Temperature dependence of optical transitions between electronic energy levels in semiconductors

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We propose a model to describe temperature-dependent electronic transitions using an effective electron-ion interaction. We present a nonperturbative calculation of the temperature dependence of the forbidden energy gap of CdTe crystals. The results are compared with similar calculations using the statistical-function method and both give good agreement with experimental data. It is also demonstrated that the thermal expansion of the lattice plays a minor role for the temperature variation of the electronic energy levels.

I. INTRODUCTION

The understanding of the temperature dependence of electronic energy levels of perfect and imperfect semiconductors is important for technological applications. The corresponding theoretical models as well as the results of their application to particular crystals and the comparison with experimental data was reviewed by Cohen and Chadi,[1] and is also given in a number of recent papers.[2–7] Two methods are currently used to describe the temperature variation of the electronic energy levels in semiconductors: the perturbative treatment of the electron-phonon interaction, and the statistical-function method. In the perturbative treatment the electron-phonon interaction, which depends on temperature through the atomic displacements, is regarded as a correction to the adiabatic approximation. In the statistical-function method the temperature variation follows from the change of the Gibbs free energy for the corresponding electronic states. In particular, these methods are used for the calculation of the temperature variation of the forbidden energy gap. They are not related to each other and are inapplicable for the calculation of the temperature variation of energy levels of localized defects.

The temperature variation may be separated into an explicit harmonic and an implicit anharmonic part. Usually the explicit contribution is remarkably larger than the implicit one. We here present a temperature-dependent effective electron-ion interaction potential which accounts for the large contribution of the electron-phonon interaction. Using this model we perform a direct, nonperturbative calculation of the temperature variation of the forbidden energy gap. The method also serves to understand the temperature variation of the luminescence of the A center in CdTe crystals.[8] The observed shift of the emission energy has a maximum at a temperature of about 20 K, which is not far from the minimum of the thermal-expansion coefficient of CdTe at 25 K. In order to understand such temperature-dependent transitions between electronic energy levels in semiconductors, we first study the temperature variation of the forbidden energy gap of CdTe crystals. Our results are in good agreement with experimental data, and we explain why the explicit contribution is large compared to the implicit one. We also demonstrate that there are no numerical differences between our direct calculation and the statistical-function method.

The paper is organized as follows. In Sec. II we give a theoretical background for the calculation of the temperature dependence of optical transitions between electronic energy levels of semiconductors. In Sec. III the theoretical model of the temperature-dependent electron-ion interaction is described, and we indicate the difference between the conventional perturbative treatment and our direct method. The results of our calculations of both methods are compared with experiments for CdTe in Sec. IV.

II. TEMPERATURE DEPENDENCE OF OPTICAL TRANSITIONS

Here we describe crystals consisting of N_N nuclei and N_E electrons by a Hamiltonian of the form

$$H=T^I+T^E+V^{E-I}+V^{E-E}+V^{I-I}\ , \tag{1}$$

where T^I gives the kinetic energy of the nuclei,

$$T^I=-\sum_{I=1}^{N_N}\frac{\hbar^2}{2M_I}\Delta_I\ , \tag{2}$$

and M_I denotes the nuclear masses. The Hamiltonian Eq. (1) may be used for an all-electron calculation by applying the frozen-core approximation. In the latter case there are N_N rigid ions and N_E valence electrons. The kinetic energy of the electrons is given by

$$T^E=-\sum_{i=1}^{N_E}\frac{\hbar^2}{2m}\Delta_i\ . \tag{3}$$

We denote the coordinates of the electrons by $\mathbf{r}_i$, $i=1,2,\ldots,N_E$, and of the nuclei or ions by $\mathbf{R}_I$, $I=1,2,\ldots,N_I$. The potential energy of the electrostatic repulsion of the electrons is

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$$V^{E\text{-}E}=\frac{e^2}{8\pi\varepsilon_0}\sum_{\substack{i,j\\ i\neq j}}^{1,\ldots,N_E}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\,, \tag{4}$$

and of the ions is

$$V^{I\text{-}I}=\frac{e^2}{8\pi\varepsilon_0}\sum_{\substack{I,J\\ I\neq J}}^{1,\ldots,N_N}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\,, \tag{5}$$

where Z_I denotes the charges of the nuclei or ions. The potential energy of the electron-ion interaction may then be written in the form

$$V^{E\text{-}I}=\sum_{i=1}^{N_E}\sum_{I=1}^{N_N}v_I(|\mathbf{r}_i-\mathbf{R}_I|)\,, \tag{6}$$

where v_I is the spherically symmetric electron-ion interaction potential. In the method adopted here we do not consider spin-orbit interaction or other relativistic effects.

We write the Born-Oppenheimer approximation of H in the form

$$H\approx H^{\mathrm{el}}+H^{\mathrm{vib}}\,, \tag{7}$$

with

$$H^{\mathrm{el}}=T^E+V^{E\text{-}I}(\mathbf{R}_I^0)+V^{E\text{-}E}+V^{I\text{-}I}(\mathbf{R}_I^0) \tag{8}$$

and

$$H^{\mathrm{vib}}=T^I+E_\nu^{\mathrm{el}}(\mathbf{R}_I)-E_\nu^{\mathrm{el}}(\mathbf{R}_I^0)\,. \tag{9}$$

Here E_ν^{el} are the eigenvalues of the electronic Hamiltonian H^{el}, and the vibrations of the crystal are obtained by introducing the positions $\mathbf{R}_I^0$ of the minimum of the Born-Oppenheimer electronic total-energy surface $E_\nu^{\mathrm{el}}(\mathbf{R}_I)$ defined by

$$\left[\frac{\partial E_\nu^{\mathrm{el}}(\mathbf{R}_I)}{\partial \mathbf{R}_I}\right]_{\mathbf{R}_I=\mathbf{R}_I^0}=0\,, \tag{10}$$

so that the $\mathbf{R}_I^0$ depends on the electronic state considered. We further describe the ionic motion in the harmonic approximation so that the vibrational Hamiltonian may be written in the form

$$H^{\mathrm{vib}}=\sum_j \hbar\omega_j(a_j^\dagger a_j+\tfrac{1}{2})\,. \tag{11}$$

According to Eq. (9) the vibration frequencies ω_j depend on the electronic state considered, and $a_j^\dagger$ and a_j are the corresponding creation and annihilation operators, respectively. The eigenvalues E of the Hamiltonian H of Eq. (7) are then given by

$$E_{\nu\mu}=E_\nu^{\mathrm{el}}+E_{\nu\mu}^{\mathrm{vib}}=E_\nu^{\mathrm{el}}+\sum_j\hbar\omega_j(n_j+\tfrac{1}{2})\,, \tag{12}$$

where $n_j=0,1,2,\ldots$ are the occupation numbers of all the vibrational states, and $\mu=\{n_1,n_2,\ldots\}$ describes the vibrational spectrum $E_{\nu\mu}^{\mathrm{vib}}$.

The Born-Oppenheimer approximation allows us to calculate the eigenvalues of the Hamiltonian in Eq. (7) as a function of the crystal volume V defined by the nuclear coordinates $\mathbf{R}_I^0$. For a semiconductor in thermodynamic equilibrium, we then consider a canonical ensemble for which the partition function is given by[9]

$$Z(T,V)=\exp\left\{-\frac{E_0^{\mathrm{el}}(V)}{k_BT}\right\}\sum_\mu\exp\left\{-\frac{E_{0\mu}^{\mathrm{vib}}(V)}{k_BT}\right\}, \tag{13}$$

where k_B is the Boltzmann constant. The electronic ground state E_0^{el} of a perfect semiconductor crystal is nondegenerate, but in the case of imperfect crystals we have to multiply the right-hand side of Eq. (13) by the degeneracy of the electronic ground state. This gives an additional contribution to the Helmholtz free energy, for example of $-k_BT\ln 2$ for a twofold spin-degenerate electronic state. Equation (13) holds in the case of $E_\nu^{\mathrm{el}}-E_0^{\mathrm{el}}\gg k_BT$ for all excited electronic states ν. We will assume that this condition is valid for the semiconductors considered here. This means that the system cannot be brought to an excited *electronic* state by *thermal* excitation. We then obtain the Helmholtz free energy by

$$F(T,V)=-k_BT\ln Z(T,V)\,, \tag{14}$$

which may be separated into an electronic and a vibrational part:

$$F(T,V)=E_0^{\mathrm{el}}(V)+F^{\mathrm{vib}}(T,V)\,. \tag{15}$$

Because of the harmonic approximation using Eq. (12) we find

$$F^{\mathrm{vib}}(T,V)=\sum_j\left[\tfrac{1}{2}\hbar\omega_j+k_BT\ln\left[1-\exp\left\{-\frac{\hbar\omega_j}{k_BT}\right\}\right]\right]. \tag{16}$$

Using the definitions for entropy

$$S(T,V)=-\left[\frac{\partial F}{\partial T}\right]_V \tag{17}$$

and pressure

$$p(T,V)=-\left[\frac{\partial F}{\partial V}\right]_T \tag{18}$$

we can calculate the Gibbs free energy by solving the equation of state (18) for the volume $V=V(T,p)$:

$$G(T,p)=F+pV\,. \tag{19}$$

Here the difference between F and G can be neglected at normal pressure. The Gibbs free energy G is thus calculated as a function of the nuclear positions $\mathbf{R}_I^0$ and the equilibrium positions $\mathbf{R}_I^e$ are defined by

$$\left[\frac{\partial G}{\partial \mathbf{R}_I^0}\right]_{T,p}=0\,. \tag{20}$$

Due to Eq. (13) the Gibbs free energy and other properties of the thermodynamic equilibrium are determined by the *electronic ground state* of the semiconductor only. The reason for this is that the semiconductor cannot be brought to the excited *electronic* state by *thermal* excita-

tion. The situation is different, however, when a crystal is brought to an excited electronic state by *optical excitation*. The application of the Born-Oppenheimer approximation means practically that we consider the semiconductor to consist of two subsystems: the inhomogeneous electron gas, described by the electronic part of the Hamiltonian, and the ionic system, described by the vibrational part of the Hamiltonian. The interaction of the two subsystems (the electron-phonon coupling) is small, and both subsystems are considered to be in contact with a heat bath at temperature T. Therefore, applying quantum statistics the equilibrium state defined by the Gibbs free energy is found from the partition function calculated, taking all many-electron and vibrational energy levels into account.[10]

We assume that the initial state is the thermodynamic equilibrium. Then, in the case of absorption of a photon by the electronic subsystem, the Franck-Condon principle postulates that the absorption process is so fast that the final state is not a thermodynamic equilibrium but is characterized by an appropriate electronic state, whereas all the nuclear positions are kept fixed. In a second step the system then relaxes to new nuclear positions. In the third step the system may release its electronic energy by an optical emission process, which again does not lead to a thermodynamic equilibrium. In a fourth step the system finally relaxes its nuclear coordinates to their equilibrium positions as in the initial state. This leads to the Stokes shift between absorption and emission lines, and is usually interpreted using the so-called configuration-coordinate diagram.

The band-to-band transition of a perfect cubic crystal is a special case because the only configuration coordinate is the lattice parameter or crystal volume (a phase transition to a different crystal structure requires much more energy). The change of the crystal volume due to a photon of, say, 1 eV is so small that it can neither be measured nor calculated directly. The smallness of the corresponding volume work also cannot cause a measurable Stokes shift for band-to-band transitions. The situation is different, however, for transitions involving electronic defect levels where the nearest-neighbor atoms may relax their position as a consequence of an optical transition. These processes, described by the four steps, can be calculated using the following method. The initial state of thermodynamic equilibrium is calculated using a canonical ensemble and the Born-Oppenheimer approximation.[11] The Gibbs free energy is obtained from the partition function Eq. (13) which contains the electronic ground state only. After the absorption of the photon the excited nonequilibrium state is described by a partition function Z_x similar to Eq. (13), modified by replacing E_0^{el} by the excited electronic energy level E_x^{el}. We here assume that there are no other electronic energy levels within the region of $k_B T$. We further assume that E_x^{el} is nondegenerate, because this would result in entropy changes of the electronic subsystem leading to an energy exchange with the heat bath. The lattice relaxation, described above as step 2, can now be found from $G_x(T,p,\mathbf{R}_I)$ derived from Z_x and using Eq. (20) accordingly. Keeping these relaxed nuclear coordinates fixed, the system may release its energy to the electronic ground state in step 3 giving $G(T,p,\mathbf{R}_I)$. The following lattice relaxation of step 4 leads to equilibrium positions $\mathbf{R}_I^e$ by use of Eq. (20).

Therefore, in case the lifetime of the excited electronic state is sufficiently large to allow for the relaxation of the atomic nuclei, we obtain a different crystal volume, different equilibrium positions $\mathbf{R}_I^e$ of the nuclei, and different vibration frequencies $\hbar\omega_j$ compared with the values for the electronic ground state.

In the case of a perfect semiconductor crystal there are many other excited electronic energy levels above the energy gap E_g within $k_B T$. We will assume that these excited electronic states give approximately the same vibration frequencies, so that the Helmholtz free energy again may be separated into electronic and vibrational parts.

When a semiconductor in an excited electronic state emits a photon and returns to the electronic ground state, then, due to the Franck-Condon principle, the energy difference is given by the difference between the Helmholtz free energies in the excited state F_x and ground state F_0:

$$h\nu=\Delta F=F_x-F_0=E_x^{\mathrm{el}}-E_0^{\mathrm{el}}+F_x^{\mathrm{vib}}-F_0^{\mathrm{vib}} \tag{21}$$

and this difference has been separated into electronic and vibrational parts. Equation (21) describes transitions between electronic states which both refer to the same positions $\mathbf{R}_I^0$ of the nuclei, which are equilibrium positions of the initial state. We further neglect the same variation of the volume in the electronic excited and ground states related to the change of the electronic configuration.

Equation (21) does not give a rigorous description of optical transitions in semiconductors, but contains simple approximations to describe the temperature shift of optical transitions. The electron-phonon interaction is taken into account in a more indirect way by assuming different vibration frequencies for the electronic ground and excited states.[6] Due to this, Eq. (21) cannot be used to describe properties such as line shapes, which depend on many details of the electron-phonon interaction.

In order to calculate the temperature dependence of optical transitions between electronic energy levels of semiconductors, we distinguish between the implicit temperature dependence, originating from the thermal expansion, and the explicit temperature dependence, originating from the vibrational part of the Helmholtz free energy *taken at a fixed crystal volume V:*

$$\begin{aligned}\left(\frac{\partial \Delta F}{\partial T}\right)_p &= \left(\frac{\partial \Delta F}{\partial T}\right)_V + \left(\frac{\partial \Delta F}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ &= \left(\frac{\partial \Delta F}{\partial T}\right)_V - B\alpha \left(\frac{\partial \Delta F}{\partial p}\right)_T ,\end{aligned} \tag{22}$$

where ΔF is given by Eq. (21). Here B denotes the bulk modulus

$$B(T,V)=-V\left(\frac{\partial p}{\partial V}\right)_T , \tag{23}$$

and α the thermal-expansion coefficient

$$\alpha=\frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_p . \tag{24}$$

Comparing the experimentally observed temperature derivative of the energy gap E_g of various semiconductors (see Table I), with the pressure derivative of the energy gap multiplied by the bulk modulus and the thermal-expansion coefficient, we find from Eq. (22) that the implicit temperature dependence (second term) is remarkably small compared with the explicit temperature dependence (first term). We therefore restrict ourselves here to the calculation of the explicit temperature dependence of optical transitions, which can be calculated from the Helmholtz free energy at a given volume V.

According to Eq. (15) the electronic part of the Helmholtz free energy does not depend on temperature, and therefore the temperature dependence of an optical transition energy $h\nu$ is determined by the vibrational part of Eq. (21), which may be approximated in the following way:

$$h\nu(T)=E_x^{\mathrm{el}}-E_0^{\mathrm{el}}+\sum_j \frac{\partial F_0^{\mathrm{vib}}}{\partial \hbar\omega_j}\Delta\hbar\omega_j =h\nu(0)+\sum_j \frac{\Delta\hbar\omega_j}{\exp\left\{\frac{\hbar\omega_j}{k_B T}\right\}-1} , \tag{25}$$

where $\Delta\hbar\omega_j$ is the difference of the vibration energies in the electronic excited and ground states. Here $h\nu(0)$ is the photon energy at zero temperature including the zero-temperature vibrations, and we used Eq. (16) and the assumption $\Delta\hbar\omega_j \ll \hbar\omega_j$. The vibration energies $\hbar\omega_j$ are determined by the dynamical matrix obtained from the elastic potential given by $E_\nu^{\mathrm{el}}(\mathbf{R}_I)$ in the harmonic approximation.

III. THEORETICAL MODEL

In order to understand the explicit temperature dependence of an optical transition, we may use Eq. (25) and determine the change of the vibration energies $\Delta\hbar\omega_j$ due to the electronic transition at a fixed crystal volume. As can be seen from Eq. (25), the temperature dependence of an optical transition results from a sum over all vibrations of the crystal. Such an integral quantity may well be understood by simple models in order to avoid cumbersome first-principles calculations. We here present two simple approaches. The direct method is based on an effective and temperature-dependent softening of the electron-ion interaction potential, whereas in the statistical-function method the sum in Eq. (25) is reduced to a few dominating frequencies, the changes of which are obtained from simple assumptions. Both methods yield satisfactory results, and give better insights into the microscopic processes involved.

We begin by describing the direct method by which we deduce the change of the electron-ion interaction potential Eq. (6) with temperature in the classical limit of the ionic motion. In this approximation the positions of the ions $\mathbf{R}_I(t)$ are given by time-dependent displacement vectors $\mathbf{u}_I(t)=(u_{I1,}u_{I2,}u_{I3})$:

$$\mathbf{R}_I(t)=\mathbf{R}_I^0+\mathbf{u}_I(t) \tag{26}$$

for each of the ions I, and for the time average we have

$$\langle \mathbf{u}_I(t)\rangle=0 . \tag{27}$$

In the classical limit and in thermodynamic equilibrium,

TABLE I. The experimental values of the $[dE_q(\Gamma)/dT]_p$ at room temperature, and the implicit contribution $-3B\alpha(dE_g/dp)_T$ for the direct energy gap. The data for Si and Ga are taken from the paper of P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983), while other data are from K. W. Böer, *Survey of Semiconductor Physics* (Van Nostrand Reinhold, New York, 1990).

	$\left[\frac{dE_q(\Gamma)}{dt}\right]_p$	$-3B\alpha\left[\frac{dE_g}{dp}\right]_T$	$\left[\frac{dE_g(\Gamma)}{dp}\right]_T$	B	α
Crystal	$\left[\frac{\mathrm{meV}}{K}\right]$	$\left[\frac{\mathrm{meV}}{K}\right]$	$\left[\frac{\mathrm{meV}}{\mathrm{kbar}}\right]$	(Mbar)	$(10^{-6}\ \mathrm{K}^{-1})$
IV					
Si	−0.22	−0.04	5.2	0.980	2.59
Ge	−0.44	−0.17	13	0.752	5.75
III-V					
GaAs	−0.39	−0.17	11.3	0.746	6.63
InP	−0.29	−0.09	9.1	0.725	4.75
InAs	−0.34	−0.08	10.0	0.588	4.52
II-VI					
ZnS	−0.47	−0.09	5.8	0.719	6.8
ZnSe	−0.45	−0.08	6	0.606	6.9
ZnTe	−0.52	−0.10	8.3	0.500	8.19
CdTe	−0.54	−0.05	8	0.424	4.8

the mean-square displacement of an ion I is given by

$$\langle u_I^2(T)\rangle = \langle u_{Iv}^2\rangle = \frac{\hbar}{N_N M_I}\sum_j \frac{1}{\omega_j}\left[\frac{1}{\exp\left\{\frac{\hbar\omega_j}{k_B T}\right\}-1}+\frac{1}{2}\right], \quad (28)$$

where the sum goes over all vibration frequencies. Introducing Eq. (26) into Eq. (6) and applying a Taylor expansion, we obtain

$$V^{E\text{-}I}(\mathbf{R}_I) = V^{E\text{-}I}(\mathbf{R}_I^0) + \sum_I \frac{\partial V^{E\text{-}I}}{\partial \mathbf{R}_I^0}\mathbf{u}_I + \frac{1}{2}\sum_{I,J}\frac{\partial^2 V^{E\text{-}I}}{\partial \mathbf{R}_I^0 \partial \mathbf{R}_J^0}\mathbf{u}_I\mathbf{u}_J + \cdots . \quad (29)$$

Taking the time average of this expression, we make the assumption of uncorrelated phases of the displacements $\mathbf{u}_I(t)$, and find

$$\langle V^{E\text{-}I}\rangle \approx V^{E\text{-}I}(\mathbf{R}_I^0) + \tfrac{1}{2}\sum_I \sum_{v=1}^{3}\frac{\partial^2 V^{E\text{-}I}}{\partial R_{iv}^{02}}\langle u_I^2\rangle = V^{E\text{-}I}(\mathbf{R}_I^0) + \tfrac{1}{2}\sum_{i=1}^{N_E}\sum_{I=1}^{N_N}\langle u_{Iv}^2\rangle \Delta v_I(|\mathbf{r}_i - \mathbf{R}_I^0|) , \quad (30)$$

where we have used Eq. (6) and $\mathbf{R}_I^0 = (R_{I1}^0, R_{I2}^0, R_{I3}^0)$. We take advantage of the fact that the ionic potential v_I is spherical symmetric, so that the Laplacian can be replaced by the simple form ($r = |\mathbf{r}_i - \mathbf{R}_I|$):

$$\langle V^{E\text{-}I}\rangle = V^{E\text{-}I}(\mathbf{R}_I^0) + \tfrac{1}{2}\sum_{i=1}^{N_E}\sum_{I=1}^{N_N}\langle u_I^2\rangle\left[\frac{2}{r}\frac{\partial v_I}{\partial r} + \frac{\partial^2 v_I}{\partial r^2}\right] . \quad (31)$$

This is approximately equal to a Taylor expansion up to first order only, and we obtain

$$\langle V^{E\text{-}I}\rangle \approx V^{E\text{-}I}(\mathbf{R}_I^0) + \sum_{i=1}^{N_E}\sum_{I=1}^{N_N}\frac{\langle u_I^2\rangle}{r}\frac{\partial v_I}{\partial r} = \sum_{i=1}^{N_E}\sum_{I=1}^{N_N} v_I\left[|\mathbf{r}_i - \mathbf{R}_I^0| + \frac{\langle u_I\rangle^2}{|\mathbf{r}_i - \mathbf{R}_I^0|}\right] . \quad (32)$$

The physical interpretation of this result is as follows. Comparing Eq. (6) with Eq. (32), we see that the time average of the electron-ion interaction potential $V^{E\text{-}I}$ is reduced because the temperature-dependent effective distance between the electron and ion is larger than in the case of nonvibrating ions:

$$\frac{|\mathbf{r}_i - \mathbf{R}_I^0|^2 + \langle u_I^2\rangle}{|\mathbf{r}_i - \mathbf{R}_I^0|} > |\mathbf{r}_i - \mathbf{R}_I^0| . \quad (33)$$

Using the tight-binding approximation we consider only the s and p valence orbitals at every atom in the CdTe crystal. Then at the Γ point the lowest valence-band Γ_{1v} and lowest conduction-band Γ_{1c} energies result from the solution of the secular equation for the two s orbitals s_1 and s_2, and are given by[12]

$$E(\Gamma_{1c,v}) = \frac{E_{s1}+E_{s2}}{2} \pm \left[\left[\frac{E_{s1}-E_{s2}}{2}\right]^2 + V_{ss}^2\right]^{1/2} . \quad (34)$$

The upper valence-band state Γ_{15v} and the upper conduction-band state Γ_{15c} follow from the secular equation for the two p orbitals p_1 and p_2, and are given by

$$E(\Gamma_{15c,v}) = \frac{E_{p1}+E_{p2}}{2} \pm \left[\left[\frac{E_{p1}-E_{p2}}{2}\right]^2 + V_{xx}^2\right]^{1/2} . \quad (35)$$

Here E_s and E_p are the diagonal matrix elements which, in the Harrison[13] version of the tight-binding approximation, are simply atomic single-electron eigenvalues for the s and p electrons at the two atoms in the elementary unit cell. They do not depend on temperature in this approximation. V_{ss} and V_{xx} are the corresponding off-diagonal matrix elements. Harrison has demonstrated that for tetrahedral semiconductors they can be approximated by

$$V_{ss} = \eta_{ss}\frac{\hbar^2}{md^2} \quad \text{and} \quad V_{xx} = (\tfrac{1}{3}\eta_{pp\sigma} + \tfrac{2}{3}\eta_{pp\pi})\frac{\hbar^2}{md^2} , \quad (36)$$

where η_{ss}, $\eta_{pp\sigma}$, and $\eta_{pp\pi}$ are universal constants, and m and d are the electron mass and interatomic distance, respectively. In order to account for the temperature-induced reduction of the interaction potential [see Eq. (32)], we replace d^2 by the average of $d^2+u_I^2$ in the off-diagonal matrix elements [Eq. (36)]. Using Eq. (28) we then obtain the temperature dependence of the electronic energy levels in the tight-binding approximation. From the expansion of $1/(d^2+\langle u_I^2\rangle)$ in terms of powers of $\langle u_I^2\rangle$, one sees that the off-diagonal matrix elements describe the thermal shifts of electronic energy levels more accurately than to the second power in the thermal displacements. In the limit of very narrow bands (at large interatomic distance) the temperature dependence disappear. In our consideration the electron-phonon interaction is partly included in the effective interaction potential, and that part which is proportional to the odd powers of the displacements can be further used for the calculation of transition probabilities to particular states. In our direct method no extra computational effort is necessary, because the calculation at a given temperature is the same as for a calculation at zero temperature.

We may rederive the expression for the matrix elements of the tight-binding approximation using a different limiting case. In the nearly free-electron approximation the ionic potential, which is a sum of atomic potentials $v_I(\mathbf{r}-\mathbf{R}_I^0-\mathbf{u}_I)$ localized at the atomic sites $\mathbf{R}_I^0$, is developed in terms of plane waves $\exp\{i\mathbf{kr}\}$. A typical matrix element is[14]

$$\left\langle \exp\{-i\mathbf{k}'\mathbf{r}\}\left|\sum_I v_I(\mathbf{r}-\mathbf{R}_I^0-\mathbf{u}_I)\right|\exp\{i\mathbf{kr}\}\right\rangle = \sum_I \int^{i\mathbf{K}(\mathbf{r}-\mathbf{R}_I^0-\mathbf{u}_I)} v_I(\mathbf{r}-\mathbf{R}_I^0-\mathbf{u}_I) \times \exp\{i\mathbf{K}(\mathbf{R}_I^0+\mathbf{u}_I)\}d^3r = \sum_I \exp\{i\mathbf{K}(\mathbf{R}_I^0+\mathbf{u}_I)\}v_I(\mathbf{K}) , \quad (37)$$

where $\mathbf{K}=\mathbf{k}-\mathbf{k}'$ is a vector of the reciprocal lattice, and $v_I(\mathbf{K})$ is the Fourier transform of the atomic potential. In the calculation of this matrix element the coordinate $\mathbf{r}$ of the plane wave as well the position $\mathbf{R}_I^0$ of the atomic sites were taken with respect to one of the fixed lattice sites (the origin of the coordinate system). We consider a crystal with constant volume at different temperatures. An increase of temperature causes a reduction of the interaction potential. This can be seen from Eq. (37), since an increase of the vibration amplitude $\mathbf{u}_I$ causes a reduction of the Fourier transform $v_I(\mathbf{K})$ by a temperature-dependent factor. The conclusion that the vibration effectively reduces the Fourier transform $v_I(\mathbf{K})$ was generally stated in Ref. 1. The lowering of the scattering amplitudes of neutrons by atoms in crystals at increasing temperatures has been explained in a similar way.[14,15] Furthermore, in Ref. 16 the calculation of the thermal shift of electronic energies in II-V semiconductors was performed by using pseudopotentials changed by a temperature-dependent structure factor (Debye-Waller factor). This means practically that the concept of narrowing of the interaction potential was indirectly used. Apart from this our method differs from the above-mentioned one in that we account for higher powers of the atomic displacements. The above arguments and those of Sec. II lead to the conclusion that the vibrational motion reduces the effective electron-ion interaction, and the thermal shift of the electronic energy levels can equivalently be described in both tight-binding and nearly free-electron approximations. Contrary to the free-electron approximation in the linear combination of atomic orbitals (LCAO) approach, the amplitude $\mathbf{u}_I$ should not enter the corresponding phase factor $\exp\{i\mathbf{k}\mathbf{R}_I^0\}$, as this factor reflects the symmetry of the lattice and the average position of the atoms, while in the free-electron approximation the factor $\exp\{i\mathbf{K}(\mathbf{R}_I^0+\mathbf{u}_I)\}$ accounts for the electron-ion interaction.

Now we point out an important qualitative conclusion which can be obtained without the calculation of the temperature variation of the electronic energy levels. Since the pioneering work of Fan,[17] there has existed the challenge of understanding why the effect of the thermal expansion on the temperature variation of the electronic levels is small compared with the effect of the electron-phonon interaction. The direct method presented here offers an answer: The effect of the thermal expansion is equivalent to replacing the interatomic distance d in Eq. (36) with $d+\Delta d$, where Δd describes the change due to temperature. The effective reduction of the electron-ion interaction Eq. (32) at a fixed crystal volume is approximately described by $\mathbf{u}_I$, and $(d+\Delta d)^2$ in Eq. (36) is replaced by $(d+\Delta d)^2+\langle u_I^2\rangle$. We therefore have to compare Δd with $\sqrt{\langle u_I^2\rangle}$. For a simple description of the phonon spectrum we use the Einstein model with three frequencies as discussed in Sec. IV. Taking CdTe as an example, we find a thermal expansion of $\Delta d=0.002\,16$ Å and $\sqrt{\langle u_I^2\rangle}=0.59$ Å, where we used the lattice parameter $a=6.481$ Å and determined $\langle u_I^2\rangle$ according to Eq. (28). These quantities differ by two orders of magnitude, and this explains why the effect of the thermal expansion is much smaller compared with the effect of the electron-phonon interaction.

We now turn to the statistical-function method and the calculation of the temperature dependence of optical transitions according to Eq. (25). The crucial point here is an estimation of the change of the vibration energies $\Delta\hbar\omega_j$ resulting from electronic excitation. In the case of a localized state of a deep defect, an electronic transition at the defect causes a change of the interatomic forces in the vicinity of the defect. Since these forces determine the vibration frequencies, which are obtained from the eigenvalues of the dynamical matrix, the most simple assumption is that the change of energy of a local vibrational mode $\Delta\hbar\omega$ is determined by the change of an effective force constant ΔK_{eff},

$$\Delta\hbar\omega=\frac{\hbar\Delta K_{\text{eff}}}{2\omega m_{\text{eff}}}\ , \qquad (38)$$

as in the case of a one-dimensional harmonic oscillator. Here m_{eff} denotes an effective mass, which is assumed not to be changed by the optical transition. The next assumption is that the change of the effective force constant is related to the difference ΔE between the initial and final electronic states of the transition by

$$\Delta K_{\text{eff}}=\frac{\partial^2\Delta E}{\partial q^2}\ , \qquad (39)$$

where q is an appropriate configuration coordinate in view of the configuration-coordinate model for optical transitions. Assuming that the crystal phonons are unchanged by a transition between two localized states, the local vibrational modes predominantly determine the temperature dependence of the optical transition according to Eq. (25), and Eqs. (38) and (39) can be used to evaluate the right-hand side of Eq. (25).

In the case of a band-gap transition in a perfect semiconductor, the difference in electronic energies is $\Delta E=E(\Gamma_{1c})-E(\Gamma_{15v})$. The most simple assumption then is that Eqs. (38) and (39) may also be applied to find the change of the vibration energies for all relevant contributions to the right-hand side of Eq. (25). In this case the interatomic distance may serve as the appropriate configuration coordinate. For band-gap transitions at the Γ point, optical phonons with small wave vectors are mostly affected. The mean value of the masses of the atoms in the elementary unit cell are then taken as the effective mass in Eq. (39).

In order to determine the temperature variation of electronic transitions, we deduce the necessary information with the direct method from the difference of single-electron energy levels, and with the statistical-function method from the second derivative of the electronic energy levels with respect to displacements. In this way we demonstrate the compatibility of the direct and statistical-function methods. In the latter method we calculate the change of the phonon spectrum caused by the change of the electronic state, whereas in the direct method we calculate the change of the electron spectrum caused by the change of the phonon occupation numbers with temperature, as can be seen from the Bose-Einstein

distribution in Eq. (28). Finally we point out that due to the increasing randomness of the atomic movement with increasing temperature, causing an increase of entropy, the Helmholtz free energy decreases with increasing temperature.

IV. NUMERICAL CALCULATION OF $E_g(T)$ FOR CdTe

The purpose of our numerical calculation is to check the validity of the models described. In fact, part of this can be found in Refs. 2–5 in dealing with the direct method in the nearly free-electron approximation. These extensive calculations were performed for Si and Ge crystals, using the pseudopotential concept and the valence-force model for the phonon spectrum in first and second orders of perturbation theory, as well the approach of the Debye-Waller factor. The calculated temperature dependence of $E_g(T)$ was found to be in fairly good agreement with measurements, and possible errors were discussed in detail. We here perform a nonperturbative, direct calculation of the temperature dependence of the direct energy gap at the Γ point in CdTe crystals within the tight-binding approach of Harrison. This approximation is justified because the amplitude of vibration $\mathbf{u}_l$ and the thermal change of the interatomic distance Δd are small compared with the interatomic distance. Our scheme of calculation contains a number of fitting parameters, but the final step of the calculation, i.e., the temperature dependence of the top of the valence band and the bottom of the conduction band, does not include any fitting parameters except the energy gap at zero temperature. Now we proceed to the calculation of the band levels at the Γ point according to the Harrison method at $T=0$ K. For CdTe the experimental energy gap at the Γ point is 1.9 eV,[18] or, including the spin-orbit splitting, 1.606 eV.[19] The energy gap obtained using Harrison universal parameters is two times larger than the experimental value, and therefore we readjusted the parameters V_{ss} and V_{xx} entering Eqs. (34) and (35), to give $V_{ss}=2.142\,87$ eV and $V_{xx}=1.771$ eV, so that we obtain the correct value of the energy gap. Further, we need information about the phonon spectrum to calculate $\langle u_l^2 \rangle$ according to Eq. (28), which is valid only for the Bravais lattice. To this end we take advantage of experimental information about the heat capacity. We approximate the phonon spectrum by the Einstein model using three frequencies, and we assume that the Cd and Te atoms have the same vibration amplitudes, which is justified by the small mass difference of about 12%. From the density of phonon states of CdTe we select three pronounced frequencies:[20,21] $\hbar\omega_1=4.1$ meV, $\hbar\omega_2=13$ meV (for the acoustic branches), and $\hbar\omega_3=17.8$ meV (for the optical branches). Then we fit the experimental values of the heat capacity taken at temperatures below 25 K from Ref. 22, and for higher temperatures from Fig. 5 of Ref. 23. The heat capacity C_v then contains three weight factors g_1, g_2, and g_3 as fitting parameters:

$$C_v = k_B \sum_{i=1}^{3} g_i \frac{x_i^2 \exp\{x_i\}}{(\exp\{x_i\}-1)^2} , \tag{40}$$

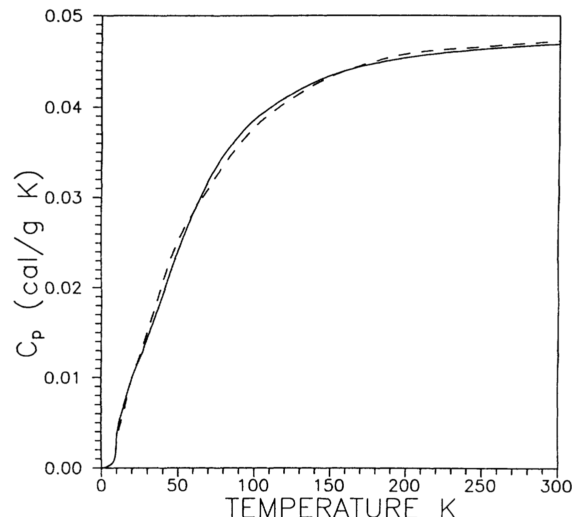

FIG. 1. Fit (solid line) of the heat capacity according to Eq. (40) using three fitting parameters g_1, g_2, and g_3. The experimental values (dashed) were taken from Refs. 22 and 23.

with $x_i=\hbar\omega_i/k_BT$. As a result of the fitting, shown in Fig. 1, we obtain $g_1=0.920$, $g_2=0.164$, and $g_3=1.830$. The sum of the weight factors of 2.914 is not far from the correct value of 3, resulting from a correct density of phonon states. From the weight factors g_i we calculate $\langle u_l^2 \rangle$ according to Eq. (28). In Fig. 2 we show the resulting temperature dependence of the energy gap together with the experimental data taken from Fig. 3 of Ref. 19. Figure 3 shows the temperature dependence of the band energies at Γ_{1c} and Γ_{15v}. These results were obtained using a fixed interatomic distance of $d=2.806$ Å. Additionally we assumed that due to our fitting the effect of the zero-temperature vibrations is included in the parameters V_{ss} and V_{xx}. This effect would change the energy

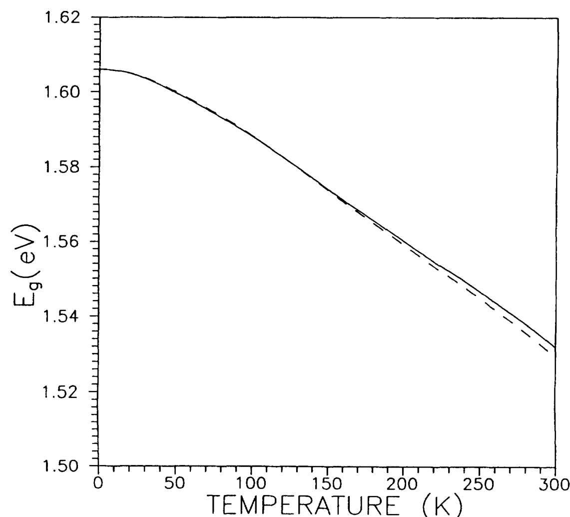

FIG. 2. Temperature variation of the energy gap at point Γ for CdTe calculated according the tight-binding approximation within the Harrison model. Experimental data (dashed line) are taken from Ref. 19.

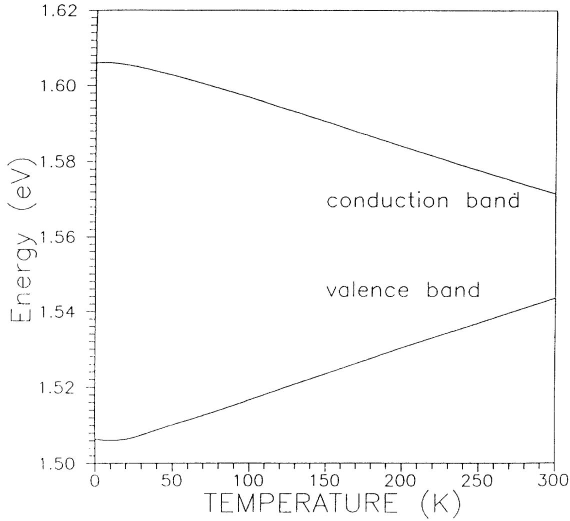

FIG. 3. Temperature variation of the valence- and conduction-band levels at the Γ point calculated according the tight-binding approximation. The valence-band level is shifted up by 1.5 eV.

gap by 9 meV. In Fig. 4 we show the change of the energy gap due to the thermal expansion only, i.e., we take $\langle u_l^2 \rangle$ as a constant and consider the effect of the temperature-dependent interatomic distance d. The calculation was performed by two methods. In the tight-binding calculation we used an interatomic distance according to the thermal expansion coefficient α [see Eq. (24)],

$$d(T)=d(0)\exp\left\{\tfrac{1}{3}\int_0^T \alpha(T')dT'\right\} . \quad (41)$$

On the other hand, we applied Eq. (22) for the implicit temperature dependence to obtain

$$E_g(T)_{\text{implicit}}=-B\frac{dE_g}{dp}\int_0^T \alpha(T')dT' , \quad (42)$$

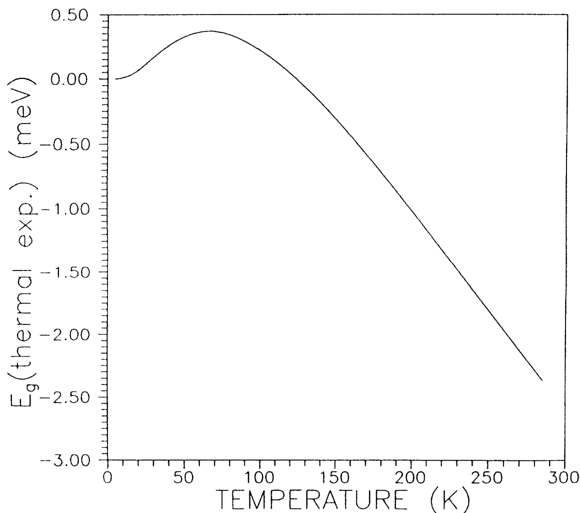

FIG. 4. Temperature variation of the energy gap due to the thermal expansion only.

where we used the bulk modulus $B=0.423$ Mbar and the pressure derivative of the energy gap $dE_g/dp=8$ eV/Mbar. Both methods give the same result shown in Fig. 4.

Applying the statistical-function method we calculated the change of vibration energies according to Eqs. (38) and (39), and obtained $\Delta\hbar\omega_1=-0.0108$ meV, $\Delta\hbar\omega_2=-0.0001$ meV, and $\Delta\hbar\omega_3=-0.0098$ meV. We here use the mean value of the nuclear masses of Cd and Te as a good approximation for the effective mass entering Eq. (39), because the difference of the nuclear masses is only 12%. With this we obtain from Eq. (25) the temperature dependence of the energy gap of CdTe shown in Fig. 5.

V. DISCUSSION

Let us first consider the details of the mechanism of the temperature variation of the energy gap. The band levels are due to the off-diagonal matrix elements V_{ss} and V_{xx} in Eqs. (34) and (35). In our model we introduce the narrowing of the electron-ion potential due to the vibration amplitudes $\mathbf{u}_l$. V_{ss} and V_{xx} become smaller with increasing temperature, and the energy gap decreases. As $V_{ss}\neq V_{xx}$ the Γ_{1c} and Γ_{15v} energy levels change their positions with different slopes but the energies at Γ_{1c} and Γ_{1v} as well as at Γ_{15v} and Γ_{15c} are shifted in opposite directions having the same absolute value of the temperature derivative. The semiempirical calculation of Ref. 24, which includes the Fan term only (the vibration amplitude $\mathbf{u}_l$ in second-order perturbation theory), shows for temperatures below 50 K that the conduction-band level Γ_{1c} is weakly dependent on T. The main variation of the energy gap with temperature comes from the variation of the valence-band level Γ_{1v}. Similar results were obtained in more accurate calculations for Si on Refs. 2 and 5. In the cases of Si and Ge (where $V_{ss}\gg V_{xx}$) the change of the energy gap is mainly due to the shift of the valence

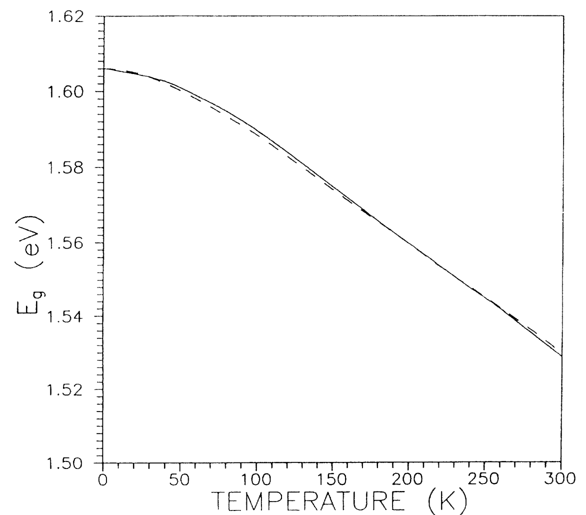

FIG. 5. Temperature-dependent energy gap calculated according to the statistical-function method. Experimental data (dashed line) are taken from Ref. 19.

band. From our calculation for CdTe we conclude that the temperature changes of the energies at Γ_{1c} and Γ_{15v} are similar, since the values of V_{ss} and V_{xx} are comparable in magnitude. It is not excluded that in more refined models, taking the 5s states into account, the temperature variation of the band levels may be slightly changed. From the mechanism of the temperature variation of electronic energy levels presented here, it follows that all longitudinal and transversal phonon branches participate for $E_g(T)$. The longitudinal phonons change the interatomic distance (causing the narrowing of v_I) along the direction of their propagation, the transversal modes those perpendicular to their propagation. This qualitative conclusion was also confirmed by the calculation presented in Ref. 6 for Si crystals. The calculated change of the energy gap originating from the zero-temperature vibration is 9 meV and therefore rather small. In Ref. 4 this effect was estimated to be 65 meV.

The experimental data for the temperature variation of the forbidden energy gap (direct or indirect) are similar for many materials. Most of these data, found in the literature, were fitted by the formula

$$\gamma(T)=\frac{\alpha T^2}{(T+\beta)} , \tag{43}$$

which contains two fitting parameters α and β. It was originally given by Varshni[25] using the behavior of $E_g(T)$ in the vicinity of zero temperature and above the Debye temperature as the best way to achieve an empirical fit. To our knowledge it has no physical foundation. From Eq. (25) we see that the temperature variation is described by the Bose-Einstein distribution. Assuming that the sum can be evaluated with a few frequencies only, selected from the peaks of the density of phonon states, the experimental data may as well be fitted with Eq. (25) using the energy shifts $\Delta\hbar\omega_i$ as parameters. A similar form was applied to fit the experimental data in Ref. 26 but no physical justification was given. In Fig. 6 we show the best fit of $E_g(T)$ by both formulas to the experimental

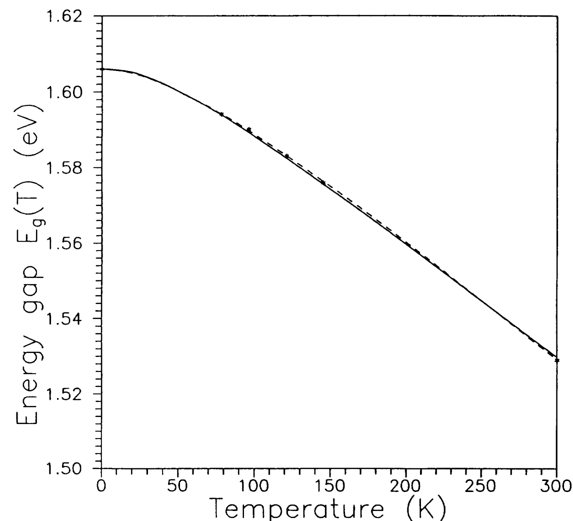

FIG. 6. Observed energy gap from Ref. 19 (points), and fits according to Eqs. (25) (solid line) and (43) (dashed line).

data for CdTe. The fit by Eq. (25) gave $\Delta\hbar\omega_1=-0.0090$ meV, $\Delta\hbar\omega_2=-0.0033$ meV, and $\Delta\hbar\omega_3=-0.0158$ meV. These values should be compared with our estimation according to Eq. (38). We conclude that the direct fit of $E_g(T)$ as well as our estimation (based on the fit of the heat capacity) predict a softening of the phonon spectrum upon electron excitation. The observed inaccuracy in the determination of $\Delta\hbar\omega_2$ from both methods is related to the small sensitivity of the fit by Eq. (25) to the experimental data.

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