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Vibronic spectra of impurity-related optical centers in diamond

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Electron-vibrational spectra of impurity-related optical centers of diamond are analyzed in terms of interaction with quasilocal and local vibrations connected with impurity atoms as well as with the short-wavelength lattice phonons. It is shown that the theoretical expressions for the energy and resonance width of quasilocal vibrations in crystals caused by heavy isotopic impurity atoms [Brout and Visscher, Phys. Rev. Lett. **9**, 54 (1962)] can be satisfactorily applied for description of the acousticlike quasilocal vibrations in the diamond lattice caused by chemically different impurities. The model of quasilocal vibrations can also be successively applied for impurities (e.g., nitrogen) with masses comparable with the mass of the host carbon atom, provided these impurities form rigid clusters with host atoms vibrating as heavy units. The model is used for analysis of the optical centers in diamond containing Ti, Cr, Zn, Ag, Tl, W, Ni, Co, Ta, Si, and N impurities. Based on the results of this analysis, atomic models of the 3.188 eV N-related, 1.249 eV Ti-related, and 2.56 eV Ni-related centers are proposed.

I. INTRODUCTION

More than 500 electronic optical centers have been detected in the absorption and/or luminescence of diamond.[1,2] Half of them are believed to be impurity related. A vast majority of these centers are due to nitrogen. No other impurity exhibits in diamond such a great variety of optical centers as does nitrogen. However, nickel and cobalt may also produce many different optical centers under certain doping, irradiation, and annealing conditions. Other impurities give rise, as a rule, to only one characteristic center per species. By now at least the following impurities have been intentionally introduced into diamond during growth or by ion implantation with the aim of creating the related optical centers: **H**, **He**, **Li**, Be, **C**, **B**, **N**, **O**, F, **Ne**, Na, Al, S, **Si**, **P**, Ar, **Ti**, V, **Cr**, Mn, Fe, **Co**, **Ni**, Cu, **Zn**, Ga, **As**, Y, **Zr**, Nb, Mo, Pd, **Ag**, Cd, Sb, **Xe**, **Ta**, **W**, Pt, Au, **Tl**, and Er. Those in bold have been found to form optical centers. A peculiarity of diamond is that it is almost impossible to predict the energy range of the radiative electronic transitions at impurity centers based on the electronic structure of these impurities when in the atomic, ionic, or molecular state, as can be done for other solids. The short and strong covalent bonds of diamond modify the electronic structure of any introduced atoms so strongly that their inherent electronic structure (even for compact multicharged ions of transition metals or rare earths) is no longer a decisive factor in formation of optical centers. Such behavior is also characteristic, though to a lesser extent, of other superhard semiconductors like cubic boron nitride and beryllium oxide,[3] the crystal fields of which may also modify the electronic structure of impurity atoms considerably. The crystal field in lattices of superhard semiconductors is so strong that even noble gases, when placed in certain lattice positions, lose their chemical inertness and form covalently bonded defects with surrounding host atoms, which can detected as characteristic optical centers.[4]

The method of impurity introduction into diamond also plays an important role in the formation of impurity-related optical centers since it may deliver the necessary intrinsic structural components (for instance, self-interstitial atoms or vacancies) to the impurity atoms. It is this peculiarity that allows some optical centers to be readily created by doping during growth, but others only when the impurity is inserted by ion implantation.

The most characteristic features of the impurity-related optical centers are the energies of their electronic transitions. The electronic structure of a defect containing an impurity atom is totally different from that of the host carbon atoms. Due to this, every impurity-related center is characterized by its optical spectrum and principally by the spectral position of the zero-phonon lines (ZPLs). The ZPL energy is usually considered to be the main parameter distinguishing and characterizing an optical center. However, though relatively seldom, some different centers may have ZPLs with almost coinciding spectral positions. In this case, when the spectral resolution of the instrument is not sufficient, there is a danger of confusion. Examples of such centers are the nitrogen-related $H3$ center with ZPL at 502.3 nm and the radiation intrinsic $3H$ center with ZPL at 502.5 nm, and the nitrogen-related $N3$ center with ZPL at 415.2 nm and a specific center with ZPL at 415.2 nm observed in luminescence of some chemical-vapor-deposited (CVD) diamond films.[1,2] Even the $GR1$ center with ZPL at 741 nm was confused with the silicon-related center with ZPL at 738 nm by several authors.

To resolve the problem of the identification of optical centers in case of coinciding ZPLs one should compare their other parameters. Fortunately, optical centers possess one more parameter that, along with the ZPL, is very specific to each center. This is the energy and relative intensity of the vibration-assisted electronic transitions (vibronic sidebands), characterizing the electron-vibrational coupling at the optical center. There are no two different optical centers in diamond that would exhibit equal vibronic sidebands. However, there are some centers showing rather similar electron-phonon coupling, for instance, the 2.526 eV center observed in natural type-IaB diamonds and the 2.523 eV center created in some natural type-Ia diamonds by ion irradiation[2,5] (Fig. 1).

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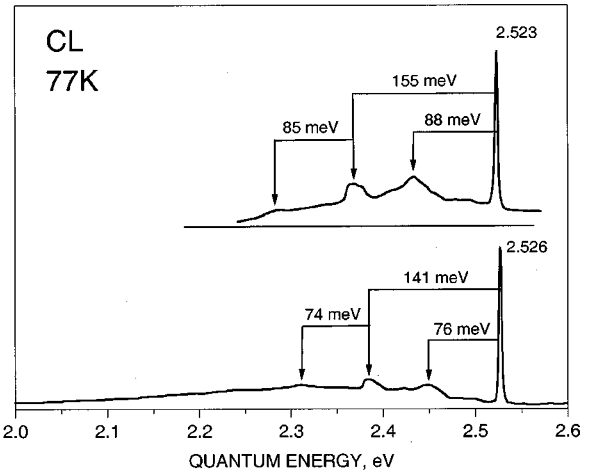


FIG. 1. CL spectra (taken at a temperature of 77 K) of the 2.526 eV center in a natural type-IaB diamond (Ref. 5) and the 2.523 eV center in a natural type-Ia diamond as implanted with Si^+ ions of energy 300 keV. The vibronic spectra of both centers have a similar structure. The energies of the zero-phonon electronic transitions are very close to each other. However, the energies of the dominating phonons differ by a coefficient of $\hbar\omega_{2.526}/\hbar\omega_{2.523} = 0.9$.

Thus, to be on the safe side, a reliable identification of optical centers must include measurements of the spectral positions of the ZPLs as well as analysis of the spectral structure of the vibrational sidebands.

The aim of the present paper is to provide further insight into the nature of the vibrational spectra of impurity-related centers of diamond with particular emphasis on the role of quasilocal vibrations. It is shown that for some centers the analysis of the vibrational sidebands provides information that is sufficient to propose atomic models of the corresponding defects.

II. ELECTRON-VIBRATIONAL COUPLING OF OPTICAL CENTERS RELATED TO HEAVY IMPURITIES

Essentially, the vibrational sideband of an impurity-related optical center is formed due to interaction with intrinsic lattice phonons as well as with local (the energy of local vibrations is above the energy range of the matrix phonons) and quasilocal (the energy of quasilocal vibrations is within the energy range of the matrix phonons) vibrations localized at atom fragments of the corresponding defect. The energy values and type of the local and quasilocal vibrations are determined by the masses of the vibrating atoms inside the defects and the interatomic forces driving these vibrations. Thus the impurity-related centers may have an additional specific characterization parameter distinguishing them from the intrinsic centers, namely, the local and quasilocal vibrations involving the impurity atoms.

The origin of the vibrational sidebands of optical centers in diamond is still an obscure subject. There are only a few publications on the subject, for instance, those analyzing the nature of local and quasilocal vibrations of the nitrogen-related centers with ZPLs at 3.188 and 2.807 eV,[6–8] of the silicon-related center with ZPL at 1.681 eV,[9] and of the intrinsic $GR1$ center.[10] A simple and effective approach to the interpretation of the vibrational sidebands was proposed by Steeds *et al.* in Ref. 11, who draw attention to the fact that the expressions for the frequency and width of the resonant peak of quasilocal vibrations involving heavy atoms obtained in Ref. 12 could very well describe the vibrational spectrum of the tungsten-related center in diamond.

When studying the spectra of the optical centers related to heavy impurity atoms, the following common peculiarities can be noticed. (i) There is relatively low electron-phonon coupling. Usually the Huang-Rhys factor for all the vibrational modes interacting with the center, $S \leqslant 1$. (ii) Several relatively narrow lines are present, the spectral width of which may range from 5 to 15 meV. Very often only one of them is fine structured. This structured line is believed to be the true ZPL of the center. (iii) The narrow lines (including the ZPL) may form an equidistant structure (in energy scale) in the low-energy range of the vibrational sideband. Usually the energy difference between the neighboring lines ranges from 20 to 40 meV. The narrow lines other than the ZPL do not exhibit any fine structure and are suspected to be due to quasilocal vibrations. (iv) Predominantly, interaction is with lattice phonos of energy above 140 meV, which are believed to be short-wavelength optical phonons of the diamond lattice.

A defect containing a heavy impurity atom of a mass M_I considerably exceeding the mass of the host atom M_C can generate only quasilocal vibrations involving this impurity. If the impurity atom does not noticeably change the forces of the interatomic interactions inside the defect (for instance, for isotopic impurities and acoustic vibrations), the frequency ω_{QL} and the resonance width $\Delta\omega_{QL}$ of the quasilocal vibration are described by the following expressions:[12]

$$\omega_{QL} = \omega_D \sqrt{M_C/3(nM_I - M_C)},$$

$$\Delta\omega_{QL} = \frac{\pi}{6}\omega_D \frac{M_C}{nM_I - M_C},$$

where $\omega_D = 150$ meV is the Debye frequency of the diamond lattice and n is the number of impurity atoms involved in the quasilocal vibration. It is important to note that the quasilocal vibration described by these expressions is an acoustic one. This means that the impurity atom and its next carbon neighbors vibrate with the same phase. For an impurity atom of mass over 30 a.m.u., the energies of acoustic quasilocal vibrations do not exceed 75 meV. That is, they get into the energy region of low vibrational density of the diamond lattice (Fig. 2). Thus, optical centers containing impurity atoms ranging from Si (28 a.m.u.) to Tl (204 a.m.u.) may exhibit in their spectra quasilocal vibrations of energies from 75 down to 22 meV with corresponding resonance widths from 59 down to 5 meV. Note that for very heavy impurities the lines due to quasilocal vibrations are expected to be almost as narrow as ZPLs.

A peculiarity of the electron-phonon coupling with lattice phonons at impurity-related optical centers is the predominant interaction with modes whose wave vectors are at critical points of the Blillouin zone boundary. There are two reasons explaining this behavior. First, the phonon density has its maximum at the critical points and, consequently, the probability of electron-phonon interaction with these modes is the highest. Secondly, at the Brillouin zone boundary the

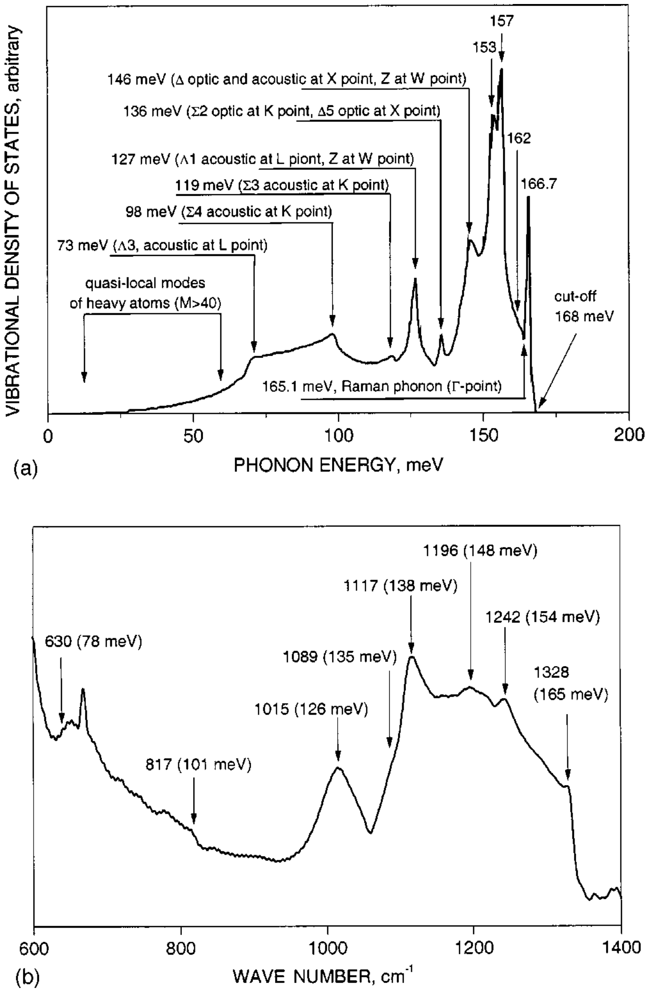


FIG. 2. (a) Calculated vibrational density of states of diamond lattice (Ref. 36). Most of the marked features can be found in vibrational sidebands of optical centers related to heavy impurity atoms. For comparison an absorption spectrum (taken at room temperature) of a natural type-IIa diamond irradiated with high-energy carbon ions is given in (b). It is seen that the experimental spectrum qualitatively resembles the calculated curve of the vibrational density of states. Some features of the spectrum have good quantitative coincidence with corresponding maxima of the calculated phonon density curve.

phonons have the shortest wavelengths. Since the impurity-related optical centers are mostly point defects (the characteristic size of point defects is of a few interatomic distances), the electron-phonon coupling at them occurs most effectively with short-wavelength vibrations, the wavelength of which is comparable with the defect size. The second peculiarity of electron-phonon interaction is particularly straightforward for acoustic phonons. Indeed, the change of interatomic distances by acoustic vibrations is inversely proportional to their wavelength. Since the vibration-related change of interatomic distances inside the defect is the main factor in its electron-phonon interaction, long-wavelength acoustic phonons scarcely participate in the electron-phonon coupling at point defects. The optical phonons behave rather differently because they provide antiphase movements of neighboring atoms at any wavelengths. For optical modes the influence of the wavelength on the change of the interatomic distance between vibrating atoms is relatively weak. An effective coupling may occur with relatively long-wavelength optical phonons. Essentially, the optical vibrations, irrespective of wavelength, cause much stronger change of the interatomic distances between the vibrating atoms in comparison with that caused by acoustic vibrations. Therefore the optical modes always dominate the electron-phonon coupling at point defects.

Based on these considerations, one can expect that the vibrational sidebands of optical centers are dominated by optical phonons and short-wavelength acoustic phonons as well as by quasilocal and local vibrations. Thus any feature in the vibrational sidebands of energy below, say, 70 meV is very probably a quasilocal vibration, and any feature of energy above 168 meV is a local vibration.

III. OPTICAL CENTERS WITH HEAVY IMPURITIES

A. Titanium

Cathodoluminescence (CL) of the Ti-related optical center in diamond was reported in Ref. 13. The center was created in natural diamonds by Ti^+ ion implantation and subsequent annealing at a temperature of 1400 °C. The CL spectrum of the center taken at 4 K is shown in Fig. 3(a). The center exhibits two relatively narrow lines at 1.217 and 1.249 eV along with broader bands with maxima at 1.13 and 1.16 eV. Only the line at 1.249 eV shows fine structure. This line is believed to be the true ZPL of the center. The other features are ascribed to vibronic replicas of the ZPL due to interaction with vibrations of energies of 32, 85, and 119 meV. The small width of the 1.217 eV line [the full width at half maximum is 5 meV] and relatively small energy separation from the ZPL (only 32 meV) suggest that this line may be caused by a quasilocal vibration due to the Ti impurity. A calculation of the energy and width of the resonance peak of quasilocal vibrations involving one Ti atom strongly conflicts with the experimentally measured values (see Table I). A much better coincidence between the experimental and calculated data is attained when assuming incorporation of two Ti atoms into the Ti-related defect. In this case there is excellent quantitative agreement for the energy of the quasilocal vibration. However, the calculated resonance width is twice as high as that observed experimentally.

The other vibrational features of energies 85 and 119 meV relate probably to the maxima at 98 and 119 meV of the vibrational density of states of the diamond lattice, both corresponding to acoustic phonons with the shortest wavelengths propagating along the ⟨110⟩ direction [Fig. 3(b)]. Based on these facts, a very tentative model of the Ti-related center could be a complex of two Ti atoms in the nearest tetrahedral (or hexagonal) interstitial positions placed along the ⟨110⟩ axis, or a ⟨110⟩ split interstitial of two Ti atoms [Fig. 3(b)]. Indeed, such a configuration looks to be particularly sensitive to the lattice deformations caused by the acoustic phonons in the ⟨110⟩ direction.

B. Chromium

A specific center with the main line at 1.673 eV (741 nm) is observed in the CL of natural low-nitrogen type-IIa diamonds implanted with Cr^+ ions and subsequently annealed at temperatures above 800 °C (Fig. 4). In addition to the

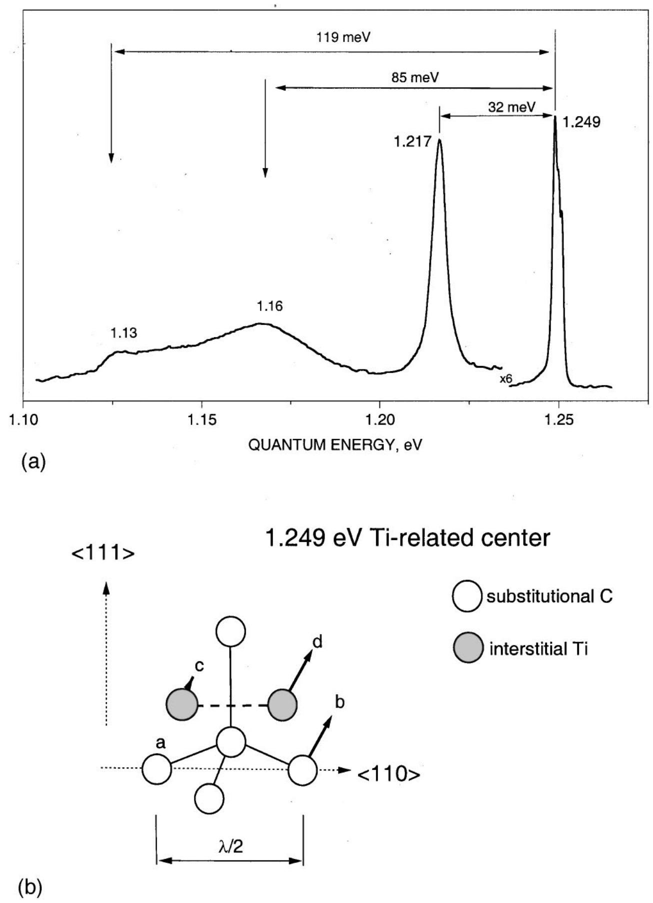


FIG. 3. (a) CL spectrum (taken at liquid nitrogen temperature) of a natural diamond implanted with Ti^+ ions at room temperature and subsequently annealed at a temperature of 1400 °C (Ref. 13). (b) A possible atomic model of the Ti-related optical center: a pair of Ti atoms in neighboring tetrahedral interstitial positions along the $\langle 110 \rangle$ axis. Note that this model assumes that the Ti-Ti bond length is shorter than one-half wavelength of the Σ phonon at the K point. The movements of the atoms involved in the Σ acoustic vibrations are shown with arrows.

main line, which is most probably the ZPL, the center exhibits several other relatively narrow peaks at 1.644 eV (754 nm), 1.61 eV (770 nm), and 1.569 eV (790 nm) separated from each other by an energy of 31 meV. Because of the low intensity of the Cr-related center, the real widths of these lines have not been measured. From the available spectrum, however, it can be assumed that the line widths are below 12 meV. It is assumed that the lines at 754, 770, and 790 nm are due to quasilocal vibrations of Cr atoms. As in the case of the Ti-related center, excellent agreement between the calculated and experimental parameters of the quasilocal vibration can be obtained by suggesting incorporation of two Cr atoms into the corresponding defect (see Table I). Due to the low intensity of the Cr-related center and its overlapping with the broad and intense *B* band (the *B* band is a very prominent feature of type-IIa diamonds subjected to implantation by any ions with subsequent annealing at temperatures above 700 °C;[1,2] see Fig. 6(a), it is not possible to recognize any vibrational features that are due to interaction with high-energy lattice phonons.

C. Zinc

The Zn-related optical center can be created in type-IIa diamonds by Zn^+ ion implantation followed by an annealing at temperatures above 800 °C. The most prominent feature of the center is its ZPL at 2.393 eV (518 nm) (Fig. 5). The ZPL is accompanied by relatively narrow lines at 2.363 eV (524.5 nm) and 2.330 eV (532 nm), as well as by a broader band peaking at 2.24 eV (553 nm). The spectral parameters of the two former lines can be well ascribed to a quasilocal vibration of energy 30 meV located at a defect involving two Zn atoms (Table I). The broad band can be attributed to interaction with the optical phonons forming the most intense peak of the diamond phonon density curve in an energy range from 140 to 165 meV [Fig. 2(a)].

D. Silver

The Ag-related optical center with its main ZPL at 3.110 eV (398.5 nm) is created by Ag^+ ion implantation and annealing at temperatures above 800 °C. This center exhibits fairly strong CL. Relatively low concentration of the Ag atoms (below $10^{18}\,cm^{-3}$) may result in a strong CL of the 398.5 nm center, when implanted into a low-nitrogen natural diamond [Fig. 6(a)]. In the spectral area around the ZPL four narrow lines can be resolved, forming two pairs of lines with a correlating intensity. It can be suggested that the lines at 3.117 eV (397.7 nm) and 3.110 eV (389.5 nm) are true ZPLs, whereas the lines at 3.095 eV (400.5 nm) and 3.089 eV (401.2 nm) are their replica, due to interaction with quasilocal vibrations of energy 21 meV. Calculation of the energy and resonance width of quasilocal vibrations involving Ag atoms gives excellent agreement, when assuming simultaneous vibration of two Ag atoms (see Table I). In addition to the quasilocal mode, the Ag-related center also interacts with optical phonons, the most intensive of which have energies of 122, 142, and 162 meV. These values are very close to the energies of corresponding maxima in the vibrational density of states of diamond (Fig. 2).

E. Thallium

Ion implantation of Tl^+ ions produces in diamond relatively strong CL of a center with ZPL at 2.019 eV (614 nm), Fig. 7. The center can first be detected after postimplantation annealing at temperatures above 700 °C. The Tl-related center exhibits a very low electron-phonon coupling with acoustic lattice modes. The main features of the vibrational sideband are two relatively narrow peaks at 1.996 eV (621 nm) and 1.974 eV (628 nm), a structured band in a spectral region from 1.89 eV (655 nm) to 1.85 eV (670 nm), and four peaks at 1.753 eV (707 nm), 1.738 eV (713 nm), 1.698 eV (730 nm), and 1.682 eV (737 nm). The former two lines can be ascribed to a quasilocal vibrational mode of energy 21 meV localized at a Tl-containing defect involving only one Tl atom. The calculated values of the energy and resonance width of the corresponding quasilocal vibration coincide well with the experimentally measured values (Table I).

The structured band is formed of features arising due to interaction with lattice optical phonons of energies 132, 140, 159, and 167 meV. All these values closely coincide with the main features of the diamond phonon density curve, actually

TABLE I. Vibrational parameters of impurity-related optical centers in diamond.

Species and atomic mass (a.m.u.)	ω_R (meV) (number of impurity atoms in parentheses)	$\Delta\omega_R$ (meV)	Impurity content	Phonons (meV)
Ti(48)	experiment: 32	5	2 Ti	85, 119
1.249 eV center	calculations: 51 (1Ti); 32.7 (2Ti)	26 (1Ti); 11.2 (2Ti)		(Σ acoustic at *K* point)
Cr(52)	experiment: 31	$<$12	2Cr	not detected
1.673 eV center	calculations: 47 (1Cr); 31.3 (2Cr)	24 (1Cr); 10 (2Cr)		
Zn(65)	experiment: 30	8	2Zn	152
2.393 eV center	calculations: 41.2 (1Zn); 27.6 (2Zn)	17.7 (1Zn); 8 (2Zn)		
Ag(108)	experiment: 21	4	2Ag	122, 142, 162
3.110 eV center	calculations: 30.6 (1Ag); 21 (2Ag)	9.8 (1Ag); 4.6 (2Ag)		
Ti(204)	experiment: 21	6	Ti	132, 140, 159, 167
2.019 eV center	calculations: 21.6 (1T1)	4.6 (1T1)		
W(184)	experiment: 24	5.5	W	165
1.735 eV center	calculations: 23 (1 W)	6 (1W)		
Ni(58.7)	experiment: ~50	~30	Ni	99, 127, 165
1.4 eV center	calculations: 44 (1Ni)	20 (1Ni)		
Ni(58.7)	experiment: 24; 36	8 for both	2Ni	125 (147?)
2.56 eV center	calculations: 44 (1Ni)	20 (1Ni)		
	29.2 (2Ni)	8.9 (2Ni)		
	35.7 (1Ni+2C)	13.3 (1Ni+2C)		
	24.2 (2Ni+4C)	6.1 (2Ni+4C)		
Ni(58.7)	experiment: 26	9	2Ni	157
3.1 eV center	calculations: 44 (1Ni); 29.2 (2Ni)	20 (1Ni); 8.9 (2Ni)		
Ni(58.7)	experiment: 26	8	2Ni	85, 165
2.292 eV center	calculations: 29.2 (2Ni)	8.9 (2Ni)		
Co(59)	experiment: 44	13	Co	
1.852 eV center	calculations: 43 (1Co)	20 (1 Co)		
Co(59)	experiment: 25; 56	~13; ~20	2Co	119
1.989 eV center	calculations: 44 (1Co); 29 (2Co)	20 (1Co); 8.8 (2Co)		
Co(59)+Ni(14)	experiment: 38	~13	Co+N	100 (for the 2.277 eV center)
2.367 and 2.277 eV centers	calculations: 38.4 (1Co+1N)	15.4 (1Co+1N)		
Ta(181)	experiment: 26	~10	Ta	not detected
1.774 eV center	calculations: 23	6		
Si(28)	experiment: 64; 41	6; 30	2Si	90, 125, 148, 155, 163
1.681 eV center	calculations: 75 (1Si); 45 (2Si)	59 (1Si); 21 (2Si)		
N(14)	experiment: 58 (57 in ^{13}C); 178.8	~20	N	73, 98, 116, 125, 131, 137,
3.188 eV center	calculations: 58.8 (1N+2C) (57.8 in ^{13}C);	36 (1N+2C)		151, 154, 162, 165, 190.4 (Λ_1
	174 (C_4N-$C_{(I)}$)			phonons at *L* point dominate, ⟨111⟩ direction)

reproducing the phonon density curve in a range from 130 to 168 meV (Fig. 2). This peculiarity suggests that the Tl atom does not change the symmetry of the surrounding diamond lattice and does not disturb the density distribution of short-wavelength optical phonons. To satisfy this condition the Tl atom should occupy a tetrahedral position. Since the Tl atom is a large one, the most likely position is expected to be the tetrahedral interstitial one.

The final most energetic four lines of the vibrational sideband are merely two-phonon replicas due to interaction with optical phonons. The energy positions of these lines relative to the ZPL are exactly twice the energies of the features that form the structured band at 660 nm.

F. Tungsten

Luminescence of the tungsten-related center is excited in CVD diamond films grown by the hot-filament method using a tungsten filament (Fig. 8).[11,14,15] The center is excited in both cathodo- and photoluminescence. A specific feature of the W-related center is the presence of at least five ZPLs in a spectral region from 1.761 (704) to 1.738 eV, (713 nm). The most intense ZPL (the *W*5 center) is at 1.735 eV (713 nm). The vibrational sideband of the center is dominated by a quasilocal vibration of energy 24 meV involving one W atom[11] (Table I). In CL a relatively broad band is observed at 125 meV away from the main ZPL. Comparing this energy with the phonon density curve of diamond, one can see good

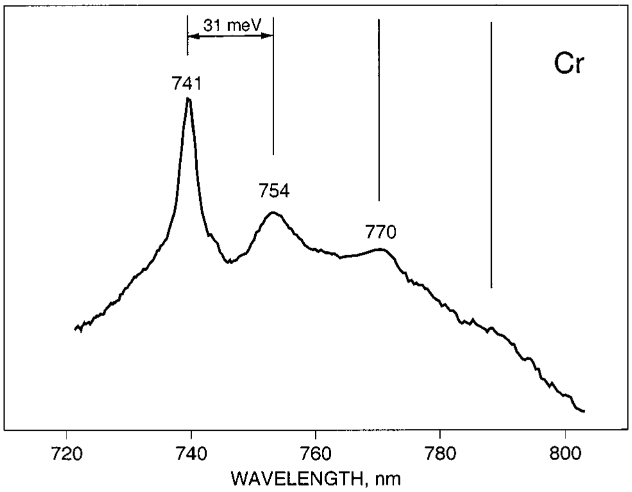


FIG. 4. CL spectrum (taken at 80 K) of a very-low-nitrogen natural diamond implanted with 300 keV Cr^+ ions at a dose of $10^{14}\,\mathrm{cm}^{-2}$ and subsequently annealed at a temperature of 1400 °C. Vertical lines show structure due to interaction with quasilocal vibrations of two Cr atoms.

agreement with one of the strong features of the phonon density of diamond, which could originate from $\Lambda1$ acoustic phonons at the L point, $\Sigma1$ acoustic vibrations at the K point, or Z phonons at the W point.

G. Nickel

Ni produces many optical centers in diamond, depending on doping method. The most well known of them are the centers with ZPLs at 1.4 eV (885 nm), 2.56 eV (484 nm), and 3.1 eV (400 nm) (Figs. 9–11). The centers at 1.4 and 2.56 eV are readily created when doping diamond with Ni both during growth and by ion implantation. Both centers are active in luminescence and absorption. In contrast, the 3.1 eV center is observed only in absorption. Up to now, there

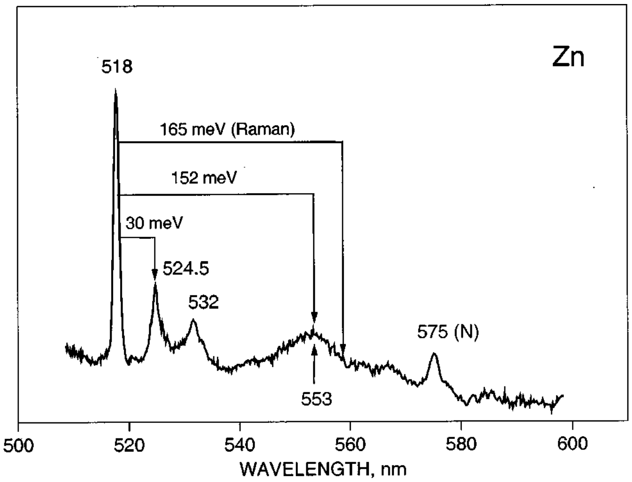


FIG. 5. CL spectrum (taken at 80 K) of a very-low-nitrogen natural diamond implanted with 350 keV Zn^+ ions at a dose of $10^{14}\,\mathrm{cm}^{-2}$ and subsequently annealed at a temperature of 1400 °C. The phonon-assisted spectrum of the Zn-related center spreads to the Raman phonon energy. The peaks at 524.5 and 532 nm are replicas of the ZPL due to interaction with quasilocal vibrations of Zn atoms.

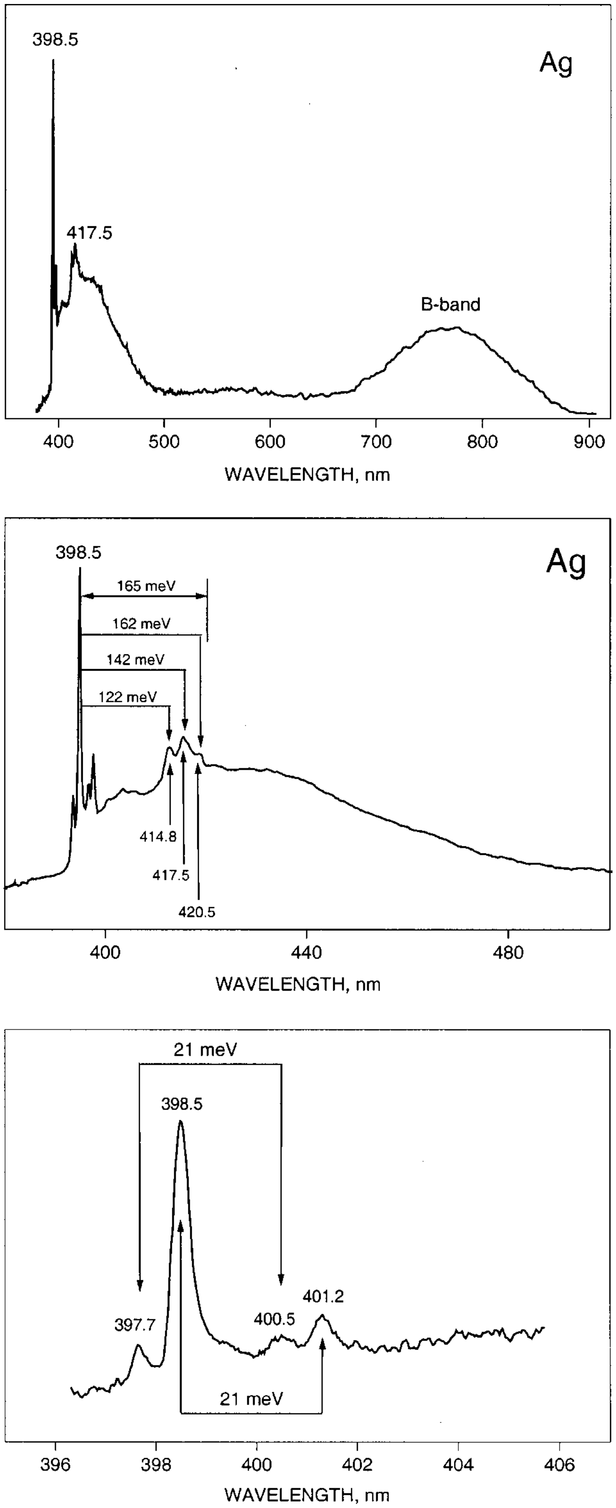


FIG. 6. CL spectrum (taken at 80 K) of a very-low-nitrogen natural diamond implanted with 350 keV Ag^+ ions at a dose of $10^{14}\,\mathrm{cm}^{-2}$ and subsequently annealed at 1400 °C. The lines at 414.8, 417.5, and 420.5 nm are replicas due to interaction with short-wavelength optical phonons of energy 122, 142, and 162 meV.

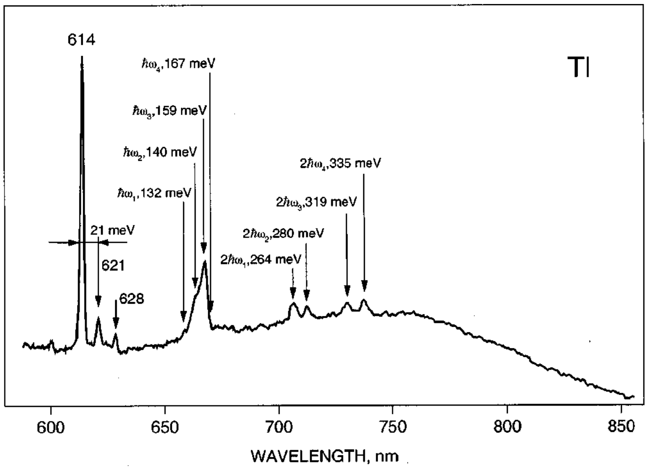


FIG. 7. CL spectrum (taken at liquid nitrogen temperature) of a very-low-nitrogen natural diamond implanted with 350 keV Tl^+ ions at a dose of $10^{14}\,cm^{-2}$ and subsequently annealed at 1400 °C. The narrow lines at 621 and 628 nm are due to interaction with quasilocal vibrations involving one Tl atom. The band at 667 nm is a vibrational sideband due to interaction with optical phonons.

are no reports on creation of the 3.1 eV center by Ni^+ ion implantation.

1. The 1.4 eV center

The vibronic band of the 1.4 eV center is dominated by a broad maximum at an energy of 60 meV apart from the ZPL. This maximum can be fitted by a superposition of a Gauss-shaped band of width 30 meV lying about 50 meV from the ZPL and the low-energy tail (below 70 meV) of the diamond phonon density. Assuming that the origin of the 50 meV band may be a quasilocal mode related to the Ni impurity, its energy can be compared with energies of quasilocal vibrations calculated for one and two vibrating Ni atoms. Qualitative agreement is obtained for the quasilocal vibration involving one Ni atom (Table I). Other features of the vibronic sideband of the 1.4 eV center are those of energies 99, 127, and 165 eV. All these vibrations can be ascribed to lattice phonons corresponding to the maxima of the phonon density curve. Thus the model of quasilocal vibrations assumes incorporation of one nickel atom in the atomic structure of the 1.4 eV center. It is in agreement with the one-Ni-atom-atom-model of Refs. 16 and 17 based on analysis of the fine structure of the ZPL related to different Ni isotopes. Indeed, the ratio of the experimentally measured intensities of the ZPL components deviates from the natural abundance of Ni isotopes within a 13% error. In contrast, when assuming incorporation of two Ni atoms in the 1.4 eV center, the experimental and calculated data differ by a factor of 3.5 (see Table II).

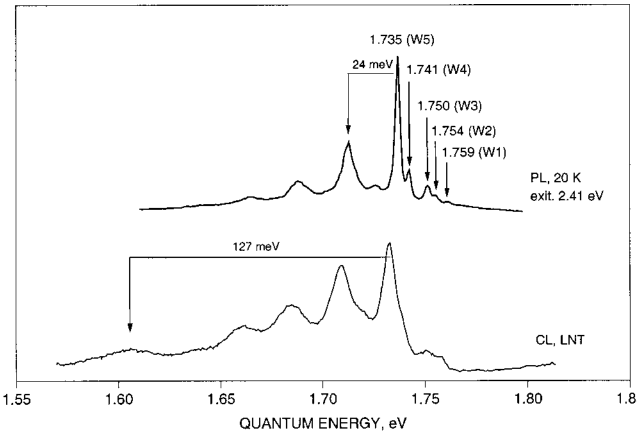


FIG. 8. PL and CL spectra (recorded at liquid nitrogen temperature and at 20 K, respectively) of CVD diamond films grown using a tungsten filament. The lines W1 through W5 are believed to be ZPLs of the W-related center (Refs. 11, 14, and 15). The 24 meV quasilocal vibration of the W atom dominates the spectrum.

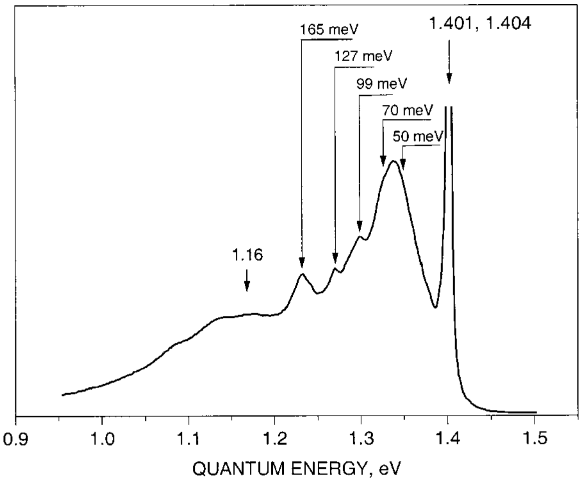


FIG. 9. CL spectrum (taken at liquid nitrogen temperature) of the 1.4 eV Ni-related center showing spectral structure of its vibrational sideband (Ref. 37).

2. The 2.56 eV center

The spectrum of the 2.56 eV nickel-related center exhibits a fine-structured ZPL and relatively narrow bands, which are separated from the ZPL by energies of 24, 36, 125, and 147 meV. The first two bands are believed to be due to quasilocal vibrations.[18] Relatively good agreement can be obtained for a quasilocal vibration involving two Ni atoms (Table I). It is

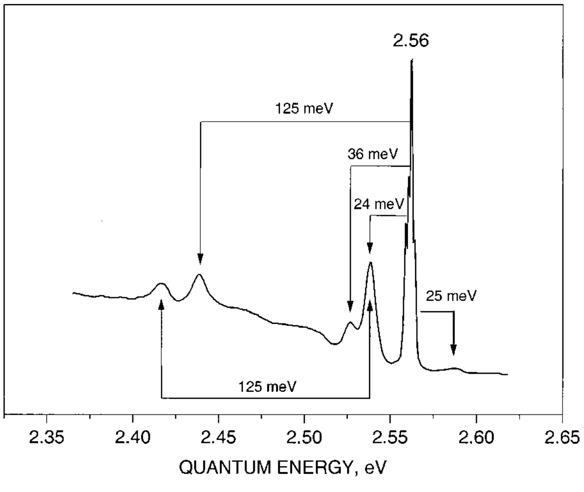


FIG. 10. CL spectrum (taken at liquid nitrogen temperature) of the 2.56 eV Ni-related center showing spectral structure of its vibrational sideband.

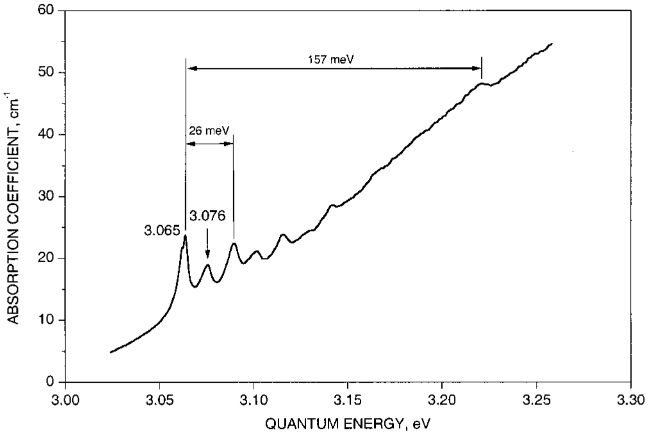


FIG. 11. Absorption spectrum of the 3.1 eV center taken from octahedral growth sector of a synthetic diamond grown employing a nickel catalyst with 2.5 at. % Ti added (Ref. 19). The 26 meV quasilocal vibration of two Ni atoms forms a periodic structure in a spectral range from 3.06 to 3.12 eV. The center clearly exhibits interaction with optical phonons of energy 157 meV (maximum of the diamond phonon density).

interesting that the calculated value of 29.2 meV for the 2Ni quasilocal vibration lies in between the two peaks observed experimentally (24 and 36 meV). Two tentative explanations can be proposed to account for the origin of these two peaks. First, they might be due to two types of quasilocal vibrations involving two Ni atoms. For instance, they could be vibrations of different orientations: along and perpendicular to the Ni-Ni pair. These vibrations could have somewhat different energies, producing two separate vibronic transitions. A more speculative explanation of the splitting of the quasilocal vibration of the 2.56 eV center can be proposed, assuming that every Ni atom strongly interacts with two adjacent carbon atoms, so that they form rigid three-atom clusters, each vibrating as a unit. A quasilocal vibration of these three atoms Ni+2C would possess an energy of 35.7 meV, which is very close to the experimentally measured value of 36 meV. Then the vibration of the defect as the whole, that is 2(Ni+2C), would give an energy of 24.2 meV. This value is also in very good agreement with the experimentally observed vibration 24 meV (Table I). According to this model, the 2.56 eV Ni-related center may have an atomic structure of $C_2{=}Ni{-}Ni{=}C_2$. The bands peaking at about 2.42 eV (512 nm) and 2.44 eV (508 nm) are possibly vibrational replicas of the ZPL and the 24 meV vibronic band, both interacting with one and the same 125 meV phonon mode. It is interesting that the energy 125 meV coincides with that of the $\Lambda 1$ acoustic phonon at the L point. It might be an additional argument in favor of the model, indicating that the Ni-Ni pair is oriented along the $\langle 111 \rangle$ direction (for instance, a split interstitial of two Ni atoms, or two interstitial Ni atoms in neighboring tetrahedral positions along the $\langle 111 \rangle$ axis).

A particular feature of the 2.56 eV center is a relatively weak line at 2.585 eV (479.5 nm) lying about 25 meV from the ZPL toward greater quantum energies. Interestingly the relative intensity of this line strongly increases with temperature. This is natural behavior, if we assume that the 2.585 eV line is merely the anti-Stokes vibronic replica of the ZPL due to interaction with the 24 meV quasilocal vibrations involving the whole $C_2{=}Ni{-}Ni{=}C_2$ cluster.

The most reasonable alternative model of the 2.56 eV nickel-related center discussed in the literature is a substitutional Ni^- ion of T_d symmetry proposed in Refs. 18 and 39. However, this model is not consistent with optically detected magnetic resonance experimental results that assume a lower symmetry of the corresponding defect.

3. The 3.1 eV center

The primary ZPL of the 3.1 eV center is a fine-structured band at 3.065 eV (404.4 nm) (Fig. 11).[19] The vibronic structure of the center is dominated by a 26 meV vibration originating most likely from a quasilocal vibration involving two Ni atoms (Table I). There is also a band at 3.076 eV (403.0 nm), which also shows a sequence of vibronic replicas due to interaction with the vibration of the same energy, 26 meV. Though the 3.076 eV band does not show any apparent structure, it should also be ascribed to a ZPL, because of the very small energy difference (about 11 meV) between this line and the primary ZPL. Indeed, 11 meV is far too small an energy for any quasilocal vibration in the diamond lattice. In order to fit this value, the vibrating mass has to be assumed to be over 700 a.m.u., which is, of course, far too big to be realistic. The weak broad feature lying 157 meV away from the ZPL is most probably a vibrational replica due to interaction with optical phonons forming the most intensive region of the phonon density of diamond.

4. Ni-related centers in ion-implanted diamond

A great variety of Ni-related optical centers can be induced in low-nitrogen diamond by Ni^+ ion implantation (Fig. 12). There is no evidence that these centers are formed immediately during implantation. All of them can be detected only after postimplantation annealing at temperatures above 600 °C, when the damaged diamond lattice is sufficiently recovered. The spectral region from 2.69 eV (460 nm) to 1.97 eV (630 nm) is the most highly populated with

TABLE II. Intensities of 1.4 eV center ZPLs related to different Ni isotopes compared with those calculated assuming incorporation of one and two Ni atoms.

Stable Ni isotope	^{58}Ni	^{60}Ni	^{61}Ni	^{62}Ni	^{64}Ni
Experiment (arb. units)[a]	100	33.6	~2.2	5.3	2.0
One-Ni-atom model	100	38.2	1.9	5.3	1.7
Two-Ni-atom model	100	77.1	3.7	25.5	7.6
(most intense components)	^{116}(2Ni)	^{118}(2Ni)	^{119}(2Ni)	^{120}(2Ni)	^{122}(2Ni)

[a] References 16 and 17.

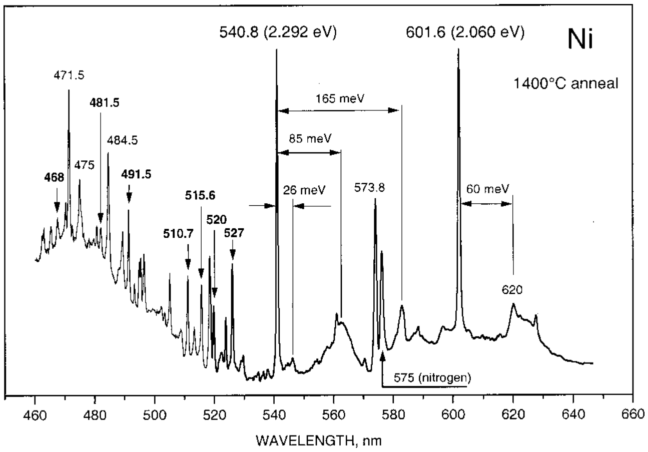


FIG. 12. CL spectrum (at liquid nitrogen temperature) of a natural type-IIa diamond implanted with 340 keV Ni^+ ions at a dose of $10^{14}\,cm^{-2}$ and subsequently annealed at a temperature of 1400 °C. Most of the narrow lines in the spectrum are expected to be ZPLs of nickel-related centers. The line at 575 nm is the ZPL of the 575 nm nitrogen-related center. The lines marked with arrows were found in (Ref. 38) in absorption of HPHT synthetic diamonds doped with Ni during growth.

optical centers. Many of these centers have been suggested to originate from interstitial-type defects containing Ni atoms.[20,21] The two most prominent centers, the vibrational spectral structure of which can be isolated from the general spectrum, are those with ZPLs at 2.292 eV (540.8 nm) and 2.060 eV (601.6 nm).

The 540.8 nm center interacts with a 26 meV vibration, which is likely to be due to a quasilocal vibration involving two Ni atoms (Table I). Two relatively broad bands lying 85 and 165 meV away from the ZPL also belong to the center. The origin of the latter band is quite clear: it originates from interaction with optical phonons. The shape of this band is very similar to that observed in the electron-vibrational spectra of the Tl-related center (see above) or the 3.188 eV, (389 nm) N-related center.

In the electron-vibrational sideband of the 601.6 nm center one can recognize only a band peaking at 2.00 eV (620 nm). The energy difference between this band and the ZPL is 60 meV. This value coincides with the energy of the most intensive vibronic band of the 1.4 eV center. It can be assumed that the 60 meV vibration is localized on the same atomic fragment in both centers. So far, the 601.6 nm center is suggested to be partially analogous to the 1.4 eV center. The difference is that the former contains interstitial atoms, whereas the latter is a defect containing only substitutional atoms.

H. Cobalt

Cobalt, when introduced in diamond during growth, produces many optical centers.[22] However, attempts to create Co-related centers by ion implantation have still not been successful. Of the variety of these centers two, namely, those with ZPLs at 1.852 eV (669.3 nm) and 1.989 eV (623.2 nm), are analyzed. The 1.852 eV center is observed only in absorption (Fig. 13). It is characterized by interaction with only one vibrational mode of energy 44 meV. Since 44 meV is too small an energy to be ascribed to a feature of the phonon density curve of diamond, a more probable explanation is a quasilocal vibration. Calculating the energy of the quasilocal vibration involving one Co atom, one can obtain good agreement with the experimental data (Table I).

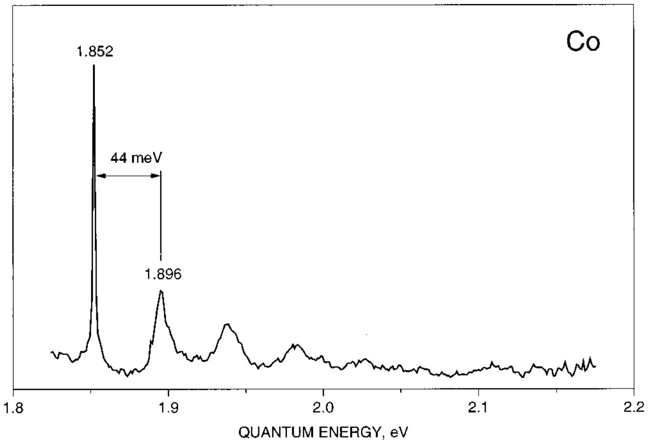


FIG. 13. Absorption spectrum of the 1.852 eV Co-related center (Ref. 22).

The spectral structure of the 1.989 eV center is more complicated than that of the 1.852 eV center (Fig. 14). In the electron-vibrational spectrum of the 1.989 eV center, three bands can be resolved, which correspond to vibrations with energies of 25, 56, and 119 meV. The two former vibrations can be qualitatively interpreted as quasilocal vibrations involving two and one Co atom, respectively (Table I). The 119 meV vibration is most likely due to interaction with $\Sigma 3$ acoustic phonos at the *L* point. The appearance of quasilocal vibrations with one and two Co atoms of similar intensities is a hint that the Co atoms are not bound strongly to each other.

I. Cobalt and nitrogen

When a Co impurity is introduced during growth into high-nitrogen synthetic diamonds, several specific optical centers result, which are absent from the spectra of nitrogen-free diamonds.[22] On the basis of this fact it has been concluded that these centers are due to defects incorporating

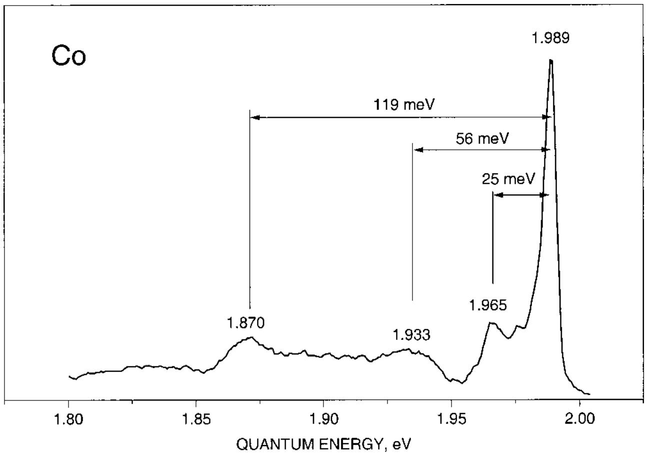


FIG. 14. PL spectrum of the 1.989 eV Co-related center (Ref. 22). This center is one of the Co-related centers that is believed to be nitrogen-free.

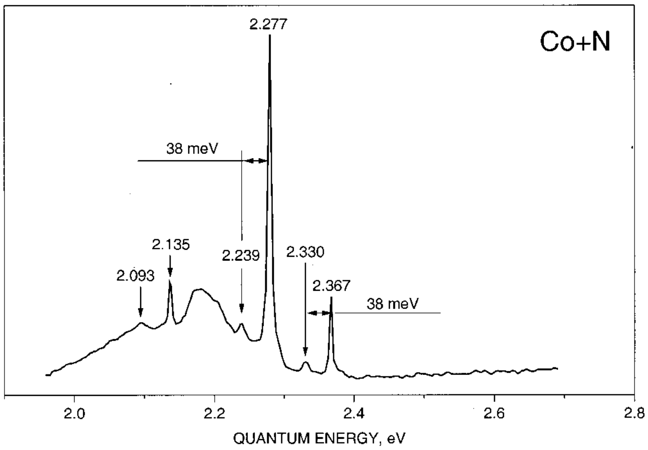


FIG. 15. PL spectrum of a synthetic diamond grown with Co catalyst after it had undergone a 1500 °C annealing (Ref. 22). The spectrum was recorded with a 1μs delay in order to isolate the long-time Co-related centers. The centers dominating the spectrum are believed to be due to Co+N complexes.

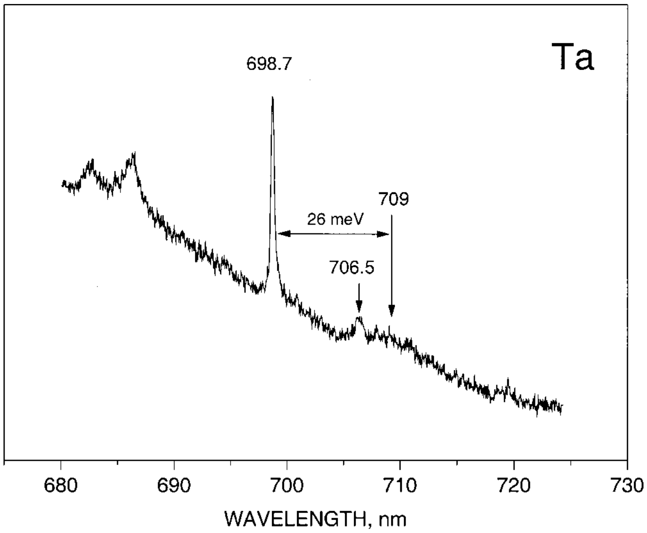


FIG. 16. PL spectrum (taken at a temperature of 78 K) of a CVD diamond film exhibiting the Ta-related center. Excitation with 514 nm Ar-laser line.

both Co and N atoms. The photoluminescence spectrum of the two most intense (Co+N)-related centers, namely, those with ZPLs at 2.277 eV (544.4 nm) and 2.367 eV (523.7 nm), are shown in Fig. 15. Both centers exhibit prominent interaction with a quasilocal vibration of energy 38 meV and a resonance width of 13 meV. Both these figures are in close agreement with the calculated values of the energy and resonance width of a quasilocal vibration involving one Co and one N atom provided both atoms vibrate as one unit (see Table I). Thus there is one more proof that the 2.277 and 2.367 eV centers indeed relate to defects containing one Co atom and one N atom.

J. Tantalum

The optical center related to Ta impurity in diamond was found in photoluminescence (PL) of CVD diamond films grown by the hot-filament method using Ta filament.[23] The center is characterized by a sharp ZPL at 1.774 eV (698.7 nm) and very weak electron-phonon coupling (Fig. 16). The relative intensity of the center may be enhanced in films of low quality. A weak relatively broad band at 1.75 eV (709 nm) (the spectral width of the band is about 10 meV) can be recognized in the electron-vibrational side band of the center. This feature can be tentatively ascribed to a quasilocal vibration of energy 26 meV involving one Ta atom (Table I). A relatively sharp weak line at 706.5 nm observed in the spectrum probably does not belong to the 1.774 eV Ta-related center.

K. Silicon

Although the silicon atom is not really a ''heavy'' one in comparison with carbon, nevertheless it is interesting to apply the model of quasilocal vibrations to silicon-related optical centers also. A silicon impurity in diamond gives rise to the very well-known optical center with ZPL at a wavelength of 738 nm (1.681 eV). This center is created by any method of doping: during high-pressure high-temperature (HPHT) growth, during CVD deposition, or by ion implantation. The electron-vibrational sideband of the center has been studied in detail in Refs. 9 and 25–27 (Fig. 17). The electron-phonon coupling at the Si-related center is relatively weak. In luminescence the strongest interaction occurs with a mode of energy 64 meV. In addition, several other electron-vibrational features can be recognized in the spectrum (Table I). Different atomic models have been proposed to explain the behavior of the center: (i) a substitutional silicon atom bound to a vacancy, the complex being in the neutral charge state;[28–30] (ii) a defect containing silicon and nitrogen atoms;[31,32] (iii) two Si atoms located along the ⟨111⟩ axis and bound to vacancies, as well as a two-silicon-atom model.[9,33,34] The main difference between these models is the number of incorporated Si atoms: one or two. Calculation of the parameters of possible quasilocal vibrations involving Si atoms gives energies of 75 meV for one Si atom and 45 meV for two Si atoms (Table I). These values are qualitatively comparable with the energies of two features in the vibrational sideband

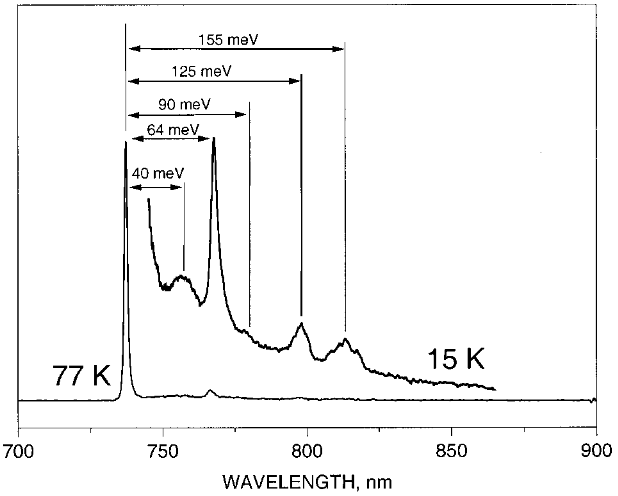


FIG. 17. PL spectrum of Si center taken from a CVD diamond film (Ref. 9). The vibrational structure of the center is shown for a temperature of 15 K (excitation at a wavelength of 737 nm).

TABLE III. Intensities of ZPLs of the Si center related to different Si isotopes compared with those calculated assuming incorporation of one and two Si atoms.

Stable Si isotopes	^{28}Si	^{29}Si	^{30}Si		
Experiment[a]	100	11.2	~7		
One-Si-atom model	100	5.1	3.2		
Two-Si-atom model	100 ^{56}(2Si)	10.2 ^{57}(2Si)	6.7 ^{58}(2Si)	0.4 ^{59}(2Si)	0.1 ^{60}(2Si)

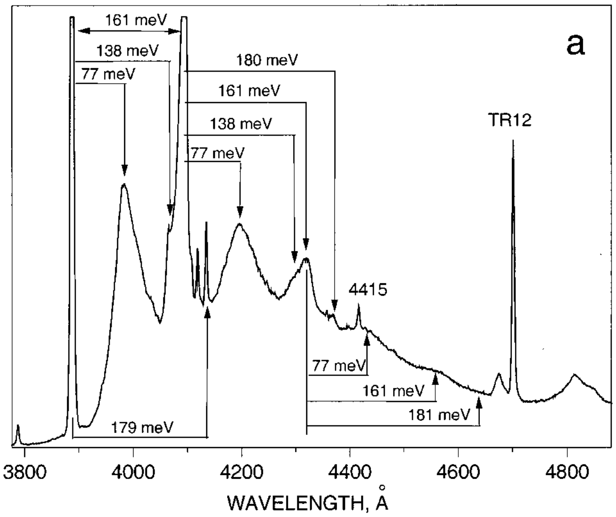
[a] From Ref. 24; average off luminescence and absorption values.

of the center, namely, those peaking at 64 and 41 meV from the ZPL. So far, it can be assumed that both modes are quasilocal modes of a defect containing two Si atoms. The high-energy quasilocal vibration is localized on one Si atom, whereas the low-energy one is localized on two Si atoms. The other vibrational features observed in the spectrum are due to interaction with the lattice phonons. The corresponding maxima can be found in the curve of diamond phonon density.

The Si-impurity-related nature of the center was proved in Ref. 35, where it was shown that the fine structure of the ZPL can be well explained by electron-phonon interaction in Si centers containing different stable Si isotopes. However, no explicit statement on the number of Si atoms in the Si center was given in the paper, although the authors compared the experimental spectrum with a calculated one based on the one-Si-atom model. Nevertheless, when comparing the measured intensities of the ZPL components with those calculated for the two-Si-atom model, better agreement is achieved (Table III). This might be an additional proof that the Si center does contain two Si atoms.

L. The 3.188 eV nitrogen-related center

Whereas the Si atom can still be considered to some extent as a ''heavy'' impurity in diamond, this is not the case at all for nitrogen. Consequently, the model of quasilocal vibrations cannot be directly applied to nitrogen-containing defects. However, there might be a chance to use the model in cases when nitrogen atoms from stable rigid clusters with surrounding carbon atoms, providing vibrating masses considerably exceeding the mass of carbon atom. An example of such a defect could be the well-known nitrogen-related optical center with ZPL at 389 nm (Fig. 18). The vibrational sideband of this center is almost completely formed of features related to intrinsic phonons of the diamond lattice [Fig. 18(b)]. The intrinsic origin of the vibrational sideband of the 389 nm center was unambiguously shown in Refs. 7 and 8, where the spectrum of the center was studied on diamonds synthesized of different carbon isotopes. All the vibrational features except two exhibit a shift of their energies with respect to the ZPL at a ratio ranging from 0.965 to 0.968, which is close to the ratio of the energy change of the C-C vibrations, when substituting ^{12}C for ^{13}C. The two mentioned features, namely, a sharp line due to a local vibration lying 178.8 meV from the ZPL and a very weak broad hump separated from the ZPL by an energy of 58 meV, show considerably lower isotopic shifts, characterized by factors of 0.977 (for the sharp peak) and 0.983 (for the weak hump).



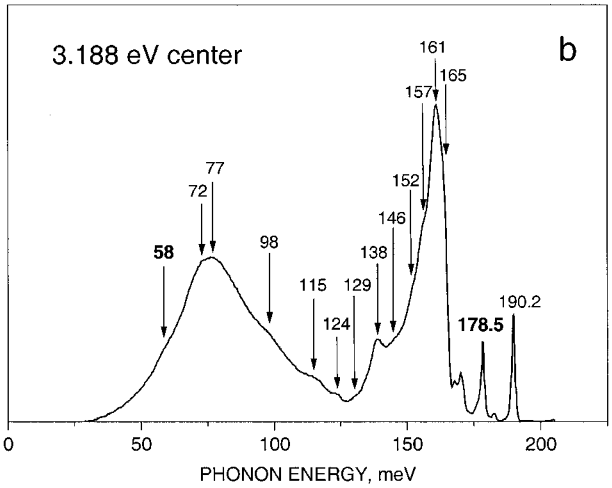


FIG. 18. (a) CL spectrum (at liquid nitrogen temperature) taken from a nominally nondoped CVD diamond film as irradiated with high-energy carbon ions (ion energy of 10 MeV/a.m.u.) at a dose of 3.5×10^{15} cm^{-2}. The vibronic sideband of the center exhibits all the features characteristic of the phonon density of states of the diamond lattice. The third-order vibrational replica can be detected. The bands at 4195 and 4320 Å are vibronic replicas of the 4094 Å band. The 4396 Å band is the second replica of the 4135 Å band. (b) First-order vibrational spectrum of the center. The quasilocal and local vibrations involving the nitrogen atom are numbered in bold.

The lower rate of the isotopic shift of the 178.8 meV local vibration has been explained by the presence of a nitrogen atom involved in the vibration. By analogy, it can also be suggested that the 58 meV vibronic feature is formed from a quasilocal vibration also involving a nitrogen atom. Very good agreement with the experimental data can be obtained, when suggesting simultaneous vibration of a cluster formed of one nitrogen and two carbon atoms (total mass 38 a.m.u.; see Table I). The measured energy of this quasilocal vibration in ^{13}C diamond is about 57 meV. The calculated energy of the quasilocal vibration of a cluster $^{13}C_2N$ is 57.8 meV (the Debye frequency of ^{13}C diamond $\omega_{D(^{13}\mathrm{C})}$ is assumed to be equal to $\omega_{D(^{13}\mathrm{C})}=\omega_{D(^{12}\mathrm{C})}\sqrt{M_{^{12}\mathrm{C}}/M_{^{13}\mathrm{C}}}$). Thus the calculated ratio of the isotopic shift of the quasilocal vibration is

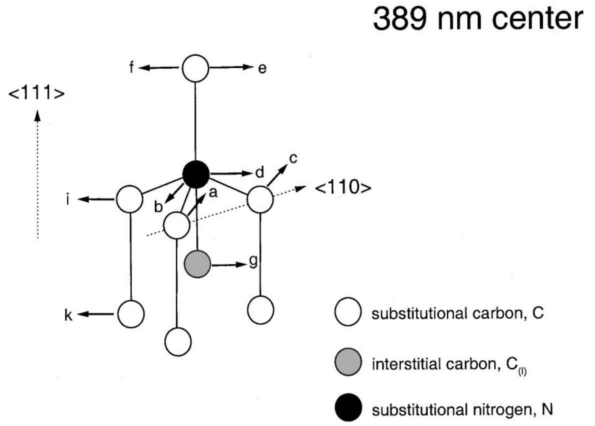


FIG. 19. Atomic model of the 389 nm nitrogen-related center: substitutional nitrogen atom bound to a carbon atom in the nearest tetrahedral interstitial position. The arrows show atomic movements at the following vibrations: *abc*, transverse optical [polarized normal to the (110) plane] $\Sigma 2$ phonon at the *K* point; *ed* and *ik*, transverse acoustic $\Lambda 3$ phonon at the *L* point; *edg*, quasilocal vibration of the C-N-$C_{(I)}$ fragment.

0.983, which exactly coincides with the experimentally measured one.

Additional information related to atomic models of optical centers can be obtained by analyzing the types of phonons dominating the electron-phonon coupling. In the case of the 389 nm nitrogen center, these are phonons with energies within a range from 150 to 165 meV. Two further features dominating the electron-phonon sideband of the center are a strong broad band at about 73 to 77 meV and a weaker band at 138 meV. These features originate most likely from the transverse acoustic $\Lambda 3$ phonons at the *L* point and the transverse optical [polarized normal to the $(1\bar{1}0)$ plane] $\Sigma 2$ phonons at the *K* point.[36] That is, the atomic structure of the 389 nm center appears to be particularly sensitive to transverse vibrations along the $\langle 111\rangle$ and $\langle 110\rangle$ directions. A possible atomic configuration sensitive to such vibrations could be a C-N-C chain oriented along the $\langle 111\rangle$ direction. Thus the following atomic model of the 389 nm center is proposed: a substitutional single nitrogen atom N bound to the carbon atom $C_{(I)}$ in the nearest tetrahedral interstitial position (atomic configuration of the defect C_4N-$C_{(I)}$, symmetry C_{3V}), Fig. 19. This model is well consistent with most experimental spectroscopic data on the 389 nm center, as well as with peculiarities of formation of this center during diamond growth and irradiation. The geometry of the C_4N-$C_{(I)}$ cluster appears indeed to be sensitive to short-wavelength transverse acoustic vibrations propagating along the $\langle 111\rangle$ direction, because of a strong bending deformation of the C-N-$C_{(I)}$ chain during the vibrational motion (note that the length of the C-N-$C_{(I)}$ chain is about half of the wavelength of Λ phonons at the *L* point). The movements of the lattice atoms involved in $\Lambda 3(L)$ and $\Sigma 2(K)$ vibrations are shown in Fig. 19. It is interesting that the C-N-$C_{(I)}$ atomic configuration appears to be insensitive to the longitudinal acoustic vibration along the $\langle 111\rangle$ axis, since in this case the $C_{(I)}$ atom moves toward the hexagonal interstitial position almost freely and does not change the geometry of the cluster. This might be the reason that the longitudinal $\Lambda 1$ phonons at the *L* point (energy of 126 meV) are almost absent from the electron-phonon sideband of the 389 nm center in contrast to the dominating 73 meV band due to the transverse acoustic $\Lambda 1$ phonons at the *L* point. The geometry of the C_4N-$C_{(I)}$ defect appears also to be sensitive to the short-wavelength transverse optical vibrations propagating along the $\langle 110\rangle$ direction. This is possibly the reason for a relatively intense 138 meV feature in the vibrational sideband of the center (compare Fig. 2 and Fig. 18).

The atomic model of the 389 nm center as a C_4N-$C_{(I)}$ cluster gives the opportunity to explain the origin of the local (178.5 meV) and quasilocal (58 meV) vibrations. Since the mass of the nitrogen atom is higher than that of carbon, the only possibility to create a true local vibration with an energy exceeding the highest vibrational energy of the diamond lattice is to increase the force driving the vibrations of the nitrogen atom. In the proposed model the nitrogen atom is surrounded by five carbon atoms, each forming a covalent bond. Assuming that the strength of each N-C bond is about that of the C-C covalent bond, one can compare the vibration frequencies of the fourfold-coordinated carbon atom ω_{C4C} and the fivefold-coordinated nitrogen atom ω_{C5N}:

$$\omega_{\mathrm{C4C}}/\omega_{\mathrm{C5N}}=[(4f/M_{\mathrm{C}})/(5f/M_{\mathrm{N}})]^{0.5}=1.035.$$

The vibrational energy of the fourfold-coordinated C atom is the highest one of the diamond lattice, of energy 168 meV (see Fig. 2). The ratio of this energy to that of the nitrogen-related local vibration gives a value $178.5/168=1.063$, which qualitatively agrees with the calculated ratio.

The quasilocal nitrogen-related vibration of energy 58 meV can be assigned to a transverse acoustic-type vibration of the C-N-$C_{(I)}$ group in a plane parallel to the $\langle 111\rangle$ crystallographic axis. This is actually an analog of the $\Lambda 1$ (at the *L* point) transverse lattice phonons, which are characterized by the vibration of two-atom C-C groups in planes parallel to the $\langle 111\rangle$ axis. Since the driving forces of the vibrations of both the C-N-$C_{(I)}$ and C-C groups are the same (note that the $C_{(I)}$ atom is actually bound only to the N atom and does not change the interatomic forces in the chain of carbon atoms along the $\langle 111\rangle$ direction), the frequency ratio of these vibrations can be calculated as $\omega_{\text{C-C}}/\omega_{\text{C-N-C}_{(I)}}=[(2M_{\mathrm{C}})/(2M_{\mathrm{C}}+M_{\mathrm{N}})]^{0.5}=0.795$. The ratio of the energies of the quasilocal vibration (58 meV) and $\Lambda 1$ (at the *L* point) transverse lattice phonon (the 73 meV band) exactly coincides with this value: $58/73=0.795$.

IV. CONCLUSIONS

It has been shown that quasilocal acoustic-type vibrations are common features of electron-vibrational sidebands of the optical centers related to heavy impurities in diamond. Diamond is a very suitable material for revealing such vibrations because of the low mass of carbon atom. A common feature of the electron-vibrational interaction with quasilocal vibrations is a relatively low coupling strength characterized by a Huang-Rhys factor $S<1$. The energies and resonance widths of these vibrations can be calculated quite satisfactorily with formulas given in Ref. 12. Since the deformation of interatomic bonds by acoustic vibrations is relatively small, the acoustic-type quasilocal vibrations will not depend noticeably on the bonding strength of the impurity atom with the surrounding host atoms. This means that the chemical nature of the impurity atom does not much influence the energy of its quasilocal vibration. Due to this peculiarity the formulas of Ref. 12 describe fairly well the quasilocal vibrations of chemically different atoms and even atom clusters. Indeed, for all the optical centers considered above, irrespective of the nature of the impurity, the energies of the quasilocal vibrations can be calculated by taking into account only the total masses of the vibrating atom clusters.

The applicability of the model of quasilocal vibrations can be extended even to optical centers related to light impurity atoms, provided these atoms combine with carbon atoms to make rigid clusters vibrating as heavy units. Fortunately, nitrogen, the most important optically active impurity of diamond, appears to be such an impurity. If so, the electron-vibrational sidebands of the nitrogen-related optical centers can be analyzed with the aim of recognition of the quasilocal vibrations involving nitrogen atoms. No doubt the information obtained in this way would be very helpful for structural modeling of the corresponding defects, as has been shown above for the 389 nm center.

Measurement of the energy of the quasilocal vibrations appears to be a simple and effective method to determine the number of impurity atoms involved in the vibration and, consequently, constituting the impurity-related optical center. It is interesting to note that the incorporation of two impurity atoms seems to be a quite common feature of impurity-related optical centers in diamond. However, for very heavy atoms like Tl or W the incorporation of single atoms is preferable.

Finally, it should be noted that the model of quasilocal vibrations in the vibronic spectra of optical centers is not restricted to diamond only. Nothing prevents its extension to other crystals. The only important factor is the mass of the impurity atom, which must be considerably greater than the masses of atoms constituting the host crystal lattice. Heavy impurities result in quasilocal vibrations of energies low enough to get into the low-density region of long-wavelength lattice acoustic vibrations and, consequently, to provide characteristic vibronic features in the electron-vibrational sidebands.

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