PHYSICAL REVIEW B **95**, 094113 (2017)

Anharmonicity effects in impurity-vacancy centers in diamond revealed by isotopic shifts and optical measurements

E. A. Ekimov,[1] V. S. Krivobok,[2] S. G. Lyapin,[1] P. S. Sherin,[3,4] V. A. Gavva,[5] and M. V. Kondrin[1,*]
[1]*Institute for High Pressure Physics RAS, 142190 Troitsk, Moscow, Russia*
[2]*Lebedev Physical Institute RAS, 117942, Leninsky pr. 54, Moscow, Russia*
[3]*International Tomography Center SB RAS, 630090, Institutskaya Street 3A, Novosibirsk, Russia*
[4]*Novosibirsk State University, 630090, Pirogova Street 2a, Novosibirsk, Russia*
[5]*Institute of Chemistry of High-Purity Substances RAS, 603950, Tropinina Street 49, Nizhny Novgorod, Russia*
(Received 21 October 2016; revised manuscript received 24 February 2017; published 15 March 2017)

We studied isotopically enriched nano- and microdiamonds with optically active GeV^- centers synthesized at high pressures and high temperatures in nonmetallic growth systems. The influence of isotopic composition on optical properties has been thoroughly investigated by photoluminescence-excitation (PLE) and photoluminescence (PL) spectroscopy to get insight into the nature and electronic structure of this color center. We have demonstrated that the large frequency defect (difference between oscillation frequencies in the ground and excited electronic states) does bring about large discrepancy between PLE and PL spectra and comparatively high isotopic shift of the zero phonon line. Both effects seem to be rather common to split-vacancy centers (for example SiV^-), where the frequency defect reaches record high values. Isotopic substitution of carbon atoms in the diamond lattice results in even larger shifts, which are only partially accounted for by a redistribution of electron density caused by the volume change of the diamond lattice. It was shown that the vibronic frequency in this case does not depend on the mass of carbon atoms. The greatest part of this isotopic shift is due to anharmonicity effects, which constitute a substantial part of vibronic frequency observed in this center. The exact physical mechanism, which leads to significant enhancement of anharmonicity on substitution of $^{12}\mathrm{C}$ to $^{13}\mathrm{C}$, is yet to be clarified.

DOI: 10.1103/PhysRevB.95.094113

I. INTRODUCTION

Bright and practically monochromatic luminescence of the recently discovered GeV center [1–4] in diamond makes it an interesting object for applications as a marker in medicine, biology, high-resolution microscopy, or as a single-phonon emitter in prospective projects such as quantum computing and cryptography. Synthesis of nanodiamonds from hydrocarbons using high-pressure, high-temperature (HPHT) techniques makes it possible to produce individual nanoparticles with single-impurity centers, which are quite chemically inert and stable, so they are safe enough to be used *in vivo*.

Experimental data (e.g., angular dependence of electronic paramagnetic resonance [5]) suggests that this center is isostructural to the more thoroughly studied SiV center [6–13]. Thus, SiV^- and GeV^- belong to the same type of so-called split-vacancy center with D_{3d} ($\bar{3}m$) symmetry [9]. This impurity center can be thought of as formed by two adjacent vacancies in a diamond matrix and a dopant atom located exactly between them.

Ab initio calculations demonstrate that the highest occupied and partially occupied impurity levels (the Kohn-Sham orbitals) of the GeV^- center consist of two doublets—filled e_u about 0.2 eV below the valence band top, and partially occupied (with 3 electrons) e_g levels about 1.75 eV above it. Symmetry analysis [14] shows that the ground and excited (with one electron promoted from e_u to e_g levels) multielectron functions built using these orbitals have ^2E_g and ^2E_u symmetry. Since the electron levels in the ground and excited states are degenerate and partially filled, both of them are Jahn-Teller unstable. It is believed that the actual mechanism that lifts this degeneracy is caused by spin-orbital coupling; therefore both doublets are split. Experimental data suggest splitting energies of 4.6 meV (1.1 THz) and 0.75 meV (181 GHz) for e_u and e_g orbitals, respectively, so the zero phonon line (ZPL) of this center consists of four well-resolved lines (see Fig. 1).

From the symmetry considerations it also follows that two quasilocal vibrational modes can be expected (corresponding to the movements of the impurity atom along the trigonal axis and in the plane orthogonal to it). Nonetheless in the recent analysis [15], only one mode was demonstrated to contribute to the optical sideband of a split-vacancy center (SiV^- was considered as an example). Still we believe that further experimental evidence, which can be obtained from complementary measurements of isotopic effects and optical properties, is required.

In the previous works careful investigation of the influence of the isotopic constitution of dopant on the position of the ZPL [2] and its first vibronic peak [4] allowed authors to associate unambiguously the "2.059 eV" luminescence line, observed in the synthetic diamonds grown in the presence of germanium, with the Ge impurity. Since HPHT synthesis allows one to exert finer control over the isotopic composition of the impurity, it makes it possible to introduce isotopically pure dopant into a carbon matrix. Consequently, this enables us to deeper understand more subtle microscopic properties of this center, which otherwise are not easily caught by other experimental methods or *ab initio* calculations. Besides, in this paper we will also discuss the influence of isotopic

---

[*] mkondrin@hppi.troitsk.ru

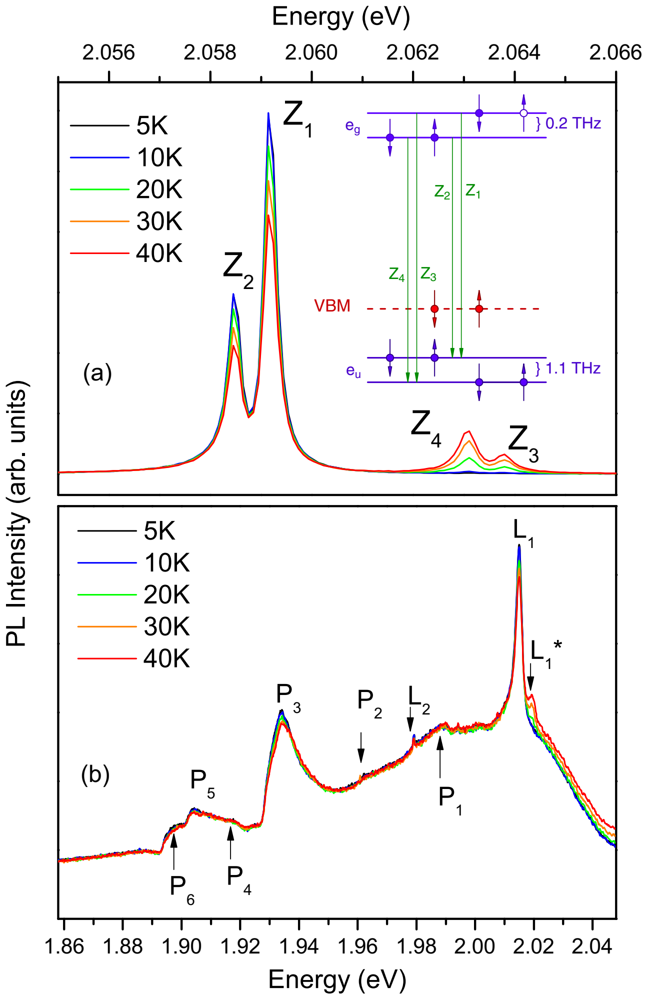

FIG. 1. (a) Temperature dependence and fine splitting of the ZPL of the GeV$^-$ center. (b) Temperature evolution of the vibronic sideband of the GeV$^-$ center in the ^{76}Ge -^{12}C sample. Peaks marked with L are quasilocal modes and broad features marked with P are due to bulk phonon modes in the diamond lattice (see text). The schematic view of impurity levels in the vicinity of the valence band maximum is shown in the inset where electron configuration corresponds to the ground state (^2E_g); the empty symbol stands for the unoccupied electron state.

composition of the carbon matrix on optical properties of the color center, which remains a controversial issue since the first seminal work of Collins *et al.* [16].

II. METHODS

A. Synthesis

Our concept of producing Ge-doped diamond with high structure perfection is based on HPHT synthesis from organic compounds, which provides formation of very small diamond crystals free of strain-generating metallic impurities. In contrast to the Ge-C [2] or Ge-Mg-C [17] growth systems, the synthesis of diamond in the Ge-C-H (naphthalene-germanium) system at 8 GPa takes place at lower temperatures of 1600–1900 K [4,13,18]. At these temperatures germanium does not act as a carbon/diamond-forming solvent for the diamond synthesis, which provides opportunity to control doping of diamond by changing germanium content in the carbon-hydrogen-based growth medium. Microcrystals of up to 10–15 μm in size with perfect shape and nanocrystals of 50–300 nm in size are detected in as-synthesized samples (Fig. 2). Diamonds enriched with carbon isotope ^{12}C were synthesized from mixtures of naphthalene and Ge (C-H-Ge growth system), while diamonds enriched with isotope 13C were produced from mixtures of Ge with amorphous carbon in the presence of distilled water (C-H-O-Ge growth system).

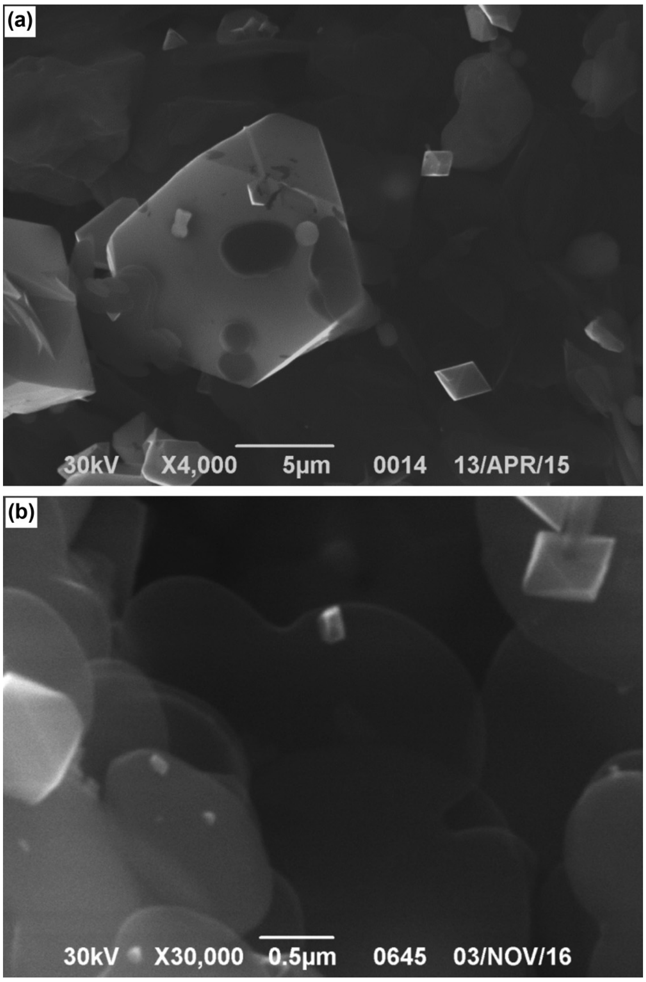

FIG. 2. (a) Micro- and (b) nanocrystalline diamonds synthesized under high-pressure conditions in the C-H-Ge growth system.

Under the synthesis, water interacts with carbon to form hydrocarbons in one growth system, and some amount of oxygen is inevitably present as an impurity in the other, which makes two these growth media similar and should lead to the same set of impurities in synthesized diamonds. Indeed, apart from carbon isotope shift, no changes in optical spectra of the diamonds were detected, which indicates their structural identity. Crystals of diamond enriched with either one or the other carbon isotope have the same color, morphology (mostly octahedral), and grain-size distribution; no metal impurities were detected in the samples by EDX microanalysis. Since samples were synthesized under the same conditions which should provide the same crystal nucleation and growth rates, the difference in growth strain for the samples is unlikely. Repeated synthesis with variation in pressure and temperature results practically in the same line position in the luminescence spectra, which rules out a significant influence of mechanical stresses on the line position in luminescence spectra of the samples obtained. Moreover, random strain present in nano- and microdiamonds would inevitably lead to inhomogeneous broadening of optical lines which was not observed in our samples where the ZPL's FWHM was in the range 0.2–0.5 meV. Interestingly that intake of hydrogen or oxygen into the diamond in the form of a structural impurity is not known for HPHT synthesis [19–22]. One can conclude therefore that HPHT synthesis of diamond from the C-H-O growth systems has a high potential for production of diamonds with a high purity and structural quality.

B. Optical measurements

Due to the very low concentration of impurity centers produced by the HPHT synthesis, no direct absorption measurements were possible. Instead we used the more sensitive photoluminescence-excitation (PLE) method. PLE and optical absorption in general yield similar results, so these two experimental techniques are usually regarded as interchangeable [23]. PLE spectra were further considered as absorption spectra of GeV$^-$ centers.

Photoluminescence excitation and emission spectra were recorded with the FLSP920 spectrofluorometer (Edinburgh Instruments, UK) equipped with a low-noise micro-channel-plate photomultiplier. Diamond crystals were placed in a quartz tube (2.0 mm in diameter) and all photoluminescence experiments were performed in the reflective mode with a cylindrical quartz Dewar vessel at room temperature or 77 K. All obtained spectra were corrected for the wavelength-dependent sensitivity of the detection.

Low-temperature emission spectra were recorded with a grating spectrograph (Princeton Instruments SpectraPro 2500, 1200 grooves/mm grating) equipped with Pylon CCD detector (eXcelon, front-illuminated). Spectral resolution better than 0.1 meV was provided by the entrance slit width of 20 μm and the same CCD pixel size.

Samples were immersed in the optical cryostat (Utreks1 RTA) and cooled by continuous flow of helium vapor. A steady-state semiconductor laser (40 mW) operating at a wavelength of 472 nm was used as an excitation source. An approximately 2.5 times enlarged image of the excitation spot with an approximate size of 500 μm was focused at the entrance slit of the spectrograph using a quartz lens (100 nm focal length).

III. ISOTOPIC EFFECTS

The isotopic substitution of the impurity atom leads to the change in the frequency of quasilocal phonon modes caused by oscillations of this atom. However, identification of these modes is not always trivial and in the vibronic sideband we have selected two sharp features [marked with L_{1-2} in Fig. 1(b)]. These two peaks, from our point of view, can be attributed to oscillations of the impurity atom. Several other broader peaks marked as P_{1-6} present in Fig. 1(b) are presumably caused by bulk phonons, which are routinely observed in the optical sidebands of impurity centers in diamond [24]. The energy evolution of one (the most intense) ZPL peak and its first vibronic peak (L_1) with respect to isotopic composition of the dopant is depicted in Fig. 3 (see also Table I). The shoulder visible in the first vibronic peak (marked as L_1^*) corresponds to a weaker doublet in the ZPL (Z_{3-4}), which explains similar energy splitting and temperature evolutions of these two features. The relative energy (measured from the strongest Z_1 line) of the first vibronic peak follows relation $1/\sqrt{m}$ (where m is the mass of Ge isotope), which enabled the authors of Ref. [4] to demonstrate the connection of this center with the Ge impurity. However, in the limited range of the isotope's mass it will be convenient to approximate isotopic shifts of the first vibronic peak (L_1) and the ZPL (Z_1) by linear dependence. This yields two respective coefficients $\delta L_1/\delta m = -0.28 \pm 0.01$ and $\delta Z_1/\delta m = -0.065 \pm 0.001$ meV/amu. The last value is similar to but somewhat higher than -0.06 ± 0.01 reported earlier [2] for the same center.

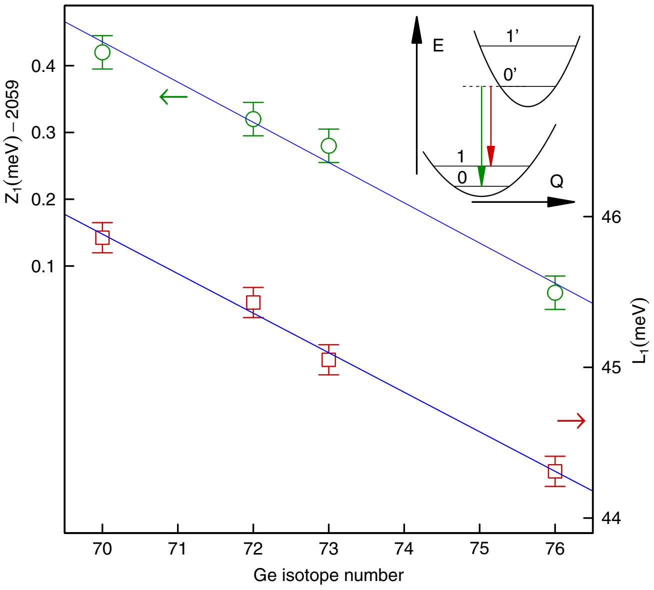

FIG. 3. Dependence of absolute energy of the most intense component of ZPL (Z_1: ○) and the first vibronic peak (L_1: □) on isotope number of the Ge impurity (see also Table I). Corresponding transitions in the Huang-Rhys model between vibronic levels of the excited (n') and ground (n) electronic states are shown in the inset. Thin lines are linear approximations of experimental data.

TABLE I. Position of the most intense ZPL component and four strongest sideband peaks (energies of lines L_1, L_2 and P_3, P_5 in Fig. 1 relative to Z_1) with respect to isotopic composition of impurity center.

Composition	Z_1 (eV)	L_1 (meV)	L_2 (meV)	P_3 (meV)	P_5 (meV)
^{70}Ge -^{12}C	2.05942	45.86	80.06	125.20	155.32
^{72}Ge -^{12}C	2.05932	45.43	80.05	125.17	155.57
^{73}Ge -^{12}C	2.05928	45.05	80.02	124.96	154.70
^{76}Ge -^{12}C	2.05906	44.31	79.96	125.16	154.83
^{73}Ge -^{13}C	2.06193	45.02	80.05	120.13	148.70

In our opinion, a rather strong dependence of the absolute ZPL position on the mass of the impurity might be brought about by a large frequency defect present in this center. In stand alone molecules this defect was reported to exceed 20% [25]. Taking into account the Huang-Rhys model [26] (schematically depicted in the inset of Fig. 3) and estimations of isotopic shifts provided earlier, the oscillation quanta of the impurity center in the excited state can be evaluated using the equation

$$\nu_e = \nu_g \frac{2\delta Z_1/\delta m + \delta L_1/\delta m}{\delta L_1/\delta m}. \tag{1}$$

Here $\nu_g \equiv L_1 = 45$ meV is the oscillation quanta in the ground state. So Eq. (1) yields $\nu_e = 67$ meV, which is almost 50% higher than ν_g. This means that in the excited state the impurity atom is significantly more tightly bound to the carbon lattice than in the ground state.

The derivation of Eq. (1) is based on two assumptions: the oscillators are harmonic (so zero energy is half of the oscillation quanta above the minimum of the potential surface, hence factor 2 in the numerator) and the impurity atom's mass does not influence the energy minimum of this potential surface. The latter condition is justified because this energy depends only on the electron density in the vicinity of the defect, so it mostly depends on geometry of the neighborhood. Thus, the fraction in Eq. (1) is a ratio of zero energy change rates in the excited and the ground electronic states, which under these assumptions should be equal to the ratio of the oscillation quanta in the same states. Note that Eq. (1) can be further simplified into an approximate relation between the frequency defect and the ZPL's isotopic shift: $\nu_g - \nu_e \approx 4m\delta Z/\delta m$. This relation practically coincides with the result predicted in Ref. [27].

The value ν_e can be directly measured in optical absorption experiments. In the absorption sideband beside the peak associated with the transition $0 \to 1'$ (we will mark with tick marks the vibronic levels of the excited electronic state), transitions with no change of vibronic quantum numbers should be also present (like $1 \to 1'$ and so on). This additional transition is possible due to the frequency defect (otherwise they would coincide with the ZPL corresponding to transition $0 \to 0'$). At low-temperature conditions, where the vibronic sideband is the most easily observed, the occupation of higher vibronic levels strongly diminishes. Thus, considering transitions only between a few lowest levels (0–3) in many cases would be enough. However, there is a subtle issue of level parity (see Appendix for details).

Photoluminescence excitation and emission spectra of the GeV$^-$ center recorded in the same experiment at 77 K are depicted in Fig. 4. PLE is a highly sensitive technique of optical absorption measurements, applicable in the case of low concentrations of color centers [23]. Despite lower experimental precision as compared with luminescence spectra presented earlier in Fig. 1, the first vibronic peak L_1 with energy ≈46 meV is easily discernible at the emission part of Fig. 4(a). So, this result reproduces data already known from luminescence measurements and also gives an experimental error of absorption measurements (about 2 meV).

Two peaks in the absorption spectrum [Fig. 4(b)] with energies 25 meV and 73 meV can be attributed to quasilocal vibration of impurity atoms. The last one of these peaks is significantly larger in intensity than the similar peak in emission, which is ascribed to the bulk phonons. This difference of spectral density is due to the transition $0 \to 1'$ with energy 73 meV, while the first weaker peak (with energy 25 meV) is attributed to the transition $1 \to 1'$. The energy difference between these two transitions yields the ν_g value. This equality is indeed satisfied within the range of experimental error (48 meV vs 45 meV obtained in luminescence experiments).

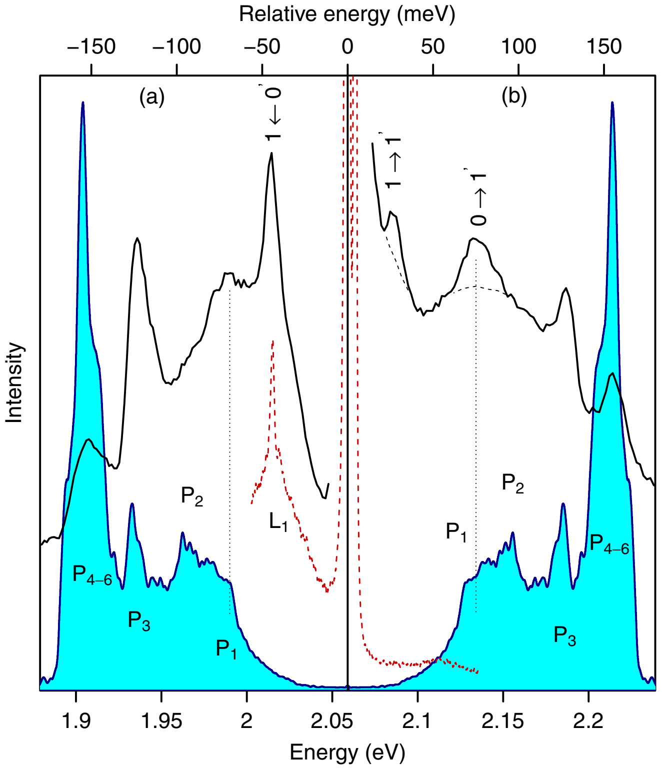

FIG. 4. PL (a) and PLE (b) sidebands of the GeV$^-$ center (solid lines) recorded at $T = 77$ K. Zero of the top axis corresponds to the position of the Z_1 line. Below the emission and adsorption curves the experimental density of the bulk phonon modes [28] in pure diamond (shaded areas) symmetrically mirrored around ZPL energy is drawn. For comparison the region around the ZPL of the curve taken at $T = 40$ K from Fig. 1 (dotted curve in the middle) is shown. It demonstrates that in the vicinity of the $1 \to 1'$ peak there are no additional impurity lines. Dashed curves on the PLE spectrum trace assumed background used for calculation of relative intensities of peaks corresponding to transitions $0 \to 1'$ and $1 \to 1'$ in the Appendix.

Nonetheless, even if one takes into account this experimental error, there is still a considerable gap between values ν_e obtained by direct absorption experiments (73 meV) and estimations made earlier from isotopic effects (67 meV). We assume that this deviation is caused by anharmonicity effects, which invalidate the equality between the zero energy and half of the oscillation quanta, used earlier in the derivation of Eq. (1). So, this difference also provides an upper limit on anharmonicity effects, which can be expected in this defect center—about 5%. This observation in fact corroborates the almost obvious conclusion that the anharmonicity effects are rather small in diamond.

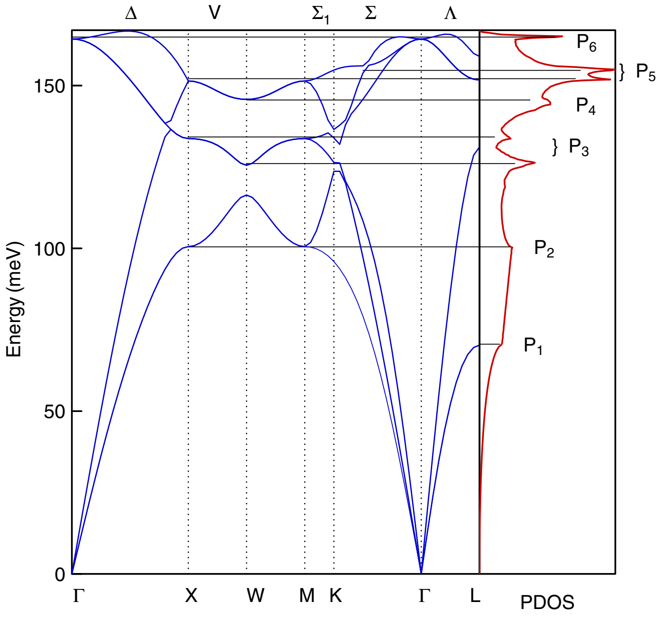

FIG. 5. Attribution of observed bulk phonon modes P_{1-6} to the Van Hove singularities in the Brillouin zone of pure diamond. Note that P_3 and P_5 peaks are in fact doublets corresponding to pairs of singularities in the different points of the Brillouin zone. Dispersion curves and phonon density of states were calculated using QuantumESPRESSO and Phonon software packages [29] by slight modifications of examples provided with them.

Moreover, these experiments give us the opportunity to assign other peaks visible in the luminescence sideband of GeV$^-$ [Fig. 1(b)]. In Fig. 4 we demonstrate correspondence between some lines in experimental emission and absorption sidebands of the GeV$^-$ center's ZPL and density of phonon states in pure diamond [24,28]. From this picture it immediately follows that broad features P_{1-6} in Fig. 1(b) with relative energies ≈70, 100, 128, 145, 155, and 165 meV correspond to bulk phonon modes in the diamond lattice excited by oscillations of impurity atoms (see also Fig. 5). These phonon modes are symmetrically located on both side of the ZPL in Fig. 4 in absorption and emission panels. So, one must conclude, they do not depend on whether the impurity atom is in either the excited or ground state. This behavior is totally different from the local modes, which are (as was mentioned earlier) very sensitive to the electronic excitation state of the impurity center due to the strong frequency defect found in the GeV$^-$ center. Another way leading to the same attribution of the P_{1-6} lines is the approximate invariance of their positions with respect to the mass of the impurity atom and very strong dependence on the isotopic composition of carbon lattice (see Table I). Note that the shifts of both P_3 and P_5 lines in ^{73}Ge-^{13}C and ^{73}Ge-^{12}C diamonds are almost equal to $\sqrt{13/12}$ as one would expect from the harmonic oscillator formula.

So, the only sharp peak which remains unattributed in the luminescence sideband is L_2 at ≈80 meV. This peak was always registered in our experiments (see Table I) but its position weakly depends both on the mass of the impurity atom as well as on the isotope composition of the carbon lattice. Although we find that this isotopic dependence is very unusual and cannot rule out the possibility that this line is due to some unknown impurity, nonetheless we believe that this peak belongs to the vibronic sideband of the GeV$^-$ center. The only known impurity center in diamond with a ZPL at 1.979 eV is a rather uncommon center produced by special optical treatment at low temperatures of irradiated Ib diamonds [21,30], so it is highly improbable that it can be unintentionally obtained in our experiments.

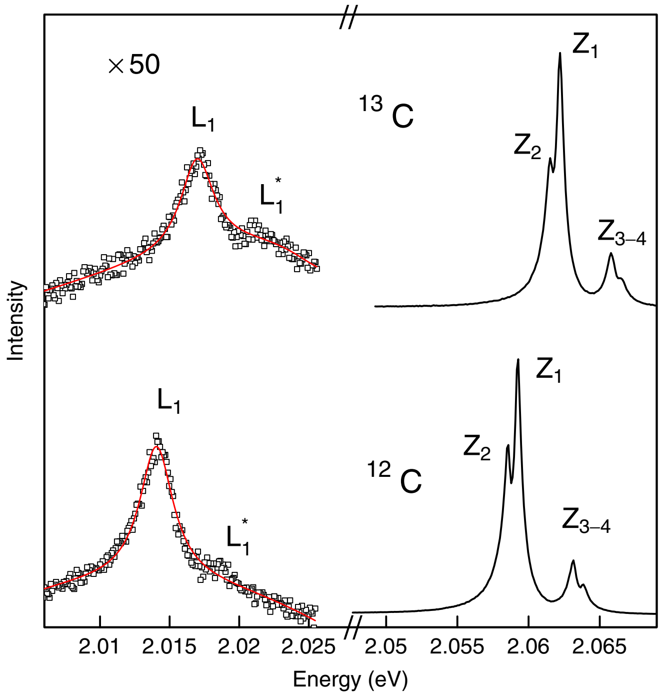

FIG. 6. The ZPL and the first vibronic peak of the GeV$^-$ center (^{73}Ge) in isotopically pure ^{12}C and ^{13}C diamonds.

IV. EFFECTS OF ^{12}C TO ^{13}C SUBSTITUTION

The most intriguing effect found in our experiments is the influence of the variation of carbon matrix isotopic composition on the position of the ZPL of the GeV$^-$ center, which moves by 2.65 meV on substitution of ^{12}C with ^{13}C (see Table I and Fig. 6). The similar values for other types of impurity-vacancy complexes (like the NV center or neutral vacancy GR1) of about 2–3 meV were previously reported in the work of Davies [31]. In his paper two possible explanations of this effect were proposed; one of them takes into account the vibronic effect (similar to the one used above to explain the shift caused by isotopic substitution of the Ge impurity), and the second one, specific isotopic compression of the carbon lattice.

These two possible explanations in the Huang-Rhys model (see inset in Fig. 3) correspond to either vertical shift of potential surfaces of the ground and excited states or to the change of curvature of any one (or both) of these surfaces. The linear term (which is the change of the stable coordinate position in the ground or excited state in the ^{13}C diamond) or the shift of the two surfaces in the horizontal direction does not directly influence the energy of the ZPL although it can change the relative intensities of corresponding optical transitions and the overall background. In the case of a strong sideband with significant background (like in the NV$^-$ center) such a change of relative intensities would indirectly influence the observable ZPL position shift, but in the GeV$^-$ center (due to the weakness of its sideband) such a possibility can be safely neglected.

Nonetheless, careful analysis of both factors demonstrates that both of them cannot be responsible for such large isotopic shift of the GeV$^-$ center ZPL. Indeed, isotopic compression of the diamond lattice is a well studied effect. According to literature data [32–34] it produces a relative diminishing of the unit volume of the ^{13}C diamond with respect to the ^{12}C one (practically natural diamond) $\Delta V/V = 5 \pm 1 \times 10^{-4}$. This effect is rather small, so it could not be measured by straightforward diffraction techniques that, in its turn, leads to a comparatively large error in the determination of its amplitude. If one is interested only in the effect which this volume change produces on the impurity's electron levels, then it seems natural to ignore whether this change is produced by isotopic substitution or by the external pressure. We will show that there is a difference and it is very significant. In natural diamond the equivalent compression can be attained by application of relatively small pressures (assuming that the bulk modulus of diamond is about 500 GPa, this pressure is equal to 0.25 GPa). Recent measurements of pressure dependence of the ZPL of GeV$^-$ [35] centers yield the value of energy shift equal to 3.1 meV/GPa (it is blueshifted with pressure rising). Thus, at best this volume change accounts for only 0.8 meV of 2.65 meV of the observed effect.

Although one might suppose that the rest of this shift ($2.65 - 0.8 = 1.85$ meV) can be attributed to the effect of mass change of vibrating atoms, it can be demonstrated that this is not the case. In fact, the oscillations of carbon atoms practically do not contribute to the energy of the first two oscillating levels (0 and 1) of the ground electronic state. Indeed, as follows from Table I (see also Fig. 6), the oscillation frequency of the first level in ^{12}C-^{73}Ge and ^{13}C-^{73}Ge remains practically unchanged (45.05 meV). So, one might expect that the zero-point energy (assuming oscillator to be harmonic) does not change either. Research at high pressure [35] also corroborates this conclusion: in the pressure range up to 6 GPa the value ν_g does not change significantly.

The only loophole in these arguments is the supposition that the isotopic compression and vibronic effects do significantly influence only the excited electron state (which cannot be directly measured in luminescence experiments). Nonetheless, we argue that it cannot produce such a large isotopic shift. Indeed, let us assume that the oscillations in the excited electronic state do involve movements of adjacent carbon atoms. Therefore, the substitution of ^{12}C to ^{13}C might produce some difference in the frequency of these oscillations, but the increase of oscillating atom mass should lead to decrease of its frequency. Taking into account that the ground electronic state remains unchanged, this would result in decrease of the ZPL energy. That is, this effect has an opposite sign than the actually observed one. So, the best case is to suppose that the carbon atom is not involved in the oscillations of the excited as well as the ground electronic states and the entire isotopic shift caused by isotopic substitutions of carbon matrix is due to the volume change. However, as was already shown, it only accounts for 0.8 out of 2.65 meV of the total shift.

The last resort is to ascribe this difference to anharmonicity effects, which are hard to register by direct experimental methods. As was demonstrated earlier, in the excited electronic state almost 5% of oscillation quanta ($\approx$3 meV) is due to anharmonicity. Some deviations of this value by substitution of carbon atoms with heavier isotopes would produce the desired effect. Nonetheless, the exact mechanism of such anharmonicity enhancement is not known. In other words we have demonstrated that the Grüneisen coefficients $\gamma = V/Z_1 \partial Z_1/\partial V$ obtained from the shifts of Z_1 line significantly differ in ^{12}C and ^{13}C diamonds.

There is one more remark. In some theoretical treatments (see, e.g., [36,37]) which take into account possible interaction of local vibration with long-wave acoustic phonons, the temperature shift of the ZPL is regarded as a possible indication of frequency defect sign. For the positive frequency defect ($\nu_e - \nu_g > 0$) these theories predict that the ZPL should be blueshifted with temperature rising. It is opposite to the actually observed effect: according to [4] on heating from the liquid helium to the room temperature the ZPL of the GeV$^-$ center is redshifted by about 2 meV. So, we believe that the basic assumptions of these theories are not applicable in the case of this color center.

Instead, there is a rather straightforward explanation obtained by taking into account thermal expansion of crystal lattice (in application to the SiV$^-$ center it was proposed in Ref. [38]) which predicts the right sign and by the order of magnitude realistic values of temperature shift. Indeed, thermal expansion of diamond from 4.2 to 300 K produces relative volume change $\Delta V/V = 8 \pm 1 \times 10^{-4}$, so, simply reproducing the arguments from above, we conclude that it will result in a redshift of the Z_1 line of about 1.4 meV. The discrepancy of this value from the experimental one may be caused by more subtle effects (such as softening of carbon bonds at higher temperatures which results in even more severe redshift) not taken into consideration in this simple model.

V. CONCLUSIONS AND FINAL REMARKS

As a final remark we apply the same arguments to the isostructural defect SiV$^-$. Effects caused by isotopic variations of the impurity were already studied by investigation of single-photon emitters in CVD diamond [39] and produced two isotopic shift coefficients $\delta Z_1/\delta m = 0.38$ and $\delta L_1/\delta m = 1.1$ meV/amu. Substitution of these values and $\nu_g = 65$ meV into Eq. (1) yields $\nu_e = 105$ meV. This value can be independently verified by optical absorption data on CVD diamond [40] (Fig. 7). In this experiment two broad vibronic features were observed with relative energies 29 and 95 meV, which can be attributed to transitions $1 \rightarrow 1'$ and $0 \rightarrow 1'$ respectively. Slight ($\approx$10%) overestimation of ν_e might be caused by anharmonicity effects.

We should note that different pieces of this model were earlier discovered by different research, but the whole picture remained elusive. The isotopic effect was theoretically predicted by Keil [27], the possible connection of the isotope effect in the SiV$^-$ center with the frequency defect was proposed in Ref. [39] (but without any numerical estimations), and the discrepancy between absorption and luminescence sidebands in some color centers is also a well-known effect

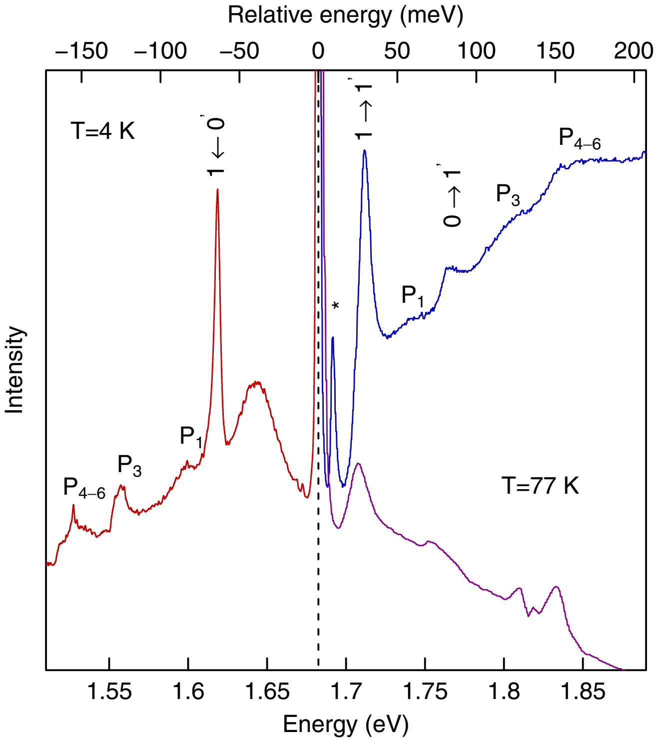

FIG. 7. Luminescence [39] (left) and absorption [40] (right) sidebands of the SiV$^-$ center in diamond. Two absorption spectra were collected on two different samples of different origin. The dashed line marks the position of the ZPL's strongest component. Transitions responsible for excitation of quasilocal modes are shown beside respective peaks. Features marked with P correspond to bulk phonon modes which are similar to that of the GeV$^-$ center (cf. Fig. 1). The line marked with an asterisk presumably is due to either some unidentified impurity or to weak quadruplet lines (Z_{3-4}) which are strongly blueshifted by the internal strain present in this sample.

which can be traced back to the works of a half century ago (see, e.g., Ref. [25]). The discrepancy between the absorption and luminescence sidebands of the SiV$^-$ center was even observed experimentally [41], but the authors did not pay any attention to this difference. However, the optical spectra in this work were collected on CVD samples of poor quality (it can be deduced from the too wide ZPL present in their plots) which can be caused by imperfections of CVD technology of their time, but still the transition $1 \rightarrow 1'$ can be detected in their data as a shoulder on the high-energy flank of the ZPL. We should stress once more that the technology of diamond HPHT synthesis from hydrocarbons was a crucial element which allows us to investigate simultaneously correlation between isotopic effects and optical properties of the impurity centers in diamond.

In summary, in this case, as well as in the GeV center, the large frequency defect causes disparity between absorption and emission (luminescence) spectra and rather strong dependence of the ZPL on the impurity's isotopic composition. Informally speaking, the isotope substitution of impurity atoms results in a modification of curvatures of potential surfaces in the ground and excited electron states without changing the energy difference between them. The isotope substitution of the carbon matrix does not influence (on the average) their curvatures but produces a small relative shift of these surfaces. In the latter case the shift is also accompanied by the significant deformation of potential surfaces that increases anharmonicity of the potential. The exact physical mechanism of such anharmonicity enhancement is yet to be discovered.

ACKNOWLEDGMENTS

The authors are grateful to Marina N. Popova and Boris Z. Malkin for fruitful discussions and critical remarks. The authors acknowledge prompt advice from Kirill N. Boldyrev and his help in accomplishment of experiments. The authors thank Tatiana V. Kotereva for preparation of germanium isotopes. This work was supported by RFBR Grants No. 15-02-05603, No. 16-02-01120, and No. 17-52-50075. PLE measurements were supported by FASO Russia (Project No. 0333-2014-0001).

APPENDIX: RELATIVE INTENSITIES OF ABSORPTION PEAKS

The theory of impurity centers in crystals with a frequency defect was developed by Keil [27]. Although he considered a simplified model ("quadratic" in his terms, with the minima of two harmonic potentials of the ground and excited states located at the same point or, in other words, without the Stokes shift), but in his treatment the isotopic shift for the ZPL was already predicted. Keil did not consider a generalized model with shifted potentials ("linear-quadratic" or "the third case" in his terms), because he believed that this is a simple generalization of his model lacking "new physical insight." We will show that in the generalized model the transitions between oscillatory levels of different parity, forbidden in Keil's model, become allowed and manifest themselves in the relative intensities of peaks observed in the absorption sideband of the impurity center.

One of the reasons why Keil did not consider a generalized model is that the linear term (or the Stokes shift) in the defects possessing the center of inversion is allowed only for even oscillatory modes. In the case of split-vacancy centers which belong to this class, these modes are A_{1g}, A_{2g}, and E_g. For all other oscillatory modes in split-vacancy centers the "quadratic" model is the simplest possible. Thus, if the frequency defect is accompanied with the nonzero Stokes shift, that indicates the parity of oscillatory modes involved in the optical transition.

In the GeV$^-$ absorption band relative intensities of peaks corresponding to transitions $0 \rightarrow 1'$ and $1 \rightarrow 1'$ can be evaluated using the data depicted in Fig. 4 and yield the value $I \equiv I(1 \rightarrow 1')/I(0 \rightarrow 1') \approx 0.2$. Obviously, for SiV centers shown in Fig. 7 the value I is totally different and larger than unity. So, this parameter is very sensitive to the individual characteristics of isostructural optical centers. Moreover, the transition $0 \rightarrow 1'$ takes place between oscillatory levels of different parity, so it is forbidden in the Keil model (where $I \rightarrow \infty$).

The value I is proportional to the ratio of corresponding Franck-Condon overlap integrals of respective wave functions squared (here $b = m\nu_e$, $a = m\nu_g$, and c is a coordinate shift of the two potentials):

$$I \propto \left(\frac{a \int x(x-c)\exp\{-ax^2/2 - b(x-c)^2/2\}dx}{\sqrt{2}\int (x-c)\exp\{-ax^2/2 - b(x-c)^2/2\}dx} \right)^2.$$

By taking a few Gaussian integrals we obtain

$$I \propto \frac{[1 - bac^2/(a+b)]^2}{2c^2 a} = \frac{\nu_g}{4E_{\rm Stokes}}\left(1 - \frac{2E_{\rm Stokes}\nu_e}{\nu_g(\nu_g+\nu_e)}\right)^2.$$

Here $E_{\rm Stokes} \equiv \nu_g ac^2/2$ is the Stokes shift in the ground state (or the energy of the ground state at the minimum of excited state potential surface relative to the minimum of the ground state potential). By setting $c = 0$ the Keil quadratic model is recovered and $I \to \infty$. So, the presence of both transitions $0 \to 1'$ and $1 \to 1'$ in the absorption sideband of split-vacancy centers demonstrates nonzero Stokes shift in them though its value significantly differs in SiV and GeV centers. For the GeV$^-$ center an experimental value $E_{\rm Stokes} \approx 27$ meV was earlier reported in Ref. [2] which corresponds to the value $I = 0.02$.

[1] T. Iwasaki, F. Ishibashi, Y. Miyamoto, Y. Doi, S. Kobayashi, T. Miyazaki, K. Tahara, K. D. Jahnke, L. J. Rogers, B. Naydenov, F. Jelezko, S. Yamasaki, S. Nagamachi, T. Inubushi, N. Mizuochi, and M. Hatano, Sci. Rep. **5**, 12882 (2015).

[2] Y. N. Palyanov, I. N. Kupriyanov, Y. M. Borzdov, and N. V. Surovtsev, Sci. Rep. **5**, 14789 (2015).

[3] V. G. Ralchenko, V. S. Sedov, A. A. Khomich, V. S. Krivobok, S. N. Nikolaev, S. S. Savin, I. I. Vlasov, and V. I. Konov, Bull. Lebedev Phys. Inst. **42**, 165 (2015).

[4] E. A. Ekimov, S. G. Lyapin, K. N. Boldyrev, M. V. Kondrin, R. Khmelnitskiy, V. A. Gavva, T. V. Kotereva, and M. N. Popova, JETP Lett. **102**, 701 (2015).

[5] V. Nadolinny, A. Komarovskikh, Y. Palyanov, I. Kupriyanov, Y. Borzdov, M. Rakhmanova, O. Yuryeva, and S. Veber, Phys. Status Solidi A **213**, 2623 (2016).

[6] V. S. Vavilov, A. A. Gippius, A. M. Zaitsev, B. V. Deryagin, B. V. Sinitsyn, and A. E. Alekseenko, Fiz. Tekh. Ploluprovodn. **14**, 1811 (1980) [Sov. Phys. Semicond. **14**, 1078 (1980)].

[7] C. D. Clark, H. Kanda, I. Kiflawi, and G. Sittas, Phys. Rev. B **51**, 16681 (1995).

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

[9] J. P. Goss, P. R. Briddon, M. J. Rayson, S. J. Sque, and R. Jones, Phys. Rev. B **72**, 035214 (2005).

[10] C. Hepp, T. Müller, V. Waselowski, J. N. Becker, B. Pingault, H. Sternschulte, D. Steinmüller-Nethl, A. Gali, J. R. Maze, M. Atatüre, and C. Becher, Phys. Rev. Lett. **112**, 036405 (2014).

[11] L. J. Rogers, K. D. Jahnke, M. W. Doherty, A. Dietrich, L. P. McGuinness, C. Müller, T. Teraji, H. Sumiya, J. Isoya, N. B. Manson, and F. Jelezko, Phys. Rev. B **89**, 235101 (2014).

[12] L. J. Rogers, K. D. Jahnke, M. H. Metsch, A. Sipahigil, J. M. Binder, T. Teraji, H. Sumiya, J. Isoya, M. D. Lukin, P. Hemmer, and F. Jelezko, Phys. Rev. Lett. **113**, 263602 (2014).

[13] E. A. Ekimov and M. V. Kondrin, Phys. Usp. (2017), doi:10.3367/UFNe.2016.11.037959.

[14] A. Gali and J. R. Maze, Phys. Rev. B **88**, 235205 (2013).

[15] A. Norambuena, S. A. Reyes, J. Mejía-Lopéz, A. Gali, and J. R. Maze, Phys. Rev. B **94**, 134305 (2016).

[16] A. Collins, G. Davies, H. Kanda, and G. S. Woods, J. Phys. C: Solid State Phys. **21**, 1363 (1988).

[17] Y. N. Palyanov, I. N. Kupriyanov, Y. M. Borzdov, A. F. Khokhryakov, and N. V. Surovtsev, Cryst. Growth Des. **16**, 3510 (2016).

[18] V. A. Davydov, A. V. Rakhmanina, S. G. Lyapin, I. D. Ilichev, K. N. Boldyrev, A. A. Shiryaev, and V. N. Agafonov, JETP Lett. **99**, 585 (2014).

[19] J. E. Field (ed.), *The Properties of Natural and Synthetic Diamond* (Academic Press, London, 1992).

[20] T. Ando, H. Haneda, M. Akaishi, Y. Sato, and M. Kamo, Diamond Relat. Mater. **5**, 34 (1996).

[21] A. M. Zaitsev, *Optical Properties of Diamond: A Data Handbook* (Springer Science & Business Media, Berlin, Heidelberg, 2013).

[22] G. Thiering and A. Gali, Phys. Rev. B **94**, 125202 (2016).

[23] K. Iakoubovskii and G. Davies, Phys. Rev. B **70**, 245206 (2004).

[24] A. M. Zaitsev, Phys. Rev. B **61**, 12909 (2000).

[25] E. F. Sheka, Sov. Phys. Usp. **14**, 484 (1972).

[26] K. Huang and A. Rhys, Proc. R. Soc. London A **204**, 406 (1950).

[27] T. H. Keil, Phys. Rev. **140**, A601 (1965).

[28] A. Bosak and M. Krisch, Phys. Rev. B **72**, 224305 (2005).

[29] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter **21**, 395502 (2009).

[30] A. T. Collins and S. Rafique, Proc. R. Soc. London A **367**, 81 (1979).

[31] G. Davies, Physica B **273-274**, 15 (1999).

[32] H. Holloway, K. C. Hass, M. A. Tamor, T. R. Anthony, and W. F. Banholzer, Phys. Rev. B **44**, 7123 (1991).

[33] M. Muinov, H. Kanda, and S. M. Stishov, Phys. Rev. B **50**, 13860 (1994).

[34] P. Gillet, G. Fiquet, I. Daniel, B. Reynard, and M. Hanfland, Phys. Rev. B **60**, 14660 (1999).

[35] A. A. Razgulov, S. G. Lyapin, A. P. Novikov, and E. A. Ekimov, in *Proceedings of 59th Moscow Institute of Physics and Technology Conference "Challenges of Fundamental and*

Applied Science in Physics," 21–26 November, Moscow, 2016 (in Russian).

[36] Z. Cheng, Phys. Rev. B **60**, 15747 (1999).

[37] V. Hizhnyakov, H. Kaasik, and I. Sildos, Phys. Status Solidi B **234**, 644 (2002).

[38] E. Neu, C. Hepp, M. Hauschild, S. Gsell, M. Fischer, H. Sternschulte, D. Steinmüller-Nethl, M. Schreck, and C. Becher, New J. Phys. **15**, 043005 (2013).

[39] A. Dietrich, K. D. Jahnke, J. M. Binder, T. Teraji, J. Isoya, L. J. Rogers, and F. Jelezko, New J. Phys. **16**, 113019 (2014).

[40] A. Zaitsev, B. Deljanin, A. Peretti, M. Alessandri, and W. Bieri, in *Contributions to Gemology, 14*, edited by A. Peretti (DR Peretti Co. Ltd, Bangkok, Thailand, 2014), pp. 41–55.

[41] K. Iakoubovskii and G. J. Adriaenssens, Phys. Rev. B **61**, 10174 (2000).