

Effect of isotope concentration on the lattice parameter of germanium perfect crystals

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The difference in lattice parameters between germanium crystals of natural isotopic composition and an isotopically enriched crystal of ⁷⁴Ge was calculated and measured by using a double-beam triple-axis x-ray spectrometer. The measured relative fractional difference was $(-6.3 \pm 0.3) \times 10^{-6}$ and $(-14.9 \pm 0.3) \times 10^{-6}$ at room and liquid-nitrogen temperatures, respectively. The corresponding calculated values are -6×10^{-6} and -12×10^{-6} . The agreement is very good, given uncertainties in the values of physical constants used for the theoretical calculations.

INTRODUCTION

The atomic volumes (i.e., the lattice parameters) of two chemically identical crystals formed by different isotopes are not equal as a result of the zero-point motion of the atoms. An atomic volume difference of 10% was observed between ³He and ⁴He (Ref. 1) while this difference reduces to 0.2% for ²⁰Ne and ²²Ne (Ref. 2). A similar, though much smaller, effect is expected for crystals of higher atomic mass. The availability of high-perfection crystals, such as silicon and germanium, with low concentrations of impurities and of other defects, and the development of highly sensitive x-ray methods for measuring lattice parameters, makes these investigations possible. The isotope effect on the lattice constant of natural germanium (mass 72.6) and of an isotopically enriched ⁷⁴Ge crystal³ was calculated. The theoretical values were compared with the experimental results obtained by using a spectrometer which was designed and built for high-precision measurements of lattice parameters of perfect single crystals.⁴

THEORY

Consider two crystals with atomic masses M and $M + \Delta M$, respectively. The equation of state of the first crystal is

$$P + \left[\frac{\partial F}{\partial V} \right]_T = 0, \tag{1}$$

where P is the pressure, V the volume, T the temperature and F is the Helmholtz free energy given by

$$F(V, T, M) = U_0(V) + \sum_i \left[\frac{1}{2} \hbar \omega_i + kT \ln(1 - e^{-\hbar \omega_i / kT}) \right], \tag{2}$$

$U_0(V)$ being the binding energy of the crystal made of atoms with infinite mass, k Boltzmann's constant, and ω_i the frequency of the i th phonon mode.

The summation extends over all such modes. The dependence of the free energy on isotopic mass M is incorporated in the frequencies ω_i . The anharmonicity of the crystals is taken into account by supposing that each phonon mode frequency ω_i depends on the volume V . A measure of this variation is given by a Grüneisen constant defined for each mode according to the standard definition $\gamma_i = -\partial(\ln \omega_i) / \partial(\ln V)$.

The dependence of ω_i on M follows from the equation of motion of the lattice and is $\omega_i \propto M^{-1/2}$. Since ΔM is small, it follows from Eq. (1) that

$$\frac{\Delta V}{V} = -\Delta M \frac{\partial^2 F / \partial V \partial M}{V \partial^2 F / \partial V^2} = -\kappa \Delta M \frac{\partial^2 F}{\partial V \partial M}, \tag{3}$$

where κ is the isothermal compressibility. Equations (3) and (2) yield

$$\frac{\Delta V}{V} = -\frac{1}{2V} \kappa \left[\frac{\Delta M}{M} \right] \sum_i \gamma_i (E_i - C_i T). \tag{4}$$

In Eq. (4) E_i and $C_i = dE_i / dT$ are the contributions arising from the i th mode to the internal energy and to the heat capacity of the crystal, respectively. The limits of zero and high temperatures are of particular interest. At zero temperature $E_i = \frac{1}{2} \hbar \omega_i$, while if $T \gg \hbar \omega_i / k$ for all ω_i , $E_i - C_i T \approx \sum_i \gamma_i (\hbar \omega_i)^2 / 6kT$ is greater than zero.

$\sum_i \gamma_i E_i$ at zero temperature is estimated as follows. Suppose the Grüneisen parameters for optical and acoustical modes to be γ_o and γ_a , respectively, and assume a Debye spectrum for the acoustic phonons and constant frequency for the optical branches of the vibrational spectrum. Then the relative change in lattice constant is given by the expression

$$\frac{\Delta a}{a} = -\frac{\kappa}{a^3} \frac{\Delta M}{M} (\gamma_o \hbar \omega_o + \frac{3}{4} \gamma_a k \Theta), \quad (5)$$

where Θ is the Debye temperature.

The measurements reported in this work were obtained using a sample of Ge containing 95.8% of ^{74}Ge (average mass 73.93). The average atomic mass of a crystal of natural Ge is 72.59. Using $\kappa = 1.29 \times 10^{-12} \text{ cm}^2/\text{dyn}$,⁵ $\gamma_o = 1.12$,⁶ $\gamma_a = 0.40$, $\Theta = 374 \text{ K}$,⁵ and $\hbar \omega_o = 5.97 \times 10^{-14} \text{ erg}$ (Ref. 7) we obtain $\Delta a/a = -12 \times 10^{-6}$. Thus the lattice constant of ^{74}Ge should be 12 parts per 10^6 smaller than that of natural germanium.

The value of γ_a was estimated in the following manner: at high temperatures ($kT > \hbar \omega_o$) the average Grüneisen constant is

$$\gamma = \frac{1}{2} \gamma_o + \frac{1}{2} \gamma_a;$$

γ_o is 1.12 from the piezospectroscopic effect on the Raman spectrum⁶ and γ at high temperature is equal to 0.76.⁸

The value of $|\Delta a/a|$ thus obtained decreases as the temperature increases. The difference in $\sum_i \gamma_i (E_i - C_i T)$ between temperature T and 0 K can be expressed as

$$\int_0^T [\gamma(T') C(T') - \gamma(T) C(T)] dT'$$

with $\gamma(T) = \sum_i \gamma_i C_i(T) / C(T)$,

where $C(T)$ is the heat capacity at temperature T . A numerical calculation of this quantity using the results of Carr, McCammon, and White⁹ leads to a 50% reduction of $|\Delta a/a|$ at room temperature, thus $\Delta a/a \approx -6 \times 10^{-6}$.

There remains to be determined the change in lattice parameter with an isotopic mixture. If a crystal is made of atoms of mass M , the secular equation for the pure crystal is a polynomial expression $\sum_{n=0}^{3N} a_n (M \omega^2)^n = 0$ in $M \omega^2$, of degree $3N$. Suppose now $\nu = cN$ atoms of mass $M + \Delta M$ are introduced at random positions into the lattice, the term in $a_{3N} \omega^{6N}$ becomes $M^{3(n-\nu)} (M + \Delta M)^{3\nu} = M^{3N} (1 + \Delta M/M)^{3cN}$. On the average, the coefficient of $a_n \omega^{2n}$ will be $M^n (1 + \Delta M/M)^{cn}$. Thus, the frequencies change, if $(\Delta M/M) \ll 1$, by $\Delta \omega = -(c \Delta M / 2M) \omega$. This result validates the use of the average isotopic mass in the previous discussion.

EXPERIMENTAL METHOD AND RESULTS

The x-ray double-beam triple-axis spectrometer used for this experiment has been described elsewhere.⁴ A schematic drawing of the spectrometer is shown in Fig. 1. This spectrometer was designed and used to measure the difference in lattice parameters between a standard silicon crystal and another silicon crystal of unknown lattice parameter located close together in a cryostat. The Si monochromator, located at the first axis, was cut and sputtered polished, with the (511) planes at an angle with the surface. When the Si crystal surface was oriented at an angle equal to about 0.2° with respect to the x-ray beam coming from the source (a standard tube with a Cu target) the characteristic $\text{Cu } K\alpha_1$ radiation was reflected by the (511) planes. Owing to the highly asymmetric Bragg

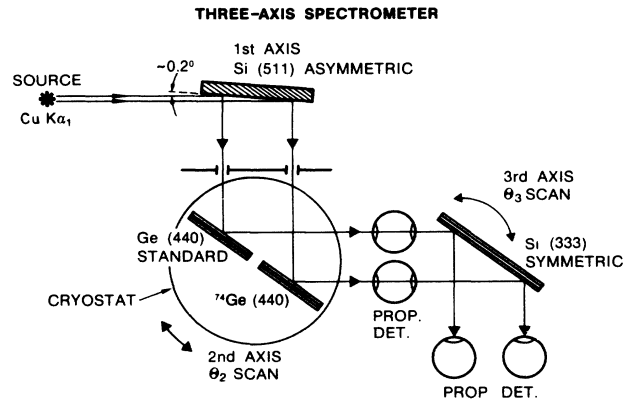


FIG. 1. Schematic drawing of the double-beam three-axis spectrometer described in Ref. 4. Four argon-filled proportional counters were used (indicated as PROP. DET. in the drawing), two to monitor the split beam, reflected by the sample and the standard, during the second axis scan and the other two to monitor the two beams reflected by the Si crystal during the 3d axis scan.

reflection, the divergence of the reflected $\text{Cu } K\alpha_1$ radiation was as small as $0.2''$.

Two Ge crystals were placed on the second axis: the standard was a highly perfect crystal of natural isotopic composition (average $M = 72.59$), the second was isotopically enriched, containing 95.8% of ^{74}Ge (average $M = 73.93$). These crystals were set to reflect (symmetrically) on the (440) planes.

The two crystals were adjusted until their reflection peaks were superimposed in a second-axis scan, as shown in Fig. 2(a). If the two Ge crystals have the same lattice

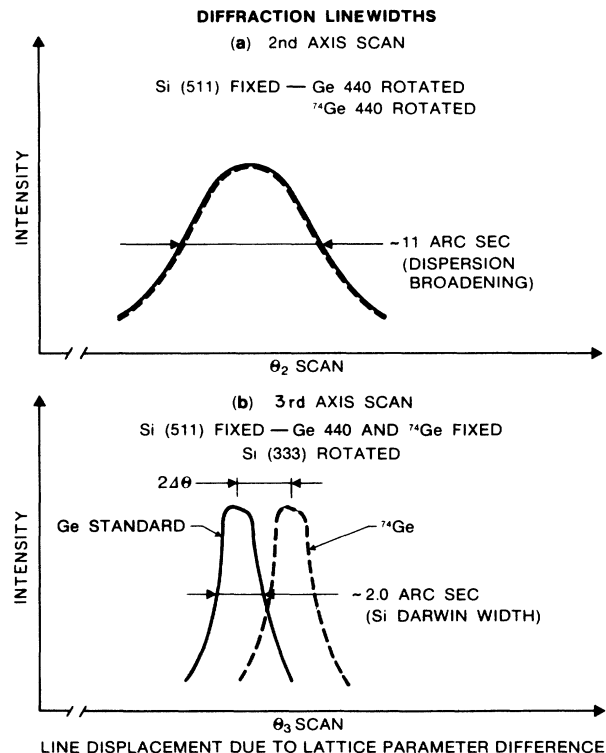


FIG. 2. Diffraction linewidths obtained with (a) the second axis scan and (b) the third axis scan.

parameter, their reflected beams are parallel and a $3d$ axis scan, with a Si crystal, cut and oriented to diffract symmetrically from the (333) planes on this third axis, would result in superimposed peaks. A lattice parameter difference Δd is indicated by a separation $\Delta\theta$ of these $3d$ axis peaks [see Fig. 2(b)]; the following simple relation gives the value of $\Delta d/d$ from a measurement of $\Delta\theta$:

$$\Delta d/d = -\cot\theta \Delta\theta. \quad (6)$$

The high sensitivity of the method comes from measuring small angular differences of narrow lines in the $(n, -n, n)$ mode. For Ge, $d_{440} = 0.99 \text{ \AA}$ instead of $d_{333} = 1.045 \text{ \AA}$ for Si. Then, with Ge crystals placed on the second axis instead of Si, there is a significant dispersion effect. Diffraction linewidths increase from $2''$ for Si to $11''$ for Ge in a second-axis scan [Fig. 2(a)]. This reduces the sensitivity from $\pm 3 \times 10^{-8}$ to $\pm 3 \times 10^{-7}$. However, the $3d$ axis scan gives the inherent $2''$ width of the Si crystal placed on this axis [Fig. 2(b)]. This effect is explained by using DuMond diagrams¹⁰ as described elsewhere.¹¹ Briefly, the two Ge crystals placed on the second axis act as mirrors and do not contribute any appreciable width to the $3d$ axis rocking curve.

Previous measurements of the same Ge sample, by a single-crystal method, showed larger linewidths and a reduction of -23×10^{-6} in lattice parameter at room temperature, instead of -6×10^{-6} expected from theory. When the surface was etched to remove the surface damage due to the ultrasonic cutting used in original fabrication, the rocking width of the second-axis scan decreased from $50''$ to $11''$ confirming that the surface was badly strained. In thermal conductivity measurements¹² on this ^{74}Ge sample, it was found a reduction in phonon scattering smaller than that indicated by theory. In light of the above-mentioned results this additional scattering may have been due to the strained surface of the crystal.

The two Ge crystals on the second axis were placed on a cryostat designed to operate between 78 and 400 K with long-term temperature and mechanical stability. A high-sensitivity system of multiple levers and elastic bearings within the cryostat was used to adjust independently the vertical and horizontal orientations of the two Ge crystals to within $0.02''$.

For low-temperature measurements extreme care is re-

TABLE I. Fractional lattice-parameter difference of ^{74}Ge with respect to natural isotopic Ge.

Calc. values	Expt. values
-12×10^{-6} (0 K)	$(-14.9 \pm 0.3) \times 10^{-6}$ (78 K)
-6×10^{-6} (300 K)	$(-6.3 \pm 0.3) \times 10^{-6}$ (300 K)

quired to avoid any temperature gradient between the sample (^{74}Ge) and the standard in the cryostat at the second axis position. The first and third crystals remain at room temperature. To avoid possible difficulties with distortions in the first and third axis crystals as well as possible temperature gradients, two natural germanium crystals with the same lattice parameter were measured before and after measurements with the standard and the isotope sample.

In addition, runs were made with the standard and isotope samples interchanged. Long runs, over several hours, with the spectrometer under computer control, helped average out small drifts in peak positions. Measurements at liquid-nitrogen temperature required an initial 10 h to reach thermal equilibrium.

The values of $\Delta d/d$, obtained from the experimental measurements of $\Delta\theta$ by using formula (6), are given in Table I. They are the result of the average of many individual runs. The error is an estimated overall error. The agreement between calculated and measured values is very good considering the uncertainties of the Grüneisen parameter values used in the theory.

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³The isotopically enriched ^{74}Ge crystal was made available to us through the courtesy of AT&T Bell Laboratories. This crystal had a dislocation density of about 10^4 lines/cm² and contained residual impurities—as measured electrically—of about 1.2×10^{13} atoms/cm³. The dislocation density and impurity content were too low to affect appreciably the observed lattice parameter variations.

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