



	Experiment title: Low temperature thermal expansion of cuprite	Experiment number: CH-1250
Beamline: BM16	Date of experiment: from: 18/02/2002 to: 20/02/2002	Date of report: 09/07/02
Shifts: 6	Local contact(s): Michela Brunelli	<i>Received at ESRF:</i>
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Report:

The low temperature thermal expansion of cuprite was measured by high resolution powder diffraction between 9 and 298 K, with temperature intervals of 7 K. Cuprite structure exhibits a peculiar thermal behaviour: it has a negative thermal expansion below 200 K, and a positive, but extremely small [1], one above room temperature. Its shear modulus is unusually low, and it increases with increasing temperature [2]. Moreover, intense symmetry forbidden *eeo* reflections have been observed in the diffraction pattern [3], [4]. The aim of the work is to resolve the controversial issue about the nature of the negative thermal expansion and to evaluate the presence of a phase transition in the investigated temperature range [5]. The local thermal behaviour of cuprite was investigated by means of extended X-ray absorption fine structure (EXAFS) between 25 and 410 K (Experiment HS-1720). Such a multidisciplinary approach is believed to improve the knowledge of vibrational properties of copper and oxygen atoms within cuprite structure. The aim is to explain the thermal expansion of cuprite within the different temperature ranges: as powder diffraction produces excellent results in determining cell expansion/reduction with temperature, complementary techniques (EXAFS, together with single crystal neutron diffraction data [6]) will be used in order to clarify the innermost reasons for this peculiar behaviour. The combined data should yield information on the vibrational behaviour of the copper and oxygen atoms in the structure, and transverse librations of the atoms.

Cuprite cell variations with temperature is shown in Fig. 1 (top), together with its thermal expansion coefficient α (Fig. 1, bottom), evaluated as the first derivative, with respect to temperature, of the 4th order polynomial used to fit cell data. The thermal expansion is negative up to 240 K, constant up to room temperature, and then positive (data over room temperature were collected with our lab diffractometer). No sign of discontinuity, originated by phase transitions, was found in the investigated temperature range, as already pointed out by Shafer & Kirfel [7], with neutron powder diffraction.

As the data quality appeared to be particularly good, anisotropic thermal parameters for copper were refined (oxygen thermal parameter, due to site symmetry, is isotropic), with the aim of comparing the mean square displacements (MSD) evaluated by XRD with those found by EXAFS (MSRD). With EXAFS, MSRD ($\langle u_j^2 \rangle = \langle [(\underline{u}_j - \underline{u}_o) \cdot R]^2 \rangle$) of both the Cu-O 1st-shell and Cu-Cu 2nd-shell distances are evaluated by the cumulant method [8]. The MSRD is composed by the sum of the mean square displacement for Cu and O (or for Cu and Cu), from which the Displacement Correlation

Function (DCF) is subtracted. The difference between XRD and EXAFS can therefore provide a measure of the correlation in the vibrational motion of the two pairs of atoms. The analysis here performed gives only MSD values relative to the lowest temperature spectrum. Absolute values are obtained by fitting an Einstein model to the temperature dependence of the relative values; only thermal disorder is thus taken into account [9]; the non-zero intercept at 0 K represents the zero-point vibrational energy. The MSD from EXAFS are compared in Fig. 2 with the uncorrelated MSD measured from diffraction: for each pair of atoms, the components of thermal vibrations along the bond directions have been added, and the values rigidly shifted to correspond to an Einstein behaviour, in order to cancel the contributions from static disorder. As it can be clearly seen from Fig. 2, DCF is much bigger for the first than for the second shell, providing therefore useful information about vibrational behaviour of Cu₄O tetrahedra: according to our results, they are more resistant to stretching along Cu-O bond, than to bending along Cu-Cu direction.

Some of these results have already been submitted to Nuclear Instruments & Methods B (Dapiaggi, M., Tiano, W., Artioli, G., Sanson, A., Fornasini, P. 'The thermal behaviour of cuprite: a combined XRD-EXAFS approach')

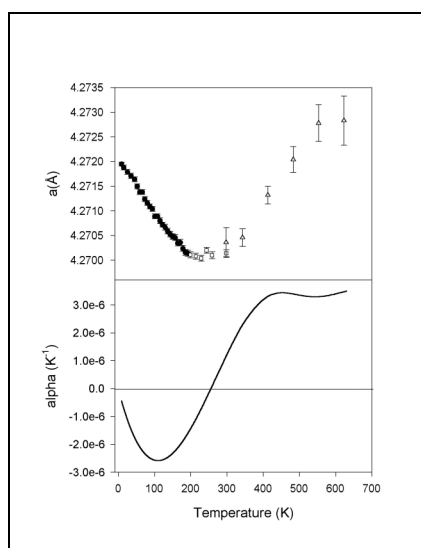


Fig. 1 – Cuprite cell parameter (Å, top) and thermal expansion coefficient (K⁻¹, bottom), as a function of temperature

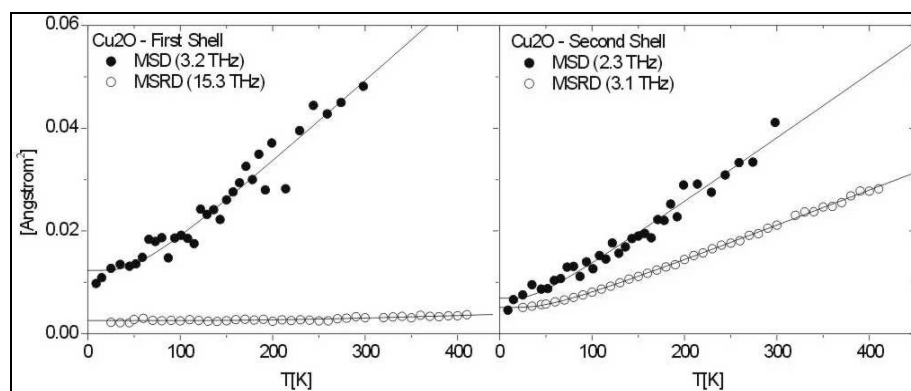


Fig.2 – Comparison of (MSD) found by XRD and MSD found by EXAFS, in the first (left) and in the second (right) shell, as a function of temperature

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