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Electronic properties of *A* centers in CdTe: A comparison with experiment

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The temperature variation of the *A*-center (a cadmium-vacancy halogen-donor pair) luminescence has been calculated using a temperature-dependent electron-ion interaction. The photoluminescence lines of the *A* center show a pronounced shift with temperature between 4 and 50 K. The zero-phonon line is explained in terms of a donor-acceptor pair transition and the temperature dependence is not due to the thermal expansion of the CdTe crystal. It results from excitations of electrons from shallow levels of isolated halogen donors and from transitions from the conduction-band edge to the deep acceptor level of the *A* center.

I. INTRODUCTION

Photoluminescence (PL) and optically detected magnetic resonance (ODMR) measurements[1] in II-IV crystals provide valuable information about the microscopic structure of the defects and their distribution. However, the interpretation of PL and ODMR data is not straightforward because of the variety and complexity of the defects and their interactions. Recently,[2–5] the recombination luminescence of chlorine-doped CdTe crystals was investigated as a function of temperature. The resolved structure contains a zero-phonon line (ZPL) at 1.473 eV and longitudinal-optical (LO) phonon replicas [see Fig. 1(a)] with an energy of 21.2 meV. This structure exhibits a characteristic temperature dependence. One can see that the maximum energy of the emission at about 20 K (see Fig. 1) is not far from the minimum of the thermal-expansion coefficient[6] of the CdTe crystal at about 25 K, which is negative in this region. We demonstrate, however, that the temperature shift of the luminescence lines is not due to the thermal-expansion coefficient.

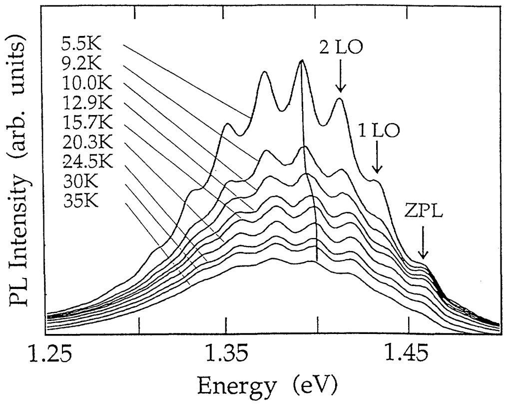

FIG. 1. The photoluminescence spectrum of the *A* center in CdTe as a function of temperature. ZPL and two of the LO-phonon replicas are marked. The extra solid line across the third LO-phonon replica is a guide for the eye to show the variation of the luminescence peak with temperature.

To understand the observed temperature dependence of the recombination lines we present a calculation of the electronic structure of the *A*-center complex which is in agreement with the fine structure obtained from ODMR measurements. In our previous papers[7,8] we developed a new, temperature-dependent electron-ion potential which takes the electron-phonon interaction into account. The determination of the temperature dependence of electronic energy levels can thus be reduced to well-known electronic-structure calculations. We performed our investigation within the Harrison[9] approximation of the linear combination of the atomic orbitals (LCAO) method. The structure of the electronic energy bands at the Γ point and the temperature dependence of the direct energy gap of CdTe crystals were found to be in good agreement with recent experimental data. Here we use a similar procedure to describe the temperature variation of the local electronic energy levels of the *A* center in CdTe. First we will derive the local electronic energy levels of the deep *A* center. Then we demonstrate that the obtained structure of these levels is consistent with the experimental data (luminescence and ODMR measurements), and finally we investigate the temperature variation of these levels.

II. ELECTRONIC STRUCTURE AND RADIATIVE TRANSITIONS

To calculate the electronic energy levels of the *A* center, we use a 16-atom supercell with periodic boundary conditions. The supercell contains a Cd vacancy nearest-neighbor Cl pair (V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$). We classify the electronic states according to the point symmetry of the defect, i.e., according to the irreducible representations of the symmetry group C_{3v}. Using a supercell of the same size for the perfect crystal, we obtain the same electronic levels at the Γ, L, and X points in the Brillouin zone as it results from conventional band-structure calculations. This is so because the results for the perfect crystal do not depend on the size of the supercell. However, the boundary condition must represent the correct translational symmetry. The energy levels of the perfect and imperfect crystals then have the same common energy reference. We found that a 16-atom supercell is large enough so that the artificial defect-defect interaction will not affect the results discussed here. The A center[10] is usually described as a complex defect consisting of a vacancy-donor pair (see Fig. 2). For CdTe it is a vacancy at the cation (Cd) site and an impurity halogen atom (F, Cl, Br, or I) at the nearest-neighbor anion (Te) site. We account for the vacancy at the Cd site by taking the diagonal and off-diagonal elements of the tight-binding energy matrix according to this site equal to zero. This gives a level of T_2 symmetry (assuming no symmetry-breaking lattice relaxation) in the forbidden energy gap around 200 meV above the top of valence band (see Fig. 3). The vacancy also has a level of A_1 symmetry approximately 350 meV above the bottom of the conduction band.

However, the observed luminescence is related with another a_1 level which lies a few meV below the bottom of the conduction band. In fact, the A center is a more complicated defect. During the doping of the CdTe crystal by halogen atoms, some of them are not bound at a Cd vacancy. Instead they occupy isolated Te sites and produce donor levels of A_1 symmetry, which are occupied by one electron in the neutral charge state. We calculate the position of these levels under the assumption that the diagonal elements of the tight-binding energy matrix are equal to the corresponding atomic energy levels. The off-diagonal matrix elements are taken the same as for the perfect crystal. Other types of defect levels are created by the Cd-vacancy halogen pair V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$. The substitutional halogen atom at the nearest Te site of a vacancy can be modeled by taking the diagonal elements of the tight-binding energy matrix equal to the atomic energy levels of this atom. As the Harrison method does not give correct values for the off-diagonal matrix elements between the halogen and the nearest Cd atom, we take these elements to be the perfect crystal, i.e., as in the case of Te-Cd. The point symmetry of the defect is C_{3v} and this is confirmed by ODMR measurements showing the respective g-factor anisotropy. The symmetry reduction from tetragonal symmetry causes the splitting the t_2-energy level of the isolated vacancy into a twofold degenerate e state and an a_1 state, both corresponding to the point group C_{3v}. This splitting of the order of 228 meV is shown in Fig. 3, and the lower a_1 level is shifted into the valence band. The observed luminescence is related to an electronic transition from the donor state of an isolated substitutional halogen atom and the vacancy t_2 level split by the nearest-neighbor halogen atom. This halogen atom, bound to the Cd vacancy, has no donor levels in the band gap, but other local levels deep in the valence band. The role of this halogen atom for the process of the A-center luminescence is that it lowers the symmetry and therefore splits the t_2 level of the Cd vacancy.

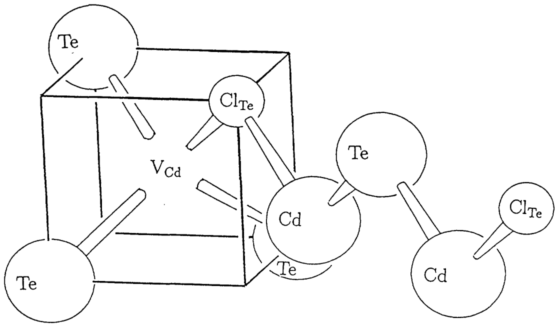

FIG. 2. A model of the A center for a CdTe crystal. A V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair gives rise to the split acceptor level, while the donor level is related to a more distant Cl atom. The distance between the isolated Cl atom and the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair may be larger than shown schematically in this figure.

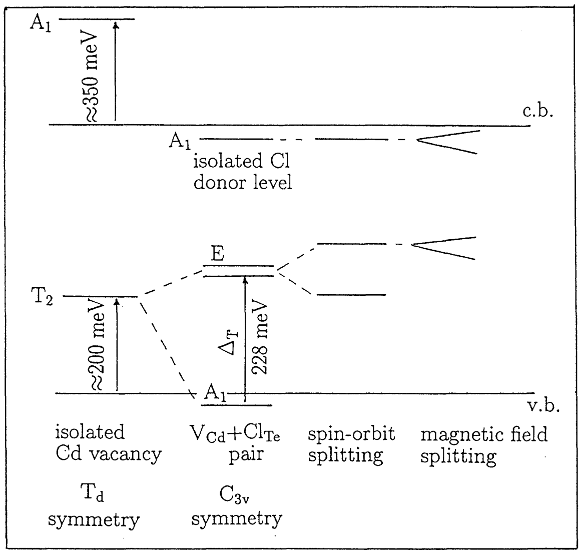

FIG. 3. The electronic energy level scheme of the A center in CdTe.

In the following we want to distinguish between two types of isolated donor centers, namely those which are not far away from the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair, say less than 20–40 Å. In this case the donor wave function overlaps with the wave function of the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair. For such a complex the luminescence can take place directly from the donor to the acceptor level, or when the temperature is high enough, from the conduction band to the acceptor level. The donor levels are not occupied because they lose their electrons to the acceptors and fill them completely (six electrons). For Cl donors, which are farther away and therefore do not overlap with the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair, the transition to the acceptor state can take place only via the conduction-band states.

The static dielectric constant of CdTe is equal to 9.6 and the Bohr radius of the donors in the ground state is about 45–55 Å. We assume that the number of vacancies in CdTe is smaller than the number N_D of Cl donors. Therefore, the number of V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pairs, which are the origin of the acceptor levels, is smaller than N_D. In the case of a homogeneous distribution of $N_D \sim 10^{17}$ cm^{-3} donors, their average separation is 210 Å. If the number of V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pairs is of the same order of magnitude as N_D, then the ratio c of the number of donors, which do not overlap with a V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pairs, to the number of overlapping donors is about $c \approx 10-100$.

III. THE LUMINESCENCE SPECTRUM

It is well known that optical transitions at deep centers in II-VI compounds are usually observed together with a number of phonon replicas. Perfect crystal optical phonons and local vibrational modes often give rise to well-resolved lines in the sidebands of the ZPL. The reason for this is that for such vibrations nearest-neighbor atoms vibrate against each other, and due to their opposite effective charge there is a strong interaction with the electromagnetic field of the photon. In case of the A-center luminescence both the initial (an electron in a donor state) and final states (an electron in the deep acceptor state) are localized states. The transition between such two separate states is associated with a charge transfer, which not only causes a change of the atomic positions around the defect, but also a change of the long-range Coulomb potential due to the change of the charge state of the defect. It is therefore expected that optical phonons with small wave vectors have the strongest interaction with the photon. This explains the observed dominance of the longitudinal-optical phonon at the Γ point with an energy of $\hbar\omega = 21.2$ meV in the luminescence spectra of the A center.[2-4] The emission spectrum consists of m discrete lines at frequencies $m\hbar\omega$. Due to the spin-orbit splitting the acceptor level can be considered as an orbital singlet. The position of this singlet strongly depends on the breathing configuration coordinate which is changed compared to the perfect crystal value. This change depends on the chemical nature of the nearest halogen atom. In contrast the donor level is nearly independent of the configuration coordinate as it has a largely extended wave function. The shape of the emission spectrum between such a donor-to-acceptor (having orbital singlet) recombination is well described by a shape function[11] proportional to $S^m e^{-S}/m!$, where S is the dimensionless Huang-Rhys factor. The donor level is not sensitive to the lattice relaxation but the factor S depends on the lattice relaxation around the defect site. Therefore, there should exist some correlation between the energy position of the acceptor level and the value of the Huang-Rhys factor.

IV. THE g FACTORS

In order to confirm our calculations of the splitting of the T_2 energy level of the Cd vacancy, we also calculated the Zeeman splitting and compared it with the experimentally observed g factor of the A-center luminescence. An exact determination of g factors is quite complicated because the wave function of the defect includes components of many atoms close to the defect site. Additionally, we do not know accurately the spin-orbit coupling parameter for the different atoms in CdTe. Due to this we will confine ourselves to a rough estimation only. In spite of these limitations the calculation confirms the correctness of our electronic energy level scheme. In the crystal-field approximation we use electronic wave functions of T_d symmetry localized at the nearest neighbors of the vacancy only, an assumption which is justified by the measured Te-hyperfine interaction.[3,4] Taking the spin-orbit interaction by first and second orders of perturbation theory into account, we obtain the energy-level scheme shown in Fig. 3. A calculation up to second-order perturbation theory gives, for the g factors,

$$g_{\parallel} = g_0 \quad \text{and} \quad g_{\perp} = g_0 - \frac{\zeta}{\Delta_T} , \tag{1}$$

where $g_{\parallel}$ corresponds to the magnetic field parallel and $g_{\perp}$ to the magnetic field perpendicular to the trigonal axis of the defect. Using the spin-orbit coupling parameter $\zeta = 420$ meV, which is the value of an isolated Te atom, and the calculated value of the trigonal crystal field splitting of $\Delta_T = 228$ meV, we obtain $g_{\parallel} \sim 2$ and $g_{\perp} \sim 0.2$. The corresponding experimental values[3,4] are $g_{\parallel} = 2.2$ and $g_{\perp} = 0.4$. Our rough estimation thus reproduces the large reduction of $g_{\perp}$ with respect to the free-electron value $g_0 = 2.0023$. Further corrections to the g factor arise from contributions of the T_1, E, and A_2 electronic energy levels by second-order perturbation theory. The direct products $T_2 \times T_1$, $T_2 \times E$, and $T_2 \times A_2$ contain the T_1 representation of the orbital momentum operator. A more precise calculation should include covalent bonding. However, even this simple estimate of the g factor together with the general agreement of the calculated electronic energy-level scheme with those deduced from the observed emission spectrum confirms the correctness of the adopted energy-level scheme shown in Fig. 3.

V. TEMPERATURE DEPENDENCE OF THE DONOR-ACCEPTOR LUMINESCENCE

The luminescence originating from the A center in CdTe (Ref. 3) in the temperature region 5–30 K, shown in Fig. 1, exhibits a shift of the ZPL of 4–5 meV toward higher energies. For temperatures above 30 K the observed luminescence lines are shifted to lower energies. A possible explanation for the temperature variation of the luminescence lines is the following. At low temperatures the emission takes place only from a nearby donor to the acceptor level. When the temperature is increased, a number of electrons from donor levels are excited into the conduction band and they also contribute to the luminescence at a slightly higher energy.

Let us consider first the temperature dependence of the luminescence due to transitions from an overlapping donor to the acceptor state. At a given temperature T the fraction w_1 of neutral donors and w_2 of positively charged donors is given by

$$w_1=\frac{1}{1+\exp\left\{-\dfrac{\epsilon}{k_BT}\right\}}\quad\text{and}\quad w_2=\frac{1}{1+\exp\left\{\dfrac{\epsilon}{k_BT}\right\}}\,, \tag{2}$$

with

$$\epsilon=E_c-E_d\quad\text{and}\quad w_1+w_2=1\;. \tag{3}$$

Here E_c denotes the bottom of the conduction band and E_d the energy of the donor level, and k_B is the Boltzmann constant. The direct transition from the donor to the acceptor level E_a occurs at the energy E_d-E_a, whereas the transition via the conduction band is at E_c-E_a. The luminescence line is a superposition of the two transitions leading to a temperature-dependent average energy of

$$E_l=w_1(E_d-E_a)+w_2(E_c-E_a)\;. \tag{4}$$

The calculated luminescence spectrum at $T=20$ K, according to Eq. (4), is shown in Fig. 4. The solid line shows the spectrum of the direct transition only, while the dashed line is obtained by including both donor and conduction-band states. The difference, however, is very small.

We now will modify Eq. (2) in order to include the transitions from the Cl donor states which do not overlap with the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair. At low temperatures the electron is trapped at the isolated donor state and cannot release its energy by a transition to the acceptor level as in the case of overlapping donors. However, when the temperature is increased the electron can be excited to the conduction band and from there releases its energy by a transition to the acceptor state. We denote with c the ratio of the number of nonoverlapping donors to the number of overlapping donors, then the average energy of the donor-acceptor luminescence is given by Eq. (4) with

$$w_1=\frac{1}{1+c\,\exp\left\{\dfrac{\epsilon}{k_BT}\right\}}\,,\qquad w_2=\frac{c\,\exp\left\{-\dfrac{\epsilon}{k_BT}\right\}}{1+c\,\exp\left\{-\dfrac{\epsilon}{k_BT}\right\}}\;. \tag{5}$$

Figure 5 shows the calculated luminescence spectrum at $T=20$ K with $\varepsilon=5.1$ meV and $c=10$, which is close to the experimental one. The energy of the luminescence ZPL between $T=0$ and 300 K, calculated by Eqs. (4) and (5), is shown in Fig. 6. Figure 7 shows the temperature variation of all the levels under consideration. The average energy exhibits a maximum around 20 K and then decreases as the temperature increases. It can be seen from Fig. 7 that the conduction band at the Γ point as well as the donor level E_d, continuously decrease in energy with increasing temperature, whereas the acceptor level E_a increases in energy. Therefore, the maximum of the luminescence around 20 K is related to the thermal excitation of the donor electrons to the conduction band followed by a recombination. Because of the smallness of the total variation of the conduction band and the donor and acceptor levels with temperature, this effect is observed only at temperatures below 30 K. In the calculation of the luminescence spectrum, shown in Fig. 4, we used $\varepsilon=5.1$ meV, which is close to the value of 5 ∓ 1 meV obtained from the temperature variation of the intensity of the luminescence lines. The ground-state level of the donor is deeper, but there are a number of excited

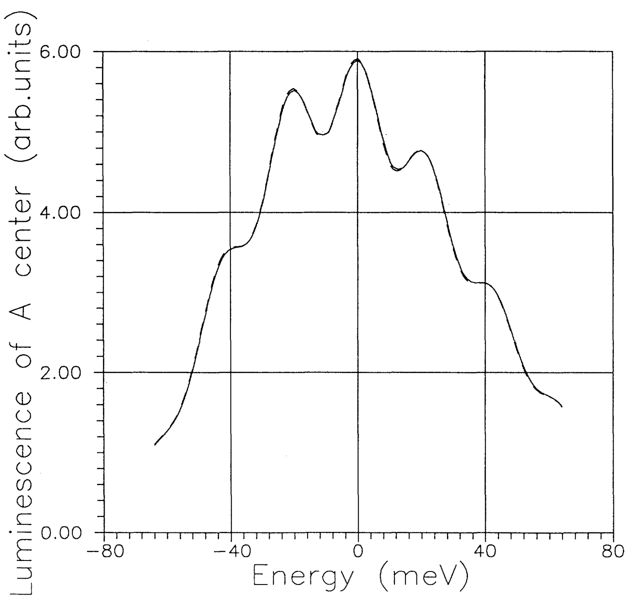

FIG. 4. The calculated luminescence spectrum of an isolated V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair.

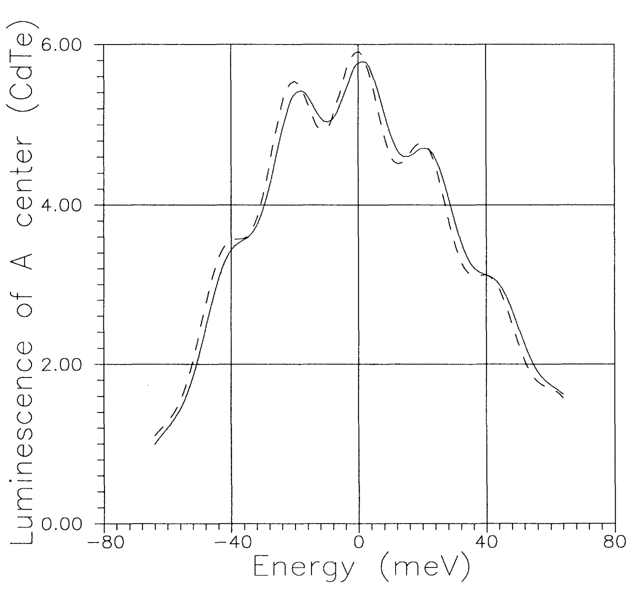

FIG. 5. The calculated luminescence spectrum of the A center taking isolated $\mathrm{Cl}_{\mathrm{Te}}$ donors into account, $c=10$ (see text).

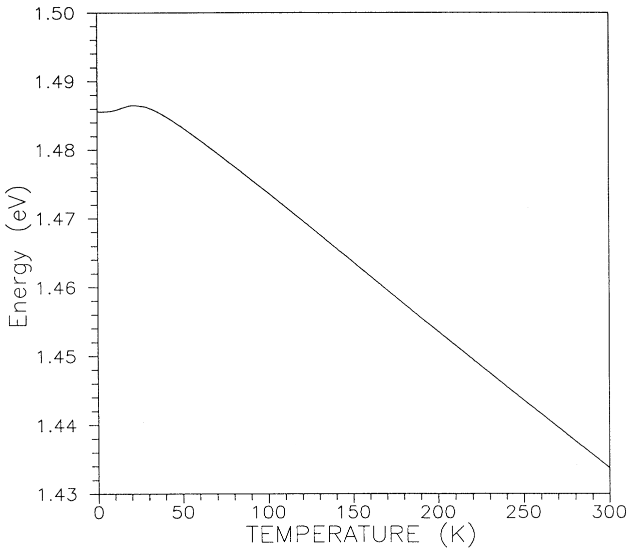

FIG. 6. The calculated average energy of the A-center luminescence ZPL, shown in Fig. 5, as a function of temperature.

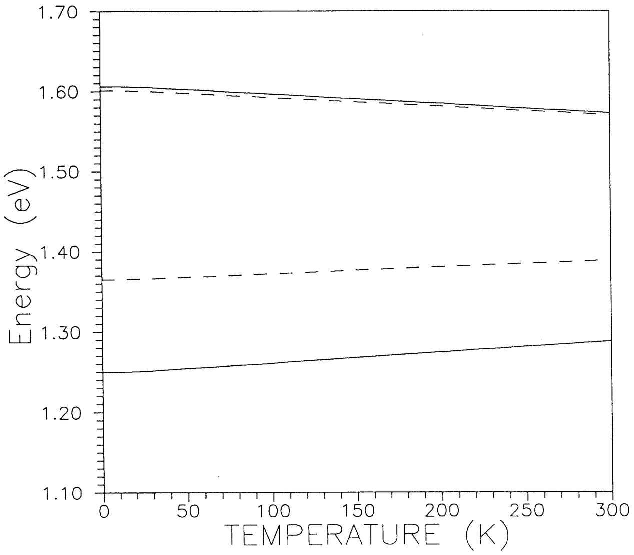

FIG. 7. The temperature variation of the Γ point of the conduction band (upper solid line), and donor level (upper dashed line), the acceptor level (lower dashed line), and the Γ point of the valence band (lower solid line). The acceptor and valence-band energies were shifted up by 1.25 eV.

states so that we used an effective energy of $\varepsilon = 5.1$ meV in our calculation.

VI. DISCUSSION

In Sec. V we explained the increase of energy of the donor-acceptor transition with temperature by means of the thermal excitation of donor electrons to the conduction band and subsequent recombination. We also investigated the temperature variation of the donor-acceptor luminescence with respect to the negative thermal expansion coefficient of the CdTe crystal.[2] The minimum of the expansion coefficient is around 25 K, i.e., close to the maximum energy of the luminescence ZPL at about 20 K (see Fig. 6). We have calculated the effect of the thermal expansion and found that it cannot explain the observed temperature shift of the luminescence line position. First, the influence of the thermal expansion of the crystal on the temperature variation of electronic energy levels is small compared with the harmonic contribution of the crystal vibrations. The anharmonic contribution, causing the thermal expansion, increases $E_d - E_a$, not more than 0.5 meV. This effect is concealed by the larger contribution of opposite sign resulting from the harmonic contribution, which comes from the reduction of the effective electron-ion potential leading to a decrease of $E_d - E_a$, Second, as the effect of the anharmonic contribution enters the corresponding equations as an integral over the expansion coefficient, its largest contribution is between 50 and 60 K. Thus, comparing with the maximum energy shift of the luminescence line, the anharmonic contribution is largest at temperatures above 30 K. Therefore, the effect of the anharmonic contribution is too small and it is in a different temperature region compared with the observed increase in the luminescence line position.

We also checked the possible influence of local vibrational modes coupled to the V_{Cd}-$\mathrm{Cl}_{\mathrm{Te}}$ pair. The change of the interatomic force constants with respect to the perfect crystal comes from the breaking of the neighboring bonds at the vacancy. We have estimated the local vibrational modes at the vacancy using a simple valence-force model. We found modes of A_1 and T_2 symmetries at energies around 3 and 19 meV. The vibrational amplitudes of the atoms around the vacancy, participating in the local vibrational modes, may be different from those of the perfect crystal atoms. This may slightly change the temperature dependence of the acceptor level (see Fig. 7), but not the top of the valence band. Therefore, it is unlikely that the calculated energetic distance between the donor and acceptor levels will be increased considerably by the local vibrational modes.

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[1] For a review, see B. C. Cavenett, Adv. Phys. **3**, 475 (1981).
[2] D. M. Hofmann, B. K. Meyer, U. Probst, and K. W. Benz, J. Cryst. Growth **101**, 536 (1990).
[3] D. M. Hofmann, P. Omling, H. G. Grimmeiss, D. Sinerius, K. W. Benz, and B. K. Meyer, Mater. Sci. Forum **83-87**, 1235 (1992).
[4] D. M. Hofmann, P. Omling, H. G. Grimmeiss, B. K. Meyer, K. W. Benz, and D. Sinerius, Phys. Rev. B **45**, 6247 (1992).

[5] C. B. Norris and C. E. Barnes, Rev. Phys. Appl. (France) **12**, 219 (1977), and references therein.

[6] T. F. Smith and G. K. White, J. Phys. C **8**, 2031 (1975).

[7] S. Biernacki, U. Scherz, and B. K. Meyer, in *Proceedings of the 21st International Conference on the Physics of Semiconductors,* edited by P. Jiang and H.-Z. Zheng (World Scientific, Singapore, 1993), p. 1681.

[8] S. Biernacki, U. Scherz, and B. K. Meyer (unpublished).

[9] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), Chaps. 2 and 3.

[10] F. F. Morehead and G. Mandel, Phys. Rev. **137**, A924 (1965).

[11] R. K. Watts, *Point Defects in Crystals* (Wiley, New York, 1977), Chap. 3.