Comment on ''Electronic structure of the N-*V* center in diamond: Theory''

J. P. Goss and R. Jones
Department of Physics, Stocker Road, University of Exeter, Exeter, Devon EX4 4QL, United Kingdom

P. R. Briddon
Department of Physics, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, United Kingdom

G. Davies, A. T. Collins, and A. Mainwood
Physics Department, King's College London, Strand, London WC2R 2LS, United Kingdom

J. A. van Wyk
Department of Physics, University of Witwatersrand, Johannesburg, South Africa

J. M. Baker and M. E. Newton
Department of Physics, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom

A. M. Stoneham
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

S. C. Lawson
DTC Research Centre, Belmont Road, Maindenhead, Berks SL6 6JW, United Kingdom

(Received 16 August 1996)

It is argued that the model advanced by Lenef and Rand [Phys. Rev. B **53**, 13 441 (1996)] for the nitrogen-vacancy center in diamond, exhibiting the 1.945-eV luminescence is incorrect. Lenef and Rand argue that the electronic ground state consists of two electrons occupying a_1 states localized on N and C, respectively, and are decoupled from the other three electrons occupying gap states. This model is inconsistent with experiments and other theoretical works. The existence of a Jahn-Teller state 46 cm^{-1} above the excited state of the defect is also in conflict with previous experiments. [S0163-1829(97)02147-4]

Recently, Lenef and Rand (LR) [Phys. Rev. B, **53** 13 441 (1996)] have analyzed the electronic structure of the 1.945-eV nitrogen-vacancy [N-*V*] optical defect in diamond with a simple molecular-orbital prescription. They argued that the five electrons associated with N and the three C radicals fall into two noninteracting groups containing two and three electrons, and (a) the group of three electrons does not participate in the magnetic or optical properties of the trigonal defect; (b) the $S=1$ ground state associated with the ground state of the transition arises from the two-electron configuration $u^{\uparrow}v^{\uparrow}$ of the *neutral* N-*V* center, where the u and v are orbitals with a_1 symmetry localized on N and C, respectively; (c) the optical excited state arises from the promotion of the electron in the v orbital to an empty e level. The transition (in absorption) is then $^3A_1 \rightarrow {}^3E$; and (d) the 46-cm^{-1} splitting in the excited ^3E state is due to a Jahn-Teller (J-T) effect and there are smaller splittings attributed to strain and spin-spin coupling.

We believe that this model is inconsistent with the general understanding of vacancy-related centers and with a number of theoretical and experimental studies and can be refuted. We argue that the 1.945-eV optical center is $[\text{N-}V]^-$, whose composition was originally suggested by Davies and Hamer[1] and charge state by Loubser and van Wyk.[2]

(1) Our understanding of vacancy-derived defects in diamond and silicon comes from occupation and splittings of the a_1 and t_2 levels arising from the four C or Si radicals.[3] This has led to a successful description of vacancy-defect states in a great many cases. For example, the J-T effects arising from the $a_1^2 t_2^2$ configuration of the neutral vacancy explains both qualitatively and semiquantitatively the properties of the GR1 center,[3] whereas the $S=3/2$ state of V^- naturally arises from the configuration $a_1^2 t_2^{\uparrow\uparrow\uparrow}$.[4] This model requires that the neutral *V*-N defect contains five electrons in a configuration derived from levels of the vacancy.

(2) The trigonal symmetry caused by N in the N-*V* defect splits t_2 level into a N-related a_1 level lying beneath the C-related e level with a single electron in the latter. This defect with $S=1/2$, as noted by LR, could not explain the $S=1$ ground state associated with the 1.945-eV transition. However, $[\text{N-}V]^-$ in the configuration $e^{\uparrow\uparrow}$ has a $^3A_2$ ground state (confirmed by *ab initio* calculations[5]) that is again consistent with magnetic resonance experiments.[2,6] The $[\text{N-}V]^-$ model associates the 1.945-eV transition in absorption with the promotion of an electron from the a_1 to e level leading to a $^3A_2 \rightarrow {}^3E$ transition consistent with uniaxial stress data.[1] Hence the final state has exactly the same symmetry as considered by LR although the ground state is $^3A_2$ rather than $^3A_1$. Their difference lies in whether the final state has an e level containing a single hole or a single electron and it is necessary for the photon-echo experiment[7] to distinguish these.

(3) It is known from magnetic resonance experiments[6,2] that the ground state has very little spin density at and near the N nucleus. The isotropic and anisotropic hyperfine data indicate less than 0.2% spin density on N. The value of the quadrupole coupling constant also implies very weak localization on the N atom.[8] All this is consistent with the partially occupied e levels arising from the three C radicals having little overlap with N. On the other hand, the LR model requires a single occupancy of the a_1 orbital related to N and the implied N hyperfine and quadrupole interactions conflict with experiment.

(4) Further support for the $[\text{N-}V]^-$ model comes from recent observations[9] on heavily irradiated diamonds, which have been interpreted in terms of a conversion of $[\text{N-}V]^-$ defects into neutral N-V ones with a consequent drop in the intensity of the 1.945-eV transition in favor of a 2.156-eV optical line due to an $^2E \rightarrow {}^2A_2$ transition. This transition is entirely consistent[10] with the excitation of the neutral N-V center as in $a_1^{\uparrow\downarrow} e^{\uparrow} \rightarrow a_1^{\downarrow} e^{\uparrow\uparrow}$.

(5) LR rule out the assignment to the charged $[\text{N-}V]^-$ defect by referencing an earlier study,[11] which they claimed showed that annealing irradiated type Ib diamonds at 1500 °C led to the diffusion of substitutional N atoms to stable N-V defects resulting in the creation of H3 centers. This is a misunderstanding of this work, which suggested instead that N-V diffuses to N, and we cannot understand how this could exclude the possibility that the 1.945-eV center is $[\text{N-}V]^-$.

(6) There is no evidence from uniaxial stress measurements on the 1.945-eV optical line for a J-T derived state 46 cm^{-1} above the excited state. Indeed, the stress studies of Davies and Hamer[1] show splittings of the 1.945-eV line that are linear in the applied stress and perturbations of up to 100 cm^{-1} were recorded. The existence of an A vibronic state only 46 cm^{-1} above the E state would have been detected in a gross nonlinearity in the shift rates of components observed in the [001] or [110] stress directions (depending on the A_1 or A_2 character of the A state). Transitions involving the A vibronic level would also be induced by the interaction, increasing from zero intensity at zero stress to becoming equal in intensity to the zero-phonon component at the stresses used in the experiment. Furthermore, the mirror image of the absorption and luminescence band shapes confirm the unimportance of J-T effects. This must cast doubt on the interpretation of the photon-echo experiment.[7]

(7) LR incorrectly state that Davies and Hamer[1] dismissed the possibility of a J-T effect. In fact, Ref. 1 reported stress-induced dichroism in the luminescence bands, which allowed them to estimate that *no more than 10%* of the vibronic coupling was caused by a J-T effect. In this measurement, they made a small correction for the depolarization effects caused by random stresses in the crystal.

To summarize, the LR model is wholly inconsistent with the hyperfine data discussed above (3), the effects of further irradiation (4), and previous results on the absence of important J-T effects (6). On the other hand, the $[\text{N-}V]^-$ model is consistent with *all* the experiments and theoretical calculations performed to date. In conclusion, we see no reason why the assignment of the 1.945-eV optical transition to $[\text{N-}V]^-$ should be modified in the light of the photon-echo experiments, even less for believing in a two-electron model of the defect, and in the existence of a J-T state 46 cm^{-1} above the E excited state.

[1] G. Davies and M. F. Hamer, Proc. R. Soc. London, Ser. A **348**, 285 (1976).

[2] J. H. N. Loubser and J. A. van Wyk, *Diamond Research* (Industrial Diamond Information Bureau, London, 1977), Vol. 77, p. 11.

[3] A. M. Stoneham, *Defects in Solids* (Oxford University Press, London, 1975).

[4] S. J. Breuer and P. R. Briddon, Phys. Rev. B **51**, 6984 (1995).

[5] J. Goss, R. Jones, S. J. Breuer, P. R. Briddon, and S. Öberg, Phys. Rev. Lett. **77**, 3041 (1996).

[6] X.-F. He, N. B. Manson, and P. T. H. Fisk, Phys. Rev. B **47**, 8816 (1993).

[7] A. Lenef, S. W. Brown, D. A. Redman, S. C. Rand, J. Shigley, and E. Fritsch, Phys. Rev. B **53**, 13 427 (1996).

[8] O. D. Tucker, M. E. Newton, and J. M. Baker, Phys. Rev. B **50**, 15 586 (1994).

[9] Y. Mita, Phys. Rev. B **53**, 11 360 (1996).

[10] G. Davies, J. Phys. C **12**, 2551 (1979).

[11] T. Collins, J. Phys. C **13**, 2641 (1980).