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EXAFS and negative thermal expansion in CdTe

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Abstract. CdTe is affected by a low-temperature negative thermal expansion (NTE) of the lattice parameter, whose strength and temperature interval are intermediate between those of the iso-structural crystals Ge and CuCl. EXAFS measurements have been performed on CdTe from 19 to 300 K. The first-shell analysis has led to an accurate evaluation of the bond thermal expansion and of the parallel and perpendicular MSRDs. The values of the relevant parameters measured by EXAFS for CdTe are intermediate between the corresponding values previously found for Ge and CuCl.

1. Introduction

The interest towards negative thermal expansion (NTE) has been renewed in the last decade by the discovery of materials exhibiting strong NTE in large temperature intervals, such as ZrW2O8 [1]. The observed macroscopic expansion is generally considered the net result of a positive bond stretching contribution and a negative contribution due to tension effects [2]. New perspectives for getting deeper insights on the local origin of NTE have been recently opened by the progresses in EXAFS analysis and interpretation ([3] and references therein), that led to the possibility of accurately measuring (a) the thermal expansion of the nearest-neighbours bond distance and (b) the perpendicular mean square relative displacement (MSRD) and the anisotropy of relative vibrations.

To evaluate strengths and limitations of EXAFS for quantitative studies of NTE materials, it is convenient to focus the attention on crystals of relatively simple structure and lattice-dynamical properties, such as tetrahedrally bonded semiconductors with the diamond-zincblende structure. In these systems, NTE is frequently observed at low temperatures, and its strength and temperature range increase with the bond ionicity; NTE is quite weak in Ge, and the strongest in CuCl [4]. In both crystals, recent EXAFS studies [5, 6] have shown that the bond thermal expansion is always positive and the relative atomic vibrations are anisotropic; the results suggest the existence of a correlation between the NTE properties and some quantities measured by EXAFS. To confirm this correlation and search for its quantitative assessment, we have performed EXAFS measurements on CdTe, whose NTE properties are intermediate between those of Ge and CuCl. The preliminary results of the first-shell analysis of the Cd K-edge EXAFS are here presented.
2. Experimental
Cadmium Telluride powders, 99.999% pure (from Alfa Aesar), were structurally tested by X-ray diffraction and then deposited on polytetrafluoroethylene membranes. Surface densities of about 50 mg/cm$^2$ allowed us to obtain an edge jump $\Delta \mu x \approx 1$ at the Cd K edge. Transmission EXAFS measurements were done at the BM29 beam-line of ESRF in Grenoble, France [7]. Electron energy and average current were 6 GeV and 190 mA, respectively. The x-ray beam was monochromatized by two parallel silicon crystals with flat (311) reflecting faces. The incoming and outgoing photon fluxes were measured by ionization chambers filled with krypton gas (pressures 140 and 500 mbar, respectively). Measurements at the Cd K edge were done from 19 to 300 K. The sample was immersed in the He gas atmosphere of a liquid-helium cryostat; the temperature control was achieved through an electric heater, controlled by a feedback loop. Thermal stabilization was guaranteed within 0.01 K. Two or three spectra were collected at each temperature, to allow an evaluation of the experimental uncertainty.

3. Data analysis and results
At the beginning of the analysis, the edges of all spectra were carefully aligned to within 0.1 eV, in order to guarantee a resolution better than 0.001 Å in distance variations. The EXAFS functions $k\chi(k)$ at three selected temperatures are shown in Figure 1. The first-shell contribution (four Te atoms at 2.8 Å) has been Fourier filtered and quantitatively analyzed by two different procedures:

(a) Separate analysis of phases and amplitudes of the filtered signals by the ratio method [8], taking the 19 K spectra as reference. At each temperature, different plots of phase differences and logarithms of amplitude ratios were obtained from different pairs of data files; the fitting range at each temperature was chosen as the $k$ range were the different plots were in good agreement. The output of the analysis were the relative values of the first four cumulants of the effective distribution of distances, $\delta C_i = C_i(T) - C_i(19 K)$, $i = 1, 2, 3, 4$. The relative values of the cumulants of the real distribution $\delta C_1^*$ were obtained by a standard procedure, assuming a mean free path $\lambda = 9 \pm 3$ Å[8].

(b) Non-linear fit of theoretical spectra, calculated by the FEFF6 code [9], to the experimental spectra, using the Artemis graphical interface of FEFFIT [10]. The values of $E_0$ and $S_0^2$ were left free in a first trial analysis; average values were then calculated and maintained fixed in subsequent analyses.

The relative values of the first four cumulants (say their temperature dependences) determined by the two procedures (a) and (b) were in very good agreement.
The first EXAFS cumulant gives the expansion of the average inter-atomic distance (for
short, bond expansion) $\delta C_1^* = \delta \langle r \rangle$, which is compared in Figure 2 with the expansion $\delta R_c$ of
the distance between average positions, proportional to the lattice expansion determined from
Bragg diffraction. The bond expansion is positive over the entire temperature range.

From the difference $\delta C_1^* - \delta R_c$ one can calculate the temperature dependence of the
perpendicular MSRD $\langle \Delta u_\perp^2 \rangle$ [8]. The temperature dependence of the parallel MSRD $\langle \Delta u_\parallel^2 \rangle$ is
directly given by the relative values of the second cumulant $\delta C_2^*$. Absolute values of both
parallel and perpendicular MSRDs have been obtained by fitting correlated Einstein models to
their relative values [11]; the result is shown in Figure 3. The large difference between
$\langle \Delta u_\perp^2 \rangle / 2$ and $\langle \Delta u_\parallel^2 \rangle$ is a clear indication of the anisotropy of relative vibrations.

![Figure 2. Cd–Te expansion from EXAFS compared with the expansion from Bragg diffraction.](image1)

![Figure 3. Temperature dependence of the parallel MSRD $\langle \Delta u_\parallel^2 \rangle$ and of the halved perpendicular MSRD $\langle \Delta u_\perp^2 \rangle / 2$.](image2)

4. Discussion

The main properties measured in CdTe – positive nearest-neighbours bond expansion and
anisotropy of MSRDs – are shared by all other NTE materials up to now studied by EXAFS. A
deeper insight can be gained by a comparison with the results previously obtained for Ge [5]
and CuCl [6]. The values of the parameters used for the comparison are listed in Table 1.

The linear coefficient of lattice thermal expansion at low temperatures, $\alpha_{\text{low}}$, can be considered
as a measure of the strength of NTE; its absolute value increases when going from Ge to CdTe to
CuCl. The coefficient of bond thermal expansion measured by EXAFS, $\alpha_{\text{bond}}$, is always positive;
its average value increases when the NTE strength increases. The effective force constants $k_\parallel$
and $k_\perp$ are obtained from the Einstein frequencies $\nu$ best fitting the parallel and perpendicular
MSRDs, respectively: $k = 4\pi^2 \nu^2 \mu$ ($\mu$ is the reduced mass). Their values can be considered as
a measure of the effective resistance against stretching and bending, respectively, of the bond
between two nearest-neighbours atoms embedded in a crystal. The force constant $k_3$, evaluated
by best fitting a theoretical model [12] to the third cumulant, is a measure of the anharmonicity
of the effective pair potential. The ratio $C_3/C_2^{3/2}$ measures the distribution asymmetry.

The increase of $\alpha_{\text{bond}}$ in going from Ge to CdTe to CuCl is accompanied by the decrease of
both $k_\parallel$ and $|k_3|$ and by the increase of the asymmetry parameter $C_3/C_2^{3/2}$. The increase of
the difference between the positive bond expansion and the crystallographic expansion, again in going from Ge to CdTe to CuCl, is due to the increasing influence of normal modes with negative Gr"uneisen parameter. The effect of these modes reflects in the perpendicular MSRD, and is measured by the decreasing value of the force constant \( k_\perp \).

The strength of NTE is correlated also to the perpendicular to parallel anisotropy of relative atomic vibrations; a temperature-independent measure of the anisotropy is the ratio \( \xi = k_{||}/k_\perp \), which should be \( \xi = 1 \) for perfect isotropy \([3]\), and increases from 2.94 for Ge to 5.38 for CuCl; it is worth noting that the thermal ellipsoids of single atoms determined from the refinement of Bragg peaks in diamond-zincblende structures are isotropic for symmetry reasons.

**Table 1.** Comparison of three crystals with the diamond-zincblende structure. \( \alpha_{\text{low}} \) is the crystallographic linear thermal expansion coefficient at low temperature, \( \alpha_{\text{bond}} \) is the average coefficient of bond thermal expansion from EXAFS. \( k_{||} \) and \( k_\perp \) are the 2nd-order effective force constants, \( k_3 \) is the third order force constant, \( C_3/C_2^{3/2} \) measures the distribution asymmetry.

|        | \( \alpha_{\text{low}} \) (10^{-6}K^{-1}) | \( \alpha_{\text{bond}} \) (10^{-6}K^{-1}) | \( k_{||} \) (eV/\AA^2) | \( k_\perp \) (eV/\AA^2) | \( \xi = k_{||}/k_\perp \) | \( k_3 \) (eV/\AA^3) | \( C_3/C_2^{3/2} \) (at 300 K) |
|--------|------------------------------------------|------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Ge     | -0.05                                    | 8                                        | 8.5                  | 2.89                 | 2.94                 | -4.8                 | 0.15                 |
| CdTe   | -3                                       | 18                                       | 3.76                 | 0.9                  | 4.17                 | -2.05                | 0.25                 |
| CuCl   | -8                                       | 43                                       | 1.4                  | 0.26                 | 5.38                 | -1.2                 | 0.61                 |

5. Conclusions

The comparison of different crystals sharing the same structure confirms that a correlation can be established between some quantities measured by EXAFS and the NTE properties. CdTe, characterised by a relatively strong NTE and a relatively weak anharmonicity, is a promising candidate for further investigations, both in bulk and in nanostructured systems.

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