

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 31, NUMBER 2

15 JANUARY 1985

Neutron scattering study of the pressure-induced phase transformation in ReO_3

J. D. Axe and Y. Fujii

Brookhaven National Laboratory, Upton, New York 11973

B. Batlogg

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

M. Greenblatt and S. Di Gregorio

Rutgers University, New Brunswick, New Jersey 08903

(Received 24 July 1984)

We have studied the pressure-induced phase transformation in a large single crystal of ReO_3 at 300 K and (0–6)-kbar hydrostatic pressure. Inelastic measurements at 1 bar show a pronounced minimum in the T_1 mode near the Brillouin-zone boundary (M point). Above $P_c = 5.2$ kbar superlattice reflections with intensities consistent with M_3 -like rotations of ReO_6 octahedra appear. The transformation seems to be continuous (second order), but an anomaly in the superlattice intensity at $P = 5.4$ kbar suggests a further transformation. The M_3 phonon softens dramatically as $P \rightarrow P_c$ from below, but no substantial changes occur in the long-wavelength acoustic velocities between 0 and 6 kbar.

I. INTRODUCTION

ReO_3 is a metal and crystallizes in the undistorted, ideal perovskitelike structure consisting of corner-linked oxygen octahedra, with Re occupying the center of the octahedra. Among the numerous perovskitelike compounds ReO_3 is unique in that the undistorted cubic structure is stable at atmospheric pressure and all temperatures. The thermal expansion and elastic constants,^{1–3} however, point to an incipient lattice instability. Unlike many other members of the W-bronze family ReO_3 does not become superconducting above 20 mK, a fact which has been ascribed to a weak electron-phonon coupling.⁴ The first indication for some kind of a pressure-induced transformation came from de Haas–van Alphen studies which revealed a pronounced increase of the Fermi-surface cross sections above 3 kbar.⁵ In a detailed study employing, in addition, NMR and x-ray diffraction under pressure, the transformation was found to be the result of a symmetry change of the lattice.⁶ “Buckling” of the Re-O-Re chains was invoked to explain the increase of the compressibility in the high-pressure phase. The proposed (space-group) symmetry change from $Pm\bar{3}m$ (O_h^1) to $Im\bar{3}$ (T_h^3) is further supported by a recent structure study at 15 kbar (Ref. 7) and by the observation of new parts of the Fermi surface which are created as the bands are folded into the new, smaller Brillouin zone.⁸ High-precision

volume-strain measurements up to 30 kbar revealed a divergence of the compressibility at the transformation and a large volume strain that grows proportional to the $\frac{2}{3}$ power of the pressure for $P > P_c$.^{9,10} The novel P - V relationship is ascribed to either highly nonlinear restoring forces counteracting the buckling of the O-Re-O chain or to a Lifshitz-type transition.

II. EXPERIMENTAL RESULTS

The single crystals of ReO_3 were grown by iodine-vapor transport and the sample investigated here was $\sim 5 \times 5 \times 5$ mm³ in size. The mosaic spread is smaller than 0.2°. The neutron scattering measurements were performed at the Brookhaven National Laboratory High Flux Beam Reactor with a conventional three-axis spectrometer. (002) pyrolytic graphite (PG) reflections were used in both the monochromator and analyzer and filtering of unwanted orders was accomplished with PG filters using either 14.8- or 30.5-meV neutrons. The individual collimation elements were either 20' or 40' full width at half maximum depending on the measured signal strength. The Al-alloy cell used for the high-pressure measurements has been described previously,¹¹ with He gas as the pressure transmitting medium. The pressure, estimated from a calibrated manganin resistor, is thought to be accurate to ± 30 bar.

A. Inelastic scattering

A summary of inelastic neutron scattering measurements at room temperature and $P=1$ bar are shown in Fig. 1. The energies of the L and T branches for $\vec{q}=(\xi,0,0)$ as well as the L and T_2 branches for $\vec{q}=(\xi,\xi,0)$ were measured with an (hkk) scattering plane. The $T_1(\xi\xi0)$ branch was measured in the $(hk0)$ scattering plane. The scans were designed to optimize scattering from acoustic branches only but no strong indications of additional optic branches were seen for $\Delta E \leq 30$ meV. Both the $T(\xi00)$ and $T_2(\xi\xi0)$ modes have anomalously low frequencies extending to the zone boundaries, which is characteristic of oxides with the perovskite structure.¹²⁻¹⁴ But the most remarkable feature is the pronounced reduction in frequency of the $T_1(\xi\xi0)$ mode near the M -point zone boundary. This behavior has been previously observed in both CsPbCl_3 (Ref. 15) and Na_xWO_3 (Refs. 14 and 16) and both systems undergo M -point phonon condensations at low temperatures. Although we devoted some effort to the search we could find no evidence for pronounced Kohn anomalies such as were seen in the $\text{LA}[100]$ phonon in Na_xWO_3 by Kamitakahara *et al.*¹⁶

Figure 2 shows the evolution of the $T_1(\frac{1}{2}\frac{1}{2}0) \equiv M_3$ phonon (which we will henceforth call the soft M -point phonon) with increasing pressure. For $P \leq 5$ kbar the phonon group shifts to lower energy, broadens, and becomes less distinct. There is also unmistakably a third quasielastic central component that grows with increasing pressure. Such central components have been seen in many soft-mode-driven transformations¹⁷ and have been extensively discussed.¹⁸ We have made no quantitative study of the central mode, which would require a careful

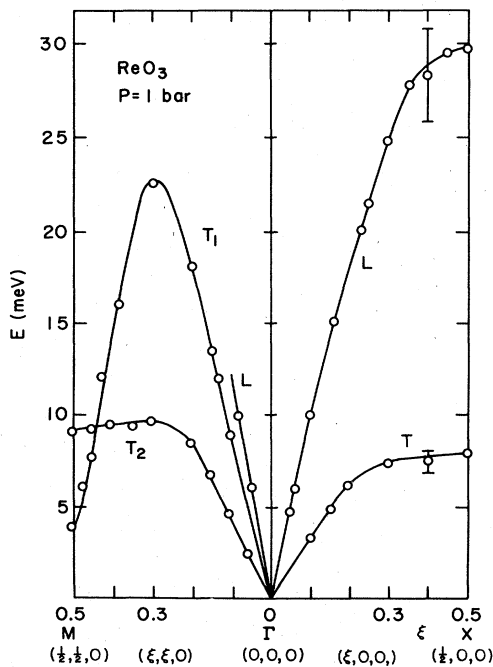


FIG. 1. Dispersion of low-energy phonon modes at room temperature and 1 atm.

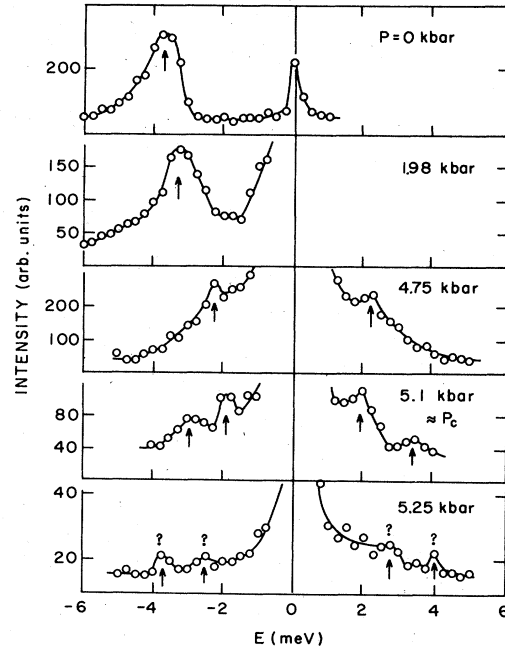


FIG. 2. Evolution of the soft M -point phonon with applied hydrostatic pressure. The statistical error is equal to the square root of the intensity.

subtraction of the scattering from the pressure cell itself. [Note in this connection that the data from Fig. 2(a) were taken *outside* the pressure cell.] For this same reason we have refrained from any detailed fitting of the observed data to an empirical three-peak response function,¹⁷ but summarize instead the behavior of the energy of the observed peak intensity versus pressure in Fig. 3. The shaded portion of the figure indicates schematically the region over which substantial quasielastic scattering is present as well. Since we cannot precisely define the real part of the

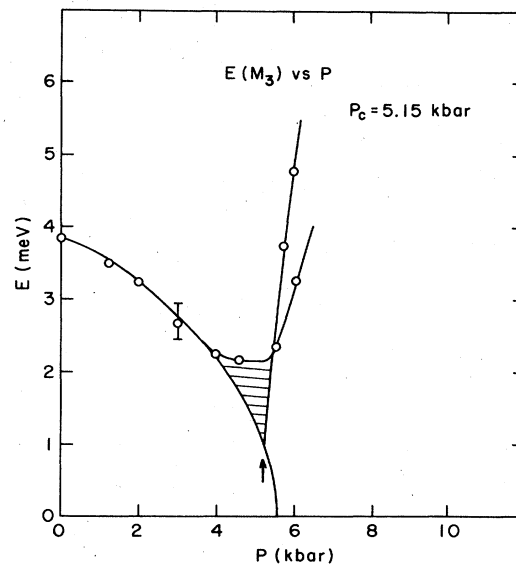


FIG. 3. Nominal soft phonon energy vs pressure. Substantial quasielastic scattering is present in the shaded region.

phonon self-energy from this data, exact significance of Fig. 3 is uncertain, but it seems clear that there is a substantial finite-energy peak at pressures very close to P_c . Above P_c evidence of splitting of the phonon group is shown in Fig. 2, as would be expected due to domain effects in the lower-symmetry high-pressure phase.

The data of Figs. 1–3 strongly suggest that the primary distortions present in the high-pressure phase should be those associated with an M_3 phonon condensation. The remaining experimental results are elastic scattering measurements which test this suggestion.

B. Elastic scattering

An M -point phonon condensation results in general in superlattice reflections of the type $\frac{1}{2}(hkl)$, with $(h+k+l)$ even. The displacements associated with the M_3 mode depend upon only one parameter (which may, for example, be taken as the angular rotation of an elementary ReO_6 octahedron). This means that the pattern of relative intensities of superlattice peaks is easily calculated,¹⁵ and is compared in Fig. 4 with our observations. The calculation assumes equal populations of equivalent domains. The good agreement confirms the correctness of the M_3 -mode condensation.

Figure 5 shows the growth of the intensity of a typical superlattice peak. The transformation appears to be second order as there is no indication of a discontinuity in $I(P)$ near P_c , which we find to be at 5.15 ± 0.05 kbar. There is, however, a sharp and reproducible spike in $I(P)$ at $P' \approx 5.35$ kbar, which we tentatively associate with a further phase transformation. To bolster this claim we have also monitored the behavior of the (200) normal Bragg reflection in the vicinity of P_c . It increases rapidly at $\sim P_c$, saturates, begins to decrease at $\sim P'$, and ultimately returns to about its low-pressure value. These changes are also reversible and we believe that they are associated with the modification of the effective mosaic spread of the sample due to elastic strains. At $P=1$ bar the mosaic spread of our sample was $\ll 0.15^\circ$ which is the instrumental resolution, and extinction is undoubtedly

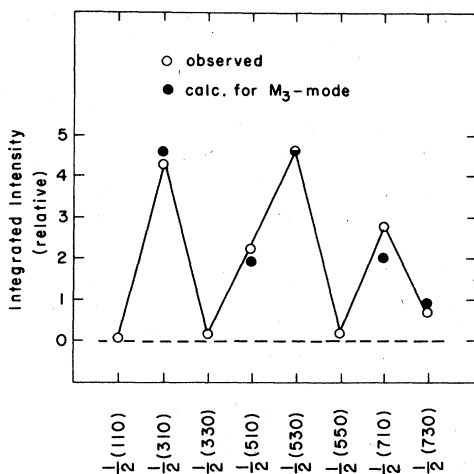


FIG. 4. Comparison of measured superlattice intensities with those calculated for M_3 -mode condensation.

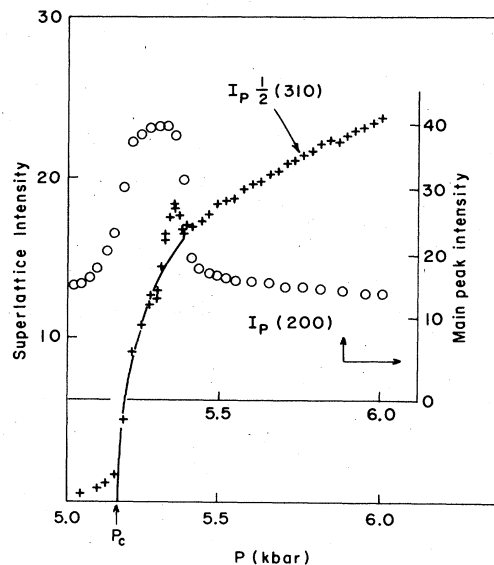


FIG. 5. Growth of superlattice intensity vs pressure (crosses), showing an anomalous peak near $P' = 5.35$ kbar. An anomalous intensity increase is also observed in the normal (200) reflection (open circles) in the region between P_c and P' . Statistical errors are roughly equal to the size of the indicating cross or circle.

severe for a strong reflection such as (200). If this mosaic is increased due to elastic strains associated, for example, with domain mismatch effects above P_c , extinction will be partially relieved and the intensity will increase. Such effects have been previously observed in connection with displacive phase transformations. Our suggestion is that the above mechanism is responsible for the behavior of $I(200)$ for $P_c < P < P'$ and that at $P = P'$ another transformation occurs which reduces the elastic strain, thereby increasing the extinction. This speculation will be discussed further in the following section.

III. DISCUSSION

We first consider some further evidence pointing to the existence of a second phase transformation at $P' \approx 5.3$ kbar and speculate about its nature. Batlogg and co-workers^{9,10} noted a small but distinct deviation from the otherwise highly accurate power-law behavior of the excess volume strain near P' . In addition these same investigators found an anisotropy in the spontaneous strain in the same region. Our rocking curves of the (200) reflection for $P_c < P < P'$ are consistently broader than for $P > P'$. This evidence together with that based on the intensity anomalies noted in the preceding paragraph lead us to believe that it is highly likely that ReO_3 is not cubic on a microscopic scale just above P_c , but instead consists of a random mixture of lower symmetry (e.g., tetragonal) domains. This should not be surprising. Clarke¹⁹ has shown that Na_xWO_3 passes with temperature through two different noncubic structures between the cubic high-temperature phase and the ultimate cubic low-temperature phase. These lower symmetry phases arise naturally as a result of the degenerate nature of the rotational order parameter, a point to which we next turn. We believe a

similar sequence may occur in ReO_3 with increasing pressure, again with the ultimate high-pressure phase restored to cubic symmetry. Note, however, that no evidence for successive phase transformations is evident in the NMR data of Schirber *et al.*²⁰

We turn now to a discussion of the connection between the octahedral rotations which are the principle concern of this work and the large excess volume strain. The observed phonon softening suggests that the former are the primary (driving) effect and the latter are a secondary driven response. The argument is as follows. The M_3 phonons are triply degenerate, reflecting the independent nature of coordinated rotations of octahedra about the three cubic axes. It is straightforward to consider how the amplitude of these three order parameters (ϕ_x, ϕ_y, ϕ_z) coupled to macroscopic strain. The lowest-order terms are linear in strain and quadratic in ϕ_i :

$$U_{\phi\epsilon} = s \left[\sum_i \phi_i^2 \right] \epsilon_0 + t \left[(2\phi_z^2 - \phi_x^2 - \phi_y^2) \epsilon_1 + \sqrt{3}(\phi_x^2 - \phi_y^2) \epsilon_2 \right], \quad (1)$$

where $\epsilon_0 = 3^{-1/2}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$ is the isotropic strain and $\epsilon_1 = 6^{-1/2}(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})$ and $\epsilon_2 = 2^{-1/2}(\epsilon_{xx} - \epsilon_{yy})$ represent tetragonal distortions. Let us consider the effect of the first isotropic term. A conventional classical Landau-theory description minimizes the elastic energy

$$U = \frac{1}{2}(C_0\epsilon_0^2 + C_1\epsilon_1^2 + C_2\epsilon_2^2) + U_{\phi\epsilon} \quad (2)$$

with respect to ϵ_0 and predicts that ϵ_0 is a secondary order parameter driven by the isotropic component of the spontaneous rotation,

$$\epsilon_0 \approx \left[\sum_i \phi_i^2 \right] \approx \langle \phi \rangle^2.$$

Simple geometrical arguments concerning corner-shared octahedra can be used to estimate the coupling constant and show that $\Delta V/V = 3^{1/2}\epsilon_0 \approx \frac{1}{2}\langle \phi \rangle^2$. It would be of some interest to attempt to verify this relation by accurate crystallographic investigations at high pressures, particularly since the predicted rotations ($\langle \phi \rangle > 10^\circ$ for $P > 10$ kbar) are large.²¹ Note in this connection that ReO_3 is unusual among ABO_3 perovskites in having unoccupied A sites, perhaps allowing for more rotational freedom.

If ϵ_0 is proportional to $\langle \phi \rangle^2$, then the spontaneous strain measurements show that $\langle \phi \rangle \sim (P - P_c)^\beta$ with $\beta = \frac{1}{3}$ to high accuracy at least up to 30 kbar. The ReO_3 M -point condensation belongs to the same Heisenberg

TABLE I. Spontaneous strains from Eq. (2).

Phase	ϵ_0	ϵ_1	ϵ_2
Cubic I	0	0	0
$\phi_x = \phi_y = \phi_z = 0$			
Tetragonal I	$-(s/c_0)R^2$	$-(2t/c_1)R^2$	0
$\phi_x = \phi_y = 0; \phi_z = R$			
Tetragonal II	$-(s/c_0)R^2$	$(t/c_1)R^2$	0
$\phi_x = \phi_y = R/\sqrt{2}; \phi_z = 0$			
Cubic II	$-(s/c_0)R^2$	0	0
$\phi_x = \phi_y = \phi_z = R/\sqrt{3}$			

critical-point universality class as do the well-studied R -point [$\bar{q}_R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$] soft-mode transformations in SrTiO_3 and LaAlO_3 , for which theory predicts an order-parameter exponent $\beta \approx 0.38$.²² Experimentally, these latter systems have been found to exhibit $\beta \approx \frac{1}{3}$ within the "critical" region ($\phi < 1^\circ$) in reasonable agreement with theory, and to revert to "classical" behavior, $\beta \approx \frac{1}{2}$, for larger rotations.²³ It is possible that these ideas explain, at least on a phenomenological level, the observed strain behavior, but it implies that the critical region in ReO_3 is surprisingly large both in comparison to SrTiO_3 and LaAlO_3 and in absolute terms. Direct crystallographic measurements of $\langle \phi(P) \rangle$ would be helpful in sorting this out. Unfortunately, the measured superlattice intensities shown in Fig. 4 undoubtedly begin to suffer from extinction effects at large ($P - P_c$), which greatly complicates any quantitative interpretation. However, more reliable data will be available shortly.²¹

Finally, we briefly consider the effect of $U_{\phi\epsilon}$ in a possible noncubic phase. The basic Hamiltonian symmetry, discussed in Ref. 14, is identical to that of SrTiO_3 and LaAlO_3 .²⁴ We consider three possible nontrivial ordered phases corresponding, respectively, to the three ordered phases observed by Clark¹⁰ in Na_xWO_3 . Equation (2) is minimized ($\partial U/\partial \epsilon_i = 0$) for values of ϕ_i describing these phases. The resulting spontaneous strains are as shown in Table I, and are in agreement with Clark's observations. The failure to directly detect the anisotropic strain associated with the corresponding postulated noncubic phase(s) in ReO_3 may reflect a small coupling constant, t , in this material in comparison with Na_xWO_3 .

ACKNOWLEDGMENTS

The research at Brookhaven National Laboratory was supported by the Division of Basic Energy Sciences, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016.

¹T. D. Pearsall and L. A. Coldren, *Solid State Commun.* **18**, 1093 (1976).

²N. Tsuda, Y. Sumino, I. Ohno, and T. Akahane, *J. Phys. Soc. Jpn.* **41**, 1153 (1976).

³N. Matsumo, M. Yoshimi, S. Ohtake, T. Akahane, and N. Tsuda, *J. Phys. Soc. Jpn.* **45**, 1541 (1978).

⁴C. N. King, H. C. Kirsch, and T. Geballe, *Solid State Commun.* **9**, 907 (1971).

⁵F. S. Razavi, Z. Altounian, and W. R. Datars, *Solid State Commun.* **28**, 217 (1978).

⁶J. E. Schirber and B. Morosin, *Phys. Rev. Lett.* **42**, 1485 (1979); J. E. Schirber and D. L. Overmyer, *Solid State Commun.* **35**, 389 (1980).

⁷J. E. Schirber, B. Morosin, R. W. Alkire, A. C. Larson, and P.

- J. Vergamini, *Phys. Rev. B* **29**, 4150 (1984).
- ⁸J. E. Schirber and L. F. Mattheiss, *Phys. Rev. B* **24**, 692 (1981).
- ⁹B. Batlogg, R. G. Maines, and M. Greenblatt, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981).
- ¹⁰B. Batlogg, R. G. Maines, M. Greenblatt, and S. Di Gregorio, *Phys. Rev. B* **29**, 3762 (1984).
- ¹¹J. Eckert, W. B. Daniels, and J. D. Axe, *Phys. Rev. B* **14**, 3649 (1976).
- ¹²J. D. Axe, J. Harada, and G. Shirane, *Phys. Rev. B* **1**, 1227 (1970).
- ¹³W. G. Stirling, *J. Phys. C* **5**, 2711 (1972).
- ¹⁴M. Sato, B. Grier, G. Shirane, and T. Akahane, *Phys. Rev. B* **25**, 6876 (1982).
- ¹⁵Y. Fujii, S. Hoshino, Y. Yamada, and G. Shirane, *Phys. Rev. B* **9**, 4549 (1974).
- ¹⁶W. A. Kamitakahara, B. N. Harmon, J. G. Taylor, L. Kopp, H. R. Shanks, and J. Rath, *Phys. Rev. Lett.* **36**, 1393 (1976).
- ¹⁷See, for example, S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, *Phys. Rev. B* **6**, 4332 (1972).
- ¹⁸B. Halperin and C. Varma, *Phys. Rev. B* **14**, 4030 (1976).
- ¹⁹R. Clarke, *Phys. Rev. Lett.* **39**, 1550 (1977).
- ²⁰J. E. Schirber, L. J. Azevedo, and A. Narath, *Phys. Rev. B* **20**, 4746 (1979).
- ²¹Such a crystallographic study using neutron powder diffraction is presently underway [J. D. Jorgensen, J. E. Jorgensen, B. Batlogg, and J. D. Axe (unpublished)].
- ²²See, for example, A. D. Bruce, *Adv. Phys.* **29**, 1 (1980).
- ²³K. A. Müller and W. Berlinger, *Phys. Rev. Lett.* **26**, 13 (1971).
- ²⁴H. Thomas and K. A. Müller, *Phys. Rev. Lett.* **21**, 1256 (1968).