Disorder-induced phonon self-energy of semiconductors
with binary isotopic composition

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(May 29, 2001)

Abstract

Self-energy effects of Raman phonons in isotopically disordered semiconductors are deduced by perturbation theory and compared to experimental data. In contrast to the acoustic frequency region, higher-order terms contribute significantly to the self-energy at optical phonon frequencies. The asymmetric dependence of the self-energy of a binary isotope system $m_1-xM_x$ on the concentration of the heavier isotope mass $x$ can be explained by taking into account second- and third-order perturbation terms. For elemental semiconductors, the maximum of the self-energy occurs at concentrations with $0.5 < x < 0.7$, depending on the strength of the third-order term. Reasonable approximations are imposed that allow us to derive explicit expressions for the ratio of successive perturbation terms of the real and the imaginary part of the self-energy. This basic theoretical approach is compatible with Raman spectroscopic results on diamond and silicon, with calculations based on the coherent potential approximation, and with theoretical results obtained using \textit{ab initio} electronic theory. The extension of the formalism to binary compounds, by taking into account the eigenvectors at the individual sublattices, is straightforward. In this manner, we interpret recent experimental results on the disorder-induced broadening of the TO (folded) modes of SiC with a $^{13}$C-enriched carbon sublattice.
I. INTRODUCTION

The mass-fluctuations (of a single element) induced by isotopic disorder can be described by the weighted \( n \)-th moments of the relative mass differences with respect to the average mass \( \overline{m} = \sum_i c_i m_i \) of the virtual crystal defined as

\[
g_n = \sum_i c_i \left( \frac{m - m_i}{\overline{m}} \right)^n,
\]

where \( i \) runs over the different isotopes with masses \( m_i \) and concentrations \( c_i \). According to Eq. (1), \( g_1 = 0 \) within the virtual crystal approximation (VCA), i.e. if \( \overline{m} \) is used as the atomic mass.

For a two-isotope system \( m_{1-x}M_x \) with \( M \) being the heavy mass and \( x = c_M \), Eq. (1) reads

\[
g_n(x) = (1 - x) \left( \frac{\overline{m} - m}{m} \right)^n + x \left( \frac{\overline{m} - M}{m} \right)^n.
\]

Equation (2) can be rewritten as follows, using \( \Delta m = M - m \)

\[
g_n(x) = \left( \frac{m}{\Delta m + x} \right)^n \times x(1 - x) \left( x^{n-1} + (-1)^n (1 - x)^{n-1} \right).
\]

For the elements under consideration here, the first factor of Eq. (3) leads to a weak \( x \)-dependence that slightly breaks the odd or even symmetry of \( g_n(x) \) with respect to \( x = 0.5 \). Neglecting this dependence (i.e. for \( x \ll m/\Delta m \)) we can write

\[
\left( \frac{m}{\Delta m + x} \right)^{-n} \simeq (\Delta m/m)^n.
\]

The lowest-order moments of \( g_n \) thus read (see Fig. 1):

\[
\begin{align*}
g_2 &\simeq (\Delta m/m)^2 x (1 - x) & (5a) \\
g_3 &\simeq (\Delta m/m)^3 x (1 - x) (2x - 1) & (5b) \\
g_4 &\simeq (\Delta m/m)^4 x (1 - x) (1 - 3x(1 - x)) & (5c) \\
g_5 &\simeq (\Delta m/m)^5 x (1 - x) (2x - 1) (1 - 2x(1 - x)) & (5d)
\end{align*}
\]
Hence, the contribution to the self-energy is even (odd) with respect to \( x = 0.5 \) for even (odd) values of \( n \). In particular, \( g_2 \) represents a parabola with the maximum at \( x = 0.5 \), while \( g_3 \) is odd with respect to \( x = 0.5 \), i.e. \( g_3(0.5) = 0 \).

The disorder-induced phonon self-energy is defined as

\[
\Pi_{\text{dis}}(\omega) = \Delta_{\text{dis}}(\omega) - i \Gamma_{\text{dis}}(\omega)/2,
\]

where \( \Delta_{\text{dis}} \) denotes the disorder-induced shift, and \( \Gamma_{\text{dis}} \) the disorder-induced broadening corresponding to the full width at half maximum (FWHM). The self-energy can be decomposed into individual contributions that are proportional to the various moments of \( g_n \) with \( n = 2, 3, 4, \ldots \)

\[
\Pi_{\text{dis}}(\omega) = A_2 x (1 - x) + A_3 x (1 - x) (2x - 1) + A_4 x (1 - x) (1 - 3x(1 - x)) + \ldots
\]

In order to estimate the contributions of higher-order perturbation terms, Eq. (7) is fitted to experimental and theoretical data of group-IV semiconductors (see Sec. III for diamond, Si, Ge, \( \alpha \)-Sn and Sec. IV for SiC). In Eq. (7) the fit parameters \( A_i = A_i,\Delta + iA_i,\Gamma \) are complex numbers; in practice, we perform individual fits to \( \Delta_{\text{dis}} \) and \( \Gamma_{\text{dis}} \), thus obtaining the two sets of fit parameters \( A_i,\Delta \) and \( A_i,\Gamma \). In the following section we show that, in general, the asymmetries with respect to \( x = 0.5 \) are not identical for \( \Delta_{\text{dis}} \) and \( \Gamma_{\text{dis}} \).

For a characterization of the contribution of the third-order perturbation term with respect to the second-order term, we define the ratio

\[
\frac{r_s}{A_2,s} \quad (8)
\]

with \( s = \Delta, \Gamma \). For the maximum self-energy \( x_{\text{max},s} \) we find

\[
x_{\text{max},s} = \frac{1}{2} \pm \frac{1}{6} \left( \sqrt{3 + \frac{1}{r^2_s}} - \frac{1}{|r_s|} \right),
\]

where the positive (negative) sign corresponds to \( r > 0 \) (\( r < 0 \)).
II. PERTURBATION THEORY

In this section, explicit expressions for the disorder-induced self-energies of a two-isotope elemental crystal are derived by perturbation theory. For the calculations we use $\Pi_{\text{dis}} = \Pi = \Delta + i\Gamma$ with $\Delta = \Delta_2 + \Delta_3 + \ldots = \Delta_{\text{dis}}$ and $\Gamma = \Gamma_2 + \Gamma_3 + \ldots = -\Gamma_{\text{dis}}/2$. The zero-temperature phonon propagator $D(\omega, \omega_i)$ for an isotopically pure crystal is the sum of the propagators $D_+(\omega, \omega_i)$ and $D_-(\omega, \omega_i)$ for positive and negative frequencies, respectively,

$$D = D_+(\omega, \omega_i) + D_-(\omega, \omega_i)$$

$$= \frac{1}{\omega - \omega_i - i\gamma} + \frac{1}{-\omega - \omega_i - i\gamma}$$

$$= \frac{2\omega_i}{\omega^2 - \omega_i^2 - i2\omega_i\gamma},$$

where $\gamma \to 0$ if anharmonicity is neglected. $\omega_i$ denotes the absolute value of the phonon frequency. Since we are interested in the self-energy of the Raman mode, to which the largest contributions stem from close-lying optic phonon states, the propagator $D_-$ can be neglected because $|\text{Re}\{D_\pm\}| \ll |\text{Re}\{D_+\}|$ and $|\text{Im}\{D_\pm\}| \ll |\text{Im}\{D_+\}|$. In the following we thus set $D = D_+$ with

$$D_+(\omega, \omega_i) = \frac{1}{\omega - \omega_i - i\gamma}$$

$$= \frac{\omega - \omega_i}{(\omega - \omega_i)^2 + \gamma^2} + i\frac{\gamma}{(\omega - \omega_i)^2 + \gamma^2}$$

$$= P_i(\omega) + iL_i(\omega).$$

$D_+(\omega, \omega_i)$ consists of $P_i(\omega)$, with a pole at $\omega_i$, and a Lorentzian $L_i(\omega)$. For the complex self-energy of the Raman phonon of a semiconductor with diamond structure, $n$th-order perturbation theory yields

$$\Pi_n(\omega, x) = \frac{g_n(x)}{2^n} \omega \left(\frac{1}{6N_c}\right)^{n-1}$$

$$\times \sum_{i,j,\ldots,n} \omega_i D_i \cdot \omega_j D_j \cdots \omega_n D_n$$

$$= \frac{g_n(x)}{2^n} \omega \left(\frac{1}{6N_c} \sum_i \omega_i D_i\right)^{n-1}. $$
with $D_n = D(\omega, \omega_n)$ and $N_c$ the number of unit cells. The second-order term ($n = 2$)

$$
\Pi_2(\omega, x) = \frac{g_2(x)}{4} \omega \left( \frac{1}{6N_c} \sum_i \omega_i (P_i + iL_i) \right)
$$

contains the real part

$$
\Delta_2(\omega, x) = \frac{g_2(x)}{4} \omega \left( \frac{1}{6N_c} \sum_i \omega_i \frac{\omega - \omega_i}{(\omega - \omega_i)^2 + \gamma^2} \right)
$$

and the imaginary part

$$
\Gamma_2(\omega, x) = \frac{g_2(x)}{4} \omega \left( \frac{1}{6N_c} \sum_i \omega_i \frac{\gamma}{(\omega - \omega_i)^2 + \gamma^2} \right).
$$

For $\gamma \to 0$, Eq. (13c) simplifies to a sum over $\delta$-functions, which represents the one-phonon density of states (DOS) $\rho_1(\omega)$,

$$
-\Gamma_2(\omega_0) = \frac{\pi}{24} g_2(x) \omega^2 \rho_1(\omega).
$$

If $\Delta_2(\omega)$ and $\Gamma_2(\omega)$ do not depend strongly on $\omega$ near the Raman phonon at $\omega_0$, then $-\Gamma_2(\omega_0)$ of Eq. (13d) represents the half width at half maximum (HWHM) of the disorder-induced broadening.

The third-order self-energy can be written as

$$
\Pi_3(\omega, x) = \frac{g_3(x)}{8} \omega \left( \frac{1}{6N_c} \right)^2 \times \sum_{i,j} \omega_i \omega_j (P_i + iL_i)(P_j + iL_j),
$$

yielding the following real and imaginary parts

$$
\Delta_3(\omega, x) = \frac{g_3(x)}{8} \omega \left( \frac{1}{6N_c} \right)^2 \times \sum_{i,j} \omega_i \omega_j (P_i P_j - L_i L_j),
$$

$$
\Gamma_3(\omega, x) = \frac{g_3(x)}{4} \omega \left( \frac{1}{6N_c} \right)^2 \sum_{i,j} \omega_i \omega_j P_i L_j.
$$

The corresponding fourth-order terms read
\[ \Delta_4(\omega, x) = \frac{g_4(x)}{16} \omega \left( \frac{1}{6N_c} \right)^3 \times \sum_{i,j,k} \omega_i \omega_j \omega_k (P_i P_j P_k - 3L_i L_j P_k), \]  

(15a)

\[ \Gamma_4(\omega, x) = \frac{g_4(x)}{16} \omega \left( \frac{1}{6N_c} \right)^3 \times \sum_{i,j,k} \omega_i \omega_j \omega_k (3P_i P_j L_k - L_i L_j L_k). \]  

(15b)

The ratios of the third-order to the second-order perturbation terms for the real and imaginary part of the self-energy is simply related to the disorder-induced shift \( \Delta_2 \) and broadening \( \Gamma_2 \):

\[ \frac{\Delta_3}{\Delta_2} = \frac{g_3(x)}{2g_2(x)} \left( \frac{1}{6N_c} \right) \frac{1}{\sum_i \omega_i P_i} \left( \sum_i \omega_i L_i \right)^2 - \left( \sum_i \omega_i L_i \right)^2 \]

\[ = 2 \frac{g_3(x)}{g_2(x)} \omega \left[ \frac{\Delta_2^2 - \Gamma_2^2}{g_2} \right]_{x=x_0} \]  

(16a)

\[ \frac{\Gamma_3}{\Gamma_2} = \frac{g_3(x)}{g_2(x)} \left( \frac{1}{6N_c} \right) \sum_i \omega_i P_i \]

\[ = 4 \frac{g_3(x)}{g_2(x)} \omega \left[ \frac{\Delta_2}{g_2} \right]_{x=x_0} \]  

(16b)

The ratios \( r_s \) (Eq. (8)) for a certain phonon mode at \( \omega_0 \) can be determined from the dilute limits \( x \to \{0, 1\} \) and the experimental shifts and broadenings for \( x_0 = 0.5 \). Under the approximation of Eq. (4), the expressions of Eq. (16a) and Eq. (16b) simplify to

\[ r_\Delta \simeq 8 \frac{m}{\Delta m} \frac{1}{\omega} \left[ \Delta_2^2 - \Gamma_2^2 \right]_{x=0.5} \]  

(17a)

\[ r_\Gamma \simeq 16 \frac{m}{\Delta m} \frac{1}{\omega} \left[ 2\Delta_2^2/(\Delta_2^2 - \Gamma_2^2) \right]_{x=0.5} \]  

(17b)

For phonons of crystals whose \( |\Delta_2(\omega_0, x_0)| \) and \( |\Gamma_2(\omega_0, x_0)| \) are comparable, such as for the Raman mode of diamond or the TO Raman modes of SiC, the asymmetry of \( \Delta(\omega_0, x) \) also depends on \( \Gamma_2(\omega_0, x_0) \) and \( r_\Gamma /r_\Delta \propto 2\Delta_2^2/(\Delta_2^2 - \Gamma_2^2) \) \( (r_\Gamma /r_\Delta \approx 8/3 \) for the Raman mode of diamond).

For phonons with \( |\Gamma_2(\omega_0)| \ll |\Delta_2(\omega_0)| \), such as the Raman modes of Si, Ge, and \( \alpha \)-Sn, Eq. (17a) can be further simplified. In these cases, \( r_\Delta \propto \Delta_2 \) and \( r_\Gamma /r_\Delta \approx 2 \). The fact
that, generally, the contributions of higher-order terms to the self-energy are not equally distributed among the real and the imaginary part \( r_\Delta \neq r_\Gamma \) means, that the asymmetries of \( \Delta(\omega_0, x) \) and \( \Gamma(\omega_0, x) \) have different shapes resulting in different concentrations of maximum self-energies \( x_{\text{max},\Delta} \neq x_{\text{max},\Gamma} \). The ratios of the next successive-order terms read

\[
\frac{A_{4,\Gamma}}{A_{3,\Gamma}} = \frac{3}{4} \frac{A_{3,\Gamma}}{A_{2,\Gamma}} = \frac{3}{2} \frac{A_{4,\Delta}}{A_{3,\Delta}} = \frac{3}{2} \frac{A_{3,\Delta}}{A_{2,\Delta}}.
\] (18)

Figure 2 shows the dependence on \( r_s \) of the concentration \( x_{\text{max}} \), at which the self-energy has a maximum, if \( |\Gamma_2(\omega_0)| \ll |\Delta_2(\omega_0)| \) (valid for Si, Ge, and \( \alpha \)-Sn).

General expressions for the ratios of successive-order perturbation terms for phonons with \( |\Gamma_2(\omega_0)| \ll |\Delta_2(\omega_0)| \) can be easily found using

\[
\left( \sum_i \omega_i D_i \right)^n \propto (P + iL)^n = \eta^n e^{in\theta} = \eta^n (\cos(n\theta) + i\sin(n\theta)) \simeq \eta^n (1 + in\theta),
\] (19)

where \( \eta = |D| \) and \( \theta = \text{Arg}\{D\} \). They are:

\[
\frac{\Delta_{n+1}}{\Delta_n} = \frac{g_{n+1}}{2g_n} \frac{1}{6N_c} \sum_i \omega_i P_i
\] (20a)

\[
\frac{\Gamma_{n+1}}{\Gamma_n} = \frac{g_{n+1}}{2g_n} \frac{n}{n-1} \frac{1}{6N_c} \sum_i \omega_i P_i
\] (20b)

\[
= \frac{n}{n-1} \frac{\Delta_{n+1}}{\Delta_n} = \frac{n}{n-1} \frac{\Delta_3}{\Delta_2}
\] (20c)

According to Eq. (17a), negative values for \( r_\Delta \) are possible if \( |\Gamma_2| \) exceeds \( |\Delta_2| \), but this does not occur for the Raman phonons of elemental semiconductors. One could also obtain \( r_\Gamma < 0 \) (Eq. (17b)) for phonons with \( q \neq 0 \) that exhibit a negative disorder-induced shift.\(^6\) The latter originates from the fact that the shift is related to the Kramers-Kronig transformation of the broadening, which displays a change of sign of \( \Delta_{\text{dis}}(\omega) \) near maxima of \( \Gamma_{\text{dis}}(\omega) \). In such a case the asymmetry would be flipped with respect to \( x = 0.5 \), i.e. the maximum of the self-energy would occur at a concentration \( x_{\text{max}} < 0.5 \).
III. COMPARISON WITH EXPERIMENTAL AND THEORETICAL RESULTS

In this section, we display a compilation of the disorder-induced self-energies for the Raman phonons of elemental crystals (diamond, Si, Ge, α-Sn) which have been obtained either by Raman spectroscopy or from theoretical calculations by several research groups during the past decade. Raman studies that address the variation of the self-energy with the isotopic composition have been conducted for diamond and Si. The coherent potential approximation (CPA) has been employed for diamond and Si, while \textit{ab initio} electronic structure based calculations have been performed for diamond and Ge. All sets of data are analyzed with respect to the asymmetries of the self-energies and compared to the results we obtain by perturbation theory.

Figure 3 displays the Raman frequencies of diamond versus the $^{13}$C-concentration. The points (open symbols) represent experimental values. The dashed curve represents the approximately linear dependence expected in the VCA. The upward curvature of the experimental data (with respect to the VCA line) clearly demonstrates the existence of an isotopic-disorder-induced self-energy as emphasized by the solid line, which is a fit with Eq. (7) for $n = 2, 3$. The prefactors $A_2$ and $A_3$ contain all factors independent of $x$. The ratios $r_s = A_3/A_2$ of the fitted values of these prefactors are listed in Table 1 under “Raman experiments”. Note that two points, which are represented by dashed triangles, have not been included in the fit since they deviate unreasonably from the other data.

It is difficult to see with the naked eye in Fig. 3 the asymmetric behavior versus $x$, which may arise from third-order perturbation terms. The asymmetry appears, however, rather clearly when the difference between the measured (or the calculated) behavior and the VCA line is plotted, as shown in Fig. 4. In this figure, the solid line also represents the fit to all experimental data (except the dotted triangles), the dot-dashed line represents CPA calculations while the dotted line is a fit to the asterisks which indicate points obtained in the \textit{ab initio} calculations. All data in Fig. 4 show a similar asymmetric behavior, with a maximum of $\Delta_{\text{dis}}(x)$ at $x \approx 0.6$. This figure allows us to conclude that the real part
of the self-energy due to isotopic disorder is well understood for diamond, including the superposition of second-order and third-order perturbation terms.

Similar degree of understanding has been reached for $\Gamma_{\text{dis}}(x)$ as shown in Fig. 5. The $x$-position of the maxima of $\Delta_{\text{dis}}$ and $\Gamma_{\text{dis}}$ determined from the experimental data agree with those obtained by perturbation theory (Eq. (9)) and also with the CPA and \textit{ab initio} calculations (see Table 1).

Concerning the other elemental semiconductors, detailed experimental results with sufficient values of $x$ to reach quantitative conclusions of the type found for diamond, are only available for Si.\cite{12} These data for Si are shown in Fig. 6 and Fig. 7 (filled circles) together with the results of CPA calculations (filled squares). The latter show for $\Delta_{\text{dis}}(x)$ a clear asymmetry with a maximum at $x_{\text{max,}\Delta} \approx 0.56$. The quality and the number of the experimental points are not sufficient to conclude that an asymmetry exists but they cannot exclude it either. The measured absolute values of $\Delta_{\text{dis}}(x)$ almost (not quite) agree within error bars with the calculated ones.

The corresponding experimental values of $\Gamma_{\text{dis}}(x)$ (see Fig. 7) are about a factor of two lower than the calculated ones, although both show the asymmetric behavior ($x_{\text{max,}\Gamma} \approx 0.62$) predicted by Eq. (17b). The reason for the discrepancy between the calculated and measured $\Gamma_{\text{dis}}$ is to be sought in the mechanism responsible for it in Si.\cite{12} Within the harmonic approximation $\Gamma_{\text{dis}} = 0$ for Si, Ge, and $\alpha$-Sn, because the Raman frequency is at the maximum of the spectrum and thus corresponds to zero density of one-phonon states. The rather small, but non-negligible, observed value of $\Gamma_{\text{dis}}$ results from the DOS induced at the $\Gamma$-point by the anharmonic interactions responsible for the linewidth of the isotopically pure crystals. Thus, the widths observed for Si, as well as for Ge and $\alpha$-Sn, correspond to fourth-order (twice disorder and twice anharmonicity) and higher-order terms. Under these conditions, we have no guarantee that the terms included in an anharmonic CPA calculation suffice to describe the experimental data, and agreement within a factor of two between theory and the small experimental values of $\Gamma_{\text{dis}}$ is to be regarded as satisfactory at this point. Using this argument too, similar values of $\Delta_{\text{dis}}$ are to be expected for these elemental crystals.
Although isotopic-disorder-induced effects have not been studied so extensively in Ge and α-Sn, there are some experimental results available for $x = 0.5$ that can be compared with perturbation calculations. The latter, once contrasted with the measurements for $x = 0.5$, provide reliable predictions for future experiments. The corresponding data are displayed in Table I, where we compared them, in the case of Ge, with those obtained by ab initio calculations. We should add that the ab initio values of $\Delta_{\text{dis}}$ for Ge calculated by Vast and Baroni agree with the CPA calculation on Si and also represent the available experimental data rather well ($\Delta_{\text{ab initio}}(x = 0.5) = 1.14 \text{ cm}^{-1}$ compared to 1.18 cm$^{-1}$ and 1.06 cm$^{-1}$ obtained experimentally for $\Delta_2$ in Si and Ge, respectively). The ab initio calculations of $\Gamma_{\text{dis}}$ for Ge, however, give values which are an order of magnitude larger than the experimental ones, a fact that can be attributed to numerical errors in the calculated DOS near the van Hove singularity which is found at the Raman frequency.

According to the values listed in Table I, one can clearly distinguish between two different behaviors in the magnitudes of $\Delta_2$ and $\Gamma_2$. Diamond exhibits a relatively large disorder-induced shift, $\Delta_2$, whereas the other elemental crystals have much smaller values. This largely reflects the factor of $\omega$ in Eq. (13b). The difference is even more striking for $\Gamma_2$, which nearly vanishes for Si, Ge and α-Sn. This can be explained also by the different orders of perturbation theory coming into play. The overbending of the phonon dispersion of diamond introduces large (second-order) isotopic disorder effects which are not present in the case of Si, Ge, and α-Sn because of their vanishing DOS at the frequency of the Raman phonon. Such overbending of the phonon dispersion is also encountered in SiC and will be discussed in Sec. IV.

We also observe a slight but systematic upwards shift of $x_{\text{max}, \Gamma}$ of the CPA values for Si, compared to those obtained by perturbation theory. The points of the CPA calculation, which includes higher-order perturbation terms, are fitted with Eq. (7) for $n = 2, 3$ that only contains the second-order and third-order terms. As shown in Fig. 4, the higher-order terms (such as, e.g., $g_5$) emphasize even more the asymmetric appearance of the self-energy, provided that the prefactors $A_i$ are all positive. A fit with Eq. (7) for $n = 2, 3, 4$ to the CPA...
values for the disorder-induced broadening of Si can be found in Ref. [12].

IV. EXTENSION FOR BINARY COMPOUNDS

The total isotopic-disorder-induced self-energy for a phonon of a binary compound can be expressed as a sum of the self-energy contributions of the individual sublattices $\kappa$

$$\Pi_n(\omega, x) = \sum_{\kappa} \frac{g_n^\kappa(x)}{2^n} \omega |e^\kappa(\omega)|^2$$

$$\times \left( \frac{1}{3N_c} \sum_i \omega_i D(\omega, \omega_i) |e^\kappa(\omega_i)|^2 \right)^{n-1}$$

where $|e^\kappa|^2$ denotes the square of the eigenvector, averaged over all $q$'s corresponding to a given frequency. The second-order self-energy can be described in a way similar to that used for monoatomic semiconductors

$$\Delta_2(\omega, x) = \sum_{\kappa} \frac{g_2^\kappa(x)}{4} \omega |e^\kappa(\omega)|^2$$

$$\times \left( \frac{1}{3N_c} \sum_i \omega_i |e^\kappa(\omega_i)|^2 \frac{\omega - \omega_i}{(\omega - \omega_i)^2 + \gamma^2} \right),$$

(22a)

$$\Gamma_2(\omega, x) = \sum_{\kappa} \frac{g_2^\kappa(x)}{4} \omega |e^\kappa(\omega)|^2$$

$$\times \left( \frac{1}{3N_c} \sum_i \omega_i |e^\kappa(\omega_i)|^2 \frac{\gamma}{(\omega - \omega_i)^2 + \gamma^2} \right)$$

(22b)

For $\gamma \to 0$, Eq. (22b) simplifies to

$$- \Gamma_2(\omega, x) = \sum_{\kappa} \frac{g_2^\kappa(x)}{4} \omega |e^\kappa(\omega)|^2$$

$$\times \left( \frac{1}{3N_c} \sum_i \omega_i |e^\kappa(\omega_i)|^2 \pi \delta(\omega - \omega_i) \right)$$

$$= \sum_{\kappa} \frac{\pi}{12} g_2^\kappa(x) \omega^2 |e^\kappa(\omega)|^2 \rho_1^\kappa(\omega),$$

(22c)

where $\rho_1^\kappa(\omega)$ corresponds to the one-phonon partial DOS projected on the sublattice $\kappa$.

Note in Eq. (22d) that for crystals with diamond structure Eq. (13d) is recovered by setting $|e^\kappa(\omega)|^2 = 1/2$. 

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The general expression for $r_s$ can be quite complicated for binary compounds when both sublattices contain isotopic disorder. However, if there is only one isotopically disordered sublattice, the sum over $\kappa$ is replaced by a single term. In this case, it is straightforward to derive expressions similar to Eq. (17a) and (17b),

$$r_\Delta \simeq \frac{8}{\Delta m} \frac{1}{m} |e(\omega)|^2 \left[ \frac{\Delta_2^2 - \Gamma_2^2}{\Delta_2} \right]_{x=0.5}$$

$$r_\Gamma \simeq \frac{16}{\Delta m} \frac{1}{m} |e(\omega)|^2 [\Delta_2]_{x=0.5}$$

(23a)

(23b)

where $e(\omega)$ is the eigenvector component at the disordered sublattice for the phonon under consideration (e.g. a Raman phonon). Thus, the isotopic effects of a disordered sublattice in a compound is different from that for the corresponding monoatomic crystal.

We apply Eq. (23a) and Eq. (23b) to the Raman spectroscopic results on a variety of $^{nat}Si^{12}C_{1-x}^{13}C_x$ polytypes, recently reported by Rohmfeld et al [2]. We have performed a fit with Eq. (3) for $n = 2, 3$ to the linewidth of the transverse optic (TO) modes of the 6H-SiC polytype measured in Ref. [2] for $^{13}C$-concentrations ranging from $x = 0.15$ to $x = 0.40$. These experimental results are displayed together with our fits in Fig. 8. The fit performed in Ref. [2] was based on the asymmetric curve obtained by CPA calculations for diamond [8]. This curve was first fitted to the data points of the TO(2/6) mode and further adjusted to the TO(0) and TO(6/6) modes by multiplication with the constant scaling factor $\omega^2 \rho_1(\omega)$ assuming constant eigenvectors (see Eq. (22c)). Instead, we have considered each TO mode separately and performed fits with Eq. (3) for $n = 2, 3$ in the same manner as for the elemental semiconductors in Sec. III. We used, however, parameters appropriate to SiC, not to diamond. In this way, we rigorously conclude that the behavior of $\Gamma_{\text{dis}}$ versus $x$ is asymmetric. This fact cannot be derived from the data in Fig. 3 of Ref. [2] which were obtained only for $0.15 < x < 0.40$. The latter can be fitted equally with either a symmetric or an asymmetric curve.

Using Eq. (22c) for a single disordered sublattice, together with the assumption of a constant eigenvector $|e_{\text{TO}}^C(q)| = 0.84$ [5] we have calculated the imaginary part $\Gamma_2(\omega)$ for 6H-SiC and 3C-SiC using the DOS of Hofmann et al. [19]. The corresponding real part, $\Delta_2(\omega)$,
is obtained by the Kramers-Kronig relations. The frequency dependence of $\Delta_2$ and $\Gamma_2$ for 6H-SiC, as well as $\Gamma_2$ for zincblende SiC (3C-SiC) is shown in Fig. 9 for the region of the TO modes. The three parallel lines cut the $x$-axis at the frequencies of the TO(0), TO(2/6) and TO(6/6) phonons, and the crossing with $\Delta_2(6H)$ gives the (approximate) disorder-induced shift of the corresponding Raman peak.

Raman experimental results extracted from Fig. 8 are compared in Table II with those found by the perturbation scheme of Eq. (23a) and (23b). The fit to the TO(0) mode is symmetric, but the large scattering of data points still allows reasonable asymmetric fits with similar curvature than for the other two modes. The two numbers given for the ratio $r_{\Delta}$ of the TO(0) mode represent maximum and minimum values and correspond to 6H-SiC and 3C-SiC, respectively. For the cubic polytype the DOS vanishes at the Raman frequencies in the harmonic approximation. Therefore, we performed a convolution of the imaginary part with the anharmonic broadening $\Gamma_{\text{anh}} = 1.4 \text{ cm}^{-1}$ [20] in order to estimate the finite value. Note that the phonon dispersion of the hexagonal polytypes, calculated in Ref. [19], exhibits an overbending of the TO branches, which mainly occurs around the K-point of the Brillouin zone. The relatively large value of $\Gamma_2$ observed for the TO(0) mode compared to those of Si, Ge and $\alpha$-Sn (see Table I) provides evidence of a non-vanishing DOS caused by an overbending of the phonon dispersion. The experimental results from Ref. [21] support therefore the DOS calculated with the bond charge model by Hofmann et al. [19].

The striking feature in Table II, which is added to the general behavior of the Raman phonons of elemental crystals, is the negative values of $r_{\Delta}$ obtained for the TO(2/6) and TO(6/6) phonons. This change of sign implies a reversed asymmetry, i.e. the maximum is now shifted to lower concentrations of the heavier isotope ($x < 0.5$). Since in Ref. [2] the phonon frequency was used for the determination of the $^{13}$C-concentration, no experimental information can be extracted about the disorder-induced shift. Within our interpretation, however, a negative $r_{\Delta}$ has been already observed indirectly for a two-phonon combination in isotopically tailored diamond by cathodoluminescence. The fact that some absolute values of $r_{\Delta,\Gamma}$ are much larger than unity is caused by a strong difference in magnitude between $\Delta_2$
and $\Gamma_2$ or by a vanishing $\Delta_2$ (see Eq. (23a) and Eq. (23b)). The latter occurs at frequencies near the maximum of the phonon DOS where $\Delta(\omega)$ changes sign.

V. CONCLUSIONS

General analytic expressions are given which allow the calculation of the real and imaginary parts of the self-energy of phonons due to isotopic disorder in elemental crystals (e.g. diamond-type semiconductors) to various orders of perturbation theory. The results are used to analyze the asymmetric behavior of these self-energies versus the isotopic concentration in crystals containing two different isotopes. The asymmetry is found to originate primarily from a combination of second-order and third-order contributions to the phonon self-energies and can be determined from the second-order perturbation terms without the need of additional parameters. These results are extended to binary crystals (e.g. zincblende or wurtzite-type semiconductors) and used to interpret quantitatively recent experimental data for SiC versus the isotopic composition of the carbon component. The possible asymmetric behavior of the self-energy in this material, which contrary to the statement in Ref. [4] does not follow from the available data for $0.15 < x < 0.40$ only, is clarified on the basis of our analytical expressions.

ACKNOWLEDGMENTS

We would like to thank W. Kress for a careful reading of the manuscript. J. S. acknowledges support from the Max-Planck-Gesellschaft and the Ministerio de Educación y Cultura (Spain) through the Plan Nacional de Formación del Personal Investigador.
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$g_n / (\Delta m/m)^n$ vs $x$ for different values of $n$: $n=2$, $n=4$, $n=5$, and $n=3$. The graph shows the behavior of $g_n / (\Delta m/m)^n$ as $x$ varies from 0 to 1.
\[ \Delta_2 + \Delta_3, \Gamma_2 + \Gamma_3 \]

\[ \Delta_2 + \Delta_3 + \Delta_4 \text{ with } A_4/A_3 = A_3/A_2 \]

\[ \Gamma_2 + \Gamma_3 + \Gamma_4 \text{ with } A_4/A_3 = 3/4 \text{ A}_3/A_2 \]
\[ x \left( \frac{12}{13}C_{1-x}^{13}C_x \right) \]

Chrenko
Hass et al.
Spitzer et al.
Hanzawa et al.
Vogelgesang et al.

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VCA

FIG. 3
FIG. 5
FIG. 6

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- Experiment
- CPA

\[ \Delta_{\text{dis}} \text{ (cm}^{-1} \text{)} \]

\[ x \left( ^{28}\text{Si}_{1-x}^{30}\text{Si}_x \right) \]

0 0.2 0.4 0.6 0.8 1

0 0.2 0.4 0.6 0.8 1

\[ \Delta_{\text{dis}} \text{ (cm}^{-1} \text{)} \]

\[ x \left( ^{28}\text{Si}_{1-x}^{30}\text{Si}_x \right) \]
\[ \Gamma_{\text{dis}} \ (\text{cm}^{-1}, \text{FWHM}) \]

FIG. 7

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- Experiment
- CPA

\[ x \left( ^{28}\text{Si}_{1-x}^{30}\text{Si}_x \right) \]
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- TO(0)
- TO(2/6)
- TO(6/6)

\[ \Gamma_{\text{dis}} (\text{cm}^{-1}, \text{FWHM}) \]

\[ x \left( \text{nat}^{12}\text{Si}^{13}\text{C}_{1-x} \right) \]

FIG. 8
FIG. 9
FIG. 1. Mass-fluctuations $g_n(x)$ for various $n$-th moments (Eqs. (5)) of an elemental, i.e. monoatomic, crystal (or each sublattice of a compound) containing a binary isotope system. $x$ denotes the concentration of the heavier mass isotope.

FIG. 2. Dependence of the value of $x_{\text{max}}$ at which the maximum of $\Delta$ and $\Gamma$ is found, including second-order and third-order perturbation terms (solid line) and also fourth-order terms (dashed and dotted lines).

FIG. 3. Raman shift of isotopically disordered diamond. The open symbols represent experimental values [6–11]. The dashed line indicates the harmonic scaling of the phonon frequency within the VCA ($\omega \propto m^{-1/2}$). The solid line corresponds to a fit with Eq. (6) for $n = 2, 3$ to all experimental data, added to the VCA-scaling. The two experimental data points at $x = 0.1$ and $x = 1$, represented as dotted symbols, were excluded from this fit.

FIG. 4. Disorder-induced shift of the Raman phonon of diamond as a function of the $^{13}$C-concentration. The open symbols are Raman experimental data [6–11] whereas the asterisks correspond to $ab$ initio calculations [13,14]. The solid line is a fit with Eq. (7) for $n = 2, 3$ to all experimental data except for the two points at $x = 0.1$ and $x = 1$ indicated as dotted symbols. The dotted and dot-dashed lines represent the fits to theoretical values obtained from $ab$ initio and CPA calculations, respectively.

FIG. 5. Disorder-induced broadening of the Raman phonon of diamond as a function of the $^{13}$C-concentration. The filled circles have been obtained from the Raman data of Refs. [6–10] by taking into account the corresponding instrumental resolutions and subtracting the anharmonic broadening, $\Gamma_{\text{anh}} \approx 2 \text{ cm}^{-1}$ (FWHM). The solid line is a fit with Eq. (8) for $n = 2, 3$ to these points. The dotted and dot-dashed lines are the corresponding fits to the values obtained from $ab$ initio [13,14] and CPA [7,8] calculations, respectively.
FIG. 6. Disorder-induced shift of the Raman phonon of Si as a function of the $^{30}\text{Si}$-concentration [12]. The solid line is a fit with Eq. (7) for $n = 2, 3$ to the experimental data. The dot-dashed line represents the corresponding fit to the values obtained from CPA calculations.

FIG. 7. Disorder-induced broadening of the Raman phonon of Si as a function of the $^{30}\text{Si}$-concentration [12]. The solid line is a fit with Eq. (7) for $n = 2, 3$ to the experimental data. The dot-dashed line represents the corresponding fit to the values obtained from CPA calculations.

FIG. 8. Disorder-induced broadening of the TO Raman modes of the 6H-SiC polytype versus the $^{13}\text{C}$-concentration of the carbon sublattice. The data are taken from Ref. [2]. The solid lines represent fits with Eq. (7) for $n = 2, 3$ to the data points that correspond to the TO(0), TO(2/6), and TO(6/6) phonon modes.

FIG. 9. Disorder-induced shift $\Delta_2(\omega)$ and broadening $\Gamma_2(\omega)$ for 3C-SiC and 6H-SiC. We obtain $\Gamma_2(\omega)$ from the DOS that has been calculated by Hofmann et al. [19] using the bond-charge model. $\Delta_2(\omega)$ is determined by a Kramers-Kronig transformation.
TABLE I. Characterization of the asymmetry of the phonon self-energy with respect to $x = 0.5$ through the ratio $r_s = A_{3,s}/A_{2,s}$ and the concentration $x_{\text{max},s}$ with $s = \Delta, \Gamma$. These quantities are displayed for each elemental crystal that is realized as a binary isotopic system $m_{1-x}M_x$, with separate rows for the corresponding real and imaginary part. The Raman data are compared with theoretical results that are derived from perturbation theory (PTh, this work), the coherent potential approximation (CPA), and $ab\ initio$ calculations. The values of the self-energies ($\Delta_2, \Gamma_2$) are for $x = 0.5$.

| $m_{1-x}M_x$ | Raman experiments | PTh | CPA | $ab\ initio^e$ |
|--------------|------------------|-----|-----|---------------|
|              | $\Delta_2$ (cm$^{-1}$) | $\Delta$ | $x_{\text{max},\Delta}$ | $\Delta$ | $x_{\text{max},\Delta}$ | $\Delta$ | $x_{\text{max},\Delta}$ |
| $-\Gamma_2$ (cm$^{-1}$) | $\Gamma$ | $x_{\text{max},\Gamma}$ | $\Gamma$ | $x_{\text{max},\Gamma}$ | $\Gamma$ | $x_{\text{max},\Gamma}$ |
| $^{12}\text{C}_{1-x}^{13}\text{C}_x$ | $\approx 6^a$ | 0.31 | 0.57 | 0.33 | 0.58 | 0.35 | 0.58 | 0.22 | 0.55 |
| $\approx 3^a$ | 0.61 | 0.62 | 0.88 | 0.66 | 0.66 | 0.63 | 0.53 | 0.61 |
| $^{28}\text{Si}_{1-x}^{30}\text{Si}_x$ | 1.18$^b$ | $\approx 0$ | 0.50 | 0.26 | 0.56 | 0.25 | 0.56 |
| 0.03$^b$ | 0.53 | 0.61 | 0.52 | 0.61 | 0.64 | 0.63 |
| $^{70}\text{Ge}_{1-x}^{76}\text{Ge}_x$ | 1.06$^c$ | 0.33 | 0.58 | 0.30 | 0.57 |
| 0.03$^c$ | 0.66 | 0.63 | 0.74 | 0.64 |
| 1.8$^d$ | 0.67 | 0.63 |
| $^{112}\text{Sn}_{1-x}^{124}\text{Sn}_x$ | 0.02$^d$ | $\approx 1$ | $\approx 0.67$ |
| 0.02$^d$ | 0.7$^d$ | 0.41 | 0.59 |
| $^{116}\text{Sn}_{1-x}^{124}\text{Sn}_x$ | 0.02$^d$ | 0.82 | 0.65 |

$^a$Values taken as average from Refs. [6–11].

$^b$Ref. [12].

$^c$Ref. [13].

$^d$Ref. [16].

$^e$Refs. [13,14].
TABLE II. Asymmetry of the phonon self-energies of isotopically disordered SiC, characterized by the ratio \( r_s = \frac{A_{3,s}}{A_{2,s}} \) and the concentration \( x_{\text{max},s} \). Experimental results from Raman spectroscopy of the TO-phonons of 6H-SiC \([2]\) are compared with calculations using perturbation theory (PTh, this work). The values of the self-energies \( (\Delta_2, \Gamma_2) \) are for \( x = 0.5 \).

| \( \) | \( \Delta_2 \) (cm\(^{-1}\)) | \( r_\Delta \) | \( x_{\text{max},\Delta} \) | \( \Delta_2 \) (cm\(^{-1}\)) | \( r_\Delta \) | \( x_{\text{max},\Delta} \) |
|-----|-----------------|---------|-----------------|-----------------|---------|-----------------|
| natSi\(^{12}\)C\(_{1-x}\)\(^{13}\)C\(_x\) | \( \Delta_2 \) (cm\(^{-1}\)) | \( r_\Delta \) | \( x_{\text{max},\Delta} \) | \( \Delta_2 \) (cm\(^{-1}\)) | \( r_\Delta \) | \( x_{\text{max},\Delta} \) |
| TO(0) | \( \approx 0.55 \) | \( \approx 0 \) | \( \approx 0.5 \) | 0.12-0.90 | 0.58 | 0.62 |
| TO(2/6) | \( \approx 3.8 \) | 0.71 | 0.64 | 3.8 | 0.76 | 0.64 |
| TO(6/6) | \( \approx 9.7 \) | 0.66 | 0.63 | 7.3 | 0.53 | 0.61 |

* Note that for negative values the asymmetry is flipped with respect to \( x = 0.5 \), i.e. the maximum of the self-energy occurs at \( x < 0.5 \).