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

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We present insights into the electronic structure and relaxation of N-*V* color centers in diamond which support the contention that Jahn-Teller effects may play a very significant role in the excited *E* state. We also consider several opposing arguments, but show that the unusual relaxation behavior of the N-*V* center can mask common signatures of the Jahn-Teller effect, and that it remains a strong candidate for the dominant interaction determining excited-state splittings. [S0163-1829(97)05748-2]

In their Comment, Goss and co-workers[1] have correctly pointed out that the six-electron nitrogen-vacancy [N-*V*] model proposed by Loubser and van Wyk[2] for the 1.945-eV center in diamond is consistent with many previous experiments. They doubt that electronic properties of this center could result from a Jahn-Teller (J-T) effect in the excited *E* state or that the center could be of neutral charge, possibilities (among others) considered in our recent paper.[3] In this Reply we respond to their critique and expand on possible alternatives discussed in our publication.[3] In particular, we point out what we view as shortcomings of the Loubser–van Wyk (LVW) theory in relation to experiments published by several groups, we explain why (on experimental grounds) a standard indicator for the presence of J-T effects may fail in the N-*V* center, we discuss the question of the charge state of the defect further, and we make specific suggestions for future theoretical work on this intriguing center.

Firstly, it is generally conceded that two unpaired electrons are responsible for the measured properties of the N-*V* center. Models developed in our paper follow LVW theory in this regard, although they are based on different total numbers of defect electrons. The issues raised by Goss and coworkers relate exclusively to the origin of the two unpaired electrons, the overall charge state of the center, and whether a strong J-T effect is present. And indeed, were it not for recent measurements discussed below, there would be little motivation to reconsider the theory. It has been argued[4] that the negatively charged LVW model already fits a trend for several diamond centers.

Regrettably, however, calculations based on the LVW model with spin-orbit and strain, but negligible Jahn-Teller interactions do not simultaneously predict the existence of an electronic state 46 cm^{-1} above the excited *E* state of the 1.945-eV transition[6] together with wavelength-independent spin splittings. Yet the large splitting and the wavelength-independent spin splittings are well documented in numerous hole-burning,[6–8] double-resonance,[9] and photon-echo experiments.[5] A $\sim$40-cm^{-1} splitting in the excited *E* state was first inferred from microwave double-resonance experiments[9] and ascribed to orbital splitting. However, if spin-orbit interactions are not quenched in any of the existing models, then the introduction of strain in concert with spin-orbit interaction leads to spin splittings which are strongly wavelength-dependent, in contradiction to the experimental results.[5] Conversely, quenching is a strong indicator of Jahn-Teller distortions.[10] Our calculations showed that a six-electron model which included only spin-orbit, strain, and spin-spin interactions resulted in an energy-level term diagram incompatible with experimental hole burning and four-wave mixing determinations of transitions between levels. (An exception in the extremely high strain limit[7] was addressed in our paper[3].) It was also decidedly unexpected that the prevailing LVW model predicted only a single spin-spin splitting in the lowest of two groups of excited states in the ^3E manifold, whereas experiments clearly revealed two. Interested readers can make a careful comparison of Fig. 4 of Ref. 3 (theory) and Fig. 14 of Ref. 5 (experiment). On the other hand, the observed excited-state structure was at least consistent with calculations including a Jahn-Teller interaction in the *E* electronic state. In our work, we therefore turned to alternative interactions seeking avenues for improved agreement.

We considered only three plausible models: $[\text{N-}V]^+$, $[\text{N-}V]^0$, and $[\text{N-}V]^-$ which contained four, five, and six electrons, respectively. Of these models, only the $[\text{N-}V]^-$ yielded the correct ground-state symmetry directly. On this basis the $[\text{N-}V]^+$ model was discarded. For the $[\text{N-}V]^0$ model, however, we found that if three carbon electrons were passivated by some means, the remaining two nitrogen electrons yielded a ^3A ground state also, as required. Consequently, more refined calculations were done with only the $[\text{N-}V]^0$ and $[\text{N-}V]^-$ models. The $[\text{N-}V]^0$ model (the $n=2$ model of Lenef and Rand[3]) fared no better in predicting observed excited-state structure on the basis of spin-orbit and spin-spin calculations than the $[\text{N-}V]^-$ model. However, it had some analytic merit in that it yielded two-electron wave functions simple enough to examine matrix elements of new excited-state interactions for clues as to the origin of the unexplained GHz splittings, as well as the larger overall splitting of the ^3E state by 46 cm^{-1}.

Neither of the models we considered reproduced the observed fine structure when only spin-orbit, spin-spin, or random strain interactions were taken into account. Yet a Jahn-Teller effect strong enough to quench the spin-orbit interaction could easily account for the excited-state splittings, earlier discussions of J-T effects notwithstanding.

Strong coupling of the E electronic state to a vibrational model could explain the ultrafast dephasing of the blue-shifted component of the ZPL transition,[5] as well as the absence of a vibrational E-mode feature in absorption, which is not uncommon in itself.[11] At the same time, fast population decay of the upper to the lower ZPL component would be expected to mask ''normal'' effects of Jahn-Teller coupling in emission. Only emission from the lower component of the excited state would be observed, in view of the extremely rapid, nonradiative relaxation of the upper component.[5] Subsequently, even if the lower component of the ZPL were vibrationally coupled to the lattice, ultrafast dephasing would flatten any vibrational feature in the emission spectrum, resulting in perfect mirror symmetry more typically taken as a signature of the *absence* of J-T effects.[11] The temperature dependence of dephasing of the blue component should follow a T^3 dependence in the presence of J-T coupling, and a dependence consistent with this was indeed observed experimentally.

Although Goss and co-workers offer no explanation for the ^3E-state splitting, they argue that if there were a significant J-T effect in the E state of the N-V center, the presence of an A vibronic state 46 cm^{-1} above the E state as depicted in our model should have caused an avoided crossing and an inflection of the E-state curve in uniaxial strain measurements reported previously.[12] This is an interesting point. However, the raw data in Ref. 12 do show small deviations from linearity which may simply correspond to an unexpectedly small reduced matrix element $\langle A \| V_E \| E \rangle$ in the presence of a strong J-T effect. This situation can arise when the phonon coupling experienced by the A and E states is very different. The observed dephasing time is much shorter for the vibronic A than the E. Hence only experiments performed on a time scale less than the coherence time (as in Ref. 6) reflect pure A-E coupling and retain any coherent cross-coupling terms.

It is interesting to estimate the J-T energy for the N-V center by assuming that the model which couples to the excited state is at the dominant phonon energy 63 meV ($\omega_E \sim 500\ \mathrm{cm}^{-1}$).[12] Combining this with a rough value of strain parameter $V_1 \sim 15\,000\ \mathrm{cm}^{-1}$ unit strain[13] in the trigonal plane bounded by the C nuclei to estimate the linear electron-phonon coupling for the E mode, one finds a J-T energy of $V_1^2/2M\omega_E^2 \sim 600\ \mathrm{cm}^{-1}$. This value is higher than the dominant phonon energy. Consequently, the lowest-energy vibronic states should at least be radially confined at low temperatures in the vibronic adiabatic potential. This is precisely the strong-coupling regime described in our paper, in which a tunneling model with a second-order warping potential is appropriate to describe the A-E vibronic-state splitting.[14] Hence the J-T effect remains a strong candidate for explaining the ^3E-state splitting, in our opinion.

After publication of our theory, research by Mita[15] provided experimental evidence for the first time that the N-V center may be negatively charged. If Mita's analysis is correct, our picture of a five-electron model producing spin one from a total of five electrons by passivation of three carbon spins would be erroneous. That is, the two active electrons in the N-V center would then have to originate from a total of six defect electrons, in close agreement with the conclusions of He and co-workers based on elegant hyperfine interaction measurements.[16] On the other hand, whether the center is neutral or negative, the difficulty of explaining the zero-field splitting patterns with transitions of the two unpaired electrons *would remain*. Our position is that detailed calculations of excited-state interactions, including especially the Jahn-Teller effect, need to be performed for the six-electron center using accurate wave functions for the two active electrons.

It should be interesting to see whether, in future work, a six-electron model can be devised to reproduce the hole-burning and echo results without invoking a Jahn-Teller effect in the E state. Further experiments are clearly needed also, perhaps using single-molecule spectroscopy[17] to eliminate ensemble averaging. However, great care will be needed in interpreting the role of time scale and dephasing in future theory and experiments. Even a single center would experience ultrafast dephasing (hence extreme broadening) of one of the E components but not the other, making it difficult to confirm the large excited-state splitting. Only the long-lived component would be observed in luminescence excitation under conditions of low signal-to-noise ratio.

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