

# Isotope effects on the electronic critical points of germanium: Ellipsometric investigation of the $E_1$ and $E_1 + \Delta_1$ transitions

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**Abstract.** Within the past years the optical excitations of electrons have been measured for semiconductor samples of different isotope compositions. The isotope shift observed have been compared with calculations of the effects of electron-phonon interaction on the electronic band structure. While qualitative agreement has been obtained, some discrepancies remain especially concerning the  $E_1$  and  $E_1 + \Delta_1$  transitions. We have remeasured the effect of isotope mass on the  $E_1$  and  $E_1 + \Delta_1$  transitions of germanium with several isotopic compositions. The results, obtained by means of spectroscopic ellipsometry, confirm that the real part of the gap self-energies induced by electron-phonon interaction is larger than found from band structure calculations, while the imaginary part agrees with those calculations, which are based on a pseudopotential band structure and a bond charge model for the lattice dynamics. Our results agree with predictions based on the measured temperature dependence of the gaps. We compare our data for  $E_1$  and  $E_1 + \Delta_1$  with results for the lowest direct ( $E_0$ ) and indirect ( $E_g$ ) gaps. The measured values of  $\Delta_0$  and  $\Delta_1$  increase noticeably with increasing isotope mass. Similar effects have been observed in the temperature dependence of  $\Delta_1$  in  $\alpha$ -Sn and GaSb. A microscopic explanation for this effect is not available.

**PACS.** 71.38.+i Polarons and electron phonon interactions – 78.40.Fy Semiconductors – 63.20.Kr Phonon-electron and phonon-phonon interactions

## 1 Introduction

Changes in the electronic energy gaps of elemental semiconductors with isotopic composition have been measured, in the past 10 years, for diamond and Ge [1]. For Ge, both the indirect gap  $E_g$  [2–5], and the direct gaps  $E_0$  [5] and  $E_1$  [6] have been investigated. A part of these observed effects can be related to the dependence of the lattice constant on isotope mass  $M$  [3, 5, 7], but additional, often dominant contributions directly attributable to electron-phonon interaction have been found to exist [3, 5]. These effects are similar to those involved in the temperature dependence of gap energies. They correspond in fact to the renormalisation of the electron states by the zero temperature vibrations, *i.e.* a quantum effect.

At low temperatures, where isotope effects on energy gaps can be seen [1], the gap energies are proportional to  $M^{-1/2}$ , as expected for the effect of electron-phonon interaction [6]. The lattice constant changes with isotope mass (volume effect) and the energy of the gaps depends on the volume, a dependence which is given by the hydrostatic deformation potential. The resulting contribution to the dependence of the gap on mass is also proportional to  $M^{-1/2}$ . Thus, at low temperatures, the two contributions

have the same mass dependence and the total effect on the gap energy can be written as [5]:

$$E = E_\infty + \frac{B}{\sqrt{M}}, \quad (1)$$

where  $E_\infty$  is the “bare” unrenormalised gap and  $B$  a constant. It should be mentioned that  $M$  in equation (1) is the average isotope mass when several isotopes are present. In the case of Ge, the mass fluctuations are known to be too small to induce localisation of phonons [8].

At high temperatures, the electron-phonon contribution to the gaps becomes independent of  $M$  [6]. The temperature dependence can be expressed by a Bose-Einstein occupation factor based on the electron-phonon interaction with an average effective phonon [9],

$$E = a - b \left( 1 + \frac{2}{\exp(\Theta/T) - 1} \right), \quad (2)$$

where  $a$  is the unrenormalised gap energy at  $T = 0$  K,  $-b$  the renormalisation at  $T = 0$  K, and  $\Theta$  corresponds to an average phonon frequency ( $\omega = k_B \Theta / \hbar$ ). The temperature dependence of the gap energies is also often described by the empirical expression [10]:

$$E = a - \frac{\alpha T^2}{\beta + T}, \quad (3)$$

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where  $a$ ,  $\alpha$ , and  $\beta$  are constants used as fitting parameters. Analogously to the isotope mass dependence, the temperature dependence of a gap can also be decomposed into two contributions: that of the electron-phonon interaction and that of the thermal expansion (volume effect). While equation (2) was postulated for the electron-phonon interaction only, it has been shown that it can also include the corresponding volume effect [11].

The isotope dependence of the imaginary part of the self-energy, the width  $\Gamma$ , which causes a lifetime broadening of the energy state [12] has a  $M^{-1/2}$  dependence, represented by an equation similar to equation (1) [6]. The temperature dependence of these widths is given by an expression similar to that for the energy shifts (Eq. (2)) [9].

In general gap renormalisations comprise two contributions: one due to electron-phonon interaction, the other due to the volume effect. The former is due to phonons interacting with electrons in the harmonic approximation, while the latter is due to anharmonic effects [13]. In order to compare the electron-phonon coupling as determined from isotope mass dependence to the one determined from the temperature dependence, we subtract the volume effect from the experimental data in both cases. In the following we use the term renormalisation for the contribution from the electron-phonon interaction only. The zero temperature renormalisation can be obtained from the dependence of the gap energy on isotope mass by extrapolating equation (1) to infinite mass. It can also be obtained by extrapolating the linear dependence of the gaps on  $T$  to  $T = 0$  K, which when using equation (2) yields  $-b$  and using equation (3)  $\alpha\beta$ .

In this paper, we analyse the dependence of the  $E_1$  and  $E_1 + \Delta_1$  transitions of Ge on isotope mass, as obtained from spectroscopic ellipsometry. We compare our results with those for  $E_g$  [5] and  $E_0$  [5], and with results obtained from the temperature dependence of the gap energies [9,10,14]. Also for the widths  $\Gamma$ , we compare the dependence on  $M$  at low  $T$  with the temperature dependence of  $\Gamma$  found at higher temperatures [9].

## 2 Experiment

Three samples were used: natural Ge, which has an average atomic mass of 72.6 (denoted  $^{72.6}\text{Ge}$ ),  $^{70}\text{Ge}$ , and  $^{75.6}\text{Ge}$ . The samples were single crystals and the surfaces to be measured were polished with Syton [15]. The measurements were performed on (111) surfaces of the  $^{70}\text{Ge}$  and  $^{72.6}\text{Ge}$  samples, and on a (110) surface of the  $^{75.6}\text{Ge}$  sample. These samples were of high purity with less than  $10^{12} \text{ cm}^{-3}$  electrically active impurities. A  $^{70}\text{Ge}$  sample, with an impurity concentration of  $7 \times 10^{16} \text{ cm}^{-3}$ , which was used in a previous investigation [6], was remeasured. The ‘‘electrical’’ purity of our samples was so high that changes in their transition energies due to differences in doping [16] should be negligible in comparison with those found experimentally (see below). The  $^{70}\text{Ge}$  sample was 99.99% isotopically pure, as determined by mass spectrometry, while the  $^{70}\text{Ge}$  sample from the previous investigation [6] had a composition of 96.3%  $^{70}\text{Ge}$  and 3.7%

$^{72}\text{Ge}$ . The  $^{75.6}\text{Ge}$  sample had a composition of 13.5%  $^{74}\text{Ge}$  and 86.5%  $^{76}\text{Ge}$  (The isotopical composition of natural Ge is 21.2%  $^{70}\text{Ge}$ , 27.7%  $^{72}\text{Ge}$ , 7.7%  $^{73}\text{Ge}$ , 35.9%  $^{74}\text{Ge}$ , and 7.4%  $^{76}\text{Ge}$  [5]).

Ellipsometry was used to measure the dielectric function of the samples, which were placed in high vacuum ( $10^{-7}$  mbar after baking at  $100^\circ\text{C}$  for 12 h) in a cryostat [17] with strain-free silica windows. The samples were attached to a cold finger inside the cryostat with silver paste [18]. Measurements were performed at room temperature and at  $30 \pm 5$  K.

The ellipsometer [19], of rotating analyzer type, had a Xe-lamp as a light source and a double monochromator with 1200 lines/mm gratings. Mirror optics was used. The polarizer and analyzer were Rochon prisms and the detector was a photomultiplier tube. The spectral range of our measurements was 1.7–5.5 eV ( $\sim 730\text{--}225$  nm) while the data were taken with intervals of 0.05 eV in the entire range, and of 0.005 eV in the 1.95–2.75 eV range, *i.e.* around the  $E_1$  and  $E_1 + \Delta_1$  transitions. The relative resolution was  $\Delta E/E = 6 \times 10^{-3}$ . The angle of incidence was  $67.5^\circ$  while the incident light was linearly polarized at an angle of  $30^\circ$  with respect to the plane of incidence. The light was collimated by means of irises. Conventional calibration procedures [20] were used prior to each measurement. The measurements were repeated three times for each sample.

## 3 Results

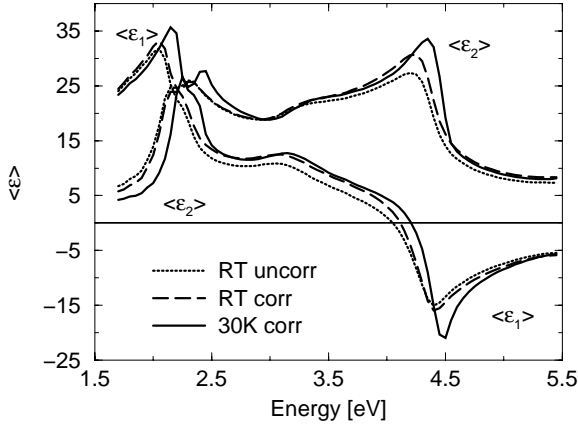
### 3.1 Analysis of optical spectra

The dielectric function was obtained from the ellipsometric measurements using standard methods [21], *i.e.* it was calculated from the ellipsometric angles using a three phase model (bulk-oxide-air) with sharp interfaces. The room temperature data were used to determine the thickness of the oxide overlayers. Literature data were used for the dielectric functions of Ge [22] and the oxide [23]. The oxide thickness was found to be typically 1 nm. The dielectric function at  $T = 30$  K was then determined by using the oxide thickness found at room temperature and the dielectric function of the oxide. It was assumed that the dielectric function of the oxide was temperature independent [24]. Figure 1 shows the pseudodielectric function of  $^{72.6}\text{Ge}$  at room temperature and at 30 K, and the effect of the overlayer correction.

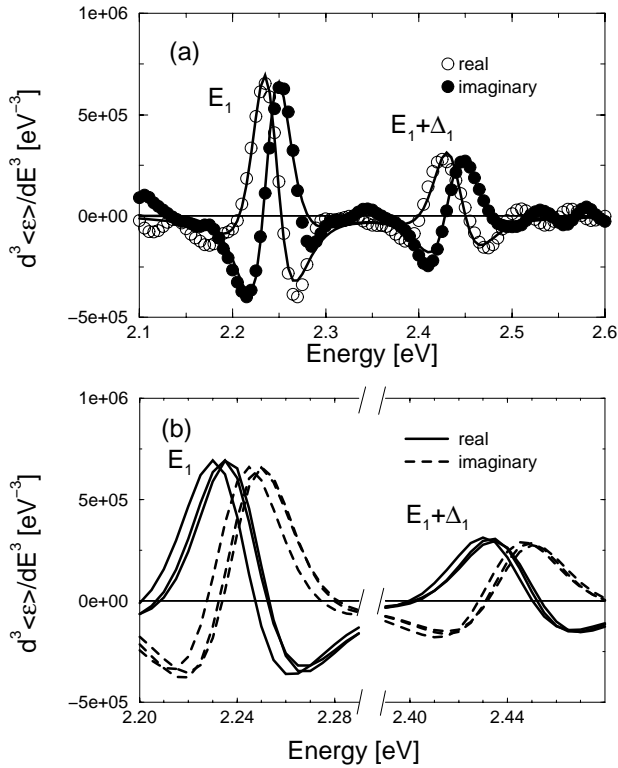
In order to determine the transition energies of the  $E_1$  and  $E_1 + \Delta_1$  interband critical points for the different isotopes, the third derivative of the dielectric function with respect to photon energy was analysed. The  $E_1$  and  $E_1 + \Delta_1$  transitions in Ge can be described by a mixture of a 2D minimum and a saddle point, whose analytical lineshape is given by [9]:

$$\varepsilon(\hbar\omega) = -A \ln(E_1 - \hbar\omega - i\Gamma)\exp(i\phi), \quad (4)$$

$A$  being its strength,  $E_1$  its transition energy,  $\hbar\omega$  the photon energy,  $\Gamma$  the width and  $\phi$  the phase angle which

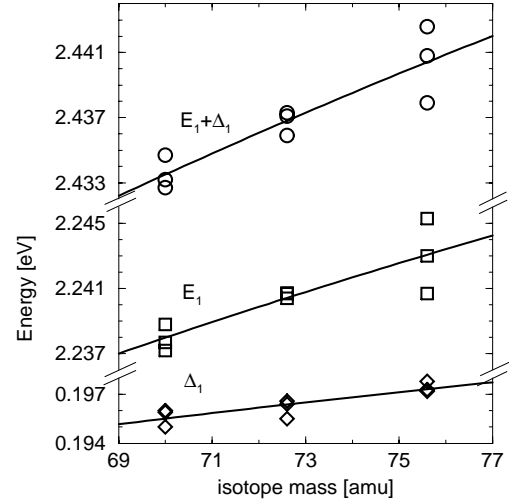


**Fig. 1.** Pseudodielectric function of natural Ge at room temperature and at 30 K, as measured with a rotating analyzer ellipsometer. The effect of the correction for an oxide overlayer is also illustrated.



**Fig. 2.** (a) The third derivative with respect to photon energy of the dielectric function of natural Ge in the vicinity of the  $E_1$  and  $E_1 + \Delta_1$  transitions. The solid lines are fitted to the experimental data using the analytical line shape of equation (4). (b) Fitted curves for the  $^{70}\text{Ge}$ ,  $^{72.6}\text{Ge}$  (natural), and  $^{75.6}\text{Ge}$  samples, respectively.

accounts for excitonic effects. The  $E_1 + \Delta_1$  transition was modeled by the same type of expression as the  $E_1$  counterpart (Eq. (4)). The third derivative of the pseudodielectric function of  $^{72.6}\text{Ge}$  is displayed in Figure 2, together with curves calculated with equation (4) to fit the experimental ones. The phase angle  $\phi$  was taken to be



**Fig. 3.** Energies of the  $E_1$  and  $E_1 + \Delta_1$  transitions in Ge, vs. isotope mass. Also shown is the dependence of the spin-orbit splitting,  $\Delta_1$ , on isotope mass. The solid lines are fits to  $E = E_\infty + BM^{-1/2}$ .

the same for the  $E_1$  and  $E_1 + \Delta_1$  transitions, but the other parameters were fitted independently. The fits were also made with different  $\phi$  values for  $E_1$  and  $E_1 + \Delta_1$ , although this procedure did not result in any significant changes of the isotope dependence of the transition energies and widths. The shifts between the spectra of the different isotopes are small, as illustrated in the inset of Figure 2. Notice that not only the energies, but also the widths depend on the isotope mass. The fitted transition energies vs. isotope mass are given in Figure 3, while the widths are given in Figure 4. The energies and widths of the less pure  $^{70}\text{Ge}$  sample used in a previous investigation [6], were not significantly different from those found for our  $^{70}\text{Ge}$  sample and shown in Figures 3 and 4.

### 3.2 Isotope shifts

Equation (1) was used to fit the isotope shifts of the  $E_1$ ,  $E_1 + \Delta_1$ , and  $\Delta_1$  parameters. The fitted values,  $E_\infty$  and  $B_{exp}$ , are given in Table 1. Also given are the isotope shifts of the lowest direct gaps  $E_0$  and  $E_0 + \Delta_0$  and the indirect gap  $E_g$ , as measured by Parks *et al.* [5]. The widths,  $\Gamma$ , were fitted to an expression of the same type, *i.e.*  $\Gamma = \Gamma_\infty + BM^{-1/2}$ . The constant term  $\Gamma_\infty$  should be interpreted as caused by spurious broadening due to the approximate nature of equation (4), the numerical third derivative, and the finite resolution of the monochromator. The fitted parameters are given in Table 2. The spurious broadenings are small. The errors in Tables 1 and 2 correspond to statistical errors in the data in Figures 3 and 4. Systematic errors in the measurements and the numerical processing of the data should be similar for all measurements and samples and were hence neglected. The isotope mass dependences of  $E_0$  and  $E_1$  have the same sign and are of the same order of magnitude. Notice that both the spin-orbit splittings  $\Delta_0$  and  $\Delta_1$  have been found to depend on isotope mass.

**Table 1.** Isotope mass dependence of some gaps of Ge, as represented by the parameters  $E_\infty$  and  $B$  (here denoted  $B_{exp}$ ) of equation (1), which was fitted to the data. The dimension of  $E_\infty$  is (meV) and those of the B's (meV amu<sup>1/2</sup>). Also given is the calculated contribution of the volume effect to the isotope dependence,  $B_{vol}$ . For this calculation, literature data for the hydrostatic deformation potentials and the dependence of the lattice parameter on isotope mass were used (see text). The contribution from the electron-phonon interaction,  $B_{el-ph}$  was taken to be the difference between  $B_{exp}$  and  $B_{vol}$ .

Transition	$E_\infty$	$B_{exp}$	$B_{vol}$	$B_{el-ph}$
$E_g$	$793 \pm 2^a$	$-445 \pm 12^a$	$-108 \pm 14^b$	$-337 \pm 26^{a,b}$ $-463^c$
$E_0$	$959 \pm 2^a$	$-606 \pm 11^a$	$-291 \pm 32^b$	$-315 \pm 43^{a,b}$ $-511^c$
$E_0 + \Delta_0$	$1291 \pm 5^a$	$-926 \pm 39^a$	$-308 \pm 30^b$	$-618 \pm 69^{a,b}$
$\Delta_0$	$332 \pm 7^a$	$-319 \pm 50^a$	$-9 \pm 30^b$	$-310 \pm 80^{a,b}$
$E_1$	$2373 \pm 28^b$	$-1129 \pm 239^b$	$-149 \pm 17^b$	$-980 \pm 256^b$ $-404^c$
$E_1 + \Delta_1$	$2616 \pm 31^b$	$-1530 \pm 261^b$	$-157 \pm 18^b$	$-1373 \pm 279^b$
$\Delta_1$	$243 \pm 11^b$	$-401 \pm 90^b$	$-9 \pm 30^b$	$-392 \pm 120^b$

<sup>a</sup> Ref. [5], <sup>b</sup> This work, <sup>c</sup> Theory, Ref. [6].

**Table 2.** Isotope dependence of the widths  $\Gamma(E_1)$  and  $\Gamma(E_1 + \Delta_1)$ , fitted to  $\Gamma = \Gamma_\infty + BM^{-1/2}$ . Also shown is the width  $\Gamma(0)$  at  $T = 0$  K obtained from the isotope mass and temperature dependence of  $\Gamma$ .

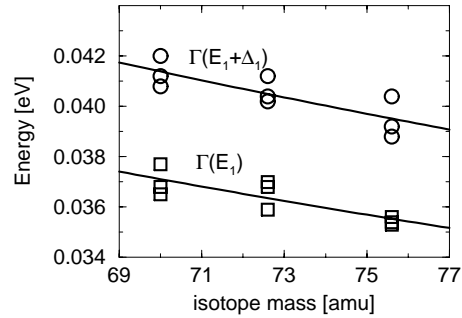
Width	$\Gamma_\infty$ (meV)	$B$ (meV amu <sup>1/2</sup> )	$\Gamma(0)$ (meV)
$\Gamma(E_1)$	$-4.6 \pm 11^a$	$349 \pm 90^a$	$41 \pm 11^a$ $25 \pm 3^b$ $288^c$ $33.8^c$
$\Gamma(E_1 + \Delta_1)$	$-8.2 \pm 14^a$	$415 \pm 113^a$	$49 \pm 14^a$ $43 \pm 5^b$ $310^c$ $36.4^c$

<sup>a</sup> From isotope mass dependence at 30 K, this work,

<sup>b</sup> From the temperature dependence of the dielectric function (100 – 800 K), Ref. [9],

<sup>c</sup> Theory, from Ref. [6].

As already mentioned, there are two contributions to the isotope mass dependence of the gaps: one is due to the electron-phonon interaction and the other arises from the difference in lattice parameter between different isotopes (volume effect) [5]. The latter can be calculated from the measured change in lattice parameter with isotope mass and the corresponding hydrostatic deformation potential [5]. We use a recently measured value by Kazimirov [25],  $V^{-1}(dV/dM) = -2.2 \times 10^{-5}$  amu<sup>-1</sup> at  $T = 55$  K, for the change in lattice parameter. (This value is smaller than that of Buschert *et al.* [7],  $V^{-1}(dV/dM) = -3.29 \pm 0.07 \times 10^{-5}$  amu<sup>-1</sup> at  $T = 78$  K.) We also used the new value for correcting the data of Parks *et al.* [5], but we used the same hydrostatic deformation potentials ( $a(E_g) = -3.8$  eV [26],  $a(E_0) = -10.9 \pm 0.8$  eV [27], and  $a(E_0 + \Delta_0) = -11.2 \pm 1$  eV) [27]. For the hydrostatic de-



**Fig. 4.** Widths,  $\Gamma$ , of the  $E_1$  and  $E_1 + \Delta_1$  transitions in Ge, *vs.* isotope mass. The solid lines are fits to  $\Gamma = \Gamma_\infty + BM^{-1/2}$ .

formation potential of  $E_1$  we used  $D_1^1 = -9.6 \pm 0.8$  eV at  $T = 77$  K, reported by Chandrasekhar and Pollak [27]. For  $\Delta_0$  there is a small volume effect (*i.e.* the hydrostatic deformation potential is different for  $E_0$  and  $E_0 + \Delta_0$ ). We have not found any measured difference in the hydrostatic deformation potential of  $E_1$  and  $E_1 + \Delta_1$  in the literature. Theoretically it has been found that  $\Delta_1$  has the same logarithmic derivative *vs.* volume as  $\Delta_0$ , within a few percent [28]. We therefore use the same value for the logarithmic derivative *vs.* volume for  $\Delta_1$ , as for  $\Delta_0$ .

The calculated values of the isotope mass dependence of the gap energies, resulting from the volume effect,  $B_{vol}$ , are given in Table 1. The errors in  $B_{vol}$  include the errors in the deformation potential and that in the change in lattice parameter with isotope mass. The electron-phonon contribution was obtained by subtracting  $B_{vol}$  from the experimental dependence on isotope mass,  $B_{exp}$ . The estimated errors in the volume dependence of  $\Delta_0$  and  $\Delta_1$  are so large that not even the sign is certain; the sign given in Table 1 is however consistent with the theoretical one [28]. For  $E_1$  and  $E_1 + \Delta_1$  the volume contribution to the

**Table 3.** Zero temperature renormalisation (in meV) of some gaps of Ge, as determined from their dependence on isotope mass and on temperature. The renormalisations due to electron-phonon interaction (*el-ph*) were determined from experimental data (*exp*) after subtracting the volume contribution.

Transition	isotope-shift		temp.dep.	
	<i>exp</i>	<i>el-ph</i>	<i>exp</i>	<i>el-ph</i>
$E_g$	$-52.2 \pm 1.5^{a,b}$	$-39.6 \pm 4^{a,b}$ $-54.3^f$	$-96 \pm 30^{c,d,e}$	$-74 \pm 27^{c,d,e}$
$E_0$	$-71.1 \pm 1.3^{a,b}$	$-37.0 \pm 6^{a,b}$ $-60.0^f$	$-70 \pm 10^{g,h,i}$ $-266 \pm 65^{c,h,i}$	$-36 \pm 5^{g,h,i}$ $-102 \pm 29^{c,h,i}$
$E_0 + \Delta_0$	$-109 \pm 4.6^{a,b}$	$-72.5 \pm 9^{a,b}$		
$\Delta_0$	$-37.4 \pm 5.9^{a,b}$	$-36.4 \pm 10^{a,b}$		
$E_1$	$-132 \pm 28^{j,k}$	$-115 \pm 30^{j,k}$ $-47.4^f$	$-120 \pm 40^{g,l,m}$ $-163 \pm 95^{c,l,m}$	$-94 \pm 37^{g,l,m}$ $-111 \pm 72^{c,l,m}$
$E_1 + \Delta_1$	$-180 \pm 31^{j,k}$	$-161 \pm 33^{j,k}$		
$\Delta_1$	$-47 \pm 10^{j,k}$	$-46 \pm 14^{j,k}$		

<sup>a</sup> 6 K, <sup>b</sup> Ref. [5], <sup>c</sup> Varshni fit (Eq. (3)), <sup>d</sup> 0 – 400 K, <sup>e</sup> Ref. [10], <sup>f</sup> Theory, Ref. [6],

<sup>g</sup> Bose-Einstein fit (Eq. (2)), <sup>h</sup> 19 – 420 K, <sup>i</sup> Ref. [14], <sup>j</sup> 30 K,

<sup>k</sup> This work, <sup>l</sup> 100–800 K, <sup>m</sup> Ref. [9].

isotope shifts is small in comparison with the contribution of the electron-phonon interaction. For the indirect gap  $E_g$ , the electron-phonon contribution is larger than the volume contribution, but the latter is far from negligible. For  $E_0$  and  $E_0 + \Delta_0$ , the volume and electron-phonon contributions are of the same order.

The renormalisation at  $T = 0$  K can be determined from the dependence of the gap energies on isotope mass by extrapolating them to infinite mass. In Table 3, the renormalisations at  $T = 0$  K of the different gaps thus obtained from the data in Table 1 are presented. The zero temperature renormalisations as estimated from the total shifts in energy with isotope mass,  $B_{exp}$ , *i.e.* without subtracting the the volume effect, are given together with those determined solely from electron-phonon interaction,  $B_{el-ph}$ . It can be seen in Table 3 that for Ge, the volume effect cannot be neglected when determining the zero temperature renormalisation from experimental data. In Table 2, the corresponding extrapolations of the widths,  $\Gamma(0)$ , are given; they represent the widths due to the lattice vibrations at  $T = 0$  K, a typical quantum effect.

Notice that there is a significant difference in the zero temperature renormalisation between  $E_1$  and  $E_1 + \Delta_1$ . A similar effect is seen for  $E_0$  and  $E_0 + \Delta_0$ . These differences result from the different isotope mass dependence of  $E_1$  and  $E_1 + \Delta_1$  and  $E_0$  and  $E_0 + \Delta_0$ , respectively.

### 3.3 Comparison with the temperature dependence of gaps

The renormalisation at  $T = 0$  K can be estimated, not only from the isotope dependence of gaps, but also from their temperature dependence. There are contributions also to the latter from electron-phonon interaction and

from thermal expansion (volume effect). The volume effects can be calculated from data for the thermal expansion and the hydrostatic deformation potentials [14]. The electron-phonon contribution is obtained by subtracting the volume contribution from the experimental data. In Table 3, the zero temperature renormalisations for some gaps of Ge are given as determined from their temperature dependence. As in the case of the isotope mass dependence, the zero temperature renormalisations are given as estimated both with and without subtracting the volume effect. For  $E_1$  we used the experimental data of Viña *et al.* [9]. For the thermal expansion [29] and for the hydrostatic deformation potential we took data from the literature ( $D_1^1 = -8.6 \pm 0.5$  eV at room temperature [30]). The volume effect was subtracted at each temperature, and equations (2, 3) were used to fit the remaining electron-phonon contribution. For  $E_g$ , we subtracted the volume contribution from the fitted curve in reference [10] using data for the thermal expansion and the hydrostatic deformation potential ( $a = -2.3$  eV at 80 K) from the literature [29]. We used when possible data for the hydrostatic deformation potentials measured in the middle of the temperature ranges. The errors in the renormalisation of  $E_g$  and  $E_1$  (from temperature dependence) are our estimates based on the “robustness” of these fits. Notice that the zero temperature renormalisation strongly depends on the model used to fit the temperature dependence. As in the case of the isotope mass dependence, the volume effect cannot be neglected when estimating the zero temperature renormalisation from temperature dependence of the gap energies of Ge (Tab. 3).

For both  $E_0$  and  $E_1$ , equation (3) gives a higher value for the renormalisations at  $T = 0$  K than equation (2). For  $E_0$  the agreement between the isotope and temperature dependence data for the zero temperature renormalisation

(*el-ph*) is good if equation (2) is used, but poor if equation (3) is used for fitting the temperature dependence. The latter overestimates the zero temperature renormalisation. For  $E_1$ , the renormalisations obtained from the temperature and isotope dependences are in good agreement. The errors are, however, large and one cannot say which of the two models, equations (2, 3), is the better one.

For the widths at  $T = 0$  K,  $\Gamma(0)$ , the agreement between temperature and isotope values is good (Tab. 2).

## 4 Discussion

It was found above that the zero temperature renormalisations determined from the temperature dependence of the gap energies strongly depend on the model used to fit that dependence. This was the case in particular for  $E_0$ . Notice that the temperature interval available in the  $E_0$  measurements is considerably smaller than that of the  $E_1$ -measurements. Since the renormalisation was determined by extrapolating the linear part of the temperature dependence (which is found at high temperatures) to 0 K, it is obvious that a large temperature interval is preferable. It has been recently suggested that analytical expressions other than equations (2) or (3) should be used to model the temperature dependence of gaps of elemental [31] and compound semiconductors [32,33]. As shown in this paper, a criterion for the usefulness of different models for the temperature dependence of gaps could be that they give zero temperature renormalisations in agreement with data from the isotope mass dependence.

For Ge,  $E_1$  and  $E_1 + \Delta_1$  are too close to allow a separate experimental determination of their temperature dependence ( $\Delta_1 = 0.187$  eV [9]). The spin-orbit splittings in  $\alpha$ -Sn,  $\Delta_1 = 0.47$  eV [34], and GaSb,  $\Delta_1 = 0.43$  eV [35], are considerably larger. Therefore the separate measurement of the temperature dependence of  $E_1$  and  $E_1 + \Delta_1$ , separately becomes possible. For  $\alpha$ -Sn the renormalisation at  $T = 0$  K of the  $E_1$  transition – without correction for thermal expansion – was found to be  $90 \pm 40$  meV ( $138 \pm 60$  meV) using equation (2) (Eq. (3)), and the renormalisation of the  $E_1 + \Delta_1$  transition was found to be  $130 \pm 40$  meV ( $189 \pm 98$  meV), from the temperature dependence in the interval 100–350 K [34]. In the same way (temperature interval 10–740 K) the renormalisation of the  $E_1$  transition of GaSb was found to be  $74 \pm 16$  meV ( $100 \pm 45$  meV), and of the  $E_1 + \Delta_1$   $81 \pm 14$  meV ( $118 \pm 53$  meV), using equation (2) (Eq. (3)) [35]. Thus, in both materials, the renormalisation is larger for  $E_1 + \Delta_1$  than for  $E_1$ , which agrees with what was found for Ge from isotope effects.

It would be of interest to measure the isotope effect on the large spin-orbit splittings in  $\alpha$ -Sn. Tin has stable isotopes with masses ranging from 112 to 124. A comparison with the temperature dependence could then be made for  $E_1$  and  $E_1 + \Delta_1$ , separately.

The spin-orbit splitting is normally the same in an atom and in a solid containing the same element, to within a factor close to one. For free atoms the spin-orbit

splittings are different for different isotopes [36]. These shifts are, except for hydrogen, several orders of magnitude smaller than the effect we find for germanium crystals [36]. We therefore conclude that the isotope effect seen in  $\Delta_0$  and  $\Delta_1$  of Ge does not have its origin in an atomic effect. Moreover, the volume effect is much too small to explain the isotope shift of  $\Delta_0$  and  $\Delta_1$  (*cf.* Tab. 1). We therefore conclude that the effect is likely to be due to electron-phonon interaction, although we have not been able to figure out the details of the corresponding perturbation terms (Feynman diagrams).

It should be mentioned that the new value for the change in lattice parameter with isotope mass [25], gives slightly better agreement between the zero temperature renormalisation as estimated from the temperature and the isotope mass dependence of the gaps, respectively, than the value reported by Buschert *et al.* [7],

We also note that the theoretically calculated isotope dependences of the gap energies  $E_g$ ,  $E_0$ , and  $E_1$  (and hence their renormalisations at  $T = 0$  K) are only in qualitative agreement with experiment, while the agreement for the widths,  $\Gamma(E_1)$  and  $\Gamma(E_1 + \Delta_1)$ , is satisfactory. The explanation for this dichotomy is probably that different phonons are active in the electron-phonon interaction. This follows from the fact that the perturbation expressions for  $\Gamma$  involve only real transitions, while the energy shifts are obtained from a sum over all possible virtual transitions to intermediate states. The latter will contain pseudopotential form factors with small wave vectors which are rather poorly known since they must be obtained from extrapolation instead of interpolation of the empirical values corresponding to exact reciprocal lattice vectors (see Fig. 2 in Ref. [37]).

## 5 Conclusions

While the effect of isotope mass  $M$  on the indirect,  $E_g$ , and lowest direct gap,  $E_0$ , of Ge has been discussed rather thoroughly in the literature, only a limited set of data exists for the  $E_1$  and  $E_1 + \Delta_1$  gaps [6]. These data present a nonmonotonic dependence on the three isotope masses used. In contrast to  $E_0$  and  $E_g$ , measurements of the dependence of the critical point parameters of  $E_1$  and  $E_1 + \Delta_1$  on  $M$  yield not only the energy renormalisation but also the widths  $\Gamma$  (both due to electron-phonon interaction). We have presented ellipsometric measurements of these parameters performed on three isotopically different samples of high chemical purity. The measurements confirm the widths,  $\Gamma$ , and their dependence on  $M$ . These widths agree with those calculated with the empirical pseudopotential method and also with the estimates obtained from the measured temperature dependence of the widths.

In contrast, the zero temperature renormalisations of the  $E_1$  and  $E_1 + \Delta_1$  gap energies, *i.e.* the real part of the self energy, and their dependence on  $M$  are a factor of two larger than the calculated values, although they agree well with the estimates based on the temperature dependence of the gaps. This agreement adds additional

support to the experimental determination of the isotope shifts of  $E_1$  and  $E_1 + \Delta_1$ . It also allows us to conjecture that the disagreement with the pseudopotential calculations may be related to an inappropriate extrapolation of the pseudopotential factor to small wavevectors.

We have found an unexpected increase of the spin-orbit splitting  $\Delta_1$  with increasing isotope mass which we also have tentatively attributed to a renormalisation by electron-phonon interaction. Although the details of the renormalisation process are not known, it is worth mentioning that similar effects are found for the isotope mass dependence of the  $E_0$  gap of Ge and also for the temperature dependence of the  $\Delta_1$  splitting in GaSb and  $\alpha$ -Sn.

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