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NV-NV electron-electron spin and NV-N_S electron – electron and electron-nuclear spin interaction in diamond

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Abstract

Features associated with the cross relaxation between spin of the ground electric state of the nitrogen vacancy centre (NV) and other impurity spins, mainly substitutional nitrogen, N_S, are observed as changes of the emission intensity as a function of external magnetic field. The features are attributed to NV-NV electron-electron spin interaction, NV-N_S electron–nuclear spin interaction and NV electron spin interaction with simultaneous change of an N_S electron and nuclear spin change.

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1. Introduction

The NV centre has an electron spin of $S = 1$ and has the property of becoming spin polarized when optically excited [1]. The emission is greater when spin polarised than when not and conversely if the polarization is reduced the emission is reduced [2] and one way this can occur is through the application of a magnetic field. With increase in magnetic field strength there can be some gradual changes and also some sharp changes in emission. These are measured in this work and explained in terms of either the electronic structure of the NV or interaction of the NV spin with those of other defects in the diamond.

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2. Spin Polarization

The nitrogen adjacent to a vacancy forms a defect centre with trigonal symmetry and a strong optical transition in the visible region of the spectrum [3]. Under optical excitation of this transition at zero magnetic field, the centre becomes spin polarised in the $S=1$ ground state [1] and this can be explained in terms of the energy level diagram in Fig. 1 [2]. The ground and excited states both have spin $S=1$ and the optical transitions conserve the spin projection. However, when in the excited $M_S = \pm 1$ state there is an alternative decay via a singlet (or singlets) to the $M_S = 0$ ground state. The presence of this alternative decay has two consequences: the ‘dark’ decay means the $M_S = 0$ emission is stronger than that for $M_S = \pm 1$, with cycling population is transferred to $M_S = 0$. This one way transfer from $M_S = \pm 1$ to $M_S = 0$ causes the spin polarisation and clearly the emission will be stronger when the system is spin polarised.

When M_S is not a good quantum number the optical cycling is less effective at causing spin polarisation and the emission is reduced. This is the situation with a magnetic field, as the component of a magnetic field transverse to the NV symmetry axis mixes the $M_S = 0$ and $M_S = \pm 1$ spin states. This mixing is dependent on the magnitude and the direction of the magnetic field, and affects the intensity. In this study the emission intensity is measured as a function of the magnetic field.

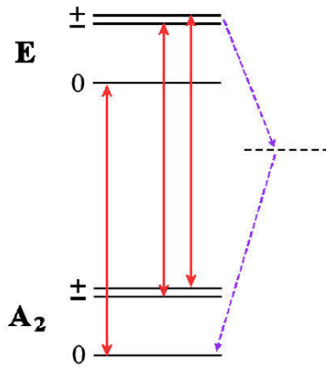


Fig. 1 Simplified NV energy diagram.

The emission intensity can be affected by another process. This is when the spin polarization is reduced through cross relaxation between NV spins and those of other defects. It occurs when there is a coincidence in the separation of the NV spin levels with those of another adjacent spin system [4,5]. The second impurity will not be polarised, and consequently cross relaxation with the NV will have the effect of reducing the NV spin polarisation and, hence, the emission intensity. The cross relaxation arises through dipole-dipole interaction and the strength of this interaction will have to be sufficient for the rate to be comparable with the optical pumping rate. In the present measurements the coincidences in the energy separations come about through the application of a specific magnetic field and are also be studied by monitoring the emission as a function of magnetic field.

3. Experimental Method

A type I b diamond crystal of dimensions 1mm by 2mm by 2mm containing a estimated concentration of 10^{19} substitutional nitrogen atoms of per cm^3 . The crystal was irradiated with electrons and annealed to give a concentration of 3×10^{18} NV defect centres per cm^3 . The sample was held between the poles of an electro-magnet with the $\langle 111 \rangle$ axis aligned with the field. The crystal was excited parallel to the magnetic field through a hole in one of the poles of the electromagnet using 100 mW laser at 532 nm. The magnet could be swept from 0 to 1450

gauss at a typical rate of 36 gauss per second. The emission at right angles was detected using a 610 nm high pass filter and a silicon diode.

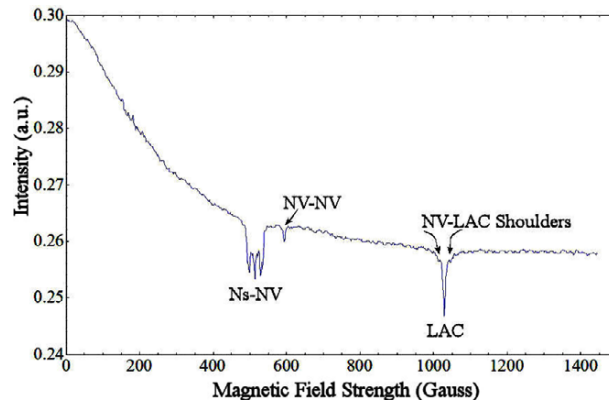


Fig. 2 Emission Spectrum of magnetic field scan

4. NV – NV cross relaxation

The emission is recorded as a function of the strength for a magnetic field aligned close to the $\langle 111 \rangle$ crystallographic axis and this is shown in Fig. 2. It can be seen that there are several sharp changes in intensity. One feature in this figure can be used to improve the alignment of the crystal and will be discussed first. The feature of interest arises from the interaction between differently aligned NV centres and gives the sharp decrease at ~ 600 gauss. The trigonal NV centres in diamond can have four possible orientations as shown in Fig. 3. When the external magnetic field is aligned along the axis of one (NV 1) the other three (NV 2,3,4) will all have an equivalent angle 70.5° to the field. The Zeeman splitting for a field at 70.5° is entirely different to that of the linear splitting axial case and these are indicated in Fig. 4. However, the significance is that at ~ 600 gauss there is a coincidence in separations of the two spin systems. In the case of the non-axial centres the spin states will be mixed and the centres will not be spin polarized. Consequently with cross relaxation the effect is to reduce the spin polarisation of the axial centre and give an overall reduction of emission intensity. Should the field be close to the $\langle 111 \rangle$ direction but not exact, each set of cross relaxations will result in a sharp decrease in emission and so there will be three features not one. However, by adjusting the alignment these can be collapsed to one to give the situation for perfect alignment. The trace shown in Fig. 2 & 4 is for this case. Therefore, the one sharp feature at 600 gauss is due to the cross relaxation between pairs of NV centres.

To achieve spin polarization the rate for optically induced spin polarization has to be faster than spin-lattice relaxation (typically MHz). This is the situation for the axial centre at all fields except where the emission is reduced. To reduce the emission the cross relaxation rate has to be comparable to or faster than the optical rate inducing the spin polarization. For the light intensities used the spin polarization rate is estimated at 10 MHz and for magnetic dipole-dipole interaction to be comparable the two NV centres would have to be within 30 nm to be effective and this is reasonably consistent with a concentration of 3×10^{18} NV per cm^3 . This change of emission due to NV–NV interaction has not been reported previously but presumably occurs here because of the high NV concentration in these samples. The interaction has been observed using other techniques. For example the cross relaxation inhibits resonant zero-phonon hole burning and the depth of the hole shows a reduction in depth as a

magnetic field [5] is swept through a value of 600 gauss. It also changes spin-lattice relaxation and the interaction has been studied using EPR [4].

It is significant to note that the gradual change in emission background from 0 to 600 gauss observed in Fig. 2 is associated with the emission from these other three non-aligned centres (NV 2, 3, 4) [6]. Under optical excitation they will be spin polarized at zero field and give high emission. The emission is reduced with the field mixing and this reduction is very obvious in the 0 – 200 gauss range. By 600 gauss there will be negligible spin polarization consistent with the fact that with cross relaxation they quench the spin polarized of the axial centre (NV 1, Fig. 3).

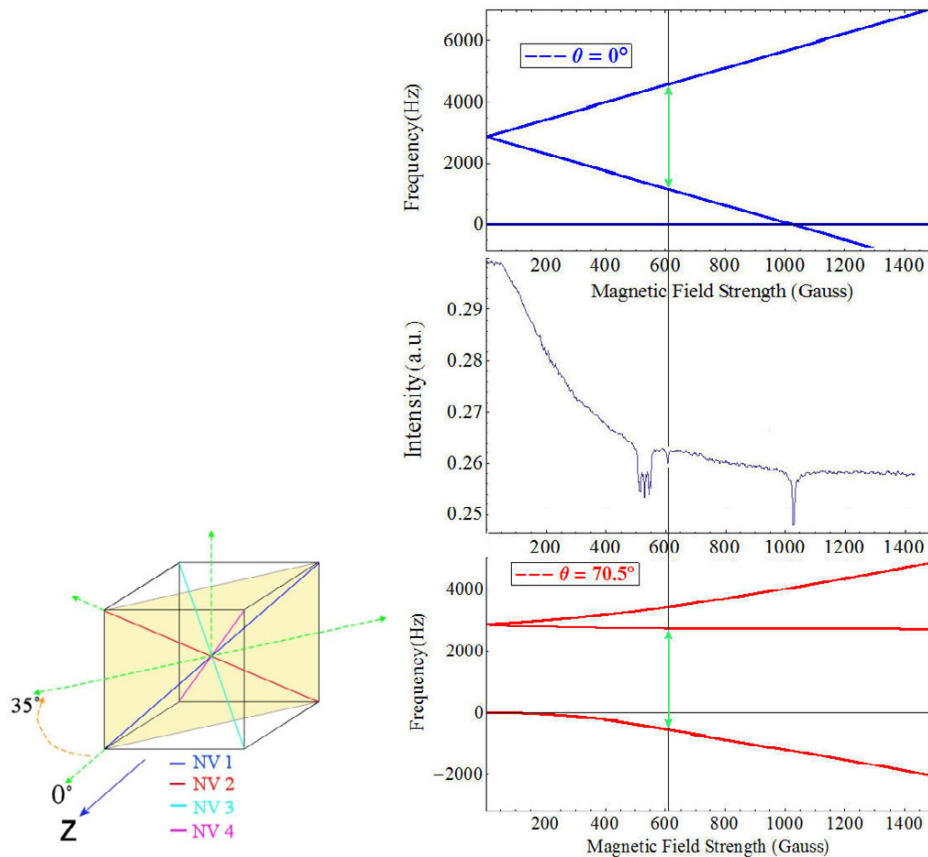


Fig. 3. Orientations of the NV centre.

Fig. 4 Spin levels and coincidence of energy separation of spin levels for NV centres aligned with a magnetic field (NV 1; $\square = 0^\circ$) and those aligned in an alternative direction (NV 2, 3, 4; $\square = 70.5^\circ$) occurring at ~ 600 gauss.

5. NV – N_S cross relaxation

There are other features in Fig. 2 that arise from cross relaxation. For example at ~ 514 gauss there is a complex set of features that arise from cross relaxation between the axial NV centre and substitutional nitrogen atoms (N_S) [7]. The field value this occurs is easily understood. The g-values for the NV and N_S are both near $g=2$, and the NV centre with $S = 1$ has a zero field splitting of 2.88 GHz whereas N_S with $S = \frac{1}{2}$ is not split. The consequence of the

Zeeman shifts is that there is a matching of separations at ‘half field’; half the field required for the $S = 1$ system to have a zero crossing (Fig 4). The zero-crossing is at 1028 gauss (discussed later) and the half field, hence, at 514 gauss. Had both centres only involved electrons there would be a single magnetic field at which energies would match and there would be a single decrease in emission. However, nitrogen has a nuclear spin of $I = 1$ and, hence, there are three hyperfine levels associated with each centre. The hyperfine associated with NV is not resolved but that associated with N_S is of the order of 114 MHz and gives three field values at which there is interaction with the NV. In addition the N_S centre has trigonal symmetry and so there are four orientations, although only two different orientations are relevant (as with NV in previous section). One centre has an axis parallel to the field and to the NV of interest. This will give interaction for three field values. A further three N_S centres will be at an angle of 70.5° to the relevant NV and the combine to give a further three interactions. The central line of the two sets of three coincide and so results in a five line pattern in the emission intensity v magnetic field trace, as shown in Fig. 5. The numbers in the spectrum indicate the number of pairs contributing. Such structure has been reported previously in holeburning spectrum [5], in EPR [4] and equivalent measurements to this using single site detection [7]. The effect has also been exploited in several other single site experiments [9,10]

In the present experiments extra structure associated with the latter features are observed. These are a pair of weaker peaks equidistant from the central feature spaced approximately half way between the central peak and the strong side peaks. The features can be attributed to cross relaxation between the NV electron spin transition and a N_S spin transition where there is a simultaneous change of the electron spin and nuclear spin state (transitions indicated in Fig. 5). The cross relaxation reduces spin polarization and hence emission. The reason for the occurrence of this feature in the present crystal is presumably due a high N_S concentration so the average NV – N_S distance is less than for material used by others.

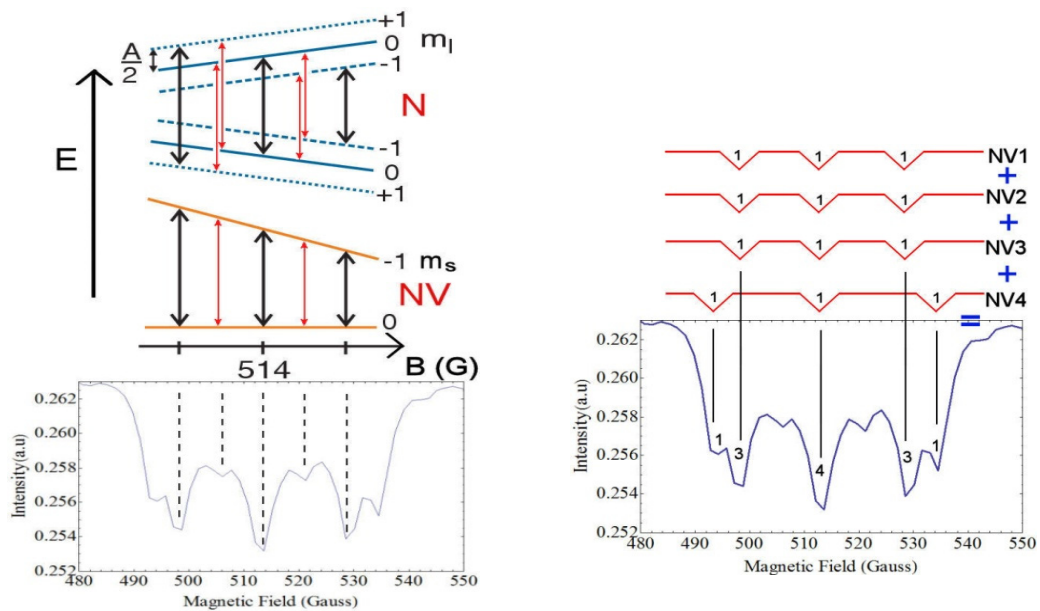


Fig. 5 Resonant spin transfer with substitutional nitrogen atoms.

6. Level Avoided Crossing of Ground State

As discussed earlier, the ground state triplet is split in zero magnetic field by a crystal field of $D=2.88\text{GHz}$ into a spin singlet and a spin doublet. The degeneracy of the $M_S = \pm 1$ doublet is split linearly with a axial magnetic field and at a field of 1028 G, the $M_S = 0$ and $M_S = -1$ levels cross (Fig 3). However, even with good alignment with the $\langle 111 \rangle$ direction there will still be a small transverse field and this causes the states to mix and the ‘crossing’

becomes an avoided crossing. The spin states are mixed and full spin polarisation cannot be attained. The result is a sharp drop of emission intensity for the avoided crossing situation [8]. This feature has been reported previously and a fuller study will be reported elsewhere.

What is new is the structure observed on either side of the level avoided crossing feature (Fig. 6). The extra peaks are attributed to cross relaxation at low frequency (~ 50 MHz) between the electron spin of the axial NV centre and a nuclear spin change of the substitutional nitrogen, N_S . This interpretation is supported by the spacing of the features matching the structure associated with the nitrogen hyperfine structure observed at 514 gauss and this comparison is shown in Fig. 6.

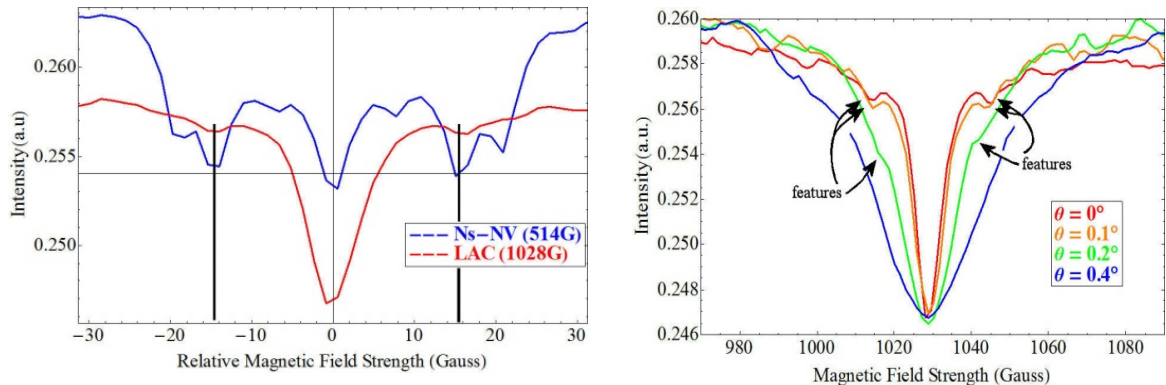


Fig. 6. LAC shoulders and comparison with cross relaxation at 514 gauss.

The reason the features are observed are again due to the high nitrogen concentration in the sample. Before the extra features can be observed it is also essential for the alignment of magnetic field with the $\langle 111 \rangle$ axis to be good and this has been achieved here by the technique described in section 4 using NV-NV interaction. If the misalignment is greater than 0.2° the features are not distinguishable due to the broadening of the avoided crossing feature. This is illustrated in Fig. 6. The reason that they are not observable in the latter situation is, of course, that with spin mixing there is no polarisation to be quenched by cross relaxation.

7. Conclusions

Several of the effects observed here have been reported previously. For example effects arising from level avoided crossings [8]. In the present work the NV ground state crossing is only mentioned briefly and level crossing in the excited state not treated at all. Studies of these crossing will be reported in a separate publication. The NV- N_S cross relaxation is also only briefly treated as the interaction has been studied extensively by others [8-13].

The main new observation is that of features arising from spin-spin cross relaxation but where there is a change of nuclear spin. This occurs combined with an electron spin flip in the case of NV and N_S or a direct electron-nuclear spin flips in the case of NV and N_S near an electron spin crossing. In the latter case the interaction could be used to polarize the N_S nuclear spin.

Another situation not observed previously through emission changes is that associated with NV-NV interaction. It also occurs through dipole-dipole interaction requiring the centres to be reasonably close and is observed here due to the use of high concentration of NV centres. The dipole-dipole interaction is of great importance in the use of the centre in quantum information processing applications and of contributions to dephasing. However, there is much

interest in the NV-NV as a multi-qubit system and the observations here indicate how in single site measurements emission may be used to search for such a pair centre in low doped crystals.

8. Acknowledgements

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9. References

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