EXAFS parameters and VDOS in zincblende structures

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Abstract. The local dynamical behaviour of the tetrahedrally coordinated semiconductors Ge, CdTe and CuCl, affected by negative thermal expansion at low temperatures, has been recently investigated by EXAFS. Parallel and perpendicular first-shell mean square relative displacements (MSRDs) are here discussed in terms of correlation and anisotropy. The Einstein frequencies are compared with the vibrational densities of states (VDOS). For all considered systems, the perpendicular Einstein frequency is situated between the VDOS structures due to transverse and longitudinal acoustic modes, while the parallel frequency is situated between the VDOS structures due to longitudinal acoustic and optic modes.

1. Introduction
The parallel mean square relative displacement (MSRD) of nearest-neighbour atoms can be directly obtained from the analysis of the EXAFS signal [1]. The comparison of the nearest-neighbours bond thermal expansion measured by EXAFS with the lattice thermal expansion measured by Bragg diffraction gives information on the perpendicular MSRD [2]. The knowledge of both parallel and perpendicular MSRDs allows a deeper understanding of the local vibrational dynamics, in terms of correlation of vibrational motion and of anisotropy of relative thermal ellipsoids.

Three crystals with the diamond or zincblende structure, characterized by different ionicity values and different strength of low-temperature negative thermal expansion (NTE), have been recently investigated by EXAFS: Ge [3], CdTe [4] and CuCl [5]. The comparison shows that a correlation exists between the bond ionicity, the negative thermal expansion strength and a number of quantities measured by EXAFS, the stronger is the NTE, the larger are the positive bond expansion, the relative atomic vibrations perpendicular and parallel to the bond, as well as their anisotropy [4].

In this paper, the local dynamic properties of the three systems are further discussed and the Einstein frequencies of the parallel and perpendicular MSRDs are phenomenologically compared with the vibrational densities of states (VDOS).
2. MSRDS correlation and anisotropy

The main properties of the parallel and perpendicular thermal MSRDS $\langle \Delta u^2 \rangle_\parallel$ and $\langle \Delta u^2 \rangle_\perp$, respectively, can be synthesised by the frequency $\nu$ of the best-fitting correlated Einstein models

$$\langle \Delta u^2 \rangle_\parallel = \frac{h}{8\pi^2\mu_\parallel} \coth \left( \frac{h\nu_\parallel}{2kB_T} \right), \quad \langle \Delta u^2 \rangle_\perp = \frac{h}{4\pi^2\mu_\perp} \coth \left( \frac{h\nu_\perp}{2kB_T} \right).$$ (1)

The two models differ by a factor 2 because the perpendicular MSRD is defined as a 2-dimensional projection of the total MSRD on the plane perpendicular to the bond [6].

For all crystals here considered, the perpendicular MSRDS are significantly larger than twice the parallel MSRDs. Correspondingly, the perpendicular Einstein frequencies $\nu_\perp$ are smaller than the parallel frequencies $\nu_\parallel$ (Table 1, where the data for copper are shown for comparison). This difference corresponds to a stronger parallel than perpendicular correlation and gives rise to a non-negligible anisotropy of relative vibrations.

The extent of correlation can be measured by the dimensionless correlation parameters [7, 8]

$$\phi_\parallel = \frac{U^{(b)}_\parallel + U^{(a)}_\parallel - \langle \Delta u^2 \rangle_\parallel}{2 \left[ U^{(b)}_\parallel + U^{(a)}_\parallel \right]^{1/2}}, \quad \phi_\perp = \frac{U^{(b)}_\perp + U^{(a)}_\perp - \langle \Delta u^2 \rangle_\perp}{2 \left[ U^{(b)}_\perp + U^{(a)}_\perp \right]^{1/2}},$$ (2)

where $U_\parallel$ and $U_\perp$ are the uncorrelated MSDs of absorber and backscatterer atoms parallel and perpendicular to the bond direction, respectively, which can be calculated from the anisotropic displacement parameters (ADP) $U_{ij}$ measured by diffraction. The correlation parameters for copper and for the three diamond-zincblende structures here considered are listed in Table 1. The parallel and perpendicular correlations are very similar for copper, strongly different for Ge and still more different for CdTe and CuCl.

The parallel Einstein frequency $\nu_\parallel$ is connected to an effective bond-stretching force constant $k_\parallel = \mu(2\pi\nu_\parallel)^2$, where $\mu$ is the reduced mass. Similarly, the perpendicular Einstein frequency can be connected to an effective force constant $k_\perp = \mu(2\pi\nu_\perp)^2$. One should not confuse these effective force constants with the force constants of the Born-von Karman models of lattice dynamics [4]. The effective force constants (Table 1), being independent of masses, can be more suitable than the frequencies to compare different isostructural compounds. Actually, the frequency values $\nu = (k/\mu)^{1/2}/2\pi$ represent the response of the pair of atoms to the interaction force, and depend on the inertia, which is measured by the reduced mass. As is evident in Table 1, the effective force constants show a neat decreasing trend when passing from Ge to CdTe to CuCl, while the Einstein frequencies for CdTe and CuCl are nearly equal.

| Table 1. | Einstein frequencies $\nu$, correlation parameters $\phi$, effective force constants $k$ for parallel and perpendicular MSRDS, and anisotropy parameters $\xi = k_\parallel/k_\perp$. The data of Cu are shown for comparison. |
|----------|----------------|----------------|----------------|----------------|
|          | Cu  | Ge  | CdTe | CuCl |
| Einstein frequencies |       |     |      |      |
| $\nu_\parallel$ (THz) | 4.9  | 7.7  | 3.89  | 3.93  |
| $\nu_\perp$ (THz) | 4.6  | 4.6  | 1.83  | 1.66  |
| Correlation |       |     |      |      |
| $\phi_\parallel$ | 0.44 | 0.76 | 0.83  | 0.8   |
| $\phi_\perp$ | 0.42 | 0.31 | 0.19  | -0.2  |
| Force constants |       |     |      |      |
| $k_\parallel$ (eV/Å$^2$) | 3.2  | 8.5  | 3.71  | 1.4   |
| $k_\perp$ (eV/Å$^2$) | 2.6  | 2.9  | 0.81  | 0.26  |
| Anisotropy |       |     |      |      |
| $\xi = k_\parallel/k_\perp$ | 1.2  | 2.9  | 4.6   | 5.4   |
The perpendicular to parallel anisotropy of the nearest-neighbours relative vibrations can be measured by the ratio \( \langle \Delta u^2_\perp \rangle / 2 \langle \Delta u^2_\parallel \rangle \), which is generally temperature dependent. Fig. 1 (a) shows the ratios of the best-fitting perpendicular and parallel Einstein models for Ge, CdTe and CuCl. A temperature independent measure of anisotropy can be obtained by considering the high-temperature asymptotic behaviour of the Einstein models

\[
\xi = \frac{\langle \Delta u^2_\perp \rangle}{2 \langle \Delta u^2_\parallel \rangle} \rightarrow \frac{2k_B T/k_\perp}{2k_B T/k_\parallel} = \frac{k_\parallel}{k_\perp}. 
\tag{3}
\]

The ratio \( \xi = k_\parallel/k_\perp \) is equal to one for perfectly isotropic relative motion. For copper, \( \xi \) is nearly one; for the three diamond-zincblende crystals here considered, \( \xi \) is significantly larger than one: the ellipsoids of relative thermal displacements are disk-shaped. The value of \( \xi \) increases in going from Ge to CdTe to CuCl (Table 1), say increasing the ionicity. It is worth noting that the atomic thermal displacements measured by Bragg diffraction are isotropic for symmetry reasons.

The extent of the parallel and perpendicular force constants as well as the anisotropy of relative vibrations can be correlated to the strength of negative thermal expansion [4].

3. Comparison with the vibrational densities of states

The MSRDs depend on the contributions of all normal modes; for the parallel MSRDs [1]

\[
\langle \Delta u^2_\parallel \rangle = \frac{1}{N} \sum_{\vec{q},s} \langle |Q(\vec{q},s)|^2 \rangle \left( \left( \frac{\bar{w}_b(\vec{q},s)e^{i\vec{q} \cdot \vec{R}}}{\sqrt{m_b}} - \frac{\bar{w}_a(\vec{q},s)}{\sqrt{m_a}} \right) \cdot \vec{R} \right)^2 
\tag{4}
\]

where \( \vec{q} \) and \( s \) are mode wavevector and branch index, respectively.

Figure 1. (a) Perpendicular to parallel MSRD ratios \( \langle \Delta u^2_\perp \rangle / 2 \langle \Delta u^2_\parallel \rangle \) for Ge, CdTe and CuCl. (b) VDOS for Ge [9], CdTe [10] and CuCl [11]. The vertical arrows correspond to the Einstein frequencies best fitting the parallel and perpendicular MSRDs.
A reliable reproduction of parallel and perpendicular MSRDs requires a homogenous sampling of the first Brillouin Zone, taking into account the inter-cell phaseshifts of each mode as well as the mode eigenvectors, their phase relationships and their projection along the bond direction and in the perpendicular plane. The knowledge only of the VDOS is clearly insufficient to this purpose; nevertheless, interesting qualitative clues can be obtained from the comparison of the MSRDs Einstein frequencies and the VDOS.

The VDOS for Ge [9], CdTe [10] and CuCl [11] are shown in Fig. 1 (b). Three structures can be identified in the VDOS of the three crystals: a low-frequency structure due to the transverse acoustic (TA) modes, an intermediate structure due to the longitudinal acoustic (LA) modes and a high-frequency structure due to the optic modes.

The terms “longitudinal” and “transverse” of lattice dynamics are relative to the direction of the normal mode wavevectors \( \vec{q} \), which densely and isotropically fill up the first Brillouin zone, while the attributes “parallel” and “perpendicular” of MSRDs refer to the nearest-neighbour bonds, limited to the \( \langle 111 \rangle \) directions for the diamond-zincblende structures.

In spite of this non trivial difference, a neat correlation can be found between the Einstein frequencies of the MSRDs and the VDOS structures. For all crystals here considered: a) the perpendicular Einstein frequency \( \nu_\perp \) is situated between the VDOS structures due to the TA modes and the LA modes, respectively; b) the parallel Einstein frequency \( \nu_\parallel \) is situated between the VDOS structures due to the LA modes and the optic modes, respectively.

The contribution of normal modes to the MSRDs is inversely proportional to the square of the frequency, since \( \langle |Q(\vec{q}, s, t)|^2 \rangle = \langle E(\vec{q}, s) \rangle /\omega^2(\vec{q}, s) \). As a consequence, optic modes are relatively less important than acoustic modes.

4. Conclusions
The first-shell parallel and perpendicular MSRDs of Ge, CdTe and CuCl have been comparatively analyzed. When the ionicity of the system increases (from Ge to CdTe to CuCl), both parallel and perpendicular effective force constants decrease, the parallel correlation increases, the perpendicular correlation decreases and the perpendicular to parallel anisotropy increases.

A phenomenological correlation has been established between the Einstein frequencies of the parallel and perpendicular MSRDs and the VDOS structures due to TA, LA and optic modes for Ge, CdTe and CuCl.

Accurate dynamical calculations sampling the eigenfrequencies and the eigenvectors within the first Brillouin zone would help to quantitatively evaluate the contribution of the different vibrational modes to the parallel and perpendicular MSRDs.

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