

Local behaviour of negative thermal expansion materials

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Abstract

EXAFS can represent a powerful probe of the local behaviour of negative thermal expansion (NTE) materials, thanks to the possibility of measuring the expansion of selected inter-atomic bonds and the perpendicular relative atomic displacements. The effectiveness of EXAFS for NTE studies is illustrated by a comparison of results recently obtained on germanium, CuCl and the cuprites Cu₂O and Ag₂O.

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1. Introduction

Negative thermal expansion (NTE) affects a number of systems [1]: a weak NTE is observed, for example, in some tetrahedrally coordinated crystals, like silicon, germanium, GaAs and CuCl, within a small low-temperature interval. The interest towards NTE has been recently renewed by the discovery of materials characterised by NTE extending over very large temperature intervals, like ZrW₂O₈ [2] or crystals with the delafossite structure [3] and even of zero thermal expansion (ZTE) materials [4,5].

Thermal expansion is a critical parameter in many scientific and technological applications [6]. The discovery of materials characterised by NTE or even ZTE in wide temperature intervals opens new perspectives for realising composite materials, able to exhibit predetermined values of the expansion coefficient. A more refined understanding of the microscopic mechanisms of NTE [7,8] would facilitate the development of new materials on the basis of a codified knowledge rather than through semi-empirical procedures.

While in two-atomic molecules the anharmonicity of the interaction potential induces positive thermal expansion, in many-atomic systems like crystals, where the potential is defined in a many-dimensional configurational space, the situation is by far more complicated and thermal expansion can also be negative. From a microscopic point of view, qualitative clues on the vibrational origin of NTE have been proposed on the basis of simple central-force mechanisms [8]. The anharmonicity of the pair potential induces positive thermal expansion, via a bond-stretching effect, like in two-atomic systems. Geometrical tension effects, connected to vibrational motion perpendicular to the bond direction, induce a negative contribution to the thermal expansion, which can in some cases overcome the positive bond-stretching contribution and give rise to NTE. Tension effects can be claimed as origin of NTE in many systems, although different peculiar mechanisms have to be envisaged for different cases.

A deeper quantitative understanding of the microscopic mechanism of NTE requires the availability of accurate experimental information concerning the local behaviour. The distinction between positive or negative thermal expansion refers to the sign of the thermal expansion coefficient, such as can be measured by macroscopic techniques, like

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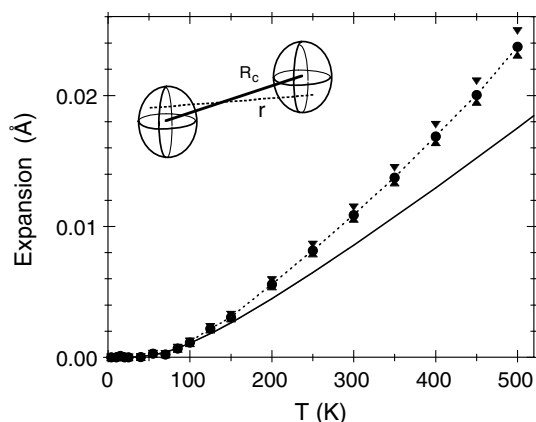


Fig. 1. Thermal expansion of the nearest-neighbour distance in copper. The continuous line is the distance between the average positions (centers of thermal ellipsoids) $R_c = |\langle \vec{r}_2 \rangle - \langle \vec{r}_1 \rangle|$ as measured by Bragg diffraction. The circles represent the average of the instantaneous distances $\langle r \rangle = \langle |\vec{r}_2 - \vec{r}_1| \rangle$ as measured by EXAFS [14].

dilatometry. From a microscopic point of view, one is interested in the expansion of the distances between neighbouring atoms (nearest-neighbours, next-nearest-neighbours, etc.), which will be for short indicated as “bond expansion” [8]. The “true” bond expansion is defined as the variation of the average distance $\langle |\vec{r}_2 - \vec{r}_1| \rangle$, while the “apparent” bond expansion is defined as the variation of the distance between average positions $|\langle \vec{r}_2 \rangle - \langle \vec{r}_1 \rangle|$ (see inset in Fig. 1). Bragg diffraction measures the apparent bond expansion, which is directly connected to the macroscopic expansion. The measurement of the true expansion of selected bonds and its comparison with the corresponding apparent expansion is crucial for understanding the origin of NTE. Actually, the difference between true and apparent expansions is mainly due to perpendicular vibrations and thus connected to the tension effect.

An estimation of the true expansion from Bragg diffraction experiments can be done only in indirect and approximate way, for example using a riding motion correction [3] or refinements based on TLS models [9]. A direct measurement of the true bond expansion is now possible, thanks to investigation tools like total scattering [10] and EXAFS, which rely on the properties of last-generation synchrotron radiation and neutron sources and on refined data analysis procedures.

In this paper, we will focus our attention on the potential of EXAFS for the study of NTE materials. In Section 2 an up to date account will be given of the state of the art in EXAFS studies of thermal disorder. In Section 3 some recent results obtained by EXAFS on NTE materials will be critically compared. Section 4 is dedicated to conclusions.

2. EXAFS and local dynamics

EXAFS studies of thermal properties require accurate temperature dependent measurements, possibly down to

liquid helium temperature. The data analysis is conveniently done by the cumulant method [11,12], whose effectiveness has been recently checked on several model systems, like germanium [13] and copper [14]. The convergence of the cumulant series is self-consistently checked by monitoring the temperature dependence of cumulants.

When the first-shell contribution can be safely Fourier filtered, the ratio method [11], using the lowest temperature spectrum as reference, gives accurate relative values of the cumulants (typically the first three or four) of the real distribution of inter-atomic distances. The first cumulant δC_1^* directly measures the true bond expansion; resolutions of the order of 0.001–0.002 Å are quite easily achieved and for some systems, like germanium, also better than 0.001 Å. The second cumulant corresponds to the parallel mean square relative displacement (MSRD); absolute values $\langle \Delta u_{\parallel}^2 \rangle$ are generally obtained by fitting a phenomenological correlated Einstein model to the experimental relative values. The third cumulant describes the asymmetry of the distance distribution. No direct information can be obtained on bond thermal expansion (both true or apparent) from the third cumulant [14]; the inclusion of the third cumulant in the data analysis is however important to get accurate values of the first cumulant; besides, the temperature dependence of the third cumulant can be compared with the expected theoretical behaviour to check the overall reliability of the data analysis.

The difference between the true bond expansion (from EXAFS) and the apparent bond expansion (from Bragg diffraction) is shown in Fig. 1 for the first coordination shell of copper. The difference between true and apparent expansion gives the temperature dependence of the perpendicular MSRD; absolute values $\langle \Delta u_{\perp}^2 \rangle$ can be obtained by fitting a suitable Einstein model to the experimental relative values [14]. The comparison of perpendicular and parallel MSRDs can give significant hints on the local dynamics, with reference to NTE. A perfectly isotropic situation would correspond to a ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle = 2$ [12]. In the case of the first shell of copper, the experimental value γ is larger than two, but smaller than 3, indicating a slight perpendicular/parallel local anisotropy. In the case of the first shell of germanium, the experimental ratio tends to an high-temperature value $\gamma \simeq 6$, in agreement with theoretical calculations. It is reasonable to expect that the rather strong perpendicular/parallel anisotropy is a measure of the tension effect considered responsible for the NTE.

The knowledge of the true bond expansion of outer shells is very important for NTE studies, since the tension effect is expected to produce NTE beyond the first shell. The EXAFS signals of outer shells are however generally difficult to disentangle by Fourier filtering and contaminated by multiple scattering (MS) contributions. Their analysis has then to rely on the theoretical simulation of EXAFS signals of the leading scattering paths and on the determination of physical parameters by non-linear best-fitting procedures. The amount of information that can

be reasonably obtained depends on the quality of experimental data and the effectiveness of simulation procedures, together with the theoretical limit to the number of independent parameters. In a recent study of copper [14], the second, third and fourth shell contributions were analyzed as a whole, including the relevant MS paths. While accurate values of the parallel MSRD were separately obtained for the three shells, only an average value of thermal expansion could be reliably evaluated.

3. EXAFS and negative thermal expansion

A few EXAFS studies of NTE materials have been up to now performed. While interesting partial results have been obtained on several crystals, a definitive picture cannot be drawn as yet. In the following, we will compare the results obtained for two different groups of systems:

- (a) Crystals with the diamond or zincblende structure. Here each atom is tetrahedrally coordinated, and NTE is attributed to low-energy transverse acoustic modes, which induce a reduction of the next-nearest-neighbours distance via a ‘guitar-string’ tension effect [8]. EXAFS has been measured on germanium [13], where macroscopic NTE extends from 15 to 40 K and is very weak ($\alpha_{\min} = -0.07 \times 10^{-6} \text{ K}^{-1}$) and on CuCl, where NTE extends up to 100 K and is by far more intense ($\alpha_{\min} = -8.3 \times 10^{-6} \text{ K}^{-1}$) [15].
- (b) Framework structures. Here, the situation is complicated by the presence of structural units and NTE could be attributed to rigid unit modes (RUM) [7,16]. EXAFS has been measured on Ag_2O [17] and Cu_2O , whose structure is formed by two interpenetrating chains of M_4O tetrahedra ($\text{M} = \text{Cu}, \text{Ag}$), where each O atom is tetrahedrally coordinated to four M atoms and each M atom is linearly coordinated to two O atoms. According to diffraction, NTE extends up to about 200 K in Cu_2O (average $\alpha \simeq -2.4 \times 10^{-6} \text{ K}^{-1}$) and up to about 500 K in Ag_2O (average $\alpha \simeq -6 \times 10^{-6} \text{ K}^{-1}$) [18].

In all the systems here considered, the true first-shell bond expansion, directly measured by the first EXAFS cumulant, is positive. This is not surprising, since the nearest-neighbour true distance is affected both by the asymmetry of the pair potential and by the effect of perpendicular vibrations. It is remarkable that a stronger macroscopic negative expansion is accompanied by a stronger positive first shell expansion and, as a consequence, by a stronger perpendicular MSRD.

Within each of the two groups, the system with the stronger NTE is characterised by both a stronger parallel MSRD and a higher value of the ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle$. The parallel MSRD is five times higher in CuCl than in Ge and two times higher in Ag_2O than in Cu_2O ; the high-temperature value of the ratio γ increases from about 6 in Ge to about 11 in CuCl and from about 6 in Cu_2O to about

22 in Ag_2O . These results confirm that a relationship exists between NTE and anisotropy of the relative thermal motion of nearest-neighbours. To find a quantitative expression for this relationship is however far from trivial. For the zincblende structures, where NTE increases with increasing ionicity, EXAFS measurements on systems with NTE intermediate between Ge and CuCl, like CdTe and HgTe, are expected to give further hints. In cuprites, the relatively open framework structure and the linear O–M–O coordination is expected to favour the anisotropy of relative thermal vibrations and the permanence of NTE at relatively high temperatures; the remarkable difference between the γ values of Cu_2O and Ag_2O represents however a puzzling problem. In all cases, the availability of accurate lattice dynamics calculations, including eigenvectors of the dynamical matrix and possibly anharmonicity effects, are necessary for a sound interpretation of experimental data.

Further experimental information can be obtained from the outer coordination shells, provided the effects of multiple scattering are effectively taken into account. Reliable and rather unexpected results have been obtained concerning the second-shell behaviour of Cu_2O and Ag_2O . The 12 M–M second-shell distances can be grouped into two sets, six distances (type A) connecting M atoms on the edges of M_4O tetrahedra, the six others (type B) connecting M atoms belonging to the two different networks of tetrahedra. In both compounds, EXAFS measures a negative expansion of type A distances and a positive expansion of type B distances; correspondingly, the parallel MSRD is higher for type B than for type A distances. These results suggest a rather complex local dynamics, inconsistent with simple RUM models (EXAFS directly measures the strong deformation of M_4O tetrahedra). NTE seems to originate within each of the two networks of connected tetrahedra, while the relative movements of the two networks induce positive expansion.

4. Conclusions

The possibility of directly measuring the true expansion of selected inter-atomic bonds and, by comparison with diffraction data, the perpendicular MSRD, makes EXAFS a very appealing tool for studying the local origin of negative thermal expansion. The results up to now obtained have given new original insights in the case of cuprites and stimulate further developments of alternative phenomenological NTE models as well as an accurate knowledge of lattice dynamical properties. EXAFS studies of NTE materials would greatly benefit from an improvement of the standard accuracy of experimental data and of the reliability of EXAFS simulations.

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