EXAFS and XRD Studies with Subpicometer Accuracy: The Case of ReO₃

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Abstract. EXAFS has been measured on ReO₃ from 30 to 600 K; XRD has been contemporarily measured above 300 K. In this way, it has been possible to compare the expansion of the lattice parameter (XRD) and of the bond lengths (EXAFS), measured at the same time. EXAFS was interpreted by the cumulant approach, using ReO₃ measured at low temperature as reference. According to our results, ReO₃ shows a complicated behavior of thermal expansion: (i) ultra low or negative expansion below 100 K, (ii) moderate positive expansion above 150 K up to 500 K, (iii) negative expansion from 500 K up to the decomposition temperature. The EXAFS parallel and perpendicular MSRD (mean square relative displacements) have been calculated for the 1st and 4th shells. An unexpected result is that the perpendicular MSRD of the first coordination shell has a weak temperature dependence.

Keywords: EXAFS, XRD, ReO₃, Thermal expansion, Cumulants.

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INTRODUCTION

ReO₃ has a unique perovskite-type structure (ABO₃), with a simple-cubic Bravais lattice composed of ReO₆ octahedra joined by corners and the A sites vacant. The empty A sites permit large rotations of the ReO₆ octahedra, resulting in an enhanced compressibility and ultra low or negative thermal expansion [1]. Unfortunately, the few published results on thermal expansion of cubic ReO₃ are an example of controversy [2].

The aim of the present work is to resolve the controversial issue about the nature of the ultra low or negative thermal expansion (NTE) of ReO₃. The availability of a novel experimental setup at ESRF [3], designed to measure both EXAFS and XRD, facilitates the study of such fine effect as NTE.

EXPERIMENTAL AND ANALYSIS

The rhenium trioxide sample used in the present work was prepared from commercial 99.9% polycrystalline ReO₃ (Metalli Preziosi S.p.A.). The ReO₃ powder was finely ground and homogeneously deposited on a membrane. The thickness of the sample was optimized to have the value of the Re L₃ absorption jump equal to one.

EXAFS and XRD measurements were performed in vacuum at the ESRF BM29 beam line. The EXAFS spectra at the Re L₃-edge were measured in the energy range 10200-11940 eV in transmission mode. The synchrotron radiation was monochromatized using a Si(111) double-crystal monochromator, and harmonic rejection was achieved by 30% detuning the two crystals from the parallel alignment. The spectra were recorded by two ionization chambers filled with argon gas. The white line edge positions were reproducible with a precision better than 0.1 eV.

Low temperature EXAFS measurements were done from 30 K to 350 K. The temperature during each measurement was stabilized within 2 degrees. High temperature EXAFS and XRD measurements were done in the temperature range from 300 K to 603 K. The sample was placed in a graphite cell mounted in a multipurpose vacuum oven. The temperature was stabilized within 5 degrees during each measurement.

XRD measurements were done in energy scanning x-ray diffraction (ESXD) mode [3] using a set of four detectors placed at fixed 2θ scattering angles. The scans were performed, using acquisition time of 4
seconds per point and an energy step of 5 eV, in six energy intervals. As a result, the Bragg-scattering from a number of ReO₃ planes (100), (110), (210), (211), (222), (320) and (321) was recorded. The lattice parameter \( a(T) \) was determined from the positions of the Bragg peaks by a best-fit least-squares procedure.

The EXAFS signals have been extracted following the standard data analysis procedure as in our previous works [4, 5]. The Fourier Transforms (FT) of the EXAFS \( \chi(k)k^2 \) signals are shown in Fig. 1 at selected temperatures. A significant decrease of the peak heights, when temperature increases, is evident. However, on the whole, the shapes of both the EXAFS signals and their FTs remain similar up to the highest temperature. The origin of the peaks in the FTs was investigated and explained in previous works [4, 5].

![Fourier Transform](image)

**FIGURE 1.** Temperature dependence of the experimental EXAFS Fourier transforms (modulus and imaginary part).

The analysis of the temperature dependent EXAFS signals was performed using a best-fit procedure within the cumulant approximation [6], with the experimental amplitude and phase shift functions taken from the lowest temperature (30 K) EXAFS signal. We used the same methodology as in our previous study of the thermal expansion of crystalline germanium [6].

The relative values of the first three cumulants \( \Delta C_i(T) = C_i(T) - C_i(30 \text{ K}) \), \( i=1,2,3 \), were treated as free parameters, while the coordination numbers were constrained at crystallographic values. Besides, since the \( E_0 \) value (\( E_0 \) - photoelectron zero energy in EXAFS) and the amplitude scaling factor \( S_0^2 \) are not temperature dependent, they were set to the same values at all temperatures.

Here we will only present the analysis of the first and fourth coordination shells. The corresponding peaks in the FT (0.7 Å to 2.0 Å and 4.3 Å to 5.6 Å, respectively) are well isolated, and their contributions can be easily singled out by Fourier back-transform.

The EXAFS signals from these shells (Re-Oᵢ, Re-Re₄) are dominated by the single-scattering processes. Therefore, a conventional single-scattering analysis can be used to extract the cumulant values.

The statistical uncertainty of the fitting and cross-comparison procedures is represented by error bars in the figures. Systematic errors of individual files can be estimated by the scattering of the cumulants values with respect to a smooth temperature dependence.

**RESULTS AND DISCUSSION**

The parallel MSRDs shown in Fig. 2 for the first and fourth shells are in agreement, within the error bars, with our previous studies [4, 5] for the Re-Oᵢ atom pair at low temperatures (\( T < 350\text{K} \)) and for the Re-Re₄ atom pair in the whole interval of temperatures.

![Temperature dependence of the MSRD](image)

**FIGURE 2.** Temperature dependence of the MSRD for the first (parallel - circles; perpendicular - squares) and for the fourth (parallel – triangles) coordination shells.

The main difference with our previous works [4, 5] occurs for the Re-Oᵢ parallel MSRD at high temperatures (\( T > 350\text{K} \)) and is attributed to the different experimental conditions of the experiments. Our previous experiments [4, 5] were performed in air, and this fact led to a distortion of the first-shell ReO₅ octahedra at temperatures above 350 K. In the present work, all experiments were performed in vacuum, and no distortion of the first shell was observed. Such difference in the behavior should not be surprising, since it is known that the decomposition of ReO₃ at 673 K proceeds by two different routes in vacuum and in air, the final products being solid ReO₂ and gaseous Re₂O₇, respectively.

The knowledge of the parallel MSRD allowed us to calculate the temperature variation of the first cumulant of the real distribution of distances \( \Delta C_i \) from the first cumulant \( \Delta C_i \) of the effective distribution of both first and fourth shells, according to a well established procedure.
The values $\Delta C_4^{\text{th}}(T)$ correspond to the “true” thermal expansions of the Re-O$_i$ and Re-Re$_q$ bonds. They are in principle different from the “apparent” thermal expansions measured by Bragg diffraction, the difference being due to the perpendicular MSRDs [7,8]. The perpendicular MSRD is twice the parallel MSRD only for perfectly isotropic relative vibrational motion of absorber and backscatterer atoms. On general grounds, the anisotropy of relative motion is larger for nearest neighbors, and decreases with increasing distance. The first-shell perpendicular MSRD is experimentally obtained from the difference between EXAFS and Bragg diffraction thermal expansions. In the present case, however, no XRD data were available below 300 K.

We tried then to evaluate the “apparent” thermal expansion below 300 K from the fourth-shell “true” thermal expansion $\Delta C_4^{\text{th}}(T)$ measured by EXAFS, assuming perfect isotropy for the Re-Re$_4$ relative motion. This assumption is justified by the fact that rhenium atoms show isotropic MSD in diffraction below 100 K, (ii) a moderate positive expansion above 300K (diamonds) and Variation with temperature of the Re$^{0}$ lattice parameter, measured by XRD above 300 K (Fig. 3, squares and diamonds). This assumption is justified by the fact that rhenium atoms show isotropic MSD in diffraction experiments [9], and by the relatively large distance. By imposing that the perpendicular MSRD is twice the parallel MSRD, one could recover the “apparent” expansion of the Re-Re$_4$ bond below 300 K. The corresponding lattice thermal expansion is in good agreement with the lattice expansion directly measured by XRD above 300 K (Fig. 3, squares and diamonds).

We tried then to evaluate the “apparent” thermal expansion below 300 K from the fourth-shell “true” thermal expansion $\Delta C_4^{\text{th}}(T)$ measured by EXAFS, assuming perfect isotropy for the Re-Re$_4$ relative motion. This assumption is justified by the fact that rhenium atoms show isotropic MSD in diffraction below 100 K, (ii) a moderate positive expansion above 300 K, (iii) a negative expansion above 500 K up to the ReO$_3$ decomposition temperature.

Once determined the expansion of the lattice parameter over the full temperature interval from 30 to 600 K, it was possible to compare the “true” bond expansions for the Re-O$_i$ bond (from EXAFS first cumulant $\Delta C_4^{\text{th}}$) with the “apparent” expansion (corresponding for ReO$_3$ to half the expansion of the lattice parameter), and evaluate the temperature dependence of the corresponding perpendicular MSRD (Fig. 2). Rather surprisingly, the parallel and perpendicular MSRDs of the Re-O$_i$ bond have similar temperature dependence, notwithstanding the absolute values of the perpendicular MSRD are generally found to be at least twice the absolute values of the parallel MSRD in other crystals.

Large amplitude of the oxygen absolute MSD vibrations in the direction perpendicular to the Re-O-Re bonds and strong anisotropy of the corresponding thermal ellipsoids were previously determined at every temperature by diffraction [9]. The EXAFS results suggest instead a strong correlation of the perpendicular relative Re-O$_i$ vibrations, which increases with temperature faster than the correlation of parallel relative vibrations [6, 7].

Finally, our experience at the beam-line BM-29 on ReO$_3$ shows that also 10 femtometer (10$^{-14}$Å) “barrier” is now attainable, even though such determination is far from trivial. A very high stability and reproducibility in the energy axis $\Delta E(E-E_0)$ about 2·10$^{-4}$ guarantees an accuracy of 2·10$^{-4}$Å (20 femtometer) and consequently $\Delta R/R \simeq 10^{-4}$ in the determination of variation of interatomic distances (R) in the first (Re-O$_i$) and fourth (Re-Re$_4$) coordination shells.

**REFERENCES**