<table>
<tr><td> </td><td>Experiment title:
Negative thermal expansion materials at low temperature: CuCl and ReO3</td><td>Experiment number:
CH-2031</td></tr>
<tr><td>Beamline:
ID31</td><td>Date of experiment:
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<tr><td>Shifts: 12</td><td>Local contact(s): Prof. Andy Fitch</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
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Report:

Negative thermal expansion (NTE) materials have received attention in the last few years because of their challenging physico-chemical behaviour and also for their interesting applications (Sleight, 2003; Barrera et al., 2005). Two more materials were added to the collection of materials studied by means of the comparison between EXAFS and diffraction data.

Rhenium oxide. Cubic ReO3 (space group Pm-3m) shows negative thermal expansion below 340 K (Matsuda et al. 1978). This is the only paper on the thermal expansion of this compound, in which the variations of the unit cell were measured by interferometry on a single crystal. ReO3 has a unique perovskite-type cubic structure composed of corner sharing [ReO6] octahedra with vacancies in the A sites. The bending modes, in which an oxygen vibrates perpendicular to Re-O-Re bond, are thought to be responsible for the negative thermal expansion, so an accurate analysis of the thermal expansion of this material, together with the evaluation of thermal vibrations as a function of temperature, could provide an insight on the negative thermal expansion behaviour.

Copper chloride. CuCl (space group F4-3m) has a framework structure composed of tetrahedra [CuCl4], similar to the sphalerite one (also called zinc-blend). Its thermal expansion at low temperature was measured by Barron et al. (1977) on a polycrystalline sample by means of a dilatometric technique up to 90 K. The structure was found to exhibit a strong negative thermal expansion up to about 50 K. The authors claim that the thermal properties should depend strongly on the balance between a negative Gruneisen parameter (due to the softening of the shear modulus under pressure) and the presence of a certain degree of covalency in the bond introducing directional forces that stiffen the shear modulus. Again, a more accurate evaluation of the cell parameters (which can be determined, with ID31 data, with a standard error of about 10-5 Å) and of the

anisotropic thermal parameters could provide the Mean Square Displacements to be compared with EXAFS MSRD in order to assess the stiffness of the bonds within the tetrahedra (Dapiaggi et al., 2003)

The data were collected with a wavelength of 0.4007256(1) Å, from 5 to 300 K, with very small temperature intervals: from 3 K in the low temperature range (where the two compounds show a negative thermal expansion) to 10 K in the higher temperature range (where the thermal expansion becomes positive). The data were collected up to 65° 2θ, in order to be able to perform a Pair Distribution Function (PDF) analysis, which needs a high Q maximum and an accurate data collection. In this case, Qmax is about 20 $Å^{-1}$. The aim of a PDF analysis is to check for the presence of local distortions in the structure, and their possible influence on the thermal behaviour of these materials. This kind of analysis has not been performed yet.

Both compounds showed a negative thermal expansion: ReO3 up to about 200 K and CuCl below 100 K, as expected. ReO3 is also a very low thermal expansion material, with variations on the cell parameter on the 5th decimal place (in Å). The standard error of the refined cell parameter is on the 6th decimal place. A lot of attention has to be given to all possible errors affecting peak position: from goniometer zero to variations of wavelength during the run, to errors in the measurement of temperature. The only way to deal with those is to use silicon thermal expansion to check for errors and their dependence on cryostat alignement and monochromator errors due to ring refills.

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