radiation. An interpretation of these effects is given which involves transitions of trapped carriers accompanied by atomic relaxation. The traps may be valence-alternation pairs.[9]

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"Compressibility Collapse" Transition in ReO_3

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We have used Fermi-surface pressure-derivative measurements at 2 K and single-crystal and powder x-ray studies as a function of pressure at room temperature to demonstrate that recently published anomalous Fermi-surface and lattice properties of ReO_3 are related to a novel second-order phase transition. This transition probably involves a tetragonal distortion of the lattice accompanying a displacement of the O atoms from the linear O-Re-O chains of cubic ReO_3 to a "hinged" arrangement at the oxygens and is characterized by an enormous increase in the compressibility of the high-pressure phase.

The compound ReO_3 has been shown to have many surprising properties. It is a bright red metal, with a conductivity within a factor of 6 of that of Cu at room temperature, which can be prepared in single crystals of sufficient perfection to permit observation of strong quantum oscillations in the magnetization[1] and thermal properties.[2] With some shifting of the bands, Mattheiss[3] was able to derive a band structure in agreement with both the Fermi-surface results and the optical data. Pressure studies[4] of the Fermi surface could be accounted for by a volume-dependent band structure by Myron, Gupta, and Liu.[5] Thus the electronic structure of this compound seemed to be rather well understood.

Razavi, Altounian, and Datars[6] recently reported an extension of the study of the pressure effect on the Fermi surface to higher pressures. The original work[4] gave only the initial derivatives determined by a method which requires pressures < 25 bars. Razavi, Altounian, and Datars found that the pressure derivatives for all the sheets of the Fermi surface suddenly increased at a much larger rate beginning at about 3 kbar. They speculated that this might be related to either (i) movement of the oxygens from their positions similar to the distortions that are observed in the related perovskites, or (ii) wave-function overlap changes with pressure, enhancing covalency in the compound and thus changing the Fermi surface.

Other investigators have reported anomalies in the lattice properties of ReO_3. Tsuda *et al.*[7] found that the elastic constants were very anisotropic, seriously violating the Cauchy relations. Pearsall and Coldren,[8] who also measured the elastic constants, suggested a phase transition might occur at low temperature although no direct evidence for such has been reported. Finally Matsuno *et al.*[9] very recently reported that ReO_3 has a negative thermal expansion below 340 K, again indicating anomalous phonon structure and possibly lattice instability.

With this background in mind, we have undertaken several experiments to try to identify the cause of this anomalous behavior. These experiments include (1) a very accurate measurement of the Fermi-surface pressure derivatives of a selected de Haas-van Alphen (dHvA) frequency to verify the existence of the transition and to pinpoint the pressure at which it occurs at low temperatures; (2) measurement of the room-temperature compressibility of ReO_3 above the transition; (3) an attempt to determine the symmetry of the high-pressure phase.

Samples were those used in our initial studies of the Fermi surface of ReO_3 grown by vapor transport. The dHvA sample was a 0.5-mm×0.5-mm×2-mm natural parallelepiped with the long axis along [100]. The sample was held in the 3200-turn counterwound pickup coil with a small amount of stopcock grease. Pressures to ~ 6 kbar were generated by careful isobaric freezing of He.[10] Magnetic fields to 100 kG were generated in a rotatable split superconducting coil. The pressure derivatives of the dHvA frequency were determined by the solid-He phase-shift technique.[11] Here the derivative of the frequency F (proportional to the cross-sectional area of the Fermi surface) is given by $F^{-1}dF/dP = B^{-1}\Delta H/\Delta P$; ΔH is the shift in the dHvA oscillation with a pressure increment ΔP at an applied field B. The room-temperature compressibility was determined in a diamond cell[12] with a powdered specimen mixed with Ag, the latter serving as an internal pressure calibration.

The structure determinations were made in a Be pressure vessel that attaches to either a Weissenberg or precession camera and permits single-crystal studies to a maximum pressure of 4 kbar at room temperature.[13] The Weissenberg camera employs Straumanis-Levinš film loading.

The shift in phase for the β oscillations of ReO_3 for $\vec{H} \parallel [110]$ as a function of pressure at 100 kG is shown in Fig. 1. The data shown constitute four separate excursions from low pressure to high pressure through the transition. The solid-He phase-shift technique improves the accuracy of the determination of the pressure derivative, which is given by the relation $d\ln F/dP = (\Delta\Phi/\Delta P) \times B/2\pi F$, substantially (probably by an order of magnitude) over what can be achieved by direct measurement of the frequency at various pressures. We thus verify unequivocably the change in derivative of the Fermi surface cross section and establish the transition pressure to be 2.4 ± 0.1 kbar at 2 K.

The results of our room-temperature lattice constant versus pressure measurements are shown in Fig. 2. The low-temperature slope was determined from single-crystal measurements at pressures $\leqslant 4$ kbar. The high-pressure points were determined by direct comparison with the lattice constant of Ag. We observe a large in-

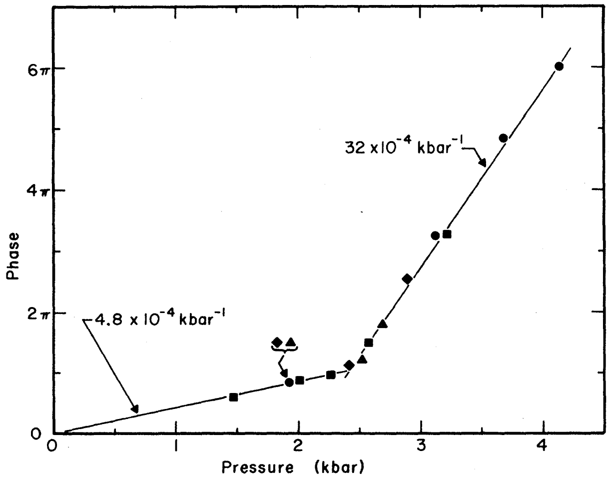

FIG. 1. Shift in phase vs pressure for the β frequency of the Fermi surface of ReO_3 for $\vec{B}$ parallel to [110] and of magnitude equal to 100 kG. These data consist of four passes through the transition shown with different symbols, all with increasing pressure.

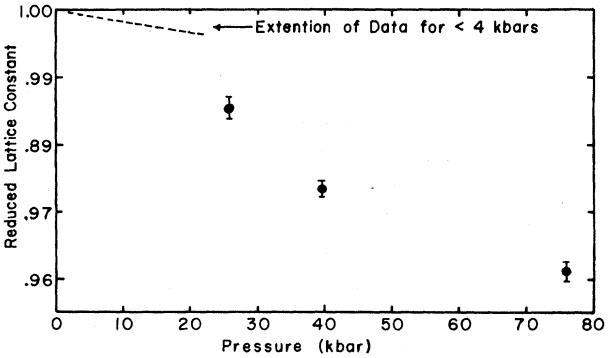

FIG. 2. Reduced lattice spacing of ReO_3 vs pressure at room temperature. The dashed line is from our earlier work in hydrostatic fluid to 3 kbar. Pressures were determined in the diamond cell with an internal Ag standard.

crease in the value of the compressibility from the low-pressure values of $(5.2\pm 0.3)\times 10^{-4}$ kbar^{-1} to $(30\pm 6.0)\times 10^{-4}$ kbar^{-1} in the 20–50-kbar pressure regime. We observed a broadening of the ReO_3 lines in these measurements which was barely detectable because the geometry of our diamond cell precludes observation of high-index lines but which seemed to increase with increasing pressure. This broadening would be consistent with a very small tetragonal distortion. We could detect no change in symmetry in our single-crystal Weissenberg camera studies to 4.1 kbar, indicating either that the transition is above this pressure at room temperature or that the distortion is too small to produce splitting of x-ray spots at a 2θ value of 160°.

The latter result is somewhat surprising in that Matsuna *et al.*[9] reported a negative thermal expansion below 340 K which would suggest that the transition might occur at a lower pressure at room temperature than at 2 K. Our measurements of the lattice constant at 300 K, 3.7479(2) Å, and ~100 K, 3.7474(2) Å, indicate that the thermal expansion is positive but quite small. This value would lead to a room-temperature transition near 3.5 kbar if nearest-neighbor distances were the only consideration. Since we observed no distortion to about this pressure we must conclude either that the transition is somewhat higher than 4.1 kbar at room temperature or that the distortion is indiscernible at this pressure.

Based upon our admittedly fragmentary results we propose that the large increase in compressibility occurs because of a shift in the oxygen positions from the O-Re-O perfectly aligned mutually orthogonal chains to a "hinged" arrangement which allows a much easier diminution of the overall lattice constant with pressure. Such shifts of the O atoms from the high-symmetry positions is not unusual in the perovskite lattices which are similar to the ReO_3 lattice but the enormous increase in compressibility is to our knowledge unprecedented in any material with a second-order phase change. We are confident that the transition is second order because of the smooth variation of the Fermi-surface cross section through the transition. The phase-shift technique we used was sensitive under the condition of this experiment to changes in phase of about $0.02\times 2\pi$ which corresponds to a volume change of about 2 parts in 10^5 in the low-pressure phase. On the other hand, the apparent compressibility increases at 2 K by a factor of nearly 7.

We present data demonstrating that ReO_3 undergoes a second-order phase transition in which the compressibility jumps to a much higher value in the high-pressure phase. Our data are consistent with a very slight tetragonal distortion of the lattice presumed to occur when the oxygen atoms shift from their octahedral arrangement around the Re atoms. This apparently changes the mutually orthogonal O-Re-O chains from rigid alignment to "hinged" arrangements at the oxygen which are far more easily compressed. The distortions are sufficiently small that we cannot detect them at 4.1 kbar at room temperature (or the transition is higher at this temperature). At much higher pressures, low 2θ lines seem to broaden progressively in our diamond cell above 20 kbar consistent with a tegragonal distortion of the lattice. Further study will be required to definitively probe the details of this unusual transition.

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