

Assignment of the NV⁰ 575-nm zero-phonon line in diamond to a ²E-²A₂ transition

N. B. Manson,^{1,*} K. Beha,² A. Batalov,² L. J. Rogers,¹ M. W. Doherty,¹ R. Bratschitsch,³ and A. Leitenstorfer²

¹*Laser Physics Center, RSPE, Australian National University, Canberra, ACT 0200, Australia*

²*Department of Physics and Center for Applied Photonics, University of Konstanz, D-78457 Konstanz, Germany*

³*Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany*

(Received 15 January 2013; revised manuscript received 21 March 2013; published 25 April 2013)

The time-averaged emission spectrum of single nitrogen-vacancy defects in diamond gives zero-phonon lines of both the negative charge state at 637 nm (1.945 eV) and the neutral charge state at 575 nm (2.156 eV). This occurs through photoconversion cycling between the two charge states. Due to strain in the diamond the zero-phonon lines of both charge states are split and it is found that the splitting and polarization of the two zero-phonon lines are the same. From this observation and consideration of the electronic structure of the nitrogen-vacancy center it is concluded that the excited state of the neutral center has A₂ orbital symmetry. The assignment of the 575-nm transition to a ²E-²A₂ transition has not been established previously.

DOI: [10.1103/PhysRevB.87.155209](https://doi.org/10.1103/PhysRevB.87.155209)

PACS number(s): 76.30.Mi, 42.62.Fi, 78.55.-m, 81.05.ug

The nitrogen-vacancy (NV) center has attracted much attention due to many applications as a single photon source,^{1,2} in quantum information processing,^{3–5} in magnetometry^{6,7} and in bio-labeling.^{8–10} The center can exist in a neutral (NV⁰) or a negative (NV⁻) charge state and there is interest in the electronic energy levels of both of these charge states. In the case of NV⁻, the levels and their symmetries are well established. However, the situation for NV⁰ is not so well advanced. Indeed, the orbital symmetry of the excited state, which gives rise to an orange emission with a zero-phonon line (ZPL) at 575 nm (2.156 eV), has not been conclusively established¹¹ and incorrect assumptions exist in the literature.^{12–14} In this work, the symmetry of this level is determined by the analysis of the stress splitting of the NV⁰ ZPL. The one-electron orbitals of the NV center are well known from the work on NV⁻ and here they are used to develop the multielectron orbitals of NV⁰ in order to account for the observed correlation between the stress splittings of the NV⁰ and NV⁻ optical ZPLs.

The NV center is formed in diamond containing singly substitutional nitrogen (N_s) by irradiating and annealing.¹⁵ The irradiation must have sufficient energy to create vacancies. The vacancies are mobile at temperatures above 600°C and become trapped by the nitrogen impurities to form NV pairs. There are five nonbonded electrons when the pair is in the neutral charge state; two from the nitrogen and three from the adjacent carbons. When there are donors in the diamond an extra electron may be acquired to form the negatively charged center with six electrons. Both neutral and negatively charged NV centers have a single allowed transition in the visible and the presence of these defect centers is usually established by the observation of a ZPL at 575 nm in the case of NV⁰ and at 637 nm in the case of NV⁻. Both lines are accompanied by vibrational sidebands of the order of 100 nm to higher energy in absorption and lower energy in emission.^{11,15} Excitation at the wavelength of the ZPL or the sideband can convert the center via a quadratic process to the alternate charge state. This is a well-established phenomenon for low nitrogen doped samples.^{16–18} When exciting a single center at a wavelength that coincides with the sidebands of both of the charge states, the one center is converted back and forth between the two

charge states at a rate dependent on excitation power (typically faster than milliseconds).¹⁶ The emission of both charge states of the single center are thus clearly observed in a time-averaged spectrum that is averaged over several seconds.¹⁷

In the present experiment, the emission of single centers (confirmed by photon autocorrelation measurements) in a low nitrogen doped sample (nitrogen concentration <5 ppb) is monitored during continuous excitation at 532 nm, which is a wavelength within the vibrational absorption sidebands of both NV⁻ and NV⁰. The optical emission of the single centers was detected in the range from 550 to 650 nm and averaged over 100 s using a low temperature (10 K) confocal microscope system that has been described previously.¹⁷ Figure 1 depicts three time-averaged spectra corresponding to three different single centers. It is clear that the ZPLs of the negative (~637 nm) and neutral (~575 nm) charge states are present in the spectra of each of the single centers.

The sample exhibits intrinsic strain introduced by the growth process and this results in the splitting of the ZPLs of both charge states. As the emission lines of a given spectrum are associated with a single center, the splittings of the ~575 nm and ~637 nm ZPLs are clearly associated with identical strains. While the splittings vary from center to center, it was found that for a single center, the splittings of the ZPLs of the two charge states are the same within the experimental resolution of 0.01 nm. This is illustrated for the three different centers in Fig. 1, where the splittings vary between centers in the vicinity of ~0.1 nm (0.3 meV), but for a given center, there is always correspondence in the splittings of the ZPLs of the two charge states. Importantly, this indicates that the effect of internal strain in the diamond is larger than that from any modification at the site due to the change of charge state.

The polarization of the zero-phonon emission was also measured. This involved the addition of a polarizer and a monochromator to our confocal microscope system. The polarizer was immediately in front of the monochromator and a rotatable half wave plate was used to select the polarization direction of the detected emission. The combination of the half wave plate and polarizer ensured the sensitivity was independent of angle. The result of a systematic rotation of the detected polarization direction is shown in Fig. 2. As indicated

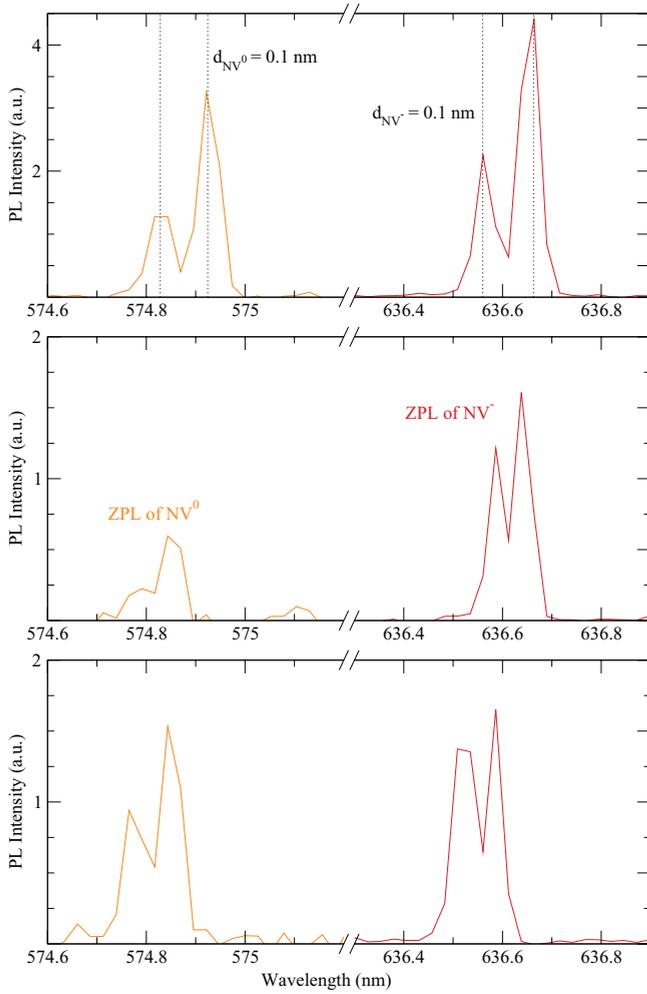


FIG. 1. (Color online) Emission spectra of single NV centers averaged over 100 s. In all cases there are ZPLs associated with NV^- at 635.6 nm (red) and NV^0 at 574.9 nm (orange). For a single site the splittings of the NV^- and NV^0 ZPLs are the same although the magnitude can vary from site to site.

by the figure, the lines are linearly polarized. The high energy ZPL components for each charge state have one polarization and the polarization of the low energy components are shifted

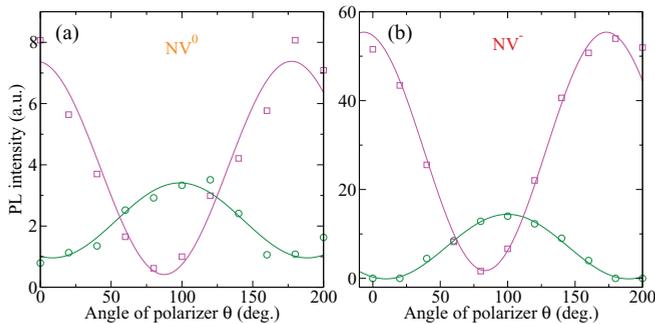


FIG. 2. (Color online) Polarization of NV ZPLs for single center shown in the upper figure of Fig. 1. Angle of polarizer for NV^0 is shown in left panel (a) and that of NV^- is shown in the right panel (b). Experimental data are given in magenta (high energy line) and green (low energy line). The lines are cosine fits to the data.

by $74^\circ \pm 2^\circ$. It is well known that for a transition between nondegenerate and degenerate levels at a site with axial symmetry, that transverse strain can lift the degeneracy and give two transitions with polarization directions that are parallel and perpendicular to the direction of the transverse strain. In the present geometry, the photoluminescence detection, and thus the polarization measurements, are for emission perpendicular to a $\langle 100 \rangle$ face, whereas the NV centers are trigonally aligned along $\langle 111 \rangle$ directions. An angle of observation inclined from the NV axis will introduce an apparent phase shift between the orthogonal polarizations of the two transitions. The direction of the local strain of the NV center can be determined from the phase shift. Indeed, Grazioso *et al.*¹⁹ have shown by measuring a number of adjacent NV^- centers (including ones with different orientations) that it is possible to determine the local strain field of the diamond lattice. This is not the purpose here. The significant observations are that all sites exhibit the ZPLs of both NV^0 and NV^- and that the ZPLs of both charge states are nearly identically split and have the same emission polarization.

The electronic structure of the NV center has been modeled by considering the one-electron symmetry adapted orbitals associated with the nitrogen and carbon atoms adjacent to the vacancy. The center's point symmetry is C_{3v} and there are four one-electron orbitals, two degenerate orbitals of E symmetry denoted by e_x and e_y and two orbitals of A_1 symmetry denoted by a_1 and a'_1 . The a'_1 orbital lies in the valence band, is always occupied, and can be neglected. Only the occupation of the a_1 and e orbitals in the band gap need be considered. The a_1 lies lower and separated from the e orbital by an energy ϵ . In the case of NV^- there are four electrons occupying the a_1 and e orbitals and, in order of increasing energy, they form the configurations $a_1^2 e^2$ ($^3A_2, ^1E, ^1A_1$), $a_1 e^3$ ($^3E, ^1E$), and e^4 (1A_1), which are to zero order in two-electron Coulomb repulsion are separated by increments of ϵ . The multielectron levels of the NV^- center are then readily determined and have been given in brackets. Considering first-order Coulomb repulsion corrections, Hund's rule gives the triplet to be the lowest energy level within the two lower energy configurations. Second-order Coulomb repulsion corrections shift only the two 1E and 1A_1 levels. The energy levels are then as indicated in Fig. 3.^{20,21} The electric dipole operator conserves spin and as the ground state has a spin $S = 1$ and there is only the one excited triplet level, the electric dipole allowed optical transition giving the ZPL at ~ 637 nm can be assigned to the $^3A_2(a_1^2 e^2) \rightarrow ^3E(a_1 e^3)$ transition.

For NV^0 three electrons occupy the one-electron orbitals and, in order of increasing energy, form the configurations (and levels) $a_1^2 e$ (2E), $a_1 e^2$ ($^4A_2, ^2A_2, ^2E$, and 2A_1), and e^3 (2E) (refer to Fig. 4). Considering first-order Coulomb repulsion corrections, within the intermediate configuration, Hund's rule determines that the quartet will have lower energy than the three doublets, but provides no information about the ordering of the doublets. There are also second-order Coulomb repulsion corrections between all of the 2E levels. As a consequence, the energy ordering of the doublets of the $a_1 e^2$ configuration cannot be readily determined. Determining their order is significant as the emitting level is likely to be the lowest state with the same spin as the ground state. The optical transition from the ground state to this level gives the ZPL at

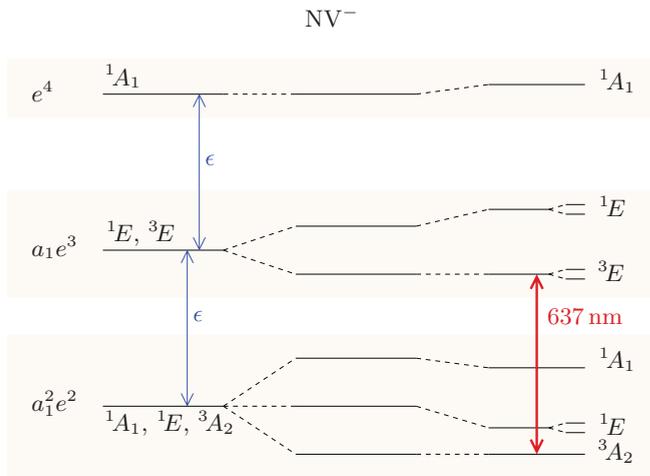


FIG. 3. (Color online) Energy levels of the lowest energy configurations of NV⁻. The diagram depicts configuration levels (left-hand side) and first-order (central) and second-order (right-hand side) corrections due to two-electron Coulomb repulsion. Splitting of the orbital E levels that can occur with strain are also indicated on the far right. The vertical arrow on the left-hand side denotes the difference in energy ϵ of the e and a_1 one-electron orbitals. The vertical arrow on the right indicates the spin-allowed optical transition from the ground state. The configurations are given in terms of four electrons. The two additional electrons in the valence band can be ignored.

~575 nm and from uniaxial stress measurements, this ZPL has been shown to correspond to a transition from an E ground state to an A excited state.¹¹ The uniaxial stress measurements,

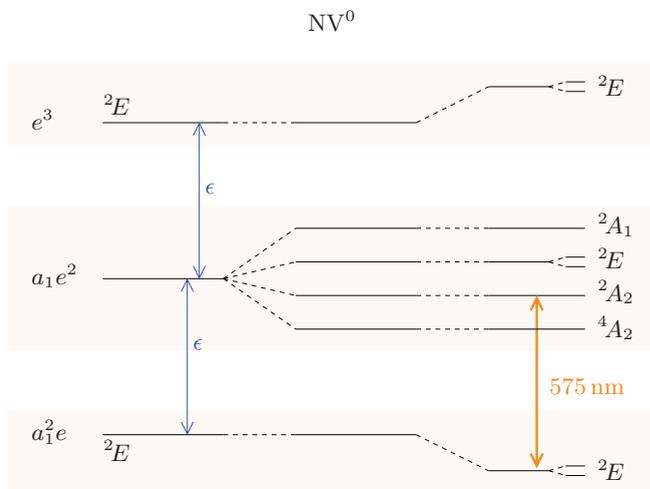


FIG. 4. (Color online) Energy levels of the lowest energy configurations of NV⁰. The diagram depicts configuration levels (left-hand side) and first-order (central) and second-order (right-hand side) corrections due to two-electron Coulomb repulsion. Splitting of the orbital E states that can occur with strain are also indicated on the far right. The vertical arrow on the left-hand side denotes the difference in energy ϵ of the e and a_1 one-electron orbitals. The vertical arrow on the right indicates the spin-allowed optical transition from the ground state. The configurations are given in terms of three electrons. The two additional electrons in the valence band can be ignored. Note that the ordering of the 2A_2 , 2E , and 2A_1 levels of the $a_1 e^2$ configuration are unknown without experimental investigation.

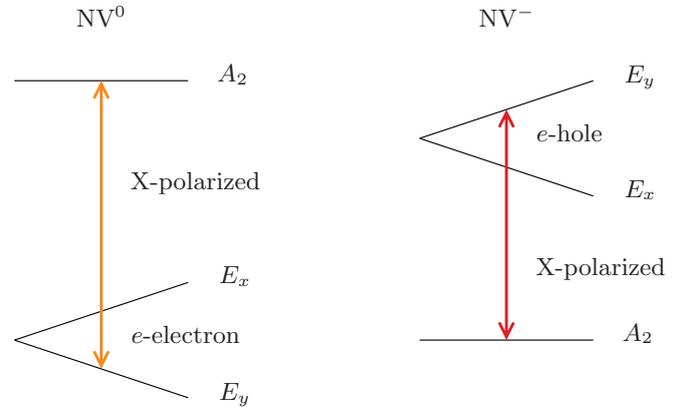


FIG. 5. (Color online) Summary of splitting due to stress for the ~575 nm NV⁰ and ~637 nm NV⁻ transitions. A transition with a common X polarization is shown and in both cases is displaced to higher energy. The transition to the E_x state is Y polarized and displaced to lower energy but, for clarity, is not shown.

however, cannot determine whether the nondegenerate state has A_1 or A_2 orbital symmetry.¹¹

The NV⁻ ZPL at ~637 nm is, therefore, definitely associated with an $^3A_2(a_1^2 e^2)-^3E(a_1 e^3)$ transition whereas the NV⁰ ZPL at ~575 nm may be associated with either a $^2E(a_1^2 e)-^2A_1(a_1 e^2)$ or $^2E(a_1^2 e)-^2A_2(a_1 e^2)$ transition. As there can be no splitting of the nondegenerate A levels, the strain splittings of the ZPLs must arise from splittings of the degenerate E levels.^{11,15} From the electronic model of the NV center, the splitting of the multielectron levels will arise from the splitting of the one-electron e orbitals. In the case of NV⁰, the splitting is in the lower $^2E(a_1^2 e)$ level, where a single electron occupies the e orbitals, whereas for NV⁻, the splitting is in the excited $^3E(a_1 e^3)$ level, where three electrons occupy the e orbitals. As four e orbital electrons (e^4) is a full shell, the latter may be considered as an e orbital hole. The situation can therefore then be summarized as in Fig. 5, with splitting of an e electron in the 2E ground state of NV⁰ and e hole in the excited 3E level of NV⁻. Clearly the splitting of a hole will be the reverse of, but equal to, that of an electron due to the charges being opposite in sign. This is analogous to the change of sign of the Zeeman splitting between an electron and a hole. The change of sign is indicated in Fig. 5 and further justified below.

For a strain along a direction X (perpendicular to center axis Z but not necessarily a symmetry direction), the one-electron e_x orbital is shifted up in energy and the e_y orbital is shifted down, resulting in a splitting of the e orbitals. Using the conclusions of the previous paragraph, this implies that the NV⁰ ground 2E (equivalent to an e electron) level is split such that the 2E_x state is shifted up and the 2E_y state is shifted down. The converse is true for the excited 3E level of NV⁻ (equivalent to an e hole), where the 3E_y state is shifted up and the 3E_x state is shifted down. Considering C_{3v} symmetry selection rules for an electric dipole transition, an A_2-E_x transition is Y polarized (orthogonal to X and Z) and an A_2-E_y transition is X polarized.^{11,15} These selection rules define the polarizations of the transitions and are depicted in Fig. 5. Since the splittings of the 2E (NV⁰) and 3E (NV⁻) levels are equal and opposite, but they occur in ground and excited levels of

the optical transitions, respectively, it is evident that the ZPLs of NV^0 and NV^- will be split by approximately the same energy and that the higher energy components of the NV^0 and NV^- ZPLs will be both X polarized and the lower energy components will be both Y polarized. This result matches experimental observation. Should the excited state of NV^0 be 2A_1 , as sometimes suggested, the polarization of the high and low energy components of the NV^0 and NV^- ZPL would each differ. This is not the case and clearly the observations prove that the emitting level of the NV^0 has A_2 orbital symmetry.

To summarize our argument for the assignment of the NV^0 ZPL to a 2E - 2A_2 transition, we first established using single centers that the ZPLs of NV^0 and NV^- have nearly identical strain splittings and that the polarizations of the split ZPLs are the same. Since the strain at a single center is approximately independent of the center's charge state, the nearly identical strain splittings of the ZPLs are clearly consequences of a correlation between the 2E and 3E electronic levels of NV^0 and NV^- , respectively. Applying the electronic model of the center, we established that the correlation is the common role of the strain splitting of the e orbital level, which is occupied by a hole in NV^- and an electron in NV^0 . Critically, this differing hole/electron occupation of the e orbital level does not affect the magnitude of the strain splitting, but it does imply that the E_x and E_y orbital sublevels of the 2E and 3E electronic levels of NV^0 and NV^- , respectively, are energetically shifted in different directions. Accounting for the final difference that the 3E level is the emitting level of NV^- , while the 2E level is the ground level of NV^0 , selection rules imply that the strain split ZPLs of NV^0 and NV^- can only have identical polarizations if the other levels involved in the transitions have identical orbital symmetry. Hence, since the orbital symmetry of the ground level of NV^- is known to be 3A_2 , the emitting level of NV^0 must be 2A_2 .

Stress measurements by themselves cannot distinguish between A_1 - E and A_2 - E transitions and this has been made very clear by Davies in his discussion of the results of uniaxial studies of NV^- ¹⁵ and NV^0 .¹¹ In the case of NV^- the uniaxial stress indicated that the ground state had orbital A symmetry¹⁵ but the 3A_2 assignment can only be made once the ground state has been identified to have $S = 1$ and modeling indicated that there is only one spin triplet in the ground configuration. It is a similar situation here for NV^0 , in that the 2A_2 assignment is required to give consistency between the electronic modeling of NV^0 and the model that is now established for NV^- .

The latter A_2 assignment could in principle be deduced from the uniaxial stress studies of the ~ 637 nm¹⁵ and ~ 575 nm¹¹ ZPLs involving ensembles and applied stress of several GPa. Certainly the magnitudes of the splitting parameters as a function of stress are better determined using controlled external stress and can provide extra information about the shift of levels involving both initial and final states. The importance of using single site measurements is that there can be no uncer-

tainty about the strain conditions and unquestionably the observed splitting and polarization are for identical strain fields. The equivalence of the splittings for the NV^- and NV^0 ZPLs in the single site measurements such as in Fig. 1 is striking.

The lowest excited doublet and emitting level of NV^0 is frequently discussed in terms of being 2A_1 rather than 2A_2 . The source of this erroneous discussion has been misreadings of Davies original work on NV^0 ,¹¹ where for the convenience of analyzing the Jahn-Teller effect in the 2E ground state of NV^0 , Davies assumes that the emitting level is an 2A_1 level. Those who have read this work and concluded that the emitting level is an 2A_1 level have likely missed Davies' statements that his observations and analysis cannot distinguish 2A_1 or 2A_2 emitting levels.

This misidentification of the emitting level of NV^0 present in the literature is often of little consequence. However, the misidentification does give difficulty in accounting for the population of the low lying quartet 4A_2 observed in electron paramagnetic resonance when the NV^0 center is optically excited.²² There is strong evidence that the quartet is populated from the emitting level at 2.156 eV, but there is no spin-orbit mixing between the 2A_2 and 4A_2 levels (as they both have A_2 orbital symmetry) and so the decay of population from 2A_2 to 4A_2 cannot arise from a conventional intersystem crossing. The details of the 2A_2 - 4A_2 intersystem crossing evidently require further investigation. Clearly it is important to allow for an 2A_2 level when calculating energy levels and it is noted that the presence of an 2A_2 can be overlooked.¹²⁻¹⁴ There is only the one calculation of Zyubin *et al.*²³ that indicates the lowest energy excited doublet is an 2A_2 . When allowing for the vibronic band their energy of 2.4 eV is in good correspondence with the experiment. The correspondence in the magnitude of the splittings observed for NV^0 and NV^- is surprising since the charge states have different numbers of electrons and therefore different electron configurations. Additionally, some redistribution of the local environment of the center is expected to occur in the photoconversion process between charge states. However, the observed correlations of the ZPLs of the charge states provides an ideal situation for comparison with theoretical calculations, as demonstrated here.

In short, the correlated energy splittings and polarizations of the NV^- and NV^0 optical ZPLs observed in the spectrum of a single NV color center in diamond is quite striking and, as shown here, imply that both transitions occur between levels of A_2 and E orbital symmetry. This leads to the first firm assignment of the 2A_2 level to the lowest energy doublet and optically emitting level of NV^0 .

The work was partly supported by Australian Research Council Grant No. DP12010223. Support from the Deutsche Forschungsgemeinschaft (FOR 1493) is gratefully acknowledged.

*neil.manson@anu.edu.au

¹C. Kurtziefer, S. Mayer, P. Zarda, and H. Weinfurter, *Phys. Rev. Lett.* **85**, 290 (2000).

²I. Aharonovich, S. Castelletto, D. A. Simpson, C.-H. Su, A. D. Greentree, and S. Praver, *Rep. Prog. Phys.* **74**, 076501 (2011).

³P. Neumann, J. Beck, M. Steiner, F. Rempp, H. Fedder, P. R. Hemmer, J. Wrachtrup, and F. Jelezko, *Science* **329**, 542 (2010).

⁴E. Togan, Y. Chu, A. S. Trifonov, J. Liang, J. Maze, L. Childress, M. V. G. Dutt, A. S. Sorensen, P. R. Hemmer, A. S. Zibrov, and M. D. Lukin, *Nature (London)* **466**, 730 (2010).

- ⁵L. Robledo, L. Childress, H. Bernien, B. Hensen, P. F. A. Alkemade, and R. Hanson, *Nature (London)* **477**, 574 (2011).
- ⁶G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, S. Chin, C. Kim, A. Wojcik, P. R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschitsch, F. Jelezko, and J. Wrachtrup, *Nature (London)* **455**, 648 (2008).
- ⁷J. R. Maze, P. L. Stanwix, J. S. Hodges, S. Hong, J. M. Taylor, P. Cappellaro, L. Jiang, M. V. G. Dutt, E. Togan, A. S. Zibrov, A. Yacoby, A. L. Walsworth, and M. D. Lukin, *Nature (London)* **455**, 644 (2008).
- ⁸K. Y. Han, S. K. Kim, C. Eggeling, and S. W. Hell, *Nano Lett.* **10**, 3199 (2010).
- ⁹J. Tisler, R. Reuter, A. Lammile, F. Jelezko, G. Balasubramanian, P. R. Hemmer, F. Reinhard, and J. Wrachtrup, *ACS Nano* **5**, 7893 (2011).
- ¹⁰L. P. McGuinness, Y. Yan, A. Stacey, D. A. Simpson, T. Hall, D. Maclaurin, S. Prawer, P. Mulvaney, J. Wrachtrup, F. Caruso, R. E. Scholten, and L. C. L. Hollenberg, *Nature Nanotechnology* **6**, 358 (2011).
- ¹¹G. Davies, *J. Phys. C: Sol. St. Phys.* **12**, 2551 (1979).
- ¹²J. P. Goss, R. Jones, P. R. Briddon, G. Davies, A. T. Collins, A. Mainwood, J. A. van Wyk, J. M. Baker, M. E. Newton, A. M. Stoneham, and S. C. Lawson, *Phys. Rev. B* **56**, 16031 (1997).
- ¹³A. Gali, *Phys. Rev. B* **79**, 235210 (2009).
- ¹⁴A. Ranjbar, M. Babamoradi, M. HeidariSaani, M. A. Vesaghi, K. Esfarjani, and Y. Kawazoe, *Phys. Rev. B* **84**, 165212 (2011).
- ¹⁵G. Davies and M. F. Hamer, *Proc. Roy. Soc. Lond. A* **348**, 285 (1976).
- ¹⁶G. Waldherr, J. Beck, M. Steiner, P. Neumann, A. Gali, Th. Frauenheim, F. Jelezko, and J. Wrachtrup, *Phys. Rev. Lett.* **106**, 157601 (2011).
- ¹⁷K. Beha, A. Batalov, N. B. Manson, R. Bratschitsch, and A. Leitenstorfer, *Phys. Rev. Lett.* **109**, 097404 (2012).
- ¹⁸N. Aslam, G. Waldherr, P. Neumann, F. Jelezko, and J. Wrachtrup, [arXiv:1209.0268](https://arxiv.org/abs/1209.0268); *New Journal of Physics*, February (2013).
- ¹⁹F. Grazioso, B. R. Patton, P. Delaney, M. L. Markham, D. J. Twitchen, and J. M. Smith, [arXiv:cond-mat/1110.3658](https://arxiv.org/abs/cond-mat/1110.3658).
- ²⁰M. W. Doherty, N. B. Manson, P. Delaney, and L. C. L. Hollenberg, *New J. Phys.* **13**, 025019 (2011).
- ²¹J. R. Maze, A. Gali, E. Togan, Y. Chu, A. Trifonov, E. Kaxiras, and M. D. Lukin, *New J. Phys.* **13**, 025025 (2011).
- ²²S. Felton, A. M. Edmonds, M. E. Newton, P. M. Martineau, D. Fisher, and D. J. Twitchen, *Phys. Rev. B* **77**, 081201(R) (2008).
- ²³A. S. Zyubin, A. M. Mebel, M. Hayashi, H. C. Chang, and S. H. Lin, *J. Comput. Chem.* **30**, 119 (2009).