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Effect of isotopic composition on the lattice parameter of germanium measured by x-ray backscattering

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We have measured, by x-ray backscattering, the lattice constant of four highly enriched Ge isotopes: $A = 70$, 73, 74, and 76 at temperatures ranging from 8 to 300 K. Comparing with ^{70}Ge, values of $\Delta a/a$ ranged from -10 to -46 p.p.m. A good quantitative agreement over the whole temperature range (8–300 K) was found with values calculated from a theory that takes into account the zero point motion and the anharmonicity of the lattice.

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Two crystals containing identical numbers of atoms of distinct isotopes of the same chemical element have slightly different volumes. This effect, most significant in the case of the *quantum solids* of helium at low temperature and under hydrostatic pressure, also manifests itself in other solids. For example, the volume per atom of a ^{12}C diamond exceeds that of a ^{13}C diamond by approximately four parts in ten thousand.[1] An accurate knowledge of the lattice constants of perfect crystals forms the basis for the determination of Avogadro's constant and related metrology investigations.[2] Measurements of lattice constants of isotopically pure crystals and their temperature dependence provide insight into the anharmonicity of forces between atoms in the crystal. The theoretical predictions of isotopic effects on atomic volume hinge on the combined effect of anharmonicity and zero point motion.

Thwelis[3] found a difference in the lattice constants of ^{6}LiF and ^{7}LiF of the order of two parts in ten thousand. Buschert *et al.*,[4] using an x-ray spectrometer which was designed and built for high-precision measurements of lattice parameters of perfect single crystals, determined the lattice parameter of an isotopically enriched (95.8%) sample of ^{74}Ge of high crystal perfection, and compared with natural Ge $(M = 72.6)$. They found a relative fractional difference of -6.3×10^{-6} at room temperature, and -14.9×10^{-6} at 78 K. Recent measurements on isotopically enriched thin films, using x-ray standing waves, have been reported for ^{76}Ge, compared to ^{70}Ge, and for ^{30}Si compared to natural Si.[5,6]

In these experiments the difference in the lattice constants of the film and that of a substrate of the same element with a different isotopic mixture will, in general, give rise to strains along their boundary, and thus *measurements in bulk crystals become necessary.* Recently it became possible to grow high quality, monoisotopic crystals of the diamond structure of carbon (diamond), silicon, and germanium, and measurements of their lattice parameters have become feasible.

We have studied four isotopically enriched bulk Ge crystals, with the following degrees of enrichment: 85.1% for ^{76}Ge, 96.8% for ^{74}Ge, $\simeq$96% for ^{73}Ge, 96.3% for ^{70}Ge. The samples were high quality single crystals in the form of slices cut from Czochralski-grown ingots. Typical dimensions were $5\times3\times0.5$ mm^3. The slices were mounted in a copper cold finger using Cry-Con conductive grease. Different samples could be selected by translating the low temperature cryostat up and down.

A backscattering technique was used for these measurements. Bragg diffraction from perfect crystals at 90° is quite

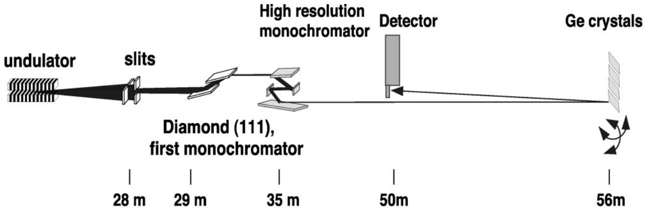

FIG. 1. The experimental layout for exact Bragg backscattering. The Ge crystals were placed in a cryostat for temperature dependent measurements. The energy tuning is performed by turning the innner channel-cut crystal of the high resolution monochromator against the outer channel-cut crystal.

special because it has some unique aspects: a very small energy bandpass and a very large angular acceptance associated with reflection widths. This was first treated by Kohra and Matsushita.[7] More recently, the application of Bragg backscattering to lattice constants measurements was discussed by Shvyd'ko *et al.*[8] The experimental arrangement of the present experiment is shown in Fig. 1. The experiment was performed at the Advanced Photon Source (Argonne) on the beam line of the SRI-CAT, sector 3, which was suitably designed for inelastic x-ray scattering experiments. The backscattered beam had a separation of 3 mm from the incident beam at a distance of 6 m from the specimen. The angle of incidence θ was therefore 89.986°. The x-ray energy was 21.56 keV, and the reflections used were the (5 1 19) and (7 7 17) reflections corresponding to the same θ angle. The reflectivity ranged from 6.3% at room temperature to 42% at 10 K. The positions of the receiving slits for the diffracted beam and the incident beam were kept fixed. The variable quantity was the x-ray energy, which was measured by making use of a high resolution monochromator[9] ($\Delta E = 1.0$ meV, corresponding to $\Delta a/a = 4.6\times 10^{-8}$).

It is known that in backscattering several reflections are excited at the same time.[10] It turns out that in conditions of perfect backscattering for the (5 1 19), ($\theta = 90°$ exactly), a total of 30 reflections are excited, including the origin (000) and the main reflection, namely, the (5119), used here for obtaining lattice constants. In principle, n-beam excitations may affect the rocking curves and introduce errors in the lattice constants. We have calculated several 30-beam diffraction profiles, under the conditions of our experiments, namely, $\theta = 89.986°$, and found that n-beam effects were negligible in all cases. Previous experience[10] shows that n-beam effects can appreciably perturb the intensity vs energy diffraction profiles only when θ is much closer to 90°.

The great virtue of the backscattering technique is that the measured Δa is relatively insensitive to θ, which is not easy to measure with great precision, nor does the accuracy with which the crystal is oriented play a critical role. It is enough to know that the Bragg diffracted beam is accepted by the receiving slit. The only quantity to be measured with great accuracy is the energy. Since the technology of high resolution monochromators is well developed at many synchrotron installations for inelastic x-ray scattering, $\Delta E/E$ can be measured very accurately with existing equipment. All measurements were done in the temperature range 300–8 K. The lattice constants were calculated from the energy of the backscattered beam, by making use of Bragg's law with an important refraction correction. In fact, a two-beam diffraction profile for the (5119) intensity vs x-ray energy, calculated from exact dynamical theory without approximations,[11] shows a peak width of 4.06 meV, at 21 550.250 eV (at 300 K). Without refraction correction the peak would have been found at a smaller energy, 45 meV below, corresponding to a substantial error in lattice constant. The lattice constants were all measured on an absolute basis, because the high resolution monochromator was calibrated against a perfect silicon crystal, whose lattice constant at room temperature is used as a standard[12] ($a = 5.43101901$ Å). Since the changes in the lattice constant due to temperature were much more important than the changes due to the isotopic composition, it was found that the best way to present and analyze the data was to consider the value, at any temperature, of $[a(M) - a(70)]/a(70)$, where $a(M)$ is the lattice parameter of ^{M}Ge and $a(70)$ is the lattice constant of ^{70}Ge. The data are presented in Fig. 2, along with results from previous experiments.[4,6] The error bars are mostly contributed by the widths of the Bragg diffraction peaks. The crystals were mounted in the sample holder with conductive grease, which was supposed to be soft at all temperatures. While all rocking curves for ^{74}Ge were extremely sharp, some broadening, impossible to control, was found for other samples. This explains the variability of the error bars visible in Fig. 2. In cases where the widths of the Bragg peaks were broad, temperature cycling helped to reduce the widths to acceptable levels, consistent with measurements at other temperatures for the same isotope. Table I shows the values of $a(70)$, for ^{70}Ge, at different temperatures, between 8 and 300 K. The data presented in Fig. 2 (triangles and bullets) are purely based on experimental observations, labeled by the nominal

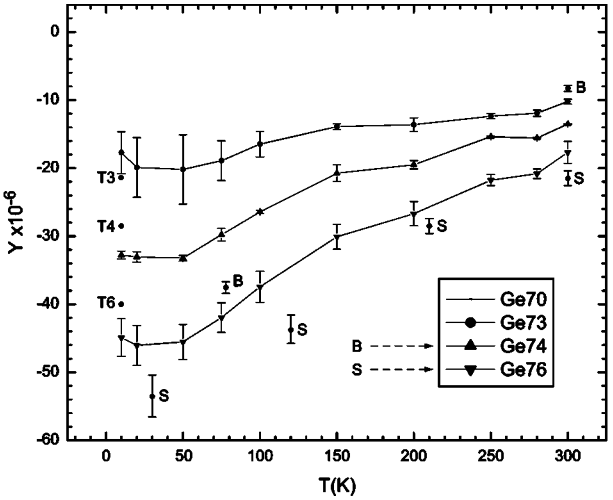

FIG. 2. Plots of $Y = [a(M) - a(70)]/a(70)$ vs temperature. $a(M)$ is the lattice parameter for ^{M}Ge, and $a(70)$ is the lattice parameter for ^{70}Ge. The points labeled B are for ^{74}Ge, and are taken from Ref. 4. The points labeled S are for ^{76}Ge, and are taken from Ref. 6. The points labeled as $T3$, $T4$, and $T6$ are from theory, and are referred to ^{73}Ge, ^{74}Ge, and ^{76}Ge, respectively. These points were calculated by making use of the theoretical value of C ($= 5.23\times 10^{-2}$ Å amu$^{1/2}$).

TABLE I. Experimental values of lattice parameters for ^{70}Ge, at different temperatures. The errors are probably less than $\pm 2 \times 10^{-6}$ Å.

T (K)	a_0 (Å)
8.0	5.652521
21.20	5.652521
38.00	5.652516
50.00	5.652518
75.00	5.652593
100.00	5.652815
150.00	5.653676
200.00	5.654924
250.00	5.656387
280.00	5.657335
298.00	5.657933
300.00	5.657983

TABLE II. Measured values of the lattice constant a at low temperatures for ^{M}Ge ($M=70$, 73, 74, and 76). The average mass M, given in amu $(=1.66053873\times 10^{-24} g)$, takes into account the level of enrichment given in the text. The masses for the pure isotopes were obtained from Ref. 13.

M	a_0 (Å)	T (K)	M (amu)
70	5.652521	8-21	70.04953
73	5.652421	8.60	72.90906
74	5.652336	10.30-10.60	73.85475
76	5.652267	9.80	75.38534

masses 70, 73, 74, and 76 of each specimen. On the other hand, the theoretical points $T3$, $T4$, and $T6$ are calculated by taking into account the effective degree of enrichment for each isotope. Scaling all the Y values to the exact isotopic masses 70, 73, 74, and 76 in Fig. 2 would shift the ^{76}Ge data to higher values by 12.6% and the ^{73}Ge and ^{74}Ge data to higher values by 5.3%, bringing our points closer to those obtained by Sozontov *et al.*[6] and the values of Buschert *et al.*,[4] the B points would yield Y values equal to -20.3 at 300 K and -48.1 at 78 K. As expected, the differences are larger at low temperature, where the quantum effects are more important. The data obtained by Sozontov *et al.*[6] are in fairly good agreement with ours, once the effective isotope composition of our samples are taken into account. In view of the experimental difficulties and considering the difference in experimental methods, we can conclude that the agreement is good.

To relate the observed results to basic principles we turn to the following considerations. If the forces between the atoms were purely harmonic the atomic volume of these crystals would be independent of the isotopic mass. In fact, even though the frequencies of the vibration under harmonic forces vary inversely as the square root of the mass of the atoms, the expectation values of the displacements from their equilibrium positions vanish. If the forces are anharmonic this is no longer the case. At the lowest temperatures, the zero point motion in combination with anharmonicity gives rise to a displacement from the equilibrium position which is larger the lighter the mass of the isotope. This occurs because the potential energy is asymmetric with respect to its minimum, being larger for negative displacements from that position than for the positive ones. Thus this phenomenon is closely related to that of thermal expansion.

To understand the dependence of the volume on the atomic mass M we consider the Helmholtz free energy $F(T,V,M)$ of an insulating solid. This quantity is the sum of $U_\infty(V)$, the energy at zero temperature if the mass M were infinite, and the well-known contribution due to the excitation of the vibrational modes of the crystal. The angular frequency of the ith mode, denoted here by ω_i, varies as $M^{-1/2}$. Thus the zero-point energy $\Sigma_i(\hbar\omega_i/2)$ is proportional to $M^{-1/2}$ It follows that the equilibrium volume V_0 and, hence, the lattice parameter at $T=0$ K behaves linearly with $M^{-1/2}$, i.e.,

$$a_0 = a_\infty + CM^{-1/2}, \tag{1}$$

where C is a constant, a_∞ is the lattice parameter if M tends to infinity, and a_0 is the lattice constant at $T=0$ K. From the measured values of a_0 (low temperature values extrapolated to $T=0$ K) displayed in Tables I and II, we find that $C = (5.93 \pm 0.0077)\times 10^{-2}$ Å amu$^{1/2}$ and $a_\infty = 5.64545 \pm 9.02 \times 10^{-4}$ Å.

A theoretical expression for C is obtained expanding the energy $U_0(V_0+\Delta V, M)$ at $T=0$ K about its equilibrium value V_0,

$$U_0(V_0+\Delta V,M) = U_0(V_0,M) + \tfrac{1}{2}(\Delta V)^2 U_0''(V_0,M) + \frac{1}{6}(\Delta V)^3 U_0'''(V_0,M) + \cdots, \tag{2}$$

where U_0'' and U_0''' are derivatives of $U_0(V,M)$ evaluated at V_0 These quantities are related to the macroscopic bulk modulus B_0 and the third order bulk modulus B_0' by $B_0 = V_0 U_0''$ and $B_0' = -(V_0^2/B_0)U_0'''$. Now the energy per primitive cell of a diamond-structure crystal is

$$H = \frac{P^{2}}{M} + 6a_0B_0u^2 - 8\sqrt{3}B_0B_0'u^3 + \cdots, \tag{3}$$

where u is the change of the nearest-neighbor distance $u = (a_0\Delta V/4\sqrt{3}V_0)$ associated with a volume change ΔV, and P is the momentum canonically conjugated with u. To first order in the cubic term in u, the expectation value of u is $\langle u\rangle = \hbar B_0'(2a_0^3B_0M)^{-1/2}$, so that

$$\begin{aligned} a_0 &= a_\infty + 2\left(\frac{2}{3}\right)^{1/2} B_0'\hbar(a_0^3MB_0)^{-1/2} \\ &= a_\infty + CM^{-1/2}. \end{aligned} \tag{4}$$

For Ge, $B_0 = 0.7653\times 10^{12}$ dyn/cm^2 and $B_0' = 4.59$,[14] yielding $C = 5.23\times 10^{-2}$ Å amu$^{1/2}$, in good agreement with the experimental value $C = 5.260\times 10^{-2}$ Å amu$^{1/2}$. The change Δa in lattice constant corresponding to an increment ΔM in isotopic mass is given by $(\Delta a/a\Delta M) = -7.5\times 10^{-6}$/amu.

At a finite temperature one must take into account the excitation of the phonon modes. The frequencies of the phonons, as a consequence of the anharmonicity of the forces between atoms, are functions of the volume. The dependence on the volume is expressed by the Grüneisen parameters $\gamma_i = -\partial(\ln \omega_i)/\partial(\ln V)$. Thus, associated with a volume change, the angular frequency of the ith vibrational mode changes by $\Delta\omega_i = -\gamma_i\omega_i\Delta V/V = -(4\sqrt{3}/a)\gamma_i\omega_i u$. To take account of these excitations to H in Eq. (3) we add the operator: $H' = -N^{-1}\Sigma_i(4\sqrt{3}/a_\infty)\gamma_i\hbar\omega_i a_i^\dagger a_i u$, where $a_i^\dagger$ and a_i are creation and destruction operators for the ith phonon mode of the crystal, and N is the number of primitive cells. This new operator has a redundant degree of freedom. Its elimination will be discussed in a future publication.

The thermal expectation value of u to first order in the deviations from harmonicity provides a satisfactory description of the temperature dependence of the lattice parameter of the four germanium isotopes used in the present experiments. We have estimated the temperature dependence of the lattice constant assuming a Debye spectrum for the acoustic vibrations, and taking the frequency of the optical phonons as constant, equal to the Raman frequency. We have further assumed average values γ_a and γ_o for the Grüneisen constants of the acoustic and optical modes from experimental data quoted in Ref. 15. Precise numerical calculations require a knowledge of the Grüneisen parameters and the vibrational frequencies at all points in the Brillouin zone of the crystal. This has been done, using density-functional perturbation theory, by Pavone and Baroni,[16] and a quantum path-integral Monte Carlo simulation was done by Herrero[17] for the case of silicon. A comparison of the expressions for the variation of the lattice constant with isotopic mass at $T = 0$ K, obtained by the thermodynamic theory, and the results of the present work lead to the identification $N^{-1}\Sigma_i\gamma_i\hbar\omega_i = B_0'\hbar(6a_\infty B_0/M)^{1/2}$.

TABLE III. Experimental and theoretical values of $Y = [a(M) - a(70)]/a(70)$, where $a(M)$ is the lattice parameter of ^{M}Ge, $a(70)$ is the lattice parameter of ^{70}Ge. Only data at the lowest temperature (8–10 K) are considered.

M	Y (expt.)$\times 10^{-6}$	Y (theor.)$\times 10^{-6}$
73	-17.7	-21.4
74	-32.7	-28.5
76	-44.9	-40.0

To summarize, a comparison of the theory based on the combination of zero point motion with anharmonicity leads to an excellent agreement between theory and experiment for the constant C in Eq. (1) at 0 K. In addition, taking into account the softening of the structure by the excitation of vibrational modes incorporating H' into Hamiltonian (3) yields a satisfactory quantitative agreement between the thermal expansion coefficient and the theoretical expression for this quantity. The degree of agreement between theory and experiment can be appreciated by comparing calculated and experimental values of $Y = [a(M) - a(70)]/a(70)$, where $a(M)$ is the lattice parameter of ^{M}Ge, and $a(70)$ is the lattice parameter for ^{70}Ge. Such comparison is presented in Table III and in Fig. 2 (see points labeled $T3$, $T4$, and $T6$). We conclude that the agreement between theory and experiment is satisfactory.

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