Phonon Dispersion of Diamond Measured by Inelastic X-Ray Scattering

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We report on a study of phonons in diamond using a new instrument for high resolution inelastic x-ray scattering at the Advanced Photon Source. We have paid particular attention to possible overbending of the most energetic branches, i.e., LO along both $\Gamma - X$ ($\equiv \Delta$) and $\Gamma - L$ ($\equiv \Lambda$) and the elliptically polarized Σ_3 branch along $\Gamma - K$ ($\equiv \Sigma$). Overbending along all three directions has been invoked in recent years to explain a famous and extraordinary peak in the two-phonon Raman spectrum. Our data reveal overbending only along Δ. [S0031-9007(98)06349-2]

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Diamond has unusual static properties when compared to other group IV tetrahedral semiconductors characterized by a small lattice parameter, a large bulk modulus, and a large cohesive energy [1]. Lattice dynamical characteristics, such as phonon dispersion and thermal expansion, are also distinctive [2].

Additionally, the occurrence of a maximum in the phonon dispersion of the most energetic phonons away from the Brillouin zone center is peculiar to diamond. A necessary condition to have such an overbending is to have sufficiently large second-nearest-neighbor force constants [2–4]. Interest in the lattice dynamics of diamond has been especially strong since the report of a sharp peak in the second-order Raman spectrum at a frequency slightly higher than twice the largest single phonon frequency, i.e., at $\omega_2 - 2\omega_0 = 2$ cm^{-1} (0.25 meV) at room temperature [$\omega_0 = E(\Gamma)$] [5]. This situation is unlike that of Si [6], and a first explanation invoked the occurrence of phonon-phonon interactions to produce a two-phonon bound state [7]. However, later theoretical work led to the conclusion that anharmonic coupling constants have the wrong sign to allow formation of a bound state [8,9]. An alternate explanation was suggested involving an unusual LO phonon dispersion with an energy maximum away from the Brillouin zone center [6,8,10]. The occurrence of this overbending for the Δ branch was supported by the valence force field model of Tubino and Birman [3]. They obtained a fluted saddle point at Γ with a maximum in energy occurring at Γ for the Λ and Σ branches. They obtained a sharp peak in the overtone density of states at $2\omega_0$ (i.e., without a shift) due to a van Hove singularity at Γ. Later, Hass *et al.* reported that the model used by Tubino and Birman does not yield the peak in the overtone density of states (DOS) [11]. However, their Raman scattering studies performed on various isotopic compositions of diamond support the occurrence of such a peak. Hass *et al.* added ad hoc a peak to the DOS to achieve agreement with their two-phonon Raman spectra.

Although an explanation for the slight shift above $2\omega_0$ had been put forward based on an extension of the bond charge model [12], more recent attention has been given to the possible occurrence of overbending for the Λ and Σ branches as well as with a true local minimum in energy occurring at Γ [9,11]. The first *ab initio* calculations by Vanderbilt *et al.* [8] found overbending along Δ. More recently, Windl *et al.* [13] have obtained such dispersion in an *ab initio* calculation along all three directions for diamond having a natural isotopic abundance. However, they obtained a two-phonon shift of 25 cm^{-1} (3 meV), an order of magnitude larger than the observed value. Although measurements obtained for diamond dispersion by inelastic neutron scattering thirty years ago were not focused on subtle features in LO phonon dispersion [14,15], overbending along Δ has been reported for recent neutron scattering measurements [16]. Close agreement with the *ab initio* calculations is purported for these neutron data based on a resolution function treatment that accounted for an admixture of TO phonons in the LO spectra due to a 2° mosaic spread of the sample. We find an overbending along Δ of 1.2 meV, a value half as large as that obtained in the *ab initio* calculations. Kulda *et al.* [16] report a measured overbending of 1.5 meV in their raw data, i.e., before processing their data to account for the resolution function. Observable [by high resolution inelastic x-ray scattering (HRIXS)] overbending along Λ or Σ was also predicted by the *ab initio* calculations, but our data do not reveal such overbending.

HRIXS is a new field that has arisen due to the availability of synchrotron radiation [17]. Energy loss spectra were obtained by angle tuning a dispersive four-reflection monochromator [18] placed downstream from a high-heat-load premonochromator that employed a water-cooled diamond crystal [19]. A focusing silicon backscattering analyzer [20] was mounted on a 2θ arm of a five-circle spectrometer at 2.7 m from the sample and was set to diffract at a fixed energy (ca. 13.84 keV) for the (777)

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reflection. Stokes-shifted phonon spectra were obtained by scanning the monochromator to higher energies. X rays with a 5 meV bandpass were focused by means of a toroidal mirror to 0.6×0.8 mm^2 at the sample. The sample was a type-IIb diamond single-crystal plate with a natural isotopic abundance. The (001) oriented plate was 1 mm thick with faceted edges and measured 5.4 mm by 4.7 mm [21]. A mosaic spread of four microradians was measured from rocking curves made with 0.76 Å x rays [22]. We made measurements using the Laue transmission geometry, and the scattering volume was thus less than 1 mm^3, a value significantly smaller than has been used in neutron scattering experiments. The full width at half-maximum of the instrumental energy resolution function was 8 meV. Our Q resolution was ≤ 0.2 Å^{-1} ($\leq 0.1\ 2\pi/a$).

LO and LA data were collected for $\vec{Q}$ of the spectrometer set along Δ ($\equiv \langle 001 \rangle$) between the (001) and (004) reciprocal lattice points. LO and LA data along Λ ($\equiv \langle 111 \rangle$) were measured between (111) and (333). Phonons along Σ ($\equiv \langle 011 \rangle$) are elliptically polarized [23], and we measured the longitudinal component between (0, 2.5, 2.5) and (0, 3.5, 3.5) (open squares in Fig. 3 below). We also measured Σ phonons in the (002) zone to obtain data near Γ, where they have predominantly LO and TO character (solid symbols). Intensities were varied as is to be expected from the phonon structure factor. A representative value for the studies of the optical phonon branches is 15 Hz aside from the measurements along Σ in the (033) zone, which yielded intensities of 5 Hz. The total counts accumulated per point was about 150, resulting in a signal-to-background ratio of 30. To achieve the precision required in analyzing the peak position, the scan step size was 0.25 meV. The spectra along Λ are shown in Fig. 1, and the complete set of dispersion data is shown in Fig. 2. As additional proof of the energy calibration, the LA phonon energies obtained from our data were compared with results from earlier neutron measurements [14,15]. The elastic scattering visible in the spectrum at a momentum transfer of 1.1 ($\sqrt{3}\,2\pi/a$) in Fig. 1 is due to scattering from a Kapton foil attached to the diamond faces. Energies for the dispersion data were obtained by fitting to a sum of a Lorentzian and Gaussian profile, where the Gaussian contribution was small. This combination also represents the best fit to the measured resolution function of the instrument [24]. We deduced from our data a precision for the phonon energies of 0.3% for the high energy phonon branches.

Our data agree quite well with the raw data from Kulda *et al.* [16]. Although they deviate from the neutron results towards the zone boundary, they show the same magnitude and position of the maximum in the phonon dispersion. The maximum obtained from this work is 1.2 meV above ω_0 and appears at the phonon wave vector $q = 0.4\ (2\pi/a)$. Kulda *et al.* measured the maximum at 1.5 meV above ω_0 and $q = 0.35\ (2\pi/a)$. However, this is in contradiction to the *ab initio* calculation presented in the same paper, which predicts a different magnitude (3 meV) and position [0.48 $(2\pi/a)$]. Kulda *et al.* used the results of their *ab initio* calculations to simulate a profile of their spectra. This simulation accounts for the instrumental resolution and the large mosaic spread of 2° (which needed to be 3.5° to provide the best fit in the simulation). The different magnitude and position of the predicted maxima are visible in the longitudinal optical phonon dispersions in Fig. 3. To make the overbending evident we draw a horizontal line at ω_0. We conclude that within our precision no additional maxima in Σ and Λ appear. Surprisingly, the raw data from the neutron measurements along Δ agree better with our data than do the results from their calculations. Effects due to instrumental resolution in our data can be neglected both because of the very small mosaic spread of our sample and because our instrumental resolution does not vary with the energy

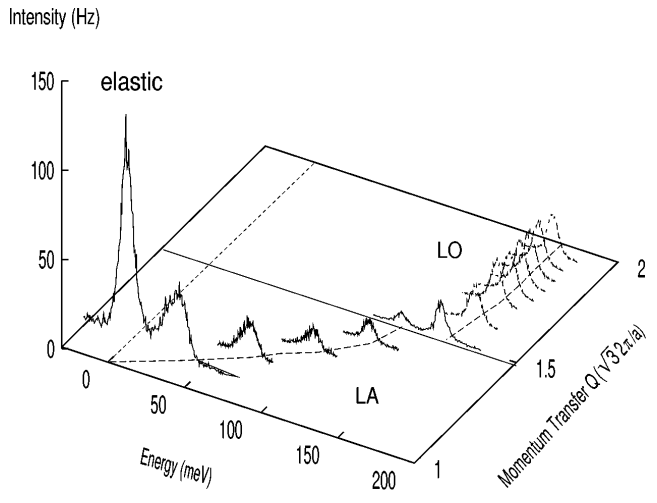

FIG. 1. HRIXS spectra of longitudinal phonons along Λ.

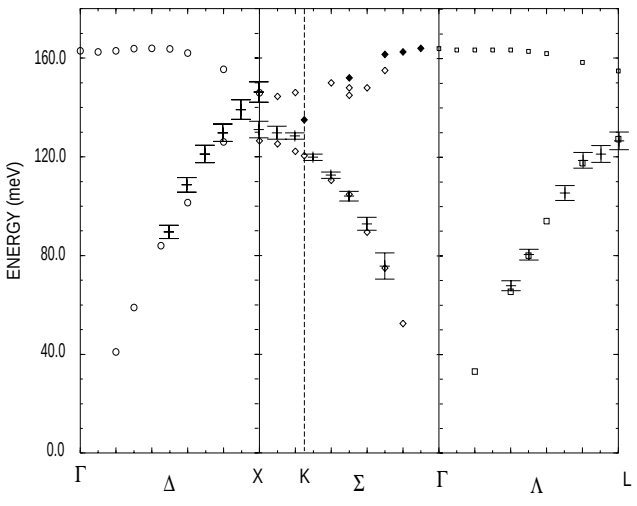

FIG. 2. Longitudinal phonon branches along Δ, Σ, and Λ: Symbols without error bars are HRIXS data; symbols with error bars were obtained by inelastic neutron scattering [14,15].

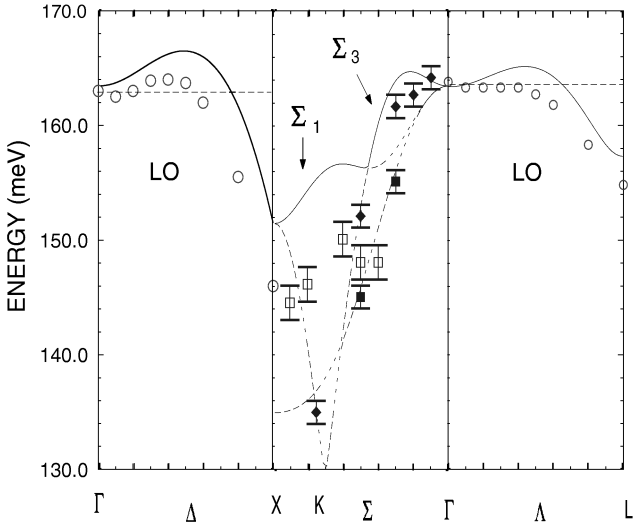

FIG. 3. Dispersion of the high energy branches as obtained by HRIXS (data points) together with *ab initio* results from Windl *et al.* [13] (lines). The error of the data is their symbol size (except along Σ). The horizontal lines indicate the phonon energy at the zone center Γ.

and momentum transfer as is the case for inelastic neutron scattering. The results from the *ab initio* calculations plotted in Fig. 3 are scaled with a factor of 0.994 to match the resulting phonon energy at the zone center with our data.

The *ab initio* calculations [13] find an overbending along Λ of 1.8 meV. Our data along Λ are taken with a precision of ± 0.3 meV. Thus, we do not find agreement with the absolute value of the *ab initio* overbending results along Δ and Λ. A value of 0.59 applies to the ratio of the overbending along Λ to the overbending along Δ resulting from the calculations. Applying this ratio to our observed overbending along Δ of 1.2 meV, a value of 0.7 meV for overbending along Λ is predicted. Our data rule this out.

Our measurements in Σ direction do not have as good a statistical precision as do our other data. But, nevertheless, at the reduced phonon wave vector of 0.8 ($\sqrt{2}\,2\pi/a$), at which point the maximum overbending for the Σ_3 branch occurs in the *ab initio* calculations [13], we observe instead a monotonic behavior in the phonon dispersion. For the same argument as used for the Λ branch, the expected maximum overbending based on the calculations is 0.5 meV. In contrast, our data falls 1.5 meV below ω_0. The difference of 2 meV is larger than our error in this measurement. To our surprise, significant scattering by longitudinal phonons of the Σ_1 branch occurs in the (033) zone. We identified the LO and TO phonons measured in the (002) zone as Σ_1 and Σ_3 phonons, based on the assignments by Warren *et al.* [15]

In summary, there have been several theoretical attempts to explain a unique high energy peak in the two-phonon Raman spectrum by assuming overbending in one or more of the most energetic optical phonon branches. Interpretation of two-phonon Raman spectra is not straightforward because the wave vectors of the phonons involved are not determined. Disagreement in the assignment of features in the Raman spectrum is the result [4,13]. However, the momentum-resolved inelastic x-ray scattering experiment that we have performed yields directly the dispersion of optical phonons. The results of this work, besides demonstrating the feasibility of HRIXS for such measurements, were the measurements of dispersion of the most energetic phonon branches along three principal directions, Δ, Σ, and Λ. These data were obtained in order to bear out the correctness of the theoretical attempts that have been made to account for the two-phonon Raman spectrum. Insofar as our data reveal overbending only along Δ, the model presented by Go *et al.*, which explains the extraordinary peak by an anomaly in the bond polarizability [12], is supported and the *ab initio* calculations of Windl *et al.* [13] are not. However, some overbending might be too small to appear in our data, especially along Σ. To our knowledge, the work by Windl *et al.* is the latest attempt to explain the famous feature in the two-phonon Raman spectrum. Improvements in the *ab initio* calculations could possibly be obtained by examining anharmonic effects as suggested by Tubino and Birman [3]. We note that the Raman measurements of Hass *et al.* [11] demonstrate the absence of the two-phonon peak for samples enriched in ^{13}C. Therefore, HRIXS on such enriched samples should be illuminating.

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