

Thermodynamic stability of neutral Xe defects in diamondD. W. Drumm,¹ M. C. Per,² S. P. Russo,² and L. C. L. Hollenberg¹¹*School of Physics, University of Melbourne, Parkville 3010, Australia*²*Applied Physics, School of Applied Sciences, RMIT, Melbourne 3001, Australia*

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Optically active defect centers in diamond are of considerable interest, and *ab initio* calculations have provided valuable insight into the physics of these systems. Candidate structures for the Xe center in diamond, for which little structural information is known, are modeled using density functional theory. The relative thermodynamic stabilities were calculated for two likely structural arrangements. The split-vacancy structure is found to be the most stable for all temperatures up to 1500 K. A vibrational analysis was also carried out, predicting Raman- and IR-active modes which may aid in distinguishing between center structures.

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I. INTRODUCTION

There are over 500 optically active defects in diamond,¹⁻³ few of which have had their structures completely determined. These defects' utilities range from potential bulk dopants to achieve superconductivity in diamond^{4,5} to bulk emissive properties in light-emitting diodes.⁶ Other example defects include the neutral-vacancy GR1,⁷ nickel-based NIRIM-1 and -2,⁸ boron acceptors,⁹ as well as the only room-temperature stable single-photon source defects such as the well-studied nitrogen-vacancy center (NV),¹⁰ the nickel-based NE8 center,^{11,12} silicon-vacancy (SiV),¹³ the unidentified 734 nm center,¹⁴ and the possibly chromium-based megahertz emission center.¹⁵ In addition, the nitrogen-vacancy (NV) center has also been shown to act as a possible qubit for quantum computing,¹⁶ as a magnetometer,¹⁷⁻²⁰ and to be useful in probing quantum decoherence.^{21,22} It has also been used to demonstrate quantum key distribution²³ using the BB84 scheme.²⁴ The optically active Xe defect, the subject of this work, was only recently characterized²⁵⁻²⁸ and is of interest as a near-IR emitter with two zero phonon lines at 794 and 813 nm.

Optically active defects in diamond have high potential for technological applications, hence it is important to also consider their thermodynamic stability over the range of temperatures to which they are likely to be subjected, including during their creation. Information on the relative stability of defects is also paramount in optimizing their manufacturing conditions. Atomistic modeling of these types of defects offers several advantages: thermodynamic stabilities (both particular and relative) of defects can be evaluated, predictions of their vibrational spectrum made (which can aid in identifying the defect structure) and examination of potential electronic or optical properties may be undertaken.

The observation in Refs. 27 and 28 of a Xe-based defect in diamond emitting at 794 and 813 nm makes the case for detailed *ab initio* studies of such centers even stronger. The site symmetry of that defect was established as trigonal by their polarization study. This defect is likely to be thermodynamically driven due to the experimental conditions under which it is formed (180–500 keV implantation with 800–1400 °C annealing), but little else has been published upon Xe-related defects in diamond other than recent studies

indicating that Xe chemically reacts with the diamond lattice,²⁹ and that the defect is comprised of one Xe atom (with assorted vacancies).²⁸

Density functional theory (DFT) (Refs. 30 and 31) has provided important insight into the nature of such defects^{32-34,29} and is excellent at predicting ground-state properties. The stability of various morphologies,³⁵ modeling of dopants,^{34,36,37} and semiconductor band-gap modification³⁸ have been characterized.

As a material, diamond offers several other attractive properties, including the largest optical transparency window, Young's modulus, and the advantage of a chemically inert host lattice.³⁹ The combination of this exceptional host material with its plethora of dopants offers much scope for investigation and development. The lack of definitive structure models for many of these defect centers requires attention.

In this paper, as the true geometric structure of the defect has not been identified by experiment, we use DFT to study the thermodynamic stability of neutral Xe-vacancy defects in diamond which both have the same symmetry as those observed by Bergman *et al.*,^{27,28} and contain one Xe atom.²⁸ We specifically consider a substitutional Xe atom with either one (Xe_s-V) or three (Xe_s-3V) vacant lattice sites directly adjacent to the Xe atom. The paper is organized as follows: in Sec. II we discuss defect formation free energies and how they may be compared; Sec. III details the DFT parameters used in calculations; Sec. IV presents relaxed defect structures; in Sec. VI vibrational results are discussed; the relative defect formation free energy is shown in Sec. V, and conclusions are drawn in Sec. VII

II. DEFECT FORMATION ENERGY AND THERMODYNAMIC STABILITY

To compare formation free energies between chemical structures requires accounting for the changes one must make to transform from one structure to the other. The defect formation free energy (ΔF_f) is the free energy required to form the defect system from a host (defect-free) lattice H . For a defect system X consisting of dopant atoms and associated lattice vacancies, which are formed by the removal of n_i atoms of chemical species i , ΔF_f becomes (for any tem-

perature T within the harmonic approximation)

$$\Delta F_f = F(X) - \left[F(H) + \sum_D n_D \mu_D - \sum_i n_i \mu_i \right] + cct. \quad (1)$$

Here $F(X)$ is the total free energy for the defected system, and $F(H)$ the total free energy of the defect-free host lattice. The chemical potentials of the dopant atom (D) and the atom(s) of chemical species i removed to create a vacancy in the defect lattice are μ_D and μ_i . The number of the dopant atoms inserted is n_D ; n_i is the number of lattice atoms removed to create vacancies. Finally, cct corresponds to charge correction terms which are added to Eq. (1) if the atoms removed or added have a charge.^{29,40}

The free-energies are defined as

$$F(X) = E(X) + F_{\text{vib}}(X) - TS_{\text{config}}, \quad (2)$$

$$F(H) = E(H) + F_{\text{vib}}(H), \quad (3)$$

where $E(X)$ is the total (DFT) energy for the relaxed defect system, and $E(H)$ is the total (DFT) energy of the relaxed defect-free host lattice. F_{vib} is the vibrational free energy contribution from the system X or host H as given by

$$F_{\text{vib}} = k_B T \int_0^\infty g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] d\omega, \quad (4)$$

where $g(\omega)$ is the (harmonic approximation) phonon density of states for system X or H . It is important to note that here $g(\omega)$ has been normalized such that

$$\int_0^\infty g(\omega) d\omega = N_p. \quad (5)$$

Here N_p is the number of phonon branches in the supercell. As written, F_{vib} also contains the zero-point energy $E_{\text{ZP}} = \int_0^\infty g(\omega) \frac{1}{2} \hbar \omega d\omega$ contribution of the X or H system, *viz.*,

$$\begin{aligned} F_{\text{vib}} &= \int_0^\infty g(\omega) k_B T \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] d\omega \\ &= E_{\text{ZP}} - k_B T \int_0^\infty g(\omega) \ln [1 - e^{-\hbar \omega / k_B T}] d\omega. \end{aligned} \quad (6)$$

The configurational entropy contribution S_{config} is given by $S_{\text{config}} = k_B \ln(\Omega_X)$, where Ω_X enumerates the possible orientations of the defect (X) within the supercell. In both cases, our defects require the Xe atom to be on a lattice site (initially), and have a distinct orientation toward one of the nearest-neighbor lattice sites. This evaluates as

$$\Omega_X = n_l n_o = 864, \quad (7)$$

where n_l is the number of lattice sites in the supercell (216) and n_o is the number of distinct orientations the Xe defect may have per lattice site (or number of nearest-neighbor C atoms, 4). While this works for Xe-3V, for Xe-V we must, as the final structure is significantly different from the initial (see Sec. IV), include a term to avoid double counting,

$$\Omega_{\text{Xe-V}} = \frac{n_l n_o}{2} = 432. \quad (8)$$

The chemical potential of the carbon atoms removed is

$$\mu_C = \frac{E_{\text{DFT}}(H) + F_{\text{vib}}(H)}{n}, \quad (9)$$

where n is the number of C atoms in the defect-free supercell of diamond. For this work we consider the formation of a neutral dopant (Xe atom) in a covalent system (diamond), thus charge correction terms may be ignored.

As we are considering two defected systems (Xe-V and Xe-3V), in determining the relative thermodynamic stability of the two defect configurations we need only consider the relative defect formation free energy

$$\Delta F_f^{\text{REL}} = \Delta F_f(\text{Xe-V}) - \Delta F_f(\text{Xe-3V}) \quad (10)$$

allowing us to divorce common bulk properties from relative stability calculations:

$$\Delta F_f^{\text{REL}} = F(\text{Xe-V}) - [F(\text{Xe-3V}) + 2\mu_C]. \quad (11)$$

As defined, $\Delta F_f^{\text{REL}} > 0$ means that the Xe-3V case is more stable than the Xe-V case.

Note that the μ_{Xe} term does not appear in the above expression, due to both our defects being comprised of one Xe dopant atom, and the μ_{Xe} terms canceling.

III. METHODOLOGY

All DFT calculations were performed using the *ab initio* total-energy and molecular dynamics package VASP (Vienna *ab initio* simulation package) developed at the Universität Wien.⁴¹ We used the generalized-gradient approximation (GGA), with the PBE exchange-correlation functional,⁴² and projector augmented-wave (PAW)⁴³ potentials for C and Xe. The plane-wave cutoff was set at 400 eV for all calculations. A $4 \times 4 \times 4$ Monkhorst-Pack k -point mesh was used as this has been found to give accurate representation of the geometry and electronic structure.^{29,34,44,45} The bulk diamond lattice constant was checked using these parameters, found to be 3.562 Å, and this value was used for all subsequent calculations.

All calculations were performed by constructing a $3 \times 3 \times 3$ simple cubic supercell of diamond (216 atoms), removing the appropriate number of carbon atoms to create vacancies and inserting Xe into a substitutional lattice site. The vacancy sites were always in first nearest neighbor positions to the Xe atom. For the defect diamond lattices, the Xe-vacancy defects were constructed such that they had trigonal crystallographic point group symmetry in accordance with experimental data.²⁷

In performing the geometry optimization the relaxation was constrained so that the supercell remained cubic in shape. After relaxation the force on a C atom was typically less than 0.001 eV/Å and in all cases the trigonal symmetry of the defect remained.

IV. DEFECT GEOMETRIC STRUCTURE

A. Split-vacancy interstitial Xe

Upon relaxation the initial Xe-vacancy geometry [Xe_s-V in Fig. 1(a)], with all atoms occupying C lattice sites,

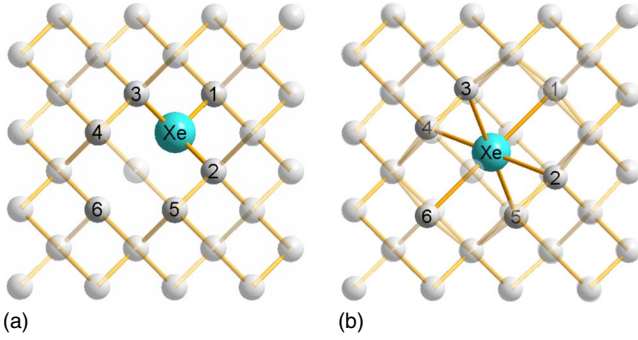


FIG. 1. (Color online) Split-vacancy Xe structure in the diamond lattice, viewed from the $[100]$ direction. Nearest-neighbor C atoms are numbered, Xe shown larger. (a) Initial structure. (b) Relaxed structure.

formed a split-vacancy interstitial structure with the site symmetry of the Xe atom being C_{3v} [Fig. 1(b)]. The Xe atom was then found to be at the center of the divacancy, where it has D_{3d} symmetry (still within the constraint of trigonal symmetry). In the relaxed structure, the Xe atom is sixfold coordinated with the nearest-neighbor C atoms, with bond lengths of 2.15 Å. The bonds form two distinct sets of three (C_{1-3} and C_{4-6}); bond angles within sets are different from those between sets. More details may be seen in Table I. This structure is commensurate with the Si-V defect in diamond studied by Goss *et al.*³²

B. Three-vacancy defect (Xe_s -3V)

The three-vacancy case [initial geometry shown in Fig. 2(a)] was also considered. Initially, the Xe is left with one nearest-neighbor C atom (C_1), and three directly adjacent vacant sites. Of the surrounding atoms, nine (C_{2-10}) are also adjacent to the vacancies. Six of these (C_{5-10}) form a coplanar hexagon about the Xe atom.

The relaxed geometry [Fig. 2(b)] shows that the Xe atom migrates 0.38 Å (out of the hexagon plane) to an interstitial position between the four vacant lattice sites (one being the initial position of the Xe atom) with the site symmetry of the Xe atom being C_{3v} . C_{1-4} move outward by 0.22 Å. The hexagon distorts slightly, with pairs of atoms expanding outward (along their perpendicular bisector) by 8.66 Å, maintaining C_{3v} symmetry. More details are located in Table II.

V. DEFECT FORMATION ENERGIES

Using the equations detailed in Sec. II, the relative defect formation free energy [ΔF_f^{REL} from Eq. (11)] was calculated

TABLE I. Bond lengths and angles for relaxed split-vacancy Xe.

Bond length/angle	Relaxed amount	Change from initial %
C_i -Xe	2.15 Å	+39.6
$\angle C_{1-3}$ -Xe- C_{1-3}	84.436°	-22.9
$\angle C_{4-6}$ -Xe- C_{4-6}	84.316°	+40.5
$\angle C_{1-3}$ -Xe- C_{4-6}	95.640°	+6.27

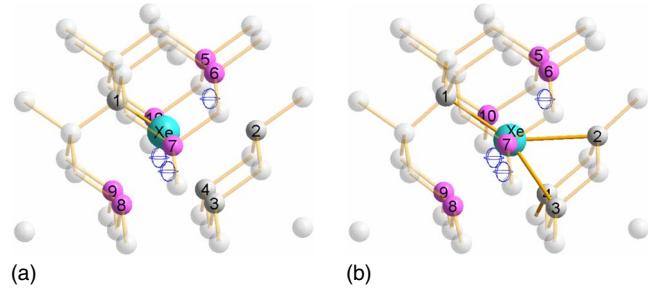


FIG. 2. (Color online) Xe_s -3V, viewed from approximately the $[110]$ direction. Nearest neighbor C atoms are numbered, Xe atom shown larger, vacant sites shown as wire ellipse frames. (a) Initial structure. (b) Relaxed structure.

over temperatures ranging from 0–1500 K and can be seen in Fig. 3. The split-vacancy defect is 2.59 eV more stable than the Xe-3V defect at all temperatures considered. The variation with temperature is small, about 3% of the total value, indicating that the difference in their behavior with respect to temperature is small compared to the other terms in ΔF_f^{REL} and that for the purpose of determining the qualitative stability ordering temperature effects are irrelevant. The relative stability of the split-vacancy defect is slightly enhanced at high temperatures. Neglecting E_{ZP} (which comes at significant computational expense compared to a simple DFT calculation), leads to a relative zero-temperature defect formation energy of -3.06 eV, overestimating the stability by $\approx 18\%$. Finally, in Fig. 4 we show the vibrational free energy contribution to the total energy as a function of temperature for each defect. The Xe-3V case (dashed line) is vibrationally more stable at every temperature studied. At 0 K, the difference is 0.83 eV, and at 1500 K, 0.25 eV. We may therefore infer that the energetic expense of removing two C atoms from the diamond lattice outweighs the steric benefit of having the extra space for the Xe atom and unpaired C electrons to inhabit.

VI. VIBRATIONAL DOS

The vibrational properties of the systems were then calculated using lattice dynamics under the harmonic approxi-

TABLE II. Bond lengths and angles for relaxed Xe-3V

Bond length/distance/angle	Relaxed amount	Change from initial %
C_1 -Xe	2.13 Å	+38.3
C_{2-4} -Xe	2.39 Å	-5.28
C_{5-10} -Xe	2.63 Å	+4.47
C_5 - C_6 (7-8,9-10)	2.67 Å	+5.86
C_6 - C_7 (8-9,10-5)	2.52 Å	+0.11
$\angle C_1$ -Xe- C_{5-10}	80.334°	-10.7
$\angle C_5$ -Xe- C_6 (7-Xe-8,9-Xe-10)	60.878°	+1.46
$\angle C_6$ -Xe- C_7 (8-Xe-9,10-Xe-5)	57.247°	-4.59
$\angle C_{2-4}$ -Xe- C_{5-10}	67.828°	+13.0
$\angle C_{2-4}$ -Xe- C_{2-4}	63.129°	+5.23

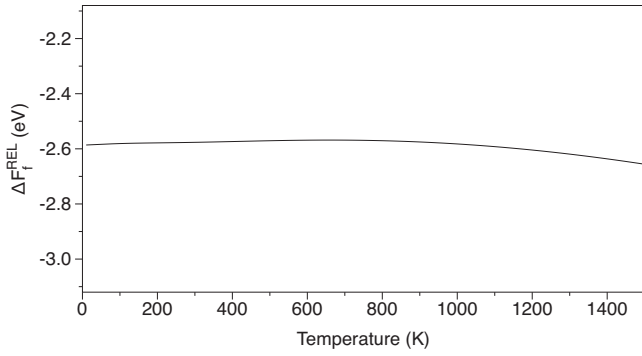


FIG. 3. Relative defect free energy of formation; $F(\text{Xe-V}) - [F(\text{Xe-3V}) + 2\mu_C]$.

mation. The derivatives of the forces required to build the dynamical matrix were obtained using a finite-difference scheme in which individual nuclei were displaced by 0.04 Å from their equilibrium positions and the resulting forces on all the nuclei calculated. Symmetry was used to reduce the number of displacements required to build the full dynamical matrix. The calculated forces were used in the program PHON⁴⁶ to construct and diagonalize the dynamical matrix to obtain the vibrational density of states (vDOS) and the thermodynamic properties of the systems.

Figure 5(a) shows the total vDOS of bulk diamond (shaded) and for the Xe split-vacancy (solid), averaged over the entire Brillouin zone. The region where the contribution from the Xe atom, the Xe-projected vDOS (dashed) is significant is shown in Fig. 5(b). Three strong Xe-localized modes are extant at the Γ point (dot-dashed). As the site symmetry of the Xe atom and the crystallographic point group symmetry of the relaxed lattice are identical (C_{3v}), the vibrational modes involving the Xe atom will be of A_1 (nondegenerate) or E -type (doubly-degenerate) symmetry. We find a nondegenerate mode with A_1 -character at 218 cm^{-1} whose eigenvector shows the displacement of the Xe atom to be in the $[111]$ direction. This displacement compresses three of the C-Xe bonds (e.g., C_{1-3}) and stretches the other three. A doubly-degenerate mode of E -character was found at 251 cm^{-1} which is more prominent in the full vDOS than the A_1 mode. All three modes are mutually orthogonal (see Fig. 6), and are both IR and Raman active. For all three modes the relative displacement of any C atom is much smaller (by an order of magnitude) than the displacement of the Xe atom, showing that the vibrations are indeed almost entirely localized on the Xe atom.

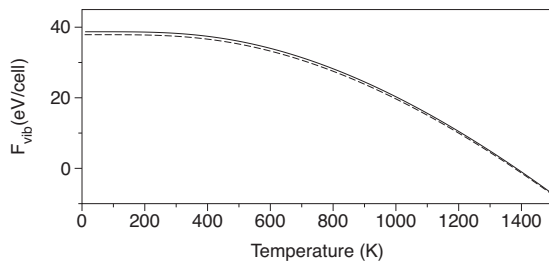


FIG. 4. Vibrational contribution to the free energy. Split-vacancy Xe defect (solid line), Xe-3V defect (dashed line).

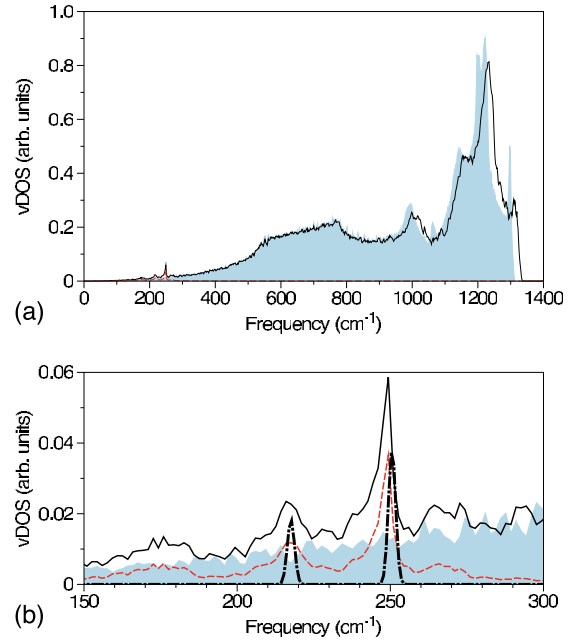


FIG. 5. (Color online) Vibrational density of states for the relaxed split-vacancy Xe defect. Total vDOS (solid line), Xe-projected vDOS (dashed line), Gaussian-smearred Xe-projected vDOS at Γ (dot-dashed line), bulk diamond vDOS (shaded background). (a) Full calculated vDOS. (b) Region where Xe-projected vDOS is significant.

The corresponding total vDOS of the Xe-3V defect (solid) and for bulk diamond (shaded) is shown in Fig. 7(a) (again averaged across the Brillouin zone). Again, the region where the Xe-projected DOS (dashed) is significant is displayed in Fig. 7(b). At the Γ point we find a nondegenerate mode at 245 cm^{-1} (dot-dashed) which displaces the Xe atom along the $[\bar{1}11]$ direction (along the Xe- C_1 bond). The relative displacement of any C atom is again smaller (by an order of magnitude) than the displacement of the Xe atom. As this mode is nondegenerate, it corresponds to an A_1 -type mode which is both IR and Raman active.

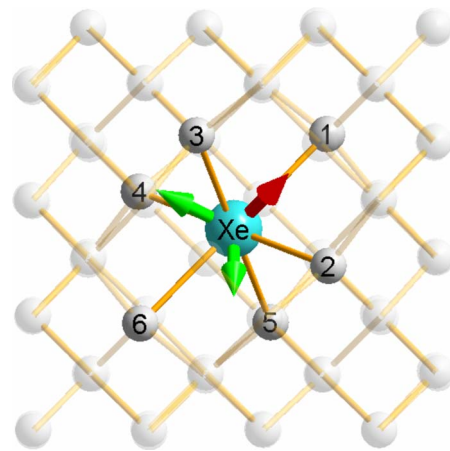


FIG. 6. (Color online) Displacements of the Xe atom under the two strongly Xe-localized vibrational modes in the split-vacancy Xe defect. A_1 mode (red arrow), doubly-degenerate E mode (green arrows).

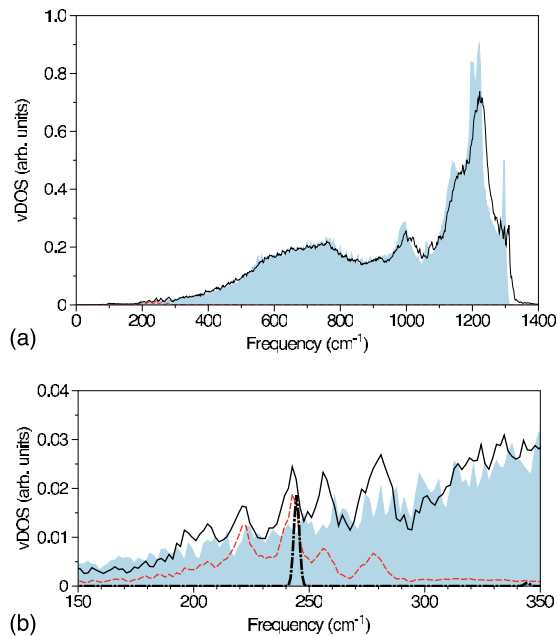


FIG. 7. (Color online) Vibrational density of states for the relaxed Xe-3V defect. Total vDOS (solid line), Xe-projected vDOS (dashed line), Gaussian-smearred Xe-projected vDOS at Γ (dot-dashed line), bulk diamond vDOS (shaded background). (a) Full calculated vDOS. (b) Region where Xe-projected vDOS is significant.

From 400 cm^{-1} , both vDOS spectra are largely unchanged from the bulk, apart from some softening of peaks and a slight shift from about 900 cm^{-1} onward. In particular, the sharp peak near 1300 cm^{-1} is significantly lower.

The predicted Raman signals should be visible and differentiable at sufficient doping density, especially if appropriate line-fitting models are used.⁴⁷ Some indications of them are present in the PL phonon sidebands seen in Martinovich *et al.*,²⁵ but a clearer signal could be obtained by looking at the sidebands nearest the pump laser frequency. This may reduce any frequency-shift effects of the electronic level excitation/de-excitation. Also, if the center in question happens to be the optically active one, pumping its optical emission could set up a dipole which may enhance the Raman signal, making detection easier. Unfortunately, none of the currently published experimental work on Xe centers provide spectra sufficiently close to the pump laser frequency to compare with.^{6,25–28}

VII. CONCLUSIONS

We have presented the results of density functional theory simulations of Xe in diamond and draw several conclusions. First, the split-vacancy neutral defect is the most stable of those considered, at all temperatures. Second, the cost of removing two extra C atoms from the lattice outweighs the vibrational benefit of the extra space. Finally, both defects have IR- or Raman-active vibrational modes at Γ which may aid in further identification of the structure of the defects studied by Bergman *et al.*^{27,28}

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