Structure of ReO_3 above the "compressibility collapse" transition

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We have determined the crystal structure of ReO_3 at ~ 15 kbar and 300 K well above the "compressibility collapse" transition (5.2 kbar, 300 K) with the use of the single-crystal diffractometer at the Los Alamos Pulsed Neutron Facility. Our data are consistent with space group $Im3$ and $a = 7.41(2)$ Å. A model was refined to an $R(F)$ value of 0.12. The octahedra are slightly rotated moving the oxygen atoms so as to form a 165° Re–O–Re angle. This structural model is consistent with a large body of recent physical data.

INTRODUCTION

A novel second-order phase transition is induced in ReO_3 by modest pressures (5.2 kbar at 300 K) resulting in a high-pressure phase with a compressibility increase of at least an order of magnitude.[1] This transition was first detected by Razavi, Altounian, and Datars[2] who noted nonlinear behavior of the Fermi-surface cross sections with pressures near 3 kbar. Schirber and Morosin[1] used very accurate differential measurements of the strongest de Haas–van Alphen frequency to determine that the transition occurred at 2.45 kbar at liquid-He temperature. Schirber, Azevedo, and Narath[3] subsequently used first- and second-order quadrupolar effects on the Re NMR to show that the symmetry at the Re site above the transition was less than cubic. The phase diagram between 4 and 300 K was mapped out accurately using the first-order quadrupolar effect. These data impose restrictions on the space group for the high-pressure phase: (i) a single Re site in the primitive unit cell, (ii) noncubic point symmetry at the Re site, and (iii) overall cubic symmetry for the unit cell.

The simplest structures not involving atomic rearrangements meeting the above characteristics have the symmetry of either the $Im3$ or $Im3m$ space groups, requiring that a body-centered Bravais lattice with a doubled lattice parameter[4] be used. The difference between $Im3$ and the higher-symmetry $Im3m$ is subtle but distinguishable with the proper diffraction experiment. The $Im3$ structure has been assigned previously to phase changes in the related perovskite structured sodium tungsten bronzes.[5] The changes from the primitive perovskite to the double-sized body-centered lattice should substantially modify the band structure and Fermi surface, and indeed new Fermi-surface sheets were observed completely consistent with the predicted band structure.[6] However, magnetic breakdown effects dominate[6] high-field experiments indicating that the superlattice gaps introduced by the change from simple cubic to body-centered cubic are small at a pressure a few kbar above the transition. An attractive feature of the proposed $Im3$ structure is that it makes plausible the large increase in compressibility. The rotation of the oxygen octahedra about each of the cube edge directions produces a buckling or hinging of the Re–O–Re chains. This hinging presumably allows much easier compression of the lattice while the octahedra remain essentially undistorted. The sample volume versus pressure has been very accurately determined by Batlogg, Maines, and Greenblatt[7] using strain gauge techniques to 30 kbar. They found no discontinuous volume change at the transition but reported an infinite slope on the volume versus pressure curve which gradually decreases with increasing pressure. They infer that the [100] LA phonon mode at zone center and one of the TA branches in [110] softens. Axe *et al.*[8] using inelastic neutron scattering observe a softening of an M-type phonon at pressures near the transition.

All of the above results are consistent with a transition to $Im3$ space group but no detailed structure determination has been reported. In this paper we report a refinement on such a structure model for ReO_3 near 15 kbar at 300 K, well above the transition which occurs at 5.2 kbar at this temperature.

EXPERIMENTAL

The sample used in this investigation is a single crystal grown by iodine-vapor transport.[9] This is the identical crystal used in earlier de Haas–van Alphen measurements[10] so it is known to have a very long electron mean free path and, therefore, high perfection. The original crystal was a 3-mm-diam faceted disk which was trimmed by spark erosion to a maximal dimensioned $3 \times 2 \times 1.5$-mm^3 specimen with the longest dimension approximately along the [12,5,0] direction.

The pressure vessel is a BeCu clamp cell of design similar to that described by Chu *et al.*[11] The crystal was mounted on a hollow Gd pedestal which, in turn, rested on Cd washers (2 mm i.d.) all inside the usual Teflon capsule. In our geometry, which is described in more detail in Ref. 12, the incoming pulsed neutron beam is directed along the axis of the pressure vessel. The Cd and Gd fixtures are designed to collimate the beam and to reduce diffraction from the BeCu closure pads. The pressure fluid was fluorinert 77 (F77, 3M Co., St. Paul, MN) and the pressure was monitored by a manganin strain gauge on the exterior circumference of the vessel. After clamping, the assembly was photographed with a flash x-ray source to identify precise crystal location; this aids in crystal centering and allows maximum shielding against scattering from the pressure vessel. The

pressure was 15 (± 1) kbar and all measurements were taken at room temperature. A 2-mm-diam beam of pulsed neutrons from the Los Alamos National Laboratory Pulsed Neutron Facility (LANL) bathed the crystal along its longest axis. The 25×25-cm Borkowski-Kopp–type[13] position sensitive proportional counter was positioned 90° from the incident beam and ~ 26 cm from the crystal. By using the Laue time-of-flight technique[14] with crystal and detector held constant during data collections, individual orders of a Bragg plane were resolved via precise time-of-flight (wavelength) information. Events on the detector are coded within a three-dimensional framework (called a histogram) consisting of 64×64 spacial (x,y) channels and a time resolution of 188 channels over a wavelength range of $0.75\rightarrow 4.0$ Å. Coverage of reciprocal (or k) space is accomplished by rotating the pressure vessel and enclosed crystal specimen about the incident beam direction.

RESULTS AND DISCUSSION

Two histograms were collected at orientations approximately 45° apart in rotation about the nominal [12,5,0] direction, each for about 24 h. A total of 130 peaks were observed and indexed on the double-sized body-centered cell. The strongest peaks were used to refine the lattice constant $a=7.41(2)$ Å. Integration of the data about the 174 predicted lattice points in these histograms yielded 129 reflections measured above background with 79 having amplitudes more than 3σ above a moderately high background.

The data reduction and least-squares refinement were performed using the Los Alamos crystal structure programs.[15] The choice of space group was made on the basis of these refinements. The refinement in $Im3m$ converged to $R=0.22$ while that in $Im3$ converged to $R=0.12$. In addition, several parameters in the $Im3m$ refinement converged to totally unrealistic values. Corrections were included for absorption effects on the beam spectrum resulting from the BeCu clamp, anisotropic temperature factors, and an isotropic extinction parameter. An additional wavelength-dependent absorption correction ($\sim 10\%$ of the total absorption correction) was required to account for multiple scattering effects of the pressure fluid and vessel. The initial lattice parameter used is double the simple cubic cell dimension 3.75 Å. In $Im3$, Re atoms occupy 8-fold (c) sites at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ while O atoms occupy 24-fold (g) sites at $(0,y,z)$ (plus symmetry equivalent sites on both atoms). The displacements of the oxygens from $(0,\frac{1}{4},\frac{1}{4})$ (the position in the perovskite, simple cubic structure) are small and pressure dependent. The symmetry requires the anisotropic thermal factors to be constrained; for Re, $U_{11}=U_{22}=U_{33}$ and $U_{12}=U_{13}=U_{23}$, while for O, $U_{12}=U_{13}=0.0$. The final parameters, with $R(f)=0.12$, are given in Table I. At 15 kbar, the Re–O distance is 1.868(7) Å with Re–Re $=\frac{1}{2}a_0=3.706(13)$ Å. The displaced oxygen from $(0,\frac{1}{4},\frac{1}{4})$ results in Re–O–Re angles of 165.1(5)° with O–Re–O angles ranging from 89.7(3) to 90.3(3)°, not significantly different from those for a regular octahedron.

TABLE I. Refined structured parameters at ~ 15 kbar.

a_0	7.41(2) Å
Mosaic block size	0.021(5) mm
ReU_{11}	0.0265(11) Å^2
ReU_{12}	0.0022(6) Å^2
Oy	0.2726(10)
Oz	0.2265(9)
OU_{11}	0.0105(15) Å^2
OU_{22}	0.0584(29) Å^2
OU_{33}	0.0504(28) Å^2
OU_{23}	0.0009(20) Å^2

These results are consistent with our earlier attempts to determine the structure above the transition. Time-of-flight neutron diffraction on an earlier powder diffractometer at LANL at ~ 8 kbar showed no superlattice peaks above the high background. However, we calculate (assuming the compression all goes into kinking the Re–O–Re chains) that the intensity would be down by nearly two orders of magnitude at this pressure near the second-order transition. Our diamond cell x-ray measurements to ~ 100 kbar involve intensities overwhelmed by the Re scattering and additionally are confined to low 2θ values because of the Mo wavelength and the geometry of the cell.

In summary, we have shown that the structure of ReO_3 above the "compressibility collapse" transition is consistent with $Im3$ symmetry. Near 15 kbar the lattice parameter is 7.41 Å. The octahedra are rotated about 7° so that the "hinge" angle is 165°. This structure is consistent with all of the physical properties data that have been accumulated over the past several years. However, the puzzle remains incomplete. Is the driving force for the transition due to mode softening as indicated by the preliminary inelastic neutron work, elastic constant,[16] and thermal expansion anomalies or is it an electronic effect perhaps related to Cr-like Fermi-surface nesting phenomena? Additional inelastic neutron data appear to be the most powerful tool to answer these questions.

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