

Experiment: HC-2132

Title: Bond compressibility and local Thermodynamics in CdTe

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Introduction

The difference between bond thermal expansion measured by EXAFS and lattice thermal expansion measured by diffraction has been measured on a number of crystalline systems (Cu, Ge, GaAs, CdTe, CuCl). The difference depends on the presence and extent of relative vibrations normal to the bond direction. This effect is larger for open structures, such as tetrahedrally bonded semiconductors, and increases with the degree of ionicity. Particularly careful are the results obtained for CdTe in the temperature range 5-300 K, which allowed the evaluation of the coefficient of bond thermal expansion [1] and of the bond Grüneisen parameter [3] have been evaluated from EXAFS [2].

Main aim of the present experiment is to measure by EXAFS the bond compressibility in the low-pressure phase of CdTe (zincblende structure, ZB, below 3.5 GPa) and to compare it with the lattice compressibility measured by diffraction. The final goal is to verify if local response functions (bond thermal expansion, bond compressibility, bond Grüneisen parameter) can be connected by a simple relation, similar to the one that connects the corresponding average thermodynamic quantities.

A second aim is to monitor by EXAFS the phase transitions in the range 3.5 to 5 GPa, to the mixed ZB-cinnabar phase and subsequently to the NaCl phase, in order to evaluate the possible original information obtainable on the local structural and dynamical behaviour.

Experiment

Transmission EXAFS measurements have been performed at the Cd K edge (26.711 keV) using a Si(311) monochromator and two Pt-coated mirrors.

The sample was loaded in a mechanical diamond anvil cell (DAC). Sintered nano-polycrystalline anvils were used, to obtain glitch-free EXAFS spectra. The sample size was about 200 μm . The beam was focalised to a size of about 5 μm on the sample.

The pressure was varied from 1 bar to 55 kBar (5.5 GPa) and measured by the ruby fluorescence method. At each pressure, a diffraction spectrum was measured at a fixed energy by a position sensitive detector.

Preliminary results

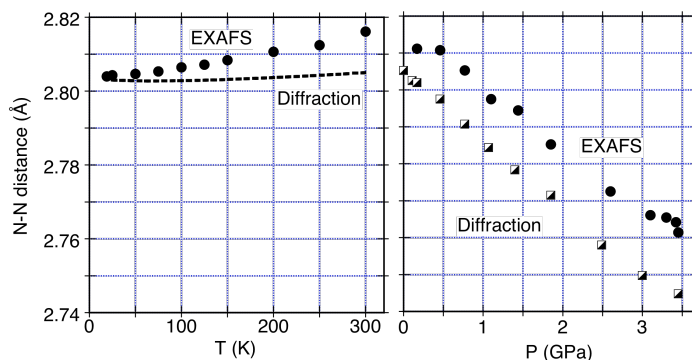
The analysis of the first-shell EXAFS in the ZB phase (below 3.5 GPa) allowed the evaluation of the pressure dependence of the bond distance and of the 2nd cumulant (EXAFS Debye-Waller exponent). It is interesting to compare the pressure dependence at 300K of these quantities with their temperature dependence at 1bar.

The bond thermal expansion measured by EXAFS (circles in the left panel) is larger than the bond expansion proportional to the lattice expansion (dashed line). The reduction of bond distance when pressure increases measured by EXAFS at 300 K (circles in the right panel) is slightly weaker than the reduction measured by diffraction (squares in the right panel).

By fitting the Murnaghan equation of state to the pressure dependence of both distances one obtains a higher value of K_0 and a much lower value of K'_0 for the EXAFS data than for the diffraction data. The diffraction values are in good agreement with the previous results of McMahon (1993) [3].

The K_0 values correspond to the following values of bond compressibility:

a) $5.8 \times 10^{-12} \text{ Pa}^{-1}$ for EXAFS measurements



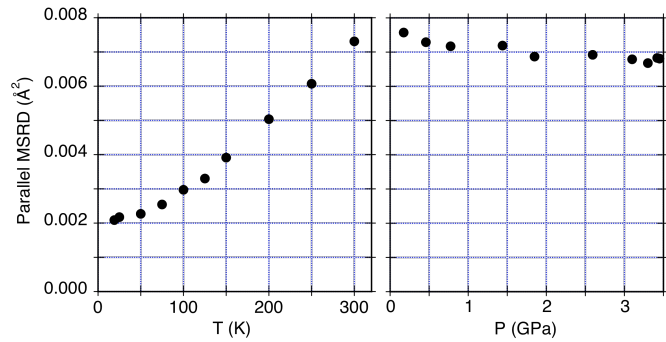
b) $7.2 \times 10^{-12} \text{ Pa}^{-1}$ for diffraction measurements

Slightly lower values of compressibility had been found from EXAFS results by other researchers, but the difference had been attributed to experimental uncertainty [4].

In view of the knowledge gained from temperature dependent measurements, it seems now more reasonable to attribute the difference to the effect of relative vibrations perpendicular to the bond direction, which allows the bond distance to be less squeezed than the lattice parameters when the pressure increase.

The parallel MSR (DW exponent) increases with temperature (left panel) at constant 1 bar pressure. At 300K, when pressure increases, the MSR slightly decreases (right panel): the Einstein frequency increases when the distance decreases, according to the Grueneisen theory.

Further work is in progress to refine and interpret the results for the ZB phase.



Two phase transitions are expected to take place in the pressure interval 3.5 to 5 GPa [3]: the first one from ZB to a mixed ZB-cinnabar phase, the second one to an NaCl phase. Both transitions are well evidenced in diffraction spectra. Weak but clear differences are noticed in the XANES region. Strong differences are evident in the Fourier transform of the EXAFS spectra. The first-shell peak slightly increases and shifts to shorter distances in the ZB phase when the pressure increases. The onset and progressive development of the cinnabar phase are accompanied by a strong progressive reduction of the first-shell peak, reasonably due to the increase of static DW factor. The NaCl phase is characterised by a quite small first-shell peak; the quantitative analysis confirms the presence of a large static contribution to the DW factor.

Further work is in progress to refine the quantitative analysis of the high-pressure phases, and in particular to interpret the large DW factor of the NaCl phase.

[1] P. Fornasini and R. Grisenti, *J. Chem. Phys.* **141**, 164503 (2014)

[2] P. Fornasini and R. Grisenti, *J. Synchrotron Rad.* **22**, 1242 (2015)

[3] M.I. McMahon M.I et al., *Phys. Rev. B* **48**, 16246 (1993)

[4] A. San-Miguel et al., *Phys. Rev B* **48**, 8683 (1993)