PHYSICAL REVIEW B VOLUME 56, NUMBER 8 15 AUGUST 1997-II

Local vibrational modes and anharmonic forces of Mg^{2+} and S^{2-} in ZnTe and CdTe crystals

S. W. Biernacki*
Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, PL-02-668 Warsaw, Poland

U. Scherz and Ch. Schrepel
Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623, Berlin, Germany

(Received 12 March 1997)

We present a simple model to describe local vibrational modes at impurities in semiconductors using a two-particle anharmonic potential. We calculated the breathing-type distortion at the impurity in the tight-binding approximation, the frequencies of the local vibrational modes associated with the Mg^{2+} and S^{2-} impurities in ZnTe and CdTe, their isotope shifts, and the anharmonic forces without any parameters adjusted to defect properties. Our results for the energies of the local vibrational modes and their isotope shifts at Mg and S impurities in ZnTe and CdTe are in good agreement with experiments. We found an inward distortion of the ligands of Mg^{2+} in CdTe, an outward distortion in ZnTe, and an inward distortion at S^{2-} in both crystals. [S0163-1829(97)06232-2]

I. INTRODUCTION

Local vibrational modes (LVM's) are easily observed by Raman spectroscopy if the mass of the impurity is significantly smaller than the mass of the host-lattice atoms. In this case, the frequencies are well above the vibrational spectrum of the host lattice and these LVM's are called split-off modes. The displacements of an impurity of such a mode are strongly peaked at the impurity site and the calculation may be done with a model, in which the impurity and its nearest neighbors are considered as a quasimolecule embedded in the host crystal. The normal modes of such a system and their frequencies can be extracted provided the adiabatic interaction surface is known.

Many properties of such a quasimolecule are determined predominantly by the bond energy. Harrison,[1,2] using the tight-binding approximation and some results following from the density-functional theory, simplified the calculation of the bond energy by expressing it in terms of one-electron atomic energies and some universal parameters. The universal parameters replace the complicated interaction integrals and are common for many covalent crystals. The model can be substantially improved by extending the linear dependence of the interatomic force on the impurity displacement with higher anharmonic terms. Because of the dependence of the frequencies of the LVM on the impurity mass, isotope substitution has been used to obtain an unambiguous proof for the localization of a LVM at a certain impurity. LVM spectra of impurities, composed of several isotopes consist of closely spaced lines resulting from different impurity masses. For example, Mg has three stable isotopes, ^{24}Mg, ^{25}Mg, and ^{26}Mg, with natural abundances of 78.99, 10.00, and 11.01 at. %, respectively. In such a case three separated peaks of vibrations are observed. The vibration frequencies are described by harmonic and anharmonic forces and these frequency shifts originate not only from the mass dependence of the dynamical matrix but also from the mass dependence of the zero-temperature vibration of the LVM.

Our investigation was stimulated by recent accurate vibrational Fourier transform spectra on Mg^{2+}, Ca^{2+}, and S^{2-} ions in ZnTe and CdTe crystals.[3] In addition to the fundamental transition (including the isotope structure) the second harmonic transition was observed. In such a situation it is possible to deduce some information about anharmonicity of the elastic potential. The calculation of the anharmonicity requires an accurate knowledge of the higher order (cubic and quartic) force constants. We therefore apply a simple analytical method to extract some information about the anharmonic contributions to the elastic potential of impurities.

II. PHENOMENOLOGICAL APPROACH

The Mg^{2+} substitutes the Zn or Cd atoms while S^{2-} replaces the Te atom. Thus both defects occupy a site of tetrahedral symmetry. The oscillator potential (referred to the cubic axes x,y,z) up to quartic terms which transforms as the identity representation A_1 of the group T_d is given by

$$V=\frac{k_h}{2}(x^2+y^2+z^2)+Bxyz+D_1(x^4+y^4+z^4)+D_2(x^2y^2+x^2z^2+y^2z^2), \tag{1}$$

where k_h, B, D_1, D_2 are the harmonic, cubic, and quartic force constants. The energy levels are given by

$$E_n=\hbar\sqrt{\frac{k_h}{\mu}}(n+\tfrac{3}{2})-\frac{\hbar^2}{24k_h^2\mu}\lambda B^2+\frac{\hbar^2}{4k_h\mu}(\mu_1D_1+\mu_2D_2), \tag{2}$$

where $n=0, 1, 2,\ldots$, and μ is the reduced mass of the oscillator. The values for μ_1, μ_2, and λ were derived from perturbation theory by Elliot *et al.* (Table 8 in Ref. 4 and Table 3.3 in Ref. 5). The first excited oscillator level E_1 is triply degenerate (either in harmonic or anharmonic approximation). The fundamental transition T_{fun} is given as

$$T_{\rm fun}=E_1-E_0=\hbar\omega-\frac{\hbar^2B^2}{6k_h^2\mu}+\frac{\hbar^2}{k_h\mu}(3D_1+D_2), \qquad (3)$$

with $\omega=\sqrt{k_h/\mu}$. The next oscillator level E_2 is sixfold degenerate only in the harmonic approximation. Its six sublevels are classified by representation A_1, E, and T_2. The anharmonic terms split these levels. The second ''harmonic'' transition $T_{\rm sh}$ to the T_2 symmetry level (which is allowed by the selection rule) is

$$T_{\rm sh}=E_2-E_0=2\hbar\omega-\frac{5\hbar^2B^2}{6k_h^2\mu}+\frac{3\hbar^2}{k_h\mu}(2D_1+D_2). \qquad (4)$$

Both the fundamental and the second harmonic transition contain contributions from the cubic and quartic anharmonic terms. If both transitions are known from experiment, we are able to deduce the anharmonic contributions from the difference

$$T_{\rm sh}-2T_{\rm fun}=-\frac{\hbar^2B^2}{2k_h^2\mu}+\frac{\hbar^2D_2}{k_h\mu}. \qquad (5)$$

Since there are two transitions (fundamental and second harmonic) and four unknown constants (k_h, B, D_1, and D_2) it is necessary to use in addition some theoretical information for unambiguous conclusions.

III. THEORETICAL MODEL

An impurity with an atomic mass significantly smaller than those of the substituted host-crystal atom, exhibits a vibrational mode with a frequency higher than the modes of the perfect crystal. The frequency increase is due to the dependence of the dynamical matrix on the inverse square root of the vibrating masses. Additionally, the substitutional defect produces a symmetric lattice distortion and we disregard here the distortions related to the Jahn-Teller effect. This directly influences the nearest neighbor interatomic force constant. To describe the vibrations quantitatively we use the Harrison model[1,2] which estimates the bonding properties of solids in a simple manner. This method was successful in the prediction of the equilibrium lattice spacing for many zinc-blende-structure compounds (see, for example, Ref. 6) as well as many other properties like the relaxation of the bond length around an isoelectronic substitutional defect. The total energy is expressed in terms of interactions between pairs of nearest neighbor atoms, i.e., in terms of the bond energy.

In the valence-bond theory of tetrahedrally coordinated crystals four orthogonal and normalized sp^3 hybrids are formed, and the valence-bond energy is given as[1,2]

$$\varepsilon_b=\frac{1}{2}(\varepsilon_h^\alpha+\varepsilon_h^\beta)-q\sqrt{V_2^2+V_3^2}+\frac{qV_2^2}{k|\overline{\varepsilon_h}|}, \qquad (6)$$

with

$$V_3=\frac{1}{2}(\varepsilon_h^\alpha-\varepsilon_h^\beta) \quad \text{and} \quad \varepsilon_h^{\alpha,\beta}=\frac{1}{4}(\varepsilon_s^{\alpha,\beta}+3\varepsilon_p^{\alpha,\beta}), \qquad (7)$$

and ε_s and ε_p are the free-atom energies for the outermost s and p states.[8] The coupling between the two atoms is determined by

$$V_2=f(\eta)\hbar^2/md^2, \qquad (8)$$

where m is the electron mass, and the function $f(\eta)$ is expressed in terms of the four universal coefficients: $\eta_{ss\sigma}=-1.40$, $\eta_{sp\sigma}=1.84$, $\eta_{pp\sigma}=3.24$, and $\eta_{pp\pi}=-0.81$. For example, in the perfect CdTe crystal, for two sp^3–sp^3 hybrids directed against each other on two neighboring atoms,

$$f_{sp^3-sp^3}(\eta)=\eta_{ss\sigma}/4-2\sqrt{3}\,\eta_{sp\sigma}/4-3\,\eta_{pp\sigma}/4=-4.373. \qquad (9)$$

The parameter q is the electron occupancy of the bond in units of the electron charge and $\overline{\varepsilon_h}$ is the average of ε_h^α and ε_h^β. The parameter k is the only one adjustable coefficient entering the theory. It is determined from the requirement that the calculated bond lengths for C, Si, Ga, and Sn crystals are equal to the experimental values. The value of k is the same for all crystals formed by elements of the same row of the Periodic Table. For example, we have for the C row $k=2.5$, for the Si row $k=1.455$, for the Ge row $k=1.33$, and for the Sn row $k=1.12$.[6] For bond lengths between atoms from different rows the interpolated value $\sqrt{k_ik_j}$ is used.

Each pair of nearest neighbor atoms with masses M_1 and M_2 can be considered as an oscillator with respect to a single bond. The vibrational frequency of such an oscillator is determined by the stretching force constant k_h and is given as

$$\omega_b=\sqrt{k_h/\mu}, \qquad (10)$$

where $\mu=M_1M_2/(M_1+M_2)$ is the reduced mass and M_1, M_2 are the masses of the two atoms in the elementary unit cell. The harmonic force constant is calculated by taking the second derivative of the bond energy with respect to the bond length d. For example, at the equilibrium distance d we have

$$k_h=\frac{4qV_2}{d^2}\left(\frac{V_2}{\sqrt{V_2^2+V_3^2}}\right)^3. \qquad (11)$$

For diamond structure crystals, the optical frequency $\omega(\Gamma)$ at the Γ point is expressed in terms of ω_b, $\omega(\Gamma)=\sqrt{4/3}\,\omega_b\approx1.16\omega_b$.

The localized vibration is here described by an impurity, connected to its four nearest neighbors by anharmonic forces. There are four equivalent bonds around the impurity. The fourfold degeneracy of the four bond stretching forces is reduced and we obtain a T_2 and a A_1 mode of the tetrahedral symmetry group. The threefold degenerate T_2 mode only causes the impurity isotope shift of the LVM, whereas the A_1 mode is localized at the nearest neighbors. Both modes arise from the same force constant but have different reduced masses. There are also two other modes of E and T_2 symmetry when taking the bond bending forces at the impurity into account. Since the force constant of bond bending is remarkably smaller than for bond stretching, these modes usually are within the crystal-phonon band and hybridize with crystal phonons. The bond length between the impurity and its nearest neighbors is usually different from the corresponding bond length of the host atoms. The substitutional defect produces a relaxation of the neighboring atoms. We calculate the relaxation of the nearest neighbors of the impurity by assuming that the positions of all other atoms are unchanged and we minimize the sum of the four bond energies. Each nearest neighbor has one bond with the impurity and three other back bonds with the second nearest neighbors of the impurity. We change the position of the nearest neighbors along the bond direction (this corresponds to the breathing mode distortion around the defect site) until the sum of the four bond energies reach a minimum. We then calculate the force constant from the second derivative at this minimum.

The elastic potential V can be obtained from an expansion of the bond energy at the equilibrium interatomic distance with respect to the mutual displacements of the atoms. Thus

$$V=\sum_{i=1}^{4} \varepsilon_{bi}=\sum_{i=1}^{4} \frac{1}{2}k_h r_i^2-\beta r_i^3+\alpha r_i^4+\dots, \tag{12}$$

where r_i are the mutual displacements between the atoms in the bond direction. It can be expressed in terms of the Cartesian displacements of the atoms, and for example, for the [111] direction we have

$$r_1=[(x_1-x)+(y_1-y)+(z_1-z)]/\sqrt{3}. \tag{13}$$

The sum in Eq. (12) runs over the four bonds. Using Eq. (12) the dynamical matrix is set up in the harmonic approximation and solved analytically. The frequencies of vibration are

$$\omega_{T_2}=\sqrt{k_h/\mu}, \tag{14}$$

$$\omega_{A_1}=\sqrt{k_h/M_L}, \tag{15}$$

where $\mu=3M_IM_L/(3M_I+4M_L)$. M_I is the impurity mass and M_L denotes the mass of the ligand. These solutions are similar to the stretching modes of a five atom molecule. In order to find the correspondence between the anharmonic force constants in Eqs. (1) and (12) it is necessary to take the displacement of the ligands from their equilibrium positions equal to zero and compare with the corresponding terms in Eq. (1). We thus find $B=-8\beta/\sqrt{3}$, $D_1=4\alpha/9$, and $D_2=8\alpha/3$.

IV. RESULTS AND DISCUSSION

We do not use any adjustable parameters in the presented model. First, we apply Eq. (6) to the perfect crystal bond. We determine the interatomic equilibrium distance d from the requirement $\partial\varepsilon_b/\partial d=0$ and the optical vibrational frequency $\omega(\Gamma)$ at the Γ point. In the case of the diamond lattice we have $\omega(\Gamma)=\sqrt{4/3}\omega_b$, where ω_b is given by Eq. (10). The results of our calculation are presented in Table I. The interatomic distance is given with more digits assuming that the initial parameters (like atomic eigenvalues) are given accurately. As can be seen from Table I, the error of the calculated d is 2% for CdTe and 0.6% for ZnTe, but we use five digits to show the later change of d with isotope mass. This overestimation effects the vibration frequencies which sensitively depend on d. For ZnTe a 0.4% increase of d results in a 12% increase of the vibrational frequency. We therefore expect a similar inaccuracy when calculating LVM's. Of course, it would be possible to adjust the interatomic distance so as to obtain the experimental value of the frequency. Then the same shift could be used to calculate the LVM. Instead, we try to describe all observable parameters for the crystal in terms of the free atomic parameters using the general Eq. (6), which can be applied for a broad class of isoelectronic defects in various semiconductors.

TABLE I. Nearest neighbor distance d and average optical phonon frequency $\omega(\Gamma)_{\rm av}=[\omega_{\rm LO}(\Gamma)+2\omega_{\rm TO}(\Gamma)]/3$.

	CdTe		ZnTe	
Parameter	Exp.	Calc.	Exp.	Calc.
d, (Å)	2.806	2.8649	2.641	2.6579
$\omega(\Gamma)_{\rm av}$ (cm^{-1})	152	109	186	163

Now we shall discuss the defect parameters. The vibrational spectra for the $\rm Mg^{2+}$, $\rm Ca^{2+}$, and $\rm S^{2-}$ defects were reported in Ref. 3. We skip the calculation of the $\rm Ca^{2+}$ because of the lack of the atomic $4p$ eigenvalues in Ref. 7, which we need in Eq. (6). The investigation of an isolated impurity-ligand bond would result in the same vibrational frequencies of $\rm Mg^{2+}$ in ZnTe and CdTe crystals. We therefore take the impurity-ligand bond together with three back bonds of the ligands into account. In this way we account for the static displacement of atoms. We calculate the relaxation of the nearest neighbor atoms only and we obtain the energy minimum by displacing the ligands (Te in the case of $\rm Mg^{2+}$ and Zn or Cd in the case of $\rm S^{2-}$) in the bond direction. We consider the sp^3 bonds as rigid and we calculate the energy due to the misalignment of the bonds between the first and second nearest neighbors numerically. The equilibrium distances between the impurity I and the ligand as well as between ligand and the second nearest neighbor are given in the first and second rows of Table II and Table III. The value of d and the harmonic force constant k_h have more digits to show the isotope mass effect.

The isotopic substitution in a crystal is a perturbation with only one parameter: the nuclear mass. Contrary to substitutions with different atoms it does not change the largest interaction in a crystal — the Coulomb interaction. As a result, the isotope dependence of the force constant is not taken into account. The determination of the bond length from the minimum of the bond energy (or from the minimum of the total energy in *ab initio* theories) is an approximation only in case the kinetic vibration energy is neglected. More accurately, the equilibrium interatomic distance must be determined not only from the electrostatic energy but also by taking the vibrational energy into account,[8] i.e., d must be determined from the minimum of the Helmholtz free energy. Since LVM's were observed at $T=5$ K,[3] we need to consider only zero-temperature vibration energy. The zero-temperature vibration energy increases the calculated equilibrium distance and decreases the vibrational frequency. Consequently, the harmonic force constant depends indirectly on mass. The isotopic dependence of the force constant is rather weak because the relative change of the isotope mass is small and because zero-temperature vibration energy is small with respect to the electrostatic bond energy.

TABLE II. Results of the stretching mode calculation and the experimental energies of the Mg^{2+} and S^{2-} ions in CdTe. The fundamental transition frequency $\omega_{\rm fun}$ is given for the lightest isotope. For heavier isotopes, the shifts in frequency are given with respect to the light isotope [for example, $\omega_{\rm fun}(^{25}{\rm Mg}) = (233.8 - 4.1)\ {\rm cm}^{-1}$]. The experimental data at $T = 5$ K are taken from Ref. 3.

Parameter	CdTe ^{24}Mg	^{25}Mg	^{26}Mg	^{32}S	^{33}S	^{34}S
d(I-ligand) (Å)	2.7279	2.7278	2.7277	2.5818	2.5817	2.5816
d(ligand-2nd shell) (Å)	2.9134	2.9135	2.9135	2.9713	2.9713	2.9714
$\omega_{\rm fun}$(cal.) (${\rm cm}^{-1}$)	233.8	-4.1	-8.0	212.40	-2.6	-5.2
$\omega_{\rm fun}$(exp.) (${\rm cm}^{-1}$)	253.3	-4.4	-8.6	254.1	-3.4	-6.5
$(T_{\rm sh} - 2T_{\rm fun})$(cal.) (${\rm cm}^{-1}$)	-3.1	-3.1	-3.1	-2.8	-2.8	-2.8
$(T_{\rm sh} - 2T_{\rm fun})$(exp.) (${\rm cm}^{-1}$)	-1.3	-1.3	-1.2	-0.6		-0.9
k_h (eV/Å^2)	3.1930	3.1935	3.1941	3.3052	3.3060	3.3067
β (eV/Å^3)	1.57	1.57	1.57	1.76	1.76	1.76
α (eV/Å^4)	1.37	1.37	1.37	1.69	1.69	1.69

We find an inward breathing mode distortion around the Mg^{2+} ion in CdTe and an outward distortion in ZnTe (see Tables II and III). Around the S^{-2} ion we find in both crystals an inward distortion. The calculated bond length of $d = 2.58$ Å for S-Cd in CdTe is a bit larger than the corresponding bond length of $d = 2.52$ Å in the perfect CdS crystal. Similarly, the S-Zn bond length of $d = 2.51$ Å in ZnTe crystal is larger than the bond length of $d = 2.34$ Å in the ZnS crystal. This is due to the influence of the back bonds between the nearest and second nearest neighbors of the impurity. For a perfect crystal with defects the loss of translational symmetry means that the normal modes of vibration can no longer be classified by a wave vector. Hence, the reduced mass for a LVM mode of T_2 symmetry is $\mu = 3M_IM_L/(3M_I + 4M_L)$ instead of $\mu = M_IM_L/(M_I + M_L)$. The last expression is valid for a two atomic molecule or for a perfect crystal with two atoms per elementary unit cell. For example, taking $M_I = M(^{24}{\rm Mg}) = 24$ and $M_L = M({\rm Te}) = 127.6$ one obtains according to the first formula $\mu = 15.77$, while the second formula (for a two-atomic molecule) gives $\mu = 20.2$. The A_1 mode is localized at the nearest neighbors. Both modes have the same stretching force constant k_h but different reduced masses. According to Eq. (15) the A_1 mode reduced mass is simply the ligand mass. As this mass is remarkably larger than the defect mass the A_1 mode lies in the perfect crystal-phonon band. For example, the A_1 mode related to the S^{2-} ion in CdTe has a frequency of $\omega = 89\ {\rm cm}^{-1}$, while in ZnTe it is $\omega = 135\ {\rm cm}^{-1}$. Although, the modes of this symmetry are not infrared active, they were observed as gap modes at energies of 106.1 ${\rm cm}^{-1}$ and 144.6 ${\rm cm}^{-1}$ in CdTe and ZnTe, respectively.[3]

The calculated fundamental transition frequencies $\omega_{\rm fun}$ are smaller than the experimental ones, and similarly the calculated $\omega(\Gamma)$ for the perfect crystal is smaller than the experimental value. This indicates that in reality the impurity-ligand distance may be shorter by $0.02 - 0.04$ Å. On the other hand, the frequencies of heavier isotopes with respect to the lightest one are reproduced correctly. In Ref. 3 the effective mass of the ligand was determined from the fit of Eq. (2) to the observed frequencies. The effective mass obtained from the fit to the Mg^{2+} spectra turns out to be different in ZnTe and in CdTe in spite of the fact that ligand mass in both cases is the Te atom mass. An energy shift of 19 ${\rm cm}^{-1}$ was reported in Ref. 3 for the fundamental transition when going from the CdTe to ZnTe crystal. Nearly, the same shift was obtained in our calculation for the Mg^{2+} ion and we attribute this to the change of the relaxation energy in both crystals.

The harmonic treatment of vibrational frequencies, discussed above, is correct only for small displacements of the atoms from their equilibrium positions with respect to the bond length. For vibrations involving the displacements of

TABLE III. Results of the stretching mode calculation and the experimental energies of the Mg^{2+} and S^{2-} ions in ZnTe.

Parameter	ZnTe ^{24}Mg	^{25}Mg	^{26}Mg	^{32}S	^{33}S	^{34}S
d(I-ligand) (Å)	2.6757	2.6756	2.6755	2.5185	2.5184	2.5183
d(ligand-2nd shell) (Å)	2.6520	2.6521	2.6521	2.7076	2.7076	2.7076
$\omega_{\rm fun}$(cal.) (${\rm cm}^{-1}$)	253.3	-4.5	-8.6	261.13	-2.9	-5.6
$\omega_{\rm fun}$(exp.) (${\rm cm}^{-1}$)	272.3	-4.7	-9.0	272.7		-7.0
$(T_{\rm sh} - 2T_{\rm fun})$(cal.) (${\rm cm}^{-1}$)	-3.3	-3.3	-3.3	-2.7	-2.7	-2.7
$(T_{\rm sh} - 2T_{\rm fun})$(exp.) (${\rm cm}^{-1}$)	-1.7	-1.6	-1.7	-1.6		
k_h (eV/Å^2)	3.7498	3.7507	3.7517	4.4349	4.436	4.4373
β (eV/Å^3)	1.89	1.89	1.89	2.23	2.23	2.23
α (eV/Å^4)	1.64	1.64	1.64	2.13	2.13	2.13

Mg or S atoms, the vibration amplitudes are rather small and the anharmonic corrections are expected to be also small. The energy shifts due to anharmonicity are calculated in Refs. 4 and 9 by perturbation theory, in which cubic terms are treated in second order (there is no first-order effect) and quartic terms are considered in the first order only. The two contributions are usually of similar magnitude. The calculation of the anharmonic corrections requires an accurate estimation of the elastic potential derivatives up to the fourth order. We therefore calculated the cubic and quartic force constants analytically, using the impurity-ligand bond energy at the equilibrium distance found for the four impurity-ligand stretching bonds including the three back bonds. The bond energy given analytically by Eq. (6) contains only one adjustable parameter. An improvement of the bond energy expression can only be made by introducing additional parameters. On the other hand the first-principles calculations give the harmonic force constant with an accuracy of around 10%, the cubic force constant with an accuracy of around 40–50 %, and the quartic force constant with a poor accuracy. The calculated anharmonic correction, i.e., $T_{\mathrm{sh}}-2T_{\mathrm{fun}}$ are presented in Table II and Table III. The theoretical results are about twice the experimental values. This may be due to the fact that our final result is the sum of cubic and quartic terms of opposite sign and both terms are sensitive to the equilibrium distance. For example, Mg^{2+} ion in CdTe has an anharmonic correction of $(-5.5+2.4)\ \mathrm{cm}^{-1}=-3.1\ \mathrm{cm}^{-1}$, where the first term in brackets is the contribution from the cubic potential. Similarly, the anharmonic correction for S^{2-} in CdTe is $(-5.1+2.3)\ \mathrm{cm}^{-1}=-2.8\ \mathrm{cm}^{-1}$.

The Mg^{2+} and S^{2-} defects, considered here, are isoelectronic with respect to replaced atoms and therefore have localized states, which are completely occupied by electrons. Since their atomic eigenvalues, entering Eq. (6), differ from the eigenvalues of the substituted host atoms, they cause a breathing mode distortion of the ligands. Some defects, like transition-metal ions, introduce additionally to the 4*s* valence states the *d* states close to the valence-band states. These *d* states are not fully occupied, hence they are orbitally degenerate. In such a case it is necessary to extend Eq. (6) by a perturbation term, which accounts for interaction between the *d* and the ligand electrons. The resulting distortion around the defect is a superposition of the breathing mode distortion[10] and the asymmetrical distortions of T_2 or E type which are known as the Jahn-Teller distortions. Because of these distortions the LVM of T_2 symmetry will be split into a doubly degenerate mode and a singly degenerate mode (because the defect site symmetry is lower than tetrahedral symmetry site). The Cr^{2+} atom in II-VI semiconductor exhibits the Jahn-Teller distortion. However, such a fine splitting has not been observed within the experimental accuracy at the fundamental transition of the LVM reported in Ref. 3. This may be due to the fact that asymmetrical static distortion is too small or that there exists a dynamical Jahn-Teller effect.

In conclusion, we applied a simple but useful model for the calculation of the vibrational properties of neutral impurities. It is free of adjustable parameters of the defect and it reproduces the dynamical properties of isovalent impurities. We calculated separately the anharmonic cubic and quartic corrections to the frequencies in the harmonic approximation. These corrections cannot be deduced from the fundamental and the second harmonic transitions because corresponding formulas [see Eqs. (3)–(5)] include four unknown parameters.

---

*Electronic address: biern@ifpan.edu.pl

[1] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, New York, 1980).

[2] W. A. Harrison, Phys. Rev. B **23**, 5230 (1981); **27**, 3592 (1983); **34**, 2787 (1986).

[3] M. Dean Sciacca, A. J. Mayur, N. Shin, I. Miotkowski, A. K. Ramdas, and S. Rodriquez, Phys. Rev. B **51**, 6971 (1995).

[4] R. J. Elliott, W. Hayes, G. D. Jones, H. F. MacDonald, and C. T. Sennett, Proc. R. Soc. London, Ser. A **289**, 1 (1965).

[5] R. C. Newman, *Infrared Studies of Crystal Defects* (Taylor & Francis, London, 1973), p. 1.

[6] J. M. Baranowski, J. Phys. C **17**, 6287 (1984).

[7] F. Herman and S. Skilman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, NJ, 1963).

[8] S. W. Biernacki and M. Scheffler, J. Phys. Condens. Matter **6**, 4879 (1994).

[9] S. Califano, *Vibrational States* (Wiley, London, 1976), Chaps. 8 and 9.

[10] S. W. Biernacki and H.-J. Schulz, Phys. Status Solidi B **200**, 173 (1997).