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Infrared absorption in ^{76}Ge and natural Ge crystals: Effects of isotopic disorder on $\mathbf{q}\neq0$ phonons

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Self-energy effects (frequency shifts and line broadenings) due to isotopic disorder on the off-zone-center ($\mathbf{q}\neq0$) phonon spectra in natural Ge have been investigated by comparing infrared transmission spectra of an isotopically enriched germanium crystal (86% ^{76}Ge) and a natural Ge crystal at temperatures of 25, 100, and 300 K. Because selection rules only allow for the observation of two-phonon (and higher-order) absorption in Ge, $\mathbf{q}\neq0$ phonons at Brillouin-zone points with high two-phonon density of states were investigated. Besides the trivial dependence of the phonon energies on the average isotopic mass $\overline{m}$ (proportional to $\overline{m}^{-1/2}$), isotopic disorder leads to additional *energy shifts* and *line broadenings* in natural Ge. The observed self-energy effects depend strongly on the phonon energy and are only significant for the transverse optical vibrations at the zone boundary (L, K, W, and X critical points), in agreement with coherent-potential-approximation calculations.

I. INTRODUCTION

The vibrational spectra of solids, along with many other physical properties, are affected by their isotopic composition.[1] Both the average *isotopic mass* and the *isotopic disorder* (atomic-mass fluctuation) influence these spectra of crystals.[2–5] For a monatomic crystal with average atomic mass $\overline{m}$, the phonon frequency should be proportional to $\overline{m}^{-1/2}$ within the harmonic approximation. But anharmonicity and defects in the material also have to be taken into account, leading to additional frequency shifts and line broadenings for real crystals.[2–4] Isotopic disorder is the only defect of relevance in this work because of the high quality of our samples and their low free-carrier densities. Its effects on vibrational spectra can be described by a complex phonon self-energy, with its real part corresponding to a frequency shift and its imaginary part to an additional phonon linewidth.[2,3]

Ge is ideal for studying isotopic-disorder effects because natural Ge is composed of five different isotopes (see Table I), and natural as well as isotopically enriched Ge can be obtained as high-purity crystals with low carrier concentrations. To investigate isotopic-disorder effects on the phonon spectra of Ge, the first-order Raman spectra of isotopically enriched crystals have been previously compared to these of high-purity natural Ge crystals.[2,3,5] Luminescence due to indirect recombination in isotopically enriched ^{76}Ge and natural Ge have been used to study the LA, TA, and TO phonons at the L point, but the accuracy of the measurements did not allow an analysis of isotopic-disorder effects.[5] Recently, we have used first-order Raman spectra to determine isotopic self-energy effects of zone-center optical phonons in Ge.[2,3] An upward shift (1.06 ± 0.4 cm^{-1}) of the $O(\Gamma)$ phonon energy in addition to the $\overline{m}^{-1/2}$ shift was observed in the natural Ge, in good agreement with coherent-potential-approximation (CPA) and self-consistent Born-approximation (SCBA) calculations.[3] The isotopic-disorder-induced width of the zone-center optical phonons in natural Ge has been found to be two orders of magnitudes smaller than the broadening due to anharmonic decay of the optical phonons.[3]

The CPA predicts self-energy shifts of the phonons in natural Ge induced by isotopic disorder that are negligible for phonon energies below about 240 cm^{-1}, but are of the order of 1–2 cm^{-1}in the TO-phonon region.[2] First-order Raman experiments are in agreement with these calculations,[3] but only probe phonons at $\mathbf{q}\approx0$. Therefore, other techniques have to be used to measure the shifts of phonons with finite $\mathbf{q}$ vectors. At present, the accuracy of inelastic neutron-scattering measurements is not sufficient to measure the small effects due to isotopic disorder.[6]

In this work we used infrared (ir) transmission data[7–10] to compare the off-zone-center phonon frequencies in the spectra of isotopically enriched Ge (86.0% ^{76}Ge) and natural Ge. The ir absorption is determined by two-phonon summation and difference processes[11–14] because one-phonon processes are forbidden by symmetry.[10] Since a photon can convert into two phonons with opposite $\mathbf{q}$, wave-vector conservation does not restrict those processes to Γ-point phonons, as is the case for one-phonon processes. Infrared spectroscopy is a suitable tool to investigate self-energy effects of zone-boundary phonons, once

TABLE I. Isotopic composition of isotopically enriched ^{76}Ge and natural Ge used in this experiment.

Isotope	Mass[a] (a.u.)	Atomic percent Isotop. enriched ^{76}Ge	Atomic percent Natural Ge
^{70}Ge	69.9243		20.5
^{72}Ge	71.9217	0.1	27.4
^{73}Ge	72.9234	0.2	7.8
^{74}Ge	73.9219	13.7	36.5
^{76}Ge	75.9214	86.0	7.1

[a] Reference 21.

the observed structures are identified by using the well-known phonon-dispersion relations.[15] The present work complements our previous Raman measurements performed on the same materials.[3]

II. EXPERIMENT

A. Experimental details

The germanium sample of natural isotopic composition was cut as a 4.53-mm-thick (111) wafer from a high-purity *n*-type single crystal. The ^{76}Ge was isotopically enriched by Eagle Picher (Quapaw, Oklahoma), and a crystal grown by Ortec (Livermore, California) cut 3.93 mm thick in the (111) orientation. The carrier concentration of the crystals, as determined from Hall measurements, was $N_D - N_A \approx 2\times 10^{13}$ cm^{-3} for the natural Ge sample, and $N_A - N_D \approx 4\times 10^{11}$ cm^{-3} for the ^{76}Ge sample at 80 K, insufficient to affect the phonon spectra.[16] The values for the isotopic composition of the Ge samples used in this experiment, obtained by mass spectroscopy, are given in Table I.

The chemomechanically polished surface of the Ge samples was cleaned with diethyl-ether and acetone prior to taking the measurements. The far-ir transmission measurements were carried out on a Bruker IFS-113v Fourier-transform interferometer in the 50–650-cm^{-1} spectral range. A He-cooled germanium bolometer was used as the detector.

B. Experimental results

The far-infrared transmission spectra of the isotopically enriched ^{76}Ge sample is shown in Fig. 1 for $T = 25$, 100, and 300 K. As expected, the lattice absorption decreases with decreasing temperature and the phonon energies shift to higher values. The corresponding spectra of natural Ge look very similar, except that the maxima and minima of the spectra are slightly shifted towards higher energies. This shift due to the different isotopic composition of the two Ge samples can be seen in Fig. 2, where the spectrum of the isotopically enriched ^{76}Ge is compared to the spectrum of natural Ge, both taken under identical conditions at 100 K.

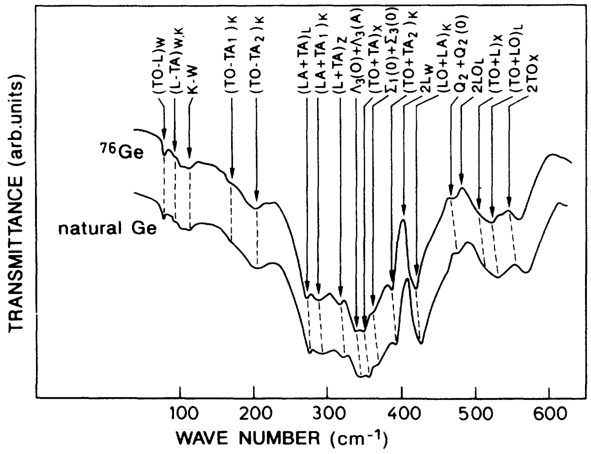

FIG. 1. Infrared transmission spectra of ^{76}Ge, at 25, 100, and 300 K.

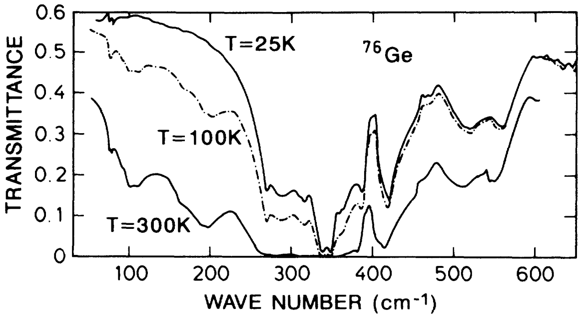

FIG. 2. Infrared transmission spectra of ^{76}Ge and Ge of natural isotopic composition at 100 K. The curve of ^{76}Ge was shifted vertically for clarity. The assignment of the transmission minima is discussed in the text.

Both samples show low-energy absorption bands below 250 cm^{-1} at room temperature that decrease in intensity for lower temperatures and are below the detection limit at 25 K. The absorption between about 250 and 400 cm^{-1}, on the other hand, was strong enough to suppress almost all the transmitted intensity in our approximately 4-mm-thick samples at room temperatures, but the lower-temperature spectra allow for an accurate analysis of the observed absorption spectra in the higher-energy region. These bands have been identified as two-phonon absorption from different critical points in the Brillouin zone where the phonon density of states exhibits pronounced maxima.[9–14] The lower-energy bands (below 250 cm^{-1}) arise from two-phonon *difference* processes[12–14] and the higher-energy bands from two-phonon *summation* processes.[9–11] The minima in the transmission spectra correspond to symmetry-allowed combinations, while the peaks arise from forbidden ones.[9]

Even though the phonon dispersion of Ge is well known from inelastic neutron-scattering data,[15] there has been some controversy about the assignment of these absorption bands[9,12,13] (see Tables II and III). The assignments we used for our analysis were done by comparing the energies of the bands with the corresponding inelastic neutron-scattering data[15] and with bond-charge-model calculations of the two-phonon density of states,[17,18] and checking the ir selection rules for the phonon symmetries under consideration.[9,10] The results of this analysis for the two-phonon difference and summation processes are listed in Tables II and III, respectively, and are indicated by arrows in Fig. 2.

As mentioned in Sec. I, the phonon frequency in our high-purity samples is affected by the *isotopic disorder* in addition to the trivial frequency shift due to the different *average isotopic mass*. We defined a virtual crystal (VC) as a perfect diamond-structure lattice with each site being occupied by a Ge atom of average isotopic mass $\overline{m}$. The frequency $\omega_{\mathrm{VC},j}$ of a branch-j phonon in the VC is shifted with respect to the corresponding phonon in ^{76}Ge according to

$$\omega_{\mathrm{VC},j} = \omega_{76,j}\sqrt{m_{76}/\overline{m}}\ , \tag{1}$$

TABLE II. Assignment of the observed ir transmission minima in natural Ge arising from absorption due to two-phonon difference processes. The phonon energies are compared to previous ir work and to inelastic neutron-scattering data (Ref. 15). All energies are given in cm^{-1}.

Observed ir transmission minima at 100 K	Inelastic neutron-scattering data at 80 K	Assignment This work	Assignment Ref. 13	Assignment Ref. 12
76.95	$(\mathrm{TO}-\mathrm{L})_W$, 72.7	$(\mathrm{TO}-L)_w$		174−99
94	$(\mathrm{L}-\mathrm{TA})_w$, 93.06	$(\mathrm{L}-\mathrm{TA})_{W,K}$		
	$(\mathrm{LA}-\mathrm{TA}_2)_K$, 94.4			
111.23	$(\mathrm{LO}-\mathrm{TA}_2)_K$, 99.74	$K-W$	$K-W$	210−109
	$(\mathrm{LO}-\mathrm{TA}_1)_K$, 136.46			
166	$(\mathrm{LA}-\mathrm{TA})_L$, 158.87	$(\mathrm{TO}-\mathrm{TA}_1)_K$	$(\mathrm{TO}-\mathrm{TA})_x$	$(\mathrm{LA}-\mathrm{TA})_L$
	$(\mathrm{TO}-\mathrm{TA}_1)_K$, 167.12			
	$(\mathrm{TO}-\mathrm{TA})_x$, 195.5			
204.92	$(\mathrm{TO}-\mathrm{TA}_2)_K$, 201.81	$(\mathrm{TO}-\mathrm{TA}_2)_K$	$(\mathrm{TO}-\mathrm{TA})_L$	$(\mathrm{TO}-\mathrm{TA})_x$
	$(\mathrm{TO}-\mathrm{TA})_L$, 226.62			

and the phonon frequency $\omega_{\mathrm{nat},j}$ in natural Ge can be written as

$$\omega_{\mathrm{nat},j}=\omega_{\mathrm{VC},j}+\Delta\omega_{\mathrm{disorder}}(\omega_{\mathrm{VC},j}) \ . \qquad (2)$$

The experimental disorder-induced self-energy shifts $\Delta\omega_{\mathrm{disorder}}(\omega_{\mathrm{VC},j})$ (see Table IV) were therefore obtained by taking the energy difference $\omega_{\mathrm{nat},j}-\omega_{76,j}$ of the corresponding bands in the ir spectra of ^{76}Ge and natural Ge, and subtracting from it the trivial $\overline{m}^{\,-1/2}$ contribution. Note that the self-energy contribution due to isotopic disorder $\Delta\omega_{\mathrm{disorder}}(\omega_{\mathrm{VC},j})$, depends on the phonon energy and can be negative or positive, i.e., the various bands in the ir transmission spectra of natural Ge may occur at higher or lower energies than expected from the difference in the average isotopic mass, depending on the point in the Brillouin zone at which the absorbing phonons are created.

It should be mentioned that anharmonic effects also contribute to the phonon energy but are negligible for our analysis. The phonon self-energy contribution due to anharmonicity is proportional to the inverse average isotopic mass $\overline{m}$ in the material[2,3] and has been calculated by Cowley to be 2.33 cm^{-1} in Ge at 100 K.[19] Due to the $\overline{m}^{\,-1}$ dependence of this self-energy contribution, it is expected to be different for the two Ge samples used in this work, but taking the calculated value of Ref. 19, the difference for the sample with $\overline{m}=72.63$ (natural Ge) and $\overline{m}=75.63$ (isotopically enriched) amounts to only 0.1 cm^{-1}, which is within the uncertainty of the measure-

TABLE III. Assignment of the observed ir transmission minima in natural Ge arising from absorption due to two-phonon summation processes. The phonon energies are compared to previous ir work and to inelastic neutron-scattering data (Ref. 15). All energies are given in cm^{-1}.

Observed ir transmission minima at 100 K	Inelastic neutron-scattering data at 80 K	Assignment This work	Assignment Ref. 9	Assignment Ref. 12
275.31	$(\mathrm{LA}+\mathrm{TA})_L$, 285.53	$(\mathrm{LA}+\mathrm{TA})_L$		174+99
290.73	$(\mathrm{LA}+\mathrm{TA}_1)_K$, 295.87	$(\mathrm{LA}+\mathrm{TA}_1)_K$		$(\mathrm{LA}+\mathrm{TA})_L$
321.76	$(\mathrm{L}+\mathrm{TA})_{W,X}$, 320.56	$(\mathrm{L}+\mathrm{TA})_Z$	$(\mathrm{L}+\mathrm{TA})_{W,X}$	210+109
344.7	$\Lambda_3(O)+\Lambda_3(A)$, 341	$\Lambda_3(O)+\Lambda_3(A)$	$(\mathrm{L}+\mathrm{TA})_{W,X}$	
	$(\mathrm{TO}+\mathrm{TA})_L$, 353.58			
355.49	$(\mathrm{TO}+\mathrm{TA})_X$, 355.57	$(\mathrm{TO}+\mathrm{TA})_X$	$(\mathrm{TO}+\mathrm{TA})_X$	
363.98	$\Sigma_1(O)+\Sigma_3(A)$, 364	$\Sigma_1(O)+\Sigma_3(A)$		
	$(\mathrm{TO}+\mathrm{TA})_W$, 392.61			
393.14	$(\mathrm{TO}+\mathrm{TA}_2)_K$, 403.28	$(\mathrm{TO}+\mathrm{TA}_2)_K$	$(\mathrm{TO}+\mathrm{TA})_W$	
409[a]	$2L_W$, 413.62[b]	$2L_W$		
427.35	$(\mathrm{LO}+\mathrm{LA})_K$, 430.3	$(\mathrm{LO}+\mathrm{LA})_K$		
	$(\mathrm{LO}+\mathrm{LA})_L$, 466.99			
472.9	$Q_2+Q_2(O)$, 474	$Q_2+Q_2(O)$		
	$(\mathrm{TO}+\mathrm{L})_W$, 485.67			
490.5[a]	$2\mathrm{LO}_L$, 490.7[b]	$2\mathrm{LO}_L$	$2\mathrm{LO}_L$	
	$(\mathrm{TO}+\mathrm{LA})_L$, 512.35[b]			
520.18	$(\mathrm{TO}+\mathrm{L})_X$, 516.02	$(\mathrm{TO}+\mathrm{L})_X$		
530.0	$(\mathrm{TO}+\mathrm{LO})_L$, 535.04	$(\mathrm{TO}+\mathrm{LO})_L$	$(\mathrm{TO}+\mathrm{LO})_L$	
552.95[a]	$2\mathrm{TO}_X$, 551.04[b]	$2\mathrm{TO}_x$	$2\mathrm{TO}_x$	

[a] Maxima in ir transmission spectra.

[b] Forbidden combination.

ment and is therefore not taken into account in the following discussion.

In addition to the *phonon-energy shift*, a comparison of the ir transmission spectra of ^{76}Ge and natural Ge also allowed the determination of the *phonon broadening* due to isotopic disorder of $\mathbf{q}\neq 0$ phonons, at least for some of the absorption bands that were strong enough to be analyzed. Unfortunately, the structure in the ir transmission spectra arising from two-phonon absorption is not only determined by the phonon frequencies and their linewidths, but is basically a mapping of the two-phonon density of states, with some modulation related to matrix elements.[11,13] This fact prevents the accurate determination of intrinsic phonon linewidths. Nevertheless, the experimental data resemble qualitatively the results obtained from CPA self-energy calculations, as will be discussed in the following section. The results for the full-width-at-half-maximum (FWHM) broadening due to isotopic disorder of the phonons in natural Ge, which are listed in Table IV, were obtained by deconvoluting the phonon lines with the method described in Ref. 2.

Thus, by comparing the far-infrared transmission spectra of isotopically enriched ^{76}Ge and natural Ge, we were able to determine experimentally the phonon self-energy shifts (described by the real part of the phonon self-energy) as well as the line broadening (described by the imaginary part of the phonon self-energy) of off-zone-center phonons induced by the isotopic disorder in Ge crystals. These results will be compared to those of CPA calculations in the following section.

III. DISCUSSION

A. Frequency shifts of $\mathbf{q}\neq 0$ phonons

The isotopic-disorder-induced shift of the phonon energy can be described theoretically in terms of the real part of the disorder-induced phonon self-energy, which has been calculated for Ge with the CPA.[2] In the CPA, the phonons in a disordered material are characterized by the dimensionless complex self-energy $\tilde{\epsilon}(\omega_{\mathrm{VC},j})$ with respect to the VC. The phonon frequency in the VC is shifted with respect to the corresponding frequency in ^{76}Ge according to Eq. (1), and the phonon self-energy shift due to isotopic disorder in natural Ge with respect to this "ideal" VC is, within the framework of the CPA, approximately given by[2]

$$\Delta\omega_{\mathrm{disorder}}(\omega_{\mathrm{VC},j}) \approx \omega_{\mathrm{VC},j}\left[\frac{1}{\sqrt{1-\mathrm{Re}[\tilde{\epsilon}(\omega_{\mathrm{VC},j})]}}-1\right] . \quad (3)$$

The phonon self-energy due to isotopic disorder has been calculated for natural Ge using the CPA,[2] and together with Eq. (3) the phonon-energy shifts can be obtained. The result for the total calculated phonon-energy difference between ^{76}Ge and natural Ge is plotted in Fig. 3, where the dashed line indicates the harmonic upward shift of the phonon energies in natural Ge with respect to

TABLE IV. Phonon energy shifts and broadenings due to isotopic disorder in natural Ge obtained by comparing the ir transmission spectra of ^{76}Ge and natural Ge (see Fig. 2). For details of the analysis see text. All energies are given in cm^{-1}.

Phonon	Observed combination	Disorder-induced energy shift $\Delta\omega_{\mathrm{disorder}}$	Disorder-induced line broadening $\Gamma_{\mathrm{disorder}}$
LA_K	$(\mathrm{LA}+\mathrm{TA}_1)_K$	+0.2	0
LA_L	$(\mathrm{LA}+\mathrm{TA})_L$	−0.2	+0.8
L_Z	$(\mathrm{L}+\mathrm{TA})_Z$	0	0
LO_K	$(\mathrm{LO}+\mathrm{LA})_K$	−0.3	0
LO_L	$2\mathrm{LO}_L$	−0.1	0.9
TO_X	$(\mathrm{TO}+\mathrm{TA})_X$	−0.5	+1.25
TO_X	$2\mathrm{TO}_X$	−0.9	
$Q_2(O)$	$Q_2+Q_2(O)$	+0.5	+2.5
TO_W	$(\mathrm{TO}\text{-}\mathrm{L})_W$	+0.5	
TO_K	$(\mathrm{TO}+\mathrm{TA}_2)_K$	−0.6	+3.5
TO_K	$(\mathrm{TO}-\mathrm{TA}_2)_K$	−0.4	
TO_K	$(\mathrm{TO}-\mathrm{TA}_1)_K$	−0.4	
TO_L	$(\mathrm{TO}+\mathrm{LO})_L$	−2.0	
$\Sigma_1(O)$	$\Sigma_1(O)+\Sigma_3(A)$	+0.5	

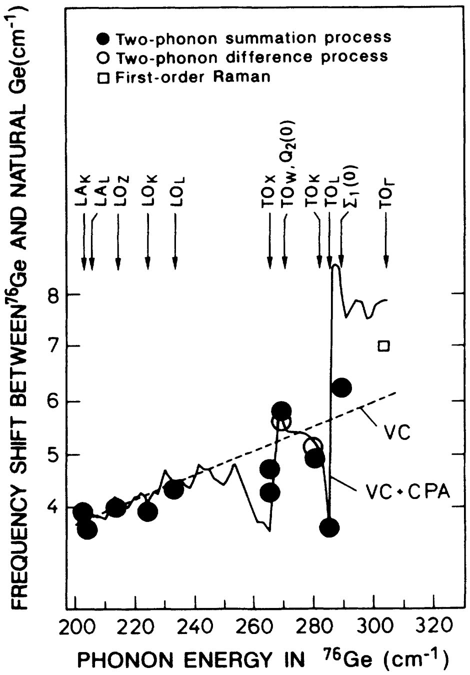

FIG. 3. Difference of the $\mathbf{q}\neq 0$ phonon energies in ^{76}Ge and natural Ge as a function of the phonon energy in ^{76}Ge. The dashed line represents the harmonic upward shift of the phonon energies in natural Ge due to the smaller average isotopic mass $\overline{m}$ [$\omega \propto \overline{m}^{-1/2}$; virtual-crystal (VC) approximation]. The solid line takes into account the additional contributions due to isotopic disorder in natural Ge, calculated with the coherent-potential approximation (CPA). The closed and open circles are the results of the comparison of the experimental ir transmission spectra of ^{76}Ge and natural Ge (two-phonon summation and difference processes, respectively). The size of the symbols gives an estimate for the accuracy of the measurements. The isotopic-disorder-induced energy shifts of the various $\mathbf{q}\neq 0$ phonons are listed in Table IV. The open square is the experimental result from first-order Raman measurements with the same samples (Ref. 3).

^{76}Ge due to the smaller average *isotopic mass* in natural Ge (VC approximation), and the solid line is the total frequency shift including both this isotopic-mass contribution and the isotopic-disorder contribution $\Delta\omega_{\text{disorder}}(\omega_{\text{VC},j})$ [see Eq. (2)].

When calculations and experimental results are compared, it has to be noted that the CPA gives the self-energy as a function of energy and not of wave vector, whereas in the experiment, the bands in the ir spectra are interpreted as arising from phonon absorption, where the phonons originate from specific critical points in the Brillouin zone with a particular wave vector. Hence, even though the ir spectra are recorded as a function of energy, the data are interpreted in terms of the wave vector of the phonons rather than their energy. Nevertheless, the results of the CPA should not differ significantly were it possible to consider the phonon branches individually. The reason for this is that the mass defects in the isotopically disorder Ge are localized perturbations (idealized as δ-function-shaped potentials at the sites of the mass defect) scattering isotropically into all possible phonon states, which makes the disorder-induced self-energy approximately independent of the phonon wave vector. Including the weak off-diagonal disorder (force-constant changes) when calculating phonon self-energies would, in principle, make it possible to obtain different self-energies for degenerate phonons in different branches.

Infrared spectra for each of the samples were taken at $T=25$, 100, and 300 K (see Fig. 1). As expected, all phonon frequencies shift to higher energies for decreasing temperatures, but no systematic change of the disorder-induced phonon self-energy could be detected. The values of $\Delta\omega_{\text{disorder}}$ listed in Table IV and plotted in Fig. 3 are, therefore, the average of the results from the different temperature runs for each sample.

The ir transmission spectra allow an accurate determination of the phonon frequencies, as discussed above, but a comparison of the absolute values of the absorption coefficient α in ^{76}Ge and natural Ge is not very meaningful. As can be seen in Figs. 1 and 2, the transmittance exceeds 47% in the low- and high-frequency range of the low-temperature spectra. With a refractive index of 4.0, which is almost independent of temperature and frequency in the range under consideration,[20] the transmitted power should not exceed 47%. Similar effects have been observed before, and they have been explained with a reduction of the beam spreading caused by refraction of non-normally-incident rays in the samples.[14] Brazis and Keilmann introduced a correction factor into Beer's law to account for this effect,[14] but such a procedure would make a comparison between ^{76}Ge and natural Ge doubtful, because this factor could vary for the different samples due to their different shapes. In addition to that, the different free-carrier densities of the samples at various temperatures may also influence the ir absorption. Hall measurements showed that due to the high compensation in the ^{76}Ge sample, the free-carrier densities were comparable at 300 K, but at 80 K the density in natural Ge was 50 times higher than in the ^{76}Ge and at 25 K even 600 times higher. A detailed study of the absolute value of the absorption coefficient as a function of isotopic disorder in the material was therefore not possible with these samples. However, the frequency shifts of $\mathbf{q}\neq 0$ phonons obtained from the transmission minima in the ir spectra could be determined with high accuracy.

B. Broadenings of $\mathbf{q}\neq 0$ phonons

The linewidths of phonons in natural Ge are determined by the lifetime of the phonons (anharmonic decay into two or more lower-energy phonons) and disorder or defect broadening (dephasing time). In our high-purity samples with the low free-carrier concentrations, the only significant defect was the isotopic disorder of the natural Ge. High-resolution first-order Raman measurements on the Ge samples used in this work revealed that the linewidth of the optical zone-center phonons in Ge is predominantly caused by the anharmonic decay of phonons.[3] Contributions to the linewidth arising from isotopic disorder were two orders of magnitudes smaller than the broadening due to the anharmonic decay for phonons at the Γ point because the phonon density of states approaches zero at the zone center.[3] For $\mathbf{q}\neq 0$ phonons, however, the phonon density of states does not vanish, and a wave-vector-dependent broadening induced by isotopic disorder is expected for phonons throughout the Brillouin zone.

The broadening due to the anharmonic decay depends on the average isotopic mass $\bar{m}$.[19] But the difference between the two Ge samples used in this experiment is too small (about 0.05 cm^{-1}) to be detected with the ir measurements,[2] and all the differences in the linewidths ob-

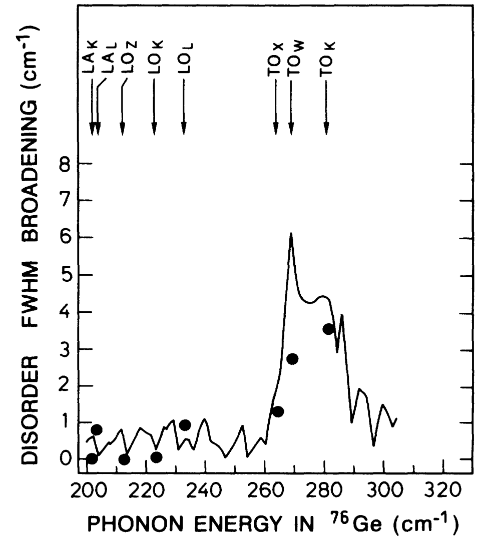

FIG. 4. Line broadening due to isotopic disorder of $\mathbf{q}\neq 0$ phonons in natural Ge, obtained theoretically with the coherent-potential approximation (solid line), and experimentally (closed circles) from the comparison of the ir transmission spectra of ^{76}Ge and natural Ge (see Fig. 2). The size of the symbols gives an estimate for the accuracy of the measurements. The isotopic-disorder-induced line broadenings of the various $\mathbf{q}\neq 0$ phonons are listed in Table IV.

served in the ir spectra were attributed to isotopic disorder in the natural Ge.

The additional isotopic-disorder-induced broadening of a phonon j in natural Ge, Γ_{disorder}, can be obtained from the imaginary part of the disorder-induced phonon self-energy:[2]

$$\Gamma_{\text{disorder}}(\omega_{\text{nat},j}) \approx -\omega_{\text{nat},j} \operatorname{Im}[\tilde{\epsilon}(\omega_{\text{nat},j})] \ . \tag{4}$$

Figure 4 shows the broadenings obtained with Eq. (4) as a function of the phonon energy, where the self-energy was calculated with the CPA, as in Fig. 3. These calculations yield considerable disorder broadening only for the transverse-optical phonons at the W, K, and L points in the Brillouin zone. Even though the results of the experimental broadenings have to be handled with some care because of the influence of the two-phonon density of states on the line shape of the ir spectra (see Sec. III A), the results agree qualitatively with the calculated predictions, as can be seen in Fig. 4.

IV. CONCLUSION

The effect of isotopic disorder on the frequencies and widths of $\mathbf{q}\neq 0$ phonons in natural Ge has been investigated by comparing the infrared (ir) transmission spectra taken from an isotopically enriched germanium crystal (86% ^{76}Ge) and a natural Ge crystal at 25, 100, and 300 K. In materials with the diamond structure such as Ge, symmetry-selection rules forbid one-phonon processes but allow two-phonon ir absorption with dominance of critical points in the Brillouin zone where the two-phonon density of states displays maxima. This makes ir transmission an excellent tool to study the behavior of phonons outside the zone center. The phonons in natural Ge have larger energy compared to ^{76}Ge due to the smaller average isotopic mass $\overline{m}$. But in addition to these trivial $\overline{m}^{\,-1/2}$ contributions to the phonon energy, an additional isotopic-disorder-induced frequency shift was observed for the phonons in natural Ge. This *energy shift* as well as the *broadening* of the phonons caused by the isotopic disorder in natural Ge is in good agreement with coherent-potential-approximation calculations. The phonon-frequency shifts as well as the additional line broadenings induced by isotopic disorder in natural Ge strongly depend on the energy of the various $\mathbf{q}\neq 0$ phonons; only the transverse-optical phonons at the L, K, W, and X point in the Brillouin zone are significantly affected by that disorder.

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