Isotope-Disorder-Induced Line Broadening of Phonons in the Raman Spectra of SiC

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The width of phonon lines in the Raman spectra of ideal isotopically pure solids is determined by inelastic scattering processes. In solids that contain a mixture of different isotopes of one atomic constituent, elastic scattering due to isotopic mass disorder opens up decay channels that result in additional line broadening. We use different polytypes of SiC with an associated number of Raman active modes in order to experimentally validate the proportionality between linewidth and phonon density of states predicted by a simple elastic scattering theory.

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The frequencies of vibrational modes in a solid depend on the interatomic force constants and the atomic masses. By changing the mass of atoms by isotopic substitution the frequencies of modes are changed in a small but characteristic way that can be monitored by Raman spectroscopy. In isotopically pure crystals the width Γ_0 of the Raman line is determined—aside from experimental resolution—by the phonon lifetime which is governed by the spontaneous anharmonic decay into phonons of lower energy [1]. In an isotopically disordered material an additional contribution Γ_{iso} to the linewidth comes from the elastic scattering of phonons via mass fluctuations and has been observed for diamond [2,3], Ge [4–7], α-Sn [8], and ZnSe [9].

Line shift and line broadening are theoretically obtained as real and imaginary parts of a complex self-energy which can be calculated in the framework of a coherent potential approximation (CPA). This theory describes, for example, frequency shift and line broadening very well in isotopically disordered diamond [3], Ge [4], and α-Sn [8]. However, the considerable computational effort that is necessary to extend this theory beyond elemental solids has prevented similar calculations for binary compounds.

A mass perturbation theory of the harmonic lattice dynamics for calculating Γ_{iso} has been developed by Tamura and applied to Ge [10], GaAs, and InSb [11]. According to this theory the mass-disorder-induced contribution Γ_{iso} is given by the elastic scattering rate τ_{iso}^{-1} which in turn depends on three factors: the relative mass variance g, the phonon density of states $\rho(\omega)$ at the frequency ω of the Raman mode, and a relevant phonon eigenvector $\mathbf{e}$:

$$\Gamma_{\text{iso}} = \tau_{\text{iso}}^{-1} = \frac{\pi}{6}\,\omega^2 g|\mathbf{e}|^4\rho(\omega)\,. \tag{1}$$

Equation (1) has the form of Fermi's golden rule in that the scattering rate τ_{iso}^{-1} of a phonon at frequency ω is, for fixed relative mass variance, directly proportional to the density of states $\rho(\omega)$ into which the phonon can scatter. Equation (1) should lend itself to a rather straightforward interpretation of experimental data. Here we utilize the unique properties of the Raman spectra of isotopically disordered $\text{Si}^{13}\text{C}_x\ {}^{12}\text{C}_{1-x}$ polytypes to confirm the linear dependence of τ_{iso}^{-1} on $\rho(\omega)$ with a slope that yields an experimental value for the phonon eigenvector $|\mathbf{e}_\text{C}|$ of the carbon sublattice.

The polytypes of silicon carbide (SiC) are an ideal testing ground for the theory of mass-disorder-induced broadening. On account of their large unit cells they yield a considerable number of Raman active zone-center phonons. Moreover, these modes and the corresponding $\rho(\omega)$ are related to each other via the backfolding concept [12]. As far as the phonon dispersion is concerned, the polytypes can be regarded as natural superlattices that originate from different stacking sequences of Si-C double layers along the [111] direction (Γ-L) of the zinc blende (3*C*) modification. Accordingly, the phonon dispersion curves of all noncubic polytypes are well approximated by folding the 3*C* dispersion along [111] into the smaller Brillouin zone of the polytypes corresponding to larger unit cells in the direction equivalent to the [111] direction. The Raman active zone-center phonon modes are thus labeled by the phonon branch (TA, LA, TO, LO) and by the fraction of their wave vector in terms of the Γ-L distance of the 3*C*-SiC Brillouin zone, e.g., TO(2/6) or TO(2/5) for a particular mode in 6*H*-SiC and 15*R*-SiC, respectively. By studying the mass-disorder-induced line broadening for SiC polytypes a stringent test of Tamura's theory is thus possible.

Crystals of 6*H*- and 15*R*-SiC polytypes were grown using a modified Lely technique (physical vapor transport method) [13] from a source material that was obtained by sintering a stoichiometric mixture of 99% pure ^{13}C and silicon powder with natural isotopic composition ($m_{\text{Si}} = 28.09$ u) in a graphite crucible. Lely platelets of 6*H*- and 15*R*-SiC with natural carbon isotopic composition ($\overline{m}_\text{C} = 12.01$ u) were used as seed crystals. Because of the incorporation of ^{12}C from the crucible the crystals contain ^{13}C with a concentration varying between 0% and

40% [14]. Raman spectra were recorded at room temperature in a Raman microprobe setup in backscattering configuration using the 514.5 nm Ar-ion-laser line. The ^{13}C concentration x was determined from the frequency shift of the TO(0) mode, which was calculated in the virtual-crystal approximation (VCA). Within the VCA each lattice site is assumed to be occupied by identical carbon atoms of average mass $\overline{m}_{\mathrm{C}} = (12 + x)$ u corresponding to the mixture of ^{12}C and ^{13}C in $^{13}\mathrm{C}_x{}^{12}\mathrm{C}_{1-x}$ [15]. For such a virtual crystal, the square of the TO(0) mode frequency is proportional to the inverse of the reduced mass μ, i.e., $\omega^2_{\mathrm{TO(0)}} \propto \mu^{-1}$ with $\mu = (1/\overline{m}_{\mathrm{C}} + 1/m_{\mathrm{Si}})^{-1}$, where m_{Si} is the average mass of the isotopic mixture of natural Si.

Raman spectra of folded transverse optic (TO) modes of natural and isotopically enriched 6*H*-SiC and 15*R*-SiC with $x = 0.26$ are shown in Figs. 1(a) and 1(b), respectively. Altogether there exists six modes which are labeled as outlined above. For the isotopically enriched samples all modes shift to lower frequencies. In addition, a broad structure around 750 cm^{-1} appears in the spectra of both ^{13}C enriched polytypes. We assign this structure to isotopic disorder-induced Raman scattering by TO phonons with $\mathbf{q} \neq \mathbf{0}$ (band modes) as reported for germanium [6]. This broad structure roughly coincides with the phonon density of states. Most important in the present context, the TO modes of 6*H*-SiC and 15*R*-SiC broaden to different degrees in the isotopically enriched samples. We assume that additional scattering due to defects and impurities is negligible in our samples, since the crystalline quality of our samples is identical to that of a standard grown crystal with a low defect density. Thus, the additional contribution to the linewidth comes from the elastic scattering of phonons. According to Eq. (1) differences in the phonon density of states at the mode frequencies account for the different broadening of the peaks of the spectra of Fig. 1 provided that $g_{\mathrm{C}}(x)$ and $|\mathbf{e}_{\mathrm{C}}|$ are constant for all TO modes in both polytypes. For fixed x, the relative mass variance $g_{\mathrm{C}}(x)$ is constant and the absolute values of the eigenvectors for all TO modes do not vary by more than 2% according to *ab initio* calculations [16].

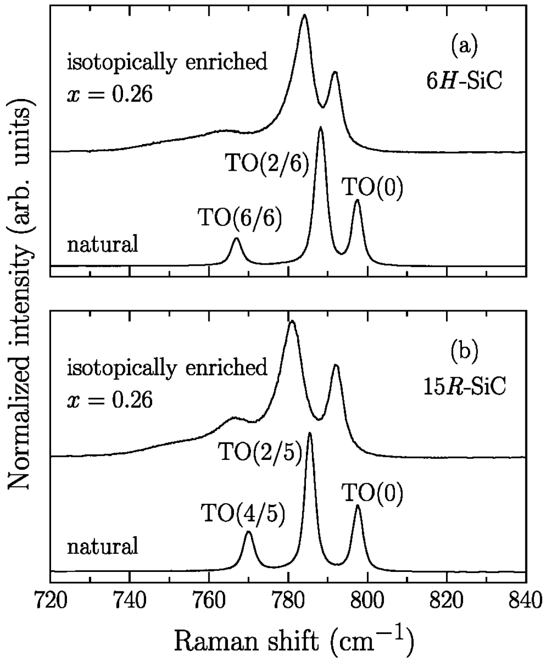

FIG. 1. Raman spectra of the TO modes of natural and isotopically mixed 6*H*-Si$^{13}\mathrm{C}_x{}^{12}\mathrm{C}_{1-x}$ (a) and 15*R*-Si$^{13}\mathrm{C}_x{}^{12}\mathrm{C}_{1-x}$ (b). The spectra are normalized to the amplitude of the TO(2/6) and the TO(2/5) mode, respectively.

The contribution Γ_{iso} to the linewidths has been obtained by fitting the spectra with Voigt profiles in which the Gaussian width was fixed to the experimental resolution (1.8 cm^{-1}). In order to account for the contribution of line broadening due to anharmonic decay and Si isotopic disorder, respectively, the linewidth Γ_0 obtained for samples with natural composition has been subtracted. In Fig. 2 the values for Γ_{iso} obtained in this way divided by the square of the phonon frequency are plotted versus the phonon density of states $\rho(\omega)$ of 6*H*-SiC as calculated in Ref. [17]. Because of the lack of theoretical data for the phonon density of states of 15*R*-SiC we have used the phonon density of states of 6*H*-SiC for both polytypes. In fact, if one compares $\rho(\omega)$ for 4*H*- and 6*H*-SiC (see Ref. [17]) one finds differences of no more than 10%. If anything, the difference in $\rho(\omega)$ for 15*R*-SiC is expected to be lower because the hexagonality, which is defined as the percentage of hexagonal stacking in the respective polytype, of 15*R*-SiC (40%) lies between that of 4*H*- (50%) and 6*H*-SiC (33%). The proportionality between Γ_{iso} and $\rho(\omega)$ is clearly maintained over 1 order of magnitude in both quantities as demonstrated by the linear regression to the experimental data indicated by the solid line. Hence, our data verify the role of the phonon density of states

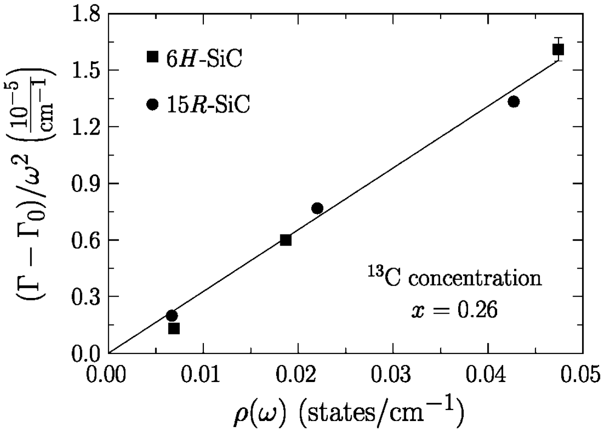

FIG. 2. Linewidths divided by the square of the phonon frequency of the characteristic modes of different SiC polytypes plotted as a function of the phonon density of states at the corresponding mode frequencies. The solid line is a linear regression to the experimental data.

for the mass-disorder-induced contribution to the phonon linewidth as expressed by Eq. (1). From the slope of the linear regression the absolute value of the phonon eigenvector $|\mathbf{e}_C|$ of the carbon sublattice can be calculated using $g_C(x = 0.26) = 1.28 \times 10^{-3}$ as obtained from Eq. (2) given below. We obtain $|\mathbf{e}_C| = 0.83 \pm 0.01$, a value in good agreement with the experimental results of Ref. [18] determined from the shift of Raman lines in SiC polytypes grown from natural silicon ($\approx ^{28}$Si) and ^{30}Si, respectively and with *ab initio* calculations which yield $|\mathbf{e}_C| = 0.84$ at the Γ point and $|\mathbf{e}_C| = 0.86$ at the L point [16].

In the following, we address the x dependence of Γ_{iso}. The linewidths Γ_{iso} of the three Raman active TO modes in 6*H*-SiC are given in Fig. 3 for ^{13}C concentrations that cover $0 < x < 0.4$. The solid lines are calculated after Tamura's theory using Eq. (1) with an absolute value of the eigenvector of $|\mathbf{e}_C| = 0.84$ and the phonon density of states from Ref. [17]. According to Eq. (1) the contribution of mass disorder to $\Gamma_{\text{iso}}(x)$ is determined by the relative mass variance $g_C(x)$ of the carbon sublattice:

$$\begin{aligned} g_C(x) &= \sum_i c_i \left(\frac{m_i - \overline{m}}{\overline{m}} \right)^2 \\ &= x \left(\frac{1 - x}{12 + x} \right)^2 + (1 - x) \left(\frac{x}{12 + x} \right)^2, \qquad (2) \end{aligned}$$

where c_i is the relative fraction of the isotope with mass m_i. $g_C(x)$ is essentially a symmetric function of x with a maximum at $x = 0.5$. The comparison between theory and experimental data in Fig. 3 indicates that Tamura's theory gives a rather poor description of Γ_{iso} as a function of x. In particular, there is no indication that the experimental linewidth reaches a maximum for $x = 0.5$. Instead, the experimental data appear to follow the asymmetric x dependence as was measured in diamond [3] and predicted by the CPA theory of Taylor [19]. In the CPA theory the linewidth is obtained as the imaginary part of the complex self-energy as stated above. This self-energy depends, in general, asymmetrically on the mass disorder: small additions of an isotope with smaller mass to a host with a larger mass isotope have a stronger effect on Γ_{iso} than the opposite case [3]. The experimental data of Figs. 2 and 3 can be recast into the simple form of Tamura's expression for Γ_{iso} by defining a modified mass-disorder function $h_C(x)$ as indicated by the dotted lines in Fig. 3. In lieu of any realistic disorder function for SiC we took the calculated asymmetric CPA curve of $\Gamma_{\text{iso}}(x)$ for diamond from Ref. [3] as a starting point. This function was first multiplied with a constant factor chosen such that an optimal fit to the linewidths of the TO(2/6) mode over the measured concentration range was achieved. In the spirit of Tamura's theory, the resulting curve represents $\Gamma_{\text{iso}}(\text{TO}(2/6)) \propto \omega^2_{\text{TO}(2/6)} h_C(x) \rho(\omega_{\text{TO}(2/6)})$. Thus, dividing $\Gamma_{\text{iso}}(\text{TO}(2/6))$ by $\omega^2_{\text{TO}(2/6)} \rho(\omega_{\text{TO}(2/6)})$ we obtain a modified mass-disorder function $h_C(x)$. The linewidth functions for the other two modes [TO(6/6) and TO(0)] were consequently derived by simply multiplying $h_C(x)$ with the factor $\omega^2 \rho(\omega)$, where ω and $\rho(\omega)$ are the frequencies and the densities of states for the other two phonon modes, respectively. To the extent that the data follow the Γ_{iso} curves constructed in this way the linear relationship

$$\Gamma_{\text{iso}} \propto \omega^2 h_C(x) \rho(\omega) \qquad (3)$$

is confirmed over the whole concentration range measured with a common, asymmetrical disorder function $h_C(x)$. We note in passing that $g_C(x)$ and $h_C(x)$ coincide at $x = 0.26$. Hence, the value of $|\mathbf{e}_C|$ derived above is not affected by substituting $g_C(x)$ with $h_C(x)$.

In summary, we have shown that the linewidth of a phonon in isotopically disordered SiC does not depend only on the degree of mass disorder but also on the frequency of the phonons. The latter point can be understood in the framework of a simple scattering theory as formulated by Tamura. In this theory, the elastic scattering by mass fluctuations contributes to the linewidth and the scattering rate is proportional to the density of final phonon states. We could confirm this proportionality between linewidth and phonon density of states. The polytypes of SiC are an ideal testing ground for that aspect of Tamura's theory, since the accessible Raman active modes cover a larger range of phonon density of states than is usually found in other materials. A further aspect of Tamura's

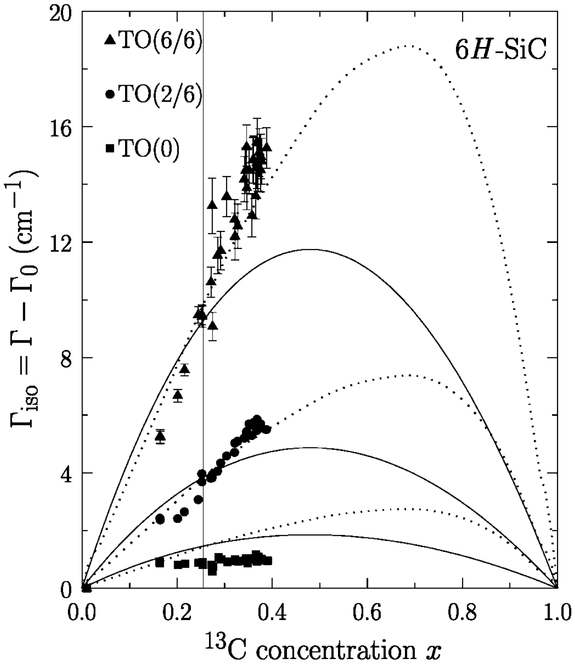

FIG. 3. Mass-disorder-induced contribution to the phonon linewidth as a function of ^{13}C concentration for the three TO modes observable in 6*H*-SiC. The solid lines are obtained from Eq. (1), whereas the dotted lines are scaled CPA diamond results from Ref. [3] as explained in the text. The vertical line marks $x = 0.26$ used for Fig. 2.

theory, namely, the linear relationship between linewidth and relative mass variance, is not fulfilled in our experiments; a more sophisticated theory is clearly needed to describe this dependence.

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