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Novel p-V relationship in ReO_3 under pressure

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High-precision strain measurements on the metallic perovskite ReO_3 across the pressure-induced phase transformation at $p_{tr} = 5$ kbar are reported. The crystals soften exponentially as the pressure approaches p_{tr} from below. The high-pressure phase exhibits large volume strain, proportional to $(p - p_{tr})^{2/3}$ up to at least 30 kbar pressure. The abnormal p-V relationship reflects either highly nonlinear restoring forces counteracting the rotations of the ReO_6 octahedra or the dominance of electron redistribution among subbands as in a Lifshitz transition.

The large group of perovskite-structured compounds with general composition ABX_3 is among the most intensively studied solid systems, particularly because of the lattice-dynamical instabilities and the associated ferroelectricity. And yet, a microscopic understanding of the structural transformations based on simple interatomic potentials is only slowly emerging.[1] Despite their importance, the oxides (ABO_3) cannot be treated by such an approach because the wave function of the O^{2-} ion is not known. Furthermore, a considerable covalency involving the oxygen p states and the s or d states of the B atom makes any treatment in terms of simple interionic potentials inappropriate. This is the long-standing problem of the "polarizability of oxygen" in solids and further experimental information is necessary for a microscopic understanding.

Here we report on a high-resolution pressure-volume study of ReO_3 across the pressure-induced structural transformation. From the observed novel p-V power law, $\Delta V \sim (p - p_{tr})^{2/3}$, we conclude that the restoring torque counteracting the rotations of the presumed rigid ReO_6 octahedra around the linking oxygens is extremely nonlinear, in fact, it is proportional to the *square* of the rotation angle. This unexpected result for the angular stiffness of the Re–O–Re bond chain has to be seen as both a new ingredient and a challenge for the microscopic description of lattice-dynamical properties of perovskites with oxygen octahedra. In an alternative interpretation along the lines of a Lifshitz transition, the $\frac{2}{3}$ power law is a consequence of a change of the Fermi-surface topology.

ReO_3 is uniquely suited to investigate the aspects of the structural stability of only the oxygen-octahedra network *alone* for the following reasons: (1) the A sites are not occupied allowing a free rotation of the corner-linked octahedra. (2) The cubic, nondistorted perovskite structure is stable at atmospheric pressure, in contrast to WO_3, which is always a distorted structure. (3) A moderate pressure of 5 kbar at room temperature induces a structural transformation. This transformation has originally been detected in Fermi-surface studies, and ReO_3 was found to be softer in the high-pressure than in the low-pressure phase.[2,3] The term "compressibility collapse transition" was coined.[3]

The single crystals of ReO_3 were grown by iodine vapor transport and we investigated several samples up to a size of $6 \times 4 \times 4$ mm^3. The mosaic spread is smaller than the experimental resolution of 0.2° in the neutron scattering experiments.[4] This high quality of the samples was a prerequisite for the high-resolution pressure-volume measurements we report here. The length change of the crystals was measured using strain gauges epoxy bonded to the natural (100) faces. One pair of gauges was mounted on the sample and another pair on a silicon reference crystal. The linear strain of ReO_3 was measured with respect to Si as the imbalance voltage of the Wheatstone bridge formed by the four gauges. A relative length change of ~ 2 ppm could be resolved. The hydrostatic pressure up to 30 kbar was generated employing the Teflon-cell technique[5] and on slow variation of the pressure a resolution of 3 bar could be achieved. All experiments were done at room temperature.

An overview of the pressure-dependent volume strain, as calculated from the linear strain assuming cubic symmetry, is shown in Fig. 1. Up to the transformation pressure $p_{tr} = 5$

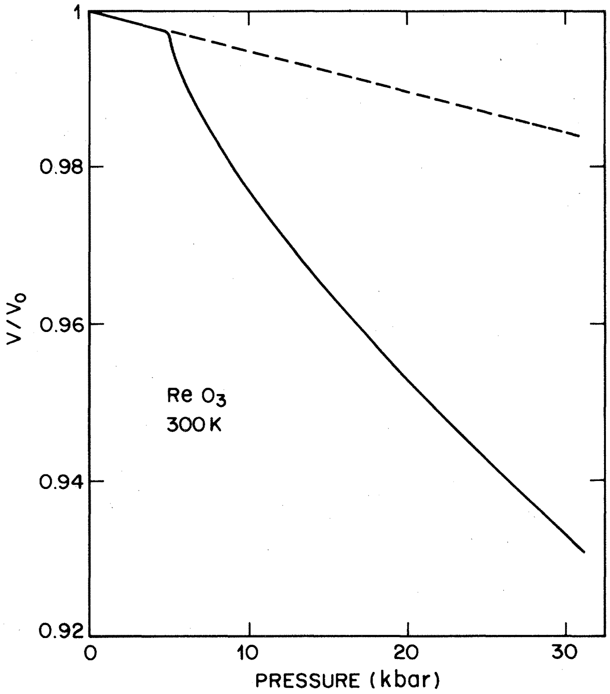

FIG. 1. Pressure-volume relationship of ReO_3 up to 30 kbar. The broken line is an extrapolation of the low-pressure behavior.

kbar ReO_3 is a hard compound and the compressibility of $(5 \pm 0.1) \times 10^{-7}$ bar^{-1} compares well with the $(5.12 \pm 0.18) \times 10^{-7}$ bar^{-1} calculated from the elastic moduli measured in ultrasonic experiments.[6,7] The adiabatic and isothermal values should be the same within less than 1% because the thermal expansion coefficient is zero around 300 K.[8] The volume strain does not increase linearly in the low-pressure phase but grows faster as p_{tr} is approached [Fig. 2(a)]. The deviation δ from linearity, as defined in Fig. 2(a), is plotted on a logarithmic scale in Fig. 2(b). This precursor effect grows *exponentially* by a factor of 10 every 2.3 kbar. The transformation at 5 kbar is continuous and marked by a drastic softening of the crystal. The value for the compressibility is only instrumentally limited and exceeds 2.5×10^{-4} bar^{-1}, equivalent to a bulk modulus of less than 4 kbar.

An extremely nonlinear p-V relationship characterizes the high-pressure phase up to at least 30 kbar. To illustrate the striking softening of ReO_3 on crossing the transformation pressure, we note that ReO_3 at 1 bar is twice as "hard" as silicon, but at ~ 7 kbar as soft as NaCl. We define an "excess volume strain" $\Delta V / V_0$ in the high-pressure phase as the difference between the measured and the extrapolated low-pressure p-V curves (see dashed line in Fig. 1). In Fig. 3 this excess volume strain is plotted on a double logarithmic scale against $p - p_{tr}$ where p_{tr} is the transition pressure. The straight-line relationship indicates a simple power law, obeyed over the entire pressure range.[9] Accordingly, $\Delta V / V_0$ is proportional to $(p - p_{tr})^{\alpha}$, with α being 0.667(5), which is close to $\frac{2}{3}$. This unusual power law in a p-V relationship is observed up to the highest pressures in all five experiments on three different ReO_3 crystals.

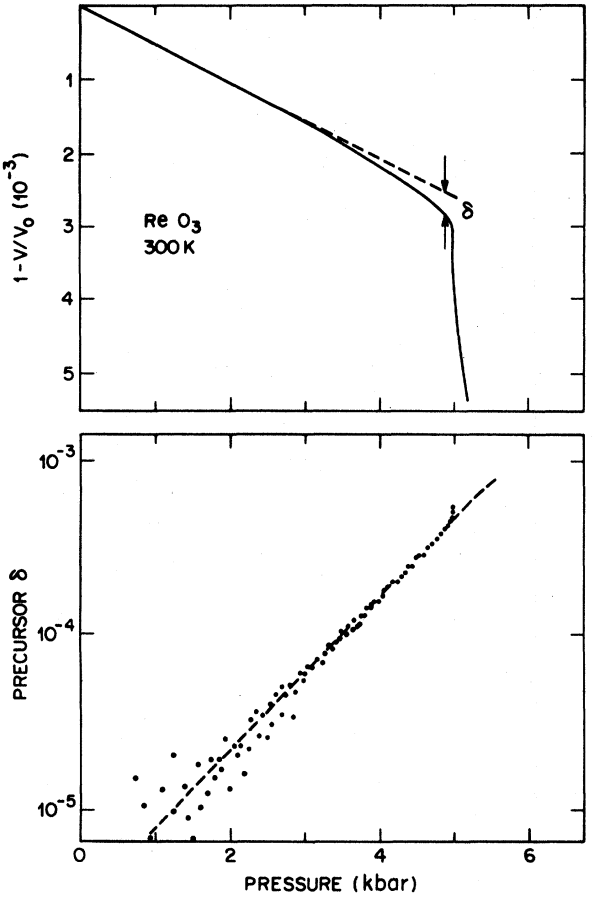

FIG. 2. Pressure dependence of the volume up to the transformation pressure p_{tr}. A precursor softening δ is observed and it grows exponentially as p_{tr} is approached (lower part).

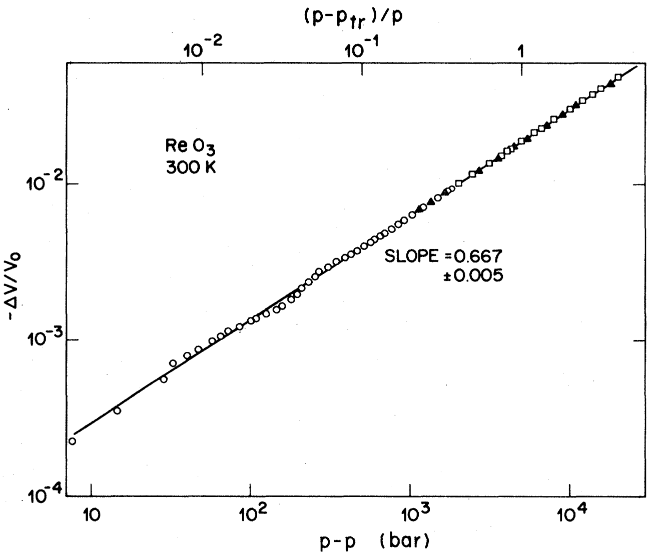

FIG. 3. Excess volume strain in the high-pressure phase is proportional to $(p - p_{tr})^{2/3}$. The various symbols represent results from three experiments and most of the data points at high pressures are omitted for clarity.

From x-ray diffraction, Fermi-surface, and NMR studies it has been concluded that the phase transformation in ReO_3 involves a rotation of the ReO_6 octahedra by an equal angle around the three principal cubic axes, enlarging the unit cell and retaining an overall cubic symmetry ($Im3$).[3] Rotations of the O_6 octahedra are widely encountered in perovskites and result from a condensation of zone-boundary phonons, in the present case of the T_2 mode at the M point.[4] In the following first interpretation we attempt to model the structure change in terms of a rotation of corner-linked *rigid* ReO_6 octahedra. A rotation of the octahedra by a small angle ϕ results in a volume strain proportional to ϕ^2. The observed $\frac{2}{3}$ power law is therefore equivalent to $\phi \sim (p - p_{tr})^{1/3}$. Taking this microscopic mechanical model one step further we connect the octahedra at their corners by torsion springs counteracting the rotations by a restoring torque $\Gamma(\phi)$. Assuming $\Gamma \sim \phi^n$ leads for small angles to $\phi \sim p^{1/(n+1)}$, where p corresponds to the externally applied pressure. Comparing this with the experimental results we conclude that the restoring torque for the static rotation increases *quadratically* with the rotation angle ($n = 2$). The angular stiffness of the Re–O–Re bond chain appears to be extremely nonlinear. This is an obvious starting point for detailed microscopic calculations and we speculate that the strongly directional bond involving the O $2p$ and Re $5d$ hybrids[10] will be important and partial charge transfer will be involved.[11] One way to reduce the angular rigidity is by coupling the occupied oxygen states and the empty Re d states. It is not clear, however, how this concept of the "chemical grip"[12] can account for the observed nonlinearities, because it predicts a *deformation* of the octahedra.

We discuss in passing the observed power law in the context of phase transformations and critical phenomena. Detailed measurements of the static order parameter ϕ in, e.g., $SrTiO_3$ and $LaAlO_3$ below the structural transformation temperature T_c, demonstrated the deviation of ϕ from the mean-field behavior.[13] The rotation angle ϕ was found to be proportional to $(T_c - T)^{1/3}$ up to $\sim 1°$ and to obey the "classical" $(T_c - T)^{1/2}$ beyond 1°. If we substitute p for T in the case of ReO_3, we conclude from our kinematic analysis that ϕ is proportional to $(p - p_{tr})^{1/3}$ for rotations up to at least 10°. Such a wide range of "critical" behavior in ReO_3 would be remarkable, particularly if we keep in mind that for ReO_3 the slope of the phase boundary in the p-T plane is more than 20 times larger than for the same type of tranformations in other perovskites.[3,14] Application of pressure is therefore expected to remove ReO_3 quite rapidly from the critical region.

Finally, an alternative explanation of the $\frac{2}{3}$ power law in the spirit a Lifshitz transition is offered. In a Lifshitz transition the topology of the Fermi surface changes as a Van Hove singularity passes through the Fermi level.[15] If the band has a parabolic density of states and moves linearly with volume strain, the change in the free energy results in a compressibility anomaly just as we find in ReO_3.[15] In ReO_3, a lattice instability occurs at p_{tr}, but the p-V relationship in the high-pressure phase would be determined by the topology of the Fermi surface which has changed due to the structural transformation. Indeed, new extremal orbits are found in de Haas–van Alphen measurements and can be ascribed to the new parts of the Fermi surface which are formed as the energy bands are folded back into the reduced Brillouin zone.[16] To analyze this unique situation, the interplay between the rotation of the oxygen octahedra, the redistribution of the electrons among the new bands, and the possible variation of the Re–O bond length has to be treated self-consistently. The involvement of the conduction electrons can be inferred also from the exponentially growing lattice softening and the anomalies in the Fermi-surface[17] precursor to the transformation. A detailed study of the Fermi surface in the high-pressure phase, with emphasis on the new parts with small cross-section areas, would be revealing. This is, however, beyond the scope of this paper.

In summary, we have observed a $\frac{2}{3}$ power law for the volume strain in the high-pressure phase of ReO_3. This power law is unique for solids.

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