prominent features appear between zero field and 150 Gauss (figure 5.9) and these are ascribed to increased N-V$\leftrightarrow$P1 cross relaxation. At high fields P1 hyperfine splittings were considered to be a function of field orientation alone. At low fields this approximation is no longer valid and off-diagonal hyperfine terms in the energy matrix (overleaf) must be considered,
The P1 ground state consists of three doublets which split apart in a magnetic field. With the field along a [111] direction there exist two magnetically inequivalent P1 centres, as for the N-V centres. Comparisons of P1 splittings with N-V centre $|+\rangle\leftrightarrow|-\rangle$ splittings yield approximately 50 crossings within the 0-150 Gauss region. Selection rules (low field - $\Delta m_F = 0, \pm 1$; high field - $\Delta m_I = 0, \Delta m_S = 0, \pm 1$) eliminate a portion of these. Under these circumstances, energy may be conserved through a pair of spin flip-flops but angular momentum may not, thus preventing the interaction from occurring, in an analogous way to the effect which occurs for magnetically equivalent centres when the field is close to [111] as discussed earlier (section 5C(ii)). There remain many more resonances than features.

Variation of the holeburning laser polarity may help to isolate which of the N-V centres gives rise to individual features, as the optical transition is only allowed in $\sigma$ polarisation. Rotation of the sample from the [111] direction should cause features to occur at different field strengths, as occurs for features at larger field strengths. The excessive number of possible fits and the small size of the features would render such techniques extremely difficult, however.

$$\begin{pmatrix}
\frac{k}{2}\cos\theta + \frac{A_\perp}{2} & 0 & 0 & -i\sin\theta & 0 & 0 \\
0 & \frac{k}{2}\cos\theta & 0 & \frac{A_\perp}{\sqrt{2}} & -i\sin\theta & 0 \\
0 & 0 & \frac{k}{2}\cos\theta - \frac{A_\perp}{2} & 0 & \frac{A_\perp}{\sqrt{2}} & -i\sin\theta \\
i\sin\theta & \frac{A_\perp}{\sqrt{2}} & 0 & \frac{k}{2}\cos\theta - \frac{A_\perp}{2} & 0 & 0 \\
0 & i\sin\theta & \frac{A_\perp}{\sqrt{2}} & 0 & -\frac{k}{2}\cos\theta & 0 \\
0 & 0 & i\sin\theta & 0 & 0 & -\frac{k}{2}\cos\theta + \frac{A_\perp}{2}
\end{pmatrix}$$
5D. CONCLUSION.

A measure of the depth of an optical hole during continuous illumination while subject to an external perturbation has been shown to provide considerable information about the optically active centre and this technique would be generally applicable. In this study, the depth of a hole in a zero phonon line associated with a nitrogen-vacancy colour centre in diamond has been measured as a function of the orientation and magnitude of an external magnetic field and found to display several critical changes. The fields at which these features occur have been found to coincide with the fields at which the triplet separations reach special conditions, either equal to zero or to another ground state separation. The transient holeburning mechanism arises from a redistribution of the population in the ground state triplet levels, therefore the changes in depth arise as there is a faster restoration of the population when the triplet reservoir involved in the holeburning is coupled to a larger ensemble of spins. The close fit between theory and results confirm these assumptions and also confirm the ground state to be $^3\text{A}$.

Quantitative statements as to the variation in relaxation times are hard to make due to the complexity of the dynamics of the N-V centre system. The spin-spin relaxation time of 2 ms has been shown to be equal to the lifetime of the hole at zero field (Reddy 1989, Runciman et al 1989, van Oort and Glasbeek 1989) proving this mechanism to be dominant under these conditions. The spin-spin relaxation time increases to 4 ms and remains at 4 ms as a magnetic field is applied (van Oort et al 1989) though the transmission of the diamond does not remain constant, possibly due to an increasing absorbance of the ground state and or to several other holeburning effects which have not been fully investigated (Harley et al 1984, Nisida et al 1989). Cross relaxation with the P1 centre returns the spin-spin relaxation time to 2 ms but this time remains at 4 ms in the level anticrossing region (van Oort and Glasbeek 1989). The dip in transmission at level anticrossing is attributed to a reduction in optical pumping due to state mixing in
the triplet ground state. A direct relationship between transmission and relaxation times is, therefore, not possible due to changes in transmission caused by state mixing.

The emission level of the N-V centre whilst excited by broad band, non-resonant laser irradiation has subsequently been found to show sudden changes at exactly the same field strengths (van Oort and Glasbeek 1989), confirming our data. In the emission study, the small changes in emission intensity must arise from differences in the strength of absorption from the individual triplet levels. A change in the triplet populations induced by enhanced spin-spin cross relaxation or a change in the optical pumping efficiency will then affect the total light absorbed and hence the emission intensity.

There are parallels between these N-V centre studies and emission studies of photoexcited triplets in molecular solids (Veeman et al 1975, Nonhof et al 1980) and ionic solids (Hond and Glasbeek 1982). In the case of this study, cross relaxation and level anticrossing cause changes in the hole depth and this is detected in transmission, whereas in the case of photoexcited triplets changes to the total emission intensity are detected. The physical phenomenon giving rise to the level anticrossing signal in the present holeburning experiment also differs from that observed for excited triplet states. Here triplet spin polarisation induced by photo-absorption, rather than by spontaneous emission, is considered to be influenced by the state mixing.
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CHAPTER SIX

RAMAN HETERODYNE DETECTION OF
ELECTRON PARAMAGNETIC RESONANCE IN THE DIAMOND
N-V COLOUR CENTRE

6A INTRODUCTION

6A(i) The Raman heterodyne signal.

Raman heterodyne detection was first reported as a method for observing nuclear magnetic resonance in solids (Mlynek et al. 1983) and radio frequency induced sub-level coherence in atomic vapours (Mlynek et al. 1984). The interactions giving rise to this phenomenon have been analysed (Wong et al. 1983) and led to a prediction that EPR could be detected using this technique. Previous studies showed that the N-V colour centre in diamond (see section 5A(i)) possessed the required properties such that EPR signals could be detected using Raman heterodyne detection.

Raman heterodyne spectroscopy requires a three-level system in which two transitions may be excited optically whilst the third, usually between two split ground state levels, may be excited by a radio frequency field (figure 6.1). The full analysis of the interactions which lead to the production of a Raman heterodyne signal involve an analysis of the density matrix equations of motion. This analysis has been completed previously (Wong et al. 1983) and so only the principles and
Figure 6.1 The three level system and allowed transitions required to produce anti-Stokes and Stokes Raman heterodyne signal fields.
assumptions are presented here.

A laser, tuned to the frequency, $\omega_E$, of the optical transition, connects the excited state to the split ground state levels through the electric vector of the laser field. The ground state levels are coupled by a radio frequency magnetic field, at a frequency $\omega_H$, chosen by the magnitude of the ground state splitting. Two optical fields may be generated as a result of the coherence created between ground states and between each ground state and the excited state. These optical fields are generated at frequencies, $\omega_E+\omega_H$ (anti-Stokes) and $\omega_E-\omega_H$ (Stokes) (figure 6.1), and may be generated simultaneously in the case that the inhomogeneous broadening of the optical transition is greater than $\omega_H$.

The separation of the ground state levels should be much less than the separation between ground and excited states, $\omega_E$. This is an important experimental consideration as the theoretical analysis assumes that the slowly varying component of the coherence between the excited state and the ground state levels is at a frequency much less than the frequency corresponding to the separation in energy of the states (condition 1).

The density matrix equations of motion must then be solved. They may be written as,

$$\frac{i\hbar}{2\pi} \frac{\partial \rho}{\partial t} = [H, \rho] + \text{damping terms} \quad (6.1)$$

where $H$ is the sum of the unperturbed Hamiltonian and the dipole interactions, $-\mu_E E_0$ (the perturbation due to the laser field, equal to the vector dot product of the electric dipole moment operator and the electric vector of the laser field), and, $-\mu_H H_R$ (the perturbation due to the radio frequency field, equal to the vector dot product of the magnetic dipole moment operator and the magnetic vector of the radio frequency field).
The resulting dipole coupling strengths are given by,

\[ \alpha_1 = \frac{E_0^{\mu_0X}}{h/\pi}, \quad \alpha_2 = \frac{E_0^{\mu_1X}}{h/\pi}, \quad \beta = \frac{H_{R^{\mu_{12}}}}{h/\pi} \]  \hspace{1cm} (6.2)

where \( \mu_{ij} \) represents the matrix element corresponding to a unitary dipole operator coupling two levels, \( i \) and \( j \), which may be the ground spin states, \( |1\rangle \) and \( |2\rangle \), or the excited state, denoted by \( |X\rangle \).

As the density matrix equations of motion are solved by a perturbative method, it is necessary that the perturbing fields, \( E_0 \) and \( H_R \), are weak, such that the dipole coupling strengths (equation 6.2) may be regarded as being small in a second order calculation (condition 2).

It is further necessary to assume that the sample is optically thin, such that the signal field, \( E_S \) at frequencies \( \omega_E - \omega_H \) (Stokes) and \( \omega_E + \omega_H \) (anti-Stokes), obeys Maxwell's wave equation for an unbounded vacuum (condition 3).

An important result of the density matrix analysis is that the signal field and the input laser field are coherent so that the total field, when summed as \( E_0 + E_S \), produces observable beats at \( \omega_H \), at a constant phase with respect to the input radio frequency field.

The Raman heterodyne signal field is averaged over the Gaussian crystal strain and the Gaussian ground state inhomogeneous lineshape. To simplify this averaging process, it is necessary to assume that the strain broadening of the optical transition is very large, such that it is much greater than the ground state splitting (condition 4).
The resulting expression for the Raman heterodyne beat signal, $l_s$, taking into account the assumptions and approximations mentioned above, may be reduced to,

$$l_s = \frac{4\pi^4 k_E \text{LN}}{\sigma_E \sigma_H h^2} \mu_1 \mu_2 k_{12} |E_0|^2 |H_R|^2 (P - p) e^{-(\Delta_E/\sigma_E)^2} e^{-(\Delta_H/\sigma_H)^2} \left( \sin(\omega_H t) + \frac{2\Delta_H}{\sqrt{\pi} \sigma_H} \cos(\omega_H t) \right)$$

(6.3)

where $k_E$ is the wavenumber of the laser field, $L$ and $N$ are the length and number density of the sample, $\sigma_E$ and $\sigma_H$ represent the inhomogeneous widths of the optical and radio frequency transitions, $\Delta_E$ and $\Delta_H$ give the offsets of the exciting radiation fields from the centres of the inhomogeneously broadened optical and radio frequency transitions and $(P - p)$ is the difference in population between spin triplet states.

6A(ii) **Raman heterodyne detection of EPR in the N-V centre**

It has been established that Raman heterodyne signals may be obtained from certain three level systems under the correct experimental conditions. When the three level system is contained within a solid, various orientations of the centre produce different signal fields. A symmetry analysis of the interference between different sites in solids may be made from simple group theoretical considerations (Taylor 1984). Expressions for all crystal symmetries have subsequently been derived (Kintzer *et al.* 1984) in terms of signal polarisation, $P_s$, laser polarisation, $P_E$, and the direction of the radio frequency field, $P_H$, in terms of the crystal axis directions. For many field orientations, interference is complete and no Raman heterodyne signal may be observed.

Diamond has cubic symmetry and signals may only be observed when $P_s$,
$P_E$ and $P_H$ are aligned along the three different crystal axes (Bloch et al 1985). The signal field is perpendicular to the laser field, in this case, and may only be detected with the use of a linear polariser between the sample and detector. At zero field, however, the $|+\rangle$ and $|-\rangle$ states are degenerate and the Raman heterodyne signals generated by the transitions from these levels to the $|0\rangle$ state may be of opposite sign, causing the signals to interfere destructively. Destructive Zeeman interference has been reported and explained for nuclear Raman heterodyne signals in YAlO$_3$:Pr$^{3+}$ and LaF$_3$:Pr$^{3+}$ (Mitsunaga et al 1984).

The large zero field splitting of the triplet ground state, 2.88 GHz, necessitates delivery of effective, similarly high radio frequencies to the diamond sample and this is technically difficult to achieve, preventing an investigation of zero field interference effects here. Application of a magnetic field along a $\langle 111\rangle$ direction of the diamond causes the $|0\rangle\leftrightarrow|+\rangle$ spin ground state splitting of the set of centres aligned parallel to the field to approach zero (see section 5A(v)) and effective radio frequency fields may be delivered to the diamond using copper coils.

Application of a static magnetic field along a $\langle 111\rangle$ direction selects a single N-V centre orientation, in that a radio frequency field resonant with the ground state splitting of an N-V centre oriented along a $\langle 111\rangle$ direction is not resonant with ground state splittings of differently oriented N-V centres, except at particular field values (see chapter 5). Consequently, in the general case, the centre symmetry, rather than the crystal symmetry, now determines whether Raman heterodyne signals may be generated. The N-V centre has $C_{3v}$ symmetry, for which several orientations of fields may generate Raman heterodyne signals (Kintzer et al 1984). The $^3A\rightarrow^3E$ electric dipole transition at 638 nm is forbidden when the laser electric field is parallel to the N-V centre local $z$ axes (along the $\langle 111\rangle$ directions) and so the orientation as shown in figure 6.2 was chosen, such that the laser and electric fields are parallel and no polariser is required to produce beating.
Figure 6.2 Orientation of fields relative to diamond crystal for Raman heterodyne detection of EPR.
The expression for the signal field (equation 6.3) shows that the beat strength is expected to be proportional to the square of the electric field laser amplitude (and therefore proportional to the laser power) and proportional to the radio frequency magnetic field amplitude. Though this suggests that high powers would give strong signals, it should be remembered that the theoretical treatment assumes weak perturbations, such that a second order treatment is valid. The N-V centre is, therefore, an appropriate system with which to test the theoretical predictions for several reasons:

(i) The three transition dipole moments are large suggesting that weak fields may be sufficient to generate Raman heterodyne signals. This is the case as spin-orbit coupling in the excited state causes transitions from all three spin quantised ground state levels to be allowed.

(ii) The population difference between spin levels is substantial due to optical pumping (see chapter 5). This prevents significant cancellation of the Raman heterodyne signal due to interference between Stokes and anti-Stokes fields.

(iii) The ground state level is a triplet spin system which, through careful alignment of the static magnetic field, goes through a level anticrossing. This facilitates fewer technical difficulties in delivering a radio frequency field to the crystal as the frequencies may be restricted to less than 1 GHz, unusual for EPR experiments.

(iv) The conditions which are made in deriving equation 6.3 may all be met; Condition 1, the slowly varying component of the coherence between the excited state and the ground state levels is at a frequency much less than the frequency corresponding to the separation in energy of the states. The coherence between the ground state levels and the excited state vary at $\omega_H$ (< $10^9$ Hz for the N-V centre near level anticrossing) and the frequency corresponding to the separation of levels is $\omega_E$ (> $10^{14}$ Hz for the N-V centre), therefore, as $\omega_H \ll \omega_E$, the condition is met.
Condition 2, the perturbing fields are weak.

From (i) and (ii) above, it is thought that weak fields may be sufficient to generate Raman heterodyne signals. This approximation is not necessarily valid throughout this study, however, as the perturbing fields are maximised in order to maximise the coherence between levels, and this will be discussed later (see section 6C(ii)).

Condition 3, the sample is optically thin.

This may seem a dubious assumption as it has been noted that our sample was 100% absorbing in white light absorption at 638 nm (see section 5A(i)). However holeburning substantially reduces the absorption when the diamond is exposed to a focussed laser beam (see chapter 5). Furthermore, the wings of the zero phonon line have a greatly reduced absorption, allowing investigation of the signal in an optically thin medium. This will also be discussed later (see section 6C(ii)).

Condition 4, the strain broadening of the optical transition is much greater than the $|0\rangle \leftrightarrow |+\rangle$ splitting.

This is satisfied for our diamond sample in which the N-V centre optical transition is broadened to 1000 GHz whereas $\omega_H$, which corresponds to the $|0\rangle \leftrightarrow |+\rangle$ splitting, is chosen to be less than 1 GHz in this study.

There are, however, slight departures from the assumptions required to derive equation 6.3. Though the optical line shape, produced by the crystal strain, is Gaussian in white light absorption, this approximation is not strictly correct for our experimental conditions in which permanent and transient spectral holes are burnt by the high resolution laser (see section 5A(ii)). It is further possible that the Gaussian ground state inhomogeneous lineshape may be changed by exposure to a radio frequency field. Also, the signal lineshape would be expected to be complicated by the hyperfine structure associated with nitrogen (figure 6.3) and which is apparent in conventional EPR (Loubser and van Wyk 1977). Further features associated with C$^{13}$ could be expected to give additional structure.
Figure 6.3 Schematic diagram illustrating the three level system in the N-V centre. As $\omega_H <<$ strain broadening, both Stokes and anti-Stokes fields are generated simultaneously. Transitions between all three nitrogen hyperfine levels are allowed.
6A(iii) Raman heterodyne detection of transient effects in the N-V centre

It has been shown in the previous section that the N-V centre in diamond possesses the required properties such that EPR signals may be detected by a Raman heterodyne technique. It follows that transient phenomena such as nutation, free induction decay and spin echoes, which involve perturbations of the ground state populations, may also be detected using this optical technique. These effects are produced by fast switching or pulsing of the radio frequency field. Any disturbance in the ground state populations may be detected by monitoring the size of the Raman heterodyne EPR signal.

(1) Nutation is the oscillation of populations in a two level system caused by the abrupt turning on of a resonant field connecting the two levels. This effect was first observed and explained for nuclear spin levels (Torrey 1949) following the first observation and explanation of nuclear magnetic resonance (Purcell et al. 1946, Bloch et al. 1946, Bloch 1946). The application of a pulse of resonant radio frequency to an ensemble that has, for instance, most of its component centres in their ground states causes the centres to be excited and to relax at the same rate. This bulk oscillation is termed nutation.

For Raman heterodyne signals to be observed in the N-V centre, a population difference between the split triplet levels must exist (equation 6.3) so that the destructive interference between the Stokes and anti-Stokes fields is not complete. When the radio frequency field is turned on, therefore, the driven oscillation between levels will appear to be stronger for one set of centres than for the other. This set, the set initially in the more strongly populated state, will dominate the nutation signal which will be caused through the varying dominance of the Stokes and anti-Stokes fields as the populations oscillate.

It can be shown that the nutation oscillation frequency is equal to the Rabi frequency, $\chi$ (Torrey 1949, Allen and Eberly 1975). For a resonant radio frequency transition this is given by $\beta/2$ (equation 6.2) and is, therefore, proportional to the
square root of the radio frequency power. In a real system, however, power broadening effects will cause centres slightly removed from resonance to be excited. For these, the Rabi frequency is given by,

$$\chi = \sqrt{\frac{\beta^2}{2} + \Delta_H^2}$$  \hspace{1cm} (6.4)

(Allen and Eberly 1975) where $\Delta_H$ is the detuning of the centre from the resonant radio frequency field (not to be confused with $\Delta_H^*$, defined earlier). The bandwidth over which non-resonant centres are excited can be shown to be $\beta/2$ (Allen and Eberly 1975) and so most of these excited centres oscillate at a frequency close to $\beta/2$, the resonant Rabi frequency, due to the addition of the detuning term being in quadrature (figure 6.4). The ensemble of oscillating centres will, nonetheless, dephase due to this variation in nutation frequency.

The dephasing of the ensemble takes place with a time constant given by,

$$\frac{1}{T} = \frac{1}{T_2'} + \frac{1}{T_2^*} + \frac{1}{T_i}$$  \hspace{1cm} (6.5)

where the $T_2'$ and $T_2^*$ terms represent the total relaxation time of the centre and $T_i$ represents a time constant which accounts for dephasing due to radio frequency field inhomogeneities.

The $T_2^*$ term represents the dephasing due to power broadening, mentioned above. This term is not random but its effect increases across the line profile thus this time constant decreases with radio frequency power. It may be calculated, if the exact distribution of non-resonantly excited centres is known, using a knowledge of the variation of Rabi frequency with detuning (equation 6.4). $T_2^*$ may be assumed to be small for driven transitions due to the nature of the detuned centre Rabi frequency variation, as described above.
Figure 6.4 Graph of oscillation frequency before and after a transition is driven by an oscillating field. Whilst driven, the Rabi frequency varies with offset from resonance as shown in the curve indicated by "driven". When the driving field is turned off, the system is free to decay at its natural frequency, indicated by "undriven". Axes are labelled in units of the resonant Rabi frequency, $\beta/2$ (see text). Note, zero refers to the resonant Rabi frequency for the "driven" curve and to the resonant driving frequency itself for the "undriven" curve.
Within the $T_2'$ term, homogeneous effects, such as radiative decay, phonon scattering and spin-spin cross relaxation are taken into account. These occur randomly and cause the interacting centre to be withdrawn from the ensemble of in phase centres. The centre will continue to be excited and relaxed at the same rate but will no longer be in phase with the ensemble. The value of $T_2'$ may be determined from spin echo decay measurements.

The $T_1$ field inhomogeneity term has a similar nature to $T_2^*$ in that its effect is to cause steady dephasing of the centres. Here the Rabi frequencies are altered by the variation in radio frequency field strength at the centre (equation 6.2) and effects similar to power broadening occur due to the linewidth of the radio frequency source. Both of these effects are likely to be small due to the small volume of crystal with which the focussed laser interacts and the high spectral purity of the radio frequency source (see section 6B).

These processes cause the spin ensembles to dephase and the oscillation is damped until an equilibrium is reached in which equal numbers of centres are switched between states but in which each centre may be considered to be independent of the others. That is, each centre is excited and relaxes at its own Rabi frequency (equation 6.4) but the ensemble gradually dephases. Despite the dephasing of the populations, there still exists a coherence between levels and a Raman heterodyne signal may still be observed.

In order to observe nutation, the period corresponding to the dephasing of the ensemble must be greater than the period corresponding to the Rabi frequency ($2/\beta$) so that the amplitude modulation of the induced fields is not damped before the populations have begun to oscillate in phase. A high Rabi frequency is, therefore, preferred experimentally and this is likely to be the case for any system for which EPR may be detected using the Raman heterodyne technique as both require the ground state transition magnetic dipole moment to be large. Higher radio-frequency field strengths further increase the Rabi frequency but this may cause the weak field assumption, essential for the analysis presented above, to
become invalid.

(2) Free induction decay is observed when the radio frequency field is abruptly turned off. As for nutation, this effect was first observed and explained for nuclear magnetic resonance (Hahn1 1950). The rate at which the coherence between the two ground state levels will collapse is still governed by the same principles that account for the damping of the nutation signal. The value of $T_2^*$ is, however, reduced. The dephasing time constant is given by the reciprocal of the bandwidth of the emission. This bandwidth is now easily calculable as being $\beta/2$, the bandwidth due to power broadening. This is because the non-resonant centres, no longer excited by the radio frequency field, are free to radiate at their natural frequency, $\beta/2+\Delta_H$, rather than at a driven frequency, close to $\beta/2$ given by equation 6.4. Where power broadening is large, the radiation, therefore, collapses anomalously quickly (figure 6.4).

This process occurs in the ground state levels and, as Raman heterodyne detection of EPR depends upon the interactions of these triplet ground states, free induction decay may be expected to be observed in the diamond N-V centre.

(3) Spin echoes were a natural progression from the work carried out on nutation and free induction decay some forty years ago. Not surprisingly, they too were first observed as a nuclear magnetic resonance phenomenon (Hahn2 1950).

To produce spin echoes, two pulses of resonant radio frequency radiation are applied to the ensemble of centres. The first pulse causes the ensemble of centres to nutate but the pulse has a period of only $1/2\beta$ (or one quarter of a period ($\pi/2$ radians) corresponding to the Rabi frequency) such that very little dephasing occurs during this time. Immediately following the pulse, free induction decay will occur and the system will quickly dephase through inhomogeneous processes though individual centres continue to oscillate. Consider two such centres oscillating at Rabi frequencies, $\omega_1$ and $\omega_2$, with waveforms $\sin(\omega_it+\phi)$, where $i=1,2$ and $\phi$ is a random phase factor. At time, $t=0$ (immediately after the first pulse), the two centres are in phase. The second pulse is applied a time, $\tau$, later and has a
width of $1/\beta$ (or half a period ($\pi$ radians) corresponding to the Rabi frequency). At this time, the phase difference between the centres is $(\omega_1 - \omega_2)t$. The application of the $\pi$ pulse again causes nutation to occur and both phases change by $\pi$ radians. The waveforms may now be expressed as $\sin(\omega_1 t + \phi + \pi)$ which is equivalent to $\sin(-\omega_1 t - \phi)$. After a second period, $\tau$, the phase difference is $(\omega_1 - \omega_2)t + (-\omega_1 + \omega_2)\tau$ or zero, a time reversal has been effected. This is the case for all interacting centres and the crystal will then radiate an 'echo'.

During the time between the first pulse and the echo, dephasing also occurs due to homogeneous effects. These are random in nature and thus a time reversal will not bring centres so affected back in phase. Consequently, the magnitude of the spin echo will decrease with increasing $\tau$, with a time constant of $T_2$.

Once again, the spin echo may be observed using the Raman heterodyne technique in which the optical transition is utilized to probe the processes occurring in the ground state.

6B EXPERIMENTAL DETAILS

The diamond crystal, the same 1 mm cube with (100), (110) and (110) faces as was used for the experiments described in chapter 5 was located in helium exchange gas within the bore of a superconducting magnet. The N-V centres' principal axes are aligned along the (111) directions of the diamond and the crystal was positioned with one set of centres aligned to within 1° of the magnetic field. The crystal could be rotated about both axes perpendicular to the magnetic field which could be varied from zero to several thousand Gauss.

The radio frequency field was applied perpendicular to the N-V centre axis by winding a 5 mm radius, 5 turn coil of copper wire around the crystal with its axis
along the direction of the laser (figure 6.5). The radio frequency field power input to
the coil was typically 5 W, delivered by a 5W1000 Amplifier Research amplifier.
Using a standing wave ratio meter, it was determined that almost all of the radio
frequency power incident on the coil was reflected above about 100 MHz. Below
this frequency, reflection steadily decreased until at 30 MHz it was about 70%.

The laser beam was oriented such that its electric vector, its direction of
propagation and the N-V centre axis were mutually perpendicular (figure 6.2). The
dye laser had a linewidth of 1 MHz, an output power of 50 mW and was tuned to
the zero phonon absorption of the N-V centre at 638 nm. The laser could be
scanned over 30 GHz or mode hopped 200 GHz to regain signal strength which is
lost due to holeburning mechanisms with time constants of the order of seconds
(see section 5A(ii)). Neither technique was found to alter the signal shape or
frequency.

Figure 6.5 shows the experimental arrangement for Raman heterodyne
detection of EPR. The light is detected by an Electrooptics PD-15 photodetector,
capable of detecting amplitude modulation at up to 9 GHz. The radio frequency
signal was generated by a Hewlett Packard 8444A tracking generator with a 200
Hz linewidth, capable of sweeping up to 1 GHz and which was typically swept in
30 ms. The detector signal was analysed by a Hewlett Packard 8554B spectrum
analyser set to a bandwidth of 300 kHz and the output from this could be signal
averaged and stored in a Data Precision Data 6000 data analyser.

Figure 6.6 details the adjustments to the apparatus required to detect and
analyse transient effects. The tracking generator generates a constant radio
frequency signal which is passed through a 50 MHz high pass filter for Raman
heterodyne detection or a 2-20 MHz band pass filter for incoherent detection. This
signal was then mixed with a portion of the input radio frequency signal in an
Anzac MD-143 5-500 MHz double balanced mixer. The mixed signal was digitally
sampled at $10^8$ points per second, signal averaged and stored by the data
analyser. Attenuators and amplifiers were used to vary the input radio frequency
Figure 6.5 Schematic diagram illustrating the experimental arrangement for Raman heterodyne detection of EPR.
Figure 6.6 Schematic diagram illustrating the apparatus used to detect spin transients using the Raman heterodyne technique.
power to the sample, to match signal strengths entering the double balanced mixer and to make signal sizes compatible with display and storage units.

6C RESULTS AND DISCUSSION

6C(i) Raman heterodyne detection of electron paramagnetic resonance

EPR signals have been observed using Raman heterodyne detection (figure 6.7) at frequencies between 30 MHz and 1 GHz. Signals could not be detected above 1 GHz due to the detection limit of the spectrum analyser. Signals could not be detected below 30 MHz due to a slight misalignment of the field from the [111] direction. A misalignment of 0.4° causes the levels to approach no closer than 30 MHz and this is consistent with the accuracy of our field alignment.

The frequencies at which signals were detected for varying magnetic field and varying field orientation have been compared to the calculated \(|+\rangle \leftrightarrow |0\rangle\) triplet splittings (see section 5A(i)). An excellent correlation is found (figure 6.8) and slight variations in experimental and theoretical values are attributed to discrepancies in measuring the angle between the field and the [111] direction. It is concluded that the signals observed are due to Raman heterodyne detection of electron paramagnetic resonance.

By adding the Raman heterodyne signal to a proportion of the input radio frequency signal, the phase of the signal could be investigated (figure 6.9). The signal is composed of three similar interfering components, split by 2 MHz. This splitting and the number of components corresponds to the hyperfine interaction between the |+\rangle triplet ground state level and the nitrogen (I=1) nuclear spin (Loubser and van Wyk 1977). This observation confirms the origin of the Raman heterodyne signal to be due to EPR of the ground state triplet.
Figure 6.7 A typical EPR signal detected using the Raman heterodyne technique.
Figure 6.8 Solid lines show theoretical splitting of triplet ground state levels in a magnetic field for various misalignments (indicated). Crosses indicate experimentally determined triplet splittings obtained from Raman heterodyne detection of EPR.
Figure 6.9 A typical Raman heterodyne EPR signal detected using the phase sensitive technique. The three nitrogen hyperfine levels, each of which give rise to a derivative lineshape, may clearly be observed.
The signal strength is expected to be proportional to the amplitude of the radio frequency field (equation 6.3) and this is confirmed qualitatively as the signal strength and effective radio frequency field decrease at higher frequencies. Signals at 30 MHz were typically 100 times stronger than at 1 GHz. A quantitative investigation of the correlation between signal strength and effective radio frequency field was not undertaken due to the difficulty of measuring the effective radio frequency field under experimental conditions and due to effects, such as holeburing (see section 5A(ii)), which prevent repeatable signal strength measurements from being made.

Holeburning also prevents a quantitative investigation of the relationship between laser power and signal size from being undertaken. The signal strength is expected to be proportional to laser power (equation 6.3) and this has been qualitatively observed. Neutral density filters placed in the laser input beam reduce the signal strength by approximately the same proportion as the laser input power.

The limit in the microwave frequency which may generate Raman heterodyne EPR signals is likely to be determined by the equipment used rather than by theoretical considerations as there is no physically realisable theoretical limit to the frequency at which this technique can be used in the N-V centre. However, when the ground state $|\uparrow\rangle \leftrightarrow |\downarrow\rangle$ splitting approaches the inhomogeneous broadening of the optical transition, at 1000 GHz, the signal will change form such that the Stokes and anti-Stokes fields may no longer be generated simultaneously. This would require a magnetic field of 30 T which is close to the limit of static magnetic fields which may be generated in a laboratory. Our results show that coils become ineffective above frequencies of about 100 MHz and resonators would, therefore, be required to develop effective radio frequency fields in the microwave region.
Important features of the Raman heterodyne electron paramagnetic resonance signal

At level anticrossing, with the field aligned along [111], no Raman heterodyne signals could be detected. The diamond was rotated in the field in 1° steps. This misalignment caused the ground state splitting at level anticrossing, and, therefore, the minimum Raman heterodyne frequency, to increase, as predicted by theory (see section 5A(i)). For each minimum, the signal disappeared until 8°, at which angle the signal at minimum frequency was greatly diminished but did not disappear.

The collapse of the Raman heterodyne signal at level anticrossing is not fully understood. At level anticrossing, electron spin quantisation breaks down and the nitrogen nuclear spin influences the state mixing through off diagonal terms in the energy matrix, causing several additional transitions between states to be allowed, which may interfere destructively, as occurs for YAlO₃:Pr³⁺ and LaF₃:Pr³⁺ (Mitsunaga et al 1984). Away from [111], the nuclear spin state mixing decreases and weak Raman heterodyne signals may be observed. Furthermore, the state mixing at level anticrossing prevents preferential relaxation from the excited state to spin quantised ground states (see chapter 5). This will cause a reduction in the population difference between the states driven by the radio frequency field to which the Raman signal is proportional (equation 6.3).

Away from level anticrossing, the signal lineshape (figure 6.9) remains steady as the hyperfine interaction remains constant in the high magnetic field regime. As predicted by equation 6.3, the component of the signal which oscillates as \( \sin(\omega_H t) \) has a Gaussian lineshape whilst the component which oscillates as \( \cos(\omega_H t) \) has a differential Gaussian lineshape. The signal lineshape observed here, for all three ground state transitions, is a differential Gaussian. The Gaussian lineshape predicted from theory has not been observed. The signal lineshape using amplitude modulation detection only, approaches zero at the centre frequency. If the Gaussian component of the Raman signal were present, it would
add vectorially to the derivative Gaussian component and could never give zero amplitude modulation. It would appear that the Gaussian component is either missing or substantially reduced in amplitude at optical and radio frequency power levels typical of this study. The assumptions made in the derivation of equation 6.3 may, under these circumstances, be questioned. It is possible that three of the conditions considered in section 6A(ii) may not be met;

(i) Optical and radio frequency holeburning may cause the respective transition lineshapes to vary. This is experimentally confirmed not to be the case by sweeping laser and radio frequencies over different frequency ranges at varying rates in order to change hole depths and shapes. Though overall signal strength shows small changes, lineshape does not.

(ii) The diamond sample is assumed to be optically thin (condition 3). The signal lineshape remains unchanged in all features other than magnitude when the laser excites the extremes of the zero phonon line. It is concluded, therefore, that the diamond is consistent with being optically thin, for the purposes of this investigation.

(iii) The optical and radio frequency fields are assumed to be weak such that second order perturbative calculations may be made (condition 2). However, a very important observation is the change in lineshape with reduced radio frequency power (figure 6.10), suggesting that the radio frequency weak field approximation may be invalid for the powers used in this study. The low field lineshape consists of three signals, split by 5 MHz, whilst a 2 MHz splitting does not appear. Subsequent investigations with improved detection equipment (He and Manson 1989) have confirmed the presence of three Gaussian-like features, split by 2 MHz, as well as the additional features split by 5 MHz, confirming the weak field approximation to be valid for low radio frequency power. The 5 MHz splitting is not understood but a subsequent theoretical investigation has confirmed the differential component of the Raman heterodyne signal to increase at high radio frequency power whilst the Gaussian component is reduced (Fisk 1989).
Figure 6.10 Variation of the EPR Raman heterodyne lineshape with radio frequency power. The 0 dB trace corresponds to a power not precisely known (see section 6B). The vertical scale is different for each trace as indicated by the noise signals close to 90 MHz.
6C(iii) Raman heterodyne detection of coherent spin transients in the N-V centre

Nutation has been detected using the Raman heterodyne technique in the N-V centre using continuous illumination with the laser beam and long pulses of radio frequency (figure 6.11). The Rabi frequency is expected to be proportional to the amplitude of the radio frequency field and therefore to the square root of the radio frequency power (see section 6A(iii)). This has been confirmed to within the limits of experimental uncertainty (figure 6.12).

The frequency analysis is complicated by the presence of two spectral components. Under some conditions, stronger signals could be obtained by detecting the transmission of the laser beam incoherently and this allowed fast Fourier transforms to be calculated by the data analyser (figure 6.13). The nutation signal was found to be composed of one or two components. This is attributed to separate signals being generated by different hyperfine levels. Indeed, a variation in the frequency spectrum is observed as nutation signals are obtained from different positions within the line profile. Figure 6.13 shows an example in which only one hyperfine level is excited (or two hyperfine levels oscillate at the same Rabi frequency), giving only one spectral component, and an example in which two hyperfine levels are excited, giving two spectral components.

The conditions under which incoherent detection techniques give larger signals are unclear as the complexity of an investigation of the parameters of these techniques is beyond the scope of this study. Both techniques give quantitatively similar values for the parameters of interest. The nutation damping time (equation 6.5) is found to be 1 μs.

Nutation frequencies have been shown to be larger than 2 MHz whilst driving the transition at high power. As discussed (see section 6A(iii)), the bandwidth over which non-resonant centres are excited is equal to the Rabi frequency. As the hyperfine splitting is only 2 MHz, it is not surprising that the Raman heterodyne EPR signals are power broadened.
Figure 6.11 Nutation signals, detected using the Raman heterodyne technique for varying power levels (0 dB power not precisely known). Note the dual frequency components, attributed to interference between adjacent hyperfine levels.
Figure 6.12 Graph of nutation frequency versus radio frequency power, using data derived from signals detected using the Raman heterodyne technique. The line indicates the theoretical slope of the graph and is drawn at an approximate best fit y-offset through the experimental data, indicated by crosses.
Figure 6.13 Nutation signals (centre), detected incoherently for two positions on the EPR Raman heterodyne lineshape (lower) and their spectral components calculated by the data analyser using a fast fourier transform algorithm (upper).
Free induction decay may not be detected incoherently. Once the ground state populations have dephased, the laser beam is no longer incoherently amplitude modulated at the Rabi frequency, hence, when the radio frequency field is turned off, the transmitted laser beam does not vary in amplitude (figure 6.13). If the amplitude modulation is being monitored coherently, however, a Raman heterodyne signal remains after the populations have dephased. When the radio frequency field is removed from the diamond, free induction decay is observed (figure 6.14). Our detection equipment, whilst studying free induction decay, was insufficiently fast to capture the signal decay time and this is evidenced by the ringing of the signal magnitude after the signal has reached zero. The signal appears to decay with a time constant less than 1 μs, the nutation damping time constant, and it can be concluded that this rapid dephasing is due to free induction decay.

Free induction decay is determined by the same expression as for nutation damping (equation 6.5) with a value for $T_2^*$ modified for free emission from the value for driven oscillation (figure 6.4). Though our detection equipment prevented a study of the variation of free induction decay time with radio frequency power, the smaller magnitude of the free induction decay time shows that the $T_2^*$ term in the expression governing dephasing time is dominant at the high radio frequency powers with which we conducted our experiments.

Spin echoes have also been observed using Raman heterodyne detection (figure 6.15). High power radio frequency pulses were applied to the diamond such that the Rabi frequency, measured as the nutation frequency, was 2 MHz. Pulse durations of 0.1 μs ($\pi/2$ pulse) and 0.2 μs ($\pi$ pulse) were applied and spin echoes were observed for pulse delays of 1 to 8 μs. The lower limit was determined by the pulse production apparatus and the upper limit is attributed to incoherent, homogeneous interactions. These interactions, such as spin-spin cross relaxation (see chapter 5) and emission, are random events and thus the second radio frequency pulse, which causes 'time reversal' for inhomogeneous processes,
Figure 6.14 Raman heterodyne detection of free induction decay, after dephasing processes have damped nutation. The rapid dephasing of the centres causes the EPR signal to collapse with a time constant smaller than that of the detection equipment, hence the ringing of the signal after 45 μs.
Figure 6.15 A typical spin echo recorded using Raman heterodyne detection. Pulses of 0.1 μs and 0.2 μs, resonant with the ground state splitting of 50 MHz, were applied to the diamond with a time delay of 2 μs.
may not cause constructive interference to occur a time, \( \tau \), later, for those centres which have dephased in this way.

These homogeneous processes are also partly responsible for the decay of the nutation signal \( (T'_2) \) accounts for these interactions in equation 6.5). The nutation signal has almost completely cancelled after 8 \( \mu \)s (figures 6.11 and 6.13) and it is concluded that the same processes dominate the decay of both nutation and spin echo magnitudes. Consequently, the decay of the nutation signal (equation 6.5) is dominated by \( 1/T'_2 \) and \( 1/T_i \) is negligibly small. The magnitudes of time constants determined by this study are summarised in table 6.1.

**Table 6.1** Experimentally determined time constants in the diamond N-V centre.

<table>
<thead>
<tr>
<th>conditions</th>
<th>( T'_2 )</th>
<th>( T_2^* )</th>
<th>( T_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>radio frequency on</td>
<td>1 ( \mu )s</td>
<td>&gt;1 ( \mu )s</td>
<td>&gt;1 ( \mu )s</td>
</tr>
<tr>
<td>(driven oscillation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>radio frequency off</td>
<td>1 ( \mu )s</td>
<td>&lt;1 ( \mu )s</td>
<td>&gt;1 ( \mu )s</td>
</tr>
<tr>
<td>(free decay)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The details of the structure of the echoes, as triplet splitting and position of radio frequency excitation within the lineshape are both varied, is complex and beyond the scope of this study and the spin echo data collected has not generally been related to specific processes in the solid, therefore. However, the spin echo structure is attributed to interference between different hyperfine levels of the \( |+\rangle \) spin state.
The N-V centre in diamond has been identified as an ideal centre for which a new method of observing electron paramagnetic resonance, Raman heterodyne detection, might be achieved. Subsequently, EPR signals detected by the Raman heterodyne method have been observed for the first time though a systematic investigation of the effect of field strengths, temperature and other experimental conditions has not been made. Signals have been obtained up to the instrumental limit of 1 GHz. Spectra displaying the 2 MHz nitrogen hyperfine structure can be observed in a 30 ms sweep over 20 MHz with an excellent signal to noise ratio of better than 100:1. The Raman heterodyne method for detecting EPR has the distinct advantages of displaying the whole spectrum on screen in real time and of not requiring strong magnetic fields. It is, nonetheless, applicable in the high field region, if desired.

The technique has been used here to study spin transients in the field split triplet ground state. Information has been obtained on the relaxation times due to various processes within the solid. The analysis of such effects is complicated by the hyperfine structure of the |\( ^+ \rangle \) spin state, in an analogous way to the Zeeman frequency modulation observed for Raman heterodyne detection of nuclear magnetic resonance in praseodymium doped lanthenum fluoride (Wong et al 1983). Further investigation of the dependence of these beating effects as line position and magnetic field strength are varied may reveal further information about the N-V centre, the Raman heterodyne technique and interactions within solids in general.

This study has demonstrated the usefulness of Raman heterodyne detection and highlighted the technical difficulties which need to be overcome so that a comprehensive quantitative study may be made of the interactions and processes which occur in the N-V colour centre in diamond. This work has indicated the importance of power broadening effects whish have yet to be fully
theoretically described. Alternatively, improved detection equipment is needed to
investigate these processes in the low power regime. This has recently been
achieved and is allowing the Raman heterodyne technique to be used to carry out
these investigations quantitatively (He and Manson 1989).

Effective radio frequency resonators and radio frequency shielding
equipment will allow the technique to be utilised at a wider range of frequencies
and, hence, investigate a greater range of materials and conditions. Of particular
interest, would be an investigation of the response of the Raman heterodyne signal
at the specific field values and orientations for which there is an accidental
coincidence between differently oriented N-V centres (see chapter 5). The radio
frequency field may then drive transitions in both sets of centres, which may
interfere, whilst increased spin-spin cross relaxation may affect ground state
populations and, hence, the Raman heterodyne signal strength (equation 6.3).
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