

# Isotopically Controlled Semiconductors

E. E. Haller

Department of Materials Science and Engineering, University of California at Berkeley  
and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA  
94720 USA

**Keywords:** semiconductors, isotopes, spectroscopies, metal-insulator transition, neutron transmutation doping, diffusion, nuclear spin

**PACS:** 31.30.Gs, 63.20.-e, 71.30.+h, 78.30.-j, 85.40.Ry

## Abstract

A review of recent research involving isotopically controlled semiconductors is presented. Studies with isotopically enriched semiconductor structures experienced a dramatic expansion at the end of the Cold War when significant quantities of enriched isotopes of elements forming semiconductors became available for worldwide collaborations. Isotopes of an element differ in nuclear mass, may have different nuclear spins and undergo different nuclear reactions. Among the latter, the capture of thermal neutrons which can lead to neutron transmutation doping, can be considered the most important one for semiconductors. Experimental and theoretical research exploiting the differences in all the properties has been conducted and will be illustrated with selected examples. Manuel Cardona, the longtime editor-in-chief of Solid State Communications has been and continues to be one of the major contributors to this field of solid state physics and it is a great pleasure to dedicate this review to him.

## 1. Introduction

Isotopes of a given element differ in the number of neutrons making up their nuclei. In crystalline solids, this difference in nuclear mass most directly affects vibrational phenomena, i.e., phonon frequencies and all phonon-related properties. These include lattice constant, thermal conductivity, electronic band gaps, localized vibrational modes and self-diffusion, to name a few. Further differences between isotopes of an element are found in their nuclear spins and in the cross sections for nuclear reactions, most importantly the capture of thermal neutrons. It is the differences in these properties which lie at the core of the series of special papers in this issue of Solid State Communications, dedicated to its longtime editor-in-chief, Manuel Cardona, a major contributor to the field of studies with isotopically controlled semiconductors in recent years.

The existence of isotopes became established over a period of time by Soddy [1], Thomson [2] and Aston [3]. Until the massive efforts during World War II which led to separation and enrichment of isotopes in the tens of kilograms, isotope separation led to minute quantities of materials, too small and too expensive to be practical for solid state studies. After WWII, the first isotopically enriched semiconductor single crystal of  $^{74}\text{Ge}$  was grown at Bell Laboratories for thermal conductivity studies [4]. The starting material came from Oak Ridge National Laboratory. At prices ranging from a few to a few tens of US dollars per milligram, any sizable quantities of enriched semiconductor isotopes remained out of reach for the typical solid state researcher.

The high costs of isotope-related semiconductor studies were no longer a limiting factor after the end of the Cold War. For some years, Russian and Ukrainian isotope enrichment plants had converted a fraction of their weapons-related isotope production to the enrichment of a wide range of elements. The resulting large reserves of isotopes of a wide variety of semiconductor-forming elements, including but not limited to C (diamond), Si, Ge and Ga, became accessible for research collaborations. This conversion from the use of isotopes for weapons to civilian applications is a classic case of “swords to plowshares” as aptly described by Cardona [5].

## 2. Growth of isotopically controlled semiconductor bulk and thin films

In principle, there is no difference in growing bulk single crystals or crystalline thin films of isotopically enriched or of natural composition Ge, Si or any other semiconductor. In practice, however, the very precious nature of highly enriched isotopes forces the experimenter to use small quantities of materials and to minimize all losses during the processing of materials. For example, a single 1 mm wide cut across a 5 cm diameter, enriched  $^{74}\text{Ge}$  single crystal with a diamond saw destroys material worth over US\$ 1,000 at regular isotope prices of a few US\$ per milligram! What is needed are crystal growth processes which can produce small quantities of high quality material with minimal losses. We were fortunate to have our research Czochralski (CZ) type ultra-pure Ge crystal puller [6] available for the growth of numerous isotopically enriched Ge single crystals weighing a few tens of grams up to one kilogram. We have grown bulk crystals of all stable Ge isotopes except  $^{72}\text{Ge}$  with enrichment in the high 90% and net residual dopant concentrations of  $\leq 10^{12} \text{ cm}^{-3}$ . Some of these crystals were used in bulk form for isotope-related studies, others served as source materials for thin film growth.

Whereas silicon is the most extensively used semiconductor, produced as single crystals in the thousands of tons per year, it is very difficult to find research quality Si crystal pullers which yield high purity material in small quantities in the range of grams to a few hundred grams. Helge Riemann at the Institut für Kristallzüchtung (IKZ) in Berlin, Germany has grown a number of very high quality floating zone (FZ) single crystals of enriched isotopes  $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$ . The polycrystalline source material came mostly from Russian laboratories. In recent years, we have developed a process to fabricate hollow cylinders of ultra-pure, enriched poly Si which have been successfully converted to single crystals by Helge Riemann. Our starting material came in the form of  $^{xx}\text{SiF}_4$  from the Electrochemical Plant in Zelenogorsk, Russia. The  $\text{SiF}_4$  gas was purified and

converted to silane ( $^{xx}\text{SiH}_4$ ) at Voltaix Corp., New Jersey. We built a silane pyrolysis reactor at the Lawrence Berkeley National Laboratory in which the Si was deposited on an electrically heated graphite rod [7]. Removing this graphite rod by drilling, grinding and chemical etching yielded the poly Si cylinders ready for FZ crystal growth.

The growth of large diamond single crystals is a challenge in itself without the additional problems related to isotope enrichment. Thomas Anthony and colleagues at General Electric have grown large gem-quality bulk diamonds with varying isotopic composition from highly enriched  $^{12}\text{C}$  to pure  $^{13}\text{C}$ . They found that enrichment occurs during bulk growth from a metal solvent and attributed this effect to the difference in the attempt frequency for a  $^{12}\text{C}$  or  $^{13}\text{C}$  atom to leave the solvent and deposit on the growing diamond crystal [8]. Anthony has grown both undoped and boron doped (blue!) isotopically enriched diamonds [9,10].

The growth of single and multiple thin crystalline films of enriched semiconductors (isotope superlattice) has been achieved in a number of places. The small volume MBE sources available today allow the economic growth of thin films. Single crystal Si layers grown by vapor phase epitaxy (VPE) on Si wafers has been achieved commercially (Lawrence Semiconductor Research Laboratory, Inc., Tempe, AZ).

In the following sections, an overview of studies on isotopically controlled semiconductors is presented. The sections are arranged according to the effects produced by the differences in isotopic mass, spin and thermal neutron absorption cross section. The selection of the specific physical phenomena discussed in the present article naturally reflect the studies in which the author has been closely involved. Authoritative detailed accounts of a number of isotope-related phenomena are featured in the present issue of Solid State Communications.

### 3. Isotope mass-related effects

#### 3.1. Lattice dynamics in bulk crystals

##### 3.1.1. Phonons

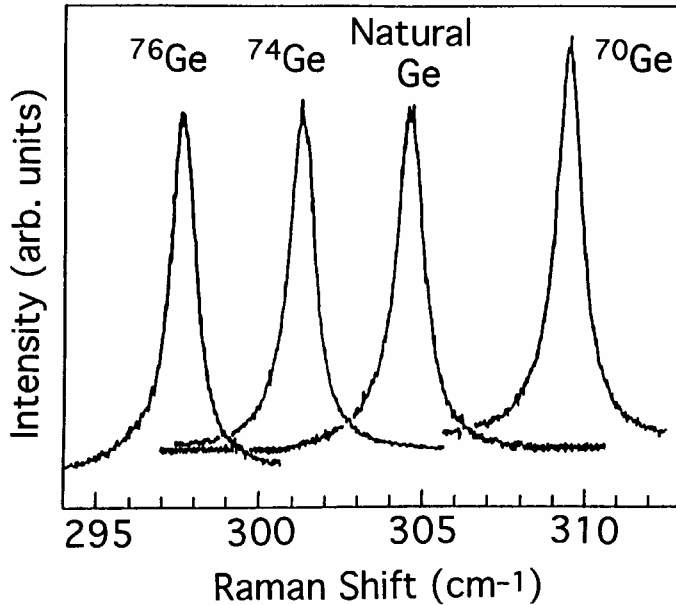
The quanta of energy of crystal lattice vibrations are called phonons. The simplest dependence of the phonon frequency  $\omega$  on mass  $M$  can be described within the virtual-crystal approximation (VCA) [11,12] by a “spring and ball” model and is given by

$$\omega \propto M^{-1/2}. \quad (1)$$

The phonon dispersion relationship describes the phonon frequencies  $\omega$  as a function of the wave vector  $\vec{k}$  for the various vibrational modes. Raman spectroscopy is ideally suited for the study of optical phonons at  $\vec{k} = 0$ . Photoluminescence in indirect band gap semiconductors requires the assistance of  $\vec{k} \neq 0$  phonons. In germanium, the recombination of an electron at the conduction band minimum

$\vec{k} = (2\pi/a)(1/2, 1/2, 1/2)$ , i.e., L-point] with a hole at the valence band maximum  $\vec{k} = 0$  requires the emission or absorption of a zone boundary phonon at the L-point to satisfy the conservation of wave vector momentum. Raman Spectroscopy and PL have been used for the study of phonons in isotopically enriched germanium crystals as well as those with controlled isotopic mixtures.

Figure 1 shows superimposed Raman lines of natural and of isotopically enriched Ge single crystals recorded near liquid nitrogen temperatures (90 K) [13]. The lines in these spectra are fully resolved instrumentally and their width is caused by homogeneous broadening. The centroid of the Raman line shifts following equation (1). What is surprising at first sight is the very weak dependence of the phonon linewidth of  $\approx 1 \text{ cm}^{-1}$  on isotopic composition. The close to constant linewidth has been explained with phonon delocalization [14-18] which can be discussed within the framework of Anderson localization [19]. If we express the relative mass fluctuations  $\Delta M/\bar{M}$  in the form of a frequency bandwidth  $(\Delta M/\bar{M}) \omega_0 = 12 \text{ cm}^{-1}$  with  $\omega_0$  being the angular optical phonon frequency at  $\vec{k} = 0$  and compare it with the bandwidth of the optical phonons in the first Brillouin zone  $\Delta\omega_0 \sim 100 \text{ cm}^{-1}$ , we immediately see that the mass fluctuation bandwidth is much smaller than the intrinsic optical phonon bandwidth. Under these circumstances phonons do not become localized on individual atoms but remain spread out over a large number of unit cells, leading to a close to perfect linear averaging of the various isotope masses.



**Figure 1.** Raman spectra of the optical zone center phonon of several isotopically enriched Ge crystals and of a natural Ge crystal at 90K (Courtesy of H. D. Fuchs *et al.* [13]).

The Raman linewidth has been shown to be due to the phonon lifetime for the anharmonic decay into two phonons. In good approximation one writes:

$$\Delta\omega_0 \cdot \tau \cong 1. \quad (2)$$

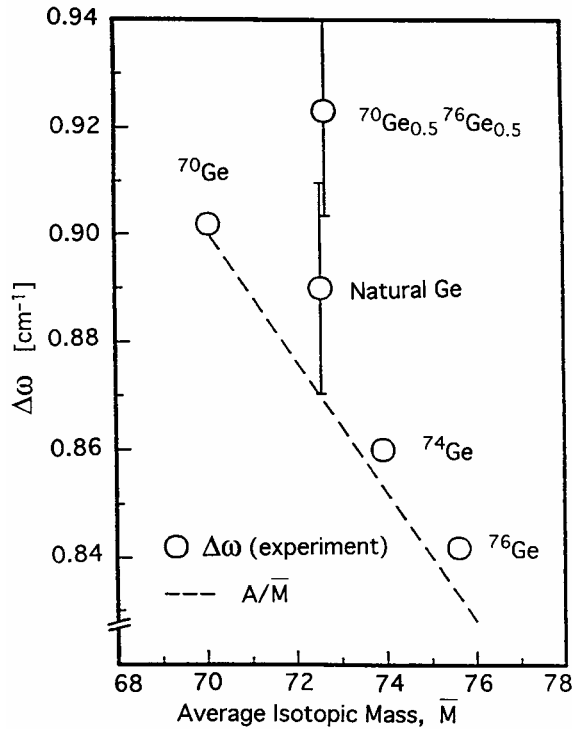
Time-resolved measurements have yielded lifetimes of 6 ps in very good agreement with the observed  $\Delta\omega_0 = 1 \text{ cm}^{-1}$  (equivalent to  $3 \times 10^{10} \text{ Hz}$ ) [14]. This natural linewidth (or lifetime) is dominated by anharmonic interactions leading to the decay of an optical phonon at  $\vec{k}=0$  into two phonons. At the low temperature where these Raman experiments were conducted, the rate for anharmonic decay ( $\tau^{-1}$ ) is proportional to the amplitudes of the two phonons created in the process:

$$\tau^{-1} = \Delta \omega_0 \propto \langle u_1^2 \rangle \langle u_2^2 \rangle = \frac{\hbar^2}{4M^2 \omega_1 \omega_2}. \quad (3)$$

Using equation (1)  $\omega \propto M^{-1/2}$ , we find:

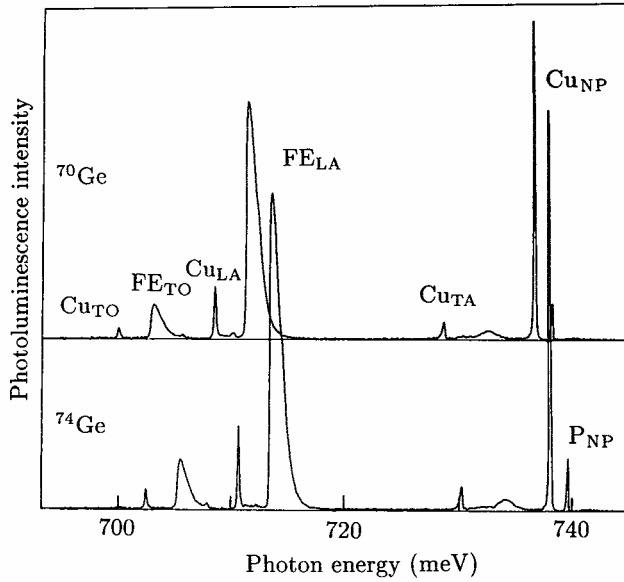
$$\Delta \omega_0 \propto M^{-1}. \quad (4)$$

The width of the Raman lines obtained from the four isotopically enriched Ge crystals indeed follow such a simple dependence (Fig. 2). The Raman linewidths for the crystals of natural composition and of maximum isotope disorder are slightly larger. Cardona *et al.* [18] have shown that this extra broadening requires the effect of anharmonicity on the density of phonon states for three-dimensional crystals. They further showed that when going to two dimensions, isotope disorder broadening can be explained in the harmonic approximation.



**Figure 2.** Full width at half maximum of the Raman lines shown in Fig. 1 and of a  $^{70}\text{Ge}_{0.5}/^{76}\text{Ge}_{0.5}$  sample. The dashed line represents the  $M^{-1}$  dependence for isotopically pure samples. (Courtesy of Fuchs *et al.*, [13]).

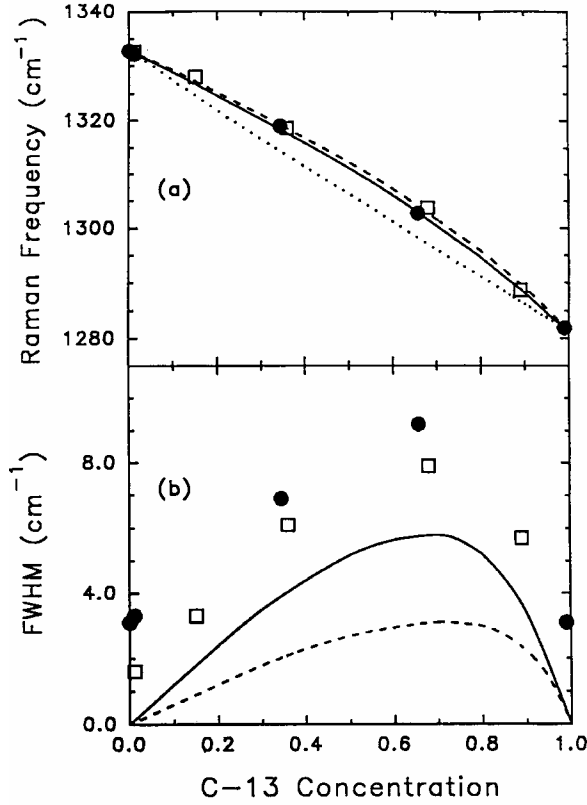
The first photoluminescence studies of several isotopically enriched Ge crystals at low temperatures were reported by Davies *et al.* [20,21] and by Etchegoin *et al.* [16]. Figure 3 shows representative luminescence spectra of highly enriched  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  crystals. The LA and the TO phonon assisted free exciton (FE) lines are clearly shifted in energy. Excitons bound to deliberately introduced substitutional Cu acceptors generate both phonon assisted (TA,LA,TO) as well as no-phonon lines (NP). In addition one observes a sharp no-phonon line due to P donors. Whereas the phonon assisted lines suffer energy shifts due to phonon and band gap energy changes, the NP lines are displaced solely because of band gap energy changes. This information allows the quantitative determination of isotope-related phonon and band gap energy changes. After correcting for the band gap shifts, the phonon energies accurately follow the frequency dependence given in Eq. (1).



**Figure 3.** Luminescence from the decay of free excitons and excitons bound to Cu acceptors and P donors in  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  at 4.2 K. The subscripts indicate the L-point phonons assisting in the exciton decay. The impurity bound excitons can decay without emission of a phonon (NP) (Courtesy of Davies *et al.*, [20]).

Stimulated in part by speculations regarding very large increases of the thermal conductivity in isotopically pure diamonds, a series of diamond crystal growth and characterization studies with extensive theoretical interpretation has been conducted. Using the well-established multiple-scattering formalism of the coherent potential approximation (CPA), Hass *et al.* [22-23] and Chrenko [24] were able to explain quantitatively the large effects of isotopic disorder on the frequencies of optical phonons at  $\vec{k} = 0$  and for the Raman linewidths for a range of isotopic compositions. Figure 4 shows the Raman frequencies and linewidths as a function of the fractional  $^{13}\text{C}$  concentration. Isotopic disorder causes the upwards bowing of the Raman frequency dependence as well as the large asymmetric increase in linewidth with isotopic composition. Both dependencies are well described with CPA theory especially when the intrinsic linewidth of the isotopically purest samples is subtracted from all the data points.

It is interesting to note that the success in describing optical phonon frequencies and Raman linewidths of isotopically mixed diamonds have not provided insights into of the very strong dependence of the thermal conductivity (which depends on acoustic phonons) on small levels of isotopic disorder.



**Figure 4.** Isotopic composition dependence of the (a) diamond Raman frequency and (b) linewidth (FW HM). CPA results for pure and adjusted "TPZ" models and VCA results in (a) shown as dashed, solid and dotted lines respectively. Open squares courtesy of Chrenko [24]; filled dots are courtesy of Hass *et al.* [23].

### 3.1.2. Thermal Conductivity

From an applications point of view, the most important phonon-related effect is the thermal conductivity of a crystalline solid. The removal of the heat produced by a modern semiconductor integrated circuit running at a clock frequency of several GHz has become one of the most important obstacles in further improvements of device performance. It is no surprise that one of the expectations for isotopically enriched semiconductors have been increases in thermal conductivity. From a number of careful recent studies of the thermal conductivity in diamond, silicon and germanium, we conclude that near and above room temperature increases in the range of at most tens of percent can be expected.

The thermal conductivity of dielectrics is given by

$$K = \frac{1}{3} C v L, \quad (5)$$

with  $C$  = specific heat,  $v$  = phonon velocity and  $L$  = phonon mean-free path [25]. Neither the velocity of low-frequency phonons nor the specific heat which has been determined by Morelli *et al.* [26] are predicted to change much at a 1% isotope impurity level. The large thermal-conductivity increases which are observed for diamonds with increasing isotopic purity must be due to changes in the phonon scattering rates. This suggestion goes back to Pomeranchuk [27].

Wei *et al.* [28] have measured a record thermal conductivity of  $410 \text{ W cm}^{-1} \text{ K}^{-1}$  at 104 K for a 99.9%  $^{12}\text{C}$  enriched diamond (Fig. 5). They fitted their data with the Callaway model [29] using four independent scattering processes. The functional form of the individual scattering rates were chosen as follows:

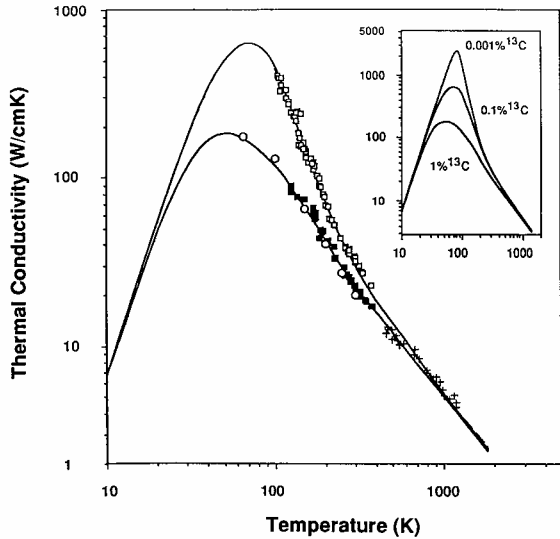
$$\tau_{\text{Normal}}^{-1} = A v T^3 \lambda^{-1} \quad (6)$$

$$\tau_{\text{Umklapp}}^{-1} = B v T \lambda^{-1} \exp(-C/T) \quad (7)$$

$$\tau_{\text{Boundary}}^{-1} = v/D \quad (8)$$

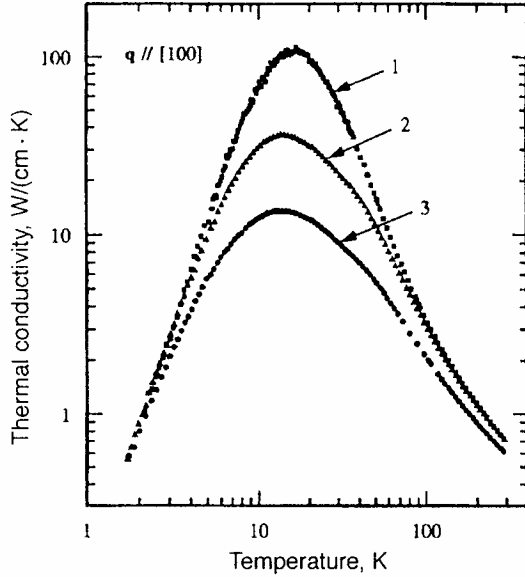
$$\tau_{\text{Isotope}}^{-1} = 4 \pi^3 v \lambda^{-4} V_0 x(1-x)(12+x)^{-2}, \quad (9)$$

with  $v$  and  $\lambda$  corresponding to the average phonon velocity and wavelength, respectively;  $x$  is the isotope fraction of  $^{13}\text{C}$ ,  $V_0$  is the atomic volume and  $T$  is the absolute temperature. The constants  $A$ ,  $B$ ,  $C$  and  $D$  were determined from the fits:  $A = 7.2 \times 10^{-11} \text{ cm K}^{-3}$ ,  $B = 1.5 \times 10^{-12} \text{ cm K}^{-1}$ ,  $C = 670 \text{ K}$  and  $D = 0.33 \text{ cm}$ . Once the constants  $A$  through  $D$  have been determined it is possible to predict the dependence of thermal conductivity on temperature and isotopic composition. This has led to their prediction of a thermal conductivity as great as  $2000 \text{ W cm}^{-1} \text{ K}^{-1}$  near 80 K, exceeding Geballe's prediction [30] that the thermal conductivity of pure diamond may surpass  $1000 \text{ W cm}^{-1} \text{ K}^{-1}$  around liquid nitrogen temperature (77K). Similar results have been reported by Olson *et al.* [31]. It should be pointed out that measurements of such extreme thermal conductivities for millimeter-size samples are extremely difficult. The samples act like close to perfect thermal short circuits.



**Figure 5.** Thermal conductivity of natural abundance (1.1%  $^{13}\text{C}$ ) diamond (lower squares), isotopically enriched (0.1%  $^{13}\text{C}$ ) diamond (upper squares). The inset shows the calculated thermal conductivity corresponding to 1%, 0.1%, and 0.001%  $^{13}\text{C}$  concentrations according to the Callaway theory [29]. (Adapted from Wei *et al.*, [28]).

Thermal conductivity studies have also been performed on very highly enriched, ultra-pure  $^{70}\text{Ge}$  crystals (Fig. 6) [32]. In these 99.99% enriched single crystals, the thermal conductivity exceeds the maximum values recorded by Geballe and Hull [4] by a factor of  $\approx 3$ . Further detailed measurements have been conducted and an in-depth analysis has been reported [33].



**Figure 6.** Temperature dependence of the thermal conductivity along the [100] direction of germanium single crystals with different isotopic composition: 1 – 99.99%  $^{70}\text{Ge}$ ; 2 – 96.3%  $^{70}\text{Ge}$ ; 3 – natural Ge [32].

The thermal conductivities of a Si single crystal of natural composition and an isotopically enriched one have been measured over a wide temperature range by T. Ruf *et al.* Their original results showed a 60% increase of the room temperature thermal conductivity of highly enriched  $^{28}\text{Si}$  over  $^{\text{nat}}\text{Si}$  [34]. Later they revised their original high temperature values of the thermal conductivity of the enriched  $^{28}\text{Si}$  from 60% to  $10 \pm 2\%$  over the values of the  $^{\text{nat}}\text{Si}$  crystal. This significantly lower value is in line with experimental observations of other groups and with theoretical estimates [35].

### 3.1.3. Lattice constant

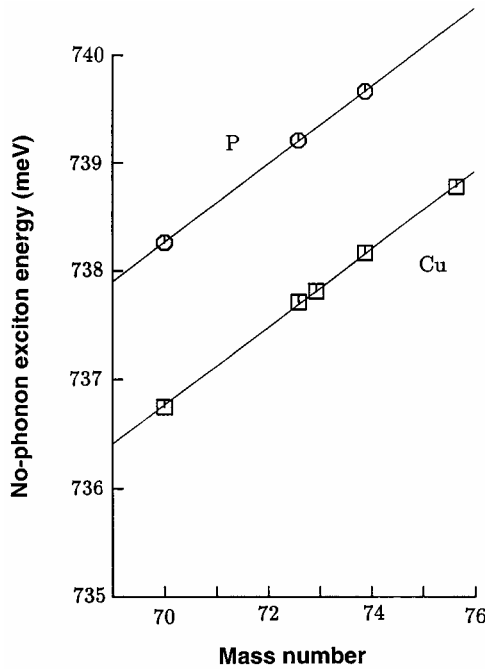
The lattice constants  $a_0$  of large, chemically pure and crystallographically highly perfect crystals can be measured with very high precision. Because of this “naturally” occurring precision there exists an interest in using the lattice constant of a suitable crystal as a length standard [36]. However, as a consequence of the zero-point motion, the atomic volumes change with isotopic composition. The resulting effect on  $a_0$  has been carefully studied for an enriched  $^{74}\text{Ge}$  crystal [37] and for a series of diamonds with varying  $^{12}\text{C}/^{13}\text{C}$  composition [38].

Using the synchrotron x-ray standing wave technique, Kazimirov *et al.* [39] performed precision lattice constant difference measurements of a thin film of  $^{76}\text{Ge}$  grown on a natural Ge substrate. Sozontov *et al.* [40] repeated such measurements with a  $^{76}\text{Ge}$  thin film grown on an enriched  $^{70}\text{Ge}$  substrate as well as a thin film of  $^{30}\text{Si}$  grown on a natural Si substrate.

More recently the lattice constants of a series of four highly enriched bulk single crystals of  $^{70}\text{Ge}$ ,  $^{73}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$  have been measured with very high precision over a wide temperature range using the Bragg backscattering technique of X-rays at the Advanced Photon Source, Argonne National Laboratory [41]. These results are the most extensive of their kind and they will be discussed in detail and compared to advanced theoretical treatments in the accompanying article by Haller, Ramdas, Rodriguez and Tsoi.

#### 3.1.4. Electronic band gaps

The width and the character (direct or indirect) of the lowest energy band gap are of paramount importance for a number of semiconductor properties and in turn for all semiconductor devices. Because of this great significance there exists a strong interest in all effects which influence the band structure.



**Figure 7.** Energies of the no-phonon lines of excitons bound to Cu acceptors (squares) and P donors (circles). (Courtesy of Davies *et al.*, [20,43])

The isotopic composition affects the band gaps through the electron-phonon coupling and through the change of volume with isotopic mass. Several groups have conducted low-temperature studies of the direct and indirect band gaps of natural and isotopically controlled Ge single crystals. Agekyan *et al.* [42] used photoluminescence, infrared absorption and Raman spectroscopy with a Ge crystal of natural composition and a crystal with 85%  $^{76}\text{Ge}$  and 15%  $^{74}\text{Ge}$ . They found an indirect band gap change  $\Delta E_{IG}=0.9$  meV and a direct band gap change  $\Delta E_{DG}=1.25$  meV with an error of  $\pm 0.05$  meV. Etchegoin *et al.* [16] and Davies *et al.* [20,43] reported PL studies of natural and several highly enriched, high quality single crystals of Ge. Measurement of the energies of impurity-bound excitons shown in Fig. 3 permits the direct determination of band gap shifts with the crystal isotope mass because the radiative recombination does not require phonon participation. Figure 7 shows the no-phonon energies of excitons  $E_{NP}$  bound to P and Cu in several isotopically controlled crystals. As may be expected from the very large Bohr orbits of the excitons, their binding energy only depends on the average

isotope mass and not on the isotopic disorder. The rate of band gap energy change which is equal to the exciton binding energy change with isotope mass as determined by Davies *et al.* [20,43] is

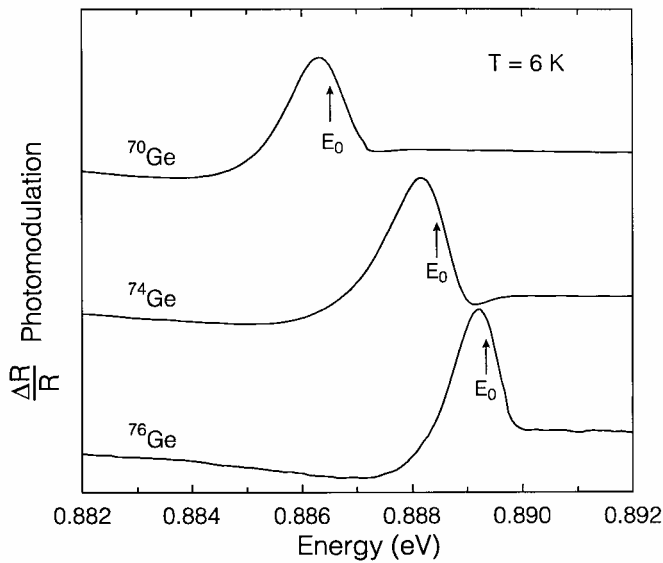
$$dE_{IG}/dA = dE_{NP}/dA = 0.35 \pm 0.02 \text{ meV amu}^{-1}. \quad (10)$$

Etchegoin *et al.* [16] obtained a very similar value.

Measurements of the direct band gap at the  $\Gamma$  point ( $\vec{k} = 0$ ) in the Brillouin zone have also been performed by Parks *et al.* [44] who used piezo- and photo-modulated reflectivity spectra of four mono-isotopic and one natural Ge crystals. These techniques do not require the extreme sample thinning which is necessary for optical absorption measurements and the derivative nature of the spectra emphasizes the small changes. Figure 8 shows the photo modulated reflectivity of three mono-isotopic Ge crystals at  $T = 6$  K. The position of the direct energy gap  $M$  is indicated by an arrow marked  $E_0$ . The excellent signal-to-noise ratio and the superb spectral resolution allow a very accurate determination of the dependence of  $E_0$  on isotopic mass. At very low temperatures, an inverse square root dependence accurately describes band gap dependence:

$$E_0 = E_0^\infty + \frac{C}{\sqrt{M}}. \quad (11)$$

A fit through five data points yields:  $E_0^\infty = 959 \text{ meV}$  and  $C = -606 \text{ meV amu}^{1/2}$ . Written as a linear dependence for the small range of isotopic masses, Parks *et al.* [44] find  $dE_0/dA = 0.49 \text{ meV amu}^{-1}$ , in perfect agreement with the results of Davies *et al.* [21]. Parks *et al.* also determined the isotope mass dependence of the sum of the direct gap and the split-off valence band ( $\Delta_0$ ) and found  $d(E_0 + \Delta_0)/dA = 0.74 \text{ meV amu}^{-1}$ .



**Figure 8.** Photomodulated reflectivity showing the direct band gap of single crystals of  $^{70}\text{Ge}$ ,  $^{74}\text{Ge}$  and  $^{76}\text{Ge}$  at  $T=6\text{K}$ . (Courtesy of Parks *et al.*, [44]).

The dependence of the indirect band gap of silicon on isotope mass has been determined by a number of groups using a variety of techniques. Karaiskaj *et al.* [45] used high resolution photoluminescence (PL) spectroscopy to determine the energy shifts of phonons and the indirect energy gap of Si crystals with different isotopic composition. Making the assumption that the binding energies of exciton bound to P donors and B acceptors are independent of the atomic mass of the Si host crystal, they determine an indirect energy gap ( $E_{IG}$ ) shift of  $(dE_{IG}/dM)_{T,V} = 1.04 \text{ meV amu}^{-1}$ . Tsoi *et al.* [46] used PL spectroscopy and wavelength-modulated transmission spectroscopy in combination to determine the isotopic mass dependence of the indirect band gap and the “wavevector conserving” phonon energies. Tsoi *et al.* [46] report  $(dE_{IG}/dM)_{T,V} = 1.01 \text{ meV amu}^{-1}$ , identical to Karaiskaj *et al.*’s results within experimental error. The experimental results are in reasonable agreement with Zollner *et al.*’s theoretical predictions [47]. Details on this topic are covered in the accompanying article by Haller, Ramdas, Rodriguez and Tsoi.

The band gaps of some III-V and II-VI semiconductor alloys have been shown to depend also on the isotope masses of the constituent elements. Just as in the case of the elemental semiconductor germanium, the values for  $(dE/dM)_{T,V}$  are typically a fraction of one  $\text{meV amu}^{-1}$  [48].

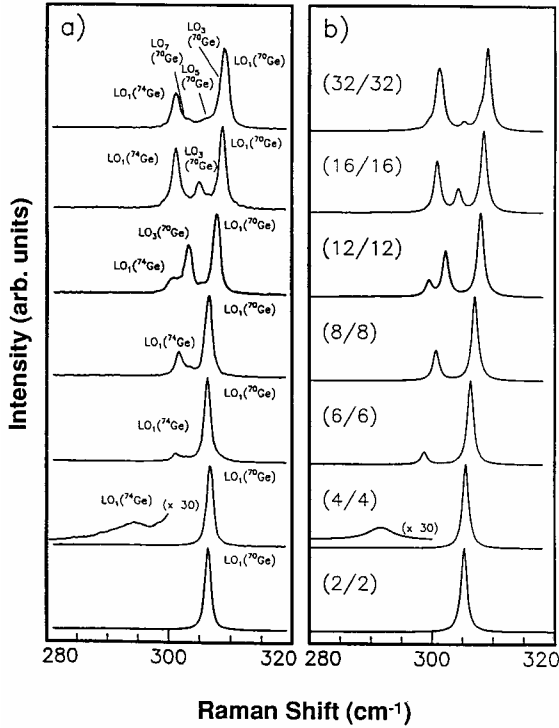
We conclude this discussion of the band gap shifts with isotope mass by observing that the effects are relatively small and most likely will not have any consequences for technological applications of Ge, Si nor any other semiconductors. However, such studies offer an excellent demonstration of the advanced state of our quantitative theoretical understanding of the subtle effects of temperature, pressure and isotope mass on the electronic band structure achieved with a wide range of spectroscopies.

### 3.1.5. Isotope Superlattices

The discussion of phonons, their dispersion and the dependence of their properties on the isotopic composition of the host crystal has so far been restricted to bulk crystals, crystals sufficiently large so as not to affect phonon properties. What do we expect when the dimensions of the crystal are significantly reduced? The discussion in this section is focused on the fascinating features displayed by short period isotope superlattices consisting of alternating layers each made up of a few atomic planes of  $^A\text{Ge}$  and  $^B\text{Ge}$ . These are ideal structures for phonon studies because the electronic band structure is not significantly affected by the isotope superlattice, i.e., the material looks bulk-like for electrons throughout the crystal layers.

The first problem to be addressed relates to the normal phonon modes of a short period isotope superlattice. The vibrational modes and the phonon dispersion relation for a  $^{70}\text{Ge}_4/^{76}\text{Ge}_4$  [001] superlattice at  $\vec{k}=0$  were calculated using the planar force constant model [49]. These theoretical results were tested with Raman studies of a series of MBE grown, short period isotope superlattices of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  [50]. The experimental and theoretical results are summarized in Fig. 9. The shortest periods studied consisted of two atomic layers each and produce a single Raman line corresponding to the Brillouin zone center optical phonon in a Ge crystal with isotope mass  $A = 72$ , the arithmetic

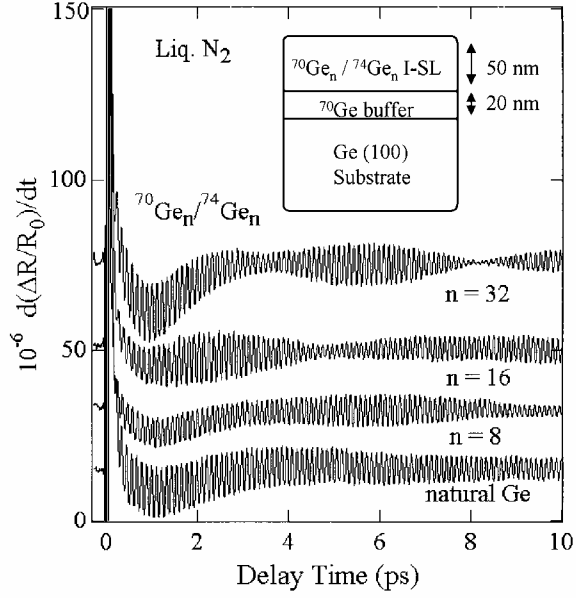
average of the two masses. Abstreiter *et al.* who grew this superlattice are quite certain that this result is not due to intermixing of more than one atomic layer during growth because they used very low growth temperatures ( $T = 350^\circ\text{C}$ ) and low growth rates ( $4 \text{ \AA}/\text{min}$ ). The  $n = 4$  superlattice shows the Raman line predicted at  $\sim 290 \text{ cm}^{-1}$  though at a slightly lower intensity. In the  $n = 12$  superlattice one observes at least three strong Raman lines. For  $n = 32$  the Raman spectra begin to approach the structure one would expect for two isotopically pure bulk crystals, one made up of  $^{70}\text{Ge}$ , the other of  $^{74}\text{Ge}$ .



**Figure 9.** (a) Measured at  $T=10\text{K}$  and (b) calculated Raman spectra for a series of isotope superlattices  $^{70}\text{Ge}_n/^{74}\text{Ge}_n$  grown along  $[001]$  with  $n = 2, 4, 6, 8, 12, 16$ , and  $32$ . A number of modes confined to the  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  layers are evident. (Courtesy of Spitzer *et al.*, [50]).

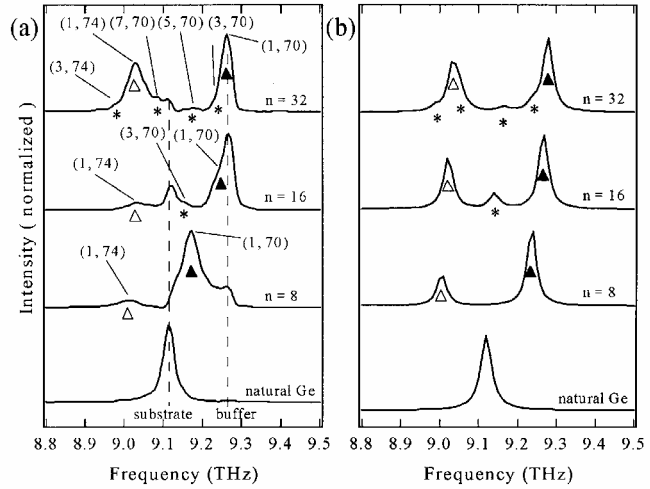
Nakajima *et al.* [51] used Ge isotope superlattices for dynamic pump-and-probe photon studies. They recorded the oscillatory reflectivity generated by high-order coherent confined phonons (Fig. 10). While these oscillations monotonically decay in natural Ge, the isotope superlattices show a beating in the oscillation amplitude. Fourier transformation of the reflection oscillations shows directly the frequencies of the LO phonons confined to the  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  layers (Fig. 11). The experimental findings are in good agreement with calculations based on a planar force constant model and a bound polarizability approach [52,53].

The first silicon isotope superlattices consisting of 8, 12 and 24 atomic layers of  $^{28}\text{Si}$  and  $^{30}\text{Si}$ , grown and studied by Kojima *et al.* [54], reveal Raman spectra associated with the various confined optical phonon modes and are well reproduced theoretically by the same model used for the germanium isotope superlattices.



**Figure 10.** Oscillatory component of the time-domain signals in  $^{70}\text{Ge}_n/^{74}\text{Ge}_n$  isotope superlattices with various layer thicknesses and in natural Ge. Inset shows the structure of  $^{70}\text{Ge}_n/^{74}\text{Ge}_n$  isotope superlattices ( $n = 8, 16$  and  $32$ : the number of monolayers); (Courtesy Nakajima et al. [51]).

**Figure 11.** (a) Fourier transformed spectra of the time-domain signals shown in Fig. 10, and (b) calculated spectra.  $(m,70)$  or  $(m,74)$  means  $m$ -th order confined modes in  $^{70}\text{Ge}$  or  $^{74}\text{Ge}$  layers, respectively. Vertical dashed lines in (a) denote LO phonon frequencies in the bulk  $^{70}\text{Ge}$  buffer layers and in the natural Ge substrate. Asterisks, and filled and open triangles denote confined LO phonon modes (Courtesy Nakajima et al. [51]).



These Raman spectroscopy studies of Ge and Si isotope superlattices demonstrate Brillouin zone folding in a direct way. The relative intensities of the Raman lines reflect the densities of states at  $\vec{k} = 0$ . It is quite impressive how well the experimental data are reproduced by the planar bond-charge and bond polarizability models. For layers thicker than approximately 30 atomic planes we observe close to perfect localization in the individual layers, i.e., bulk-like behavior.

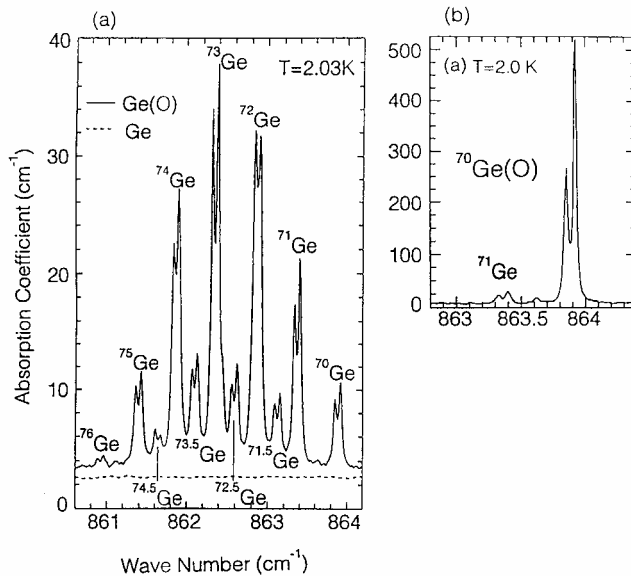
### 3.2. Local vibrational mode spectroscopy

Local vibrational mode (LVM) spectroscopy is a well-established tool for the study of defects and low mass impurities in semiconductors [55,56]. Isotope substitution has been widely used to identify the particular impurity producing a given LVM signature.

Perhaps the most widely used isotope substitution is that of H by D. With the vibrational frequency depending on the inverse square root of the isotope mass, the shift in frequency from a H- to a D-related LVM is close to 40%.

A less pronounced effect is the dependence of an LVM spectrum on the mass of the neighboring host atoms. To the extent the mass of neighboring atoms is not infinite, it is of interest to explore to what extent they participate in the vibrational motion of the impurity. Isotope control of the semiconductor host lattice offers a direct identification of the various atoms participating in the local vibration.

As an illustrative example of a LVM frequency being affected by the host atoms, we briefly review the LVM structure of O in natural and isotopically controlled Ge. To model the LVM of this bond centered impurity, one takes into account the two nearest neighbors, while the rest of the lattice appears as a small correction, called “interaction mass.” The  $^x\text{Ge-O-}^y\text{Ge}$  molecule has three fundamental modes. The “wag” mode ( $\nu_3$ ) has the highest frequency and was observed in oxygen rich Ge quite some time ago [57]. Low-temperature, high resolution studies show eleven lines, each one split into several components whose intensities depend on temperature [58]. The eleven lines result from the different mass combinations of  $^x\text{Ge}$  and  $^y\text{Ge}$ . Combinations with identical linear mass averages (e.g.  $^{72}\text{Ge}/^{74}\text{Ge}$  and  $^{73}\text{Ge}/^{73}\text{Ge}$ ) lead almost to the same oxygen vibrational frequencies.



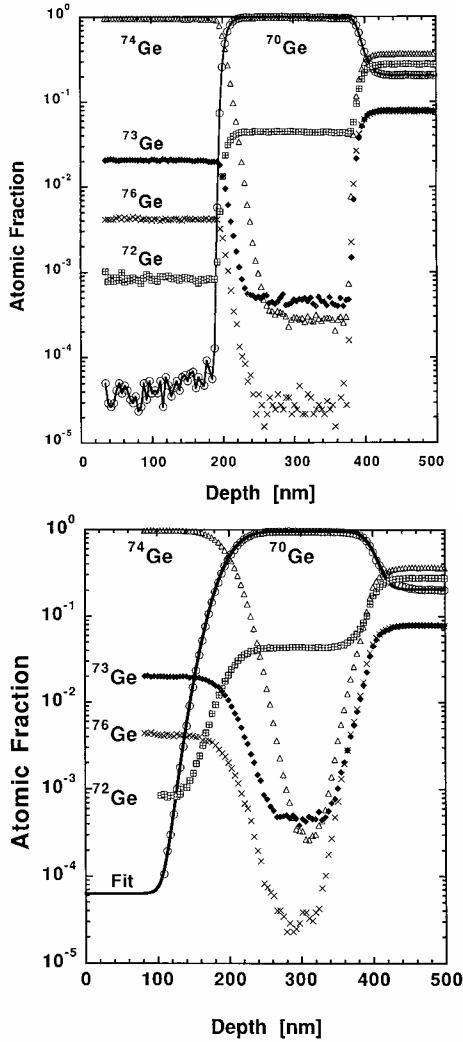
**Figure 12.** (a) Spectrum of the  $\text{Ge}_2\text{O}$  quasi molecules in natural Ge at 2.05 K. Eleven lines split by  $\nu_2+\nu_3$  coupling excitations correspond to the distinct isotopic mass combinations of the two Ge atoms in the quasi molecule. An oxygen free sample produced the dashed line. (b) The spectrum of an oxygen doped, highly enriched sample of  $^{70}\text{Ge}$ . The lines labeled  $^{71}\text{Ge}$  are caused by traces of  $^{72}\text{Ge}$  in  $^{70}\text{Ge}$ . (Courtesy of Mayur *et al.*, [59]).

The complexity of such spectra can be reduced very significantly through the use of isotopically pure (or at least highly enriched) crystals. Figure 12 shows two spectra which were reported by Mayur *et al.* [59]. They used one natural and four highly enriched Ge crystals doped with oxygen. The reduction from eleven to one LVM line is significant because it allows a quantitative study of the linewidth and of the coupling

between  $v_3$  and the other modes as a function of temperature. The splitting is a result of the nonlinear superposition of the  $v_2$  and the  $v_3$  modes. The low frequency  $v_2$  modes can be thermally populated already near liquid helium temperature.

### 3.3. Diffusion

The study of self- and dopant diffusion in semiconductors has been advanced significantly through the use of isotopically controlled multilayer structures. Diffusion measurements performed with radiotracer methods are limited by the half-lives of radioactive isotopes, by the damage produced during their introduction and by near surface effects.

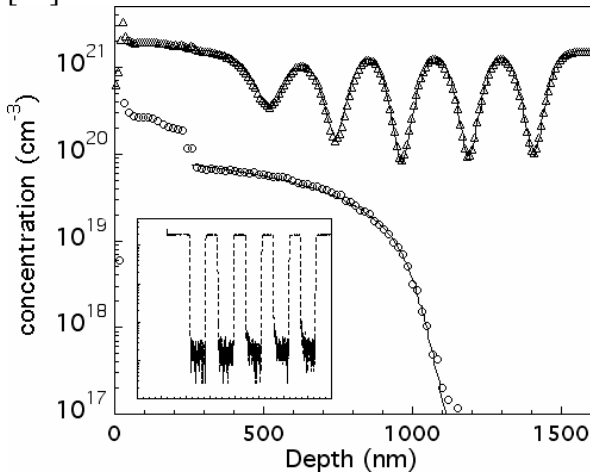


**Figure 13.** Secondary Ion Mass Spectrometry (SIMS) profile of a  $^{\text{nat}}\text{Ge}/^{74}\text{Ge}/^{70}\text{Ge}/^{\text{nat}}\text{Ge}$ -substrate structure before (top) and after annealing for 55.55 hours at a temperature of 586 °C (bottom). The self-diffusion of the  $^{70}\text{Ge}$  into the  $^{74}\text{Ge}$  layer can be modeled with a simple complementary error function to a very high level of precision. (Adapted with permission from H. D. Fuchs *et al.* [60])

In contrast, the use of Secondary Ion Mass Spectrometry (SIMS) in isotope superlattice structures provides quantitative concentration profiles of the masses of the matrix as well as the dopant atoms. In the simplest case, two layers with different isotopes of a semiconductor are grown on a substrate of natural composition. The results of annealing such a structure are illustrated in Fig. 13 for a  $^{\text{nat}}\text{Ge}/^{74}\text{Ge}/^{70}\text{Ge}/^{\text{nat}}\text{Ge}$ -substrate configuration [60]. The  $^{70}\text{Ge}$  concentration profile in the  $^{74}\text{Ge}$  layer can be fitted with a simple complementary error function (the solution to the 1-D simple Fick's law diffusion

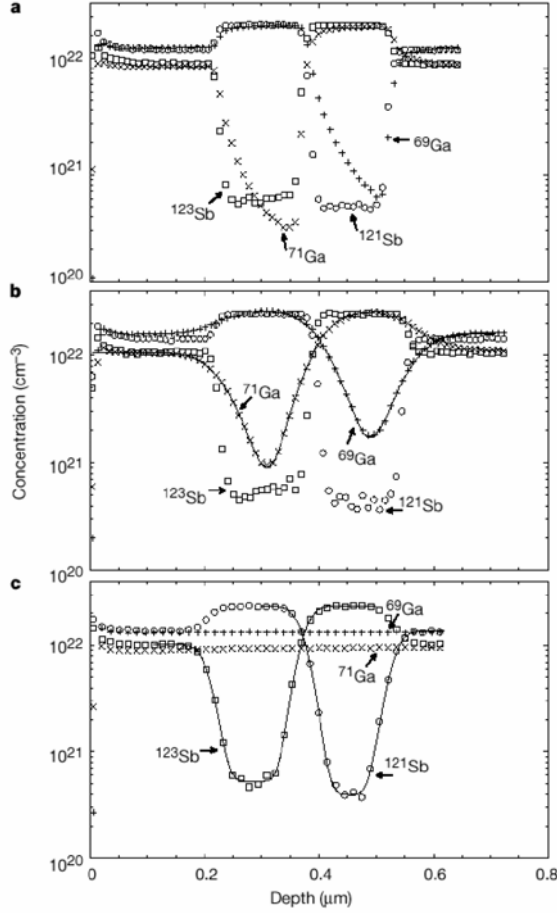
equation) over a range of four and one half orders of magnitude in concentration, yielding very precise self-diffusion data. Similar structures of silicon isotopes have been used to obtain precise measurements of the Si self-diffusion coefficient [61].

The influence of the Fermi level (and hence of specific native defects) on self- and dopant diffusion has been studied with the aid of silicon isotope multilayers capped with an amorphous layer of natural silicon. Ion-implantation into the amorphous layer was used as a source of the desired dopant and to affect Fermi level control inside the structure. Such a dopant source has been found to produce only the expected electronic effects that are due to dopant-related shifts in Fermi level position. A representative SIMS result of silicon self- and As dopant diffusion is shown in Fig. 14. The modeling of the silicon isotope and the arsenic concentration profiles yields the unambiguous result that the negatively charged interstitial is the major native defect involved in the diffusion process [62].



**Figure 14.** Depth profiles of  $^{30}\text{Si}$  (triangles) and As (circles) in an a-Si/ $(^{30}\text{Si}/^{\text{nat}}\text{Si})/^{\text{nat}}\text{Si}$  structure with 5  $^{30}\text{Si}/^{\text{nat}}\text{Si}$  periods, measured with Secondary Ion Mass Spectrometry (SIMS). Consistent modeling of both the dopant, As, and self-diffusion profiles (solid lines) shows that the singly negatively charged self-interstitial is the mediating native defect responsible for the diffusion of both species. Inset figure shows the SIMS depth profile of the as-grown isotope structure, with the same axis limits. (Adapted with permission from H. H. Silvestri, Ph.D. thesis, UC Berkeley (2004), unpublished [62]).

Isotopically controlled compound semiconductor structures offer the possibility of observing self-diffusion of each of the constituent atoms. Using this method, a very spectacular result of self-diffusion has been reported for the III-V semiconductor GaSb. Both host elements, Ga and Sb, have two isotopes occurring at comparable concentrations; a double-labeled  $^{69}\text{Ga}^{121}\text{Sb}/^{71}\text{Ga}^{123}\text{Sb}$  heterostructure was used for the study [63]. Figure 15 shows the concentration profiles of the four isotopes  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ ,  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  for the as-grown structure and after thermal annealing at different times and temperatures. The Ga host atoms diffuse by a factor of  $\sim 1000$  faster than the Sb atoms. Even after 4 days at a temperature just under the bulk melting point of GaSb and long after the labeled Ga atoms have diffused into the bulk, the Sb atoms have barely moved. The large difference can be explained with the formation of  $\text{Ga}_{\text{Sb}}$  antisites that suppress the formation of Sb vacancies required for the diffusion of this constituent. An in-depth discussion of diffusion in a number of isotopically controlled semiconductors is given in the accompanying article by Bracht, Silvestri and Haller.



**Figure 15.** Concentration–depth profiles of Ga and Sb isotopes in GaSb isotope heterostructures measured with SIMS. Data are shown for  $^{69}\text{Ga}$  (plus symbols),  $^{71}\text{Ga}$  (crosses),  $^{121}\text{Sb}$  (circles) and  $^{123}\text{Sb}$  (squares). a, Ga and Sb profiles of the as-grown  $^{69}\text{Ga}^{121}\text{Sb}/^{71}\text{Ga}^{123}\text{Sb}$  heterostructure. b,c, Profiles after annealing the isotope structure under Sb-rich conditions at 700 °C for 105 min (b) and 18 days (c). The Ga and Sb diffusion coefficients were determined by fitting the solution of Fick’s law for self-diffusion across an interface to the Ga and Sb profiles measured after annealing. Solid lines in b and c show best fits. (Adapted with permission from H. Bracht, et al., [63]).

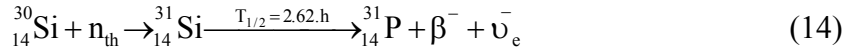
#### 4. Nuclear Spin

A number of elements found in typical semiconductors have half-odd nuclear spins  $I$  and hence magnetic moments. Examples are  $^{73}\text{Ge}$  ( $I = \frac{1}{2}$ ),  $^{29}\text{Si}$  ( $I = \frac{1}{2}$ ),  $^{31}\text{P}$  ( $I = \frac{1}{2}$ ), and both stable isotopes of Ga:  $^{69}\text{Ga}$  ( $I = \frac{1}{2}$ ) and:  $^{71}\text{Ga}$  ( $I = \frac{1}{2}$ ). The magnitude of the magnetic moment and the spin-lattice ( $T_1$ ) and transverse (decoherence,  $T_2$ ) lifetimes of non-equilibrium nuclear spin populations are measured with nuclear magnetic resonance (NMR). In high-quality single crystal material, lifetimes can be long. For example, the spin lattice relaxation time of the  $^{29}\text{Si}$  (4.67% natural abundance) nuclear spin can be as long as several hours at room temperature in high purity single crystals; decoherence times are on the order of milliseconds (ms) at cryogenic temperatures. In the case of electron spin resonance (ESR), soon after the demonstration of the effect in the late 1950’s, the effects of isotopic enrichment on the spin dynamics of donor electrons bound to  $^{31}\text{P}$  were investigated. At that time, a doubling of  $T_2$  from 0.2 to 0.5 ms was observed by removing the hyperfine spin orbit coupling interaction between the electron spin and the nuclear spin of the  $^{29}\text{Si}$ . Modern measurements on more than 99% enriched, higher purity 99%  $^{28}\text{Si}$  have demonstrated  $T_2 > 60$  ms. These and related effects are expected to be important in the development of solid state quantum computing schemes based on electron and/or nuclear spin as “qu-bits” [64-66]. An in-depth account of the state of quantum computing with isotopically controlled semiconductor structures will be given in the accompanying paper by K.M. Itoh.

### 5. Neutron absorption cross section

Among the many nuclear reactions each stable isotope can undergo, we focus here on the absorption of thermal neutrons by semiconductor forming isotopes. The major reason for this is the formation of dopant atoms as a consequence of thermal neutron capture, commonly called neutron transmutation doping (NTD).

The NTD process is typically performed in a nuclear reactor. During exposure of natural silicon to thermal neutrons all three isotopes capture neutrons with well-known capture cross sections,  $\sigma_n$ , and the following reactions occur:

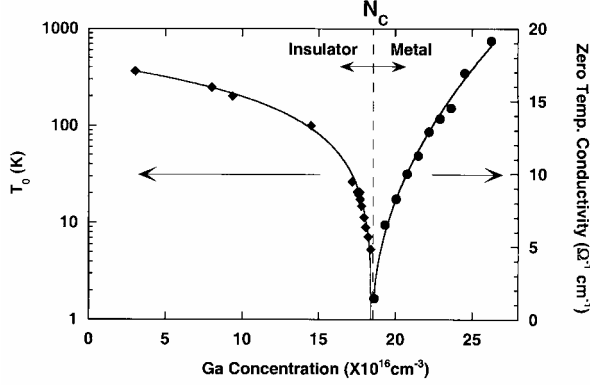


The third reaction leads to the formation of the donor P. The beta particle (electron) and the electronic anti-neutrino escape. NTD differs from other dopant technologies in that very high doping uniformity can be obtained. The unmatched doping uniformity achieved by NTD is based on three factors. First, the stable isotopes are truly randomly distributed in a semiconductor of natural composition. Second, the source of thermal neutrons is typically larger than the semiconductor crystal to be doped. This, in turn, leads to a large homogenous thermal neutron field guaranteeing identical exposure of all parts of the crystal. Third, the capture cross section for thermal neutrons is typically of the order of a few barns (1 barn =  $10^{-24}$  cm<sup>2</sup>) which means that a few centimeters of material absorb the thermal neutron flux by significantly less than 1%, maintaining the nearly uniform neutron flux throughout the depth of the sample.

The combination of isotope enrichment, ultra-purification and NTD has led to p-type <sup>70</sup>Ge crystals which are homogeneously doped with a truly random Ga acceptor distribution and a donor compensation of the order 1% [67]. A series of crystals with Ga acceptor concentrations ranging from  $3 \times 10^{16}$  cm<sup>-3</sup> to  $2.6 \times 10^{17}$  cm<sup>-3</sup> have been studied in detail on the insulator and the metal side of the transition. Figure 16 shows that the experimentally determined parameter  $T_0$  as a function of the Ga concentration on the insulator side and the zero temperature conductivity on the metal side converge precisely at the critical concentration of  $1.856 \times 10^{17}$  cm<sup>-3</sup>. The resistivity  $\rho$  on the insulator side follows the expression developed by Shklovskii and Efros [68]:

$$\rho = \rho_0 \exp (T_0/T)^v \quad .15$$

with  $\rho_0$  the prefactor,  $T_0$  a constant depending on the dopant concentration and  $v$  the critical exponent.



**Figure 16.** Conductivity parameters for NTD  $^{70}\text{Ge}$  below and above the metal-insulator transition. The left side shows the experimentally determined values of  $T_0$  (Eq. (15)) of 14 insulating samples as a function of Ga concentration ( $\blacklozenge$ ). The right side shows the zero temperature conductivity  $\sigma(0)$  obtained from ten metallic samples as a function of Ga concentration ( $\bullet$ ). The critical concentrations obtained on the insulator and on the metallic side agree to within a few percent. (Courtesy of Itoh *et al.*, [67]).

A significant amount of MIT research has been performed by the Itoh group and has been reviewed recently by Itoh *et al.* [69].

The idea of forming isotope superlattices by an epitaxial crystal growth technique and doping the various layers selectively with NTD was first proposed by this author in 1990 [70].

Isotope superlattices offer a host of new possibilities and improved processing control. The main advantage of isotope superlattices is the possibility to separate the multilayer-layer growth and the doping into two completely independent processes. The following advantages arise from this separation: i.) the growth of multilayered structures of chemically pure isotopes automatically excludes impurity auto doping, ii.) layer interdiffusion is limited to host isotope auto diffusion, the slowest diffusion process in all semiconductors, and iii.) using NTD, one can selectively dope the various layers after the growth process. The dopant concentration and species can be controlled by the proper selection of the isotope and its atomic concentration. The radiation damage caused by the fast neutrons accompanying the NTD process can be removed by the thermal annealing at temperatures which are modest compared with the epitaxial growth temperatures.

The potential of superlattices selectively doped by NTD can be best illustrated with the formation of a Ge nipi structure. The necessary donors are created by neutron transmutation of  $^{74}\text{Ge}$  into  $^{75}\text{As}$  while the acceptors are obtained from  $^{70}\text{Ge}$  by electron capture and  $^{71}\text{Ga}$  formation.  $^{72}\text{Ge}$  and  $^{73}\text{Ge}$  can be used for the intrinsic layer or to reduce the atomic concentration of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$ . This may be necessary if one wants to adjust the relative doping concentrations in the n- and p- layers. Isotopic composition and doping of a hypothetical Ge nipi structure may look like this:

$$[^{74}\text{Ge}_x\text{:As}/^{72}\text{ or }^{73}\text{Ge}_{1-x}]:[^{72}\text{ or }^{73}\text{Ge}]:[^{70}\text{Ge}_y\text{:Ga}/^{72}\text{ or }^{73}\text{Ge}_{1-y}]:[^{72}\text{ or }^{73}\text{Ge}]: \text{etc.}$$

The dopant concentrations after NTD are:

$$[\text{As}] = n_{\text{thermal}} \cdot \sigma_{74\text{Ge}} \cdot x \cdot t \cdot [^{74}\text{Ge}], \quad (16)$$

$$[\text{Ga}] = n_{\text{thermal}} \cdot \sigma_{70\text{Ge}} \cdot y \cdot t \cdot [^{70}\text{Ge}]. \quad (17)$$

Choosing the ratio of  $x$  and  $y$  to be the inverse of the ratio of the thermal neutron cross sections  $\sigma_{74\text{Ge}}$  and  $\sigma_{70\text{Ge}}$  respectively, leads to identical concentrations of As and Ga, for any neutron exposure time  $t$ .

## 6. Conclusions and outlook

An impressive amount of research with isotopically controlled semiconductors has accumulated over the past 15 years. The major effects due to the different isotope nuclear masses have been measured in many semiconductors and they are theoretically understood. The exploitation of spin properties has only started and the prospects (proposal) of an all silicon quantum computer based on the nuclear spin of  $^{29}\text{Si}$  is fascinating. Sizable quantities of isotopically enriched high quality crystalline silicon have only become available recently and have led to record resolution PL and IR absorption spectroscopy of dopants [71,72]. Many more interesting results with isotopically enriched bulk and thin film semiconductor structures can be expected, especially for II-VI alloy and compound materials, magnetic semiconductors and nano-structured materials systems. Solid state diffusion will continue to profit from isotope tracers and NTD may be used for further MIT investigations (As doped  $^{74}\text{Ge}$  is an obvious choice!). The study of NTD of enriched  $^{30}\text{Si}$  is of particular interest because only 1/30 of the neutron exposure leads to the same phosphorus concentration obtained in natural Si! The 30 times smaller fast neutron damage should result in material with larger minority carrier lifetime.

## Acknowledgments

The list of the many fruitful collaborations with isotopically enriched semiconductors is long and the number of collaborators is too large to be listed here. I owe all of them a great deal and I would like to express my sincere gratitude to each one. Much of this research became possible because of the courage of Valerii Ozhogin of the Kurchatov Institute who made the first sizable quantities of enriched  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  available for scientific collaborations. Special thanks go to Anant K. Ramdas for improving this manuscript by his detailed critical and reading.

Some of the reviewed work has been supported in part by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098, in part by U.S. NSF Grant No. DMR-0109844 and in part by a Max-Planck Society research prize. Special thanks go to Anant K. Ramdas for improving this manuscript by his critical reading.

## References

- [1] F. Soddy, "Radioactivity," Ann. Rep. Prog. Chem. **VII** (1910) 256-286; "The Radio-Elements and the Periodic Law," Nature **91** (1913) 57-58.
- [2] J. J. Thomson, "Further Experiments on Positive Rays," Phil. Mag, **24** (1912) 209-253; "Rays of Positive Electricity," Proc. Roy. Soc. A **89** (1913) 1-20.
- [3] F. W. Aston, "Mass Spectra and Isotopes," (Edward Arnold, London, 1942), pp.4-5.
- [4] T. H. Geballe, G. Hull, "Isotopic and other types of thermal resistance in Germanium," Science **250** (1958) 1194.
- [5] M. Cardona, private communication.
- [6] W. L. Hansen, E. E. Haller, "High-Purity Germanium Crystal Growing," Mat. Res. Soc. Symp. Proc **16** (1983) 1.
- [7] J. W. Ager III, J. W. Beeman, W. L. Hansen, I. D. Sharp, C. Y. Liao, E. E. Haller, M. L. W. Thewalt, and H. Riemann, "High-Purity, Isotopically Enriched Bulk Silicon," in preparation.
- [8] W. F. Banholzer, T. R. Anthony, "Isotope enrichment during diamond growth," Diamond and Related Materials **1** (1992) 1157.
- [9] W. F. Banholzer, T. R. Anthony, "Diamond properties as a function of isotopic composition," Thin Solid Films, **212** (1992) 1.
- [10] H. Kim, R. Vogelgesang, A. K. Ramdas, S. Rodriguez, M. Grimsditch, T. R. Anthony, "Electronic Raman and infrared spectra of isotopically controlled 'blue' diamonds," Phys. Rev. Lett. **79** (1997) 1706.
- [11] L. Vegard, "Die Konstitution der Mischkristalle und die Raumfüllung der Atome," Z. Phys. **5** (1921) 17.
- [12] L. Nordheim, "Zur Elektronentheorie der Metalle," Ann. Phys. **9** (1931) 607.
- [13] H. D. Fuchs, C. H. Grein, M. Cardona, W. L. Hansen, K. Itoh, E. E. Haller, "Isotopic Disorder Effects on the Phonons in Germanium," Solid State Commun. **82** (1992) 225.
- [14] H. D. Fuchs, C. H. Grein, R. I. Devlen, J. Kuhl, M. Cardona, "Anharmonic decay time, isotopic scattering time, and inhomogeneous line broadening of optical phonons in  $^{70}\text{Ge}$ ,  $^{76}\text{Ge}$ , and natural Ge crystals," Phys. Rev. B **44** (1991) 8633.
- [15] H. D. Fuchs, C. H. Grein, C. Thomson, M. Cardona, W. L. Hansen, K. Itoh, E. E. Haller, "A Comparison of the Phonon Spectra of  $^{70}\text{Ge}$  and Natural Ge Crystals: Effects of Isotopic Disorder," Phys. Rev. B **43** (1991) 4835.
- [16] P. Etchegoin, J. Weber, M. Cardona, W. L. Hansen, K. Itoh, E. E. Haller, "Isotope Effect in Ge: A Photoluminescence Study," Solid State Commun. **83** (1992) 843.
- [17] M. Cardona, C. H. Grein, H. D. Fuchs, S. Zollner, "Isotope effects on the electronic excitations and phonons in semiconductors," J. Non-Cryst. Solids **141** (1992) 257.
- [18] M. Cardona, P. Etchegoin, H. D. Fuchs, P. Molinàs-Mata, "Effect of isotopic disorder and mass on the electronic and vibronic properties of three-, two- and one-dimensional solids," J. Phys. Cond. Matter **5** (1993) A61.
- [19] P. W. Anderson, "Absence of Diffusion in Certain Random Lattices," Phys. Rev. **109** (1955) 1492.
- [20] G. Davies, E. C. Lightowers, K. Itoh, W. L. Hansen, E. E. Haller, V. Ozogin, "Isotope Dependence of the Indirect Energy Gap of Germanium," Semicond. Sci. Technol. **7** (1992) 1271.

- [21] G. Davies, J. Hartung, V. Ozhogin, K. Itoh, W. L. Hansen, E. E. Haller, "Effects of Isotope Disorder on Phonons in Germanium Determined from Bound Exciton Luminescence," *Semicond. Sci. Technol.* **8** (1993) 127.
- [22] K. C. Hass, M. A. Tamor, T. R. Anthony, W. F. Banholzer, "Effects of isotopic disorder on the phonon spectrum of diamond," *Phys. Rev. B* **44** (1991) 12046.
- [23] K. C. Hass, M. A. Tamor, T. R. Anthony, W. F. Banholzer, "Lattice dynamics and Raman spectra of isotopically mixed diamond," *Phys. Rev. B* **45** (1992) 7171.
- [24] R. M. Chrenko, "<sup>13</sup>C-doped diamond: Raman spectra," *J. Appl. Phys.* **63** (1988) 5873.
- [25] J. M. Ziman, *Electrons and Phonons*, Oxford University Press, London, 1963, p. 288.
- [26] D. T. Morelli, G. W. Smith, J. P. Heremans, T. R. Anthony, W. F. Banholzer, *Proceedings of the 2<sup>nd</sup> International Conference on New Diamond Science and Technology*, MRS, Pittsburgh, 1991, p. 869.
- [27] I. Pomeranchuk, "On the thermal conductivity of dielectrics at temperatures lower than that of Debye," *J. Phys. (Moscow)* **6** (1942) 237.
- [28] L. Wei, P. K. Kuo, R. L. Thomas, T. R. Anthony, W. F. Banholzer, "Thermal conductivity of isotopically modified single crystal diamond," *Phys. Rev. Lett.* **70** (1993) 3764.
- [29] J. Callaway, "Model for Lattice Thermal Conductivity at Low Temperatures," *Phys. Rev.* **113** (1959) 1046.
- [30] T. H. Geballe, "Cool diamonds," *Science* **250** (1990) 1194.
- [31] J. R. Olson, R. O. Pohl, J. W. Vandersande, A. Zoltan, T. R. Anthony, W. F. Banholzer, "Thermal conductivity of diamond between 170 and 1200 K and the isotope effect," *Phys. Rev. B* **47** (1993) 14850.
- [32] V. I. Ozhogin, A. V. Inyushkin, A. N. Taldenkov, A. V. Tikhomirov, G. E. Popov, E. Haller, K. Itoh, "Isotope Effect in the Thermal Conductivity of Germanium Single Crystals," *JETP Lett.* **63** (1996) 490.
- [33] M. Asen-Palmer, K. Bartowski, E. Gmelin, M. Cardona, A. P. Zhernov, V. Ozhogin, A. Inyushkin, A. Taldenkov, K. Itoh, W. L. Hansen, E. E. Haller, "Thermal Conductivity of Germanium Crystals with Different Isotopic Compositions," *Phys. Rev. B* **56** (1997) 9431.
- [34] T. Ruf, R. W. Henn, M. Asen-Palmer, E. Gmelin, M. Cardona, H. -J. Pohl, G. G. Devyatych and P. G. Sennikov, "Thermal conductivity of isotopically enriched silicon," *Solid State Commun.* **115** (2000), 243; T. Ruf, R. W. Henn, M. Asen-Palmer, E. Gmelin, M. Cardona, H. -J. Pohl, G. G. Devyatych and P. G. Sennikov, "Erratum to 'Thermal conductivity of isotopically enriched silicon' [*Solid State Communications*, 115 (2000) 243–247]," *Solid State Commun.* **127** (2003) 257.
- [35] A.V. Inyushkin, "Thermal conductivity of isotopically modified silicon: current status of research," *Inorganic Materials* **38** (2002) 427.
- [36] P. Becker, "Tracing the definition of the kilogram to the Avogadro constant using a silicon single crystal," *Metrologia* **40** (2003) 366.
- [37] R. C. Buschert, A. E. Merlin, S. Pace, S. Rodriguez, M. H. Grimsditch, "Effect of isotope concentration on the lattice parameter of Germanium perfect crystals," *Phys. Rev. B* **38** (1988) 5219.
- [38] H. Holloway, K. C. Hass, M. A. Tamor, T. R. Anthony, W. F. Banholzer, "Isotopic

- dependence of the lattice constant of diamond,” Phys. Rev. B **44** (1991) 7123; H. Holloway, K. C. Hass, M. A. Tamor, T. R. Anthony, W. F. Banholzer, “Erratum: Isotopic dependence of the lattice constant of diamond,” Phys. Rev. B **45** (1992) 6353.
- [39] A. Kazimirov, J. Zegenhagen, M. Cardona, “Isotopic mass and lattice constant: X-ray standing wave measurements,” Science **282** (1998) 930.
  - [40] E. Sozontov, L. X. Cao, A. Kazimirov, V. Kohn, M. Konuma, M. Cardona, and J. Zegenhagen, “X-Ray Standing Wave Analysis of the Effect of Isotopic Composition on the Lattice Constants of Si and Ge,” Phys. Rev. Lett. **86** (2001) 5329.
  - [41] M. Y. Hu, H. Sinn, A. Alatas, E. E. Alp, W. Sturhahn, H. C. Wille, Y. Shvid’ko, J. P. Sutter, J. Bandaru, E. E. Haller, V. I. Ozhogin, S. Rodriguez, R. Colella, E. Kartheuser, M. A. Villeret, “The Effect of Isotopic Composition on the Lattice Parameter of Germanium,” Phys. Rev. B **67** (2003) 113306.
  - [42] V. F. Agekyan, V. M. Asnin, A. M. Kryukov, I. I. Markov, N. A. Rud’, V. I. Stepanov, A. B. Churilov, “Isotope effect in germanium,” Sov. Phys. Solid State **31** (1989) 2082.
  - [43] G. Davies, “Corrigendum - Isotope dependence of the indirect energy gap of germanium,” Semicond. Sci. Technol. **9** (1994) 409.
  - [44] C. Parks, A. K. Ramdas, S. Rodriguez, K. M. Itoh and E. E. Haller, “Electronic Band Structure of Isotopically Pure Germanium: Modulated Transmission and Reflectivity Studies,” Phys. Rev. B **49** (1994) 14244.
  - [45] D. Karaiskaj, M.L.W. Thewalt, T. Ruf, M. Cardona, M. Konuma, “Photoluminescence studies of isotopically enriched silicon: isotope effects on the indirect electronic band gap energies,” Solid State Commun. **123** (2002) 87.
  - [46] S. Tsoi, H. Alawadhi, X. Lu, J. W. Ager III, C. Y. Liao, H. Riemann, E. E. Haller, S. Rodriguez and A. K. Ramdas, “Electron-Phonon Renormalization of Electronic Bandgaps of Semiconductors: Isotopically Enriched Silicon,” Phys. Rev. B. (in press).
  - [47] S. Zollner, M. Cardona, S. Gopalan, “Isotope and temperature shifts of direct and indirect band gaps in diamond-type semiconductors,” Phys. Rev. B **45** (1992) 3376.
  - [48] T. A. Meyer, D. Karaiskaj, M. L. W. Thewalt, M. Cardona, “Effect of the isotopic mass of gallium on the indirect gap of GaP,” Solid State Commun. **126** (2003) 119.
  - [49] H. D. Fuchs, P. Molinàs-Mata, M. Cardona, “Isotopic Ge superlattices: vibrational properties,” Superlatt. Microstruct. **13** (1993) 447.
  - [50] J. Spitzer, T. Ruf, M. Cardona, W. Dondl, R. Schorer, G. Abstreiter and E. E. Haller, “Raman Scattering by Optical Phonons in Isotopic  $^{70}\text{Ge}_n^{74}\text{Ge}_n$  Superlattices,” Phys. Rev. Lett. **72** (1994) 1565.
  - [51] M. Nakajima, H. Harima, K. Morita, K. M. Itoh, K. Mizoguchi, E. E. Haller, “Coherent Confined LO Phonons in  $^{70}\text{Ge}/^{74}\text{Ge}$  Isotope Superlattices Generated by Ultra-Fast Laser Pulse,” Phys. Rev. B **63** (2001), 161304(R).
  - [52] B. Jusserand and M. Cardona, Light Scattering in Solids V, edited by M. Cardona, G. Güntherodt, Springer-Verlag, Berlin, 1989, p. 49.
  - [53] P. Molinàs-Mata, M. Cardona, “Planar force-constant models and internal strain parameter of Ge and Si,” Phys. Rev. B **43** (1991) 9799.
  - [54] T. Kojima, R. Nobashi and K.M. Itoh, “Growth and Characterization of  $^{28}\text{Si}_n/^{30}\text{Si}_n$

- isotope superlattices,” *Appl. Phys. Lett.* **83** (2003) 2318.
- [55] A. S. Barker, A. J. Sievers, “Optical studies of the vibrational properties of disordered solids,” *Rev. Mod. Phys.* **47** (1975) Suppl. 2.
  - [56] E. E. Haller, “Local Vibrational Mode (LVM) Spectroscopy of Semiconductors,” *Mat. Res. Soc. Symp. Proc.* **378** (1995) 547.
  - [57] W. Kaiser, P. H. Keck, C. F. Lange, “Infrared Absorption and Oxygen Content in Silicon and Germanium,” *Phys. Rev.* **101** (1956) 1264.
  - [58] B. Pajot and P. Clauws, “High Resolution Local Mode Spectroscopy of Oxygen in Germanium,” *Proceedings 18<sup>th</sup> International Conference on the Physics of Semiconductors*, O. Engström, editor (World Scientific, Singapore, 1987), pp. 911-914.
  - [59] A. J. Mayur, M. Dean Sciacca, M. K. Udo, A. K. Ramdas, K. Itoh, J. Wolk, E. E. Haller, “Fine Structure of the Asymmetric Stretching Vibration of Dispersed Oxygen in Monoisotopic Germanium,” *Phys. Rev. B* **49** (1994) 16293.
  - [60] H. Fuchs, W. Walukiewicz, E. E. Haller, W. Dondl, R. Schorer, G. Abstreiter, A. I. Rudnev, A. V. Tikhomirov, V. I. Ozhogin, “Germanium  $^{70}\text{Ge}/^{74}\text{Ge}$  Isotope Hetero-Structures: An Approach to Self-Diffusion Studies,” *Phys. Rev. B* **51** (1995) 16817.
  - [61] H. Bracht, E. E. Haller, R. Clark-Phelps, “Silicon Self-Diffusion in Isotope Heterostructures,” *Phys. Rev. Lett.* **81** (1998) 393.
  - [62] H. H. Silvestri, “Diffusion in Silicon Isotope Heterostructures,” Ph.D. Thesis, UC Berkeley, 2004, unpublished.
  - [63] H. Bracht, S. P. Nicols, W. Walukiewicz, J. P. Silvera, F. Briones and E. E. Haller, “Large Disparity Between Gallium and Antimony Self-Diffusion in Gallium Antimonide,” *Nature* **408** (2000) 69.
  - [64] B. E. Kane, “Silicon-based quantum computation,” *Fortschritte der Physik-Progress of Physics* **48** (2000) 1023.
  - [65] K. M. Itoh, E. E. Haller, “Isotopically Engineered Semiconductors – New Media for the Investigation of Nuclear Spin Related Effects in Solids,” *Physica E* **10** (2001) 463.
  - [66] T. D. Ladd, J. R. Goldman, F. Yamaguchi, Y. Yamamoto, E. Abe, K. M. Itoh, “All-Silicon Quantum Computer,” *Phys. Rev. Lett.* **89** (2002) 011901.
  - [67] K. M. Itoh, E. E. Haller, J. W. Beeman, W. L. Hansen, J. Emes, L. A. Reichertz, E. Kreysa, T. Shutt, A. Cummings, W. Stockwell, B. Sadoulet, J. Muto, J. W. Farmer and V. I. Ozhogin, “Hopping Conduction and Metal-Insulator Transition in Isotopically Enriched Neutron Transmutation Doped  $^{70}\text{Ge}:\text{Ga}$ ,” *Phys. Rev. Lett.* **77** (1996) 4058.
  - [68] B. I. Shklovskii, A. L. Efros, *Electronic Properties of Doped Semiconductors*, Solid State Series Vol. **45**, Springer-Verlag, Berlin, 1984.
  - [69] K. M. Itoh, M. Watanabe, Y. Ootuka, E. E. Haller, T. Ohtsuki, “Complete Scaling Analysis of the Metal-Insulator Transition in  $\text{Ge}:\text{Ga}$ : Effects of Doping-Compensation and Magnetic Field,” *J. Phys. Soc. Jpn.* **73** (2004) 173.
  - [70] E. E. Haller, “Isotope Heterostructures Selectively Doped by Neutron Transmutation,” *Semicond. Sci. Technol.* **5** (1990) 319.
  - [71] D. Karaiskaj and M. L.W. Thewalt, T. Ruf, M. Cardona, M. Konuma, “‘Intrinsic’ Acceptor Ground State Splitting in Silicon: An Isotopic Effect,” *Phys. Rev. Lett.* **89** (2002) 016401.

- [72] D. Karaiskaj, J. A. H. Stotz, T. Meyer, M. L.W. Thewalt, and M. Cardona, “Impurity Absorption Spectroscopy in  $^{28}\text{Si}$ : The Importance of Inhomogeneous Isotope Broadening,” Phys. Rev. Lett. **90** (2003) 186402.