

Issues concerning the nitrogen-vacancy center in diamond

N.B. Manson*, R.L. McMurtrie

Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

Available online 28 February 2007

Abstract

The nitrogen-vacancy (N-V) center in diamond has been extensively studied and several novel properties identified. As a consequence the center has interesting applications. However, the center is not completely understood. In this work a new electronic model is proposed which accounts for the fine structure of the excited state and for many of the associated properties of the center. In addition the paper discusses the remaining difficulties and indicates the studies required to resolve the outstanding issues.

© 2007 Elsevier B.V. All rights reserved.

PACS: 42.50.Gy; 42.50.Nn; 76.30.Mi

Keywords: Nitrogen-vacancy; Color center; Electronic structure

1. Introduction

There are exciting applications of the nitrogen-vacancy (N-V) center in diamond as a single photon source [1,2] and for quantum information processing [3–6] and yet the center is not completely understood. In this paper a new model of the electronic structure of the center is outlined and shown that it can account for many of the properties. However, the purpose of the paper is to also highlight outstanding issues with the model and suggest experiments that would help to clarify the situation enabling us to obtain a complete understanding of the center.

The N-V center has C_{3v} symmetry being associated with a substitutional nitrogen atom and a vacancy aligned along a $\langle 111 \rangle$ direction. There is a single optical transition with a zero-phonon line at 637 nm. Uniaxial stress measurements show the transition is associated with an A–E transition at the trigonal site [7].

The optical transition is accompanied by a vibronic band to high energy in absorption and low energy in emission. An unusual aspect of this vibronic sideband is that the first feature in absorption gives a double peak whereas the first feature in emission is a single peak. A difference in the vibronic structure between absorption and emission is

frequently attributable to a Jahn–Teller effect. However, in uniaxial stress measurements Davies and Hamer [7] obtained the same polarization for the sideband and the zero-phonon line and established that the sidebands were associated with coupling of symmetric modes. They concluded that the variation in sideband structure was not related to a Jahn–Teller effect. They attributed the difference to the nitrogen being able to interchange positions with the vacancy and, hence, sat in a double potential well. In the excited state the depth of the well coincides with the energy of the axial mode frequency of 560 cm^{-1} (70 meV) and tunnelling between the two wells was considered to give rise to the double peak in absorption. Kilin et al. [8] have further developed this model and obtained a depth of the well in the ground states of 3000 cm^{-1} (375 meV).

With the shallow potential the excited state energy is susceptible to strain and it is improbable that at a single site the optical frequencies associated with the two wells will be the same. The well occupied can be changed by exciting at energies above the well depth ($< 600\text{ nm}$). Likewise when there is emission there can be sufficient energy to overcome the ground state potential barrier. Therefore, with single site measurements two frequencies (or sets of frequencies) should be encountered. This is not a characteristic that has been observed [9,6] and the lack of such an observation brings the double potential well model into question. With

*Corresponding author. Tel.: +61 2 612 54204; fax: +61 2 612 50029.

E-mail address: Neil.Manson@anu.edu.au (N.B. Manson).

ensembles of N-V centers optically induced re-orientations would result in long-lived spectral holes. Long-lived holes other than those associated with spin changes have been reported. However, their origin has not been established and could arise from a re-distribution of charge in the lattice. Should the holes arise from the latter process there would be little supporting evidence of nitrogen re-orientation. The situation regarding the double potential well, therefore, is a subject that requires further study.

2. Electronic model

The N-V center is recognized to have a $S = 1$ ground and excited state [10–14] and many of the interesting properties of the N-V center are associated with changes in the spin projection [15,6,16]. The electronic states are associated with six electrons occupying dangling bonds in the neighborhood of the vacancy. In C_{3v} symmetry the dangling bond orbits can be combined to give two a_1 orbits and an e orbit [17]. It would require eight electrons to form a closed shell and with six electrons it is simpler to discuss the system in terms of the two unoccupied or hole orbits. In this hole description the lower energy states are anticipated to be $^3A_2(e^2)$, $^1A_1(e^2)$, $^1E(e^2)$, $^3E(a_1, e)$, $^1E(a_1, e)$ in approximate order. The $^3A_2(e^2)$ is the ground state and the optical transition is to the $^3E(a_1, e)$ excited state and these are the only states for which the energy is known. The energy and the order of the singlets have not been established. However, regardless of their position the electronic structure and the interaction between states will be determined by the spin–orbit and spin–spin interactions. For brevity it is convenient to write the Hamiltonian in high symmetry (tetrahedral) form

$$H = V + \Delta + \lambda \underline{L} \cdot \underline{S} + \rho[(\underline{L} \cdot \underline{S})^2 + (\underline{L} \cdot \underline{S})/2 + L(L+1)S(S+1)/3] \quad (1)$$

and allowance for the lower symmetry made by making the parameters appropriate for trigonal symmetry. For example, V gives the orbital energy levels in the trigonal field. Δ is also an orbital operator and is included to allow the distort of the center by strain. The axial and transverse orbital angular momentum will be different and values are proportional to $\langle \|L_z\| \rangle = m$ and $\langle \|L_{x,y}\| \rangle = n$, respectively. The latter transverse orbital angular momentum of a doublet in axial symmetry is small and initially taken as zero. In this situation spin–orbit and spin–spin interaction do not give any mixing of the axial S_z and transverse (S_x, S_y) spin states and the spin projection (axial or transverse) can be considered as a good quantum number. Optical transitions conserve the spin projection as the electric dipole operator does not involve spin. Thus with optical cycling there will be no change of the spin projections within the system and no spin polarization.

It is known that optical excitation results in pronounced spin polarization [10,18,19] of the ground state and the spin polarization is attributed to spin–orbit induced inter-

system crossing and an account of the process has been given in a recent publication [15]. Spin–orbit mixes singlets and triplets with the same symmetry and vibrational decay becomes allowed between the mixed states. The selection rules for this inter-system crossing can then be determined from symmetry and it has been shown that if there is a single 1A_1 intermediate state between the ground and excited triplet states as in Fig. 1a the allowed decay is consistent with populating the S_z spin level. The population decaying in this way is non-radiative. Once the system is spin polarized and occupying the S_z state the absorption strength will be the same but there will be no non-radiative component. Hence, the emission will increase with polarization [15]. The observed 14% increase in emission indicates the proportion of the excited population that decays non-radiatively and this is close to the fraction of 3E states for which inter-system crossing is allowed, i.e. 1 in 6 (see Fig. 1a). This implies that for this state, $A_1(^3E)$ triplet–singlet inter-system crossing is favored over the allowed triplet–triplet radiative decay to the ground state. The situation is modified slightly by strain as the state is mixed with a second hyperfine levels or with the involvement of a 1E state discussed below. Regardless the branching ratio for the triplet–singlet inter-system crossing compared to the direct decay is surprisingly large.

Due to the extra decay path the levels associated with the inter-system crossing will have a shorter lifetime than that associated with levels only involving radiative decay. The latter have a reported lifetime of 13 ns [20], and the faster rate would then have to be of the order of 7.5 ns. There are no reports of such lifetimes. The lack of a report of a short lifetime could be due to the fact that most measurements are made with the system spin polarized when there is no fast component. The fast component will only be present when the system is unpolarized and this will require measurements using very low repetition rate lasers (<10 Hz for room temperature measurements) or introduction of microwaves to destroy spin polarization. Should two components be observed it will be important to show the presence of fast components depending on spin polarization and, hence, confirm their origin as associated with inter-system crossing. Hanzana et al. [21] have reported two lifetimes (8 and 2 ns) but observations involved high repetition rate lasers and were not taken under conditions for which the fast component would be expected. It is clear, therefore, that situation regarding emission lifetimes merits further investigation.

Carbon (and nitrogen) has low atomic number and a small spin–orbit coupling parameter of 28 cm^{-1} . The inter-system crossing is, hence, expected to be weak but this is not what is indicated with the inter-system crossing from excited triplet to the singlet of the same order as the spin allowed transitions. The singlet to the triplet is likewise reasonably efficient as the associated lifetime is of the order of 300 ns as determined from emission recovery measurements [15]. The reason for these fast inter-system crossings are not understood. One possibility is that there are two

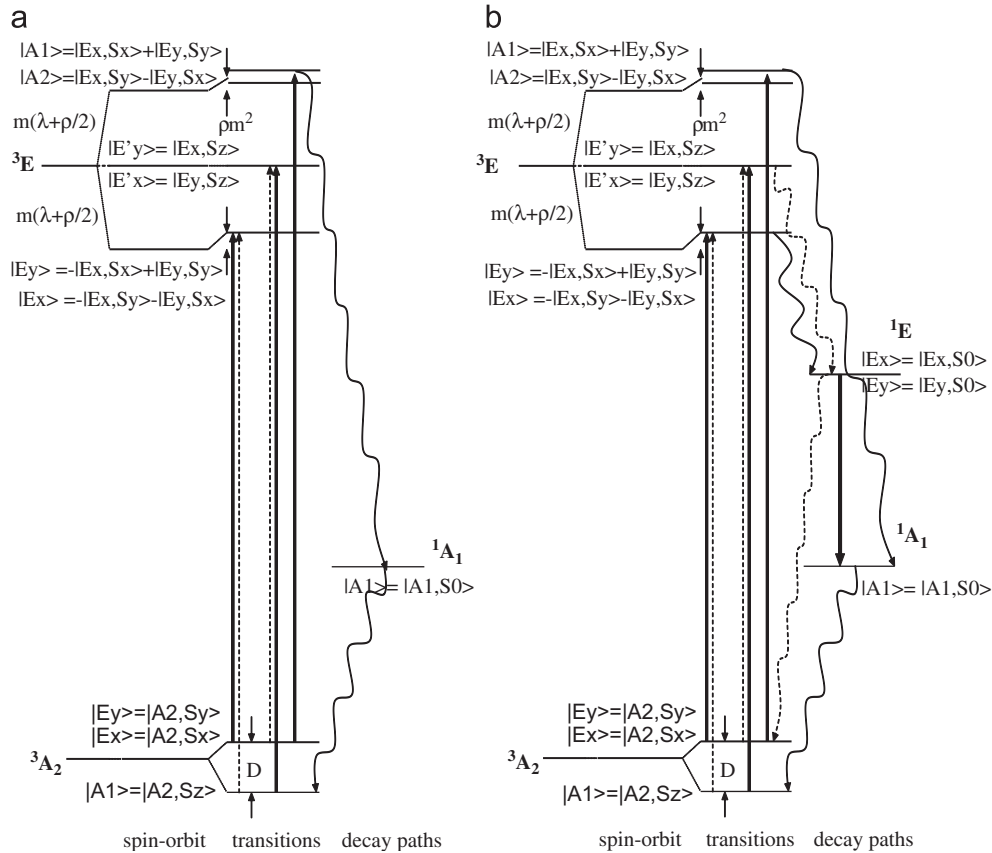


Fig. 1. Energy levels with (a) one intermediate singlet level 1A_1 and (b) with 1E and 1A_1 intermediate levels. The 3E splittings are due to spin-orbit and spin-spin terms given in text. D is the ground state splitting due to spin-spin interaction. Irreducible representation of states are indicated as well as symmetric form of wave functions. The symmetry allowed transitions are indicated by solid lines whereas the dashed lines become weakly allowed when the states E and E' are mixed by the non-axial spin-orbit interaction. The inter-system crossing is allowed through spin-orbit interaction. The dashed decay paths in (b) are weak and set to zero in the calculations.

intermediate singlet levels lying between the 3E excited and the 3A_2 ground state with one lying close to the 3E state and the other close in energy to the 3A_2 state. When energies are adjacent then there can be fast resonant transfer perhaps involving a phonon mode. A $^1E(e^2)$ singlet close to the $^3E(a, e)$ excited state and a $^1A_1(e^2)$ singlet close to the ground state as well as giving the possibility of fast inter-system crossing is consistent with the sign of the spin polarization. Fig. 1b, therefore, gives an encouraging energy level scheme.

The above energy level schemes requiring a 1A_1 to be the lowest intermediate level are inconsistent with calculation. From a local density theory model Goss et al. [22] has predicted a $^1E(e^2)$ state to be the lowest singlet. Should a $^1E(e^2)$ state lie lowest, the symmetry allowed relaxation to the ground state would populate the S_x, S_y spin projections and this is not what is observed [18]. Their calculation have given a $^1A_1(e^2)$ singlet 1000 cm^{-1} below the 3E excited state and the $^1E(e^2)$ state to be 3500 cm^{-1} above the ground state. This is the reverse order of that suggested in the last paragraph. Clearly this lack of correspondence is of significant concern and further studies will be necessary to obtain agreement.

In high intensity excitation experiments a drop in emission is obtained after 10 ns and is attributed to populating of a singlet level [15]. The population in the singlet can be appreciable and could give absorption to other singlet levels. No such induced absorption has been reported but such measurements would be useful in confirming their presence and be helpful in establishing the energies of the singlets. Should there be two well separated singlets then emission maybe observable in the infra-red. Associated with this there is the issue as to whether population in the singlet can be transferred thermally back to the triplet as has often been assumed [23]. Fast time resolved measurements at variable temperatures should be able to establish the situation.

3. 3E structure

Many of the problems of the N-V center are associated with a poor understanding of the 3E fine structure. Anticipating the structure involves establishing the parameters in the Hamiltonian. Few of the parameters are known with any degree of confidence but an estimate can be given to enabling us to obtain an indication of the 3E

fine structure. The temperature variation of the orbital Zeeman splitting suggests an axial spin–orbit splitting of 30 GHz [11,24]. However, this value is clearly over estimated as optical line widths of 15 GHz have been obtained [25] and the spin–orbit splittings have to be less than this line width. The spin–orbit splitting is, therefore, taken to be 5 GHz but clearly will require confirmation. The magnitude of the transverse spin–orbit interaction can be estimated as 0.2 GHz from state mixing obtained in two-laser hole burning experiments [25]. As Zeeman measurements [11] have given $\langle \|L_z\| \rangle = m = 0.2$, the above lead to the following parameters: $\lambda = 25$ GHz and $\langle \|L_{xy}\| \rangle = n = 0.008$.

Two-laser hole burning give additional information. The interpretation of the data indicates that when the orbital 3E state is split (even by the line width of 15 GHz) by strain the S_z spin states are lowest in each of the orbital branches [26,27]. This implies the presence of an additional interaction which displaces S_x, S_y levels relative to the S_z levels by the order of 2.5 GHz. This could arise from spin–spin interaction or with the interaction with a 1E singlet state. For example, 50 GHz interaction with a state 1000 GHz (330 cm^{-1}) lower in energy would give such a shift (clearly could also arise with a larger interaction and more distant

level). Neither this interaction nor spin–spin lifts the S_x, S_y degeneracy whereas these two spin levels are observed to be separated by the order of 0.7 GHz. The magnitude is too large to be associated with the above transverse spin–orbit interaction, but can arise from the interaction with a 1A and this is included in the following calculation.

With the above parameters the variation in the 3E energy levels as a function of strain are shown in Fig. 2a. In zero strain on the left the structure is dominated by the axial spin–orbit splitting with minor changes associated with the interaction with 1E and 1A_1 states given above. There will be allowed optical transitions from the 3A_2 ground state to each of the 3E levels but the spectrum associated with zero strain has not yet been observed. Strain splits the orbital state into two branches and leads to changes of the fine structure and the associated wave functions. There are changes with the S_x and S_y spin states but we are primarily concerned with their mixing with the S_z states. In the upper branch there is little such mixing and in Fig. 2b it is shown that it is a “pure S_z state” to within 0.3% at small values of strain. Transitions from the $S_z(^3A_2)$ spin projection of the ground state to this excited level $S_z(^3E_x)$ will be reasonably cyclic and will account for the observation of a cyclic transition and from Fig. 2b it can be seen to be maximum

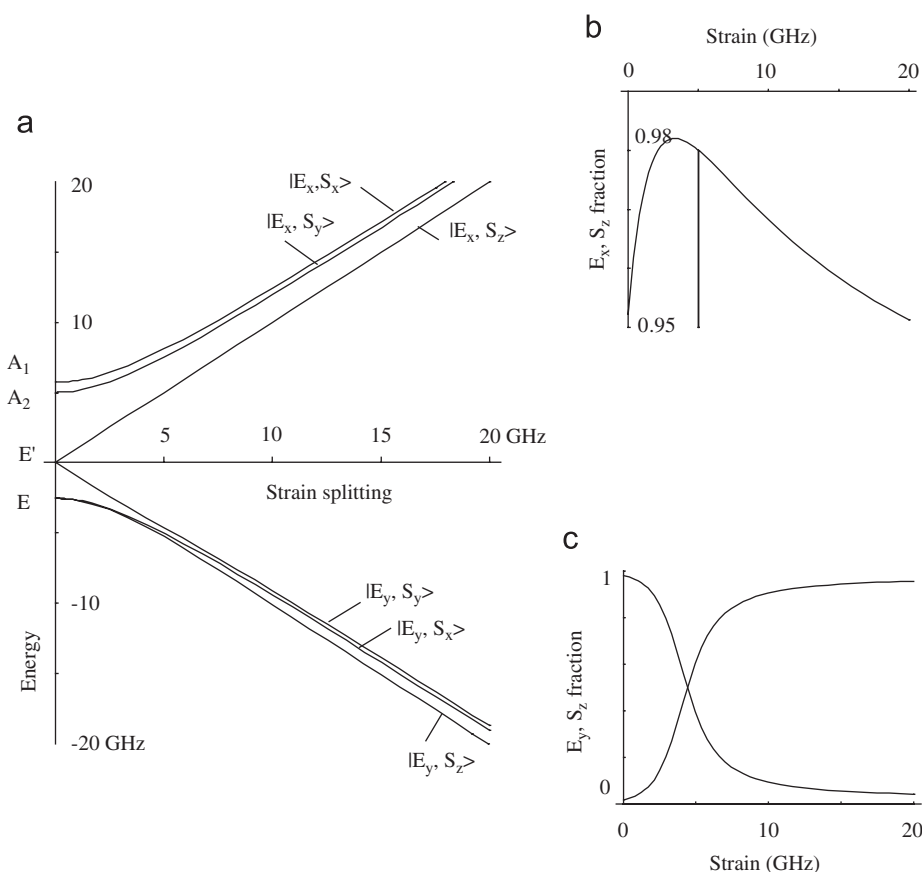


Fig. 2. (a) Energy of 3E fine structure levels as a function of strain where values have been given in text. The energy levels on the left for zero strain correspond to states given in Fig. 1. The strain considered is perpendicular to the trigonal axis but retains reflection symmetry. In the upper branch the three spin levels are well separated and there is negligible mixing of the state involving the S_z spin with any other spin state. This is shown in (b) where the fraction of S_z spin state is always greater than >0.98 . In the lower branch the S_z spin state crosses and totally mixes with the S_y state and the fraction of S_z in the two levels is indicated in (c).

with small strain splitting. This contrasts with the situation in the lower branch where the S_z and (S_x, S_y) spin levels approach and are strongly mixed (Fig. 2c). There will not be cyclic transitions in this case. In contrast there will be transitions giving rise to Λ schemes involving two-transitions to a common level. These Λ transitions in the lower orbital branch and the contrast between the upper and lower branches have been noted by Santouri et al. [25].

The parameters have been briefly justified and in this work are only taken as representative. However, the energy scheme in Fig. 2a accounts for many of the experimental trends some of which have been given above. Future work should be directed at obtaining measurements, preferably single site, of the variation of the spectrum with strain, with electric field or with magnetic field and this will allow a better determination of the parameters. Determination should include the values of axial and transverse spin–orbit interaction within the 3E state and between this state and the singlets. It is also desirable to justify the value of the interaction. For example the small value of the axial spin–orbit interaction indicated here is of concern as values closer to the spin–orbit value of 28 cm^{-1} for carbon might have been expected. Reduction in spin–orbit interaction and orbital Zeeman term is normally associated with Jahn–Teller interaction whereas the Jahn–Teller is taken from the early measurements of Davies and Hamer [7] to be small. Clearly there is an issue with the small value of the spin–orbit interaction.

Parameters for a single center are clearly site dependent and optical selection rules depend markedly on strain and which branch is involved. The values of the two branches will be averaged when operating at room temperature or when exciting within the vibronic band. Clearly for ensembles averaging will be over the distribution of strain as well as the two branches. However, the measurements of Santouri et al. [25] shows that this need not be the case as for an ensemble within a small volume the optical branches can be resolved. Thus it is possible to work with a single orbital branch and in this way select the more desirable parameters. An alternative approach is to use ensembles with high strain for which the stronger spin forbidden transitions are avoided (see Fig. 2b–c). These can be valuable considerations for some of the proposed applications of the center.

4. Center stability

Although we have been concerned with the intrinsic properties of the N–V center there are issues that are linked. For example, there is a concern regarding the situation of ionization [28–30]. The neutral N–V center has five electrons whereas the present center has six electrons and so it must obtain an additional electron from the lattice. It is not established under what conditions the center obtains the additional electron to become the stable ionization state. Also photo-ionization has been observed but it has not been established whether this is the case for all centers

and whether the process is linear or quadratic in excitation intensity. When the center is photo-ionized there is interest in the rate of recovery and whether the charge distribution about the center is also recovered. All of these issues will have effects on the behavior of the center and are important for applications.

There is further concern with the photon statistics of single sites. The statistics exhibit a bunching at high excitation intensities and a theoretical fit has only been obtained when including terms quadratic in laser excitation [31]. The origin of these quadratic effects have not been satisfactorily explained. It requires excitation to higher electronic levels or must involve photo-ionization. These are important issues particularly when using the center for quantum information processing.

5. Summary

In this paper we have introduced an electronic model to account for the fine structure of the excited state. The model has value as it provides a new understanding of many of the properties of the center. However, there are still outstanding issues and for the satisfactory adoption of the center in applications it is important these issues be resolved. Therefore, the paper also highlights some of the difficulties and suggests measurements that would be helpful. The hope is that this will stimulate further work directed at obtaining a complete understanding of the center.

Acknowledgments

The work has been supported by Australian Research Council and Defence Science and Technology Organization, by DARPA QuIST Grant through Texas Engineering Experimental Station and by STIC Grant in collaboration with University of Melbourne. The authors wish to thank Fedor Jelezko and Jorg Wrachtrup (University of Stuttgart) for useful discussions.

References

- [1] C. Kurtsiefer, S. Mayer, P. Zarda, H. Weinfurter, Phys. Rev. Lett. 85 (2000) 290.
- [2] R. Brouri, A. Beveratos, J.-P. Poizat, Philippe Grangier, Opt. Lett. 25 (2000) 1294;
A. Beveratos, S. Kuhn, R. Brouri, T. Gacoin, J.-P. Poizat, P. Grangier, Eur. Phys. J. D 18 (2002) 191;
A. Beveratos, R. Brouri, T. Gacoin, J.-P. Poizat, P. Grangier, Phys. Rev. A 64 (2002) 061802(R);
A. Beveratos, R. Brouri, T. Gacoin, A. Villing, J.-P. Poizat, P. Grangier, arXiv:Qant-ph/2061361v1.
- [3] J. Wrachtrup, S.Ya. Kilin, A.P. Nizovtsev, Opt. Spectrosc. 91 (2001) 429.
- [4] F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber, J. Wrachtrup, Phys. Rev. Lett. 93 (2004) 130501.
- [5] F. Jelezko, J. Wrachtrup, J. Phys. Condens. Matter 16 (2004) R1089.
- [6] J. Wrachtrup, F. Jelezko, J. Phys. Condens. Matter 18 (2005) S807.
- [7] G. Davies, M.F. Hamer, Proc. R. Soc. London A 348 (1976) 285.

- [8] S.Ya. Kilin, A.P. Nizovtsev, T.M. Maevskaya, A. Drabentstet, J. Wrachtrup, *J. Lumin.* 86 (2000) 201.
- [9] F. Jelezko, I. Popa, A. Gruber, C. Tietz, J. Wrachtrup, A. Nivovtsev, S. Kilin, *Appl. Phys. Lett.* 81 (2002) 2160.
- [10] J.H.H. Loubser, J.A. van Wyk, *Diamond Res.* 1 (1977) 11.
- [11] N.R.S. Reddy, N.B. Manson, C. Wei, *J. Lumin.* 38 (1987) 46.
- [12] E. van Oort, N.B. Manson, M. Glasbeek, *J. Phys. C* 21 (1988) 4385.
- [13] D.A. Redman, S. Brown, R.H. Sands, S.C. Rand, *Phys. Rev. Lett.* 67 (1991) 3420.
- [14] N.B. Manson, P.T.H. Fisk, X.-F. He, *Appl. Magn. Reson.* 3 (1992) 999.
- [15] N.B. Manson, J.P. Harrison, M.J. Sellars, *Phys. Rev. B* 74 (2006) 104303.
- [16] A. Greentree, P. Olivero, M. Draganski, E. Trajkov, J.R. Rabeau, P. Reichart, B.C. Gibson, S. Rubanov, S.T. Huntington, D.N. Jamieson, S. Prawer, *J. Phys. Condens. Matter* 18 (2006) S825.
- [17] A. Lenef, S.C. Rand, *Phys. Rev. B* 53 (1996) 13441.
- [18] J.P. Harrison, M.J. Sellars, N.B. Manson, *J. Lumin.* 107 (2004) 245.
- [19] J. Harrison, M.J. Sellars, N.B. Manson, *Diamond Rel. Mater.* 15 (2006) 586.
- [20] A.T. Collins, M.F. Thomaz, M.I.B. Jorge, *J. Phys. C* 16 (1983) 2177.
- [21] H. Hanzana, Y. Nisida, T. Kato, *Diamond Rel. Mater.* 6 (1997) 1595.
- [22] J.P. Goss, R. Jones, S.J. Breuer, P.R. Briddon, S. Oberg, *Phys. Rev. Lett.* 77 (1996) 3041.
- [23] A.P. Nizovtsev, S.Ya. Kilin, F. Jelezko, T. Gaebel, I. Popa, A. Gruber, J. Wrachtrup, *Opt. Spectrosc.* 99 (2005) 233.
- [24] I. Hiromitsu, J. Westra, M. Glasbeek, *Phys. Rev. B* 46 (1992) 10600.
- [25] C. Santori, D. Fattal, S.M. Spillane, M. Fiorentino, R.G. Beausoleil, A.D. Greentree, P. Olivero, M. Draganski, J.R. Rabeau, P. Reichart, B.C. Gibson, S. Rubanov, D.N. Jamison, S. Prawer, *arXiv:cond-mat/0602573*.
- [26] J.P.D. Martin, *J. Lumin.* 81 (1999) 237.
- [27] A.P. Nizovtsev, S.Ya. Kilin, F. Jelezko, I. Popa, A. Gruber, J. Wrachtrup, *Physica B* 340–342 (2003) 106.
- [28] Y. Dumeige, F. Treussart, R. Alléaume, T. Gacoin, J.-F. Roch, P. Grangier, *J. Lumin.* 109 (2004) 61.
- [29] N.B. Manson, J.P. Harrison, M.J. Sellars, *Diamond Rel. Mater.* 14 (2005) 1705.
- [30] T. Gaebel, M. Domhan, C. Wittmann, I. Popa, F. Jelezko, J. Rabeau, A. Greentree, S. Prawer, E. Trajkov, P.R. Hemmer, J. Wrachtrup, *Appl. Phys. B* 82 (2006) 243.
- [31] A. Beveratos, R. Brouri, J.-P. Poizat, P. Grangier, in: P. Tombesi (Ed.), *QCM-C 3 Proceedings*, Kluwer Academic Publishers, Dordrecht, MA, 2000, p. 261.