

## Acoustic-phonon dispersion in CdTe at 7.5 GPa

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The dispersion of longitudinal acoustic phonons has been measured by inelastic x-ray scattering in the sodium-chloride phase of CdTe at 7.5 GPa. A substantial increase of the phonon frequencies with respect to the dispersion curve at ambient pressure is observed in the momentum transfer region  $Q=3-10\text{ nm}^{-1}$ : This corresponds to an increase of the sound velocity from 3100 m/s to  $5100\pm 300\text{ m/s}$ , in good agreement with extrapolations based on the equation of state. [S0163-1829(97)07638-8]

The study of matter on an atomic scale under elevated hydrostatic pressures aims to relate interparticle properties to macroscopic thermodynamical parameters such as the equation of state, the critical pressure values of phase transitions, and the evolution of the interaction potential as a function of distance. Important studies deal with time-averaged structural properties such as lattice parameters, lattice symmetry, and local atomic coordinations using x-ray- and neutron-diffraction techniques and specific applications of x-ray spectroscopies. Similarly, the study of the microscopic atom dynamics in condensed matter at high densities, i.e., the study of the relative motion among particles under pressure, can give information on issues such as interatomic force constants, departures from two-body potential approximations, anharmonicity of crystal potentials, and the mechanisms driving phase transitions. Experimentally, investigations on collective dynamical properties of matter under high pressure have been undertaken using inelastic light (ILS) and neutron (INS) scattering methods. ILS using diamond anvil cells can be performed up to pressures of several gigapascals. The small magnitude of the incident photon wave vector, however, restricts this technique to momentum transfer values ( $Q$ ) in the  $10^{-3}-10^{-2}\text{ nm}^{-1}$  range, and therefore ILS cannot be used to study the pressure dependence of the typical dispersion effects observed on the phonon energies at  $Q$  values of the order of the inverse of interatomic distances. This  $Q$ -transfer limitation is overcome by INS, where the incident neutron can provide the energy ( $E$ ) and momentum transfer necessary to map out dispersion curves. The size of the neutron beam and the weak interaction between neutrons and matter, however, require samples with a scattering volume of at least several cubic millimeters: Consequently high-pressure INS studies were typically performed within a pressure limit of  $\approx 1\text{ GPa}$  due to the lack of devices capable to bring large volumes to higher pressures. Developments in neutron high-pressure techniques<sup>1,2</sup> have recently allowed to sensibly increase this pressure-range, and pressure dependent phonon dispersion curves with pressures up to 10 GPa have been measured in graphite, germanium, and zinc.<sup>3-5</sup>

Inelastic x-ray scattering (IXS) with very-high-energy resolution is another spectroscopic technique potentially suited to study the pressure dependence of phonon dispersion curves. IXS, largely profiting from the increased brilliance of third generation synchrotron radiation sources and advances in x-ray optics, can now be routinely performed with energy resolutions in the 1.5–7 meV range, corresponding incident photon fluxes of  $3\times 10^8-1\times 10^{10}$  photons/s, and lateral beam sizes on the sample of a few hundred micrometers.<sup>6</sup> The small beam size and the typical photoelectric absorption length of high-atomic-number ( $Z$ ) materials match well the geometrical constraints imposed by diamond anvil cells (DAC's), and therefore high-pressure IXS studies using these devices are coming within reach.

In this work we exploit the possibility to use inelastic x-ray scattering to study phonon excitations in a sample under high pressure in a DAC. We report IXS spectra of polycrystalline CdTe in its sodium-chloride (rocksalt) phase<sup>7</sup> at 7.5 GPa and room temperature, recorded in the  $Q$  range of  $3-10\text{ nm}^{-1}$ , and therefore extending over the first Brillouin zone. The longitudinal acoustic phonon branch is clearly observed in the whole  $Q$  region explored, and we find a large increase of the excitation energies with respect to the corresponding dispersion curve of CdTe in its zinc-blende phase at ambient pressure.<sup>8</sup> The derived sound velocity, representing an average over all crystalline directions, increases at high pressures by a factor of 1.6 to  $5100\pm 300\text{ m/s}$ . Our results demonstrate the capability of IXS to study the dynamics of systems under high pressure in a diamond anvil cell, and show the potential of this technique for high-pressure research in solids, liquids, and dense gases.

The IXS experiment was carried out at the new very-high-energy resolution inelastic x-ray-scattering beam line (BL21-ID16) at the European Synchrotron Radiation Facility (ESRF). The undulator x-ray beam was monochromatized by a cryogenically cooled Si(111) double crystal and by a very-high-energy resolution Si(777) backscattering monochromator.<sup>6</sup> This beam, with an energy of 13 840 eV and an energy resolution of 5 meV, is focused on the sample by a

toroidal mirror, yielding a spot size of  $270 \times 150 \mu\text{m}^2$  full width at half maximum (FWHM) in the horizontal and vertical planes, respectively. These incident beam dimensions were further reduced by slits to  $100 \times 100 \mu\text{m}^2$  to avoid scattering from the anvil cell gasket. The photon flux incident on the sample was  $\approx 3 \times 10^9$  photons/s. The scattered photons were collected by a spherical silicon crystal analyzer, also operating at the Si(777) reflection in backscattering and in Rowland geometry. The total instrumental resolution function, determined measuring the elastic scattering from a plastic sample at the  $Q$  value of the maximum of its static structure factor ( $Q = 10 \text{ nm}^{-1}$ ), was well approximated by a Lorentzian of 7 meV FWHM. The momentum transfer  $Q = 2k_0 \sin(\theta_s/2)$ , where  $k_0$  and  $\theta_s$  are, respectively, the wave vector of the incident photon and the scattering angle, was selected between 3 and  $10 \text{ nm}^{-1}$  by rotating the 7-m-long analyzer arm in the horizontal scattering plane. The  $Q$  resolution was set to  $0.4 \text{ nm}^{-1}$  by an aperture in front of the analyzer. Energy scans were done by varying the relative temperature between the monochromator and the analyzer crystals. Each scan took about 120 min, and each  $Q$  point was obtained by typically averaging five scans. The data were normalized to the intensity of the incident beam. Further details about the beam line are given elsewhere.<sup>6,9–11</sup> The correctness of the energy scale was checked by measuring the energy position of the longitudinal acoustic phonons in Si and LiF. The comparison with inelastic neutron-scattering data resulted in an agreement within 5%. The sample was a finely ground powder of high-purity CdTe. The diamond anvil cell was used with  $600\text{-}\mu\text{m}$  diamond-anvil culets of 1.5 mm thickness. The sample was loaded into a  $300\text{-}\mu\text{m}$  hole in a stainless steel gasket with nitrogen as pressure-transmitting medium. The sample thickness was  $\approx 20 \mu\text{m}$ . The pressure was measured before x-ray exposure using the ruby-fluorescence technique.<sup>12</sup> The measurements were made at  $7.5 \pm 0.5$  GPa, corresponding to  $\approx 4$  GPa above the zinc-blende  $\rightarrow$  sodium-chloride transition, and  $\approx 2.5$  GPa below the sodium-chloride  $\rightarrow Cmc$  transition.<sup>7</sup> The pressure cell was kept in a vacuum chamber to minimize the contribution from air scattering to the measured signal. This study was performed on a polycrystalline sample since it is very difficult, and probably impossible, to keep the single crystal structure while increasing the pressure through the structural phase transition. Consequently, the reported data correspond to an orientational average within the Brillouin zone. We have restricted the present initial experiment to  $Q$  values in the first Brillouin zone, where only longitudinal acoustic phonons can be excited, and therefore the averaging is reduced by the exclusion of all excitations with transverse symmetry.

Inelastic x-ray-scattering data as a function of transfer energy are reported in Fig. 1 at 3, 4, 6, 8, and  $10 \text{ nm}^{-1}$   $Q$  transfer values, together with the corresponding fits. The experimental data, displayed with their error bars, have been normalized to the central peak intensity. The count rates at the peak at  $E = 0$  meV were  $\approx 0.05$  count/s. For clarity, we show only the energy-loss side (Stokes) of the spectrum, although the data below  $Q = 8 \text{ nm}^{-1}$  were collected including the energy-gain side (anti-Stokes). The spectra display a line centered around zero energy transfer and an inelastic feature which disperses towards higher energies with in-

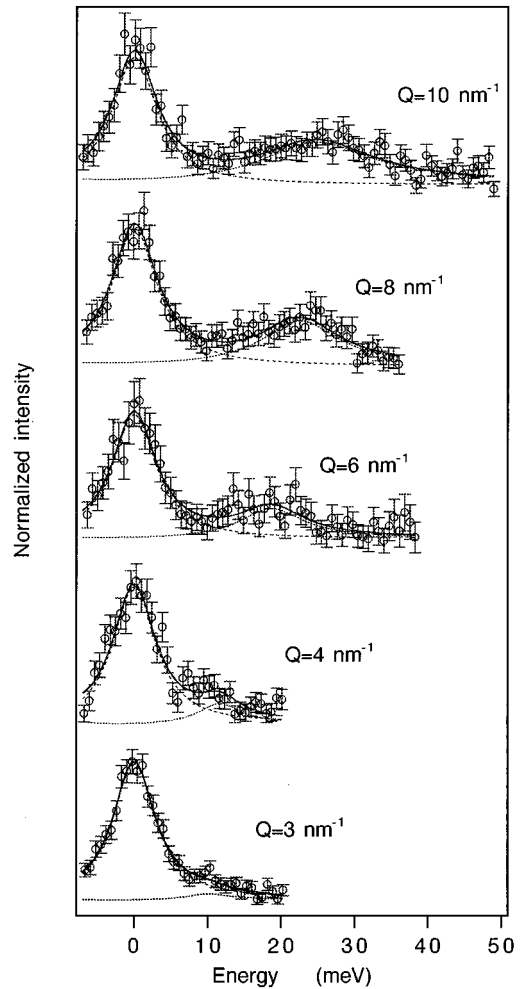


FIG. 1. Inelastic x-ray-scattering spectra of CdTe at 7.5 GPa. The experimental data (open circles), shown with the error bars, are superimposed to the fit (solid line) as explained in the text. The dashed and dotted lines represent the elastic and inelastic contributions, respectively. The data are normalized to the intensity of the central peak. The integration time for each point was typically 300 s, and the count rate at zero energy  $\approx 0.05$  count/s.

creasing  $Q$  values. The intensity centered at  $E = 0$  is due to scattering from nitrogen and from static defects in the polycrystalline CdTe sample. The longitudinal acoustic phonons of the diamond anvils have been measured previously, and yield a strong inelastic signal at energies much higher than those considered here, corresponding to a velocity of sound of  $\approx 13\,000$  m/s. The inelastic signal observed in Fig. 1 can therefore be assigned to the longitudinal acoustic phonons of CdTe, orientationally averaged in the first Brillouin zone. The energy positions and the widths of the excitations were determined fitting the spectra with a model function composed of a Lorentzian for the inelastic signal and a Lorentzian for the central peak at  $E = 0$ . For  $Q < 8 \text{ nm}^{-1}$ , a third Lorentzian was introduced to represent the energy-gain part of the spectrum: Its intensity was dictated by the detailed balance, while its energy position and width values were imposed to be those derived from the Lorentzian describing the Stokes excitation. This model function was convoluted with the experimentally determined energy resolution function, and the fit to the experimental data was performed by

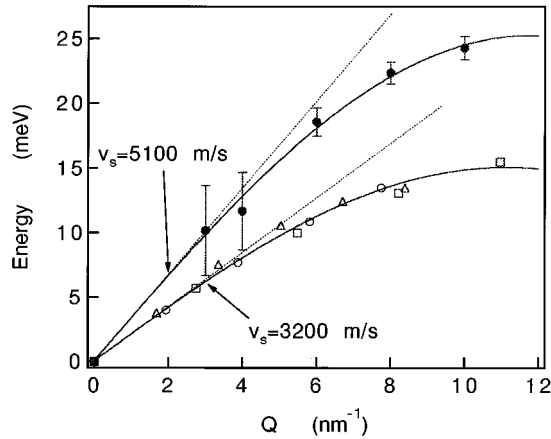


FIG. 2. Longitudinal acoustic-phonon dispersion curves of CdTe at 7.5 GPa (solid symbols) and at ambient pressure from Rowe *et al.* (Ref. 8) (open symbols; triangles correspond to the [111] direction, circles to the [100], and squares to the [110]). The solid lines through the data points represent the result of a sinus fit, and the dotted lines visualize its slope, yielding the indicated sound velocities.

standard  $\chi^2$  minimization. The results of the fit are shown in Fig. 1, with the individual elastic and inelastic components. Already from the raw data of Fig. 1, it is apparent that the phonon width increases significantly with momentum transfer. Possible reasons for this broadening could be that (i) the frequency increase of the phonon mode is different for different crystallographic directions, and therefore the orientational averaging in the polycrystal leads to the observed broadening; (ii) the pressure is not homogeneous in the scattering volume, and therefore pressure differences among microcrystals are responsible for a distribution of dispersion curves; or (iii) structural defects and/or stoichiometric fluctuations lead to a broadening of dynamical origin, essentially due to a decrease in the lifetime of the collective excitations at large  $Q$ .

The dispersion curve resulting from the energy position of the Lorentzians describing the inelastic signal of Fig. 1 is reported in Fig. 2. The IXS results are shown with their error bars as obtained from the fit. We note that for  $Q=3$  and  $4 \text{ nm}^{-1}$  the error is larger due to the reduced contrast between central line and inelastic feature. For direct comparison, we also report in Fig. 2 as a function of absolute  $Q$  values the phonon dispersion curves measured by INS in CdTe in its zinc-blende phase at ambient pressure along the [100] (open circles), [110] (open squares), and [111] (open triangles) crystallographic directions.<sup>8</sup> The high isotropy of these longitudinal acoustic-phonon branches is a consequence of the cubic structure. We notice that the high-pressure data are at energies well above those at ambient pressure, and this implies a substantial increase of the sound velocity in the high-pressure sodium-chloride phase of CdTe. This is consistent with the increase in the first-neighbor coordination, which goes from four to six atoms at high pressure and is responsible for a relevant stiffening of the average force constant acting on the constituent atoms.

The velocity of sound was estimated by fitting the dispersion relation with a sinus-law, and determining its slope in the  $Q=0$  limit. For the ambient pressure data we find

$v=3200 \text{ m/s}$ , in good agreement with known values, while for the high-pressure data we derive  $v=5100 \pm 300 \text{ m/s}$ , corresponding to a factor of 1.6 increase in  $v$ . An independent estimate for the velocity of sound increase in the high-pressure sodium-chloride phase can be obtained assuming that the elastic constants  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  have the same proportional increase at the structural phase transition: In this case, the sound velocities scale as the quantity  $\sqrt{B/\rho}$ , where  $B(P)$  and  $\rho(P)$  are, respectively, the bulk modulus and the density at the considered pressure  $P$ . The bulk modulus can be estimated from x-ray-diffraction data as a function of pressure. The pressure-volume experimental relation, in fact, can be fitted to an equation of state, yielding the bulk modulus  $B$  and its pressure derivative  $B'$  [ $B(P)=B_0+B'P$ , with  $B_0$  being the bulk modulus at a given pressure  $P_0$ ]. An analysis of existing results in CdTe gives for the rocksalt phase the values  $B_0=68.7 \pm 5 \text{ GPa}$  at the phase transition pressure ( $P_0=3.8 \text{ GPa}$ ) and  $B'=5.1 \pm 0.6$ ,<sup>13</sup> in good agreement with a recent calculation.<sup>14</sup> With this approach we find that the ambient-pressure sound velocity should increase by a factor of 1.4 in the rocksalt structure, leading to the value  $v=4300 \text{ m/s}$  at 7.5 GPa. Our experimental value is larger, and this is probably a consequence of the quite crude approximation used here. Moreover, our high-pressure results, together with the previous ambient-pressure INS results and the equation of state of CdTe, allow us to obtain an approximative value for the mode Grüneisen parameter, which is defined as  $\gamma(Q)=-d(\ln\omega(Q))/d(\ln V)$ , where  $\omega(Q)$  is the phonon frequency at a specific  $Q$  value, and  $V$  is the volume. We obtain values between 1.5 and 1.9, which are of the order of the  $\gamma(Q)$ 's, determined in other materials such as RbI (Ref. 15) and Zn (Ref. 5).

In summary, we have shown that using IXS it is now possible to detect inelastic scattering from phonon excitations in samples at very high pressure in a diamond anvil cell. In spite of the very small scattering volume, only  $\approx 20 \mu\text{m}$  in the incident beam direction and  $\approx 100 \mu\text{m}$  in the transverse directions, reasonable spectra can be obtained in high- $Z$  materials. This has allowed us to map the orientationally averaged dispersion curve of the longitudinal acoustic-phonon branch in the rocksalt phase of CdTe, and to determine a 60% increase in the velocity of sound with respect to the ambient-pressure zinc-blende phase. This study can be obviously generalized to many other systems. Substantial increases in signal rates, and, therefore the possibility to perform measurements with higher-energy resolutions (down to 1.5 meV), are well within reach. Intensity gains, in fact, will come from improvements in the beam line instrumentation, and most importantly from an optimization of the DAC volume. Finally, the possibility to keep the single-crystal phase at high pressure will allow us to overcome the orientational average, and to benefit from the large cross-section increase at higher  $Q$  transfer. This will be extremely beneficial, for example, in the study of transverse phonon softening at arbitrary points in the Brillouin zone, expected to be the driving mechanism of many structural phase transitions.

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- <sup>1</sup>J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, *Physica B* **180&181**, 907 (1992).
- <sup>2</sup>S. Klotz, J. M. Besson, G. Hamel, R. J. Nelmes, J. S. Loveday, W. G. Marshall, and R. M. Wilson, *J. Appl. Phys.* **66**, 1735 (1995).
- <sup>3</sup>A. S. Ivanov, I. N. Goncharenko, V. A. Somenkov, and M. Braden, *High Press. Res.* **14**, 145 (1995).
- <sup>4</sup>S. Klotz, J. M. Besson, M. Braden, K. Karch, F. Bechstedt, D. Strauch, and P. Pavone, *Phys. Status Solidi B* **198**, 105 (1996).
- <sup>5</sup>J. G. Morgan, R. B. Von Dreele, P. Wochner, and S. M. Shapiro, *Phys. Rev. B* **54**, 812 (1996).
- <sup>6</sup>F. Sette, G. Ruocco, M. Krisch, C. Masciovecchio, and R. Verbeni, *Phys. Scr.* **T66**, 48 (1996).
- <sup>7</sup>R. J. Nelmes, M. I. McMahon, N. G. Wright, and D. R. Allan, *Phys. Rev. B* **51**, 15 723 (1995).
- <sup>8</sup>J. M. Rowe, R. M. Nicklow, D. L. Price, and K. Zanio, *Phys. Rev. B* **10**, 671 (1974).
- <sup>9</sup>R. Verbeni, F. Sette, M. Krisch, U. Bergmann, B. Gorges, C. Halcoussis, K. Martel, C. Masciovecchio, J. F. Ribois, G. Ruocco, and H. Sinn, *J. Synchrotron Radiat.* **3**, 64 (1996).
- <sup>10</sup>C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni, *Nucl. Instrum. Methods Phys. Res. B* **111**, 181 (1996).
- <sup>11</sup>C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni, *Nucl. Instrum. Methods Phys. Res. B* **117**, 339 (1996).
- <sup>12</sup>G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975).
- <sup>13</sup>K. Strössner, S. Ves, W. Dieterich, W. Gebhardt, and M. Cardona, *Solid State Commun.* **56**, 563 (1985).
- <sup>14</sup>P. E. Van Camp and V. E. Van Doren, *Solid State Commun.* **91**, 607 (1994).
- <sup>15</sup>O. Blaschko, G. Ernst, G. Quittner, W. Kress, and R. E. Lechner, *Phys. Rev. B* **11**, 3960 (1975).