

EXAFS studies of local thermal expansion

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Abstract. Original information on local thermal expansion can be obtained through a cumulant analysis of EXAFS. The different sensitivity to correlation of the first and third EXAFS cumulants, and their comparison with crystallographic distance, can help in disentangling the contribution of potential anharmonicity to thermal expansion from geometrical effects. These possibilities are illustrated by recent experimental results. In germanium, the perpendicular Mean Square Relative Displacement has been obtained from EXAFS. In Ag_2O , whose framework structure exhibits negative thermal expansion, a positive expansion of the Ag–O bond has been measured and the deformation of the Ag_4O structural units monitored.

INTRODUCTION

Thermal expansion in crystals is basically due to the anharmonicity of the crystal potential. Geometrical effects, independent of anharmonicity, can also be relevant, for example in accounting for the difference between average interatomic distance and distance between average atomic positions [1]. As a further example, the Negative Thermal Expansion (NTE) observed in some framework structures, like ZrW_2O_8 , is often attributed to a network folding induced by low-frequency Rigid Unit Modes (RUM) [2, 3]. EXAFS oscillations are directly related to inter-atomic distance, so that temperature-dependent EXAFS can give peculiar information on local thermal expansion, in particular contributing to disentangle anharmonicity and geometrical effects.

Thermal vibrations spread atomic positions into three-dimensional distributions, and EXAFS spectra result from one-dimensional distributions of distances. In case of moderate disorder, a careful analysis of EXAFS allows to recover the basic properties of the distance distributions, parametrised in terms of lowest-order cumulants [4, 5]. The first cumulant directly measures the average distance; its comparison with the distance between average positions, measured by Bragg diffraction, gives original information on the correlation of vibrational motion. The third cumulant measures the asymmetry of the distribution, and is directly connected to the anharmonicity of the one-dimensional effective pair potential. The difference between thermal expansions measured by the first and the third cumulant in several systems has been explained in terms of a rigid shift of the effective pair potential [6, 7, 8]. A complete understanding of the relations between EXAFS cumulants and structural and dynamical properties of crystals, as well as of the relation between effective pair potential and crystal potential, is however still lacking.

This paper is a contribution to the advancement in these topics. A short account will be given of cumulants and their use for thermal expansion studies, updating and extending previous treatments [1, 5]. The still rather unexplored possibilities offered by EXAFS in this field will be illustrated by two experimental examples. In the case of the first shell of germanium, the Mean Square Relative Displacement (MSRD) perpendicular to the bond direction was for the first time obtained from EXAFS spectra [7]. In the case of Ag_2O , which is characterised by a negative thermal expansion (NTE) of the lattice parameter from 10 to 450 K, the average Ag-O nearest-neighbours distance expands upon heating, while the Ag-Ag next-nearest-neighbours distance contracts. The comparison between 1st and 3rd cumulant allows to monitor the distortion of the basic Ag_4O tetrahedral units, giving original insights on the local behaviour of a NTE solid [9].

THEORY

Let us consider the relations connecting the leading cumulants C_i^* of the one-dimensional distribution of distances $\rho(r, T)$ to the three-dimensional structural and dynamical properties of crystals. It is convenient to introduce the inter-atomic distance R_0 for an ideal classical state of absolute rest, and to decompose the instantaneous relative displacement $\Delta\vec{u}$ due to thermal motion into its projections Δu_{\parallel} and Δu_{\perp} along the bond direction and in the perpendicular plane, respectively. The instantaneous bond distance is then, to first approximation [1],

$$r = \simeq R_0 + \Delta u_{\parallel} + \Delta u_{\perp}^2/2R_0. \quad (1)$$

The distribution $\rho(r, T)$ can be connected to an effective pair potential V_e . In the classical approximation

$$\rho(r, T) = \exp[-\beta V_e(r)] \left\{ \int \exp[-\beta V_e(r)] dr \right\}^{-1}. \quad (2)$$

Relying on the quasi-harmonic approximation, the parallel relative displacement in Eq. (1) can be decomposed as $\Delta u_{\parallel} = a + (\Delta u_{\parallel})_h$, where a is the thermal expansion due to the anharmonicity of the effective potential V_e , while $(\Delta u_{\parallel})_h$ is a purely harmonic contribution.

The first EXAFS cumulant is the average distance, $C_1^* = \langle r \rangle$. We want now to clarify its relation with both the anharmonic thermal expansion a and the crystallographic distance R_c measured by Bragg diffraction. Let us consider two limiting cases. For a purely *translational* relative motion, the three-dimensional harmonic distribution of relative distances is an ellipsoid, so that $\langle \Delta u_{\parallel} \rangle_h = 0$, and

$$C_1^* \simeq R_0 + a + \langle \Delta u_{\perp}^2 \rangle / 2R_0; \quad R_c = R_0 + a. \quad (3)$$

For a purely *librational* relative motion, the ellipsoid is curved along a spherical surface, so that $\langle \Delta u_{\parallel} \rangle_h \simeq -\langle \Delta u_{\perp}^2 \rangle / 2R_0$, and

$$C_1^* = R_0 + a; \quad R_c \simeq R_0 + a - \langle \Delta u_{\perp}^2 \rangle / 2R_0. \quad (4)$$

It is worth noting that a and $\langle \Delta u_{\perp}^2 \rangle$ have finite values at zero kelvin, reflecting the effect of zero point motion. Relative translational motion exhaustively describes the behaviour of crystals with simple, highly symmetrical structures. Relative librational motion characterizes the dynamics of quasi-rigid units in molecular crystals and framework structures [10]. In both cases of translation and libration, the average distance measured by EXAFS is larger than the distance between average positions measured by Bragg diffraction, due to the effect of perpendicular MSR D:

$$C_1^* \simeq R_c + \langle \Delta u_{\perp}^2 \rangle / 2R_0. \quad (5)$$

The 2nd cumulant C_2^* measures the width of the distribution $\rho(r, T)$ and depends on the 2nd order force constant k_0 of the effective potential V_e ; to a good approximation, $C_2^* \simeq \langle \Delta u_{\parallel}^2 \rangle$. The third cumulant measures the asymmetry of $\rho(r, T)$, and depends on the 3rd order force constant k_3 of V_e . Frenkel and Rehr [11] have shown, on the basis of a perturbative quantum approach in quasi-harmonic approximation, that the quantity a appearing in Eqs. (3) and 4) can be expressed as

$$a = -3k_3 C_2^* / k_0, \quad (6)$$

where k_0 and k_3 can be obtained by fitting suitable models to the temperature dependence of the 2nd and 3rd EXAFS cumulants.

EXAFS is sensitive to an effective distribution of distances [4]. The difference between cumulants C_i^* and C_i of the real and effective distributions, respectively, is always relevant for the first one,

$$C_1^* \simeq C_1 + (2C_2/C_1)(1 + C_1/\lambda) \quad (7)$$

where λ is the photoelectron mean free path [12]. For higher order cumulants the difference is generally not considered, although in some cases it could be not negligible [5]. Actually, only a finite number of polynomial coefficients \tilde{C}_i can be derived from EXAFS analysis. The problem of the accuracy by which the polynomial coefficients \tilde{C}_n approximate the cumulants C_n has been addressed elsewhere [13, 5]. We only remember here that accurate relative values of interatomic distances, as required by thermal expansion studies, can be obtained by the ratio method, when multiple scattering effects are negligible.

GERMANIUM

In germanium only translational relative motion is expected between nearest-neighbours, and Eq. (3) should hold. The results of the 1st-shell EXAFS analysis [7] are summarised in Fig. 1. The crystallographic thermal expansion δR_c , calculated from the available literature [14], is represented by the continuous line. The temperature dependence of the quantity a , calculated from experimental EXAFS data according to Eq. (6), is shown as crossed squares. The expansion at zero kelvin, due to the zero point motion and amounting to about 0.003 Å, has been here subtracted. The good

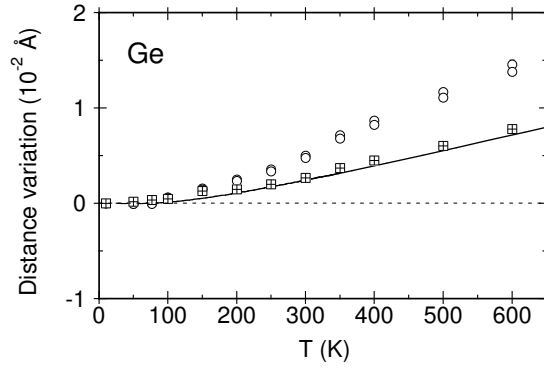


FIGURE 1. Temperature dependence of the first EXAFS cumulants C_1^* for the 1st-shell of germanium (open circles): upper and lower values correspond to a mean free path λ of 6 or 12 Å, respectively. The crossed squares refer to the anharmonicity parameter a , defined in the text and determined from the third EXAFS cumulants.

agreement between δa and the crystallographic thermal expansion δR_c suggests that the anharmonicity of the effective potential V_e reflects the anharmonicity of the crystal potential. The temperature dependence of the first EXAFS cumulant C_1^* is shown as open circles. Slightly different values are obtained by assuming different λ values in Eq. (5). The most striking feature is the difference between the EXAFS δC_1^* values and the crystallographic δR_c values, which, according to Eq. (3), is due to the perpendicular MSRD. This difference was exploited in Ref. [7] to calculate $\langle \Delta u_{\perp}^2 \rangle$ as a function of temperature. The values so obtained have been recently reproduced by D. Strauch and coworkers in Regensburg through ab initio dynamical calculations [15]. The ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle$, which is about 6 at high temperatures, is in good agreement also with the calculations made for silicon using an adiabatic bond charge model [16].

The results obtained for germanium are consistent with the following phenomenological picture. According to Eq. (3), the thermal expansion δC_1^* of the average distance is the sum of two effects: one, measured by δa , depends on the asymmetric shape, assumed temperature independent, of the potential V_e ; the other depends on the increase of the perpendicular MSRD, and is connected with a positive rigid shift of V_e with temperature. This picture has been confirmed by recent simulations: the relative motion perpendicular to the bond induces a shift of the effective potential, without significantly affecting its shape [5].

SILVER OXIDE

Silver oxide Ag_2O shares with copper oxide Cu_2O the *cuprite* structure. Each Ag atom is linearly coordinated to two O atoms, and each O atom is tetrahedrally coordinated to four Ag atoms. The structure can be also described as a framework of two interpenetrating but independent networks of corner-sharing Ag_4O tetrahedra [17]. NTE of the lattice parameter extending over large temperature ranges is frequently observed in framework structures [2], and has actually been measured also in Ag_2O from 10 to 450 K [18].

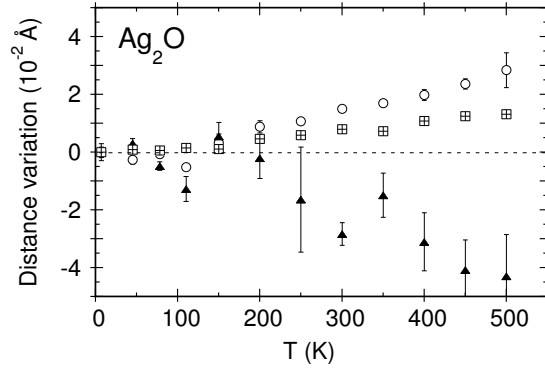


FIGURE 2. Temperature dependence of the first EXAFS cumulants C_1^* for the 1st-shell Ag–O (open circles) and 2nd-shell Ag–Ag (triangles). The crossed squares refer to the 1st-shell anharmonicity parameter a , defined in the text and determined from the third EXAFS cumulants.

The thermal expansion of framework structures results from the competition between a positive contribution of the potential anharmonicity and a negative contribution which is often attributed to a network folding induced by low frequency Rigid Unit Modes (RUM) [3]. To test RUM theories, it is important to directly measure the thermal expansion of nearest-neighbour bonds and the degree of rigidity of corner-sharing basic units. To this aim, EXAFS measurements have been performed at the K edge of silver in Ag_2O , in the temperature range from 7 to 500 K, at the Gilda beamline (ESRF, Grenoble). The main results are summarized in Fig. 2. The next-nearest-neighbours Ag–Ag distance decreases with temperature, in qualitative agreement with the lattice parameter NTE. The nearest-neighbours Ag–O distance on the contrary increases. This behaviour is consistent with the positive thermal expansion of the rather rigid nearest-neighbour bond with oxygen found in other framework structures affected by lattice parameter NTE [19].

Let us now focalise our attention on the first-shell Ag–O distance. A direct comparison of the average distance δC_1^* with the distance between average atomic positions δR_c cannot be done in this case, since no experimental data from diffraction are still available. The presence of two very different atomic species and the rather complex framework structure prevents from simply scaling the lattice parameter thermal expansion to the first-shell distance, as was done for germanium. It is then impossible to obtain $\langle \Delta u_{\perp}^2 \rangle$ by inversion of Eq. (5). Further information can be obtained by calculating the quantity a from the experimental 2nd and 3rd cumulants, according to Eq. (6). The resulting δa values are shown in Fig. 2 as crossed squares. The contribution of zero point vibrations, here subtracted, amounted to about 0.01 Å. According to Eq. (4), for a purely librational motion, as would be expected for perfectly rigid tetrahedral Ag_4O units, $\delta C_1^* = \delta a$. The discrepancy between δC_1^* and δa indicates that the nearest-neighbour relative motion is not purely librational, but contains a significant translational contribution. By properly inverting Eq. (3), one can recover the values $\langle \Delta u_{\perp}^2 \rangle_{\text{tr}}$, where “tr” indicates the translational contribution to the total perpendicular MSR \overline{D} .

The ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle_{\text{tr}} / \langle \Delta u_{\parallel}^2 \rangle$ is about 9 at high temperatures (it should be 2 for parallel-perpendicular isotropy, and is 6 for the 1st shell of germanium). The high value of γ indicates that the Ag–O bond, which is rather stiff with respect to stretching, is

much looser with respect to bending. This result is consistent with the high values found for the 2nd-shell parallel MSRD, and with diffraction measurements on Cu_2O [20]. The low-frequency modes responsible for the bond bending monitored by EXAFS cannot be identified with RUMs; the translational character of the perpendicular MSRD is instead a clear indication of a distortion of the Ag_4O tetrahedra.

CONCLUSIONS

Temperature dependent EXAFS measurements allow to directly measure the thermal expansion of nearest-neighbours bonds. The comparison between first and third cumulants and with Bragg diffraction results gives further information on the geometrical contribution to thermal expansion. These properties can be exploited to gain a deeper insight on local dynamical properties, in particular on correlation of vibrational motion. In the case of NTE framework structures, one can also monitor the degree of distortion of the basic structural units.

A generalisation of the results presented in this paper is however far from trivial, and requires further experimental work on different systems. As a matter of fact, other more subtle phenomena can influence EXAFS. For example, evidence has been found in AgI and CuBr of a negative shift of the effective pair potential at increasing temperature [6, 21]; the shift has been tentatively attributed to cluster-induced local distortions [8]. Besides, an accurate treatment of coordination shells beyond the first one is still difficult.

REFERENCES

1. Fornasini, P., *J. Phys.: Condens. Matter*, **13**, 7859–7872 (2001).
2. Evans, J. S. O., *J. Chem. Soc., Dalton Trans.*, **19**, 3317–3326 (1999).
3. Heine, V., Welche, P. R. L., and Dove, M. T., *J. Am. Ceram. Soc.*, **82**, 1793–1802 (1999).
4. Bunker, G., *Nucl. Instrum. Methods*, **207**, 437–444 (1983).
5. Fornasini, P., Monti, F., and Sanson, A., *J. Synchrotron Rad.*, **8**, 1214–1220 (2001).
6. Dalba, G., Fornasini, P., and Rocca, F., *Phys. Rev. B*, **52**, 149–157 (1995).
7. Dalba, G., Fornasini, P., Grisenti, R., and Purans, J., *Phys. Rev. Lett.*, **21**, 4240–4243 (1995).
8. Ishii, T., *J. Phys. Soc. Jpn.*, **70**, 159–166 (2001).
9. a Beccara, S., Dalba, G., Fornasini, P., Grisenti, R., Sanson, A., and Rocca, F., Local thermal expansion in cuprite structure: the case of silver oxide. (2002), submitted.
10. Willis, B. T. M., and Pryor, A. W., *Thermal Vibrations in Crystallography*, Cambridge University Press, 1975.
11. Frenkel, A. I., and Rehr, J. J., *Phys. Rev. B*, **48**, 585–588 (1993).
12. Freund, J., Ingalls, R., and Crozier, E. D., *Phys. Rev. B*, **39**, 12537–12547 (1989).
13. Dalba, G., Fornasini, P., and Rocca, F., *Phys. Rev. B*, **47**, 8502–8514 (1993).
14. Touloukian, Y. S., Kirby, R. K., Taylor, R. E., and Desai, P. D., *Thermophysical Properties of matter*, vol. 13, Plenum, New York, 1977.
15. Birner, G., Strauch, D., and Pavone, P. (2001), private commun.
16. Nielsen, O. H., and Weber, W., *J. Phys. C: Solid St. Phys.*, **13**, 2449–2460 (1980).
17. Zuo, J., Kim, M., O’Keeffe, M., and Spence, J., *Nature*, **401**, 49–52 (1999).
18. Artioli, G., and Dapiaggi, M. (2002), private commun.
19. Tucker, M. G., Dove, M. T., and Keen, D. A., *J. Phys.: Condens. Matter*, **12**, L425–431 (2000).
20. Lippman, T., and Schneider, J. R., *J. Appl. Cryst.*, **33**, 156–167 (2000).
21. Kamishima, O., Ishii, T., Maeda, H., and Hashino, S., *Solid St. Commun.*, **103**, 141–144 (1997).