

Effects of magnetic field on the low temperature emission of nitrogen vacancy centres in diamond

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Abstract

Under optical illumination in the blue or green, negatively charged nitrogen vacancy centres in diamond emit in the red. The intensity of this emission varies slightly depending on spin state occupation. Optical transitions occur predominantly without change of spin projection. However, excited $m_s = \pm 1$ states can decay non-radiatively to the ground $m_s = 0$ state via intermediary singlet states. With continuous excitation, this effect transfers most of the population to the $m_s = 0$ state resulting in decay becoming almost entirely radiative so that optical emission is stronger than when all spin states are occupied equally. However, under optical illumination the $m_s = 0$ polarization is reduced when an applied magnetic field induces avoided crossings between energy levels. The spin states are mixed and some population is diverted into the $m_s = \pm 1$ states with consequent reduction in optical emission. The change of emission can be calculated from a rate equation model involving the spin states of the ground and excited levels plus one singlet level [5].

The spin states of the excited levels are also affected by strain and in this work we calculate the variation in optical emission with changing magnetic field for various fixed values of strain.

Key words: diamond, nitrogen-vacancy centre, calculation, spin polarisation, strain

1. Introduction

Although the fine structure of the ground state spectrum of nitrogen vacancy centres (NV^-) in diamond is well established, the fine structure of the excited 3E states has only recently been established [1, 5]. In the present work we have adopted these recent theoretical calculations of the strain splitting of the fine structure [4, 1] and have extended these calculations over a larger range of strain to include the high strain situations that can occur in crystals and certainly do occur in nano-diamonds.

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For the calculation of emission intensity we consider a nominal twelve level model comprising three ground state levels (3A_2), six excited state levels (3E) and three intermediate meta-stable levels (1E and 1A_1). For our present purposes the three intermediate meta-stable levels may be regarded as a single meta-stable level effectively giving a ten-level model. On excitation with green light, the excited 3E spin ± 1 projection states decay both radiatively to the spin ± 1 projection ground state and non-radiatively (via the metastable levels) to the spin 0 projection ground state with approximate respective transition rates of 77×10^{-6} transitions per second and 30×10^{-6} transitions per second [5]. The non-radiative decay causes the system to become spin polarized with optical emission then occurring only between the excited and ground spin 0 projection states, emission between the excited and ground spin ± 1 projection states being effectively quenched [2]. Once spin polarized there is little non-radiative decay via the singlet levels and the emission of the centre is high. Whenever the spin states become mixed the situation is altered and emission becomes weaker. This can result as a consequence of an applied magnetic field or internal strain. By considering the nature of the mixing we are able to determine the variation of the emission from the rate equations of the ten level model [4]. In the calculations that follow we determine the emission for centres with given values of strain and more importantly determine how this emission varies as a function of the magnitude and direction of the magnetic field. While changes of emission can result from wave-function mixing within both the ground and the excited states, the discussion will focus on the effects resulting from wave-function mixing in the 3E states.

At temperatures greater than 10°K observations indicate that averaging over the excited orbital states occurs [5]. The model described by this paper does not address this temperature dependency and therefore pertains only to temperatures below 10°K. Also, it has been shown that the rate equation calculation is not reliable when the magnetic field is exactly along a trigonal axis [5]. However, we use it here to advantage as it indicates the presence of avoided crossings and the nature of the pertinent interactions will be discussed.

2. Parameters

In the absence of external strains and magnetic fields the energy levels of the 3E states are determined primarily by electronic spin-spin and spin-orbit interaction. The parameters used are those obtained from the recent experimental observations of Batalov et al [1] and are consistent with the low temperature theoretical description given by [5, Section 6.]:

1. A first-order spin-orbit component λ_z splits the six-fold degenerate 3E energy levels into three doubly degenerate levels comprising:

- (a) an un-displaced $m_s = 0$ doublet,
- (b) a $m_s = 1$ doublet displaced by 5.5 GHz to higher energy with respect to the $m_s = 0$ doublet and
- (c) a $m_s = -1$ doublet displaced by 5.5 GHz to lower energy with respect to the $m_s = 0$ doublet.

2. A spin-spin component D_E increases the energy of both $m_s = \pm 1$ doublets by 1.42 GHz.

3. Another spin-spin component splits the $m_s = 1$ doublet into two non-degenerate states separated by 3.1 GHz.

4. An off-diagonal spin-orbit component mixes the states in 1(a) and 1(c) (the $|\bar{1}\bar{1}\rangle$ state with the $|10\rangle$ state and the $|11\rangle$ state with the $|\bar{1}0\rangle$ state) but the interaction energy of approximately 0.2 GHz contributes little to zero field splitting compared to the much larger energy differences

of $\lambda_z - D_E$ between the $m_s = 0$ and $m_s = \pm 1$ states. In the presence of a magnetic field (H) a near isotropic spin Zeeman term $g\beta H$ is introduced with $g = 2$. (Orbital Zeeman is not included as it is small and does not change the phenomenon). As in a recent paper [4], strain is treated as a perturbation and its value is given in terms of the splitting of the orbital components in the absence of all other interactions.

3. Energy Levels As A Function Of Strain

When both strain and a magnetic field are present the labelling of the energy levels is not straightforward and are simply numbered 1 through 12 in order of increasing energy (at zero field). Levels 1 through 3 represent the 3A_2 states, levels 4 through 6 represent the meta-stable singlet states and levels 7 through 12 the 3E states with the 3E levels being of primary interest. The variation in the latter energies are calculated by including strain, the results being shown in Figure 1. At strain values below 9 GHz as shown in the left diagram, the levels are distributed over a 20 GHz energy range whereas with high strain, as shown in the right diagram, the levels are split into well separated branches having three spin levels in each branch.

The upper 3E branch exhibits little complexity. However, in the lower branch, the spin levels are close in energy and significant wave function mixing occurs. Assuming a strain that maintains the reflection plane (x-strain), spin-orbit interaction causes a mixing of levels 8 and 9 resulting in an avoided crossing as a function of strain at strain values in the region of 7.33 GHz. With x-strain, level 8 does not interact with level 7 but crosses at approximately 15.2 GHz to become the lowest 3E level at higher strain. If the strain direction is changed so that the reflection plane is lost the position of the crossing is barely changed but interaction occurs at both crossings.

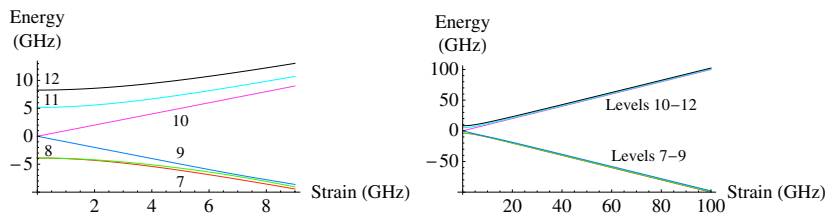


Figure 1: Energy level variation of 3E excited states with respect to strain. The left diagram gives the variation for low values of strain in the range 0 - 9 GHz. The right gives the variation over a larger range of strain, 0 - 90 GHz.

4. Single Centre Emission Under Low Strain

The left diagram of Figure 2 shows the variation in emission for a single centre with fixed strain values of 0.0, 0.5, 1.0 and 3.5 GHz when an applied magnetic field is closely aligned with the centre's trigonal axis. For these low values of strain the zero field energy levels are within a range of 12 GHz. A magnetic field of 0.4 Tesla causes a similar range of displacement with several level crossings occurring as the field is swept from 0 to 0.4 Tesla as can be seen by the example for 0.5 GHz strain on the right hand side of Figure 2. Four (8, 9, 10 and 11) of the six 3E levels become adjacent (the other two are off the figure) and some interact to give rise to four features in the emission response. When there is a crossing of a nominal $m_s = 0$ state (levels

9 and 10) with a $m_s = \pm 1$ state (levels 8 and 11) there is a decrease in emission. However, the features are either narrow or broad with the width of a feature indicating the strength of the corresponding interaction. There are two mechanisms by which the states can interact; an off-diagonal spin orbit interaction and a transverse magnetic field interaction. By applying a magnetic field very close to the axis the transverse component of the magnetic field gives rise to the delta functions whereas spin orbit interaction gives the broader lines. Clearly, if a field is applied at a significant angle the transverse magnetic field component will be larger and with the larger interaction the features will broaden. The strength of the off-axis spin orbit interaction is not dependent on field angle and, to first order, the associated features will always have the same width (or will obtain width should the interaction be dominated by the transverse field). Thus the behaviour of the feature with respect to magnetic field angle can be used to establish the nature of the interaction. The rate equation calculation with near perfect alignment is therefore useful as it both gives the magnetic field values at which a decrease in emission will occur and provides a marker indicating the nature of the interaction. It should be recognized that the narrow features do not occur in experiments as the excited states do not reach equilibrium within their radiative lifetimes [5].

In the example shown for 0.5 GHz strain, the crossing arising from the lower levels interacts via the spin-orbit interaction and, consequently, the interactions of level 8 with levels 9 and 10 give the broad features. Level 11 only interacts with levels 9 and 10 through the transverse magnetic field and, with good alignment, gives the sharp lines. Note that when the $m_s = \pm 1$ states cross (levels 8 and 11), irrespective of whether or not there is an interaction, no emission change occurs as the population of the $m_s = 0$ state is not affected.

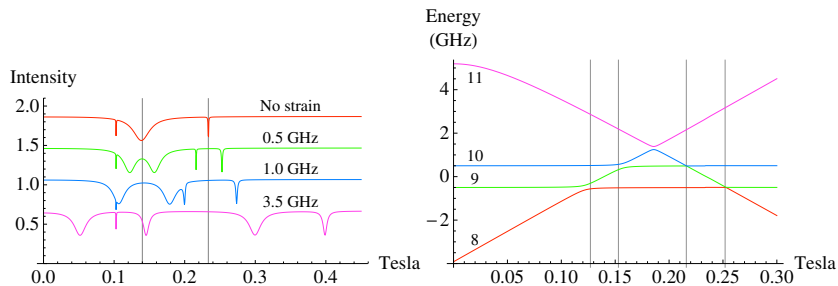


Figure 2: (left) Optical emission from a single site for strains in the range 0 to 3.5 GHz with respect to a magnetic field at 0.5° with respect to the site's symmetry axis. The spikes at about 0.1 Tesla are due to avoided crossings between 3A_2 states. (The traces are separated for clarity.) (right) 3E energy levels corresponding to the 0.5 GHz response of the left diagram.

In the left figure, for the case with no strain, depolarization occurs around 0.14 Tesla as the avoided crossings between levels 8 and 10 and between levels 8 and 11 coincide. Increasing strain progressively splits the spin zero-projection levels 9 and 10 giving a splitting of the zero-field's single broad dip. The separation of levels 9 and 10 also gives rise to splitting of the sharp feature at 0.23 Tesla due to interactions via the near zero transverse field.

In every case there is a feature at 0.104 Tesla which is due to the avoided crossing between two of 3A_2 electronic ground states. This feature is sharp for good alignment as the interaction is due to the transverse magnetic field component and, because it always occurs at the same

magnetic field strength, is useful as its width provides an indication of magnetic field alignment.

5. Ensemble Emission Under Low Strain

Should a concentrated diamond sample be measured the emission will be associated with an ensemble of nitrogen vacancy centres. There will be a range of values of strain together with contributions from the four different orientations of centres in the diamond lattice. This section indicates the spectrum expected for samples having very low strain. The left-hand part of Figure 3 shows the emission for three values of strain including contributions from centres of different orientations one quarter of which are aligned with the field with the remainder aligned in equal proportion with the other three possible ensemble orientations.

The right diagram shows the predicted emission for ensembles having a distribution of discrete strains with a weighted distribution of strains being used as an example.

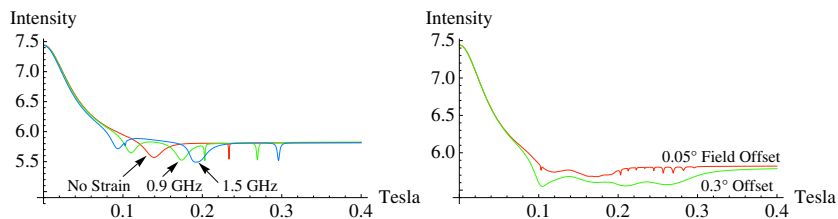


Figure 3: Optical emission from ensembles under low strain. (left) Emission from an ensemble allowing for 25% of centres closely aligned and 75% mis-aligned with the magnetic field for strains of 0.0 GHz, 0.9 GHz and 1.5 GHz. (right) Emission from an ensemble having a weighted distribution of strains covering the range 0 To 1.5 GHz for a magnetic field closely aligned with a $\langle 111 \rangle$ symmetry axis and one mis-aligned by 0.3° with this axis.

6. Single Centre Emission Under High Strain

Figure 4 shows the optical spectra predicted by our model for strains applied to a single centre in the high strain range from 50 to 400 GHz. Two broad features occur that are associated with interactions within the two orbital branches of the split excited state. Comparison with Figure 5 shows that the broader features around 0.04 Tesla are associated with contributions from the lower branch avoided crossing between levels 7 and 8 (left diagram) and from the upper branch avoided crossing between levels 10 and 11 (right diagram).

Sharper features associated with upper-lower branch crossings between levels 8 and 9 and between levels 10 and 11 are predicted for very high magnetic field (multi-Tesla) but as these fields are unlikely to be accessed are not shown.

As for the previous examples, the feature at 0.104 Tesla is caused by an avoided crossing between two of the 3A_2 ground states, the width of this feature being determined by the magnitude of the transverse field.

7. Ensemble Emission Under High Strain

This section shows the emission expected for a sample containing high values of strain. Figure 6 shows the predicted emission for a weighted distribution of strains in the range 100 to 350

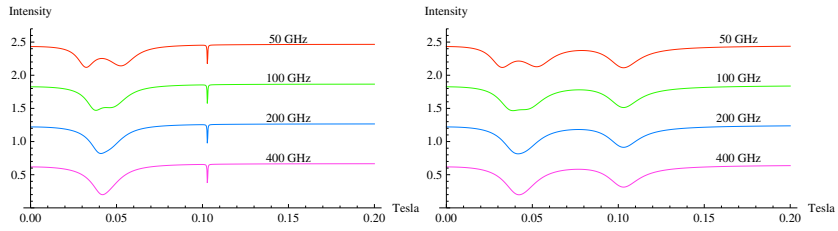


Figure 4: Optical emission from a single site at high strains. (left) For a closely aligned magnetic field. (right) For a magnetic field mis-aligned by 3° with respect to the centre’s trigonal axis of symmetry.

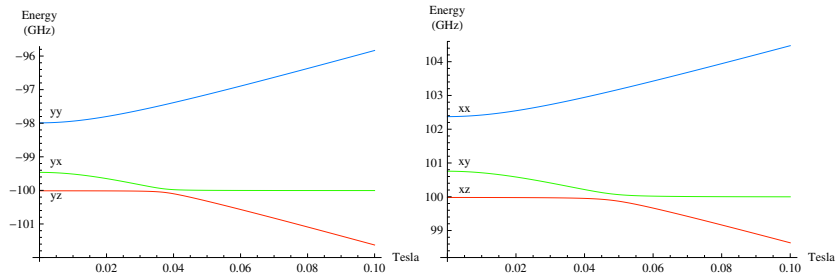


Figure 5: Energy levels with respect to applied magnetic field for strains of 100 GHz. (left) Lower branch, (right) upper branch.

GHz from an ensemble of centres. As in the previous case for an ensemble, a quarter of the centres are aligned with the field while the remainder are aligned in equal proportion with the other three possible orientations of diamond’s tetrahedrally co-ordinated lattice. The situation is shown for two orientations of the magnetic field. This situation is probably close to that realized in the experiments reported by Rogers et al [5] where a broad minimum is observed for a magnetic field of 0.05 Tesla. Although better knowledge of the distribution of strain is required to reliably calculate the spectral response for such samples the present spectrum has characteristics consistent with experiment.

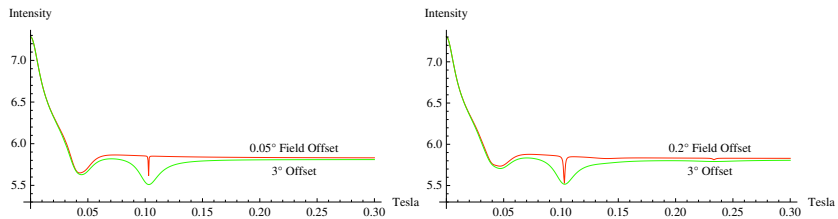


Figure 6: Optical emission from an ensemble under high strain. (left) Equally weighted strains of 100 GHz, 250 GHz and 350 GHz. (right) Variably weighted distribution of strains in the range 0 GHz to 350 GHz.

8. Conclusion

We have calculated the spectral responses of the emission intensity versus magnetic field strength for nitrogen vacancy centres in diamond over a wide range of strain and field direction for both single centres and ensembles of centres. It is anticipated that these calculations will provide guidance in the interpretation of experimentally obtained spectra. It is unlikely that we will be able to determine the distribution of strain in diamond with a concentration of NV^- and so calculation of ensembles will not be able to establish the accuracy of the present calculations. However, comparison with single site measurements should be very informative and such measurements should be undertaken.

Acknowledgements

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