ESRF	**Experiment title:** **XAFS and XRD studies with subpicometer accuracy of crystals with negative thermal expansion : case of ReO$_3$**	**Experiment number:** **HS-2270**
Beamline: **BM29**	**Date of experiment:** from: **24 September 2003** to: **30 September 2003**	**Date of report:** **March 03 2005** *Received at ESRF:*
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Report:

In the last years, the XAFS experimental techniques have undergo remarkable developments: experiments with unprecedented accuracy under extreme conditions of high pressure and temperature, that were not even conceivable just a few years ago, can nowadays be performed. New applications, stimulated by accurate experimental temperature-dependent XAFS measurements on Ge, ReO$_3$ and Ag$_2$O, can be carried out [1,2]. In parallel with the experimental techniques, XAFS theory and data analysis [1,2] have made considerable progress. ***Subpicometer*** *(*10^{-3}Å) accuracy in the determination of interatomic distances is now attainable [1,2]. Thanks to the availabolity of novel experimental apparatus [3] at the ESRF designed to the collect both XAFS and XRD, new effects can be studied, for example materials with *negative thermal expansion* [4,5].

According unique work [6], *simple cubic* ReO$_3$ shows *negative thermal expansion* below 340 K : (i) negative value at low temperatures, (ii) a rapid increase about 200 K, (iii) a moderate increase above room temperature up to 600 K. ReO$_3$ has a unique perovskite-type cubic structure (ABO$_3$) composed of [ReO$_6$] octahedra joined by corners with the A sites being vacant. Since ReO$_3$ has metallic conductivity below 500 K and the Re-O bonding is strongly covalent, it is sometimes called as "covalent metal". No evidence has been found of the phase transitions at ambient pressure previously reported up to 600 K. The stability of its cubic lattice was explained by the suppression of the screening effect on the lattice vibrations: here the screening is not free-electron like as in simple metals but has an atomic (rhenium 5*d* and oxygen 2*p*) character. The bending modes, in which an oxygen *vibrates perpendicular to Re-O-Re line*, are responsible for the *negative thermal expansion* in the rigid unit model (RUM). Therefore, cubic ReO$_3$ was an *ideal candidate* for accurate XAFS study of negative thermal expansion effect with **subpicometer accuracy.**

The goal of the present proposal was the completion of XAFS and XRD measurements on ReO_3 in the low and high temperature regions, in order to study local atomic structural and dynamical properties of materials with *negative thermal expansion*. The first set of measurements (XAFS and XRD) was done from RT to 600 K, at a step of 50 K. The second set of measurements (XAFS) was done from 25 K to 350 K, at steps of 25 K.

XAFS and XRD were measured in transmission mode on a powdered sample deposited on a Millipore filter membrane. A novel experimental apparatus [3] at the ESRF designed to the collect both XAFS and XRD was used for in-situ measurements from RT to 600 K on ReO_3 in the vacuum. The XAFS spectra at the Re L_3-edge have been measured using the Si(111) double-crystal monochromator and harmonic rejection was achieved by slightly detuning the two crystals from the parallel alignment. Experimental spectra were recorded by two ionization chambers with variable steps in the wave vector range 0.025 $Å^{-1}$, count rate 1 s per point. The energy resolution (FWHM) was 1.5 eV (Si(111)).

The experimental XAFS data were treated by software package EDA in the way similar to the one applied previously by us for high accuracy analysis of the thermal expansion of Ge [published in Phys. Rev. Letters 1999]. The XAFS was interpreted using the cumulant approach by taking into account the experimental phases and amplitudes from ReO_3 measured at low temperature.

Our experience at the beam-line BM-29 on ReO_3 shows that also *10* ***femtometer*** *(*10^{-4}Å) “barrier” is now attainable, even though such determination is far from trivial. A very high stability and reproducibility in the energy axis $\Delta E/(E-E_o)$ about $2\cdot10^{-4}$ (E_o - photoelectron zero energy in XAFS) guarantees an accuracy of $2\cdot10^{-4}$Å (20 *femtometer*) and consequently $\Delta R/R \approx 10^{-4}$ in the determination of variation of interatomic distances (R) in the first (Re-O_1), second (Re-Re_2), third (Re-Re_3) and fourth (Re-Re_4) coordination shells.

The temperature dependence of the first XAFS cumulants for the 1st, 4th, 6th - shells are larger than the crystallographic thermal expansion (increase of the distance between centres of the three-dimensional probability distribution functions) owing to the effect of thermal vibrations perpendicular to the bond direction. The apparent thermal expansion induced by the relative atomic vibrations normal to the bond has been clearly demonstrated, confirming that the first cumulant is not a reliable measure of the interatomic distance.

A “negative”thermal expansion has been observed below 100 K, very weak for the 1st shell (comparable with uncertainty), much larger for the 2nd and 3rd shell; besides, the behaviour is different for the two shells. The real (macroscopic) low-temperature negative thermal expansion of germanium is in principle too weak to be detected by EXAFS. *The present results suggest that the EXAFS sensitivity is strongly enhanced,* and in a different way for the 2nd with respect to the 3rd shell, as an effect of relative local vibrational motions, and possibly local distortions (local distortions have been recently detected in silicon by high-resolution x-ray diffraction).

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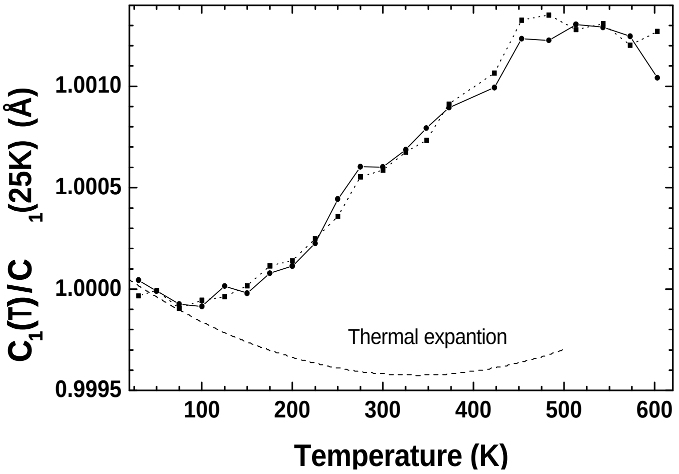

Fig. 1 Thermal expansion of bond lengths (ΔR/R) of ReO_3. Comparison between the 1st shell ($Re\text{-}O_1$) (circles) and 4th shell ($Re\text{-}Re_4$) (squares) normalised first cumulants C_1(T)/ C_1 (25K) and net thermal expansion Δ*a/a* according to Ref. [6] (dashed line).

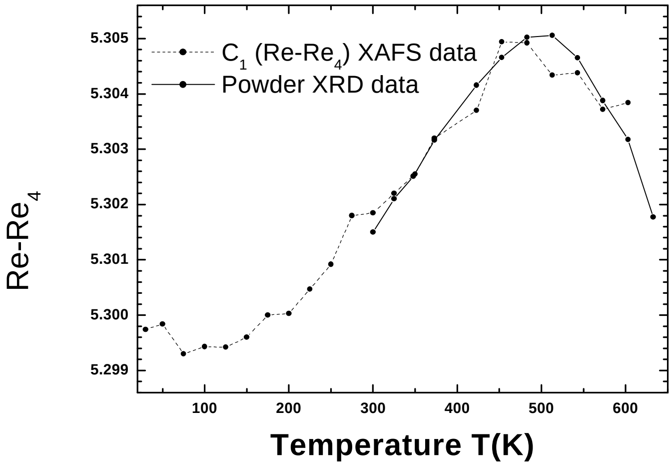

Fig. 2 Thermal expansion of ReO_3. Comparison between the 4th shell ($Re\text{-}Re_4$) first cumulant C_1 (circles connected by dashed line) and thermal expansion (full line) according this work XRD data.

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