High pressure PDF analysis of ReO_3

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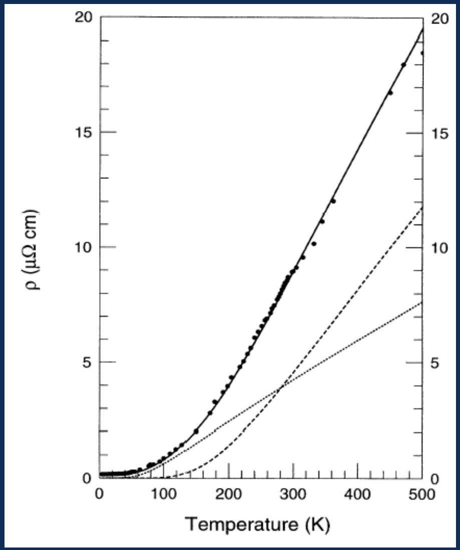
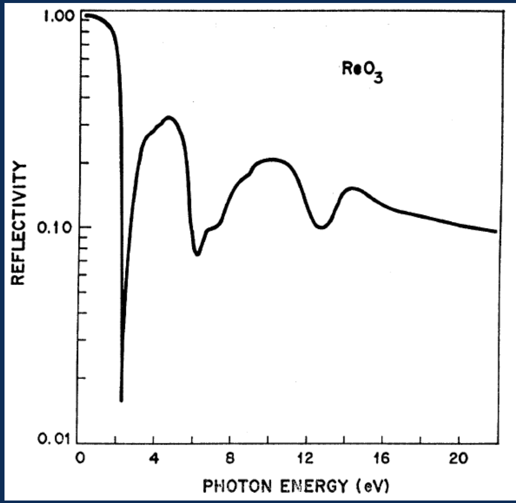
ReO_3 and its novel properties

- ReO_3 is a simple diamagnetic metallic oxide with conductivity comparable to Ag.
- Has a simple cubic perovskite structure ABO_3 with missing A atoms.
- Does not become superconducting down to 20 mK.
- Resistivity is dominated by electron-phonon coupling.
- Does not show any structural transition as a function of temperature.
- Transform to the high pressure phase at P_c = 5.2 kbar.
- High pressure phase is much more compressible than the low-pressure phase.
  ReO_3 is twice as hard as Si at ambient pressure but as soft as NaCl at P = 7 kbar.

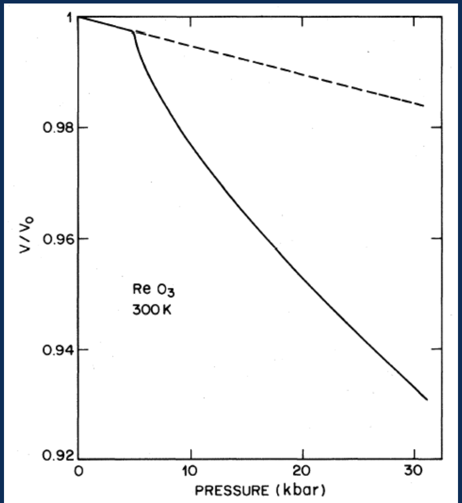
Resistivity



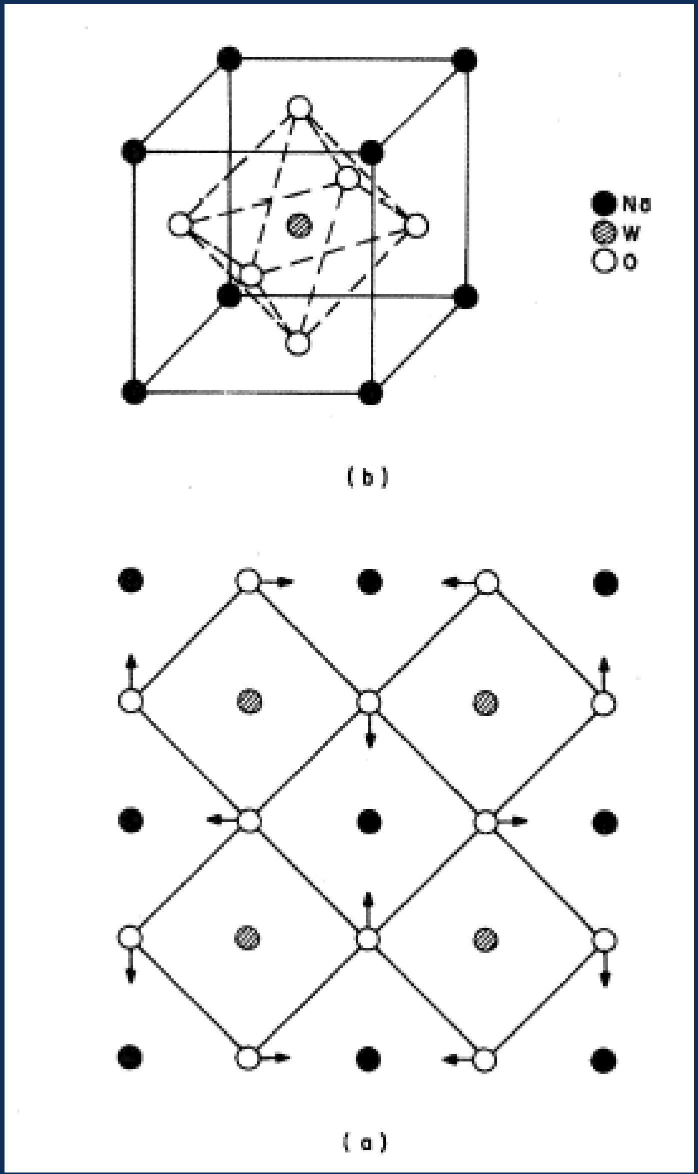
Reflectivity

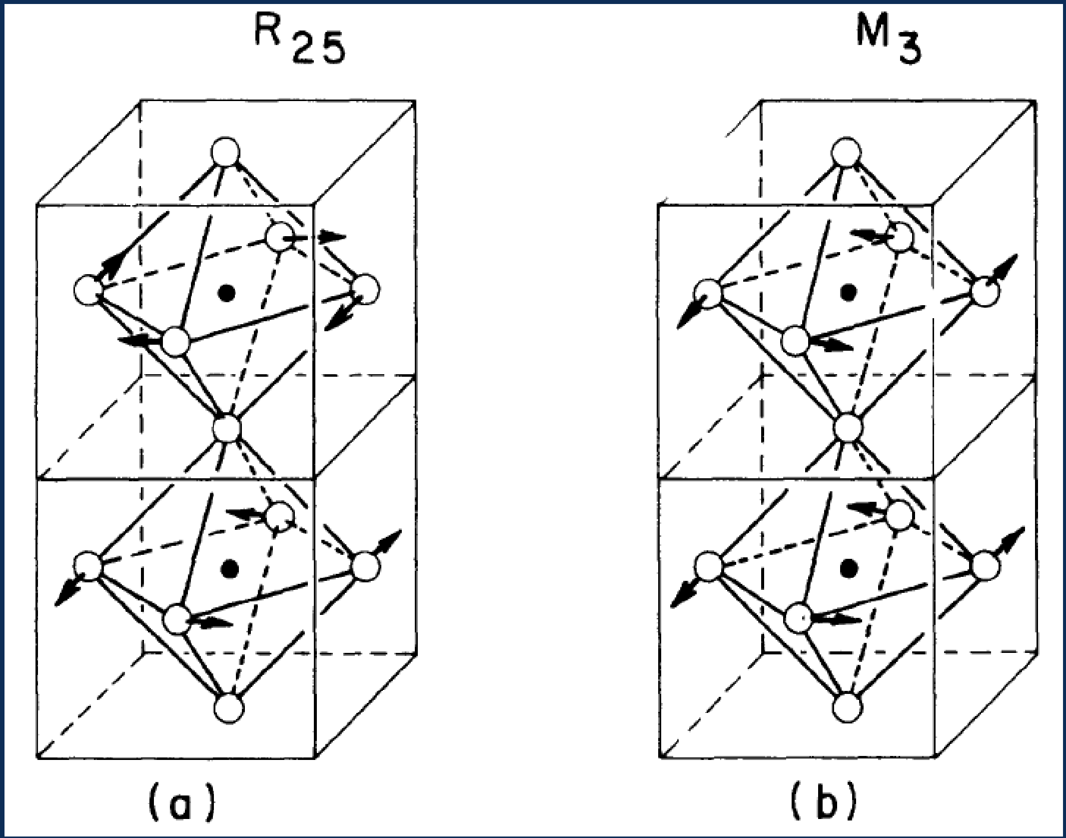


Compressibility



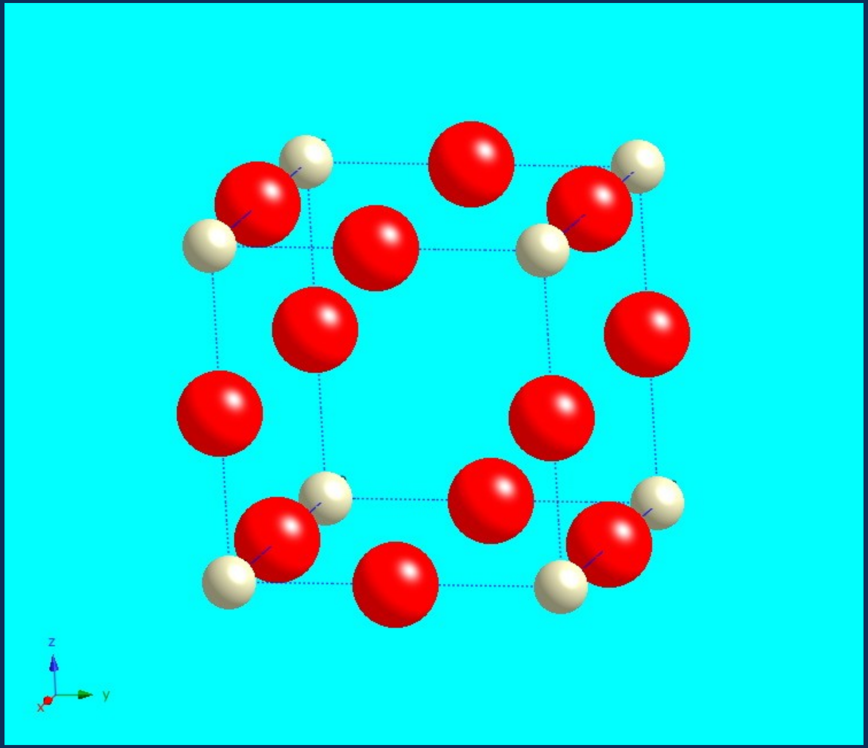
R_{25} and M_3 phonon modes in perovskite structure



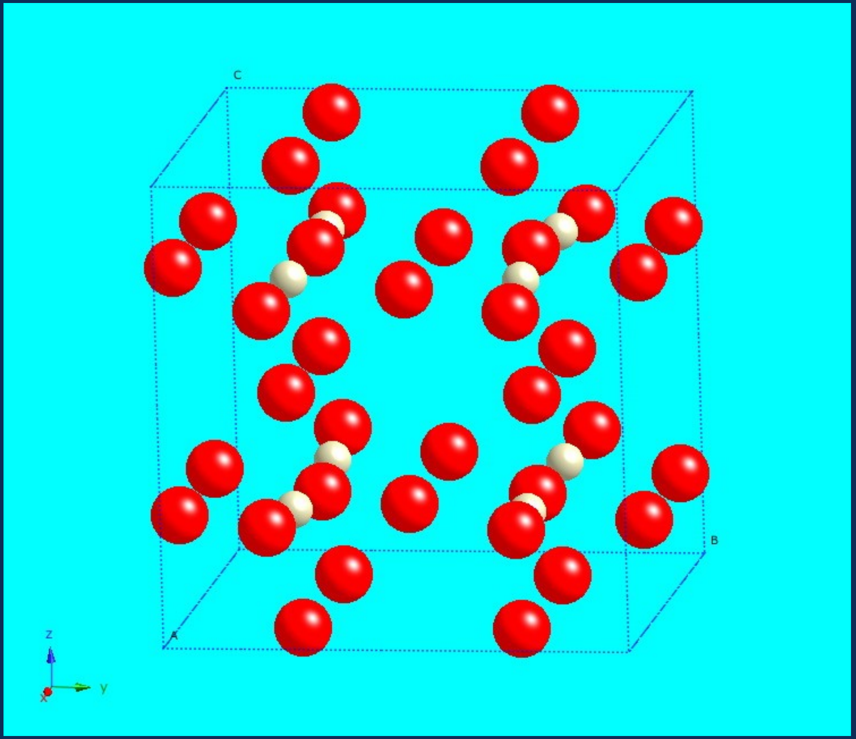


ReO_3 structure

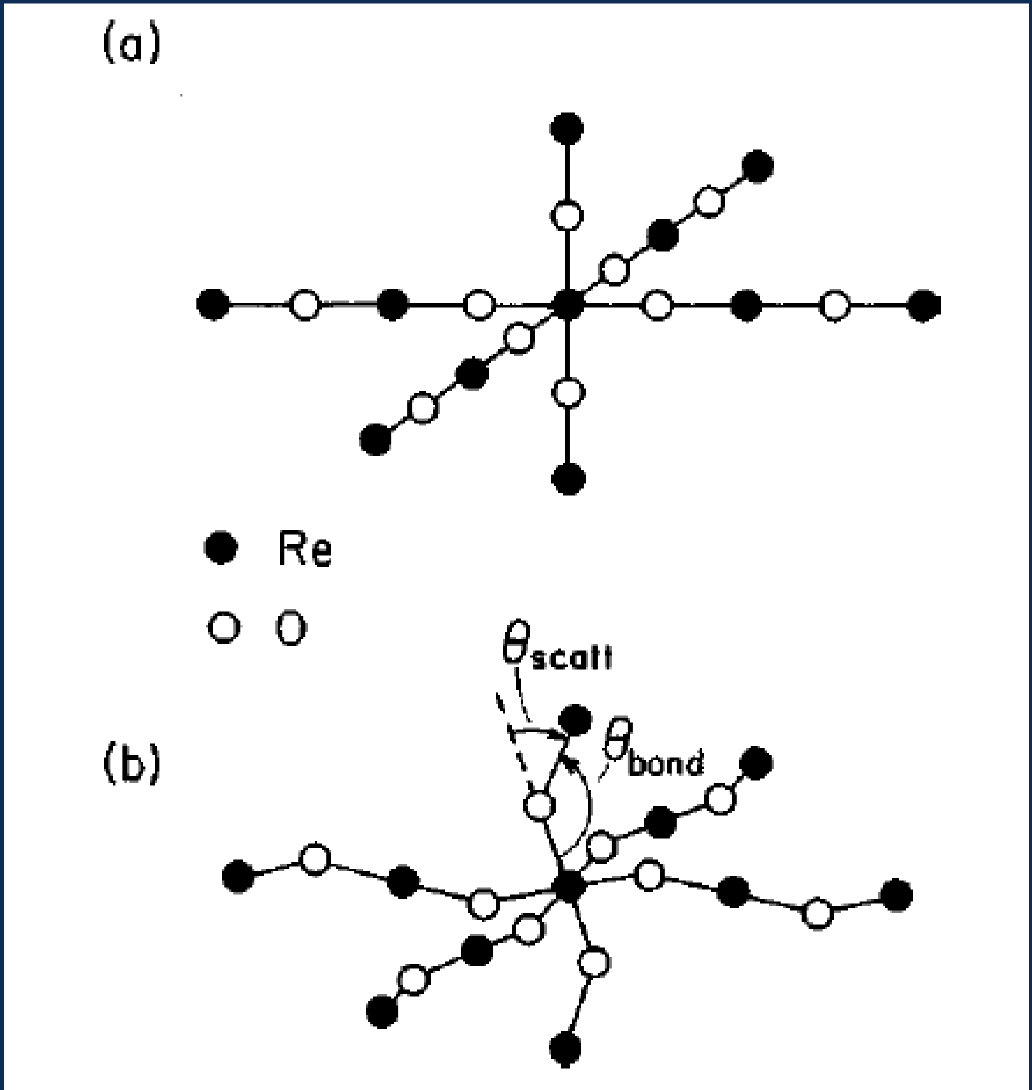
Ambient pressure phase

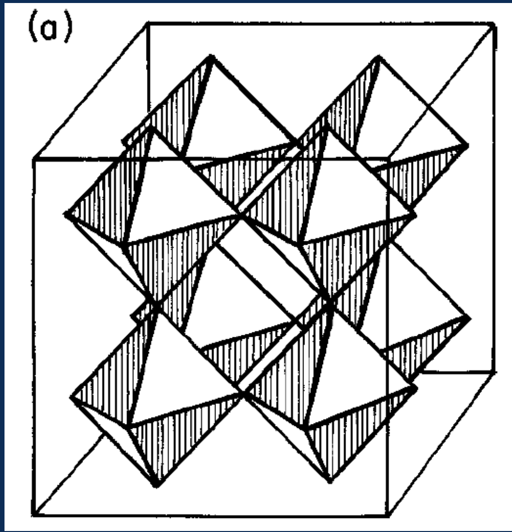


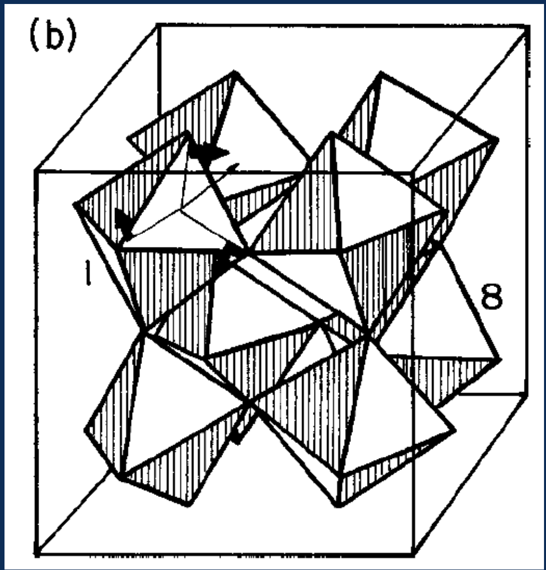
High pressure phase



Low-pressure and high-pressure structure of ReO_3

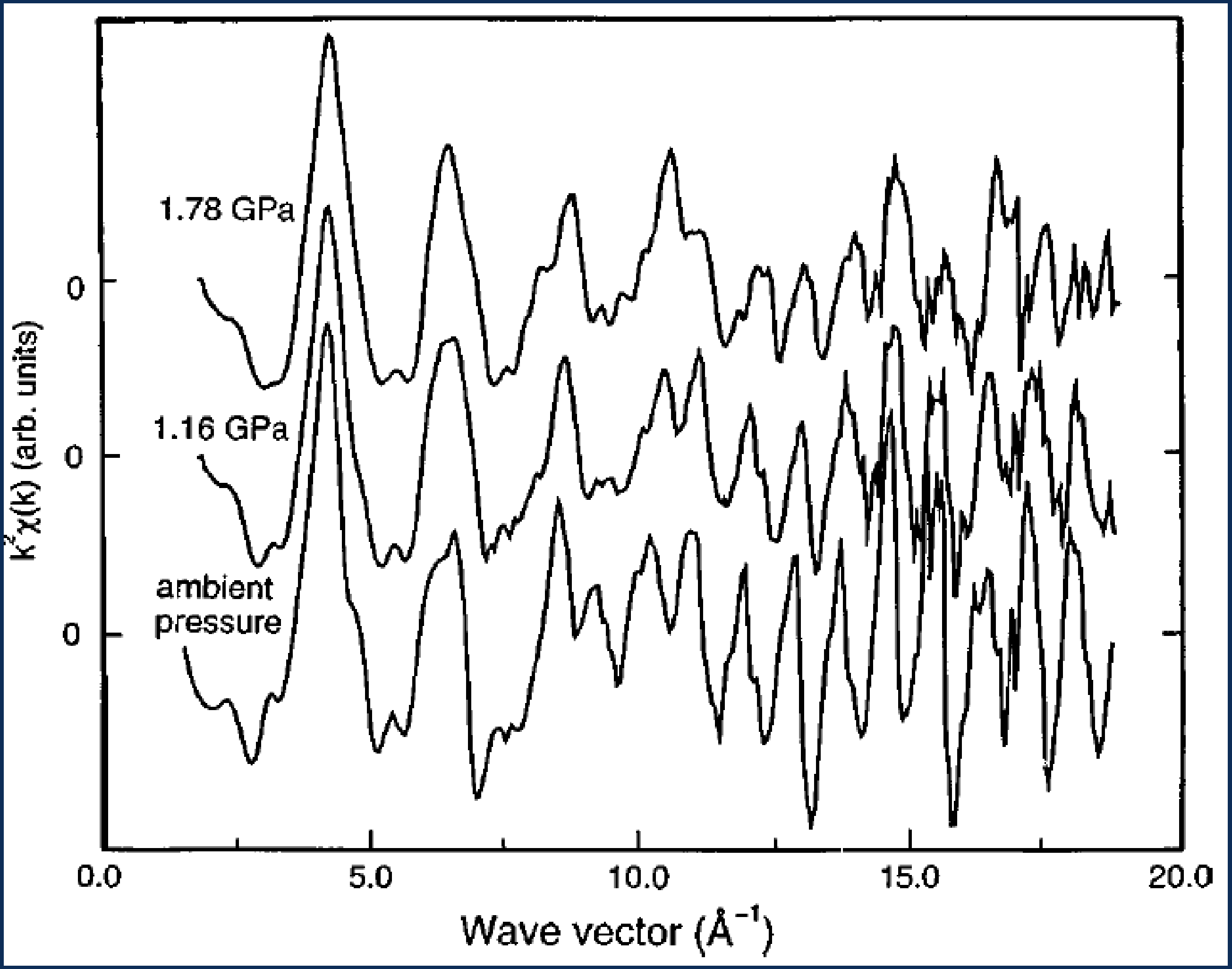






$k^2\chi(\kappa)$ from XAFS measurements at different pressure

B. Houser and R.Ingalls, Phys. Rev. B **61**, 6515 (2000).



Refinement of ReO_3 structure from powder neutron diffraction

J.E. Jorgensen et al., Phys. Rev. B **33**, 4793 (1986).

TABLE I. Structural parameters for ReO_3 at atmospheric pressure in the cubic $Pm3m$ space group. Re is in special position $1a$ (0,0,0) and O is in special position $3d$ ($\frac{1}{2}$,0,0). Numbers in parentheses are standard deviations of the last significant digit.

$a = 3.7504(1)$ Å
$\langle U^2 \rangle$(Re) = 0.0023(4) Å^2
$\langle U_{\parallel}^2 \rangle$(O) = 0.0042(8) Å^2
$\langle U_{\perp}^2 \rangle$(O) = 0.019(5) Å^2
R_{wp} = 4.60%
R_{exp} = 2.67%

Octahedral angle

$$\phi = \cos^{-1}\left[\frac{z+y}{2\sqrt{z^2+y^2-zy}}\right]$$

Re-O-Re bond angle

$$\theta = \cos^{-1}[1 - \frac{2}{9}(2\cos\phi + 1)^2]$$

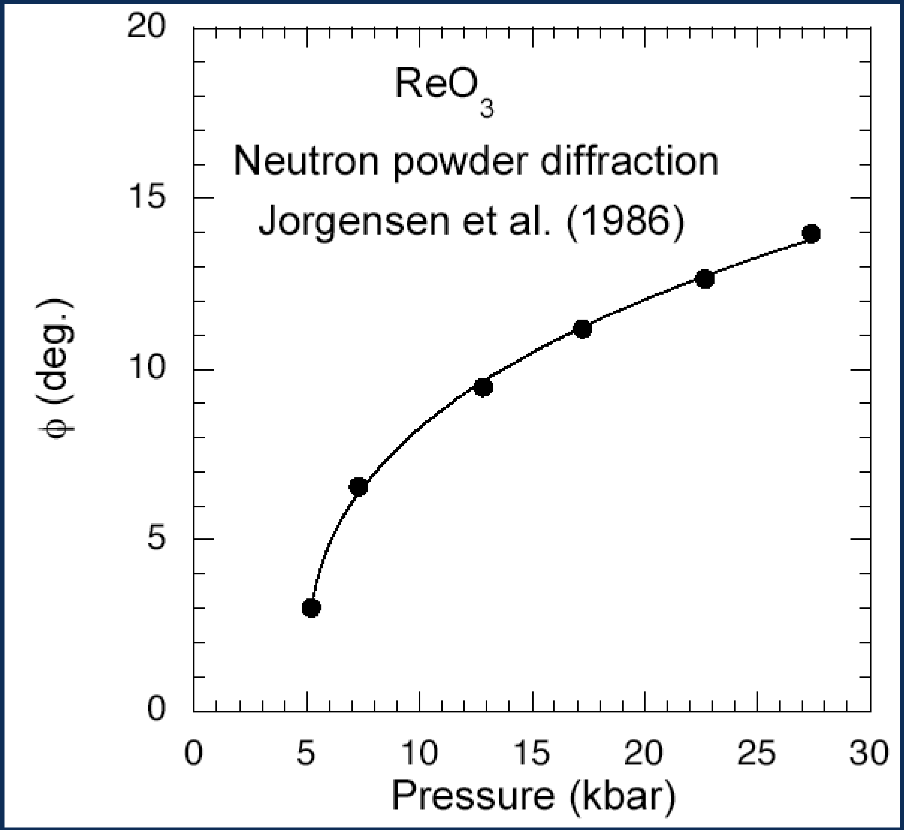
TABLE II. Structural parameters for ReO_3 versus pressure in the cubic $Im3$ space group. Re is in special position $8c$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and O is in special position $24g$ $(0,y,z)$. Temperature factors are in units of Å^2.

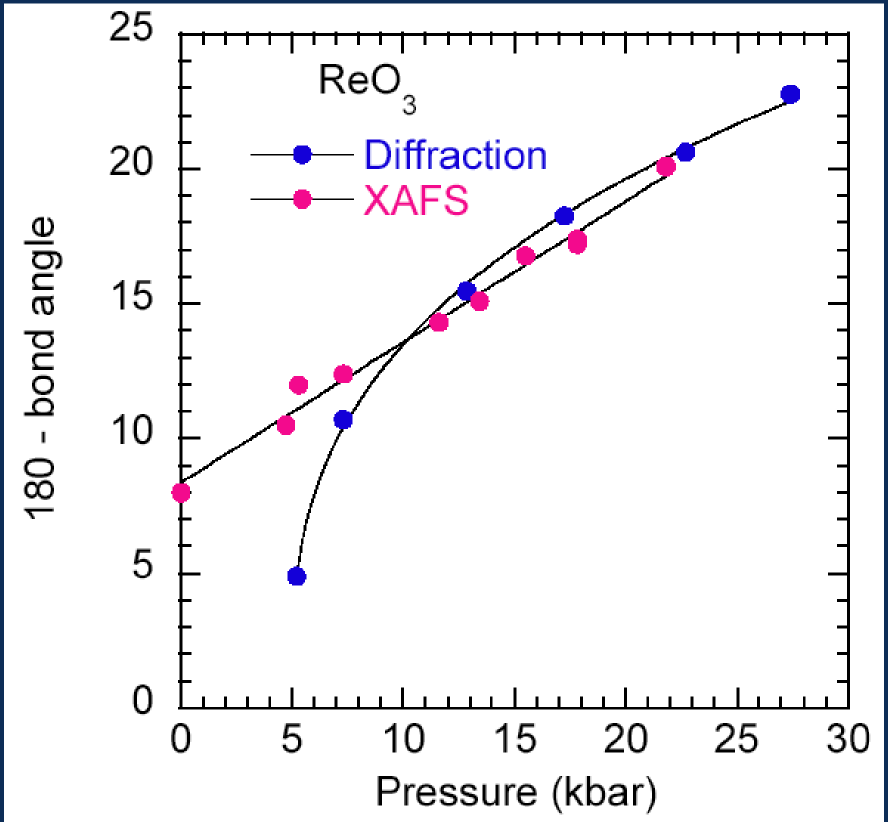
P (kbar)	7.30	12.85	17.25	22.70	27.40
a (Å)	7.4640(2)	7.4236(2)	7.3969(2)	7.3677(2)	7.3426(3)
$\langle U^2 \rangle$(Re)	0.0022(5)	0.0018(5)	0.0015(5)	0.0012(6)	0.0016(6)
y(O)	0.232(1)	0.225(1)	0.2197(8)	0.2158(9)	0.2104(9)
z(O)	0.265(2)	0.273(1)	0.2763(9)	0.280(1)	0.281(1)
$\langle U_{\parallel}^2 \rangle$(O)	0.006(1)	0.006(1)	0.005(1)	0.001(1)	0.0005(14)
$\langle U_{\perp}^2 \rangle$(O)	0.0094(9)	0.007(1)	0.0077(9)	0.008(1)	0.009(1)
R_{wp} (%)	5.86	6.18	5.52	6.64	6.90
R_{exp} (%)	3.26	3.26	3.07	3.61	3.44

Octahedral rotation and bond angle in ReO_3

Glazer notation ($a^+ a^+ a^+$)

After B. Houser and R.Ingalls, Phys. Rev. B **61**, 6515 (2000).

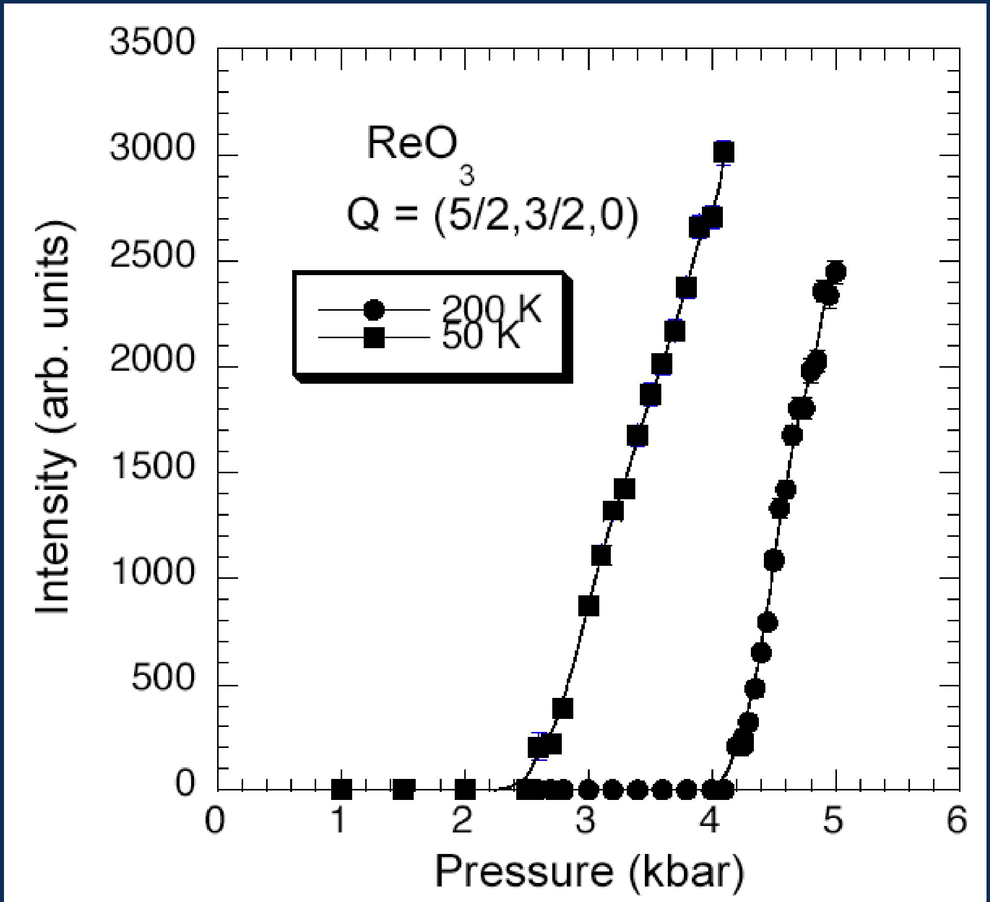


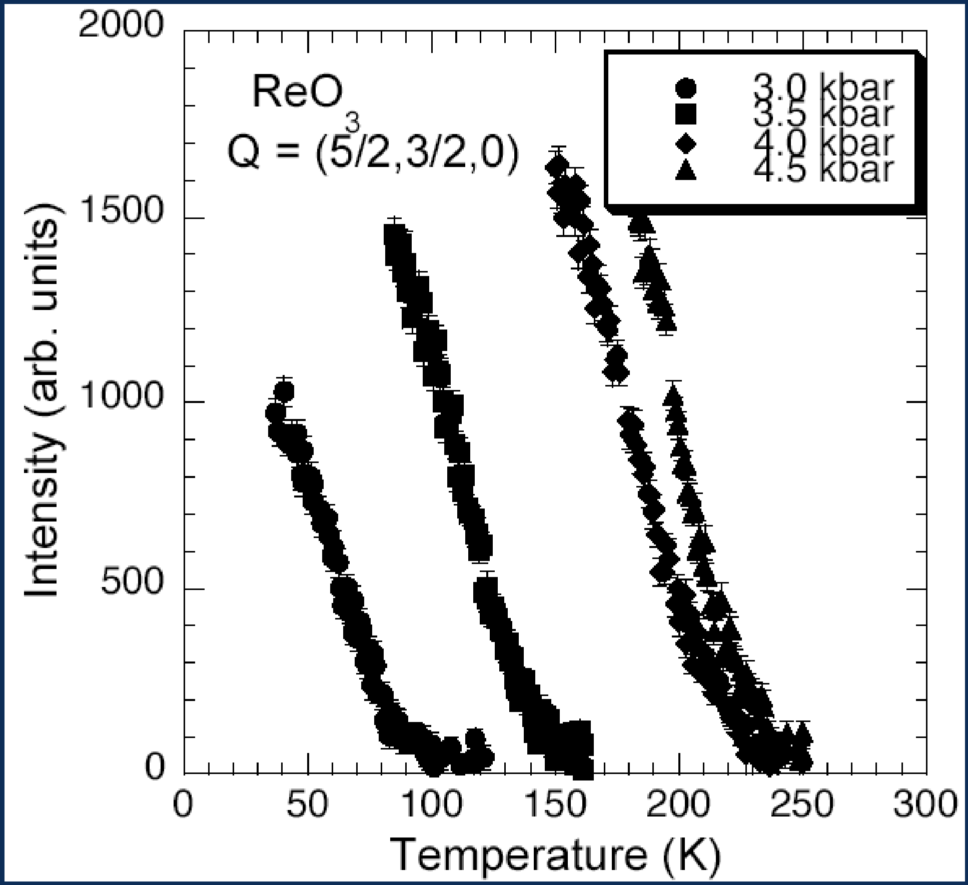


After J.E. Jorgensen et al., Phys. Rev. B **33**, 4793 (1986).

High pressure phase

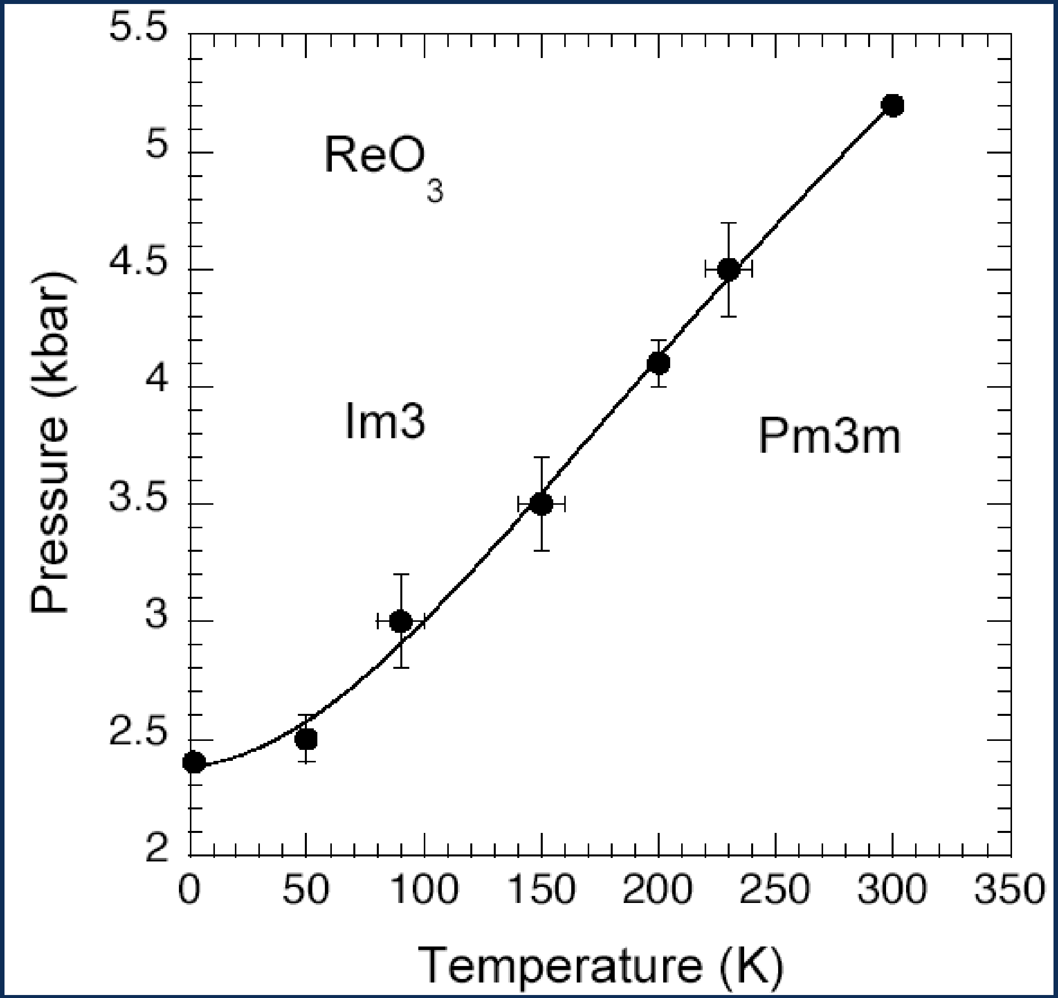
T. Chatterji and G.J. McIntyre, Solid State Comm. **139**, 12 (2006).





Pressure-Temperature phase diagram

T. Chatterji and G.J. McIntyre, Solid State Comm. **139**, 12 (2006).



We have refined the structures of Pm3m and Im3 phases from the single crystal neutron diffraction data at P = 0 and 7 kbar:

Pm3m:

$N = 286$, $N_p = 5$, $R_w = 0.069$

Im3:

$N = 949$, $N_p = 10$, $R_w = 0.091$

y(O): 0.2357(2).

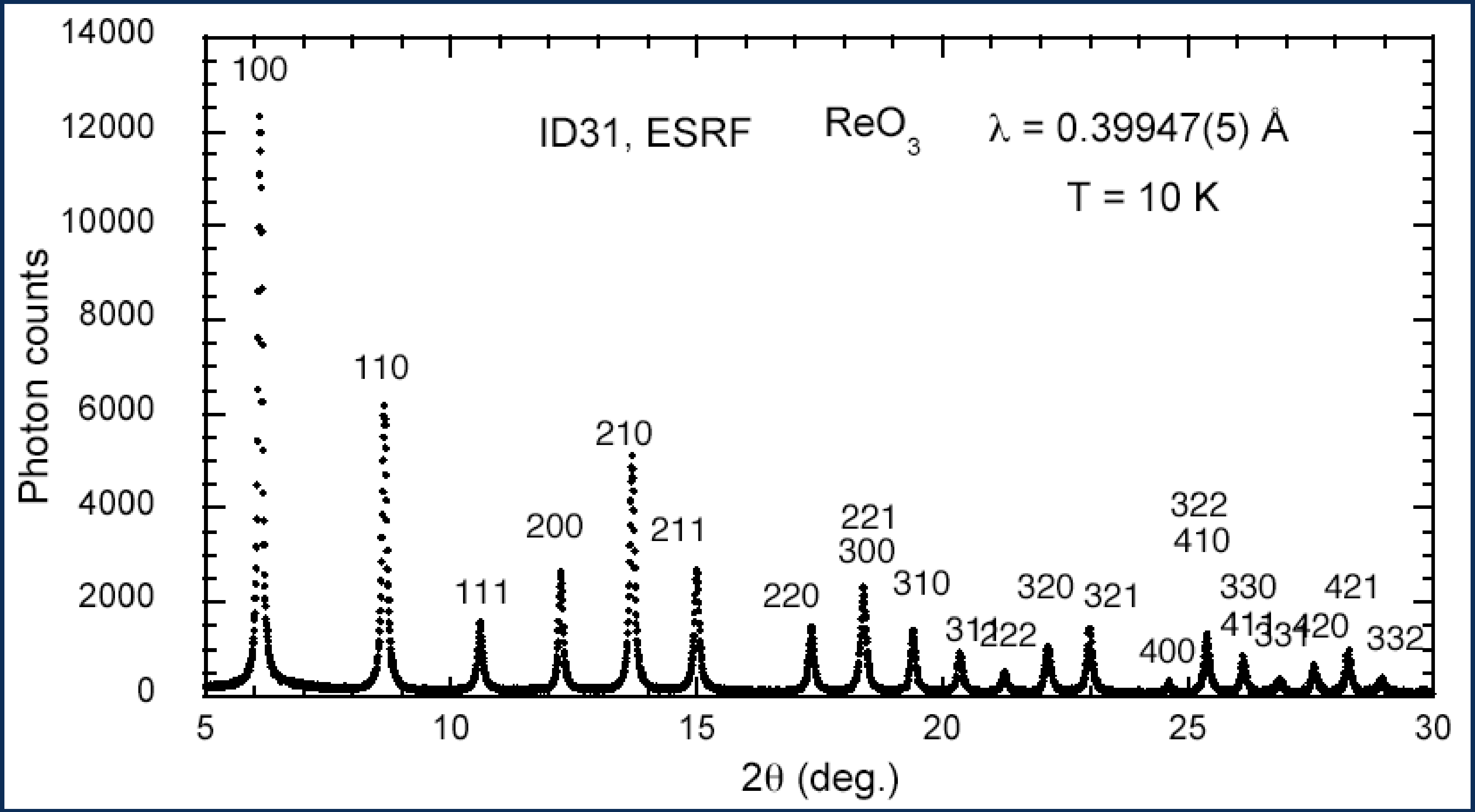
z(O): 0.2645(2).

$\phi = 5.70$ deg.

X-ray diffraction data

T. Chatterji and M. Brunelli (to be published).

Z(O) = 8, Z(Re) = 75
X-rays: useful only for determining lattice parameter.

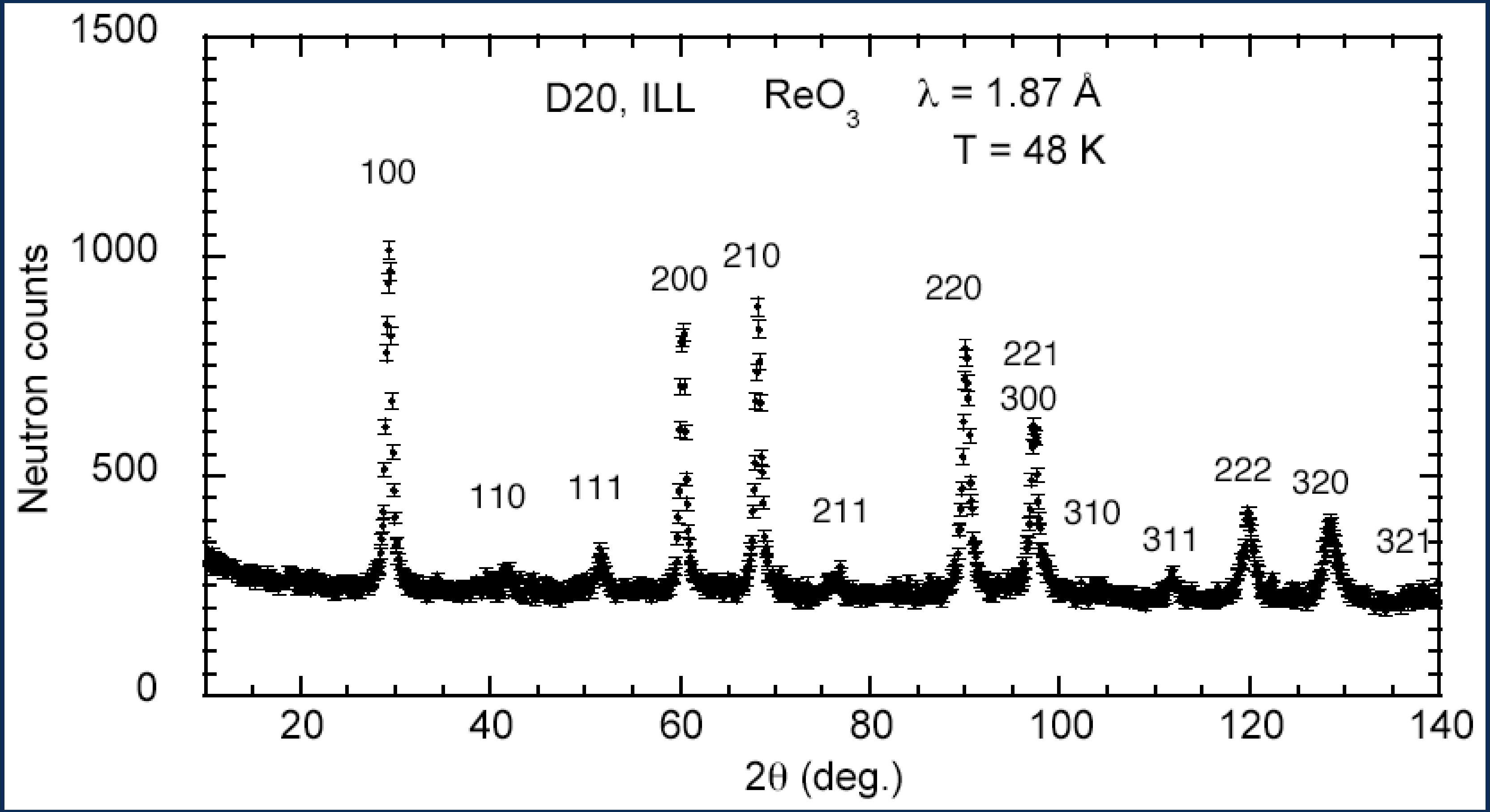


$Q_{max} = 8.1\ \text{Å}^{-1}$

Neutron diffraction data

T. Chatterji and P. Henry (to be published)

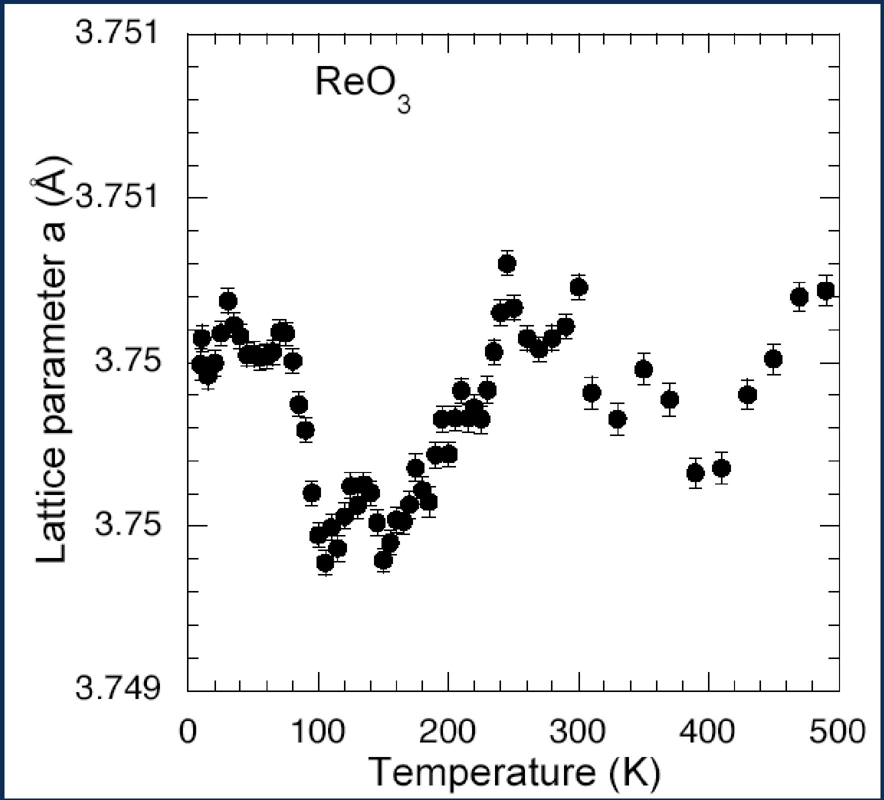
b(O) = 5.803(4), b(Re) = 9.2(2)
Neutrons: indispensable for structure.

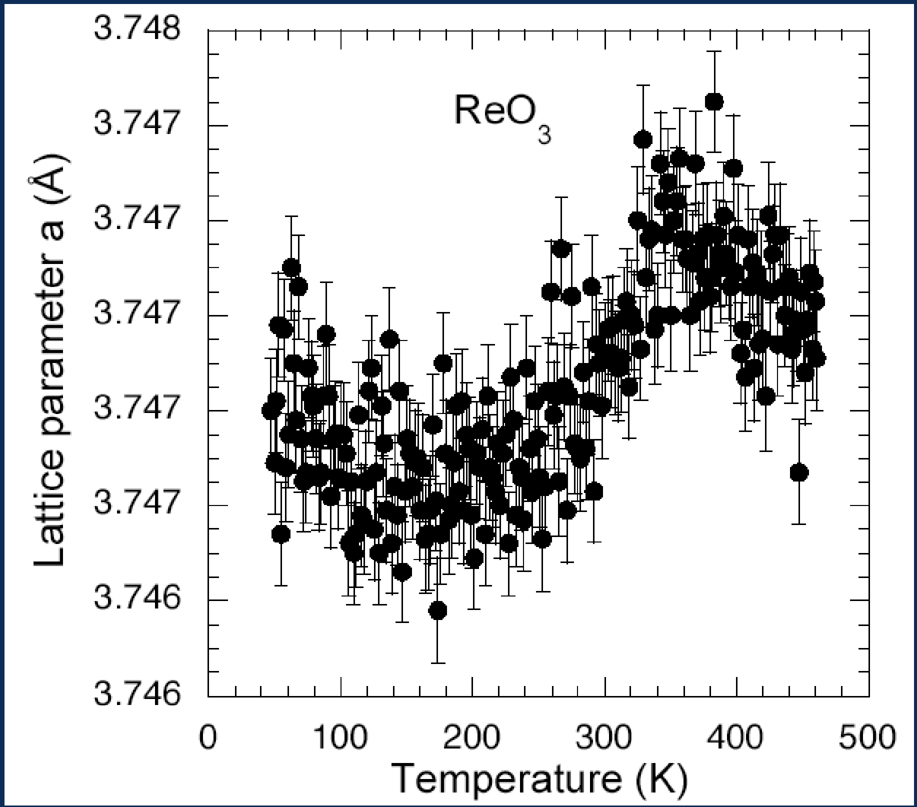


$Q_{max} = 6.3\ Å^{-1}$

Negative thermal expansion

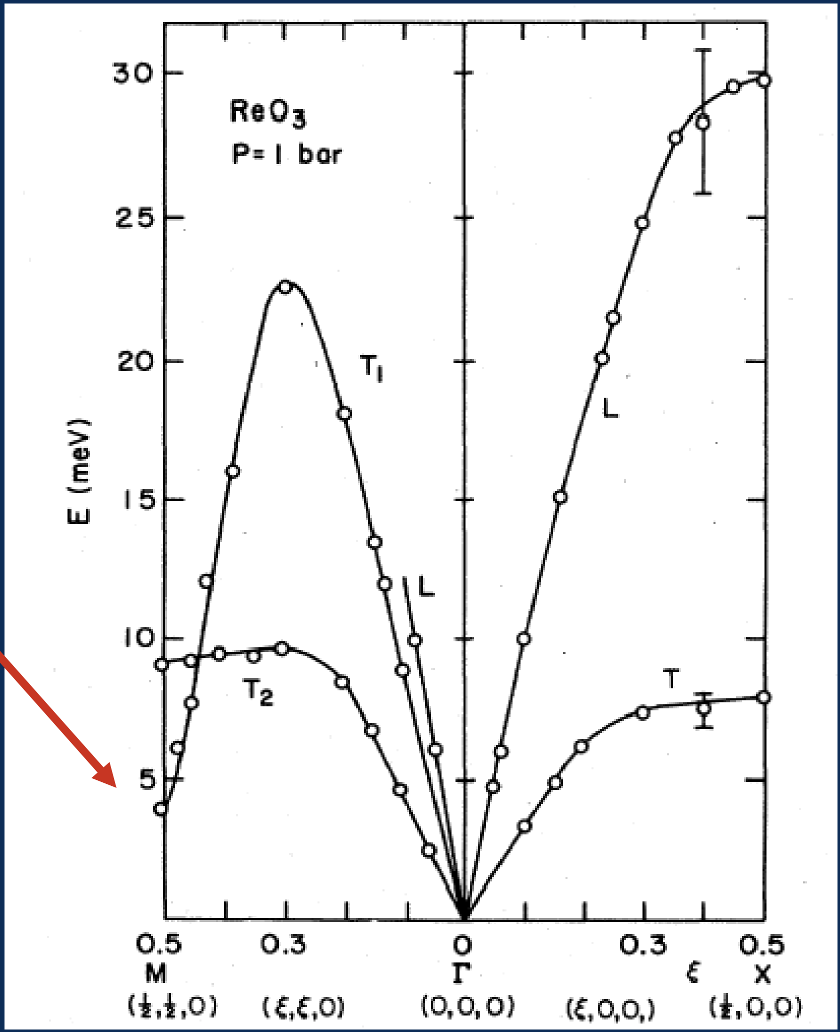
T. Chatterji, M. Brumelli and P. Henry (to be published)





Dispersion of low-energy phonon modes in ReO_3

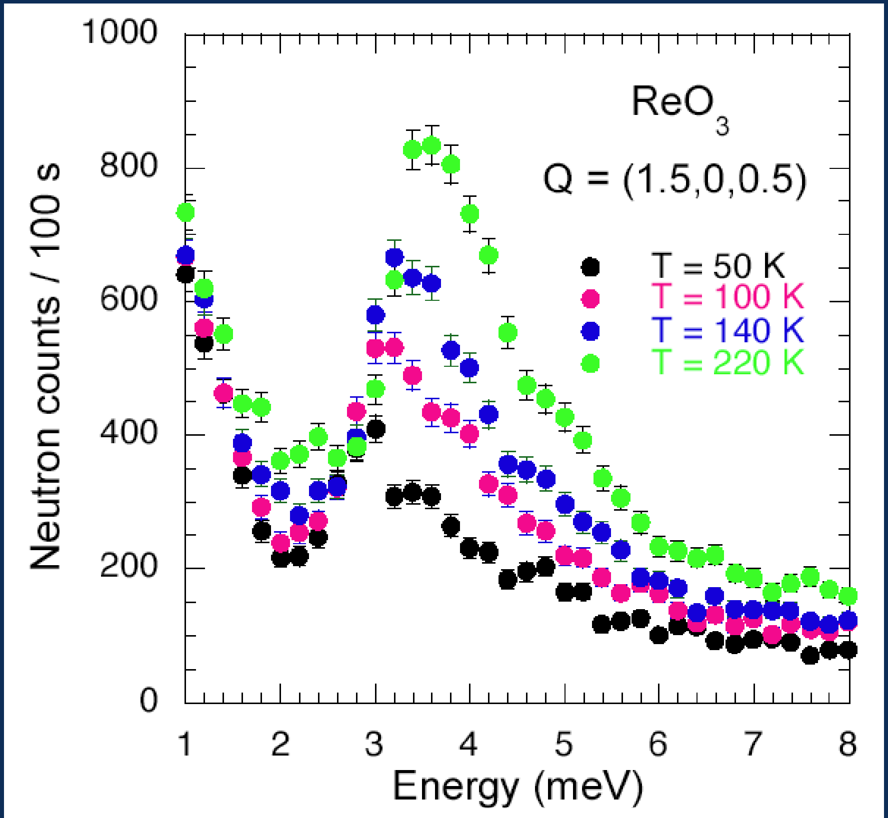
J. Axe et al. Phys. Rev. B **31**, 663 (1985).

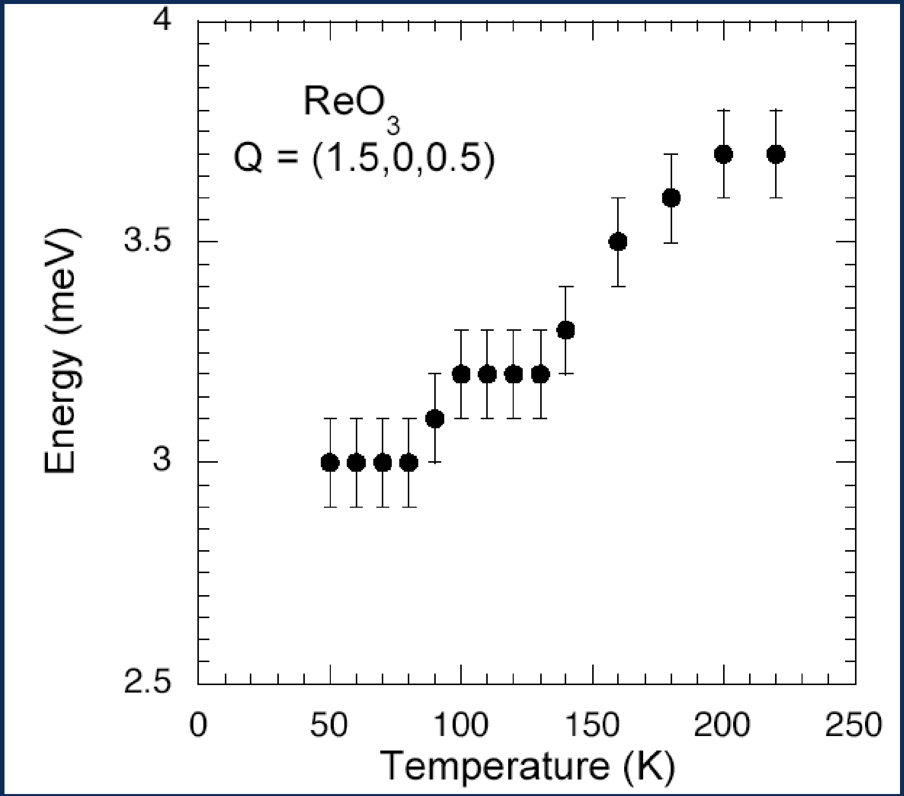


The most remarkable feature is the pronounced reduction in energy of the T1(εε0) mode near The M-point zone-boundary.

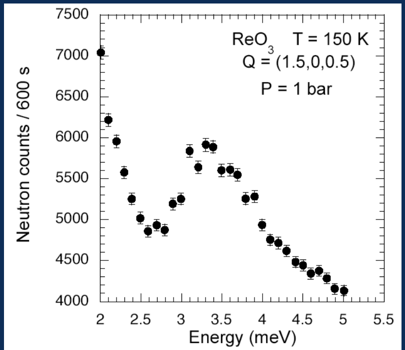
Temperature dependence of the M_3 phonon mode

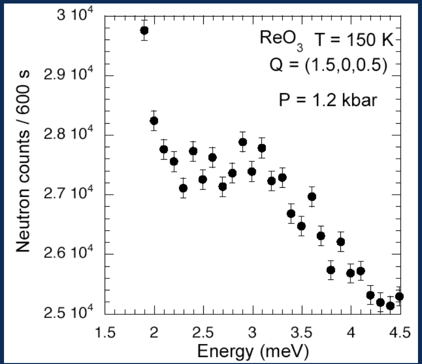
T. Chatterji, M. Jimenez-Ruiz and P. Freeman (unpublished)



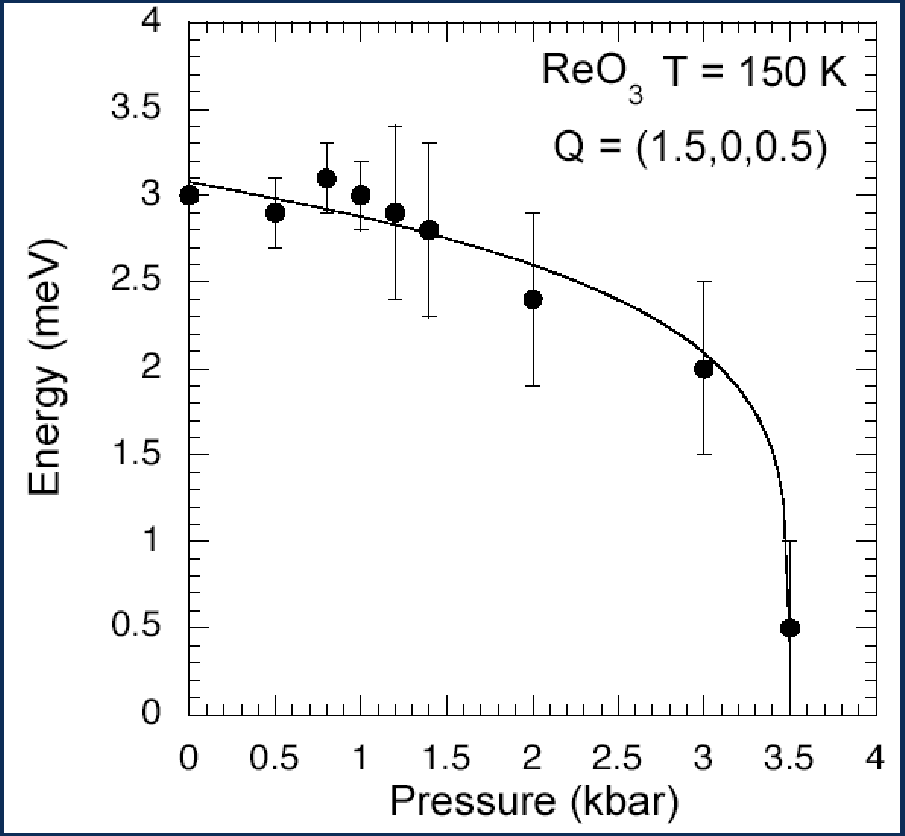


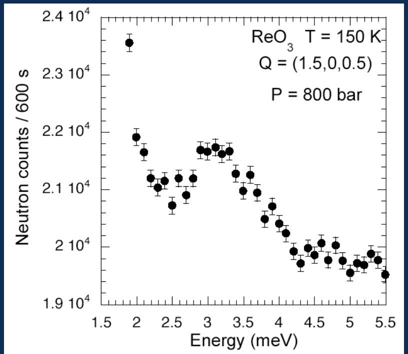
Pressure dependence of the M_3 phonon mode

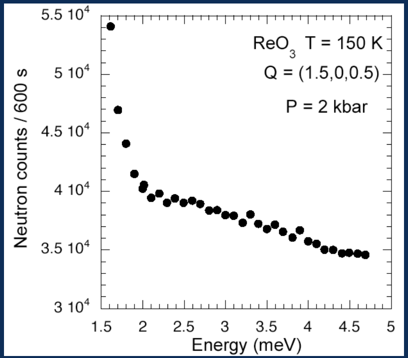


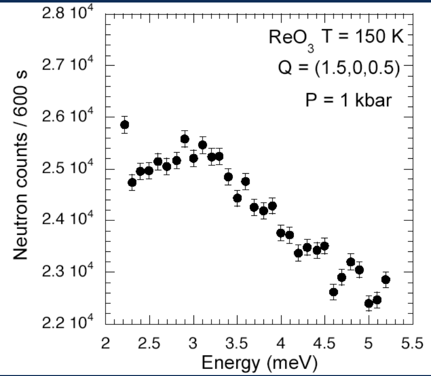


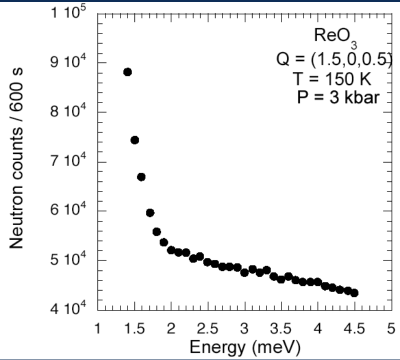
T. Chatterji, M. Jimenez-Ruiz and P. Freeman (unpublished)







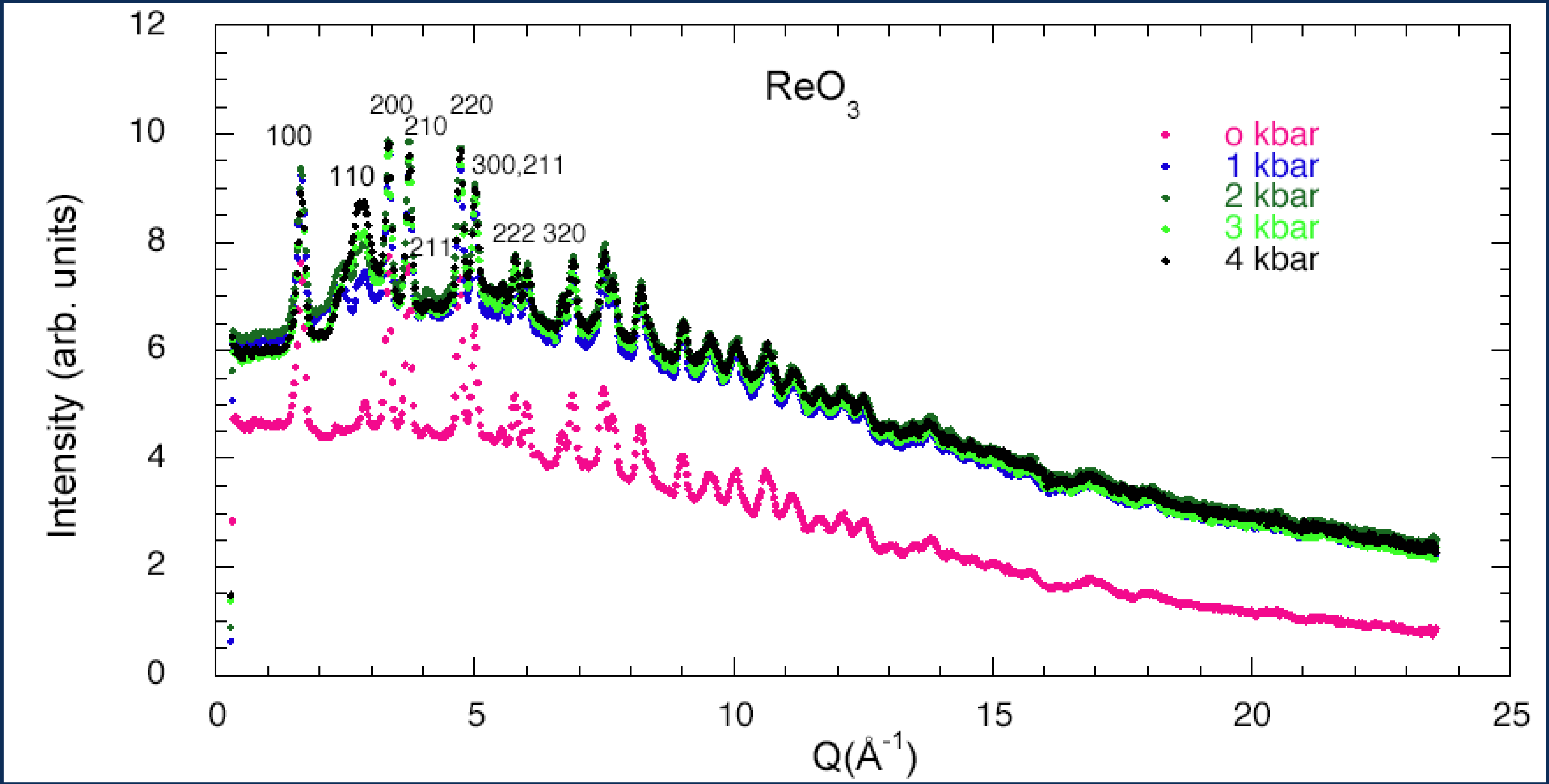




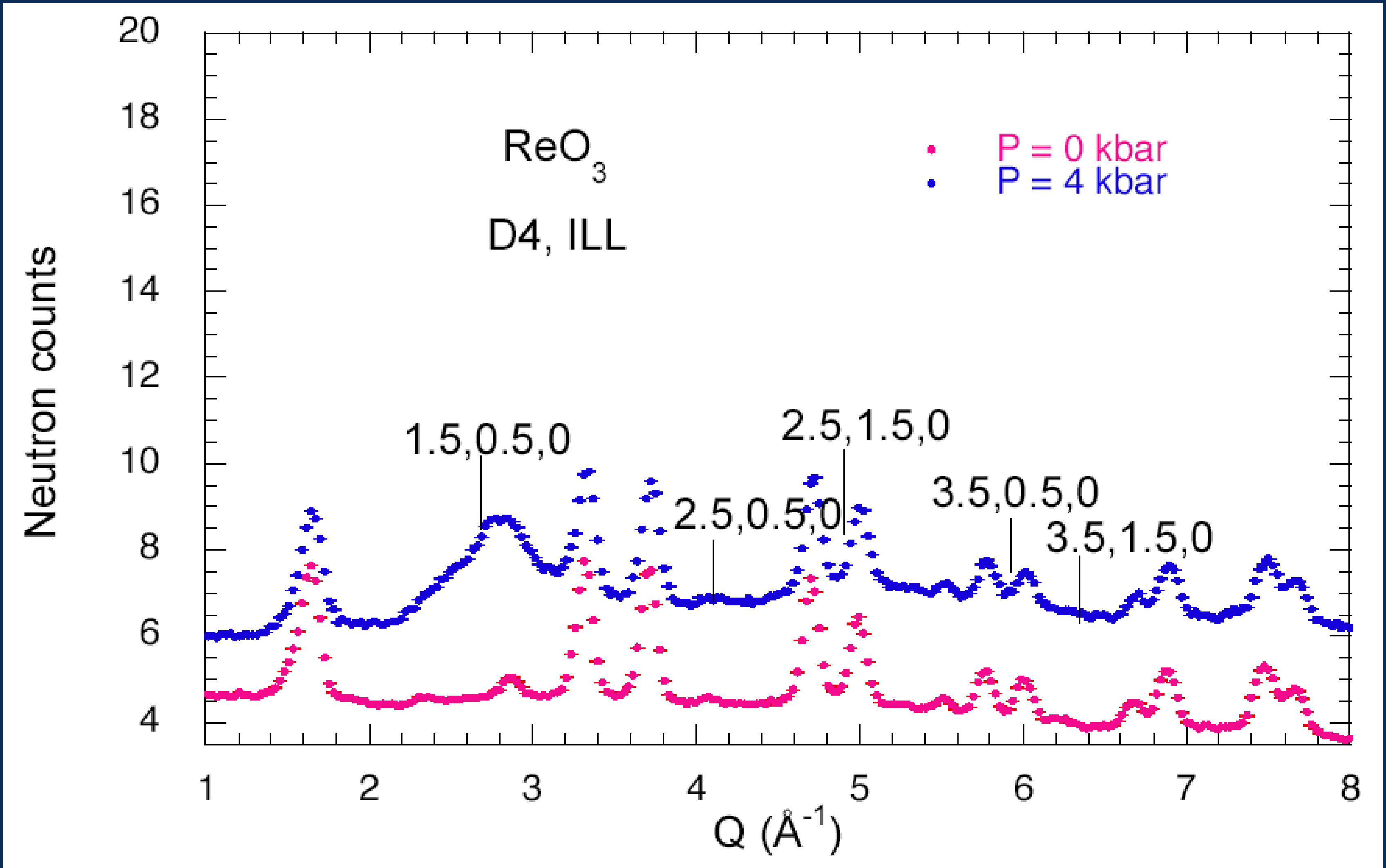
Problem to be solved

Is there any diffraction evidence for the bent Re-O-Re bonds (octahedral rotations) in ReO_3 already in the ambient pressure *Pm3m* phase?

D4 neutron diffraction data



Superlattice positions of the HP phase



Pair distribution functions

Debye (1915), Zernicke and Prins (1927), Egami and Billinge (2003)

Reduced pair distribution (PDF) function

$$G(r) = 4\pi\rho_0(g(r)-1) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

Radial distribution function

$$R(r) = 4\pi r^2\rho_0 g(r).$$

Number of neighbours

$$N_c = \int_{r_1}^{r_2} R(r)dr$$

Back transforming the PDF function

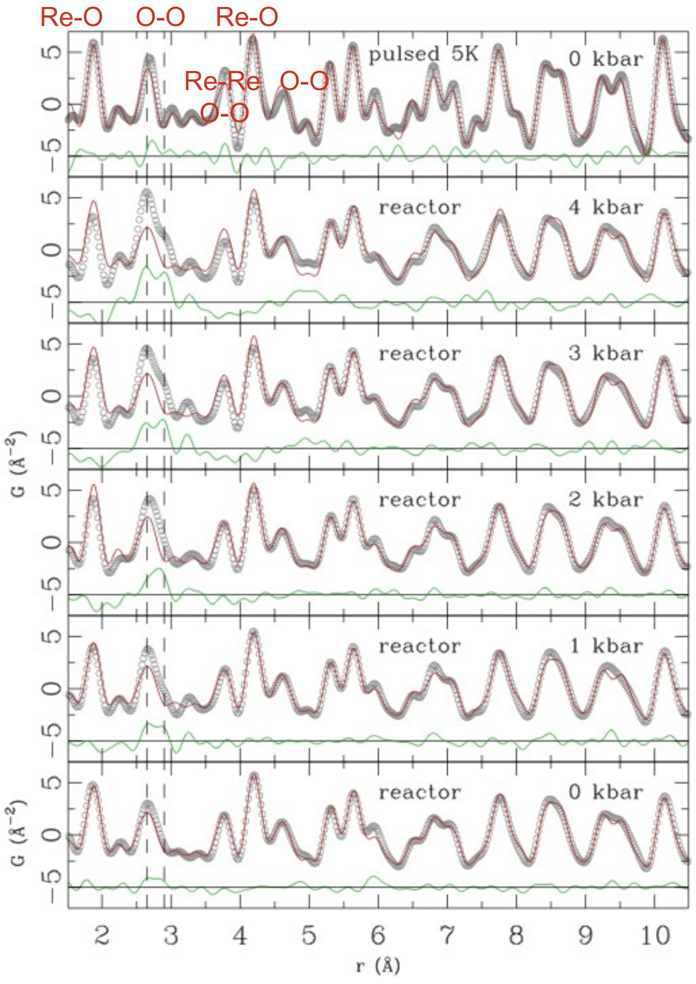
$$S(Q) = 1 + \frac{1}{Q}\int_0^\infty G(r)\sin(Qr)dr$$

Modelling radial distribution function

$$R(r) = \sum_\nu\sum_\mu \frac{b_\nu b_\mu}{<b>^2}\delta(r-r_{\nu\mu})$$

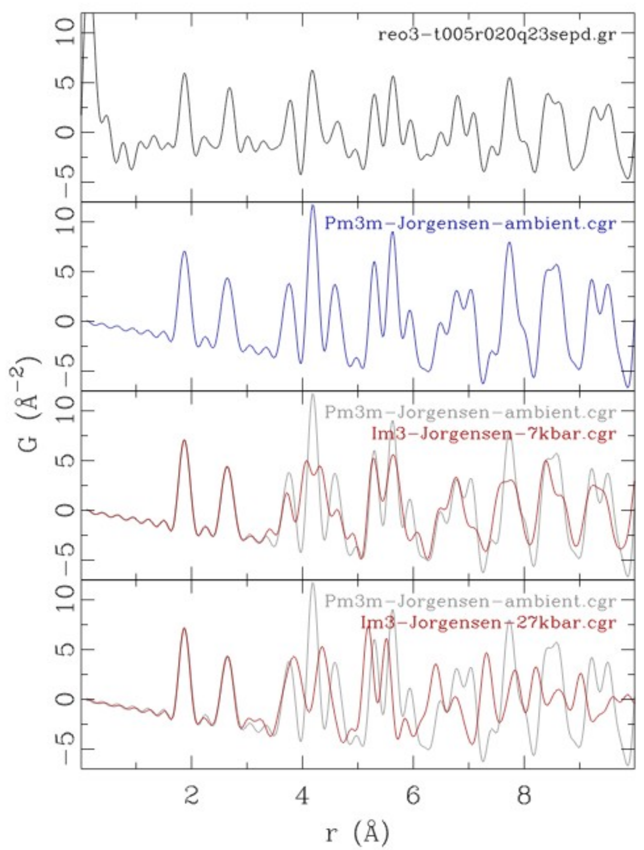
SEPD and D4 PDF data and model

Pm3m model



Re-O: 1.88,4.19 Å
O-O: 2.65, 3.75,4.59 Å
Re-Re: 3.75, 5.30 Å

Pm3m and *Im3* model



Refinement results of Im3 model

D4 (ILL) data $Q_{max} = 23$ Å^{-1}

Im3 model

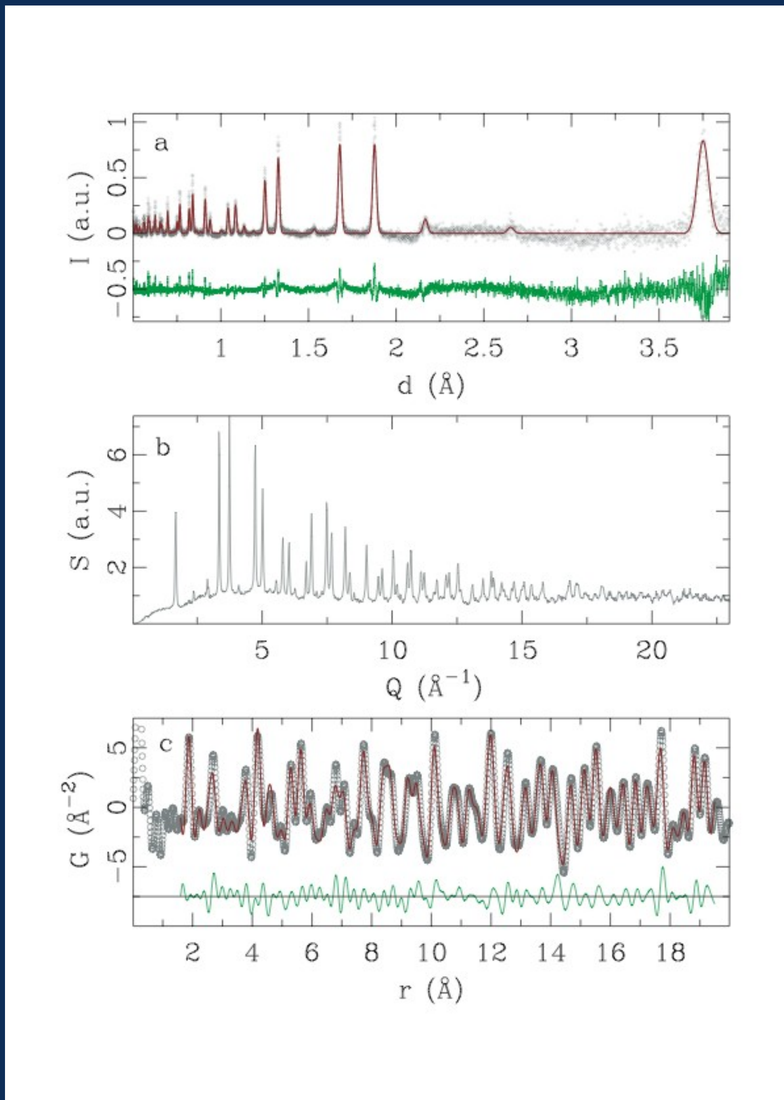
3.4-10.4 Å range

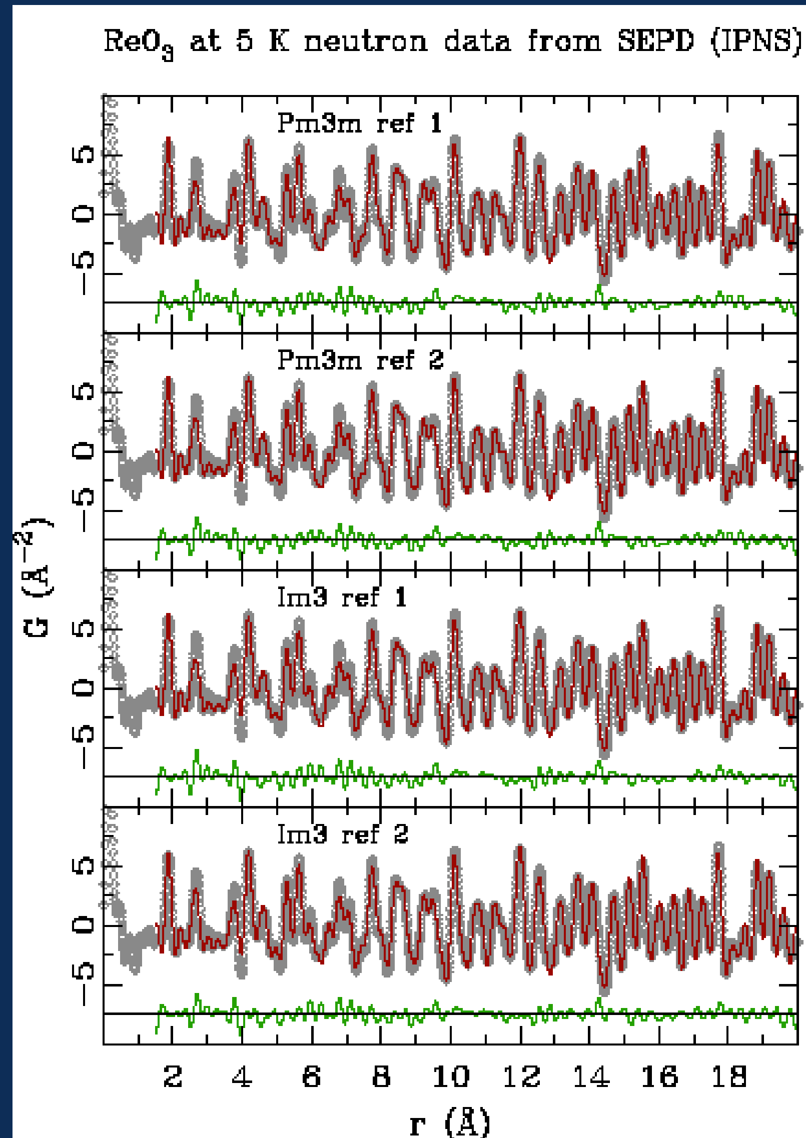
P(kbar)	ϕ(deg.)	Rw
0	0.35	0.22
1.0	2.31	0.26
2.0	2.69	0.26
3.0	0.17	0.61
4.0	3.12	0.43

5.0-10.4 Å range

P(kbar)	ϕ(deg.)	Rw
0	1.62	0.18
1.0	1.98	0.25
2.0	0.41	0.26
3.0	2.70	0.22
4.0	0.49	0.29

SEPD neutron diffraction data at T = 5 K





Pm3m: $N_p = 6$

10-20Å
$R_w = 0.147$

1.5-20Å
$R_w = 0.193$

Im3: $N_p = 7$

10-20Å
$\phi = 2.31$ deg.
$R_w = 0.145$

1.5-20Å
$\phi = 2.66$ deg.
$R_w = 0.194$

Conclusions and outlook

- So far there exist no conclusive evidence for the bent Re-O-Re bonds in ReO_3 at ambient pressure or at higher pressures below P_c in the low pressure phase.
- Better quality data are needed for making any definitive conclusion.
- New experiment on NPDF at Los Alamos has been planned.