

EXAFS studies of lattice dynamics and thermal expansion

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Accurate temperature-dependent EXAFS measurements can give original information on the correlation of thermal motion in crystals, not only along the bond direction (parallel Mean Square Relative Displacement, MSRD), but also within the perpendicular plane (perpendicular MSRD). This potential is demonstrated by the results obtained for copper and germanium, taken as model systems. Possible applications for investigating on the local origin of Negative Thermal Expansion are being supported by measurements on crystals with the cuprite structure.

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1 Introduction The acronym EXAFS (Extended X-ray-Absorption Fine-Structure) refers to the oscillations observed on the high-energy side of x-ray absorption edges in molecules and condensed systems [1]. EXAFS can be interpreted, within the framework of the time-dependent perturbation theory, as a final state effect due to the interaction of the photo-electron with the neighbouring atoms, the frequencies of oscillations being directly connected to inter-atomic distances. Selectivity of atomic species and insensitivity to long-range order make EXAFS a powerful probe of the local structure in disordered systems (glasses, random alloys, catalysts, proteins, etc.) Accurate temperature-dependent measurements can also give information on lattice dynamics of crystals, owing to EXAFS sensitivity to the correlation of atomic vibrations. The difference between the Debye-Waller factors of EXAFS and diffraction, quite early recognized [2], is due to the correlation *parallel* to the bond direction. The difference between the interatomic distances measured by EXAFS and diffraction, more recently evidenced [3], is due to the *perpendicular* relative vibrations. The sensitivity of EXAFS to the real expansion of selected atomic bonds and to the perpendicular correlation can be exploited to study the local behaviour of some crystals affected by macroscopic Negative Thermal Expansion (NTE).

In this paper, after a short account of basic concepts (Section 2), the results obtained for copper and germanium will be critically compared (Section 3). Section 4 will be dedicated to NTE and to some preliminary results on cuprite crystals. Conclusions will be drawn in Section 5.

2 EXAFS and lattice dynamics An EXAFS spectrum is the superposition of the contributions from different photo-electron scattering paths, originating from and ending at the absorbing atom. Single Scattering (SS) paths, corresponding to the first few coordination shells of the absorbing atom, are the most important. Multiple Scattering (MS) paths, although generally less important, cannot be neglected when accurate results are sought. Owing to thermal motion, the EXAFS signal of one coordination shell samples a one-dimensional distribution $\rho(r)$ of instantaneous interatomic distances r . For moderately disordered systems, phase and amplitude of the EXAFS signal can be parametrised in terms of the first odd and even cumulants, respectively, of the distribution $\rho(r)$ [4, 5]. First cumulant $C_1^* = \langle r \rangle$ and second cumulant

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$C_2^* = \langle (r - \langle r \rangle)^2 \rangle$ correspond to mean and variance of the distribution, respectively, while the third cumulant $C_3^* = \langle (r - \langle r \rangle)^3 \rangle$ measures its asymmetry. The typical outcome of an EXAFS experiment aiming at dynamical studies consists in the values of the first cumulants as a function of temperature.

Let R_c be the distance between the average positions of the central atom and one of its neighbours. The instantaneous relative thermal displacement of the two atoms, $\Delta \mathbf{u} = \mathbf{u}_j - \mathbf{u}_0$, can be decomposed into its projections Δu_{\parallel} and Δu_{\perp} along the bond direction and in the perpendicular plane, respectively ($\Delta u^2 = \Delta u_{\parallel}^2 + \Delta u_{\perp}^2$). To good approximation, the second cumulant measures the *parallel* MSRD (Mean Square Relative Displacement) [2]:

$$C_2^* = \langle \Delta u_{\parallel}^2 \rangle = \langle (\hat{\mathbf{R}}_c \cdot \mathbf{u}_j)^2 \rangle + \langle (\hat{\mathbf{R}}_c \cdot \mathbf{u}_0)^2 \rangle - \langle (\hat{\mathbf{R}}_c \cdot \mathbf{u}_j)(\hat{\mathbf{R}}_c \cdot \mathbf{u}_0) \rangle. \quad (1)$$

The first two terms on the right side are the uncorrelated MSDs, which can be obtained from diffraction, while the third term is the parallel Displacement Correlation Function (DCF).

One can also show that the average distance C_1^* , measured by EXAFS, is larger than the distance R_c between average positions, measured by diffraction, as effect of perpendicular relative motion [5]:

$$C_1^* \simeq R_c + \langle \Delta u_{\perp}^2 \rangle / 2R_c. \quad (2)$$

Accordingly, the thermal expansion measured by EXAFS is larger than the expansion measured by diffraction. Conversely, by suitably inverting Eq. 2, one can obtain the *perpendicular* MSRD $\langle \Delta u_{\perp}^2 \rangle$.

3 Local dynamics in copper and germanium The potential of EXAFS as a probe of crystal dynamics has been tested on copper [6] and germanium [7]. The signal of the first coordination shell could be satisfactorily singled out and interpreted within the SS approximation for both systems: accurate values of the first three cumulants could be obtained, and both parallel and perpendicular MSRDs could be evaluated (Figs. 1 and 2). The 1st-shell EXAFS results (parallel and perpendicular MSRDs and 3rd cumulant) were in good agreement with theoretical calculations both for copper [8] and germanium [9]. The outer shell signals could not be completely separated, and were moreover contaminated by MS contributions. As a consequence, their analysis was much more difficult, and reliable accurate values could be, up to now, obtained only for the parallel MSRDs.

3.1 Parallel MSRD As a general rule, the correlation term DCF in Eq. (1) progressively weakens when passing from the first coordination shell to the outer shells, and goes to zero at large distances. Relevant information can be gathered by fitting a Debye correlated model [2] to the experimental MSRD values. For copper, where only acoustic modes are present, the EXAFS Debye temperatures θ_i^{\parallel} of the different shells are in reasonable agreement with the ones from diffraction and specific heat measurements (Tab. 1). A slightly lower value is however found for the second shell, corresponding to a weaker correlation along the $\langle 100 \rangle$ direction, in agreement with recent dynamical calculations on fcc metals [10]. In the case of germanium, where three optical branches are present, significantly different Debye temperatures were obtained for each coordination shell (Tab. 1) [7, 11]. In particular, the high θ_1^{\parallel} value obtained for the first shell indicates a much stronger correlation between nearest-neighbours than expected for a Debye crystal. The EXAFS Debye temperatures decrease when the distance increases, and converge towards the diffraction value $\theta_M = 290$ K.

3.2 Perpendicular MSRD For a perfectly isotropic system (like a Debye crystal), the perpendicular MSRD (projection on a plane) should be exactly twice the parallel MSRD (projection along one direction). Actually, in the case of copper (Fig. 1, bottom) the perpendicular MSRD is slightly larger: the Debye temperature (301 K) is smaller than for the parallel MSRD, and the ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle$ is about 2.7 at high temperature. In the case of Germanium, the perpendicular to parallel anisotropy of relative vibrations is much larger, the ratio γ attaining the value 6 at high temperature [7].

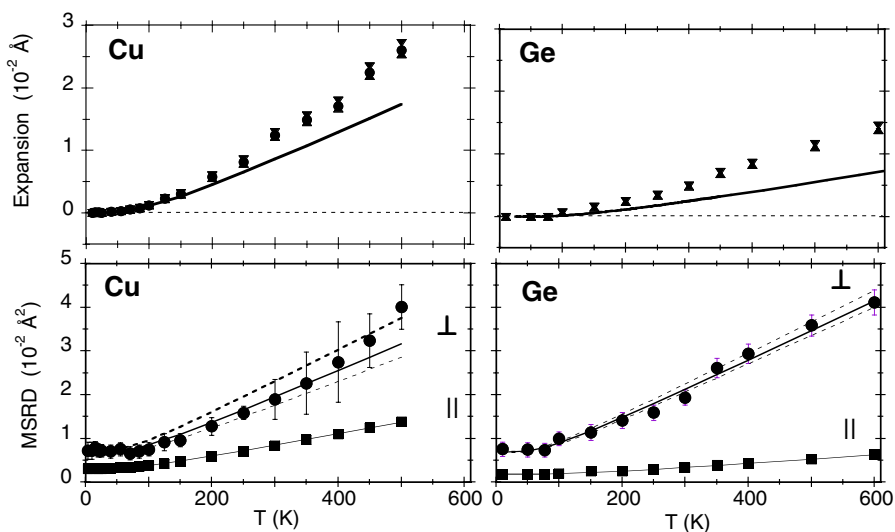


Fig. 1 Results for the first coordination shell of Copper (left) and Germanium (right). Top panels: EXAFS (symbols) and crystallographic (continuous lines) thermal expansions. Bottom panels: parallel (squares) and perpendicular (circles) MSRDS; the continuous lines are best fitting Debye models.

Table 1 Debye temperatures θ_i (in kelvin) best fitting the MSRDS of the first coordination shells of Copper ($i=1,2,3,4$) and Germanium ($i=1,2,3$). The apices \perp and \parallel refer to perpendicular and parallel MSRDS, respectively. θ_M and θ_D are diffraction and specific heat Debye temperatures, respectively.

	θ_1^\perp	θ_1^\parallel	θ_2^\parallel	θ_3^\parallel	θ_4^\parallel	θ_M	θ_D
Cu	301	328	291	322	322	312	315
Ge	234	437	312	290		290	354

3.3 Asymmetry of the distance distribution The third cumulant measures the asymmetry of the distribution of distances. It can be connected to the force constants of an effective one-dimensional pair potential through a perturbative quantum approach [12]. The introduction of the third cumulant in the EXAFS analysis is necessary to obtain accurate values of distance (first cumulant); the agreement of its temperature dependence with the quantum perturbative model (proportional to T^2 in the high temperature classical approximation) represents an important self-consistency test of data analysis (Fig. 2). Besides, the reproduction of the EXAFS third cumulant is an original benchmark for dynamical calculations including anharmonicity [8, 9].

4 Negative thermal expansion systems In many systems, negative thermal expansion (NTE) is observed in temperature ranges of different extension, and attributed to geometrical effects of low-frequency vibrations perpendicular to some inter-atomic links: guitar string effect in simple crystals with diamond or zinc-blende structure, rigid unit modes (RUM) in framework structures, etc. These vibrations induce an overall contraction, which opposes and sometimes overcomes the positive expansion due to the potential anharmonicity [13]. The possibility of measuring the real expansion of selected bonds and the perpendicular MSRDS, offered by EXAFS, can represent an effective tool for directly monitoring the local behaviour of NTE materials, complementary to Bragg diffraction and alternative to the less accurate and less simple analysis of thermal diffuse scattering in total scattering experiments. The large perpendicular/parallel anisotropy found for the first-shell MSRDS of germanium (Fig. 1) can be reasonably connected to its

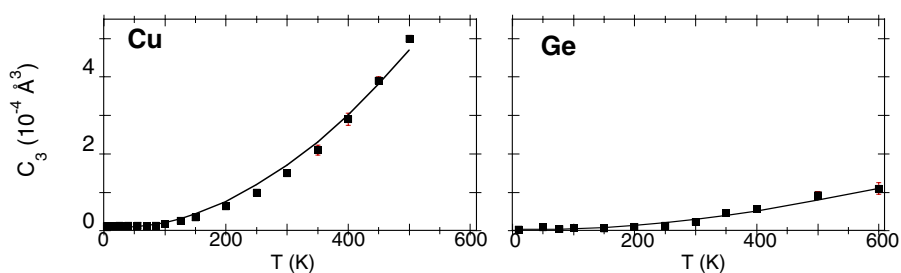


Fig. 2 Third EXAFS cumulant of the first coordination shell of Copper (left) and Germanium (right). The continuous lines are best fitting quantum perturbative models.

low-temperature NTE, which is however probably too weak to be directly detected by the first EXAFS cumulant. More effective and promising is an EXAFS study presently under way on Cu_2O and Ag_2O . The two crystals share the same cuprite framework structure, formed by two inter-penetrating networks of corner-sharing M_4O tetrahedra ($\text{M} = \text{Cu}, \text{Ag}$), and are affected by macroscopic NTE over extended temperature intervals [14]. The first results on Ag_2O [15] have revealed that the first-shell Ag-O distance regularly expands, while the second-shell Ag-Ag distance contracts; the first-shell perpendicular MSRD is much larger than the parallel MSRD, and comparable to the second-shell parallel MSRD, confirming that NTE is connected to vibrations perpendicular to the O-Ag-O chain, but also suggesting the inadequacy of a RUM model. Further work is in progress, focussing on the difference between the two compounds and on a deeper understanding of the 2nd-shell behaviour.

5 Conclusions From accurate temperature dependent EXAFS measurements on crystals, it is possible to obtain the parallel MSRD of a few coordination shells, and, for the first shell, also the perpendicular MSRD. The reproduction of both MSRDs represents an effective test of the phase relationships of calculated eigenvectors of the dynamical matrix. The reproduction of the third cumulant is a test for anharmonic calculations. The sensitivity of EXAFS to expansion of selected bonds and perpendicular MSRD can be exploited to study the local behaviour of systems affected by negative thermal expansion.

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