ISOTOPIC DISORDER-EFFECTS ON THE PHONONS IN GERMANIUM

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High-resolution (±0.02 cm^{-1}) Raman and infrared transmission (ir) measurements were used to study the effect of isotopic disorder on the vibrational properties of Ge crystals. Calculations using the coherent potential and the self-consistent Born approximations were performed and compared with the experiment. The *linewidth* of the Raman modes is predominantly determined by the anharmonic decay of the optical phonons into lower-energy phonons, with a characteristic decay time of $6.1(\pm0.1)$ ps in natural Ge. The phonon *energies* of the Raman active phonon and the transverse optical ir modes at the Brillouin zone boundary (L, K, W, X—critical point) are shifted by the isotopic disorder in the material. The frequency shifts and the line broadenings are in good agreement with the theoretical calculations.

Introduction

Many physical properties of a solid are influenced by its isotopic composition.[1] The phonon spectra in particular are very sensitive to isotopic substitution, because the *average isotopic mass* $\bar{m}$ as well as the *isotopic disorder* of the vibrating atomic cores is directly correlated with the energy and broadening of phonon modes. For a monatomic crystal the phonon frequency is proportional to $\bar{m}^{-1/2}$ in the harmonic approximation, but in a real crystal anharmonicity and defects have to be taken into account. Natural Ge is an ideal object to study isotopic disorder-effects because it is composed of five different isotopes and can be obtained in such high quality that isotopic disorder is the only relevant defect. High-quality isotopically enriched crystals are also available.

We have recently reported on Raman experiments of ^{70}Ge and ^{76}Ge and infrared transmission (ir) spectra of ^{76}Ge.[2-4] This work is complemented by the present ir and Raman spectroscopy of isotopically enriched ^{70}Ge (95.9%), ^{74}Ge (96.5%), and natural Ge. The experimental results are compared to calculations performed with the coherent potential approximation (CPA) and the self-consistent Born approximation (SCBA).

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Results

The preparation of the Ge samples and the details of the experimental setups have been described elsewhere.[3,4] The use of a 2.12-m SOPRA double monochromator allowed us to obtain high resolution (±0.02cm^{-1}). The Raman spectra of Fig. 1 exhibit some interesting features:

(i) Natural Ge does not show the individual vibrations of the various isotopes (local vibrations), as one might expect.

(ii) The spectra of natural Ge are not broadened over the whole range of vibrational frequencies corresponding to the isotopic mass distribution in the sample.

(iii) A careful analysis of the linewidths of the Raman spectra according to Ref. 2 reveals a dependence on the average isotopic mass in the material. Figure 2 shows the experimental half-width at half-maximum (Γ) as a function of the average isotopic mass after deconvolution of the instrumental broadening.

(iv) The Raman frequency of natural Ge does not follow the harmonic $\bar{m}^{-1/2}$ behavior compared with the isotopically enriched samples, but is shifted towards higher energy due to isotopic disorder in the material. This additional energy shift was measured to be 0.78cm^{-1} and 0.7cm^{-1} with respect to ^{70}Ge and ^{74}Ge, respectively.

Complementary to Raman spectroscopy we have performed ir transmission measurements with the same Ge
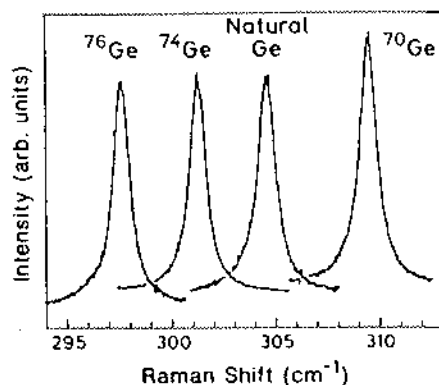
Fig. 1   First-order Raman spectra of isotopically enriched and natural Ge. The data were taken at 80 K with an excitation energy of $E_L=2.41$eV. High resolution (±0.02cm^{-1}) was achieved by measuring in tenth diffraction order of the grating (316 lines/mm) of a 2.12-m SOPRA double monochromator. The data for ^{76}Ge is taken from Ref. 3.

samples at 10, 100, and 300 K (Fig. 3). In ir spectroscopy the parity selection rule allows for the observation of only two-phonon (and higher-order) absorption in Ge.[5] Because a photon can convert into two
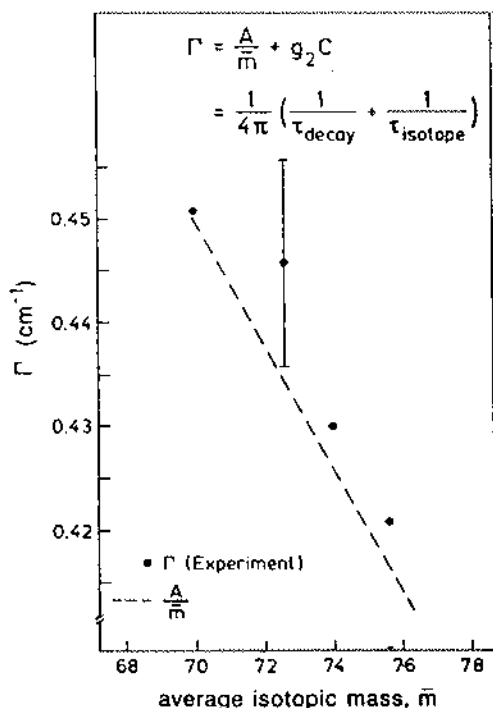

Fig. 2   Linewidths (half-width at half-maximum, Γ) of the spectra in Fig. 1. The dashed line represents the contribution due to anharmonic decay ($A/\bar{m}$) whereas the difference between this line and the experimental data points is the isotopic-disorder induced broadening (g_2C). The data for ^{76}Ge is taken from Ref. 4.
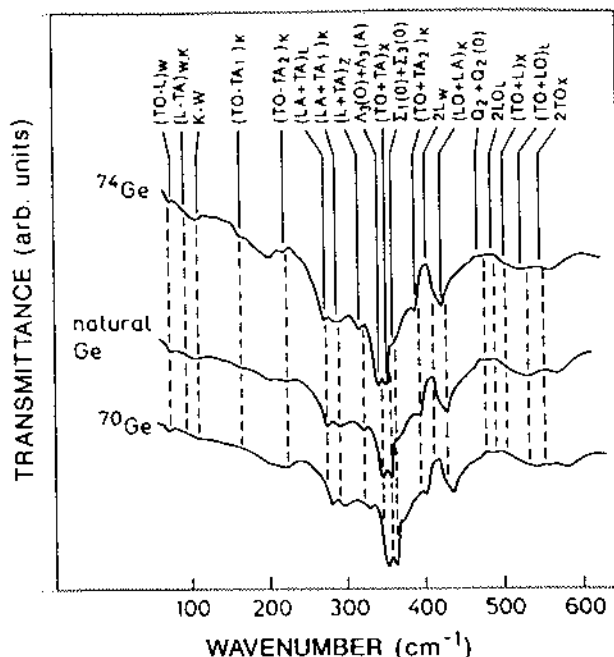

Fig. 3   Infrared transmission spectra of isotopically enriched and natural Ge at 100 K. The curves are shifted vertically for clarity.

phonons with opposite $\vec{q}$, wave vector conservation does not restrict the investigation to phonons at the Brillouin zone center ($\vec{q}=0$), as in Raman experiments. The ir absorption is therefore dominated by two-phonon processes at Brillouin zone points with high two-phonon density of states (Fig. 3). The assignment of the ir bands was done with the help of neutron scattering data for the phonon dispersion,[6] following Ref. 4.

By comparing the ir spectra of ^{70}Ge and ^{74}Ge with those of natural Ge and subtracting the trivial $\bar{m}^{-1/2}$ shift of the phonon energy, we were able to determine the isotopic-disorder-induced energy shift of the $\vec{q}\neq0$-phonons (Fig. 4). Note that this shift depends on the phonon wave vector and can be negative or positive, in good agreement with theory, discussed in the next section.

Discussion

The reason why the Raman spectrum of natural Ge in Fig. 1 does not show the local modes of the individual isotopes is that the scattering potentials for the phonons due to the mass-defects (mass fluctuations) are too small to induce bound states (i.e. Anderson localization of the phonons). A difference of the isotopic masses of at least 60% would be necessary for local modes in bulk Ge.[7] Because the actual variation of the isotope masses in Ge is only 8.6%, the phonons can not be localized at the position of the individual isotopes, and their frequencies therefore correspond to the average isotopic mass.

The lifetime of phonons, and as a result the phonon line broadening Γ, is determined by (i) the anharmonic decay of optical phonons into lower-energy phonons (Γ_{decay}) and (ii) elastic scattering from defects ($\Gamma_{isotope}$). One could expect the Raman line of natural Ge to

be strongly broadened because of a reduction of the phonon lifetime due to scattering from the mass fluctuations. As can be seen in Fig. 1 this is not the case. In second-order perturbation theory the isotopic disorder-induced line broadening $\Gamma_{isotope}(\omega)$ at a phonon frequency ω is proportional to the phonon density of states $N_d(\omega)$:

$$\Gamma_{isotope}(\omega) \propto N_d(\omega). \qquad (1)$$

Since N_d of optical phonons vanishes at the center of the Brillouin zone ($\vec{q}=0$) and Raman phonons have very small $\vec{q}$, the contribution of isotopic disorder to the linewidth according to Eq. 1 is zero. A more accurate description is given by the self-consistent Born approximation. Solving the equation

$$\Gamma_{isotope}(\omega) \propto \mathrm{Re}\,[N_d(-i\Gamma_{decay} - i\Gamma_{isotope}(\omega)] \qquad (2)$$

self-consistently yields $\Gamma_{isotope}=0.0085\mathrm{cm}^{-1}$, which is considerably less than the observed line width.[2] The conclusion is that the main contribution to the phonon linewidth arises from the anharmonic decay of the phonons.

To extract the contributions due to the anharmonic decay and isotopic disorder from the experimental data, we made use of the fact that disorder scattering is independent of $\bar{m}$ but depends on the isotopic composition, whereas the anharmonic decay time is proportional to $\bar{m}^{-1}$. This is illustrated in Fig. 2, where the dashed line represents the mass-dependent part of Γ due to anharminic decay ($A/\bar{m}$; A is a fit parameter), while the difference between this line and the experimental data points is the isotopic disorder-induced scattering contribution (g_2C; C is a fit parameter). Here the isotopic disorder is expressed in terms of m_i, the mass of isotope i with concentration x_i:

$$g_2 = \sum_i x_i \left[1 - \frac{m_i}{\bar{m}}\right]^2. \qquad (3)$$

Converting the $A/\bar{m}$-contribution to the corresponding time, we obtain the anharmonic decay time for natural Ge: $\tau_{decay} = 6.1(\pm 0.1)$ ps.[3] The experimental isotopic disorder-induced line broadening in natural Ge is $\Gamma_{isotope} = g_2C = 0.012(\pm 0.01)\mathrm{cm}^{-1}$. An analysis of the linewidths of the ir modes is not performed here because the structure in the ir transmission spectra is a mapping of the the two-phonon density of states, with some modulation related to matrix elements.[8,9] From a theoretical point of view, however, the $\vec{q} \neq 0$-phonons could have a significant isotopic disorder-broadening since N_d of optical phonons only vanishes for $\vec{q} = 0$.

The phonon energies in the various Ge samples are shifted as a result of the different average isotopic mass, but in natural Ge the transverse optical Raman and ir phonons show additional energy shifts, depending on their wavevector (see Fig. 4). This energy shift is induced by isotopic disorder and can be described in terms of the real part of the disorder-induced phonon self-energy. Results of calculations using the CPA[2,3] are shown as the solid line in Fig. 4 and agree well with the experimental data. Note that the zone center phonons observed in Raman spectroscopy display an upward shift in energy induced by isotopic disorder eventhough their line broadening is nearly unaffected.

Anharmonic effects are the main contribution to the linewidths but their influence on the phonon energy is negligible. The phonon self-energy due to anharmonicity is proportional to $\bar{m}$ and amounts to $0.1\mathrm{cm}^{-1}$, which is small compared to the observed energy shifts. It should also be mentioned that the theoretical calculations give the energy shifts as a function of phonon energy and not of wave vector, whereas the experimental data are analyzed in terms of specific points in the Brillouin zone. The results of the CPA should not differ significantly if it were possible to consider the phonon branches individually since the mass defects are localized perturbations scattering isotropically into all possible phonon states, which makes the disorder-induced self-energy approximately isotropic in $\vec{k}$-space.

Conclusion

High-resolution Raman and infrared transmission measurements of ^{70}Ge, ^{74}Ge, and natural Ge have been performed, and the experimental results were compared to calculations using the coherent potential approximation and the self-consistent Born approximation. The linewidth of the Raman modes was found to be predominantly caused by the anharmonic decay of the optical phonons into lower-energy phonons. From the linewidth the anharmonic decay time in natural Ge was determined to be 6.1 ps ± 0.1. The isotopic disorder-induced phonon self energy was found to be strongly dependent on the phonon wavevector and is only significant for the Raman active phonon and the ir active transverse optical vibrations at the zone boundary ($L, K, W, X -$ critical points). The frequency shifts as well as the line
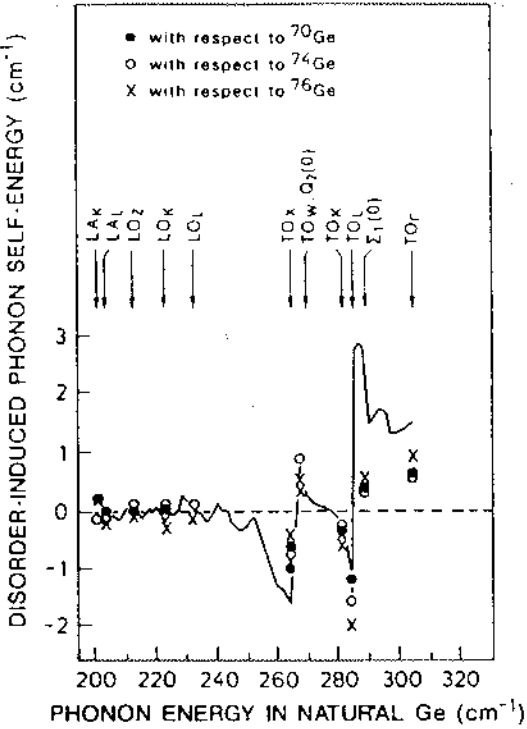

Fig. 4   Phonon self-energies of natural Ge induced by isotopic disorder. The solid line is the result of calculations using the coherent potential approximation. The experimental data were obtained by comparing the vibrational spectra of isotopically enriched and natural Ge and subtracting the trivial energy dependence on the average isotopic mass. The data for ^{76}Ge is taken from Ref. 4.

broadenings are in good agreement with the calculations.

Acknowledgement

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