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1989 J. Phys.: Condens. Matter 1 7093

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Optical hole-bleaching by level anti-crossing and cross relaxation in the N-V centre in diamond

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Received 14 December 1988

Abstract. We have studied the behaviour of an optical hole in the $^3A \rightarrow ^3E$ zero-phonon absorption of the nitrogen-vacancy centre in type 1b diamond under the influence of an externally applied magnetic field. Spin cross relaxation and level anti-crossing phenomena in the 3A ground state are displayed as sudden reductions of the optical hole depth (hole-bleaching) for specific orientations and strengths of the applied magnetic field.

1. Introduction

The N-V colour centre is created in 1b diamonds after radiation damage and annealing at temperatures over 900 K. The centre gives rise to a zero-phonon line at 638 nm with a vibronic sideband to higher and lower energy in low-temperature absorption and emission respectively. The optical line is associated with an $A \rightarrow E$ transition at a site of trigonal symmetry and is considered to arise from substitutional nitrogen accompanied by a vacancy at a nearest carbon site (Davies and Hamer 1976). It had been thought that the levels involved in the optical transition were spin singlets and that EPR of a triplet state observed during optical pumping was that of a metastable triplet level (Loubser and van Wyk 1977). However, it has been shown from two-laser hole-burning measurements (Reddy *et al* 1987) that this is not the case but rather the ground state is a triplet and hence the optical transition involved is $^3A \rightarrow ^3E$. This is substantiated by spin-coherence measurements (van Oort *et al* 1988). Further evidence for a triplet ground state is provided by the present data and, indeed, room-temperature EPR signals due to the N-V centre could be detected in the present sample without requiring optical illumination.

Transient spectral hole-burning in the 638 nm zero-phonon line of the N-V centre arises from optical pumping between levels of the spin-triplet ground state (Reddy *et al* 1987). The $^3A \rightarrow ^3E$ zero-phonon line has a large inhomogeneous width of 800 GHz and consequently the narrow-band laser only interacts with a small subgroup of the total ensemble of N-V centres in the crystal. During continuous illumination the depth of the hole depends on the balance between the optical pumping and the spin relaxation within the triplet levels. In zero magnetic field this corresponds to optical pumping between the spin-singlet and spin-doublet levels or, in the presence of a field, between all three

levels of the triplet. In this paper we report observations of sudden changes in the depth of the optical holes when magnetic fields of specific values and orientations are applied.

Spin-lattice relaxation attempts to re-establish the thermal population between the optically pumped spin levels. However, it is common for spin-spin cross relaxation involving energy-conserving spin flip-flops of neighbouring centres to be a faster process (Abragam and Bleaney 1970). For the sub group of optically active centres interacting with the laser, the flip-flop processes tend to bring the optically excited defects into equilibrium with the vast majority of non-excited triplet centres which will already be in equilibrium with the lattice. Efficient cross relaxation requires resonant conditions for the cross-relaxing spins. This is always the case for equivalently oriented centres. 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 other types of centre or inequivalent orientations of the N-V centre. The coincidence brings the two separate ensembles of centres into resonance thus providing an extra decay channel. 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 optical hole depth, that is, hole-bleaching.

Three types of cross-relaxation phenomena are illustrated by the N-V centre system. Reduction of the hole depth occurs when the separations of the energy levels of the N-V centre match those of an entirely different colour centre in the diamond. This is the paramagnetic P1 centre involving a single substitutional nitrogen site with $S = \frac{1}{2}$ electron spin ground state (Smith *et al* 1959, Cook and Whiffen 1966, Loubser and du Preez 1965) and for which room-temperature EPR signals have been reported. The P1 centre exhibits a static Jahn-Teller distortion from T_d to C_{3v} 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

$$H = \mu_B(HgS) + SA_I. \quad (1)$$

g is isotropic with a value of 2.024 and the hyperfine coupling parameters have values of $A_{\parallel} = 0.114$ GHz and $A_{\perp} = 0.081$ GHz (Smith *et al* 1959).

Similarly, a reduction of the hole depth occurs when there is a matching between the splittings of orientationally inequivalent N-V centres. Thirdly, 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.

A further situation which gives rise to a change in the hole depth is when one of the splittings within the triplet approaches zero. This phenomenon is associated with level anti-crossing.

Analogous effects have been observed for hole-burning in $\text{LaF}_3:\text{Pr}^{3+}$, 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 Pr^{3+} 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.

There are many other parallels between the present work involving cw hole-burning studies of ground-state triplets and emission studies of photo-excited triplets in molecular solids (Veeman *et al* 1975, Nonhof *et al* 1980) and ionic solids (Hond and Glasbeek 1982). Cross relaxation and level anti-crossing in the former case cause changes in the hole depth and in the latter changes to the total emission intensity. The physical

phenomenon giving rise to the level anti-crossing signal in the present hole-burning experiment differs from that observed for excited triplet states, however, in that now triplet-spin polarisation induced by photo-absorption, rather than by spontaneous emission, is influenced by the state mixing.

2. Experimental details

The diamond crystal was a cube with sides of 1 mm and 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 G s^{-1} from 0 to 1500 G. 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. 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 using phase-sensitive lock-in detection techniques. The sweeps were repeated for various field orientations. No signal averaging was required for this series of measurements. Low-field scans (0 to 10 G) were signal-averaged up to 20 times however.

3. Results and discussion

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

$$H = \mu_B(\mathbf{H}\mathbf{g}\mathbf{S}) + D[S_z^2 - S(S+1)/3] \quad (2)$$

where $|D| = 2.88 \text{ GHz}$ gives the zero-field ground-state splitting. The sign of D has not been determined. \mathbf{g} is isotropic with a value of $g = 2.0028$ (Loubser and van Wyk 1977, 1978). The energy matrix for a centre with its axis at an angle θ to the field is given by ($|x\rangle, |y\rangle, |z\rangle$ basis)

$$\begin{bmatrix} \frac{1}{3}D & -ik \cos \theta & 0 \\ ik \cos \theta & \frac{1}{3}D & -ik \sin \theta \\ 0 & ik \sin \theta & -\frac{2}{3}D \end{bmatrix} \quad (3)$$

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 and these are illustrated in figure 1. In the (110) plane of rotation indicated, defining the direction of the field 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, $\cos^{-1}(\cos \theta / \sqrt{3})$. The energy levels of any given field orientation can be obtained by diagonalising the energy matrix (3) with the appropriate values for θ and k .

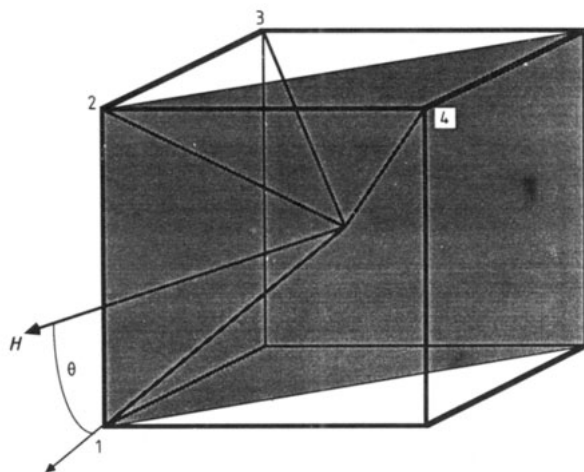


Figure 1. Orientation of trigonal centres. The experimental traces are taken as the magnetic field is varied in the (110) plane (shaded).

3.1. Cross relaxation between N-V centres and P1 centres

Because of the isotropic g value of the P1 centre, cross relaxation will occur when the N-V ground state $|0\rangle \leftrightarrow |+\rangle$ splitting derived from energy matrix (3) equals $g\mu_B H$. For a magnetic field along the axis of an N-V centre (say centre 1) this will occur when $g\mu H = D/2$ and hence at a field strength of 511 G. This is illustrated in figure 2(b). Upon rotating the field direction from the $\langle 111 \rangle$ direction to the $\langle 110 \rangle$ direction (angle θ) there is an increase in the required field strength to 770 G, as shown from the full curve in figure 3(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. 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 $\langle 110 \rangle$. Hence two lines merge at the $\langle 110 \rangle$ magnetic field orientation (figure 3).

The nitrogen hyperfine interaction gives rise to structure on each of the above N-V \leftrightarrow P1 cross-relaxation features and this is discussed for $H \parallel \langle 111 \rangle$. The P1 centres and the N-V centres are both aligned along the $\langle 111 \rangle$ axes and hence the field will also be along the axis of one P1 orientation. The hyperfine interaction shifts the aligned $m_I = \pm 1$ states by an energy of 0.114 GHz and as the splitting is 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 G from the $m_I = 0$ 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

$$(A_{\parallel}^2 \cos^2 70.5^\circ + A_{\perp}^2 \sin^2 70.5^\circ) \quad (4)$$

and hence there are two more lines separated by ± 15 G. Therefore, the inclusion of the hyperfine interaction within the P1 centre accounts for the five-line pattern observed for $H \parallel \langle 111 \rangle$ as is illustrated in figure 4. The ratio of the line sizes should be in proportion to the ratio of centres giving rise to each line, i.e. 4:3:1. The measured central line (figure 4(a)) representing all $S = \frac{1}{2}$, $g = 2$ systems is larger than expected, suggesting that it is possible there is cross relaxation with other such centres.

When the field is rotated in the (110) plane a seven-line pattern is possible but this is never resolved. Five-line patterns are expected (figure 4(b)) for the high-symmetry directions and these are confirmed experimentally. Also, for magnetic fields at an angle to the N-V centre main axis the Zeeman splittings are not a linear function of field

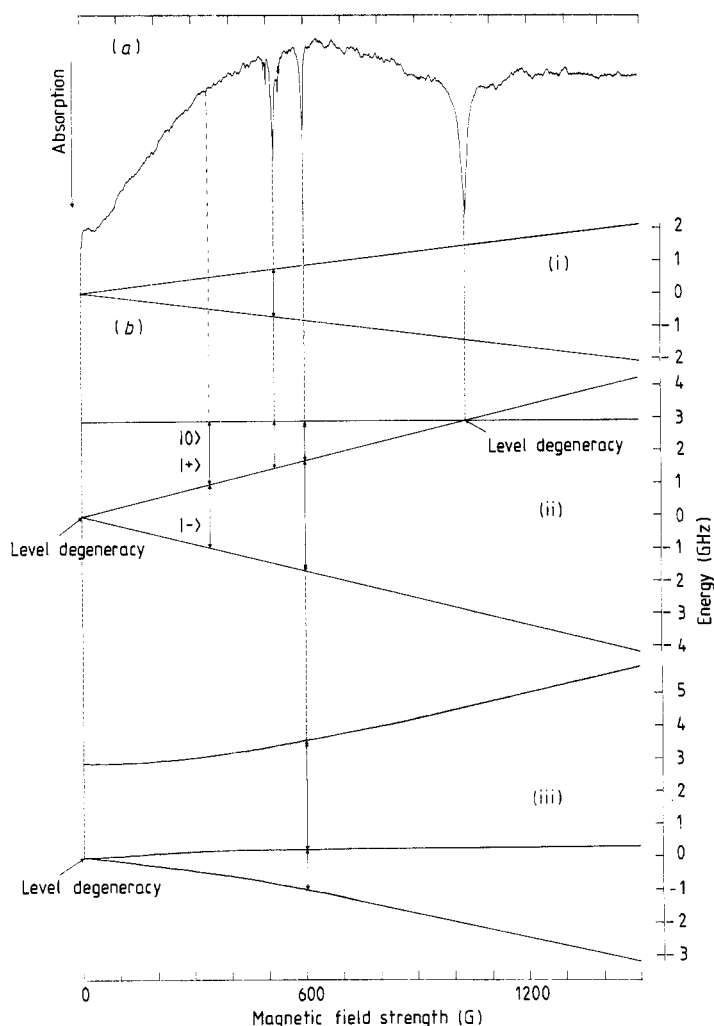


Figure 2. (a) Transmission of diamond crystal at 638 nm measured as a function of magnetic field strength in σ ($E \parallel \langle 111 \rangle$) polarisation with $H \parallel \langle 111 \rangle$. The crystal temperature was 10 K. (b) Zeeman splitting for centres when $H \parallel \langle 111 \rangle$. The three centres are (i) the $S = \frac{1}{2}$ system, (ii) the N-V centre with field along the main axis and (iii) the N-V centres with a field at an angle of 70.5° to their axes. The vertical broken lines indicate the origin of the hole-burning features and the arrows indicate the transitions involved in the cross relaxation.

strength. This results in the hyperfine features being displaced asymmetrically about the central line and the effect of this can be seen best in the trace for the $\langle 110 \rangle$ field orientation (figure 3).

3.2. Cross relaxation between N-V centres: magnetically equivalent centres

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

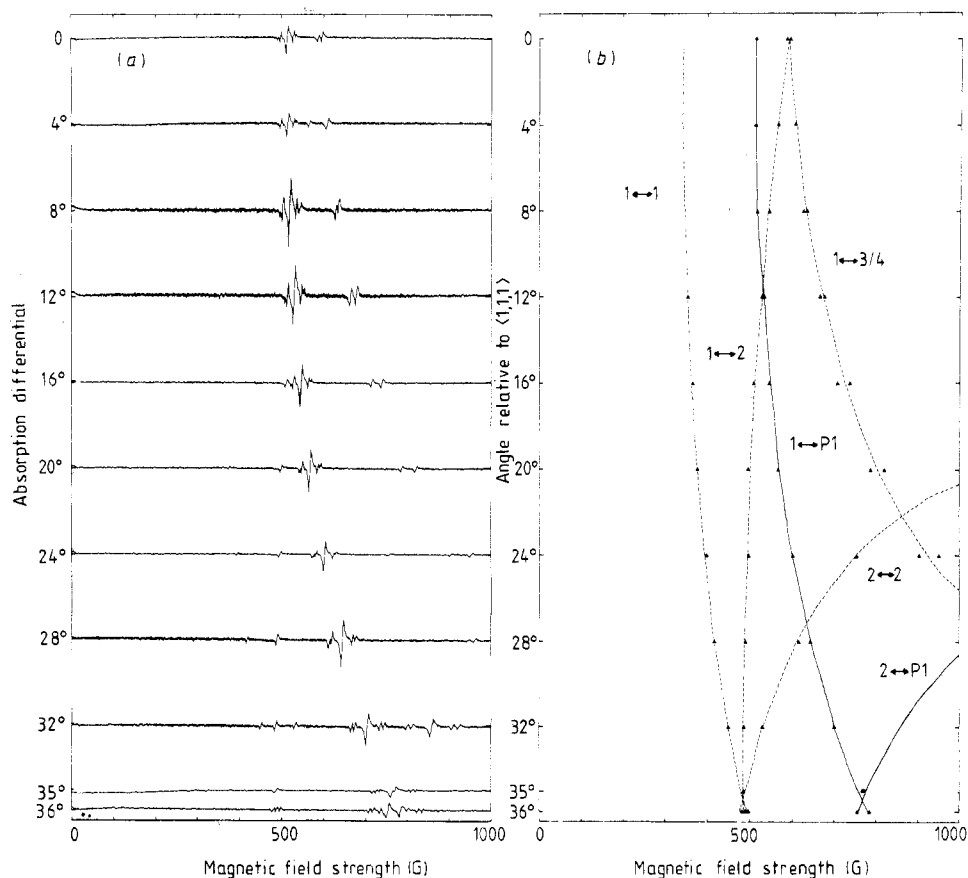


Figure 3. (a) Differential of transmission of diamond crystal at 638 nm as a function of magnetic field for field orientations between $H \parallel \langle 111 \rangle$ and $H \parallel \langle 110 \rangle$. (b) Cross-relaxation signals as a function of field orientation and field strength. The experimental values from (a) are indicated by points and calculated values are given by the full and broken curves. The full curve is the variation predicted for N-V \leftrightarrow P1 cross relaxation and the broken curves are those predicted for N-V \leftrightarrow N-V cross relaxation.

relaxation and a correspondingly faster relaxation rate; this in turn 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 (3). The eigenvalues are obtained by solving the equation for λ :

$$\lambda^3 + (-\frac{1}{3}D^2 - k^2)\lambda + [\frac{2}{27}D^3 - \frac{1}{3}Dk^2(3\cos^2\theta - 1)] = 0. \quad (5)$$

The standard solutions to such a cubic equation lead to the three energy separations (see, e.g., Stevenson 1984)

$$\nu_i = 2\sqrt{3}[(3k^2 + D^2)/9]^{1/2} \sin(\alpha/3 + \Delta) \quad \Delta = \pi/3, 2\pi/3, \pi \quad (6)$$

where

$$\cos \alpha = (9Dk^2 - 27Dk^2 \cos^2 \theta + 2D^3)/2(3k^2 + D^2)^{3/2}. \quad (7)$$

When $\alpha = \pi/2$ the magnitudes of two energy separations are equal and that of the third

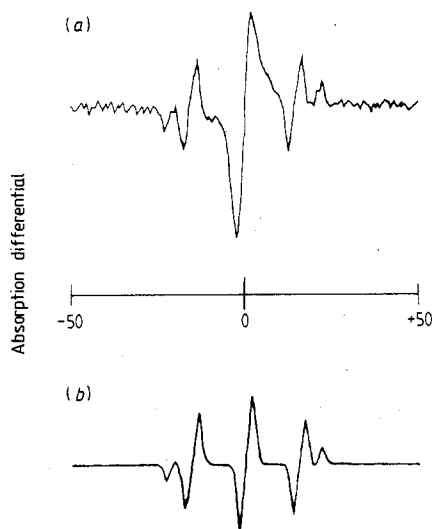


Figure 4. (a) Actual and (b) modelled illustrations of the hole-burning features associated with the P1 hyperfine structure for $H \parallel \langle 111 \rangle$. The model accounts for the theoretical separations and relative sizes of the features. The scale is calibrated in gauss relative to a zero which corresponds to 511 G.

is double the first two, i.e. the situation for equally spaced levels. Hence to have equally spaced levels, that is

$$9Dk^2 - 27Dk^2 \cos^2 \theta + 2D^3 = 0, \quad (8)$$

the field strength is given by

$$H = (D/g\mu_B)^{1/3} [2/3 \cos^2 \theta - 1]^{1/2} \quad \text{for } 0 \leq \theta \leq 54.7^\circ. \quad (9)$$

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. However, in this case spin quantisation is good and the cross relaxation required is $|+\rangle \leftrightarrow |-\rangle$ with $|0\rangle \leftrightarrow |+\rangle$ (figure 2). Thus although energy can be conserved the angular momentum cannot and 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 (9). The eigen-states are mixtures of the $|+\rangle$, $|-\rangle$ and $|0\rangle$ basis functions and the mutual spin flips become allowed. Hence the $1 \leftrightarrow 1$ feature associated with centre 1 which is forbidden for $H \parallel \langle 111 \rangle$ becomes progressively stronger as the angle is increased (figure 3). When the centre axis is at an angle to the field greater than $\cos^{-1}(1/\sqrt{3}) = 54.7^\circ$, the levels are never equally spaced and consequently there are no features associated with centre 3 (or centre 4) when H is in the (110) plane illustrated or for centre 2 when the field is close to the $\langle 111 \rangle$ direction. However, at angles close to $H \parallel \langle 110 \rangle$ centre 2 makes an angle of 35.3° to H and cross-relaxation features are observed. For $H \parallel \langle 110 \rangle$, centres 1 and 2 become equivalent and the $2 \leftrightarrow 2$ feature coincides with the $1 \leftrightarrow 1$ signal (figure 3).

3.3. Cross relaxation between N-V centres: magnetically inequivalent centres

Two magnetically inequivalent centres will give cross relaxation when there is a common ground-state resonance frequency. For two such centres, at angles θ_1 and θ_2 to the magnetic field, this will occur when there is a common value in the sets:

$$\begin{aligned} \{|\sin(\alpha_1 + 180^\circ)/3|, & \quad |\sin \alpha_1/3|, & \quad |\sin(\alpha_1 - 180^\circ)/3|\}, \\ \{|\sin(\alpha_2 + 180^\circ)/3|, & \quad |\sin \alpha_2/3|, & \quad |\sin(\alpha_2 - 180^\circ)/3|\}, \end{aligned}$$

where α_1 and α_2 are given by equation (7) with $\theta = \theta_1$ and θ_2 respectively. However, if there is one common value between these two sets then the sets are equal. This implies that for two inequivalently oriented centres the three resonances all 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 (6) or by numerical diagonalisation of the energy matrices (3).

When the magnetic field is along the $\langle 110 \rangle$ direction centre 1 becomes equivalent to centre 2 (figure 1) and hence the $1 \leftrightarrow 2$ cross relaxation should occur at the same field value as that for $1 \leftrightarrow 1$ (or $2 \leftrightarrow 2$) previously established. Away from the $\langle 110 \rangle$ direction there are three separate signals, the central one being associated with that between inequivalent centres 1 and 2. With crystal rotation the $1 \leftrightarrow 2$ signal is seen to merge with that from the $1 \leftrightarrow 3$ ($1 \leftrightarrow 4$) cross relaxation when the field is along the $\langle 111 \rangle$ direction and centres 2, 3 and 4 become equivalent. The $1 \leftrightarrow 3$ and $1 \leftrightarrow 4$ signals themselves should coincide throughout so long as the field is in the (110) plane (the observed splitting away from the $H \parallel \langle 111 \rangle$ direction is due to a slight misorientation of the field). Allowing for this misorientation the calculated field values are in excellent agreement with the observed position for the sharp decrease in the depth of the spectral hole (figure 3).

3.4. *N-V level anti-crossing*

The broader feature (half-width ~ 20 G) at 1020 G, which occurs when the magnetic field is along the $\langle 111 \rangle$ direction, is associated with the ‘crossing’ of the $|+\rangle$ and $|0\rangle$ levels. However, any small deviation of the magnetic field from the $\langle 111 \rangle$ 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 anti-crossing’. The hole-burning signal and its width will be associated with the resultant admixture of the $|+\rangle$ and $|0\rangle$ spin states in the anti-crossing region.

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 anti-crossing states can no longer provide separate population reservoirs. This mechanism is ruled out, however, by the large increase in the width of the level anti-crossing absorption dip as the field is rotated from the N-V centre main axis. 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 anti-crossing. Therefore, if the hole-bleaching was due to the approach of the triple levels to within the optical homogeneous width then the on-axis level anti-crossing dip would be broader than that for the off-axis case.

The increase in the width of the level anti-crossing 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 anti-crossing conditions implies the level state mixing gives rise to a slowing down to the optical pumping from the triplet ground state but it is not understood how this arises. Further investigations of the dynamics of the system close to level anti-crossing are required to determine the precise nature of the hole-bleaching mechanism.

3.5. *Low-field results*

A similar effect to the level anti-crossing hole-bleaching could be expected at zero field as the $|+\rangle$ and $|-\rangle$ energy levels are degenerate for all centre orientations. A sharp

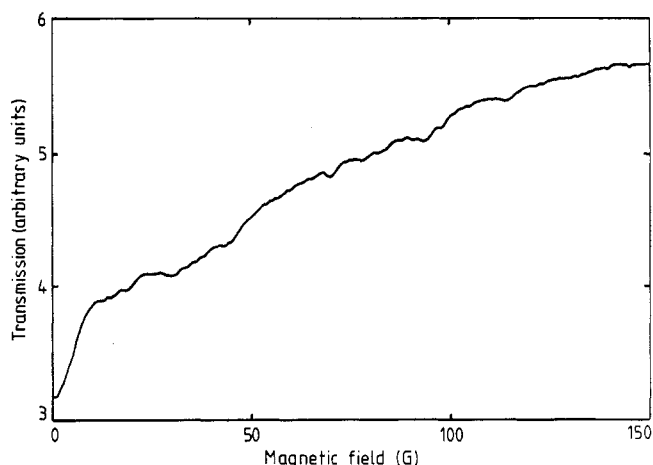


Figure 5. Transmission of the diamond crystal at 638 nm measured as a function of magnetic field strength in $\sigma(E \parallel \langle 111 \rangle)$ polarisation with $H \parallel \langle 111 \rangle$, signal-averaged over 20 sweeps. The crystal temperature was 10 K.

(~ 10 G) decrease in the hole depth near zero field has been observed (figures 1 and 5) but is considered to arise from an increased spin-spin cross relaxation; analogous to other cross-relaxation features but with an increased width due to the decreased rate at which the levels approach. In addition there is a gradual increase in the hole depth (figure 2) 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 100 G and these are ascribed to increased N-V \leftrightarrow P1 cross relaxation. Computer programs based on the theory described for high-field modelling assume a linear splitting of the P1, $S = \frac{1}{2}$ levels and the hyperfine levels dependent only on field orientation. At low fields this approximation is no longer valid and off-diagonal hyperfine terms in the energy matrix

$$\begin{bmatrix} (k/2) \cos \theta + A_{\parallel}/2 & 0 & 0 & -ik \sin \theta & 0 & 0 \\ 0 & (k/2) \cos \theta & 0 & A_{\perp}/\sqrt{2} & -ik \sin \theta & 0 \\ 0 & 0 & (k/2) \cos \theta - A_{\parallel}/2 & 0 & A_{\perp}/\sqrt{2} & -ik \sin \theta \\ ik \sin \theta & A_{\perp}/\sqrt{2} & 0 & -(k/2) \cos \theta - A_{\parallel}/2 & 0 & 0 \\ 0 & ik \sin \theta & A_{\perp}/\sqrt{2} & 0 & -(k/2) \cos \theta & 0 \\ 0 & 0 & ik \sin \theta & 0 & 0 & -(k/2) \cos \theta + A_{\parallel}/2 \end{bmatrix}$$

must be considered.

The P1 ground state consists of three doublets at zero field, which split apart in a magnetic field. With the field along a $\langle 111 \rangle$ direction, comparisons of these splittings and those for the differently aligned P1 centres with the two differently oriented N-V centre $|+\rangle \leftrightarrow |-\rangle$ splittings yield approximately 50 crossings within the 0–150 G region. Application of selection rules eliminates a portion of these but the excessive number of possible fits makes labelling of individual cross-relaxation effects difficult without further investigations.

4. Conclusion

A measure of the depth of an optical hole during continuous illumination while subject to an external perturbation is shown to provide considerable information about the optically active centre and this technique would be generally applicable. In the present 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. As the hole-burning occurs through a redistribution of the population in the ground-state triplet levels, the changes in depth arise when the triplet separations reach special conditions either equal to zero or equal to another ground-state separation. These situations give the reduced hole depths as there is faster restoration of the population within the triplet involved in the hole-burning when it is coupled to the larger ensemble of spins.

Acknowledgments

One of us (MG) acknowledges The Research School of Physical Sciences of the Australian National University in Canberra for an Invited Visiting Fellowship in the Laser Physics Centre. Support by the John van Geuns Fonds is also gratefully acknowledged. The authors are indebted to G Davies of Kings College, London, for the loan of the oriented diamond sample.

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