Local lattice dynamics and negative thermal expansion in crystals

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Abstract. The investigations on the origin of negative thermal expansion (NTE) in crystals can greatly benefit from the joint use of Bragg diffraction and extended x-ray absorption fine structure (EXAFS). In this paper, the relative merits of the two techniques are critically discussed, and recent results on CuCl (zincblende structure) and Cu\(_2\)O and Ag\(_2\)O (cuprite structure) are compared. The tension effect giving rise to NTE can be correlated to the anisotropy of the mean square relative displacements.

1. Introduction
Negative thermal expansion (NTE) affects several simple crystals, like Si, Ge and CuCl, in restricted low-temperature intervals [1]. The macroscopic expansion is the result of a competition between a positive contribution due to a bond stretching effect and a negative contribution due to a tension effect [2]. In zincblende structures, like CuCl, the tension effect prevails at low temperatures, and is progressively overcome by the stretching effect when temperature grows up [3]. The discovery that ZrW\(_2\)O\(_8\) undergoes NTE in an extended temperature interval [4] has renewed the interest for NTE. ZrW\(_2\)O\(_8\), whose structure is composed by WO\(_4\) tetrahedra and ZrO\(_6\) octahedra joined at the corners, has been extensively studied as the archetypical NTE framework structure. NTE has been attributed to the effect of low-frequency rigid unit modes (RUM), that cause rigid rotations of the basic polyhedral units [5]. A connection between RUMs and NTE cannot however be established for all framework structures [6]. Among the framework structures undergoing NTE, particularly simple are Cu\(_2\)O and Ag\(_2\)O [7], which share the cuprite structure, made up by two interpenetrating networks of corner sharing undistorted M\(_4\)O tetrahedra (M = Cu, Ag). Strong NTE is exhibited also by Zn(CN)\(_2\) [8], whose structure can be obtained from the cuprite structure by substituting Zn for O and CN for M.

A comparison between several NTE compounds is shown in Fig. 1. Two characteristics can be stressed: 

- a) The framework structures of ZrW\(_2\)O\(_8\), Zn(CN)\(_2\) and Ag\(_2\)O undergo NTE within the full explored temperature interval, indicating that the tension effect always prevails on the stretching effect: Cu\(_2\)O, in spite of having the same structure of Ag\(_2\)O, exhibits a behaviour similar to the zincblende CuCl, the tension effect prevailing only in a limited low-temperature interval.
- b) The low-temperature NTE is stronger in the zincblende CuCl, where no polyhedral
rigid units can be defined, than in the framework structure Cu$_2$O. These characteristics suggest that a deeper understanding of NTE could be obtained by a comparative study of framework and zincblende structures. A common feature of NTE materials, independent of the possible presence of polyhedral RUMs, seems to be the presence of strong vibrations perpendicular to some interatomic bonds. A significant contribution to understanding the origin of NTE can be obtained by comparing the thermal expansions and the thermal factors measured by Bragg diffraction and by extended x-ray absorption fine structure (EXAFS), thanks to the different sensitivity of the two techniques to the correlation of atomic motion.

In Section 2, a basic account of the differences between EXAFS and diffraction is given. In Section 3, some recent experimental results are discussed. Section 4 is dedicated to conclusions.

![Figure 1. Relative change in lattice parameter for different crystals: CuCl (●) [3], Cu$_2$O (○) [7], Ag$_2$O (□) [7], ZrW$_2$O$_8$ (- - - -) [4], Zn(CN)$_2$ (——) [8].](image)

2. EXAFS versus Bragg diffraction

In a diffraction experiment, an x-ray or neutron plane wave impinges on a relatively large number of atoms; the Bragg peaks reflect the long-range symmetry of the crystal. In an EXAFS experiment, the structural probe is a photoelectron emitted as a spherical wave by the atom that absorbs an x-ray photon; because of the limited range of the photoelectron, an EXAFS spectrum only gives local information, and is strongly affected by correlation. As a consequence, the structural and dynamical parameters measured by Bragg diffraction and EXAFS are intrinsically different [9, 10, 11]. From Bragg diffraction experiments, one can in principle obtain the distance $R = |\langle \mathbf{r}_2 \rangle - \langle \mathbf{r}_1 \rangle|$ between the average positions of any two atoms, as well as the anisotropic displacement parameters (ADP) $U_{ij}$ of single atoms. From the ADPs, the absolute mean square displacements (MSD) along selected directions can be calculated [12]; in particular, we are here interested in the MSDs parallel and perpendicular to the direction of inter-atomic bonds, $U_{||}$ and $U_{\perp}$ respectively. An EXAFS spectrum samples the one-dimensional distribution of interatomic distances within a few coordination shells of the absorbing atom. Very accurate information can be obtained concerning the nearest-neighbours distance distribution (first coordination shell). From the quantitative analysis, one can directly obtain the thermal expansion of the average distance $\langle \mathbf{r} \rangle = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$, as well as the mean square relative displacement of absorber and backscatterer atoms along the bond direction $\langle \Delta u_{||}^2 \rangle$ (parallel MSRD) [9], defined as

$$
\langle \Delta u_{||}^2 \rangle = \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_a)^2 \rangle + \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_b)^2 \rangle - 2\langle \hat{\mathbf{R}} \cdot \mathbf{u}_a \rangle \langle \hat{\mathbf{R}} \cdot \mathbf{u}_b \rangle,
$$

where $\mathbf{u}_a$ and $\mathbf{u}_b$ are the instantaneous displacements of the absorber and backscatterer atoms, respectively, and $\Delta \mathbf{u} = \mathbf{u}_b - \mathbf{u}_a$. The first two terms on the right-hand side correspond to the uncorrelated MSDs along the bond direction measured by diffraction, $U_{||}^a = \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_a)^2 \rangle$ and $U_{||}^b = \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_b)^2 \rangle$. The last term in (1) is the parallel correlation function. The temperature
dependence of the parallel MSRD can be connected to an effective bond-stretching force constant $k_0$, that measures the stiffness of the $a$–$b$ bond [9].

The average distance $\langle r \rangle = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$ measured by EXAFS and the distance between average positions measured by diffraction $R = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$ are connected through the equation

$$\langle r \rangle = R + \langle \Delta u^2_\perp \rangle / 2R,$$

where $\langle \Delta u^2_\perp \rangle$ is the perpendicular MSRD, say the projection of the total MSRD in the plane normal to the bond direction. Since $\langle \Delta u^2_\perp \rangle$ is positive and grows up with temperature, the EXAFS distance is larger than the crystallographic distance, and the thermal expansion measured by EXAFS is larger than the crystallographic thermal expansion. Comparing EXAFS and diffraction results, one can estimate the perpendicular MSRDs by inversion of Eq. (2) [9].

The parallel MSRD $\langle \Delta u^2_\parallel \rangle$ and the perpendicular MSRD divided by two, $\langle \Delta u^2_\perp \rangle / 2$, can be compared with the sum of the parallel and perpendicular MSDs, $U_\parallel$ and $U_\perp$, respectively, of absorber and backscatterer atoms. In both parallel and perpendicular cases, the difference between the sum of the MSRDs of absorber and backscatterer atoms and the MSRD is due to correlation. The actual extent of correlation cannot be obtained solely from diffraction measurements; the lower and upper bounds to correlation, corresponding to a perfectly in phase and perfectly out of phase motion, respectively, can however be obtained from the MSDs [13, 10].

3. Experimental results

Let us now summarize and compare the results recently obtained for the nearest-neighbours distances Cu–O in Cu$_2$O and Ag–O in Ag$_2$O [10] and Cu–Cl in CuCl [11]. Fig. 2 refers to Ag$_2$O.

In all three compounds, the expansion of the average distance $\langle r \rangle$ measured by EXAFS, say the bond expansion, is positive within the full temperature range explored (Fig. 2 a). In Cu$_2$O, both the positive EXAFS expansion and the negative crystallographic expansion are weaker than in the isostructural compound Ag$_2$O. From the difference between EXAFS and crystallographic thermal expansions, we evaluated the perpendicular MSRDs (Eq. 2). The MSRDs of Ag$_2$O, $\langle \Delta u^2_\parallel \rangle$ and $\langle \Delta u^2_\perp \rangle / 2$, are shown as full circles in Fig. 2, panels (b) and (c), respectively. The open circles are the sum of the uncorrelated MSDs of absorber and backscatterer atoms (Ag and O) along and perpendicular to the bond direction. The triangles represent the minimum and maximum possible values of the MSRDs, estimated from diffraction according to Ref. [13]. The experimental values of the parallel MSRD are very similar to the minimum possible values, indicating that the silver and oxygen atoms move in phase along the bond direction. A similarly strong correlation was found for Cu$_2$O [10], while for CuCl the correlation was weaker [11]. The perpendicular correlation is much weaker than the parallel correlation for all three crystals. A recent lattice dynamical calculation [14] gives a good reproduction of the MSRD behaviour of cuprites, qualitative for Ag$_2$O, also quantitative for Cu$_2$O.

The stiffness of the nearest-neighbours bond can be evaluated from the effective force constant; the Cu–O and Ag–O bonds ($k_0 \approx 11.6$ and 5.9 eV/Å$^2$, respectively) are much stiffer than the Cu–Cl bond ($k_0 \approx 1.4$ eV/Å$^2$). Let us now compare the extent of relative atomic vibrations perpendicular and parallel to the interatomic bond for the different compounds. The ratio $\gamma = \langle \Delta u^2_\parallel \rangle / \langle \Delta u^2_\perp \rangle$ measures the anisotropy of the relative vibrations (for perfect isotropy, $\gamma = 2$) [9]. Actually, $\gamma$ is temperature dependent; a numerical comparison can however be made by considering the high-temperature asymptotic values, that are 6, 11 and 22 for Cu$_2$O, CuCl and Ag$_2$O, respectively. The values of the ratio $\gamma$ are qualitatively correlated with the strength of NTE (Fig. 1). This is not surprising, since a common feature of NTE materials is the presence of intense motion perpendicular to a given bond. In the framework structures Cu$_2$O and Ag$_2$O, the metal atoms are linearly coordinated to two oxygen atoms, and their uncorrelated MSDs are anisotropic, the vibrations being more intense in the perpendicular than...
in the parallel direction. The anisotropy of relative M–O vibrations measured by the MSRD is anyway much stronger than the anisotropy of the absolute motion of metal atoms. In CuCl, for symmetry reasons the uncorrelated MSDs are isotropic for both Cu and Cl atoms, and thus unable to account for tension effects; the MSRD is instead strongly anisotropic, the correlation of motion along the bond direction being much stronger than in the perpendicular plane.

4. Conclusions
In the crystals up to now studied, the bond length (from EXAFS) always undergoes positive expansion, in spite of the NTE of lattice parameters (from diffraction). The difference between EXAFS and diffraction depends on perpendicular vibrations, and can be exploited to evaluate the perpendicular MSRD. The anisotropy of the MSRD, measured by the ratio $\gamma = \langle \Delta u^2_\perp \rangle / \langle \Delta u^2_\parallel \rangle$, can be correlated to the tension effects giving rise to the negative contribution to thermal expansion. A systematic investigation is in progress on different crystals, in order to gain a deeper understanding of the influence of local structure, bond stiffness, correlation and anisotropy of atomic vibrations on the negative thermal expansion.

References
[1] White G K 1993 Contemp. Phys. 34 193–204
[2] Barrera G D, Bruno J A, Barron T H K and Allan N L 2005 J. Phys.: Condens. Matter 17 R217–R252
[3] Barron T H K, Birch J A and White G K 1977 J. Phys. C: Solid State Phys. 10 1617–1624
[4] Mary T A, Evans J S O, Vogt T and Sleight A W 1996 Science 272 90–92
[5] Heine V, Welche P R L and Dove M T 1999 J. Am. Ceram. Soc. 82 1793–1802
[6] Tao J and Sleight A 2003 J. Solid St. Chem. 173 442–448
[7] Tiano W, Dapiaggi M and Artioli G 2003 J. Appl. Cryst. 36 1461–1463
[8] Chapman K W, Chupas P J and Kepert C J 2005 J. Am. Chem. Soc. 127 15630–15636
[9] Fornasini P, a Beccara S, Dalba G, Grisenti R, Sanson A, Vaccari M and Rocca F 2004 Phys. Rev. B 70 174301
[10] Sanson A, Rocca F, Dalba G, Fornasini P, Grisenti R, Dapiaggi M and Artioli G 2006 Phys. Rev. B 73 214305
[11] Vaccari M, Grisenti R, Fornasini P, Rocca F and Sanson A 2007 Phys. Rev. B 75 184307
[12] Artioli G 2002 EMU Notes in Mineralogy, vol. 4: Energy modelling in minerals ed Gramaccioli C M (Eötvös University Press, Budapest) pp 389–405
[13] Busing W R and Levy H A 1964 Acta Crystallogr 17 142–146
[14] Mittal R, Chaplot S L, Mishra S K and Bose P P 2007 Phys. Rev. B 75 174303