PHYSICAL REVIEW B VOLUME 44, NUMBER 21 1 DECEMBER 1991-I

Effects of isotopic disorder on the phonon spectrum of diamond

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(Received 13 June 1991; revised manuscript received 27 September 1991)

We examine the phonon spectrum of isotopically disordered diamond using the coherent-potential approximation (CPA). Predictions for the zone-center optic mode are compared to measurements of the first-order Raman spectrum of high-quality, single-crystal, synthetic diamonds with isotopic compositions ranging from nearly pure ^{12}C to nearly pure ^{13}C. The CPA accounts very well for the observed nonlinear composition dependence ("bowing") of the Raman mode and for its asymmetric variation in width. The maximum disorder-induced broadening predicted by the CPA for naturally abundant diamond (1.1% ^{13}C) is less than 1 cm^{-1}, nearly 2 orders of magnitude smaller than that assumed in a previous study of the possible effects of isotopic disorder on the thermal conductivity of diamond.

Interest in the role of isotopic disorder in diamond has been stimulated by the recent discovery[1] of a significant enhancement (up to 50%) in room-temperature thermal conductivity as the ^{13}C concentration is reduced below its natural abundance of 1.1%. Traditional theories of thermal conductivity consider only the effects of phonon-isotope scattering on long-wavelength acoustic modes.[2] A recent analysis by Bray and Anthony[3] suggests that such theories predict a much smaller enhancement than is actually observed. These authors instead propose that the observed effect is due to an increase in phonon-phonon umklapp scattering in less pure samples due to the disorder-induced broadening of near-zone-boundary modes. The magnitude of this broadening is estimated crudely in Ref. 3 to be as large as 50 cm^{-1} for ^{13}C concentrations as low as that of natural diamond.

In this paper we present a more complete and accurate analysis of the phonon spectrum of isotopically mixed diamond using the well-established, multiple-scattering formalism of the coherent-potential approximation (CPA).[4,5] The phonon CPA (Ref. 4) is ideally suited for this problem and reduces by symmetry in diamond[6] to its simplest "one-band" form. To test this approach, we compare our calculated shifts and broadenings of the zone-center optic mode to data on the first-order Raman peak in well-characterized, single-crystal diamonds with isotopic compositions ranging from almost pure ^{12}C to almost pure ^{13}C. The present data agree well with that of previous work[7] and confirm the main qualitative predictions of the CPA. The CPA further predicts a maximum broadening of the phonon spectrum of naturally abundant diamond nearly 2 orders of magnitude *smaller* than that estimated by Bray and Anthony.[3] This result makes it extremely unlikely that disorder-enhanced umklapp scattering plays a significant role in determining the thermal-conductivity behavior of diamond at low ^{13}C concentrations.

We begin by assuming that for any concentration x of ^{13}C isotopes, the ^{12}C and ^{13}C atoms are randomly distributed on an ideal lattice with the force constant between any two atoms independent of species. The latter assumption is often questionable in alloys containing more than one element, but in isotopically disordered systems it should be extremely reliable. The simplest approach to this problem, the virtual-crystal approximation (VCA), assumes that every site in the lattice is occupied by an atom of average isotopic mass, $\bar{M}=12+x$, in amu. Phonon states in the VCA remain perfectly sharp with frequencies that vary as $\bar{M}^{-1/2}$. In diamond, as in most other systems, this represents the dominant contribution to the shift of a given state with changing composition. The CPA treats the additional effects of scattering due to mass fluctuations by considering an effective medium characterized by a dimensionless self-energy $\tilde{\varepsilon}(\omega)$, which represents a complex "mass defect" relative to $\bar{M}$ at the frequency ω. The self-consistency condition,[4,6]

$$\bar{M}\tilde{\varepsilon}(\omega)=\frac{x(1-x)(\Delta M)^2\omega^2F(\omega^2)}{1+\omega^2[(1-2x)\Delta M+\bar{M}\tilde{\varepsilon}(\omega)]F(\omega^2)}\ , \tag{1}$$

is obtained in the CPA by requiring that the average scattering at a single site in the effective medium be zero. ΔM in Eq. (1) is the 1 amu mass difference between ^{12}C and ^{13}C and $F(\omega^2)$ is the site Green's function

$$F(\omega^2)=\frac{1}{\bar{M}}\int_0^\infty\frac{g_0(\eta)d\eta}{\omega^2[1-\tilde{\varepsilon}(\omega)]-\eta^2}\ , \tag{2}$$

which is expressed here in terms of $g_0(\omega)$, the one-phonon VCA density of states (DOS), normalized to unity. To a good approximation,[6] a given VCA state of frequency $\omega_{\rm VCA}$ is shifted in the CPA to $\omega_{\rm CPA}=\omega_{\rm VCA}[1-{\rm Re}\tilde{\varepsilon}(\omega_{\rm VCA})]^{-1/2}$ and broadened to a full width at half maximum (FWHM) of $-\omega_{\rm CPA}{\rm Im}\tilde{\varepsilon}(\omega_{\rm CPA})$. The resulting one-phonon CPA DOS is given by[3]

$$g(\omega)=-\frac{2}{\pi\omega}\int_0^\infty g_0(\eta)d\eta\,{\rm Im}\frac{\eta^2}{\omega^2[1-\tilde{\varepsilon}(\omega)]-\eta^2}\ . \tag{3}$$

Once the VCA DOS is specified, Eqs. (1) and (2) are easily solved numerically using standard techniques.[8] The reference VCA DOS used in the present work was obtained from the six-parameter valence-force model for diamond of Tubino, Piseri, and Zerbi (TPZ).[9] We first transformed this model to a Born-Von-Karman description,[10] for which the dynamical matrix is given by Herman.[11] The resulting tensor force constants were then rescaled slightly in a uniform manner to give better agreement with the experimental Raman frequency in the limit of pure ^{12}C diamond. The DOS in this limit was calculated using the tetrahedron method[12] with a mesh of over 10^4 points in the irreducible Brillouin zone. VCA densities of states for other compositions were obtained by simply rescaling this result to account for the difference in mass. We ignore here the recently observed fractional change in lattice constant of -1.5×10^{-4} from ^{12}C to ^{13}C diamond,[13] except for its effect on the Raman mode itself. For this mode, the measured contraction, together with the observed mode Grüneisen parameter[14] of 1.19, imply a frequency shift of $0.7x$, in cm^{-1}.

Figure 1(a) compares the composition dependence of the Raman frequency in the VCA and CPA (with the above small shift incorporated in both as an *ad hoc* correction) to both newly obtained and previously published[7] data on single-crystal samples. The new measurements were made on the same General Electric synthetic diamonds as were used in the above-mentioned lattice-constant study.[13] The previous x-ray measurements[13] showed all of these diamonds to be of exceptional crystal perfection with (400) Bragg peak widths in the range 12–17 arc sec. The present Raman measurements were made at room temperature using the 5145 Å line of an argon-ion laser as the excitation source. A near-normal backscattering geometry was used with the axis of the objective lens normal to a ⟨100⟩ crystal face. No polarization studies were performed. The spectra were recorded using a 1 m, $f/8$ spectrometer and a photomultiplier detector. The system was calibrated against a Hg-vapor line and found to have an instrumental linewidth (FWHM) of 1.8 cm^{-1}. The uncertainties in the peak positions in Fig. 1(a) are thus smaller than the symbol size, as are the expected uncertainties in composition.[13]

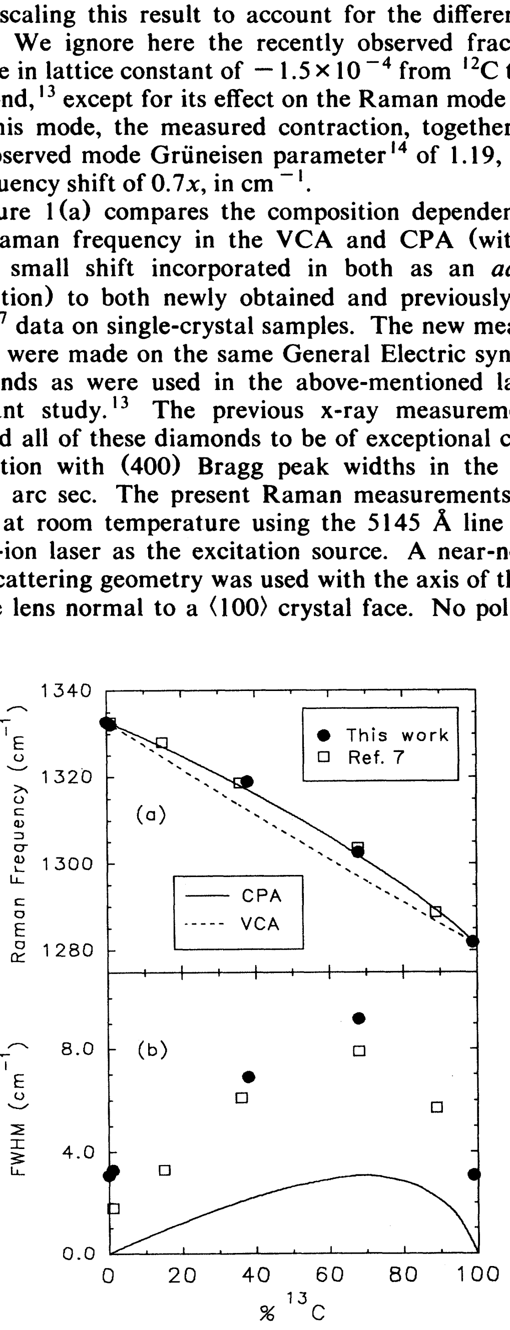

FIG. 1. Dependence of the (a) frequency and (b) width (FWHM) of the diamond Raman line on the atomic percentage of ^{13}C. Theoretical and experimental results are as labeled.

The present Raman data in Fig. 1(a) are in excellent agreement with those of Chrenko.[7] Both sets of data exhibit a pronounced "bowing" (nonlinearity) relative to the VCA that is described very well by the CPA. We conclude that the bowing is a direct consequence of the scattering due to isotopic disorder. Similar nonlinearities are observed in many other properties of alloy systems (e.g., the band gaps of semiconductor alloys).[15] Since the Raman mode occurs as or near the top of the phonon spectrum of diamond, the upward shift relative to the VCA is easily understood in terms of a repulsion from lower-lying states due to disorder-induced mixing. The recognition of this nonlinearity may be particularly important for the characterization of diamond films grown by chemical vapor deposition from ^{13}C-enriched precursors. In a recent study of this kind, Chu *et al.*[16] assumed a linear dependence of the Raman frequency on the ^{13}C concentration. Figure 1(a) shows that this assumption may lead to large errors if the location of the Raman line is used to determine the composition of the film. The failure by Chu *et al.*[16] to observe an appreciable nonlinearity in their own Raman data on *polycrystalline* films may be due to a number of factors (e.g., state of stress, impurity concentration),[17] all of which are capable of shifting the Raman lines of such films by a few cm^{-1}.

The measured Raman linewidths at different compositions are plotted in Fig. 1(b) together with the calculated CPA broadening of the zone-center optic mode. In addition to the disorder-induced contribution described by the CPA, the observed widths are also affected by instrumental resolution (1.8 cm^{-1} for our data) and anharmonic decay (on the order of 1 cm^{-1} at 300 K).[18] If we assume that the observed variation is due entirely to isotopic disorder, we find qualitative agreement in Fig. 1(b) between theory and experiment. Most notably, the CPA reproduces the strong asymmetry in the data as a function of composition, which was previously unrecognized.[16] The calculated CPA broadening, however, underestimates the variation in the observed linewidths by about a factor of 2. We believe that this discrepancy most likely reflects a problem in the underlying VCA DOS, as opposed to a limitation of the CPA itself. The precise form of the diamond DOS near the Raman mode has long been controversial[19] since it impacts on the interpretation of the "anomalous" peak that appears in the second-order Raman spectrum[20] at roughly twice the frequency of the first-order mode. The most recent studies[21,22] do not support the model of a two-phonon bound state,[23] but it is still unclear whether this peak is simply a feature of the overtone DOS (Ref. 19) (i.e., the one-phonon DOS with the frequency scale doubled) or whether it is due to matrix element effects.[24] Contrary to the results of Tubino and Birman,[19] we find that the TPZ valence force parametrization[9] used in the present work *does not* give a peak in the one-phonon DOS near the Raman mode, although we agree with their dispersion curves. This point will be discussed in detail elsewhere along with alternative dispersion relations for diamond that do give a DOS peak.[25] By artificially introducing a peak into the VCA DOS, we find that the magnitude of the CPA broadening of the Raman mode at a given composition may be increased by as much as a few cm^{-1}. This effect is easily understood in terms of the larger DOS available for scattering at the shifted position of the Raman mode. The CPA shift itself is relatively insensitive to the existence of a peak since the real part of $\tilde{\varepsilon}(\omega)$ is highly nonlocal in energy. Regardless of the precise form of the VCA DOS, the large variation in the observed widths in Fig. 1(b) strongly suggests that the Raman mode in diamond is not the absolute maximum of the one-phonon spectrum.[19] If that were the case [e.g., as it is in Ge (Ref. 6)] the additional broadening of the Raman line due to disorder would be essentially unobservable since the shifted mode would lie in a region where the VCA DOS is zero.

We now turn to more global aspects of the CPA results, which are not affected by the above uncertainties. Figure 2 shows the frequency dependence of the real (dotted) and imaginary (solid) parts of $\tilde{\varepsilon}(\omega)$ for three different isotopic compositions. In each case, $-\text{Im}\tilde{\varepsilon}(\omega)$ closely tracks the VCA DOS itself. This is to be expected here since the less than 10% mass difference between ^{12}C and ^{13}C implies that the disorder is not far from the weak-scattering,[5] Fermi's "golden rule," limit of Eq. (1). The behavior of $\text{Re}\tilde{\varepsilon}(\omega)$ is related to that of $\text{Im}\tilde{\varepsilon}(\omega)$ by a Kramers-Kronig relation.[4]

The most important thing to note about Fig. 2 is the very small scale of the results for a natural ^{13}C abundance of 1.1%. The maximum CPA broadening predicted in this case is only about 0.6 cm^{-1}, for phonons near 1240 cm^{-1}. This is almost 2 orders of magnitude smaller than the previous estimate of Bray and Anthony.[3] These authors considered only Lifshitz-like limits,[26] which are rarely realized in practice. They further assumed that the disorder-induced broadening is only significant at large wave vectors and that its maximum effect is reached by as little as 1.1% ^{13}C. The CPA broadening, by contrast, is formally independent of wave vector (although the wave vector does play an indirect role through the DOS) and has a smoother composition dependence, dominated by the $x(1-x)$ prefactor in Eq. (1). These results, and especially the smaller magnitude of the CPA broadening, raise serious doubts about the disorder-enhanced umklapp scattering mechanism proposed by Bray and Anthony.[3] Scattering rates extracted from the present CPA results at low frequencies are in excellent quantitative agreement with the standard, perturbative theory of phonon-isotope scattering.[2]

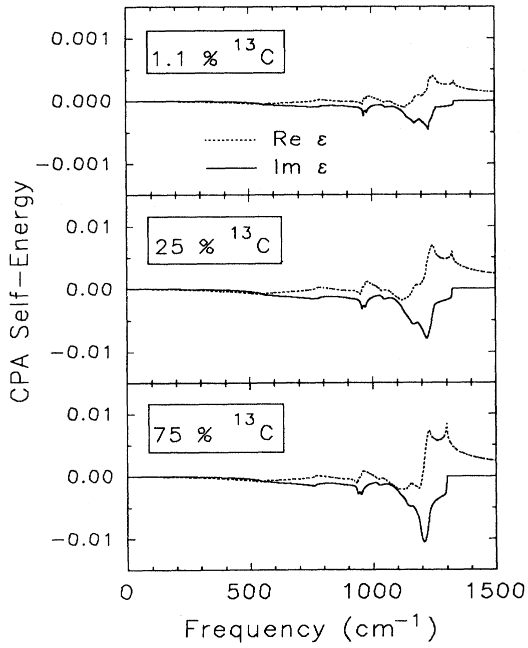

FIG. 2. Real (dotted) and imaginary (solid) parts of the CPA self-energy, $\tilde{\varepsilon}(\omega)$, in diamond containing 1.1%, 25%, and 75% ^{13}C. Note the smaller scale for the 1.1% results.

Subtle differences between the 25% and 75% ^{13}C results in Fig. 2 help to explain the asymmetric composition dependence of the Raman linewidth. For 75% ^{13}C, the highest frequency portion of the $-\text{Im}\varepsilon(\omega)$ curve is more heavily weighted than lower frequency portions; for 25% ^{13}C, the opposite behavior is observed. The qualitative difference between these two compositions reflects the fact that the maximum scattering in the CPA tends to occur in regions where the minority, or impurity, contribution to the spectrum is largest.[5] The minority ^{13}C species in a diamond with 25% ^{13}C has a heavier mass than in the VCA and therefore enhances the broadening at lower frequencies. Conversely, the minority ^{12}C species in a diamond with 75% ^{13}C has a lighter mass than in the VCA and enhances the broadening at higher frequencies. The Raman mode is thus broadened more in the 75% case since it lies near the top of the spectrum.

Figure 3 compares the VCA and CPA DOS above 1000 cm^{-1} for the midpoint of the composition range in which the total scattering [e.g., as measured by $-\int \text{Im}\varepsilon(\omega)d\omega$] is a maximum. The largest effects are seen in the vicinity of the main peak near 1210 cm^{-1}; the CPA peak is much broader and exhibits none of the Van Hove singularities of

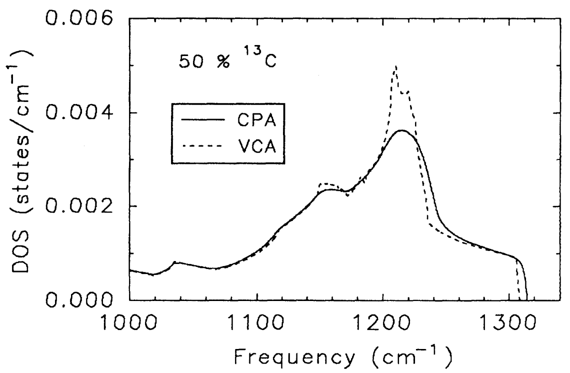

FIG. 3. Comparison of the VCA and CPA density of states (DOS) [$g_0(\omega)$ and $g(\omega)$, respectively; cf. Eq. (3)] for diamond containing 50% ^{13}C.

the VCA. This smearing is at least qualitatively consistent with preliminary measurements of the second-order Raman spectra of the most concentrated samples (38% and 68% ^{13}C) used in the present study. A more quantitative comparison is difficult, of course, since the overtone DOS represents only a crude approximation to the full second-order spectrum.[20]

In summary, we have utilized the TPZ valence force model[9] and the CPA to calculate the phonon spectrum of isotopically disordered diamond. We wish to emphasize that this system represents an almost ideal realization of the type of substitutional mass disorder for which the phonon CPA was developed.[4] The predicted disorder-induced shift and broadening of the zone-center optic mode are confirmed by Raman measurements on single-crystal synthetic diamonds with varying isotopic composition. For the lowest frequency modes most relevant to the thermal conductivity, the CPA reduces to the standard theory of phonon-isotope scattering.[2] Whether this effect is sufficient to account for the observed composition dependence of the thermal conductivity of diamond remains to be seen.

We are grateful to Jim Fleischer, Dick Chrenko, Eoin O'Tighearnaigh, and Suresh Vagarali for their help in obtaining the diamonds used in this work and to Craig Davis and Harry Holloway for helpful discussions.

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