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 (HRIXS) at the Advanced Photon Source (APS). We have paid particular attention to possible overbending of the most energetic branches [i.e., longitudinal optical (LO) along both Γ–X (≡Δ) and Γ–L (≡Λ) and the elliptically polarized Σ_3 branch Γ–K (≡Σ)]. 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.

Diamond has unusual static properties when compared to other group IV tetrahedralsemiconductors 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].

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*. [5] 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 HRIXS) overbending along Λ or along Σ was also predicted by the *ab initio* calculations, but our data do not reveal such overbending.

Energy loss spectra were obtained by angle tuning a dispersive four-reflection monochromator [6] placed downstream from a high-heat-load premonochromator that employed a water-cooled diamond crystal [7]. A focusing silicon backscattering analyzer [8] was mounted on a two-theta arm of a five-circle spectrometer at 2.7 m from the sample and was set to diffract at a fixed energy (approximately 13.84 keV) for the (777) 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 x 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 [9]. A mosaic spread of four microradians was measured from rocking curves made with 0.76 Å x-rays [10]. 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 instrumentalenergy resolution function was 8 meV. Our *Q* resolution was ≤ 0.2 $Å^{-1}$ (≤ 0.1 2π/a).

LO and longitudinal acoustic (LA) data were collected for *Q* of the spectrometer set along Δ (≡<001>) between the (001) and (004) reciprocal lattice points. LO and LA data along Λ (≡ <111>) were measured between (111) and (333). Phonons along Σ (≡ <011>) were elliptically polarized [11], and we measured the longitudinal component between (0, 2.5, 2.5) and (0, 3.5, 3.5). We also measured Σ phonons in the (002) zone to obtain data near Γ where they have predominantly LO and transverse optical (TO) character (filled 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 number of counts accumulated per point was approximately 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 and Fig. 3. As an additional proof of the energy calibration, the LA phonon energies obtained from our data are compared with results from earlier neutron measurements [12–13]. The elastic scattering visible in the spectrum at a momentum transfer of 1.1(√3 2π/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 a Gaussian profile where the Gaussian contribution was small. This combination also represents the best fit to the measured resolution function of the instrument [14]. We deduced from our data a precision for the phonon energies of 0.3% for the high-energy phonon branches.

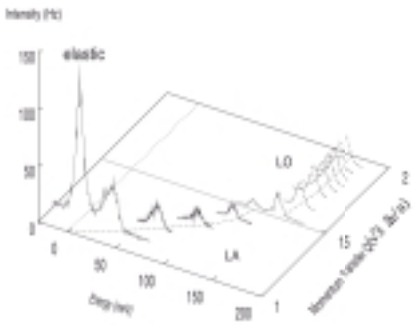

Figure 1: HRIXS spectra of longitudinal phonons along Λ.

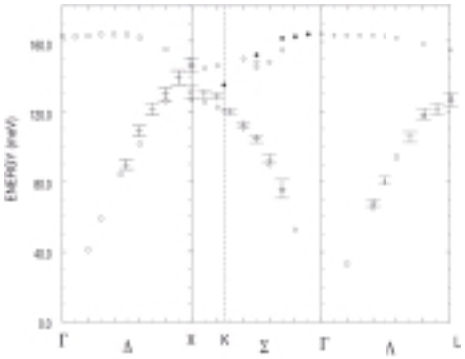

Figure 2: Longitudinal phonon branches along Δ,Σ, and Λ: Symbols without error bars are HRIXS data, symbols with error bars were obtained by inelastic neutron scattering [12–13].

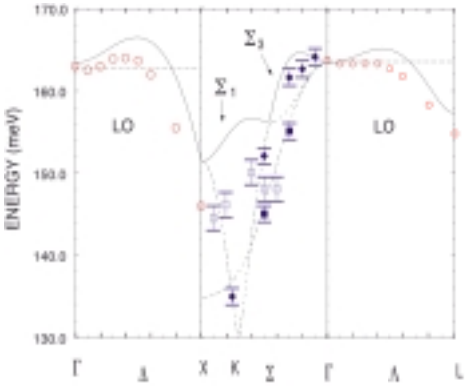

Figure 3: Dispersion of the high-energy branches as obtained by HRIXS (data points) together with *ab initio* results (lines) from Windl *et al*. [15]. The error of the data is their symbol size (except along Σ). The horizontal lines indicate the phonon energy at the zone center, Γ.

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 phonons involved are not determined. Disagreement in the assignment of features in the Raman spectrum is the result [4, 15]. 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, beside 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 examine the correctness of the theoretical attempts that have been made to account for the two-phonon Raman spectrum. In so far as our data reveal overbending only along Δ, the model presented by Go *et al*. [16] (which explains the extraordinary peak by an anomaly in the bond polarizability) is supported, and the *ab initio* calculations of Windl *et al*. [15] 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*. [17]. 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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