

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metal oxides with narrow d bands form strongly correlated Mott-Hubbard system for which conventional band theory is no longer valid [1].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.  $\text{ReO}_3$  is an example of such a simple metallic oxide. Among d-electron conductors  $\text{ReO}_3$  has a simple perovskite-like cubic structure and its conductivity is comparable to that of Ag. Although the electron-phonon coupling constant ( $\lambda = 0.34$ ) is not very small [2]  $\text{ReO}_3$  surprisingly does not show superconductivity down to 20 mK.  $\text{ReO}_3$  seems to belong to the normal class of conventional band Fermi liquids with electron-phonon interactions dominating the resistivity [2].  $\text{ReO}_3$  crystallizes in the cubic space group ( $Pm3m$ ) with the undistorted perovskite-like  $\text{DO}_9$  type structure with lattice constant  $a = 3.74 \text{ \AA}$ . The structure consists of corner-linked  $\text{ReO}_6$  octahedra with Re at the centres and linear Re-O-Re links. Among the numerous perovskite-like compounds  $\text{ReO}_3$  belongs to a small family of undistorted cubic structures which is stable at ambient pressure and at all temperatures up to its melting point. Also the  $\text{ReO}_3$  structure has a completely vacant A cation site of the  $\text{ABO}_3$  perovskite structure. This empty structure is therefore expected to allow rigid rotation of the  $\text{ReO}_6$  octahedra. High pressure X-ray neutron diffraction measurements [6, 7, 8] established that  $\text{ReO}_3$  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 ( $\text{Im}3$ ) phase. The driving force of the phase transition was shown to be the softening of the  $M_3$  phonon mode involving rigid rotation of the  $\text{ReO}_6$  octahedra and the octahedral rotation angle was identified as an order parameter of the phase transition [7, 8]. Further pressure-induced phase transitions at higher pressures have been reported [9, 10, 11]. We believe that the cubic perovskite structure in  $\text{ReO}_3$  is essentially unstable due to the softening of the  $M_3$  phonon mode involving rigid rotation of the  $\text{ReO}_6$  octahedra. 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) [12].

X-ray diffraction measurements on  $\text{ReO}_3$  powders were done on the high resolution powder diffractometer at the undulator beam line ID31 of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The polycrystalline sample were put inside a quartz capillary. The temperature variation of the diffraction intensities in the temperature range 10 – 300 K was obtained by a He-flow cryostat and that in the temperature range 320 – 500 K was obtained by blowing hot air on the sample encapsulated in quartz capillary. The wavelength of X-ray was 0.5  $\text{\AA}$ . Fig. 1 shows the diffraction diagram of  $\text{ReO}_3$  measured at  $T = 10 \text{ K}$ . Fig. 2 (a) shows the temperature variation of the cubic lattice parameter  $a(T)$ . The lattice parameter  $a$  shows two minima, one at  $T \approx 110 \text{ K}$  and another at  $T \approx 400 \text{ K}$ . Also there exist anomalous oscillations in the data beyond standard deviations. The temperature variation of the unit cell volume of cubic  $\text{ReO}_3$  is shown in Fig. 2 (b) and it behaves similarly. The total volume contraction from 10 to 110 K is about 0.056% and is rather small, but is much larger than the experimental error. The volume contraction at about  $T = 400 \text{ K}$  is somewhat smaller but is also beyond the experimental accuracy.

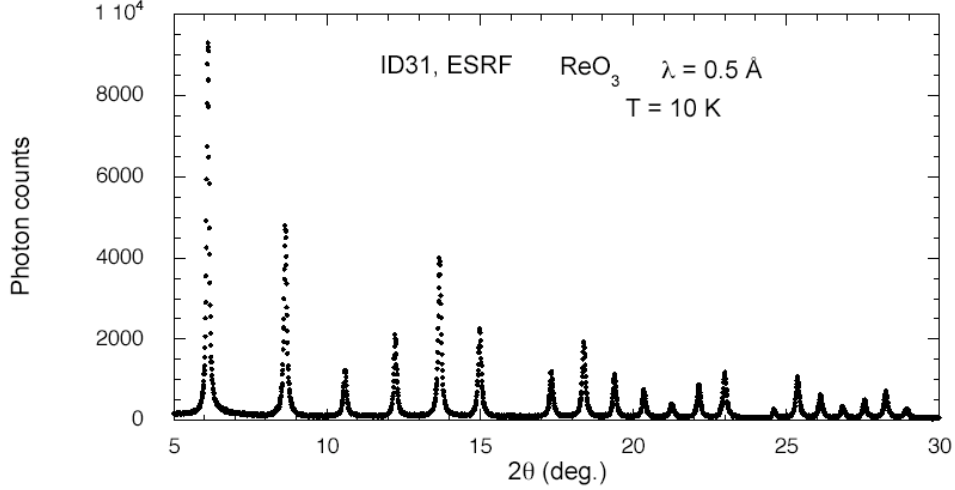


Fig. 1 - Diffraction diagram of  $\text{ReO}_3$  measured at  $T = 10$  K on ID31 of the European Synchrotron Radiation facility (ESRF).

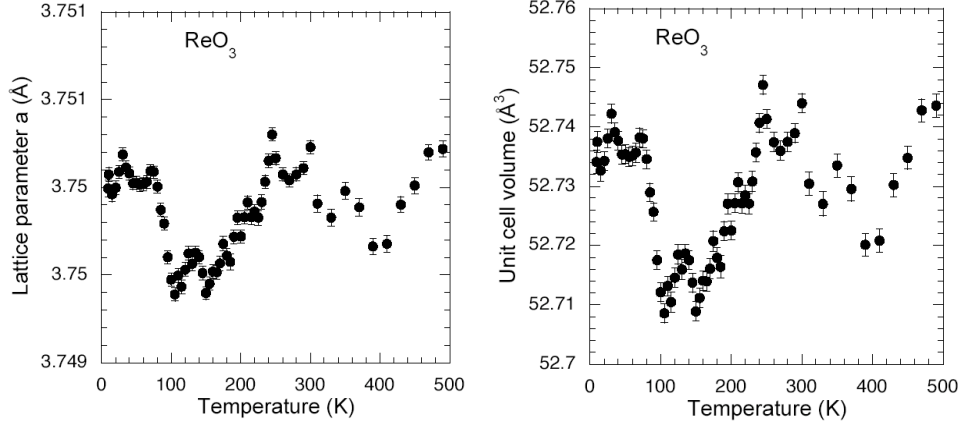


Fig. 2 - Temperature variation of (a) the lattice parameter and (b) unit cell volume of  $\text{ReO}_3$ .

One can perhaps rationalise the low temperature minimum in the lattice parameter and the unit cell volume. Axe et al. [7] determined the phonon dispersions of the low-energy transverse and longitudinal acoustic phonon modes of  $\text{ReO}_3$  by inelastic neutron scattering. Both the transverse  $T_1(\xi 00)$  and  $T_2(\xi \xi 0)$  modes have anomalously low frequencies extending to the zone boundaries. But the most remarkable feature is the pronounced reduction in frequency of the  $T_2(\xi \xi 0)$  mode near the M-point zone boundary. Axe et al. [7] have also measured the pressure dependence of the  $T_1(\frac{1}{2} \frac{1}{2} 0) \equiv M_3$  phonon that found it to decrease substantially with increasing pressure. Jorgensen et al. [9] have measured the pressure dependence of the unit cell volume of  $\text{ReO}_3$ . Combining these results one can determine the Gruneisen parameter  $\gamma_{M_3}$  of the  $M_3$  phonon which turns out to be about  $\gamma \approx -10$ . For most materials the Gruneisen parameter has the value in between 1 to 2. For  $\text{ReO}_3$  the large negative value of the Gruneisen parameter for the  $M_3$  phonon mode can lead to the negative thermal expansion at low temperatures where the low energy  $M_3$  phonon mode dominates. Similar negative thermal expansion has been observed [13] in Si and Ge for which the Gruneisen parameter  $\gamma_j(\mathbf{q})$  is negative for certain acoustic modes, which dominate the thermal expansion coefficient  $\beta$  at low temperatures because of large relative value of  $C_j(\mathbf{q})$  representing the contribution of a mode to the specific heat. The coefficient of volume expansion  $\beta$  is related to the mode Gruneisen parameter  $\gamma_j(\mathbf{q})$  by [14]

$$\beta = \frac{d}{dT} \frac{\Delta V}{V} = \frac{\kappa}{V} \sum_{\mathbf{q}_j} C_j(\mathbf{q}) \gamma_j(\mathbf{q}) \quad (1)$$

where  $\kappa$  is the compressibility and the mode Gruneisen parameter is defined as

$$\gamma_j(\mathbf{q}) = -\frac{V}{\omega_j(\mathbf{q})} \frac{\partial \omega_j(\mathbf{q})}{\partial V} = -\frac{d \ln \omega_j(\mathbf{q})}{d \ln V}. \quad (2)$$

If the dependence of the frequency  $\omega_j$  on volume can be taken to be the same for all modes, so that  $\gamma_j(\mathbf{q}) = \gamma$ , a constant, the equation (2) becomes

$$\beta = \kappa \gamma C \quad (3)$$

where  $C$  is the specific heat of unit volume. This is the Gruneisen relation. Although there is good reason to believe that  $\gamma_j(\mathbf{q})$  will not be usually the same for all modes, for many materials the coefficient of thermal expansion closely follows the variation of the specific heat.

In conclusion, we have determined the temperature variation of the unit cell volume of  $\text{ReO}_3$  in the temperature range from 10 K to 500 K and have discovered negative thermal expansion in the low temperature range 10 – 110 K and also in the high temperature range 300 – 400 K. We have ascribed the low temperature negative thermal expansion to the negative Gruneisen parameter of the zone boundary  $M_3$  phonon mode representing the anti-phase rotation of the neighbouring  $\text{ReO}_6$  octahedra. We have no explanation so far for the additional anomalous behaviour of the lattice parameter and the unit cell volume at higher temperatures.

## References

- [1] P. Fulde, *Electron correlation in molecules and solids*, Springer Verlag, Berlin Heidelberg, 1991.
- [2] P.B. Allen and W. W. Schulz, *Phys. Rev. B* **47**, 14434 (1993).
- [3] F.S. Ravazi, Z. Altounian and W.R. Datars, *Solid State Comm.* **28**, 217 (1978).
- [4] J.E. Schirber and B. Morosin, *Phys. Rev. Lett.* **42**, 1485 (1979).
- [5] B. Batlogg, R.G. Maines, M. Greenblatt and S. DiGregorio, *Phys. Rev. B* **29**, R3762 (1984).
- [6] J.E. Schirber, B. Morosin, R.W. Alkire, A.C. Larson and P.J. Vergamini, *Phys. Rev. B* **29**, 4150 (1984).
- [7] J.D. Axe, Y. Fujii, B. Batlogg, M. Greenblatt and S. Di Gregorio, *Phys. Rev. B* **31**, 663 (1985).
- [8] J.E. Jorgensen, J.D. Jorgensen, B. Batlogg, J.P. Remeika and J.D. Axe, *Phys. Rev. B* **33**, 4793 (1986).
- [9] J.-E. Jorgensen, S. Olsen and L. Gerward, *J. Appl. Cryst.* **33**, 279 (2000)
- [10] E. Suzuki, Y. Kobayashi, S. Endo and T.K. Ikegawa, *J. Phys.: Condens. Mat.* **14**, 10589 (2002).
- [11] J.-E. Jorgensen, W.G. Marshall, R.I. Smith, J. Staun Olsen and L. Gerward, *J. Appl. Cryst.* **37**, 857 (2004)
- [12] For a review see J.S.O. Evans, *J. Chem. Soc. Dalton Trans.* **19**, 3317 (1999).
- [13] G. Dolling and R.A. Cowley, *Proc. Phys. Soc.* **88**, 463 (1966).
- [14] W. Cochran, *The Dynamics of Atoms in Crystals*, Edward Arnold (Publishers) Limited, London (1973).