

Proposal: 7-02-96 **Council:** 4/2007

Title: Phonon softening in ReO₃

This proposal is a new proposal

Research Area: Physics

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Samples: ReO₃

Instrument	Req. Days	All. Days	From	To
IN8	7	7	26/09/2007	03/10/2007

Abstract:

The transition metal oxide ReO₃ is one of the few simple metallic oxide for which band theory alone is assumed to provide adequate account of their properties. However, although the phonon-electron coupling is not too small ($\lambda=0.34$), surprisingly ReO₃ shows no superconductivity down to 20 mK. ReO₃ seems to belong to the normal class of conventional band Fermi liquid with electron-phonon interactions determining the resistivity. ReO₃ undergoes a pressure induced second order structural phase transition at $P = 5.3$ kbar. Softening of the M3 phonon mode is assumed to be the microscopic reason for the structural phase transition. Our recent investigation showed negative thermal expansion (NTE) in the temperature range 0-120 K. We believe that the negative thermal expansion is related to the M3 rigid unit mode (RUM). In order to understand the pressure induced structural phase transition and negative thermal expansion we propose to investigate temperature and pressure dependence of the M3 phonon mode and the associated central mode phenomenon. We request 7 days of neutron beam time on IN8 for the proposed experiment.

Phonon softening in ReO₃

Introduction:

Transition metal oxides have been the subject of renewed interest ever since high temperature superconductivity was discovered in copper oxide materials. The transition metal oxides with narrow d bands form strongly correlated Mott-Hubbard system for which conventional band theory is no longer valid [1]. The number of transition metal oxides where band theory alone can provide adequate account of their properties is quite limited, and is confined to compounds of the 4d and 5d series. ReO₃ is an example of such a simple metallic oxide. Among d-electron conductors ReO₃ has a simple perovskite-like cubic structure and its conductivity is comparable to that of Ag. Although the electron-phonon coupling constant is not very small [$\lambda = 0.34$] ReO₃ surprisingly does not show superconductivity down to 20 mK. ReO₃ seems to belong to the normal class of conventional band Fermi liquids with electron-phonon interactions dominating the resistivity [2]. ReO₃ crystallizes in the cubic space group (Pm3m) with the undistorted perovskite-like DO₉ type structure with lattice constant $a = 3.74 \text{ \AA}$. The structure consists of corner-linked ReO₆ octahedra with Re at the centres and linear Re-O-Re links. Among the numerous perovskite-like compounds ReO₃ is unique in that the undistorted cubic structure is stable at ambient pressure and at all temperatures up to its melting point. Also the ReO₃ structure has a completely vacant A cation site of the ABO₃ perovskite structure. This empty structure is therefore expected to allow rigid rotation of the ReO₆ octahedra. High pressure X-ray neutron diffraction measurements [3-5] established that ReO₃ undergoes a pressure-induced second order phase transition at $P_c = 5.2 \text{ kbar}$ at room temperature to a tetragonal (P4/mbm) intermediate phase with a very narrow stability range in pressure and then a further transition to a cubic (Im3) phase. The driving force of the phase transition was shown to be the softening of the M₃ phonon mode involving rigid rotation of the ReO₆ octahedra and the octahedral rotation angle was identified as an order parameter of the phase transition [4,5]. Further pressure-induced phase transitions at higher pressures have been reported [6-8]. We believe that the cubic perovskite structure in ReO₃ is essentially unstable due to the softening of the M₃ phonon mode involving rigid rotation of the ReO₆ octahedra and although the average crystal structure appears cubic, the real nanoscale local structure is more complex. The rigid unit modes (RUM) involved in the structural instability should lead to negative thermal expansion (NTE) [10]. To check this we have done a high resolution X-ray powder diffraction investigation with synchrotron radiation as a function of temperature in the range 4-500 K. The lattice parameter of ReO₃ decreases continuously with increasing temperature up to about 100 K and then increases again almost linearly up to the room temperature. There is indication of a further anomaly in the lattice parameter at higher temperatures. We believe that the negative thermal expansion and the volume anomaly is intimately connected with the M₃ phonon mode.

Experimental method and results:

The goal of the present experiment was to determine the temperature and pressure dependence of the M₃ phonon mode in ReO₃. The knowledge of the temperature dependence of the M₃ phonon mode is absolutely essential in order to understand the origin of the negative thermal expansion (NTE) in ReO₃. The pressure dependence of the M₃ phonon mode in ReO₃ was investigated previously by Axe et al. [4] but the quasi-elastic central mode was not investigated carefully. This would require a careful subtraction of the scattering from the pressure cell itself. We therefore did inelastic neutron scattering investigation on ReO₃ on the triple-axis spectrometer IN8. A ReO₃ single crystal of size $4 \times 4 \times 5 \text{ mm}^3$ was first put inside an Orange cryostat with its [010] crystallographic axis parallel to the A3 axis of the spectrometer. The spectrometer configuration was: reactor – open - doubly focussed PG(002) monochromator – open – sample – PG filter – doubly focussed PG(002) analyzer – open – detector. We used the spectrometer in constant- k_f mode with k_f fixed to $k_f = 2.662 \text{ \AA}^{-1}$. We first determined the temperature dependence of the M₃ phonon mode in the temperature range 50-240 K. Fig. 1

shows the constant-Q energy scans of the M_3 phonon mode at $Q = (1.5, 0, 0.5)$ at several temperature. The energy of the M_3 phonon mode of ReO_3 increases with increasing temperature contrary to the normal behaviour of the softening of phonon energy at higher temperature. This is however consistent with the negative thermal expansion observed in ReO_3 by us [11].

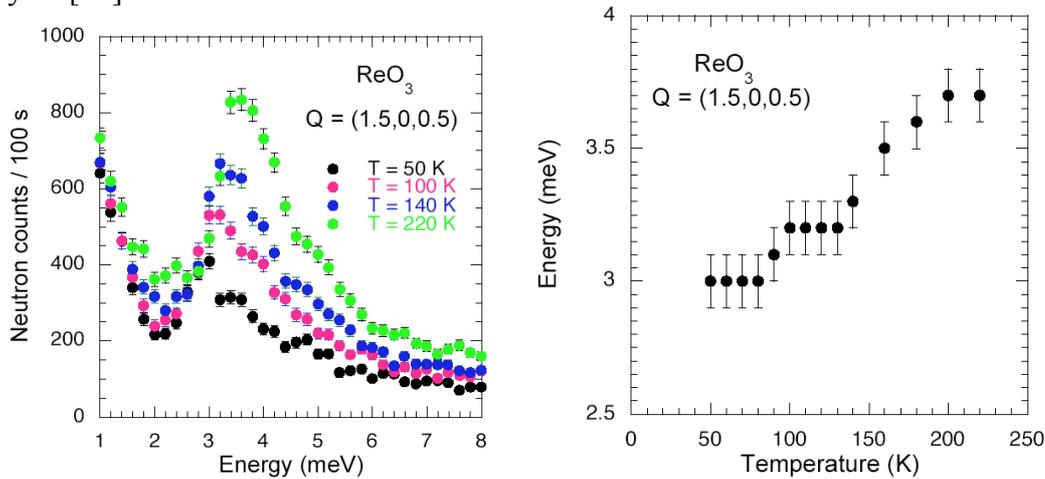


Fig. 1 – (Left) Constant-Q energy scans of the M_3 phonon mode of ReO_3 at $Q = (1.5, 0, 0.5)$ at several temperatures. (Right) Temperature dependence of the energy of the M_3 phonon mode of ReO_3 .

In the second part of the experiment we put the single crystal inside a gas pressure cell. The pressure cell was in turn put inside the He cryostat. We determined the pressure dependence of the M_3 phonon mode in ReO_3 at $T = 150$ K. This enables one to study the high pressure phase with the gas pressure cell that can generate pressure only up to 5 kbar. The lower temperature was chosen because the critical pressure of the transition in ReO_3 is considerably reduced at lower temperature [9]. The critical pressure at room temperature is $P_c = 5.2$ kbar and that at $T = 150$ K is only $P_c = 3.5$ kbar that is easily accessible with the gas pressure cell. The penalty however is the loss of phonon intensity and reduction of the energy of the phonon mode making it closer to the incoherent elastic peak. We did constant-Q energy scans of the M_3 phonon mode at several pressures. Fig. 2 (left) shows the constant-Q energy scan of ReO_3 at ambient pressure with the crystal inside the pressure cell. We notice that background is very large and is probably coming from the high pressure cell. But more surprising is that the background increases enormously at higher pressure shown in the middle and right panel of Fig. 2.

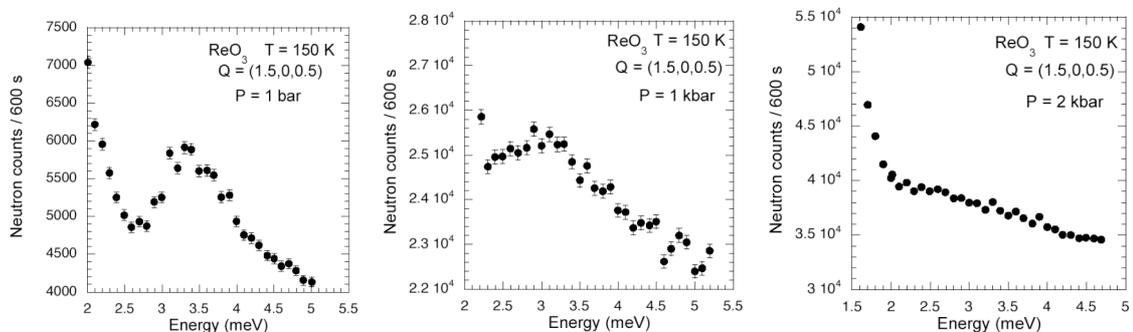


Fig. 2 - Constant-Q energy scan of of the M_3 phonon mode of ReO_3 at $T = 150$ K at several applied pressures.

Fig. 3 shows the pressure dependence of the energy of the M_3 phonon mode in ReO_3 . These results do not quite agree with those reported earlier by Axe et al [4]. The reason for this

disagreement is clear from the Fig. 2 of the Reference [4]. Axe et al. have wrongly assigned the M_3 phonon mode to sharp peaks consisting of one or two data points at higher pressure. In fact the the M_3 phonon mode is broadened considerably at higher pressure as is clearly seen from our data of Fig. 2.

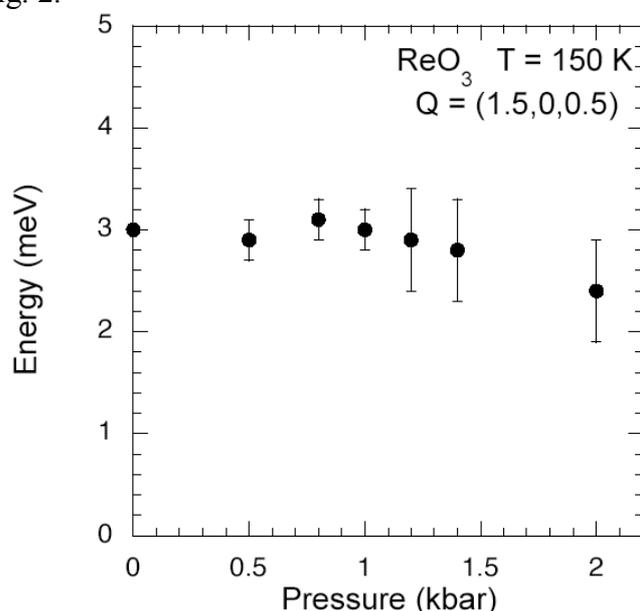


Fig. 3 – Pressure dependence of the energy of the M_3 phonon mode in ReO_3 .

Conclusions and future outlook:

In conclusion we add that although the present experiment was quite successful in determining the temperature and pressure dependence of the M_3 phonon mode in ReO_3 the detailed analysis of central mode phenomenon is difficult from the present data with a very high background. In future we would like to do this experiment by minimizing the background.

References:

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