

## LETTER TO THE EDITOR

# Isotope dependence of the lowest direct energy gap in crystalline germanium

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**Abstract.** Using optical absorption measurements we establish that the lowest direct energy gap changes with atomic mass number  $m$  at the rate  $dE/dm = 0.49 \pm 0.03$  meV at 2 K, decreasing to  $0.11 \pm 0.03$  meV at 300 K, in both isotopically pure and isotopically disordered germanium. These values are broadly consistent with a simple prediction from the measured temperature dependence of the gap and the known dependence of the lattice on the isotope. We confirm, from optical absorption data, that the lowest indirect energy gap of germanium increases at the rate  $dE/dm = 0.36 \pm 0.01$  meV, in agreement with recent photoluminescence data.

There is considerable current interest in the effects of isotope substitution on the properties of germanium. For example, at low temperature the lattice volume has been shown to change with the isotope mass number  $m$  at the rate [1]

$$d \ln V / dm = -(33.3 \pm 0.6) \times 10^{-6}. \quad (1)$$

The dependence on  $m$  of the lowest indirect energy gap  $E^{\text{ind}}$  has been measured using the luminescence emitted by electron–hole drops and free excitons [2] and by bound excitons [3]. At liquid helium temperature the combined data yield

$$dE^{\text{ind}}/dm = 0.36 \pm 0.03 \text{ meV}. \quad (2)$$

This value can be understood in terms of the change in lattice volume with isotope plus the effects of electron–phonon interaction calculated either from first principles [4] or from the temperature dependence of the energy gap [3]. Other recent work, e.g. [5, 6], has reported the effects of isotope disorder on the vibrational frequencies. However, to date the isotope dependence of the lowest direct energy gap is uncertain. The one experimental measurement shows that the gap is  $1.25 \pm 0.05$  meV larger in a mixed  $^{74}\text{Ge}/^{76}\text{Ge}$  crystal than in one of natural isotopic content [7], but the same workers underestimated the shift of the lowest indirect gap by 20%. A pseudopotential–bond-charge-model calculation has predicted a shift of 1.4 meV between these particular

isotopic abundances [4]. This letter presents accurate data on the changes in the lowest direct energy gap in isotopically purified crystals, and compares these data with the temperature dependence of the energy gap. Since the lowest indirect gap is affected by the disorder in crystals with mixtures of isotopes we will explicitly consider the effects of mixed isotopes on the direct gap. We will also use optical absorption data to confirm the isotope shift of the lowest indirect energy gap as determined recently by the photoluminescence measurements.

The Ge samples used in this work were single crystals with donor and acceptor concentrations typically below  $10^{13} \text{ cm}^{-3}$ . Samples with three different isotopic abundances, as measured by SIMS, have been used. One sample ( $^{70}\text{Ge}$ ) had contents of 96.3 at.%  $^{70}\text{Ge}$  and 3.7 at.%  $^{72}\text{Ge}$ , giving an averaged atomic mass of 70.0. A second sample ( $^{74}\text{Ge}$ ) had 0.5 at.%  $^{70}\text{Ge}$ , 0.17 at.%  $^{72}\text{Ge}$ , 2.2 at.%  $^{73}\text{Ge}$ , 96.8 at.%  $^{74}\text{Ge}$  and 0.33 at.%  $^{76}\text{Ge}$ , giving a mean mass of 73.9. A third sample ( $^{76}\text{Ge}$ ) had contents of 13.0 at.%  $^{74}\text{Ge}$  and 87.0 at.%  $^{76}\text{Ge}$ , giving an averaged atomic mass of 75.7. For an enhanced isotope disorder we have used a crystal with predominantly  $^{70}\text{Ge}$  and  $^{76}\text{Ge}$  (49.4 at.%  $^{70}\text{Ge}$ , 2.1 at.%  $^{72}\text{Ge}$ , 6.2 at.%  $^{74}\text{Ge}$  and 42.3 at.%  $^{76}\text{Ge}$ , mean mass 72.75). The samples were diamond-polished to thicknesses of several mm for the indirect gap measurements or to  $\sim 50 \mu\text{m}$  for the direct gap determination. The samples were mounted stress-free and were immersed in liquid helium pumped below the  $\lambda$  point or were held in the open laboratory

for room temperature measurements. Absorption spectra were measured using either a Nicolet 60SX Fourier transform spectrometer or a Spex 1700 monochromator fitted with a cooled North Coast Ge diode detector.

Germanium is an indirect gap semiconductor, with the conduction band minimum at the  $\langle 111 \rangle$  zone boundary and the valence band maximum at  $k = 0$ . Optical absorption with the excitation of an electron across this indirect gap occurs with the involvement of a wavevector-conserving phonon. In Ge with the natural isotope abundances, and in the limit of low temperature, these phonons have quanta of  $\hbar\omega_{TA}^L = 7.9$  meV,  $\hbar\omega_{LA}^L = 27.7$  meV,  $\hbar\omega_{LO}^L = 30.6$  meV and  $\hbar\omega_{TO}^L = 36.1$  meV. The absorption transitions of lowest energy involve the creation of a stationary exciton, with an energy of  $740.46 \pm 0.03$  meV [8], plus one of the L-point phonons. The threshold of the absorption process involving the  $i$ th phonon occurs at a photon energy  $\hbar\nu_i$  where

$$\hbar\nu_i = E^{\text{ind}} + \hbar\omega_i^L. \quad (3)$$

The transition probabilities for the indirect-edge transitions are in the ratios TA : LA : LO : TO  $\sim 0.3 : 1 : 0.05 : 0.2$ .

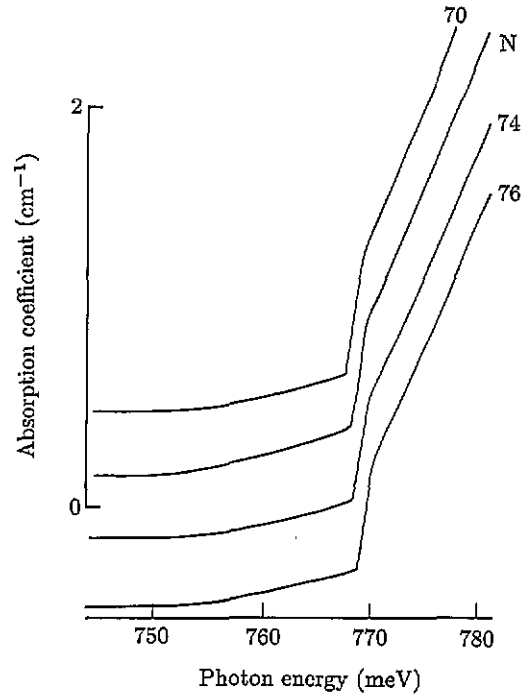
Figure 1 shows the absorption in the different isotopically doped samples for transitions across the indirect energy gap. The sharp rise near 770 meV is the dominant transition associated with the creation of one LA phonon. The energies of the wavevector-conserving phonons are known for the different crystals [6], and for approximately single-isotope crystals closely obey  $\omega \propto 1/\sqrt{m}$ , where  $m$  is the mean mass of the crystal. Subtracting the relevant phonon energy yields the change in indirect energy gap with isotope in the limit of low temperature as

$$dE^{\text{ind}}/dm = 0.36 \pm 0.01 \text{ meV} \quad (T \rightarrow 0) \quad (4)$$

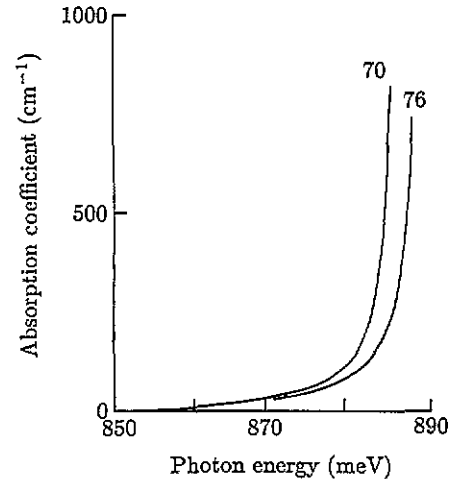
in agreement with the changes measured from photoluminescence spectra, equation (2).

With increasing photon energy the absorption produced by the indirect energy gap increases, reaching the onset of transitions across the direct energy gap near 890 meV at low temperature. The absorption increases rapidly to a maximum of  $\sim 4000 \text{ cm}^{-1}$  when the direct-gap exciton is created [9]. To measure these absorption values requires samples  $\sim 10 \mu\text{m}$  thick. Rather than risk destroying the single-isotope samples, we have measured the shift in the direct edge by using the photon energy at which the absorption coefficient has increased to  $500 \text{ cm}^{-1}$ . This energy is easy to define since the absorption coefficient is then increasing at the rate of  $\sim 200 \text{ cm}^{-1} \text{ meV}^{-1}$  (figure 2). The direct absorption edge is negligibly broadened by thermal effects at liquid helium temperature; furthermore, all the spectra can be superimposed by sliding them along the energy axis, indicating that there is no specimen-dependent broadening process which might also affect the energy gap. The change in energy gap is

$$dE^{\text{dir}}/dm = 0.49 \pm 0.03 \text{ meV} \quad (T \rightarrow 0). \quad (5)$$



**Figure 1.** Absorption at 2 K for the indirect energy gap transitions in the nominally single-isotope samples of  $^{70}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$ , and a natural germanium sample 'N'. The large increase in absorption near 770 meV is associated with the emission of the LA wavevector-conserving phonon. For clarity the spectra have been offset vertically; the absorption is close to zero at the extreme left of each curve.



**Figure 2.** Absorption at 2 K at the onset of optical transitions across the lowest direct energy gap in nominally single-isotope samples of  $^{70}\text{Ge}$  and  $^{76}\text{Ge}$ .

This value is about 20% larger than the previous determination by Agekyan *et al* [7], who underdetermined the shift in the indirect gap by the same amount.

There are two main contributions to the isotope shift. First, the lattice contraction with increasing mass (equation (1)) produces a shift (at low temperature) of

$$dE^{\text{dir}}/dm|_{\text{exp}} = a d \ln V/dm = 0.33 \pm 0.03 \text{ meV} \quad (6)$$

where the deformation potential  $a = -9700 \text{ meV}$

[10]. The uncertainty reflects the 10% spread in the experimental and calculated values of  $a$ .

The second contribution to the shift arises from the interaction of the valence and conduction band electrons with the instantaneous positions of the atoms [11]. For a lattice vibrating harmonically, an interaction that is linear in the atomic displacement  $u_i$  of the  $i$ th atom averages to zero, so that the dominant interaction arises from terms which are quadratic in  $u_i$ . The mean square displacement  $\langle u^2 \rangle$  for a harmonic oscillator of mass  $m$  and angular frequency  $\omega$  is  $\langle u^2 \rangle = \hbar[n(\omega) + \frac{1}{2}]/m\omega$  where  $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$  is the Bose-Einstein population factor. Consequently the electron-lattice interaction changes the direct energy gap by an amount  $\Delta E$  from the static lattice value where

$$\Delta E = \sum_i c_i [n(\omega) + \frac{1}{2}]/m\omega_i. \quad (7)$$

Here  $c_i$  represents the difference in electron-phonon coupling between the conduction band minimum and the valence band maximum, both at  $k = 0$ , for the  $i$ th vibrational mode. Equation (7) allows us to relate the isotope shift in the energy gap (which occurs through changes in  $m$  and  $\omega$ ) to the temperature dependence of the gap (which arises through changes in  $n(\omega)$ ). As in previous work [3] we fit the measured temperature dependence of the direct energy gap (which is known only over the limited range 0 to 300 K [9]) with the simple assumption that  $c_i$  varies smoothly with  $\omega$ . To evaluate the sum in equation (7) we use the density of phonon states given by reference [12]. The best fit to the temperature dependence is shown in the lower part of figure 3. Here the thin curve gives the calculated effect of the lattice expansion using the deformation potential  $a = -9700$  meV. The difference between the measured data and the lattice expansion effect has been fitted with  $c_i \propto \omega^{1.8}$ . Increasing the mass number of every atom in the lattice compacts the density of phonon states into a smaller range of frequencies, but does not change the  $c_i$  values (where  $i$  is identified with specific polarizations and wavevectors) since  $c_i$  is related to the change in energy per unit change in  $\langle u^2 \rangle$ . We find that the electron-lattice coupling changes the direct energy gap at 0 K by

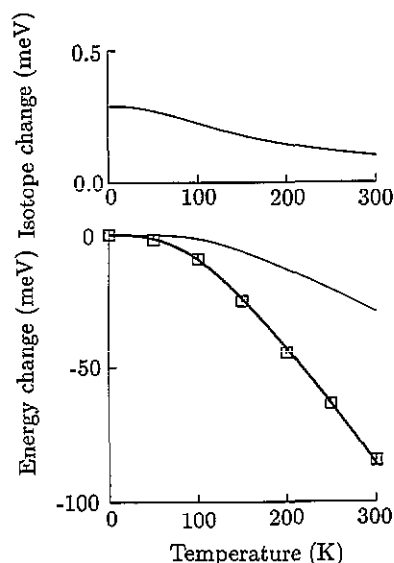
$$dE^{\text{dir}}/dm|_{c-1} \sim 0.29 \text{ meV} \quad (T \rightarrow 0). \quad (8)$$

The total predicted isotope shift is the sum of this effect plus the lattice expansion term of equation (6), giving

$$dE^{\text{dir}}/dm|_{\text{pred}} \sim 0.6 \text{ meV} \quad (T \rightarrow 0) \quad (9)$$

compared with the measured value of  $0.49 \pm 0.03$  meV (equation (5)).

This method of relating the isotope shift to the temperature dependence of the energy gap has the merit of simplicity. However, we have no guarantee that the thermal average over the phonon modes (always biased towards the lower frequencies) is appropriate for the isotope shift at 0 K (which is determined by the zero-point motion of all the modes). A graphical



**Figure 3.** The trend of the measured energies [9] of the direct gap of Ge of natural isotopic composition is shown as a function of temperature by squares in the lower diagram. The thin curve shows the calculated contribution from the lattice expansion. The thick curve is the total fit to the data using equation (7). The upper diagram shows the calculated contribution to the isotope shift from the electron-lattice term (equation (7)) when the isotope mass is increased by one unit.

illustration of the problems in determining  $\sum_i c_i/2m\omega_i$  from the temperature dependence of the gap is to note that this quantity is the difference between the energy gap extrapolated to 0 K from very high  $T$  and the actual energy gap at 0 K. Uncertainties in the high- $T$  behaviour of the energy gap probably translate into an uncertainty of about  $\pm 25\%$  in equation (8). Our calculation appears to be overestimating the shift. The much more detailed calculation by Zollner *et al* [4] overestimates the electron-lattice contribution by a similar margin.

In the limit of high temperature  $n(\omega) \rightarrow kT/\hbar\omega$  so that the mean square displacement  $\langle u^2 \rangle \rightarrow kT/m\omega^2$  and becomes independent of the isotope mass. Consequently the isotope shift is predicted to disappear at sufficiently high  $T$ . Usually this prediction cannot be tested—zero-phonon lines become too weak at high  $T$ , and indirect absorption edges become confused by phonon absorption processes as well as phonon emission processes. In contrast, the strong, well-defined absorption produced by the direct gap allows high temperature measurements. From equation (7) we predict that the electron-lattice contribution to the isotope shift will decrease as shown in the top part of figure 3, reducing to 0.1 meV at 300 K. Also, the isotope dependence of the lattice parameter decreases with increasing  $T$ . It has been measured as  $d \ln V/dm = -(14.1 \pm 0.6) \times 10^{-6}$  at 300 K [1]. With a deformation potential of  $-9700$  meV it produces a shift in the direct energy gap (cf equation (6)) of 0.14 meV per unit mass number. The total predicted shift is thus

$$dE^{\text{dir}}/dm|_{\text{pred}} \sim 0.24 \text{ meV} \quad (T = 300 \text{ K}). \quad (10)$$

We have measured a shift per unit mass number of

$$dE^{\text{dir}}/dm = 0.11 \pm 0.03 \text{ meV} \quad (T = 300 \text{ K}) \quad (11)$$

which would be accounted for by the expansion term alone: our simple model is not as temperature-dependent as reality.

Finally we note that in the highly disordered  $^{70}\text{Ge}/^{76}\text{Ge}$  sample the energy of the direct gap is indistinguishable from that expected for a single-isotope crystal of the same mean mass, to an uncertainty of  $\pm 0.06$  meV.

In this letter we have presented the first optical absorption data on the effects of changing the host lattice isotope on the lowest indirect energy gap of germanium, and have confirmed the photoluminescence data [2, 3]. We have shown that the lowest direct energy gap of germanium shifts to higher energy with increasing mass number at the rate, at low temperature, of 0.49 meV per unit mass number, and is very similar for isotopically pure and isotopically mixed crystals. At room temperature the shift is reduced by a factor of four. At low temperature the measured value is in reasonable agreement with a simple calculation based on published data for the temperature dependence of the direct gap. This study points out the need for a remeasurement of the temperature dependence of the direct energy gap over a wider range than the 0–300 K currently available.

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## References

- [1] Buschert R C, Merlini A E, Pace S, Rodriguez S and Grimsditch M H 1988 *Phys. Rev. B* **38** 5219
- [2] Etchegoin P, Weber J, Cardona M, Hansen W L, Itoh K and Haller E E 1992 *Solid State Commun.* **83** 843
- [3] Davies G, Lightowlers E C, Itoh K, Hansen W L, Haller E E and Ozhogin V 1992 *Semicond. Sci. Technol.* **7** 1271
- [4] Zollner S, Cardona M and Gopalan S 1992 *Phys. Rev. B* **45** 3376
- [5] Fuchs H D, Etchegoin P, Cardona M, Itoh K and Haller E E 1993 *Phys. Rev. Lett.* **70** 1715
- [6] Davies G, Hartung J, Ozhogin V, Itoh K, Hansen W L and Haller E E 1993 *Semicond. Sci. Technol.* **8** 127
- [7] Agekyan V F, Asnin V M, Kryukov A M, Markov I I, Rud' N A, Stepanov V I and Churilov A B 1989 *Sov. Phys.-Solid State* **31** 2082
- [8] Mayer A E and Lightowlers E C 1979 *J. Phys. C: Solid State Phys.* **12** L507
- [9] Macfarlane G G, McLean T P, Quarrington J E and Roberts V 1958 *Proc. Phys. Soc.* **71** 863
- [10] Schmid U, Christensen N E and Cardona M 1990 *Solid State Commun.* **75** 39
- [11] Allen P B and Heine V 1976 *J. Phys. C: Solid State Phys.* **9** 2305
- [12] Nelin G and Nilsson G 1972 *Phys. Rev. B* **5** 3151