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Overbending of the longitudinal optical phonon branch in diamond as evidenced by inelastic neutron and x-ray scattering

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Overbending of the longitudinal-optical-phonon branch in diamond has been evidenced along all three principal directions by a joint inelastic neutron and x-ray experiment. The observed overbending of 1.5, 0.5, and 0.2 meV (along the Δ, Λ, and Σ directions, respectively) confirms previous *ab initio* lattice-dynamics calculations, thus providing experimental proof for the explanation of the anomalous peak in the two-phonon Raman spectrum.

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Amongst the various unusual properties of diamond ranges an anomaly in the second-order Raman spectrum, observed for the first time by Krishnan.[1] A sharp peak is observed at an energy which is higher than twice the Brillouin center (Γ-point) optical-phonon frequency. Later work confirmed this observation and determined the peak to be at 2667 cm^{-1}, 2 cm^{-1} higher than twice the Raman frequency of 1332.5 cm^{-1} (165.18 meV).[2] This anomaly, not observed in other group-IV tetrahedral semiconductors, stimulated a significant amount of theoretical work. The standard explanation,[3] the simultaneous creation of two phonons, seemed to fail because of the then unknown dispersion anomaly. Cohen and Ruvalds evoked the possible existence of a two-phonon bound state,[4] but this interpretation was quickly disproved.[5] Go *et al.*[6] explained the peak by an anomaly in the model phonon-photon coupling matrix element, which does not necessitate any special features in the phonon spectra. Finally, Tubino and co-workers[7] suggested a minimum (rather than a maximum or a saddle point) of the longitudinal-optic- (LO-) phonon dispersion sheet at the Γ point of the Brillouin zone. A minimum of the dispersion sheet and a maximum in the one- and two-phonon density of states was indeed observed in an empirical tight-binding molecular-dynamics study[8] and finally in an *ab initio* density-functional response calculation.[9] The latter calculation was extended to the calculation[10] of the two-phonon Raman spectrum, thus proving in an indirect way the correctness of the upward curvature (overbending) of the LO-phonon dispersion sheet away from the Γ point as being the origin for the sharp peak in the Raman spectrum.

The origin of the overbending can be traced back to the bond-bending forces, being stiffer in diamond than in the other tetrahedrally bonded semiconductors due to the more tightly bound sp^3 hybridized electrons, which leads to particularly strong effective second-nearest-neighbor forces. This effect is also reflected in the anomalous eigenvector phase of diamond.[11]

On the experimental side, the phonon-dispersion curves of diamond have been first determined by Warren *et al.*,[12] utilizing inelastic neutron scattering (INS). However, the LO data were too scarce to provide the direct experimental observation of the overbending of the LO-phonon-dispersion sheet away from the Γ point. First inelastic x-ray scattering (IXS) data[13] suffered from poor statistics, therefore being unable to evidence small energy shifts. A conclusive observation for the Δ direction was made by Kulda *et al.*[14] using INS. After correction for resolution effects the experimental data were in excellent agreement with the theoretical results,[9] yielding a maximum overbending of 1.5 meV. A recent IXS experiment[15] has confirmed the INS result but has disputed the theoretical findings for the Λ and Σ directions, thus questioning the interpretation evoked in Refs. 9 and 10. In this Communication we present a study of the diamond LO branch along the three principal directions, using state-of-the-art neutron and x-ray three-axis instruments.

The INS experiment was carried out on the hot-neutron three-axis spectrometer IN1 at the high-flux reactor of the Institut Laue Langevin. The incident-neutron wavelength was defined by a vertically focusing copper monochromator with 30′ and 40′ collimation in front and behind it, respectively. In the first part of the experiment we have used the Cu 331 reflection to obtain the highest possible energy resolution, but finally we have found that the significantly larger intensity of the Cu 220 reflection more than compensates the effect of the accompanying increase in resolution width (20%) in the precision of the peak-position determination and, moreover, permits a direct energy calibration of the whole setup. Throughout the experiment an elastically bent perfect silicon crystal (111 reflection) was used as the analyzer in a horizontal focusing geometry, without any Soller collimators. The sample was an industrial-grade diamond single crystal of an almost spherical shape with a volume of about 0.3 cm^3 and a mosaic spread of 2° full width half maximum (FWHM). To minimize the wavelength-dependent corrections, all measurements were performed with a constant final wave vector of $k_f = 54$ nm^{-1}.

The dispersion relations of the LO-phonon branches were determined along the Δ, Λ, and Σ symmetry directions using data collected in the 600, 333, and 244 Brillouin zones, respectively. Typical INS scans recorded in the 600 zone are shown in Fig. 1. Despite the purely longitudinal geometry, the transverse phonons also contribute to the observed inten-

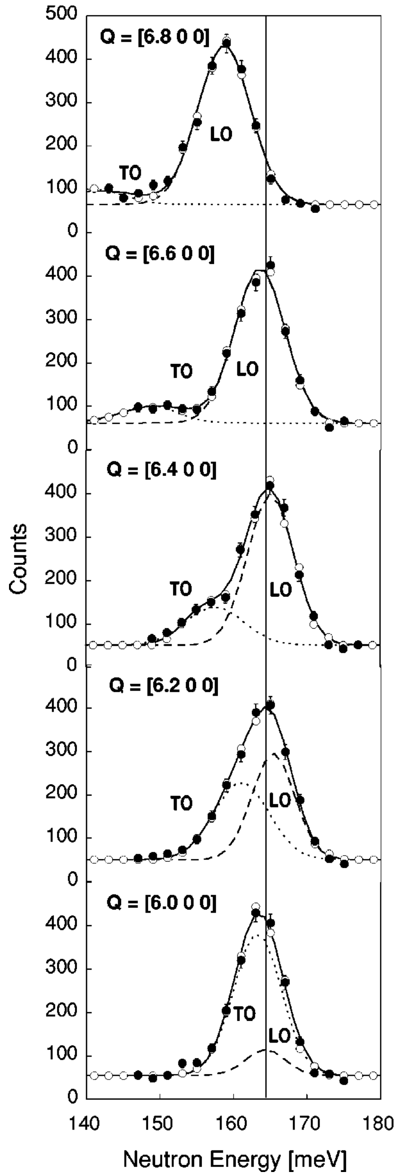

FIG. 1. INS intensities from constant-Q scans in the 600 Brillouin zone: the full circles represent the neutron counts; the open circles come from the Monte-Carlo (MC) ray-tracing simulation of the 4D resolution applied to the *ab initio* phonon calculations (Refs. 9 and 10); the full line is a Gaussian (double) fit to the MC result; the dashed and dotted lines are Gaussian fits to the LO and TO components, respectively, of the MC result. The vertical line is a guide to the eye, marking the Γ-point phonon energy.

sities because of the finite momentum resolution widths in directions perpendicular to $\mathbf{Q}$; these phonons give rise to a shoulder extending towards lower energies. In fact, their contribution is dominant at the Γ point and gradually decreases with increasing phonon wave vector to disappear almost completely for $\mathbf{Q}$ above $[6.6,0,0]$. In addition, even for the longitudinal-phonon branch the center of the energy "band" contributing to the observed intensity is generally shifted from the theoretical frequency $\omega(\mathbf{q},j)$ at the nominal $\mathbf{q}$ position (exactly on the symmetry direction), due to the curvature of the phonon-dispersion sheet. In order to account for this effect, the observed scan profiles have been fitted by a four-dimensional convolution of the theoretical scattering function $S(\mathbf{Q},\omega)$ for INS, as obtained from the complete three-dimensional (3D) *ab initio* phonon frequency set,[9] with the resolution function of the instrument generated by a Monte Carlo (MC) ray-tracing program (RESTRAX).[16] The free parameters of the fit were scale factors, renormalizing the *ab initio* intensities and frequencies of each of the phonon branches. As can be seen in Fig. 1 the result of the MC simulation reproduces the experimental spectrum very well, while the true frequency on the nominal $\mathbf{q}$ position is slightly higher than the visible maximum. All the INS results have been treated in the above-described manner, which is a further evolution of the procedure used in our preceding INS work.[14] (The overbending amplitude in the Δ direction of 1.5 meV from the older analysis[14] is now found to be 1.9 meV.) The corrected LO-phonon energies along the three principal directions are reported in Table I and Fig. 3 below.

TABLE I. LO-phonon energies (in meV) from inelastic neutron scattering (INS), inelastic x-ray scattering (IXS), and *ab initio* calculations (Refs. 9 and 10).

	ξ	E_{INS}	ΔE_{INS}	E_{IXS}	ΔE_{IXS}	E_{theo}
Δ	0.0	164.03	0.21	164.50	0.05	164.10
	0.1	164.37	0.33	164.53	0.02	164.37
	0.5	165.93	0.25	165.44	0.04	166.78
Λ	0.0	164.75	0.20	164.40	0.04	164.10
	0.1	164.67	0.31	164.69	0.03	164.71
	0.2	165.15	0.40	164.97	0.03	165.45
	0.3	164.50	0.31	163.39	0.03	164.34
	0.4	160.63	0.20	159.55	0.03	160.47
	0.5	157.00	0.24	156.31	0.03	157.00
Σ	0.0	164.26	0.20	164.18	0.03	164.10
	0.05			164.25	0.06	164.22
	0.10	163.85	0.15	164.33	0.08	164.53
	0.15			164.43	0.10	164.88
	0.20	164.38	0.26	164.13	0.09	165.09
	0.30	163.38	0.84	162.51	0.04	164.18

The error bars displayed with the neutron results correspond essentially to those obtained in the course of the profile refinement for the scaling factors of the frequencies of the corresponding phonon branches. As well, these values give a realistic measure of the reproducibility of the observed phonon energies. On the other hand, the absolute calibration of the high end of the energy scale, important for comparison with the IXS or Raman-scattering data, is only accurate to about 1–2 meV due to uncertainties related to the large differences in neutron wavelengths involved in the scattering process.

The IXS experiment was carried out at beam line ID28 of the the European Synchrotron Radiation Facility in Grenoble. The incident x-ray beam from an undulator source was monochromatized by a silicon (111) double-crystal monochromator and a high-resolution backscattering monochromator, utilizing the silicon (999) reflection order. The beam was focused onto the sample by a toroidal mirror, yielding a spot size of $270\times 70\ \mu\mathrm{m}^2$, and a beam divergence of $120\times 45\ \mu\mathrm{rad}^2$ (horizontal $\times$ vertical, FWHM). The scattered photons were collected by a spherical silicon crystal analyzer operating at the same reflection order. The FWHM of the instrumental resolution function was determined from elastic-scattering measurements of a plexiglas sample to be 2.7 meV ($\Delta E/E = 1.5\times 10^{-7}$). The momentum transfer $Q = 2k_0 \sin(\Theta_s/2)$ for the incident-photon wave vector k_0 and the scattering angle Θ_s was selected by rotating a 7-m-long analyzer spectrometer arm in the horizontal scattering plane. The total **Q** resolution was set by slits in front of the analyzer to 0.14 nm^{-1} in the scattering plane and 0.42 nm^{-1} perpendicular to it. The analyzer crystal temperature was stabilized at about 22.5 °C with a typical stability of 1 mK/24 h. The energy scans are performed by varying the monochromator temperature. Conversion from the temperature scale to the energy scale is accomplished by the relation $\Delta E/E = \alpha(T)\Delta T$, where α is the thermal-expansion coefficient of silicon.[17] The sample had a cylindrical shape with a diameter of 4 mm and a height of 2 mm. It was oriented with the $(1,\bar{1},0)$ cylindrical axis perpendicular to the scattering plane, thus allowing to access the three principal reciprocal-lattice directions by a simple rotation of the sample around its cylindrical axis. The measured mosaic spread was 0.004°.

LO phonon energies were determined along the Δ, Σ, and Λ directions, with main emphasis on the Σ and Λ directions. The zero of the energy scale was determined by recording the Stokes-Antistokes pair of a longitudinal-acoustic phonon near the Γ point at the beginning of the experiment. The energy-scale stability in the further course of the experiment was checked by repeated scans of the Γ-point LO phonon. They agreed within ± 0.04 meV for each individual Γ point. Figure 2 shows the recorded LO phonon-dispersion curves along Λ [(a), left panel] and Σ [(b), right panel] for the reciprocal-lattice units (r.l.u.) indicated on the right side of each spectrum. The experimental data are shown together with the result of a fit, obtained by standard χ^2 minimization of a Lorentzian line profile. The vertical line indicates the energy of the Γ-point LO phonon and serves as a guide to the eye. Due to selection rules the LO phonons along Σ cannot be recorded with $\vec{Q}\|[110]$. They were therefore recorded in the [3 3 1] Brillouin zone, where the intensity is largest, and the admixture of transverse modes smallest. Along this direction the data were fitted in two different manners, (i) keeping the LO to TO phonon intensity fixed at the theoretically derived value, and (ii) leaving the intensity ratio as a free parameter. Both sets yielded essentially the same LO-phonon energy. Since the effect of overbending along Σ was predicted[9] to be the weakest, each spectrum was measured three times (five times for the Γ-point phonon), and the average energy value was determined. The results are included in Fig. 3.

Table I summarizes the neutron and x-ray results, including as well the calculated phonon energies. The overall agreement is remarkable. The Γ-point LO-phonon energy is found to be identical within 0.2% (IXS) and 0.4% (INS) for the three different crystallographic directions. Within the reciprocal space probed by the present experiments the maximum energy difference between INS and IXS amounts to 0.7%. Furthermore, the overall agreement with the *ab intitio* calculations is very good, with deviations no more than 0.8%. The remaining discrepancy might be attributed to anharmonic contributions, which are not taken into account in the *ab initio* calculations.

In summary, our set of data unambiguously shows the LO overbending in all three principal directions, contrary to what has been claimed in Ref. 15. We determine the maximum of the overbending to be 1.5 meV (along Γ-X), 0.5 meV (along Γ-L), and 0.2 meV (along Γ-K). Our experimental results, in conjunction with the *ab initio* calculations,[9,10] prove that it is the LO-phonon branch overbending which is responsible for the controversially interpreted two-phonon Raman spectrum, thus answering a long-standing open question.

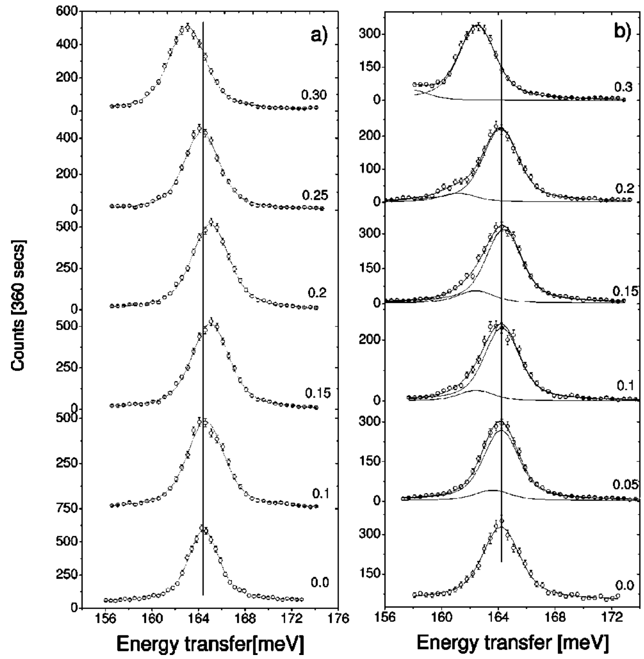

FIG. 2. Constant-**Q** scans at different q values together with the fitted curves (a) for the Λ direction and (b) for the Σ direction. The vertical lines are guides to the eye and indicate the frequency at the Γ point.

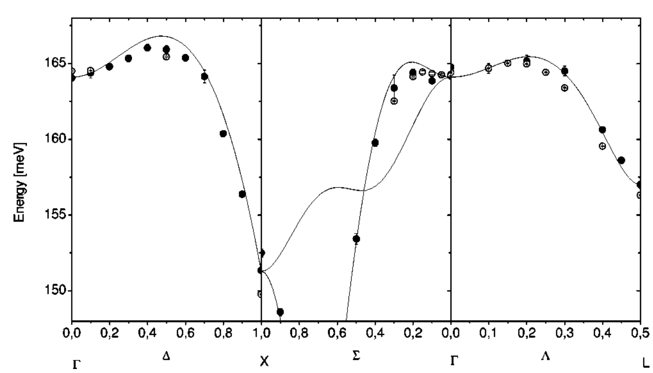

FIG. 3. LO-phonon-dispersion curves of diamond from INS (full symbols), IXS (open symbols), and *ab initio* phonon calculations (Refs. 9 and 10) (curves).

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