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Dependence of the lattice parameters and the energy gap of zinc-blende-type semiconductors on isotopic masses

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The dependence of the E_0 direct gap of Ge, GaAs, and ZnSe on isotopic masses at low temperatures has been investigated. Contributions of the variation of the lattice parameter to the gap shift of the binary compounds have been evaluated by using a volume-dependent lattice dynamics, while local empirical pseudopotential techniques have been employed to calculate gap shifts due to electron-phonon interaction. The dependence of these terms on the lattice-dynamical model and on the $q \rightarrow 0$ extrapolation of the pseudopotential form factors has been investigated. The contributions of the optical and acoustical modes to the isotopic shift are analyzed. The results are compared to previous experimental data, in the case of germanium, and to low-temperature reflectance measurements performed as part of this work on GaAs samples with different isotopic gallium composition. Particular attention has been paid to the differences in the effects of changing either the cation or the anion masses. The temperature dependence of the E_0 gap of ZnSe has also been calculated, and reasonable agreement with experiment has been found. [S0163-1829(96)02032-2]

I. INTRODUCTION

The possibility of growing isotopically enriched semiconductors has allowed us to investigate the dependence of their basic solid-state properties on isotopic masses and disorder (for an overview, see Refs. 1–4). The variation of the thermal conductivity with isotopic composition, the dependence of phonon frequencies and linewidths on the isotopic masses, and the dependence of the lattice constant and energy gaps on the average isotopic mass are some of the most interesting properties. This interest is not only of basic relevance, but technical applications have also been proposed.[5,6] A considerable amount of studies have been published during the last few years on the isotopic dependence of such properties in diamond-type semiconductors.[1–4] Interest has recently shifted to zinc-blende-type materials.[7–9]

The dependence of the electronic energy gap E_0 on the isotopic mass M_κ of a semiconductor compound (κ is the atomic species) at a constant temperature can be separated into two contributions, similar to those responsible for the temperature dependence of the gaps:[10–12]

$$\left(\frac{\partial E_0}{\partial M_\kappa}\right)_T = \left(\frac{\partial E_0}{\partial M_\kappa}\right)_{\mathrm{EP}} + \left(\frac{\partial E_0}{\partial M_\kappa}\right)_{\mathrm{TE}}. \tag{1}$$

The first term is the contribution of the electron-phonon interaction (EP) at constant volume. The second one is due to the change of the lattice constant or, equivalently, of the crystal volume with the isotopic mass. Anharmonic corrections to the crystal volume at low temperatures depend on the atomic masses through the ''zero-point'' vibrational amplitudes. The origin of this term is equivalent to that of the thermal expansion (TE) at low temperature; by analogy we shall call it the zero-point thermal expansion term.

The influence of the isotopic mass on the crystal volume has recently been calculated for diamond-type semiconductors such as C, Si, or Ge by *ab initio* total-energy techniques.[13] The results are in striking agreement with the experiment for diamond,[14] and slightly smaller than the only experimental point available for Ge.[15]

In binary semiconductors, the calculation of the dependence of volume (or lattice parameter) on isotopic masses is more complicated. It is not possible to write the relative variation of the crystal volume as a simple function of the relative variation of the mass. Phonon frequencies depend differently on the two masses, and this dependence has to be known, together with the corresponding Grüneisen parameters for all phonon modes, in order to calculate the dependence of the lattice constant on the isotopic masses. In this paper we present calculations of the dependence of the lattice constant of ZnSe on the two isotopic masses. We have employed an 11-parameter rigid-ion model[16] (RIM) at two different pressures, i.e., two different unit-cell volumes, to obtain the Grüneisen parameters. Due to the absence of a similar dynamical model for GaAs, an estimation of the variation of its lattice parameter with Ga and As (Ref. 17) masses has been performed by interpolating the ZnSe and Ge results. We find, in all cases, that the magnitude of the mass derivative of the lattice parameter is larger for the anion element than for the cation.

The dependence of electronic band gaps on isotopic masses has been extensively studied in diamond-type semiconductors. Davies *et al.*[18] studied the lowest direct gap E_0 and the indirect gap E_{ind} of Ge by means of absorption measurements at 2 K. They found a change $\partial E_0/\partial M_{\mathrm{Ge}} = 0.49 \pm 0.03$ meV/amu. There are also experimental results for the $E_0+\Delta_0$ (Ref. 19), E_1 (Ref. 20), and $E_1+\Delta_1$ (Ref. 21) critical points (cp's) of Ge. Diamond exhibits a larger isotopic shift. Collins *et al.*[22] found a difference of 14.0±0.7 meV between the lowest indirect gaps of ^{12}C and ^{13}C. Theoretical studies of the dependence of several energy gaps and linewidths on isotopic mass and temperature in diamond, silicon, and germanium have been performed by Zollner, Cardona, and Gopalan.[21] Their calculations are in rather good agreement with the experiment for diamond. In the case of germanium they slightly overestimate the isotopic mass dependence of the indirect $E_{\rm ind}$ and E_0 gaps. The calculations for the E_1 cp, however, considerably underestimate the experimental results.

We investigate in this work the dependence of the E_0 cp on the isotopic mass and temperature in several semiconductors isoelectronic to germanium. In Sec. II we present experimental results of reflectivity in the neighborhood of the fundamental gap of GaAs, obtained for several samples with different isotopic gallium compositions. Section III is devoted to the calculation of the dependence of the lattice constant on the isotopic mass at low temperature. The variation of the E_0 gap due to thermal expansion at low temperatures is discussed in Sec. IV. In Sec. V, we use the *local empirical pseudopotential method* to obtain the gap renormalization due to the electron-phonon interaction and its mass dependence in Ge, GaAs, and ZnSe. The temperature dependence of the ZnSe gap is calculated in Sec. VI, and compared with existing experimental results. Finally, in Sec. VII we summarize the main conclusions of the work.

II. EXPERIMENTAL RESULTS

A series of GaAs samples with a controlled composition of Ga isotopes has been grown by molecular-beam epitaxy on semi-insulating [001]-oriented GaAs substrates using the stable isotopes ^{69}Ga and ^{71}Ga as source materials. The thickness of the layers is 5000 Å. They were grown with a rate of 2 Å/s at a substrate temperature of 580 °C. The ratio of ^{69}Ga to ^{71}Ga in alloy samples was controlled by appropriately adjusting the individual particle fluxes via the source temperature. The average Ga masses of the samples obtained this way are 69, 69.5, 70, 70.5, and 71 amu, respectively. In addition to these specimen we have used natural GaAs (60.4% ^{69}Ga, 39.6% ^{71}Ga, 100% ^{75}As, and average Ga mass 69.8 amu) grown by liquid-phase epitaxy as a reference. The isotopic gallium composition of all samples was checked by Raman spectroscopy. We find that the frequency of the longitudinal-optic (LO)-phonon shifts with the reduced GaAs mass to a very good approximation.

To determine the fundamental band gap of GaAs, we performed reflectivity measurements at 10 K. Since the spectra are influenced by the excitonic character of the absorption edge we have taken the minimum of the reflectivity curves as a measure of the gap. Results are shown in Fig. 1. A linear least-squares fit (solid line) to the data (points) yields a slope of

$$\frac{\partial E_0}{\partial M_{\rm Ga}}=0.39\pm0.06\ \text{meV/amu}. \tag{2}$$

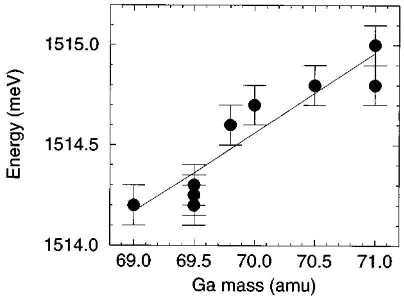

FIG. 1. E_0 gap of GaAs with isotopically controlled Ga composition obtained from reflectivity measurements at $T=10$ K. The solid line shows a linear least-square fit to the experimental data.

III. DEPENDENCE OF THE LATTICE CONSTANT ON ISOTOPIC MASSES

The equilibrium volume of a crystal at a given temperature depends, through anharmonicity, on the amplitude of the lattice vibrations. Actually, the anharmonic contribution is nonzero even at zero temperature, due to the ''zero-point'' vibrational amplitude (the minimum energy of a quantum oscillator is $\hbar\omega/2$). In order to connect the change in volume with phonon parameters we use the Helmholtz free energy F, which is related for a system of independent oscillators (phonons) through the partition function.[23] In terms of the energy of individual oscillators, F can be written as

$$F=\sum_{\nu,\boldsymbol{q}}\left\{\frac{1}{2}\hbar\omega_\nu(\boldsymbol{q})+kT\ln[1-\exp(-\hbar\omega_\nu(\boldsymbol{q})/kT)]\right\}. \tag{3}$$

The volume of a sample is related to the bulk modulus through $(\Delta V/V)_T=-\Delta p/B$, while p can be written as $p=-(\Delta F/\Delta V)_T$. Using these expressions, we find

$$V=V_0+\frac{1}{B}\sum_{\nu,\boldsymbol{q}}\hbar\omega_\nu(\boldsymbol{q})\gamma_\nu(\boldsymbol{q})[n_B(\omega_\nu(\boldsymbol{q}))+\tfrac{1}{2}], \tag{4}$$

where we have introduced the mode Grüneisen parameters $\gamma_\nu(\boldsymbol{q})$ defined as $\gamma_\nu(\boldsymbol{q})=-\partial\ln\omega_\nu/\partial\ln V$ and $n_B(\omega_\nu(\boldsymbol{q}))$ is the Bose-Einstein factor. In Eq. (4), V_0 represents the crystal volume in the limit of infinite masses. In terms of the lattice constant of the conventional unit cell (a_0 in the limit of infinite masses) for zinc-blende-type materials, Eq. (4) can be written as

$$\frac{a(M_1,M_2)-a_0}{a_0}=\frac{4\hbar}{3Ba_0^3}\sum_{\nu,\boldsymbol{q}}\omega_\nu(\boldsymbol{q})\gamma_\nu(\boldsymbol{q})[n_B(\omega_\nu(\boldsymbol{q}))+\tfrac{1}{2}], \tag{5}$$

where $a(M_1,M_2)$ is the lattice constant for a finite mass of atoms 1 and 2 in the primitive cell at a given temperature. Here we are interested in the change of the lattice parameter when one of the atomic masses changes ($\partial\ln a/\partial M_\kappa$) and in the low-temperature limit in which $n_B\approx0$. If we change the mass of atom κ ($\kappa=1,2$) from M_κ to $M_\kappa+\Delta M_\kappa$, the relative change in the lattice parameter is

TABLE I. Dependence of the lattice constant on the isotopic masses calculated for Ge, GaAs, and ZnSe, as explained in the text. The coefficients are ordered according to increasing atomic mass.

Compound	κ	Mass (amu)	$\partial \ln a/\partial M_\kappa$ (10^{-6} amu^{-1})
ZnSe	Zn	65.38	-7.95
GaAs	Ga	69.74	-6.44
Ge	Ge	72.59	-10.9[a,b]
GaAs	As	74.94	-4.44
ZnSe	Se	78.96	-2.70

[a] This coefficient corresponds to a change of the mass of the two atoms in the primitive cell.

[b] Reference 13.

$$\begin{aligned}\frac{a(M_\kappa+\Delta M_\kappa)-a(M_\kappa)}{a(M_\kappa)} &\simeq \frac{[a(M_\kappa+\Delta M_\kappa)-a_0]-[a(M_\kappa)-a_0]}{a_0}\\ &\simeq \frac{2\hbar}{3Ba_0^3}\sum_{\nu,\boldsymbol{q}} \Delta_\kappa[\omega_\nu(\boldsymbol{q})\gamma_\nu(\boldsymbol{q})]. \end{aligned} \tag{6}$$

By $\Delta_\kappa[\omega_\nu(\boldsymbol{q})\gamma_\nu(\boldsymbol{q})]$ we mean the difference of the quantity in brackets evaluated at two different isotopic masses. This term is usually negative for an increase in either of the masses. Thus it can be understood as an ''isotopic contraction'' of the lattice parameter.

The calculation of Eq. (6) requires an integration over the whole Brillouin zone (BZ). For this reason, it is convenient to define the ''lattice spectral function''

$$\mathcal{F}(M_1,M_2;\Omega)=\frac{2\hbar}{3Ba_0^3}\sum_{\nu,\boldsymbol{q}} \Omega\,\gamma_\nu(\boldsymbol{q})\,\delta[\Omega-\omega_\nu(\boldsymbol{q})], \tag{7}$$

which represents the spectral dependence of the changes in lattice parameter induced by a mass configuration, M_1 and M_2. In terms of Eq. (7), Eq. (6) becomes

$$\frac{\Delta_\kappa a}{a}=\int_0^{\Omega_{\max}} d\Omega\,\Delta_\kappa\mathcal{F}(M_1,M_2;\Omega). \tag{8}$$

In order to obtain the spectral function $\mathcal{F}(M_1,M_2;\Omega)$ for ZnSe, we have proceeded in the following way. First, we made use of the calculations of Talwar *et al.*[16] to obtain the Grüneisen parameters. These authors fitted experimental phonon dispersion data available for ZnSe at two different pressures (ambient pressure and 13.7 GPa) by using a rigid-ion model (RIM) with 11 parameters, developed by Kunc[24] (these parameters are listed in Table I of Ref. 16). We have performed similar calculations for two different isotopic masses. Once we obtained the Grüneisen parameters, the density of states was calculated with the deformable-bond approximation, in order to be consistent with the calculations of the electron-phonon interaction to be described in Sec. V.

Figure 2(a) shows the spectral functions [see Eq. (7)] corresponding to two different isotopic masses of Zn, the mass of the natural isotope (solid line), and the mass of a hypothetical isotope with five more amu (dotted line). We observe that there is a very small difference between both curves in the region of lower energies where transverse and longitudinal acoustic modes (TA and LA) contribute. This difference becomes more important in the region of optical phonons at higher frequencies (TO and LO). Figure 2(a) also shows as an inset the difference between the lattice spectral functions $\Delta\mathcal{F}$ for both masses (solid line) which enters directly into the calculation of the variation of the lattice parameter with the isotopic mass [see Eq. (8)]. The integral of $\Delta\mathcal{F}$ vs energy according to Eq. (8) is shown by the dotted line in the inset of Fig. 2(a). One can see that the main contribution to $\Delta_{\mathrm{Zn}}a/a$ comes from the region of LO and TO phonons. Due to strong oscillations in $\Delta\mathcal{F}$, large cancellations in the integral occur and the main contribution to $\Delta_{\mathrm{Zn}}a/a$ actually arises from phonons around LO$_\Gamma$, i. e., near the center of the Brillouin zone. Let us now compare this with the case in which the Se mass is changed. In Fig. 2(b) we show the spectral functions corresponding to two different Se masses (natural mass: solid line; five more amu: dotted line). The inset of Fig. 2(b) displays the difference of the spectral functions $\Delta\mathcal{F}$ (solid line) and its integral vs energy (dotted line). The units of the integral curves in both insets are those of $\mathcal{F}$ and $\Delta\mathcal{F}$ multiplied by 1 meV. In the case of Se substitution, the region of TA and LA phonons makes a higher contribution than in the case of Zn. Moreover, the energy region of optical phonons makes contributions of smaller amplitude than for Zn. Again, the magnitude and sign of $\Delta_{\mathrm{Se}}a/a$ is determined by the LO$_\Gamma$ phonons.

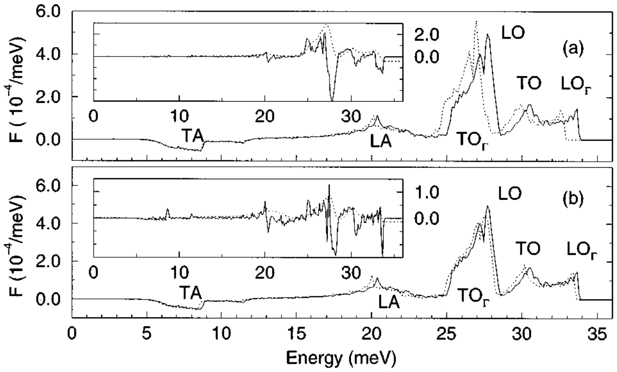

FIG. 2. Lattice spectral functions $\mathcal{F}$ [Eq. (7)] of ZnSe (solid lines: natural abundance) for (a) a change of the Zn mass and (b) the Se mass by 5 amu (dotted lines, respectively). The insets show the difference $\Delta_\kappa\mathcal{F}$ between the two spectral functions for each case (solid lines). The integral over $\Delta_\kappa\mathcal{F}$ (dotted lines in the insets) determines the change of the lattice constant according to Eq. (8).

The differences in the contributions of various phonons to the spectral functions for Zn and Se substitution can be understood by looking at the eigenvectors of the different modes at the X point of the BZ, in whose neighborhood large contributions to the density of states arise. The simplest case is that of longitudinal phonons, in which only one of the species is moving. The LA mode corresponds to vibrations of Se atoms, the LO to Zn vibrations: modes corresponding to light atoms have higher frequencies than those associated with heavy atoms. Thus the shift of the spectral function in the LA peak region, close to 20 meV, is appreciable only for Se [Fig. 2(b)], while the shift in the LO region is larger for Zn substitution. The LO peak overlaps with the TO modes. In the case of transverse phonons both atoms vibrate. How-

TABLE II. Gap shift due to isotopic contraction at $T=0$ K (TE). The values of bulk modulus and the pressure coefficient are taken from Ref. 26, unless explicitly indicated. In the binary compounds, the gap derivatives depend on the atomic species κ as indicated.

Compound	B (GPa)	$(\partial E_0/\partial p)_T$ (meV/GPa)	κ	$(\partial E_0/\partial M_\kappa)_{\mathrm{TE}}$ (meV/amu)
Ge	74.4 [a]	121	Ge	0.29
GaAs	76	111	Ga	0.163
			As	0.112
ZnSe	64.7	75	Zn	0.116
			Se	0.039

[a] Reference 41.

ever, the TA modes mostly correspond to vibrations of the Se atoms, explaining why there is a contribution in the TA region (around 10 meV) in the case of Se. When the mass of Zn is changed, the contribution of the TA modes to the differential spectral function is negligible. For the TO modes, the amplitude of the vibration is larger for Zn atoms than for Se atoms. The influence of changing the Zn mass is therefore stronger [see the inset in Fig. 2(a) in the region around 27 meV]. The differential spectral functions help us to clarify which phonon modes participate more strongly in the lattice constant renormalization. As a consequence of the oscillatory behavior (see the insets of Fig. 2, solid lines) and, consequently, strong cancellations in the integral of Eq. (8) it is hard to see by inspection of Figs. 2(a) and 2(b) which atomic species produces the larger relative variation in the lattice constant.

The numerical results obtained from the integration of the differential spectral functions (insets in Fig. 2, dotted lines) per atomic mass unit, are presented in Table I. When comparing the results for ZnSe with those for Ge obtained by Pavone and Paroni,[13] we note that the effect of changing both masses in the unit cell is nearly the same for both materials. However, whereas for Ge the two atoms contribute equally, for ZnSe the contributions of the anion and the cation are rather asymmetric. The dependence of the GaAs lattice parameter on the Ga and As masses has been obtained by linear interpolation between the values found for Ge and ZnSe because of the less extensive knowledge of Grüneisen parameters for GaAs than for ZnSe.[25] In order to perform this interpolation, the Ge data have to be divided by a factor of 2, since a change in the Ge mass means a change in the mass of the two atoms in the unit cell. The influence of the isotopic mass on the lattice constant in the different semiconductors is larger for replacement of lighter atoms. The negative signs of the coefficients reflect the fact that an increase of the mass produces a decrease in the lattice constant. The smallest value of the lattice constant is obtained for infinite atomic masses (because of anharmonicity the atoms need ‘‘space’’ to vibrate).

IV. DEPENDENCE OF THE GAP ON ISOTOPIC MASS DUE TO CHANGES IN THE LATTICE CONSTANT

The isotopic contribution to the variation of the energy gap E_0 due to zero-point thermal expansion can be written as

$$\left(\frac{\partial E_0}{\partial M_\kappa}\right)_{\mathrm{TE}} = -3B\left(\frac{\partial E_0}{\partial p}\right)_M \left(\frac{\partial \ln a}{\partial M_\kappa}\right)_p . \tag{9}$$

We have evaluated Eq. (9) by using the results of Sec. III, given in Table I, the bulk modulus, and the pressure coefficients of the gaps after Ref. 26. The results are given in Table II for Ge, GaAs, and ZnSe. The calculated value obtained for Ge, 0.29 meV/amu, as mentioned in Sec. III, has to be divided by a factor of 2 when comparing it with the change of either cation or anion masses in GaAs and ZnSe. The contribution to the gap variation, derived from Eq. (9) is of the same order in Ge and GaAs, while in ZnSe it is half of that value. This difference comes from the different pressure coefficient of the ZnSe gap, which is due in part to the larger difference in atomic term values between the cation and anion. Hence the hybridization effect becomes smaller, a fact which causes a smaller change in the gap with the pressure. Table II also shows trends of the gap shifts with the respective masses: As mentioned in the discussion of Table I, the decrease of the lattice parameter with increasing mass becomes smaller for the heavier atomic species. Analogously, the gap shift decreases with increasing mass; i.e., isotopic substitution of a heavier atom like As or Se causes a smaller gap shift than substituting a lighter one like Ga or Zn.

V. DEPENDENCE OF THE GAP ON ISOTOPIC MASS DUE TO ELECTRON-PHONON INTERACTION

The renormalization of electron energies by deformation-potential electron-phonon interaction also plays an important role in the dependence of the energy gaps on temperature and isotopic masses. The temperature dependence of the gaps in zinc-blende-type semiconductors has been widely studied, both theoretically and experimentally.[27] A rigorous derivation of the electron self-energy involved has been given by Allen.[28,29] Here we only summarize the main ideas and final expressions.

To evaluate the effect of electron-phonon coupling on the energy gap, two renormalizations have to be taken into account: The Debye-Waller effect (DW), which arises from the simultaneous interaction of an electron with two phonons with the same wave vector $\boldsymbol{q}$ and from the same branch ν (second-order electron-phonon interaction taken in first-order perturbation theory), and the real part of the self-energy (SE), which comes from the electron–one-phonon interaction taken to second-order perturbation theory. If we assume that the phonon frequencies are smaller than the lifetime broadening of the relevant electronic states, perturbed electron energies $E_n(\boldsymbol{k})$ of band n can be written in terms of the unperturbed energies $\varepsilon_n(\boldsymbol{k})$ (which correspond to infinite ion masses) as

$$E_n(\boldsymbol{k})=\varepsilon_n(\boldsymbol{k})+\sum_{\nu,\boldsymbol{q}}\left(\frac{\partial E_n(\boldsymbol{k})}{\partial n_{\boldsymbol{q}\nu}}\right)(n_{\boldsymbol{q}\nu}+\tfrac{1}{2}), \tag{10}$$

where $n_{\boldsymbol{q}\nu}$ is the occupation number of the $(\nu,\boldsymbol{q})$ vibrational mode, which is finally substituted with the Bose-Einstein factor once a thermal average is performed. The coefficients $(\partial E_n(\boldsymbol{k})/\partial n_{\boldsymbol{q}\nu})$ are the sum of the DW contributions

$$\left(\frac{\partial E_n(\boldsymbol{k})}{\partial n_{\boldsymbol{q}\nu}}\right)_{\mathrm{DW}}=-\frac{\hbar}{2N}\sum_{\substack{\kappa,\kappa',n'\\ \alpha,\beta}}\frac{\langle\boldsymbol{k}n|\partial v_\kappa/\partial R_{\kappa,\alpha}|\boldsymbol{k}n'\rangle\langle\boldsymbol{k}n'|\partial v_{\kappa'}/\partial R_{\kappa',\beta}|\boldsymbol{k}n\rangle}{\varepsilon_n(\boldsymbol{k})-\varepsilon_{n'}(\boldsymbol{k})}\left[\frac{1}{M_\kappa\omega_\nu(\boldsymbol{q})}\epsilon_{\nu,\kappa,\alpha}(-\boldsymbol{q})\epsilon_{\nu,\kappa,\beta}(\boldsymbol{q})+\frac{1}{M_{\kappa'}\omega_\nu(\boldsymbol{q})}\epsilon_{\nu,\kappa',\alpha}(-\boldsymbol{q})\epsilon_{\nu,\kappa',\beta}(\boldsymbol{q})\right] \tag{11}$$

and SE contributions

$$\left(\frac{\partial E_n(\boldsymbol{k})}{\partial n_{\boldsymbol{q}\nu}}\right)_{\mathrm{SE}}=\frac{\hbar}{N}\sum_{\substack{\kappa,\kappa',n'\\ \alpha,\beta}}\frac{\langle\boldsymbol{k}n|\partial v_\kappa/\partial R_{\kappa,\alpha}|\boldsymbol{k}+\boldsymbol{q}n'\rangle\langle\boldsymbol{k}+\boldsymbol{q}n'|\partial v_{\kappa'}/\partial R_{\kappa',\beta}|\boldsymbol{k}n\rangle}{\varepsilon_n(\boldsymbol{k})-\varepsilon_{n'}(\boldsymbol{k}+\boldsymbol{q})}e^{-i\boldsymbol{q}(\boldsymbol{\tau}_\kappa-\boldsymbol{\tau}_{\kappa'})}\frac{1}{\sqrt{M_\kappa M_{\kappa'}\omega_\nu(\boldsymbol{q})^2}}\epsilon_{\nu,\kappa',\alpha}(-\boldsymbol{q})\epsilon_{\nu,\kappa,\beta}(\boldsymbol{q}). \tag{12}$$

Here $\boldsymbol{\tau}_\kappa$ denotes the equilibrium positions of the atoms in the unit cell, N is the number of unit cells in the crystal, $\boldsymbol{R}_\kappa$ is the position of atom κ, α, and β are Cartesian coordinates, and $\boldsymbol{\epsilon}_{\nu,\kappa}(\boldsymbol{q})$ are normalized phonon eigenvectors. Here we adopt the *rigid-ion approximation*, in which the lattice potential is taken to be a sum of atomic potentials which move rigidly with the atoms. Below in Eqs. (11) and (12) we shall use atomic or ionic pseudopotentials for the potentials v_κ. Both the DW and SE corrections depend explicitly on the isotopic mass. In order to calculate the mass derivative at a constant volume, we have to calculate these corrections for two different masses. Since we are interested here in the low-temperature limit, the Bose-Einstein factor will be neglected.

In order to better display the numerical results we define, as in Sec. III, a spectral function, the electron-phonon spectral function, which now depends not only on the phonon frequency and the finite mass configuration, but also on the electron state:

$$g^2F(M_1,M_2,n,\boldsymbol{k};\Omega)=\frac{1}{\hbar}\sum_{\boldsymbol{q},\nu}\frac{\partial E_n(\boldsymbol{k})}{\partial n_{\boldsymbol{q},\nu}}\delta[\Omega-\omega_\nu(\boldsymbol{q})]. \tag{13}$$

In terms of g^2F, the energy renormalization due to electron-phonon interaction, at low temperature, is

$$\Delta E_n(\boldsymbol{k})=\frac{\hbar}{2}\int_0^{\Omega_{\max}}d\Omega g^2F(M_1,M_2,n,\boldsymbol{k};\Omega). \tag{14}$$

To perform the sum over the whole BZ in Eq. (13), we have used the tetrahedron method[30] with a discrete mesh of 89 points in the irreducible wedge of the BZ. To avoid numerical problems in the calculation of Eqs. (11) and (12), we have introduced a Lorentzian broadening of 0.01 Ry in the denominators, which corresponds to electron lifetime broadenings of 0.005 Ry. This value is probably overestimated, but we have checked that the results do not depend on its exact magnitude.

Electronic states are calculated using local empirical pseudopotentials with a basis of 59 plane waves. We have chosen the Cohen-Bergstresser[31] set of empirical pseudopotential form factors $v_\kappa(G)$. The matrix elements containing derivatives of atomic potentials are also calculated within the pseudopotential formalism. To determine these derivatives, however, it is necessary to know $v_\kappa(G)$ as a continuous function of G, not only at the few reciprocal-lattice vectors needed to calculate the band structure. This problem is solved by smoothly interpolating between the known empirical form factors and extrapolating to some judicious value at $G=0$. In our calculations, we have used two different extrapolations: (i) the traditional one[32] (GP), where the form factor takes the value of $-2\varepsilon_F/3$ at $G=0$, as in metals (ε_F is the Fermi energy, which corresponds to the valence electron density in the free-electron case), and (ii) the Bednarek-Rössler[33] extrapolation (BR), in which $v_\kappa(0)$ is taken to be zero. We have investigated in detail the dependence of the isotopic shift of the gap on the kind of extrapolation used and found it not to be critical.

Two different lattice-dynamical models have been used to obtain phonon eigenvalues and eigenvectors for Ge and GaAs: Weber's adiabatic bond-charge model[34,35] (BCM) and the 14-parameter shell model (SM) of Kunc and Nielsen.[36,37] The BCM parameters for GaAs have been taken from a recent fit to *ab initio* dispersion relations by Colombo and Giannozzi.[38] We have also used two different phonon models for the calculations of the ZnSe isotopic band-gap variation: an 11-parameter rigid-ion model[39,40] and the deformable-bond approximation[39] (DBA).

In Figs. 3(a) and 3(b) we present the electron-phonon spectral function for the E_0 gap in ZnSe, i.e., the difference

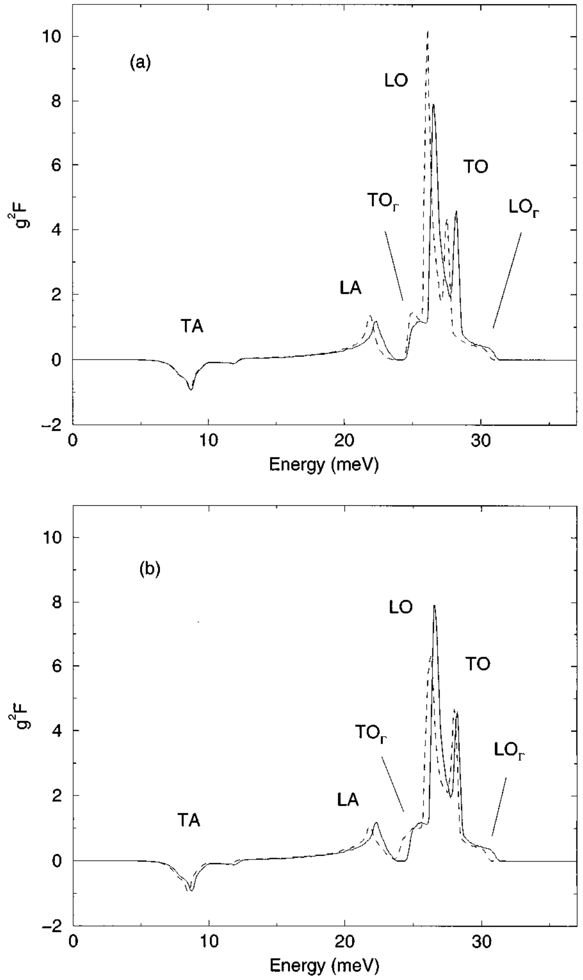

FIG. 3. Electron-phonon spectral functions g^2F for the E_0 gap of ZnSe (solid lines: natural abundance) for (a) a change of the Zn and (b) the Se mass by 5 amu (dashed lines, respectively).

between the spectral functions of Γ_1 (conduction) and Γ_{15} (valence) electronic states, for three different isotopic configurations: the two natural masses (solid lines); keeping the Se mass at its natural value and increasing the mass of Zn by 5 amu [dashed line, Fig. 3(a)]; and for the reversed situation [dashed line, Fig. 3(b)]. For the calculation of electron energies and wave functions we have employed a GP-type pseudopotential model. A 15-parameter DBA model is more realistic than the RIM model for the lattice dynamics, and gives a better approximation for the phonon density of states. This was the reason for choosing this model in our display of the electron-phonon spectral functions. As it is shown in Fig. 3, increasing the isotopic mass of any of the compounds shifts the spectral function to lower energies. The heavier the atoms are, the lower the frequencies of the corresponding vibrational modes. However, the change of the cation or the anion mass results in different spectral functions. A similar behavior was observed in the spectral function for the lattice-constant renormalization (Fig. 2). Again, the variation of the Zn mass is important only at high energies. In contrast to that, the change in the Se mass produces shifts at all energies. According to Eq. (14) the correction to the energy is proportional to the integral of the functions in Fig. 3. We find that the electron-phonon renormalization is reduced for an increase of either mass. Thus when atomic masses increase, the energy gap also increases. Increasing the atomic masses has the same effect as ‘‘freezing’’ the vibrations of the solid.

TABLE III. Electron-phonon contribution to the E_0 gap shift for different lattice dynamical (BCM, SM, RIM, and DBA) and pseudopotential models (GP and BR). The numbers in brackets are the theoretical errors of a linear regression through the results obtained for different mass increments.

			GP (meV/amu)	BR (meV/amu)
Ge		BCM	0.43(4)	0.404(16)
		SM	0.389(8)	0.364(4)
GaAs	Ga	BCM	0.285(8)	0.260(7)
		SM	0.270(7)	0.248(7)
	As	BCM	0.285(2)	0.277(3)
		SM	0.308(1)	0.300(1)
ZnSe	Zn	RIM	0.171(6)	0.147(5)
		DBA	0.186(17)	0.158(17)
	Se	RIM	0.258(16)	0.292(16)
		DBA	0.261(13)	0.288(15)

Table III shows the electron-phonon renormalization of the E_0 gap of Ge, GaAs, and ZnSe, calculated with two different pseudopotential extrapolations and different phonon models. In the case of Ge, BCM gives a slightly larger value than SM. Comparing the pseudopotential approaches, the GP extrapolation makes a larger contribution than the BR model. However, even with the lowest value, 0.36 meV/amu, the total gap shift with the isotopic mass is around 30% larger than the measured one (see Table IV). In the case of GaAs, BCM gives larger values than SM for Ga substitution, but the opposite happens when the isotopic mass of As is changed.[17] The GP extrapolation also gives larger values, similarly to the case of Ge. If we take the result corresponding to the SM and GP pseudopotential extrapolations, our theory reproduces the experimental result within the error (see Table IV). The experimental uncertainties, however, are too large to distinguish which of the proposed phonon models and pseudopotentials are best: all theoretical predictions are quite satisfactory. For ZnSe we obtain similar results for the two-phonon models and the GP and BR approaches. The GP pseudopotential gives a larger mass dependence for Zn

TABLE IV. E_0 gap shift, theoretical and experimental results (in meV/amu).

	κ	$(\partial E_0/\partial M_\kappa)_{\mathrm{EP}}$	$(\partial E_0/\partial M_\kappa)_{\mathrm{TE}}$	Total	Experiment
Ge	Ge[a]	0.36	0.29	0.65	0.49(3)[b]
GaAs	Ga	0.27	0.16	0.43	0.39(6)
	As	0.31	0.11	0.42	
ZnSe	Zn	0.19	0.12	0.31	
	Se	0.26	0.04	0.30	

[a] The Ge coefficients correspond to the simultaneous change of two masses per unit cell. They must be divided by two in order to compare them with those given for GaAs and ZnSe.

[b] References 18 and 19.

TABLE V. Contribution of acoustical and optical phonons to the isotopic shift of the E_0 gap (in meV/amu).

		Acoustical			Optical		
		DW	SE	Total	DW	SE	Total
Ge		0.184(7)	-0.099(5)	0.085	0.065(2)	0.253(5)	0.318
GaAs	Ga	0.165(4)	-0.052(5)	0.113	-0.051(6)	0.185(1)	0.134
	As	0.071(4)	-0.062(3)	0.009	0.118(9)	0.172(8)	0.290
ZnSe	Zn	0.144(9)	-0.056(9)	0.088	-0.115(5)	0.175(6)	0.060
	Se	0.154(1)	-0.080(2)	0.074	0.121(9)	0.096(6)	0.217

than the BR model, while for Se substitution the opposite is found. All the results, as in the case of Ge and GaAs, are rather similar. Since no experimental data are available, we have chosen the calculations with the DBA model and the GP pseudopotentials in order to compare them with the gap variation of Ge and GaAs in Table IV.

Table IV shows the two contributions (electron-phonon and thermal expansion) to the gap shift which we have calculated in the present work. Electron-phonon interaction causes different shifts for cation and anion isotopic substitution in compound semiconductors which are larger for the heavier constituents. This difference increases with increasing ionicity of the material. The contribution due to thermal expansion is also different for substitution of heavier and lighter elements of a compound, and the difference increases with increasing ionicity. However, the gap shifts for lighter atoms are larger than those of the heavier ones due to the larger changes in the lattice constant (see Tables I and II). This behavior is opposite to that found from electron-phonon interaction. The two effects almost cancel each other when the total gap shift is considered, which becomes nearly independent of the species being substituted.

In Table V we show separately the contribution of acoustical and optical phonons to the SE and DW terms. The results shown are obtained by using the BR pseudopotential model and BCM, SM, and RIM lattice dynamics for Ge, GaAs, and ZnSe, respectively. Generally, both corrections, SE and DW, make similar contributions. Nevertheless, there are important cancellations among them that make the result hard to understand in simple terms. For Ge, the DW term dominates in the acoustical region, while the SE contribution is more important in the optical region. In GaAs and ZnSe we can additionally distinguish between optical and acoustic DW and SE contributions when the mass of either the cation or the anion is changed. When the cation mass is changed, the DW contribution dominates in the acoustic region, while the SE contribution is larger in the optical region. This behavior is analogous to that of Ge. For anion replacement, the DW and SE contributions of As and Se almost cancel in the acoustical regime. The gap shift is thus dominated by optic modes. In general, the optical region makes the most important contribution to the energy renormalization, due to electron-phonon interaction in Ge and for anion replacement in GaAs and ZnSe, while both types of modes are almost equally important for cation substitution (Ga, Zn). An interesting trend can be observed for the DW contribution of optical modes. For Ga and Zn substitution we obtain a negative gap shift, while it is positive for replacement of As and Se. The magnitude of the shifts for either anions or cations increases with increasing ionicity. This behavior directly reflects changes of the electronic structure due to lattice vibrations. This can be qualitatively understood in simple terms by multiplying the atomic pseudopotentials v with a Debye-Waller factor, yielding expressions like $v\exp(-G^2\langle u^2\rangle/6)$ which can be used to obtain the corresponding contribution to the temperature or isotopic mass dependence of the electronic structure in an alternative way to Eq. (11). Going from Ge to GaAs and ZnSe, the difference between anion and cation pseudopotentials $v(3)$, which determine the E_0 gap energy to a large extent, increases, thus leading to larger gaps.[31] These pseudopotentials are negative for all atoms considered, with their magnitudes being larger for anions than for cations. Under these circumstances an increase of Ga or Zn masses leads to a decrease of the antisymmetric component between anion and cation pseudopotentials, and thus to a decrease of the gap. On the other hand, an increase of As or Se masses leads to an increase of the antisymmetric pseudopotentials and therefore to a larger gap.

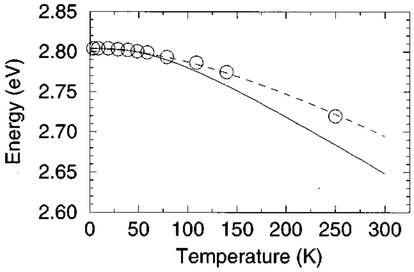

FIG. 4. Calculations of the E_0 gap of ZnSe with temperature (solid line) in comparison to experimental data (open circles: Ref. 42, dashed line: Ref. 43).

VI. TEMPERATURE DEPENDENCE OF THE ZnSe GAP

The change in the energy gap with temperature obeys the same equation [Eq. (1)] as the change with the mass, but now we have to take the derivative with respect to temperature. We have to calculate two terms, the TE and EP contributions to this energy shift. The TE term now contains the linear expansion coefficient $\alpha=\partial\ln a/\partial T$, that can be calculated by differentiating Eq. (5):

$$\alpha=\frac{4\hbar^2}{3Ba_0^3kT^2}\sum_{\nu,\boldsymbol{q}} n_B^2(\omega_\nu(\boldsymbol{q}))\omega_\nu^2(\boldsymbol{q})\gamma_\nu(\boldsymbol{q})e^{\hbar\omega/kT}. \quad (15)$$

The contribution to the EP interaction is equivalent to Eqs. (11) and (12), but now the energy shift is obtained by changing the temperature instead of the mass. In this way we have calculated the temperature behavior of the gap for ZnSe. We have used the RIM with 11 parameters and the GP pseudopotential form factors. Figure 4 shows the results of the calculations (solid line) together with experimental data of the 1S exciton associated with the E_0 direct gap obtained from luminescence[42] (open circles) and luminescence excitation[43] (dashed line) measurements. The data of Ref. 43 (dashed line) have been fitted with Varshni's formula, which yields

$$E(T)=2.804\ \text{eV}-8.59\times10^{-4}T^2/(T+405)\ \text{eV/K}. \quad (16)$$

Our calculated curve has been shifted to match the exciton energy at low temperatures. The theory somewhat overestimates the experimental temperature shifts, although the general agreement is reasonable.

VII. CONCLUSIONS

We have calculated the isotopic mass dependence of the E_0 direct gap of Ge, GaAs, and ZnSe at low temperature. A *local empirical pseudopotential method* has been employed to evaluate the electron-phonon coupling. The dependence of the electron-phonon term on the details of the pseudopotential form factors in the limit $\boldsymbol{q}\rightarrow 0$ has also been analyzed. Phonon-dispersion relations obtained with the *shell* and *bond-charge* models have been used. The calculated results are found to depend only slightly on the details of the lattice dynamics. The contributions of acoustical and optical branches to the isotope shifts of the gaps are given separately. Results of reflectivity measurements at the E_0 gap of GaAs samples with six different isotopic gallium compositions are also presented. Theoretical and experimental results compare satisfactorily. We have extended the calculations to the isoelectronic II-VI semiconductor ZnSe. The variation of the fundamental gap with both the isotopic mass and temperature is presented. Although experimental results for the dependence of the gap on isotopic mass are not yet available for ZnSe, the calculated temperature dependence is in reasonable agreement with the experimental data.

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