Lattice dynamics of ReO_3 from the quasiharmonic approximation

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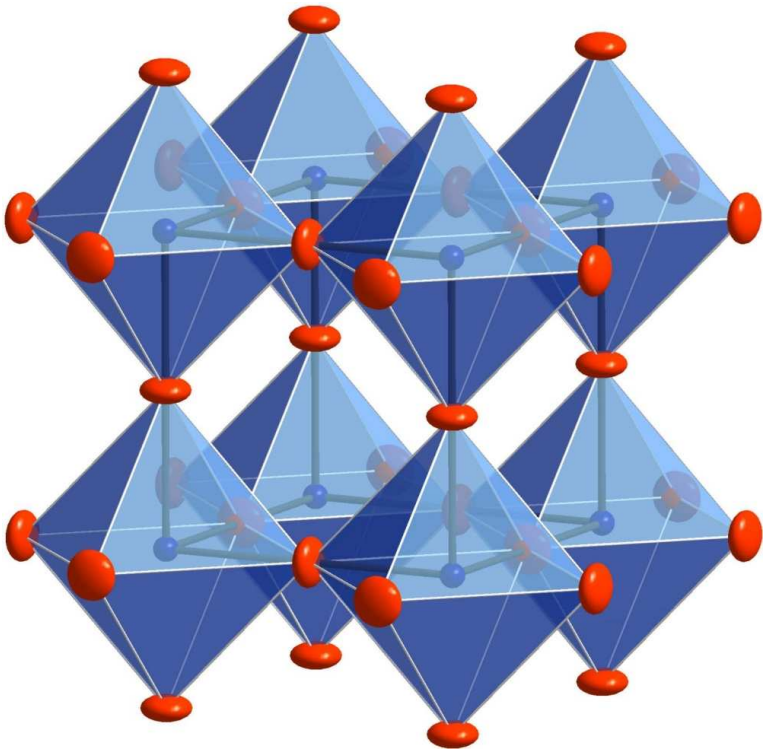
Origins of NTE

- **magnetostriction** - ferroelectric materials
- **valence transition** - intermetallic compounds, fulleride materials
- **low-frequency rigid unit modes (RUM)**
  - oxide-based framework materials
  - CN-based compounds
- materials with open framework structure - usually insulators or semiconductors

ReO_3

- metal - low electrical resistivity (comparable to Cu or Ag)
- metallic conductivity due to delocalized 5*d*-Re electrons
- highly covalent Re-O bond $\Rightarrow$ covalent metal
- properties of the lattice - not typical for metallic phase

Network of ReO_3 octahedra



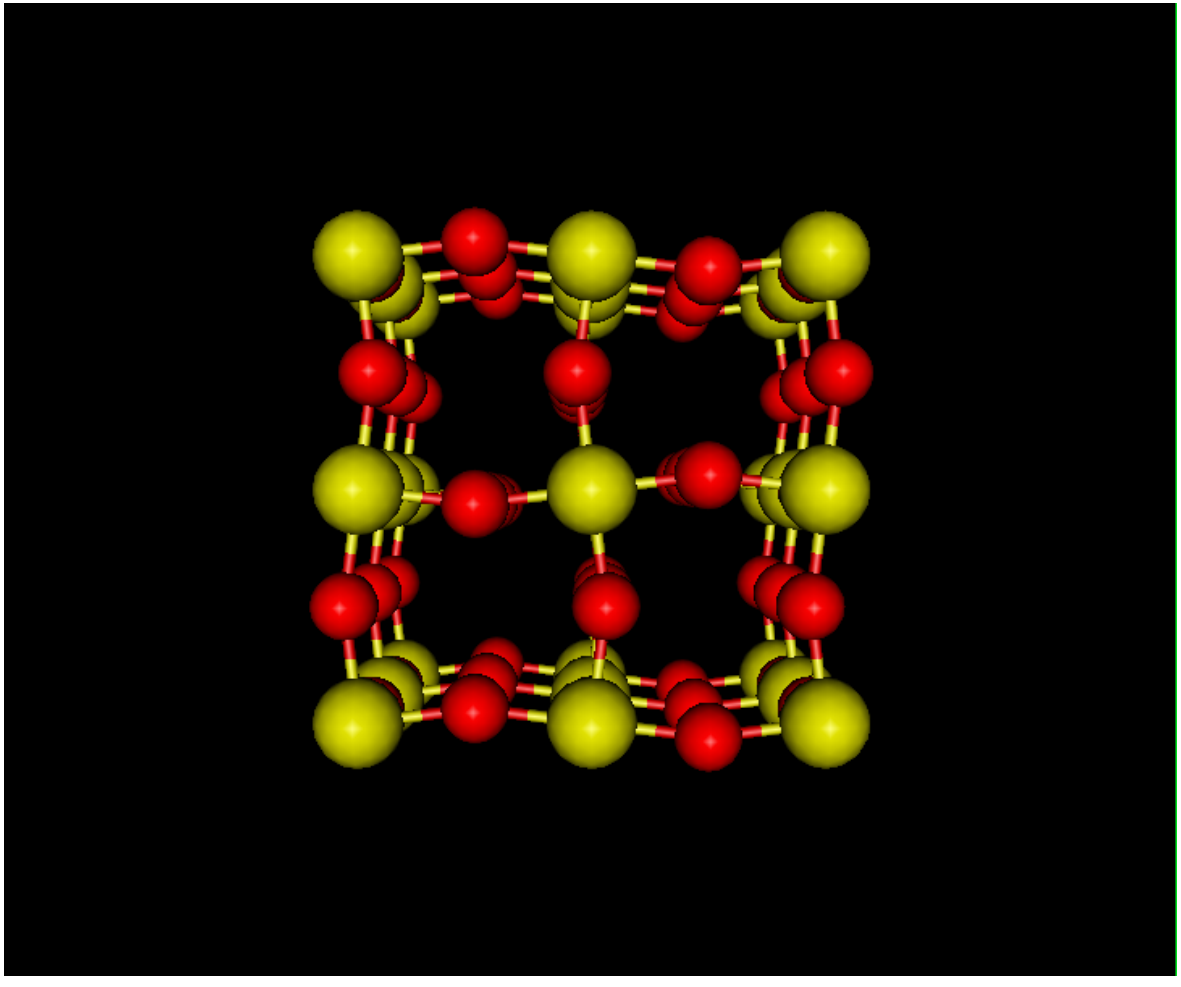
- space group $Pm\bar{3}m$
- lattice constant a = 3.74 Å

perovskite-type compound (ABO_3) with A site vacant

Rigid rotation of octahedra

- anisotropy of thermal motion
- NTE
- structural phase transitions

Rigid unit modes and M-type phonon



Experimental observations

$Pm\bar{3}m \Rightarrow Im\bar{3}$

- 5.2 kbar (RT)
- 3.5 kbar (150 K)
- 2.5 kbar (4.2 K)

Intermedite phase/phases?

$$Pm\bar{3}m \rightarrow P4/mbm \rightarrow Im\bar{3}$$
$$\downarrow$$
$$P4/mbm \rightarrow I4/mmm \rightarrow Im\bar{3}$$

NTE

- 100-340 K
  laser interferometry
- below 100 K
  x-ray diffraction, EXAFS
- up to 200 K
  neutron diffraction

NTE depends on sample quality (static disorder)

Experiment and calculations

Inelastic neutron scattering

- IN4C TOF spectrometer @ ILL
- E_i = 16.9 meV (2.2 Å)

Resolution

- ~0.6 meV @ elastic scattering
- ~4 meV @ 50 meV
- ~10 meV @ 100 meV

Corrections for multiphonon and DW contributions

MUPHOCOR by W.Reichardt
Karlsruhe Institute for Nuclear Physics

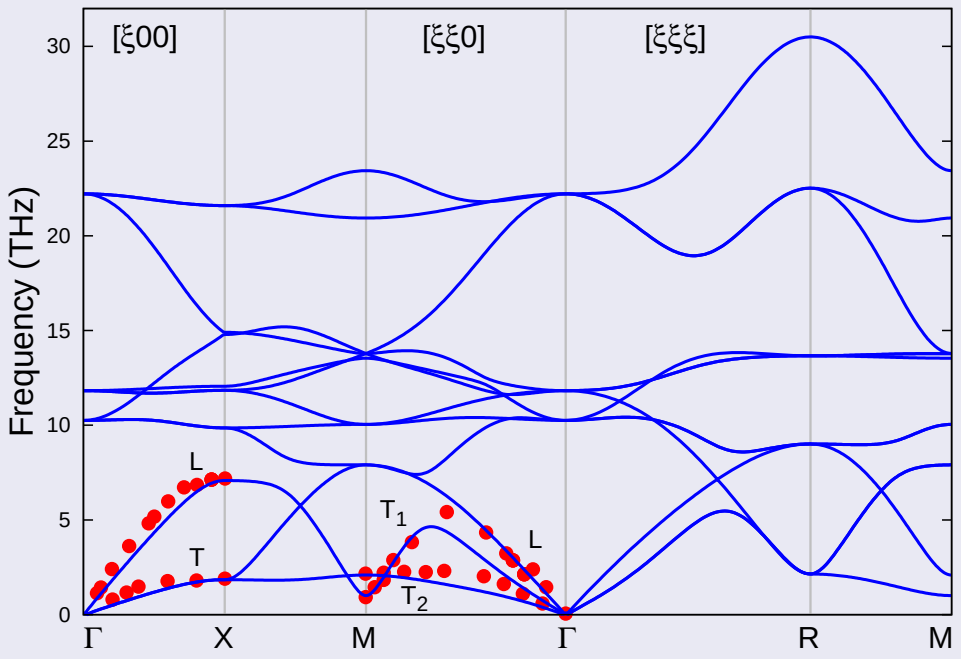
DFT calculations

- VASP code, PAW PP
- LDA approximation
  - a_{CAL} = 3.7467 Å
  - a_{EXP} = 3.7477 Å
- 2x2x2 s.c. (32 atoms)

Phonons

- Direct method - **PHONON**
- Thermal properties - **QHA**

Dispersion relations for ReO_3 at ambient pressure



Experiment: J. D. Axe *et al.* PRB 31, 663 (1985)

$T_1(\xi\xi 0)$ mode undergoes softening near the M-point

$M \equiv T_1(\frac{1}{2}, \frac{1}{2}, 0)$

Cal.	150 K	300 K
1.007	0.822	0.933

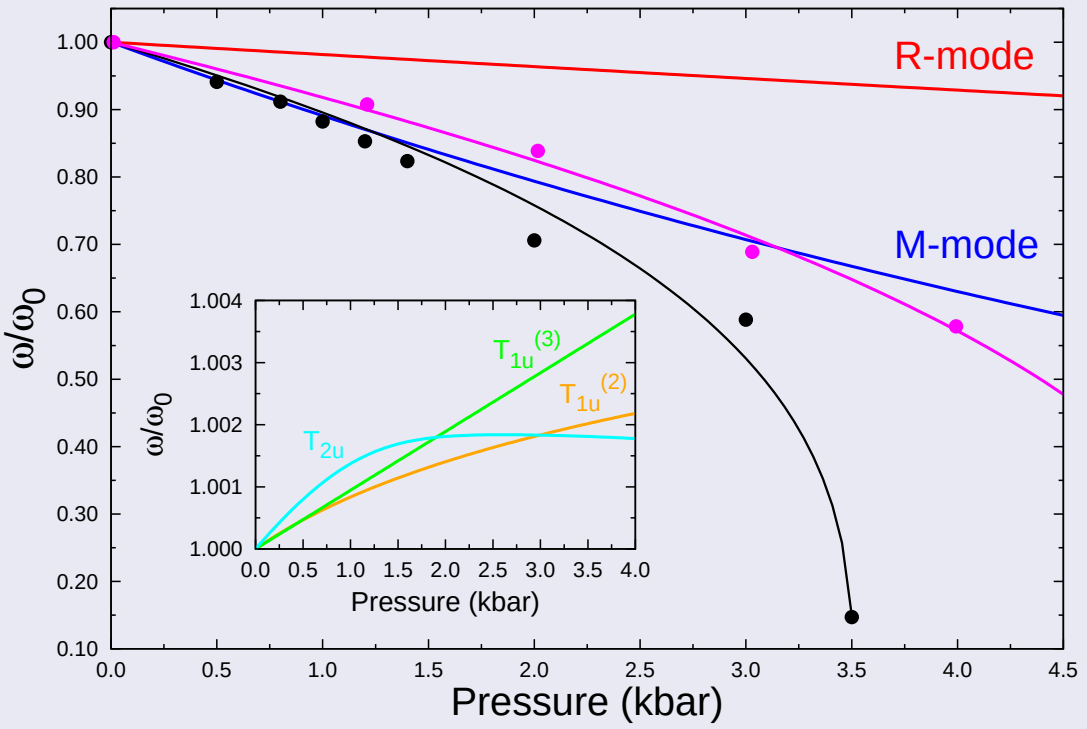
$R \equiv T(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Calculation: 2.146 THz

Γ-point modes

- **IR active**
  $T_{1u}^{(2)} \longrightarrow$ 10.255 THz
  $T_{1u}^{(3)} \longrightarrow$ 22.217 THz
- **silent**
  $T_{2u} \longrightarrow$ 11.825 THz

Rotational modes condense under compression



Grüneisen constants

$T_{1u}^{(2)}$	$T_{1u}^{(3)}$	T_{2u}
1.24	2.11	1.03

Grüneisen constants

Mode	Cal.	Exp.
M	-291	-242[1]
		-180[2]
R	-46	-

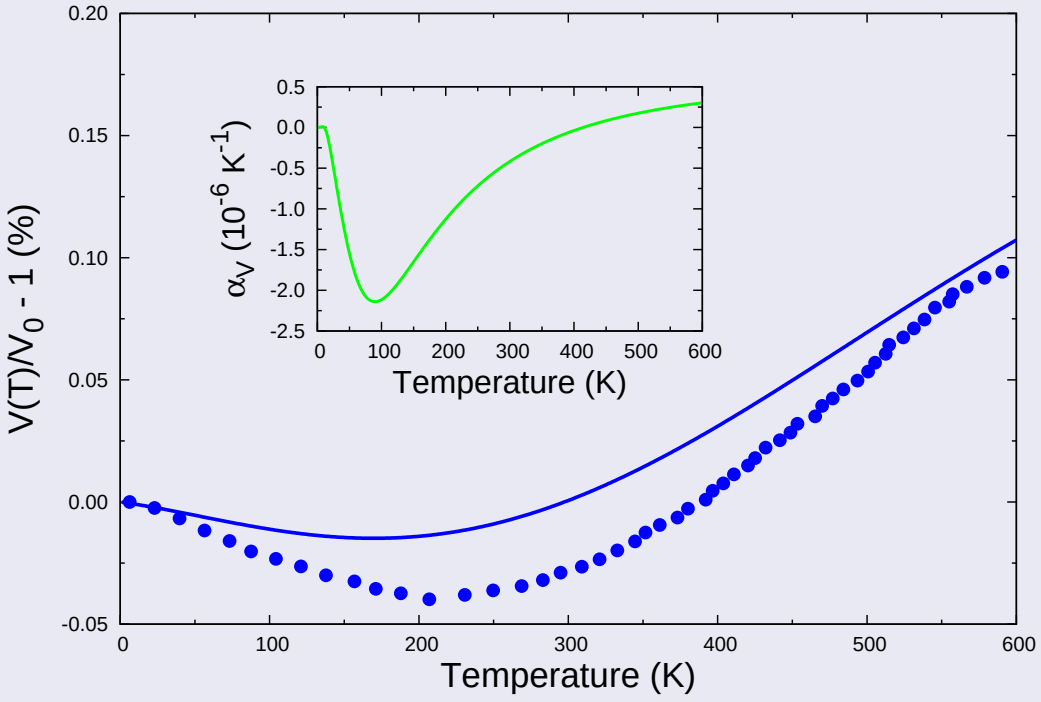
Softening rates (THz/kbar)

M	R
-0.12	-0.04

[1] T. Chatterji *et al.* PRB 79, 184302 (2009)

[2] J. D. Axe *et al.* PRB 31, 663 (1985)

Thermal expansion of ReO_3



[1] T. Chatterji *et al.* PRB 78, 134105 (2008)

[2] T. Chatterji *et al.* PRL 94, 241902 (2009)

NTE

Cal.	Neutron	LDC
170 K	200 K	350 K

Average α_V below NTE-PTE crossover temperature
$\langle \alpha_V \rangle = -1.2 \times 10^{-6}$ 1/K

QHA vs LDC

- similar expansivity below NTE-PTE
- PTE regime $\alpha_V(\text{LDC}) \sim 2\ \alpha_V(\text{QHA})$

NTE of ReO_3 and atomic thermal motion

NTE and static disorder in ReO_3

- large contribution from static disorder $\Rightarrow$ diminished NTE
- samples with less static disorder
  - high NTE-PTE crossover temperature (294 K)
  - quite large negative thermal expansivity (-1.0×10^{-6} 1/K)

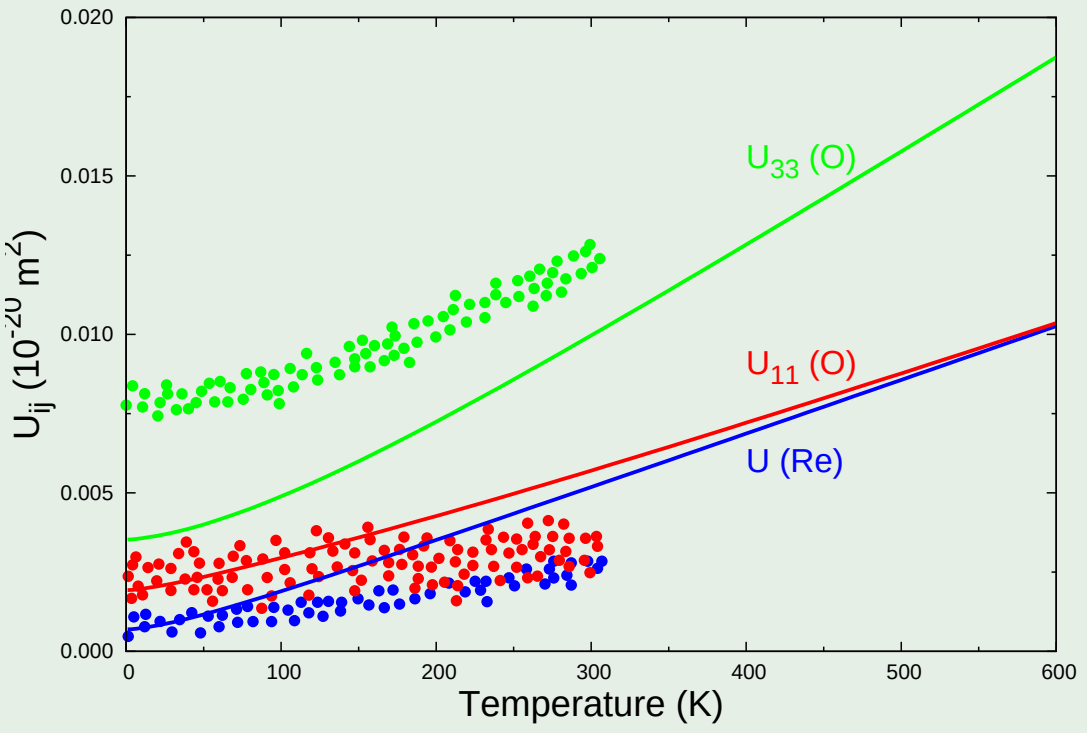
Mean-squared vibrations of ReO_3

- Experimental U_{ij} contain static and dynamic contributions
- Present calculations - dynamic component
- Re ($\bar{3}m$) $\Rightarrow$ isotropic thermal motion $\Rightarrow$ U(Re)
- O ($4/mmm$) $\Rightarrow$ anisotropic thermal motion

U_{11} (O)	oxygen vibrations $\parallel$ to Re-O bond
U_{22} (O) = U_{33} (O)	oxygen vibrations $\perp$ to Re-O bond

Atomic thermal motion in ReO_3

Thermal vibrations of Re and O



T. Chatterji *et al.* PRB 78, 134105 (2008)

Questions

1. $U_{11}(O) \approx U(Re)$?
   $\Phi(Re) \sim 1.3 \times \Phi_{xx}(O)$
2. $U_{33}(exp.) \ggg U_{33}(cal.)$
   LDC fails either !
   STATIC DISORDER

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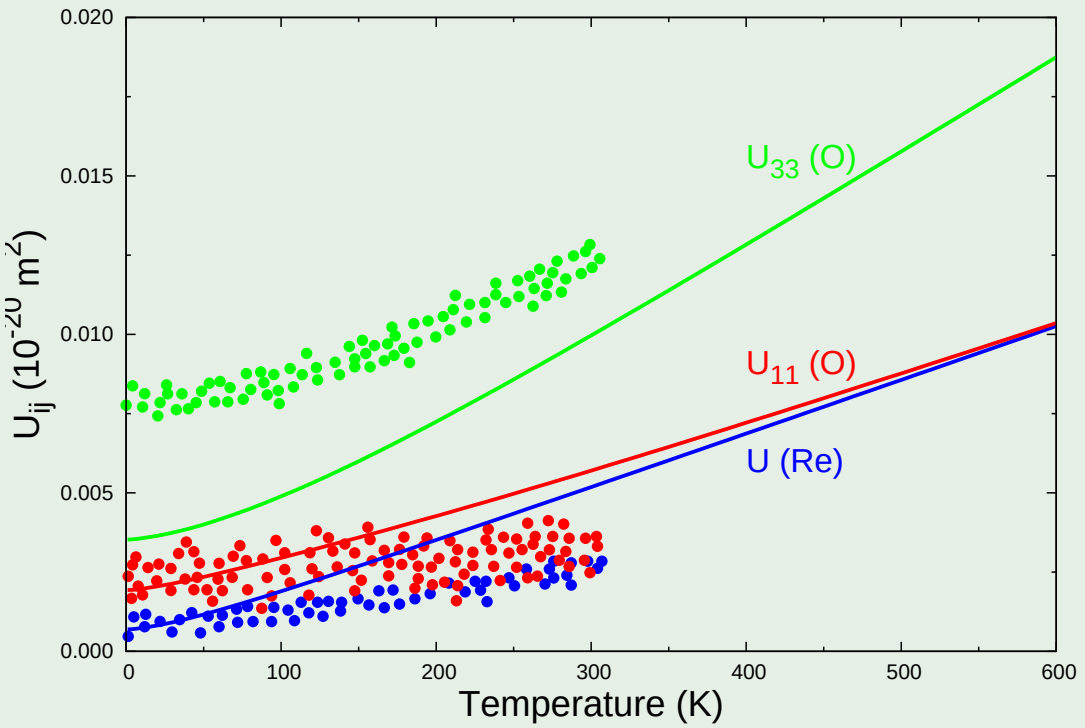

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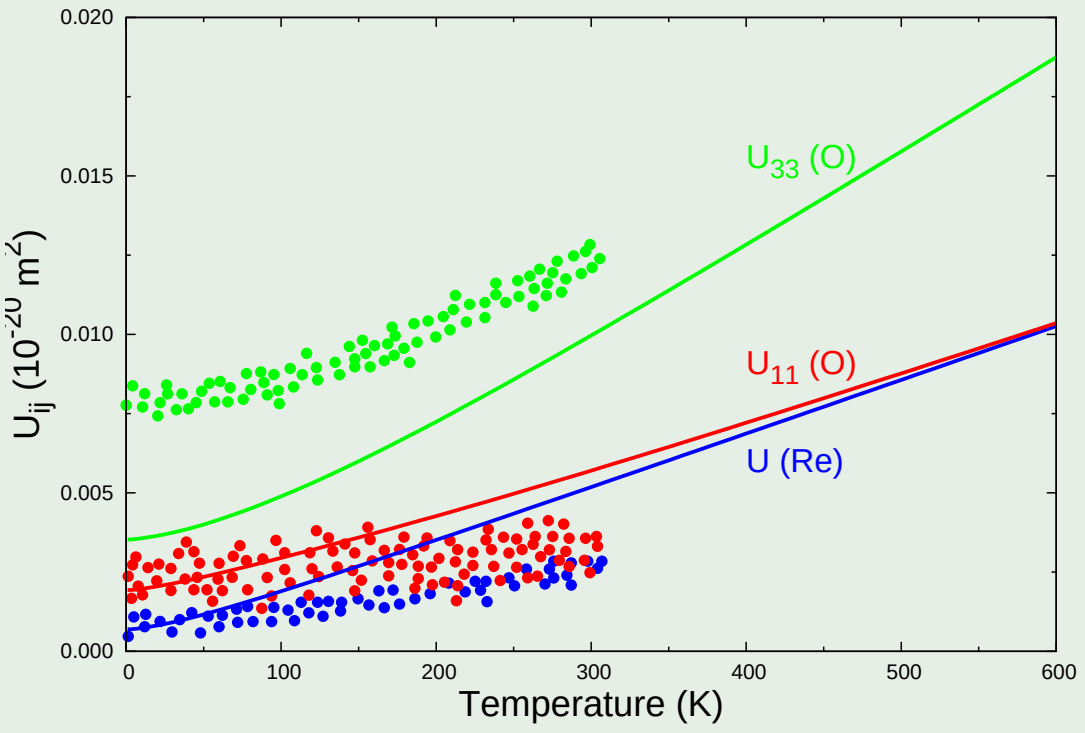

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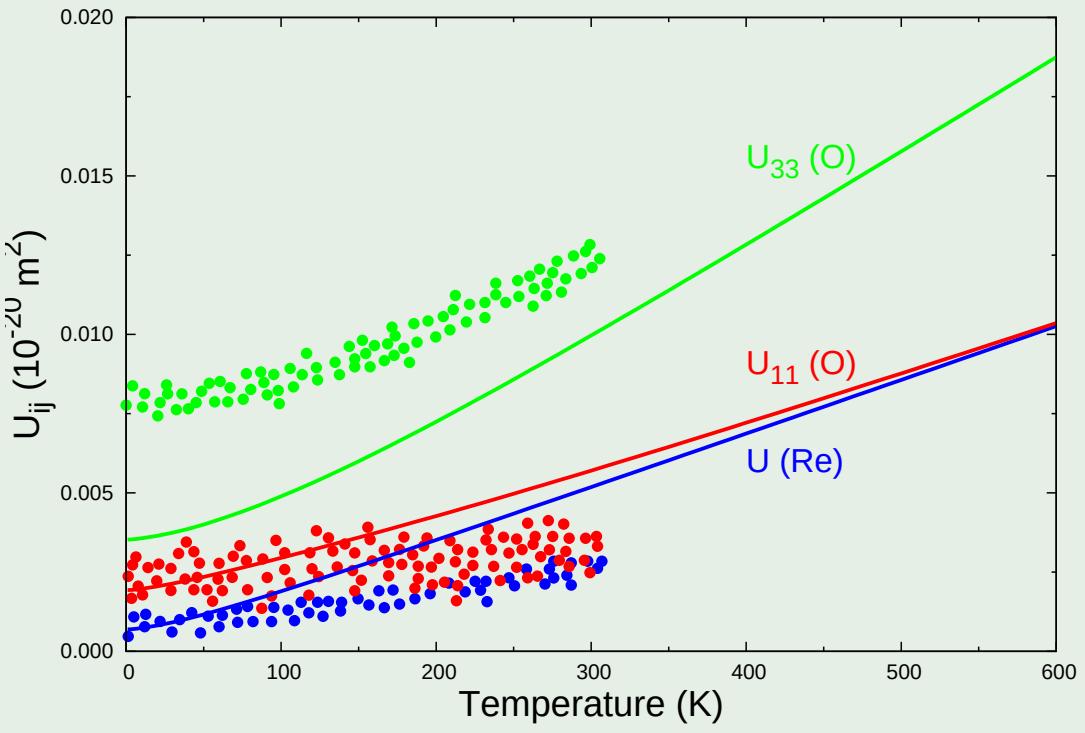

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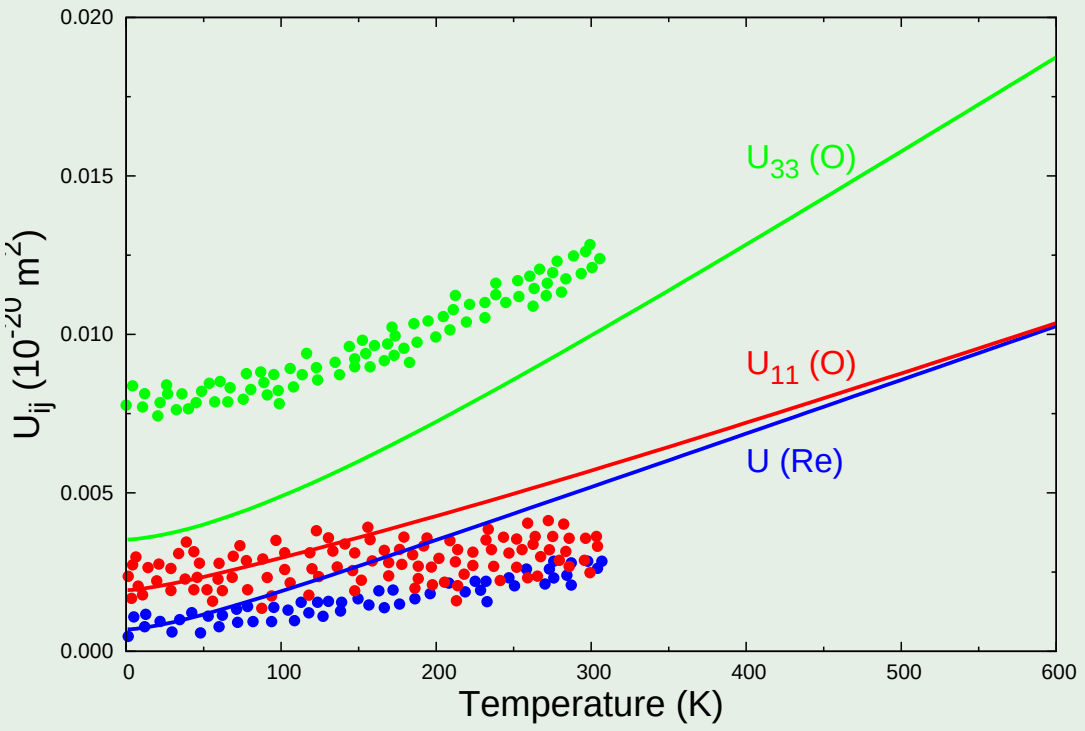

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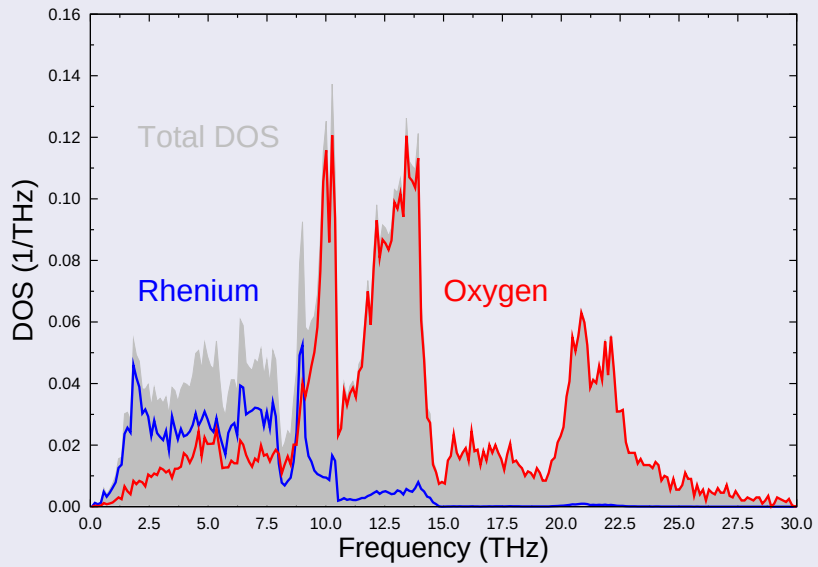
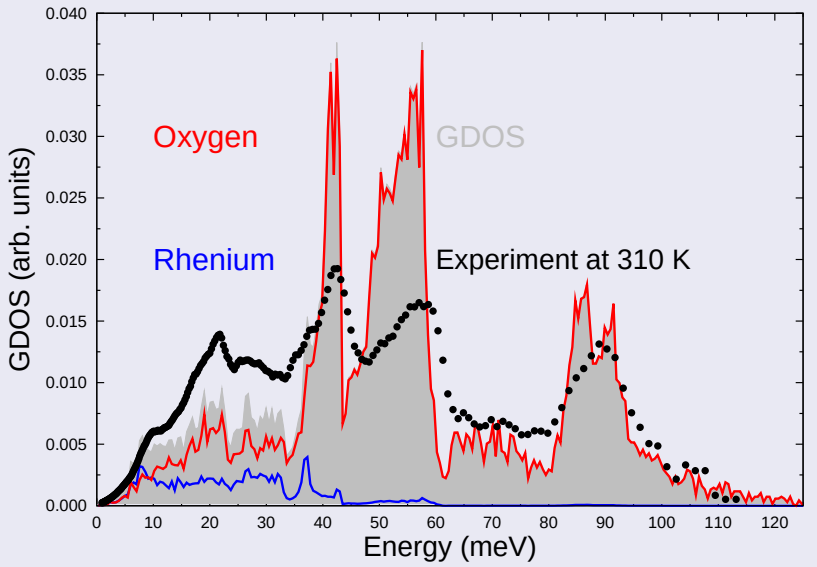
Thermal motion and static disorder of ReO_3

DOS



GDOS



α(Re)=0.062 b/amu, α(O)=0.265 b/amu
scattering dominated by oxygen (93%)

- static disorder breaks propagation of phonons throughout lattice
- shift of intensity for peaks at 41 meV and 55 meV into continuous distribution at low energies (10-35 meV)

Anisotropy of the oxygen thermal vibrations

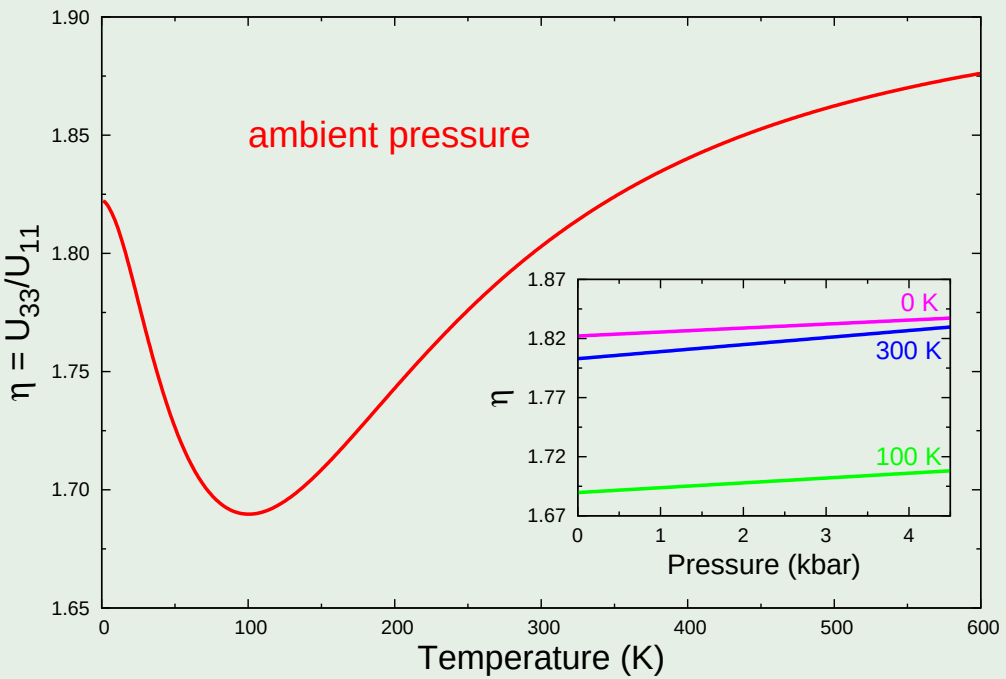
- high quality samples
  - lower gap between U_{33} and U_{11}
  - diminished anisotropy $\eta = U_{33}/U_{11}$
- low temperatures: η (exp.) $\approx \eta$ (cal.)

- η related with anisotropy in the force constants at O site
- $\Phi_{zz} \approx \frac{1}{2}\Phi_{xx}$
  $\Downarrow$
- larger amplitude of thermal vibrations in direction perpendicular to Re-O bond than along the bond

- highly anisotropic motion in a direction consistent with M-phonon mode
  $\Downarrow$
- coordinated rotations of ReO_3 octahedra

Anisotropy vs temperature and pressure

Anisotropy vs temperature



T = 100 K

- anisotropy minimum
- expansivity minimum

- NTE coincides with more isotropic thermal motion of O atoms

⇓

- reduction/enhancement in η - additional driving force converting ReO_3 from NTE to PTE

anisotropy vs pressure

- simultaneous hardening of Φ_{xx}(O) and softening of Φ_{zz}(O)
- reduction of U_{11} and enhancement of U_{33} $\Rightarrow$ increase of anisotropy

Summary and conclusions

1. Large negative values of Grüneisen constants for M and R phonons
2. M-phonon softens more rapidly than R-phonon with crystal compression
3. Anisotropy of the oxygen thermal motion in ReO_3
   - follows from the anisotropy of the force constants at the oxygen site
   - consistent with the M-phonon
   - contributes to NTE of ReO_3
   - NTE is enhanced when oxygens perform more isotropic thermal motion
4. Anisotropy - additional force driving the low-pressure phase transitions
5. Details can be found in PRB 82, 104301 (2010)