The proper identification of these peaks would substantiate our theory of minority carrier DSCR.

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Magnetothermal Oscillations and the Fermi Surface of ReO_3

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Magnetothermal oscillations have been observed in single crystals of ReO_3. The three sets of frequencies observed are in good agreement with Mattheiss's augmented-plane-wave calculations, which include open orbits along ⟨100⟩ directions.

I. INTRODUCTION

THE compound ReO_3 is a red transition-metal oxide which exhibits metallic electrical conductivity. In addition to its importance as a transition-metal oxide,[1] ReO_3 is interesting because of its relatively simple crystal structure. This structure makes it closely related to certain classes of materials of wide current interest: the perovskites and the tungsten bronzes. As such it serves as a prototype for understanding the electronic band structure of these more complicated materials.

Detailed band-structure calculations using the augmented-plane-wave (APW) method have recently been completed by Mattheiss.[2] Optical data have been reported by Feinleib *et al.*[3] and de Haas–van Alphen (dHvA) data have been reported by Marcus.[4] The optical data, as well as the lowest dHvA frequency and its effective mass, were used by Mattheiss to adjust the band-structure calculations.

Magnetothermal oscillations[5] are the Landau quantum oscillations in the temperature of an adiabatically isolated sample as the magnetic field is changed in magnitude or direction. We present here detailed data which combine rotations and field sweeps to determine precisely the frequencies and their dependence on magnetic-field direction. The dHvA data[4] were obtained at lower fields and did not include rotation data. They are roughly consistent with the present data, but the large scatter precludes any detailed comparison with the present results.

II. THEORY

The ReO_3 structure has a simple cubic Bravais lattice and is illustrated in Fig. 1. The cube corner positions are unoccupied in ReO_3 but are occupied by A atoms in the perovskite structure ABO_3, or by Na atoms in sodium tungsten bronze, Na_xWO_3.

The APW Fermi surface is illustrated in Fig. 2. The two smallest pieces, α and β, are roughly spherical and centered at Γ. The third piece γ consists of ⟨100⟩-directed cylinders intersecting at Γ and forming in the extended zone scheme a jungle-gym-like multiply connected surface. Electron orbit γ_1 and hole orbit γ_2 are illustrated in the figure. Electron orbit γ_3 is not

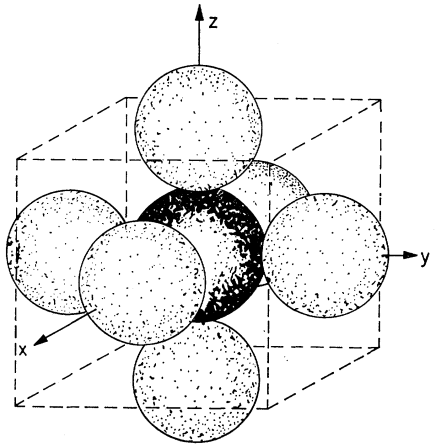

FIG. 1. Unit cell for ReO_3. The rhenium atom at the center of the cube is surrounded by six oxygen atoms located at the face centers (after Mattheiss).

[1] For a review of the transition metal oxides and their many interesting properties, see David Adler, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1968), p. 1, and references therein.
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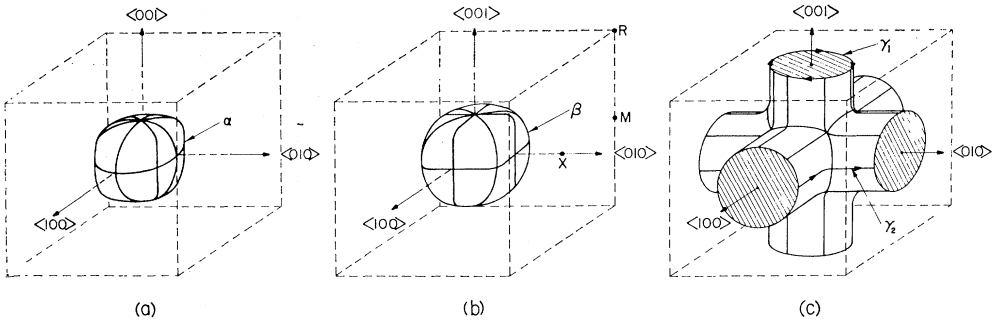

FIG. 2. Three-dimensional sketches of the three electron sheets of the APW Fermi surface in ReO_3 (after Mattheiss).

shown but it is an orbit centered at Γ with the field at or near ⟨111⟩. Various other closed orbits centered at Γ, X, or R are possible, including many which extend through more than one zone. Most of these orbits have areas considerably larger than α, β, or γ_1, and are not included in Fig. 2. Since the multiply connected surface is the classic set of interesting cylinders along ⟨100⟩ directions often used in theoretical discussions, one may find convenient illustrations of the three-dimensional extended surface in the literature.[6]

III. EXPERIMENT

The apparatus used for measuring magnetothermal oscillations has been described previously.[7] Briefly, the sample was mounted on a graphite stand inside a hollow spherical pulley free to rotate about a horizontal axis in sapphire bearings. A superconducting solenoid produced a vertical field of up to 110 kOe. The system provided very smooth rotation to angular speeds as low as 1° per 5 min. The graphite stand isolated the sample thermally from its surroundings, and a carbon thermometer attached to the sample monitored its temperature. The thermometer consisted of a 10-mil-thick "bread-loaf" slice of nominal 470-Ω, $\frac{1}{8}$-W Allen-Bradley resistor. Both circular faces of the slice were indium plated for electrical contact, and four 1-mil manganin wires, attached in pairs to each face with silver paste, served as current and potential probes. The thermometer was mounted with one face directly against the sample and attached with silver paste to optimize thermal contact. Field modulation and phase-sensitive detection[8] were used to measure dT/dH at 10–20 Hz, but this type of thermometer showed good response up to several hundred hertz. The thermometer resistance R was typically 100 Ω at room temperature, rising to ~500 kΩ at 1.1°K with sensitivity $d(\ln R)/dT \approx 3°K^{-1}$.

Two crystals were used in the present measurements. The first, grown by Ferretti by an iodide-vapor transport method,[9] was of rectangular shape with dimensions of ~2 mm and resistance ratio of 70. The second, grown in this laboratory and used for the bulk of the measurements, was a pyramidal sample of maximum dimension ~1 mm and of somewhat greater crystalline perfection. It was prepared by iodide-vapor transport of 99.95% ReO_3,[10] in a closed tube using a method slightly modified from that of Ferretti *et al.*[9] The tube (1 cm i.d., 8 cm long) contained a quantity of iodine to give a calculated initial pressure of 2 atm at the mean temperature of the tube, 352°C. It was inclined at an angle of 13° to the horizontal. The upper end was heated to 336°C and the lower end, containing the pressed-powder pellets of ReO_3, was heated to 368°C. After 15 days of heating, crystals of ReO_3 1–2 mm on a side were found at the lower-temperature end of the tube. Mass-spectrographic analysis showed the crystals contained less than 15 ppm of iodine. The resistance ratio of the small sample used in the experiment was not measured.

IV. RESULTS

Data were taken in the (100) and (110) symmetry planes and consisted of field sweeps at fixed angles as well as rotations at fixed field strength. The field sweeps were analyzed both manually and by computer calculation of their Fourier transforms.[11] The latter technique was especially needed to detect frequency β within ~30° of ⟨100⟩ in either plane because of its very weak amplitude there. Field-sweep data are represented by solid circles in Fig. 3. The smooth curves are rotation data and have been positioned vertically to give best agreement with the field-sweep data. The field-sweep data are estimated to be accurate within 1% and the rotation data within considerably less than 1%. Rotation in the (001) plane showed clearly that frequency γ_1 crosses a symmetry related branch at [110] rather than

[6] See, e.g., R. G. Chambers, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 100.

[7] M. H. Halloran and J. E. Kunzler, Rev. Sci. Instr. **39**, 1501 (1968).

[8] A similar magnetothermal system, except for the rotation mechanism and the particular thermometer construction, has been described by B. McCombe and G. Seidel, Phys. Rev. **155**, 633 (1967).

[9] A. Ferretti, D. B. Rogers, and J. B. Goodenough, J. Phys. Chem. Solids **26**, 2007 (1965).

[10] Obtained from Gallard-Schlesinger Chem. Mfg. Corp., Carle Place, N. Y.

[11] See, e.g., J. E. Graebner and J. A. Marcus, Phys. Rev. **175**, 659 (1968).

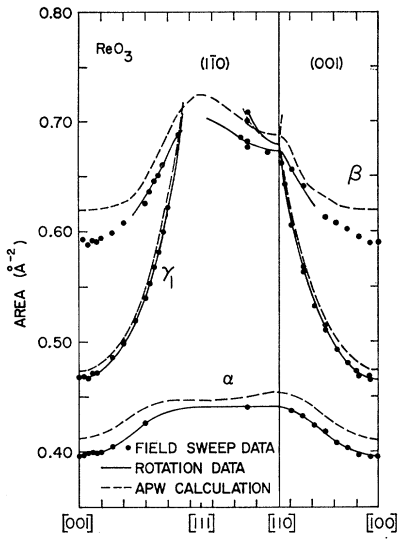

FIG. 3. Reduced magnetothermal data for the two symmetry planes (001) and (1$\bar{1}$0), compared with the calculated cross-sectional areas expected from the APW Fermi surface (dashed ines).

approaching [110] with zero slope. The higher branch was too weak to be detected in field sweeps. Exactly how far past [110] it should extend has not been determined.

Branch α in plane (1$\bar{1}$0) is nearly flat between [111] and [110]. Rotation data, however, showed that a shallow minimum occurs in that region at 23° from [110]. Frequency α is 0.0003 Å^{-2} lower at this point than it is at [111] and 0.0012 Å^{-2} lower than at [110]. The rotation data for frequency β became weak in amplitude near [100], as mentioned above, and again in a smaller angular region near [111]. The frequencies of each branch at [001], [110], and [111] are given in Table I.

TABLE I. Areas, in Å^{-2}, of the observed three pieces of Fermi surface with field along high symmetry directions.

	α	β	γ_1
[001]	0.396	0.59	0.466
[110]	0.4415	0.702	0.679
[111]	0.4406	0.673	...

V. DISCUSSION

The data are plotted in units of area[12] for comparison with the theoretical results, which are given by the dashed curves in Fig. 3. In general, the agreement is strikingly good. The worst discrepancies, occurring for β near [100], are only ~5%. The data for γ_1 indicate that the arms of the APW model should have slightly more taper in order to reduce the area at [100] by ~½% without changing the value at [110]. We note also that the observation of orbit γ_1 over the full 45° in plane (001) eliminates the possibility of open orbits along ⟨110⟩ directions that could occur with arms of larger diameter.

The APW calculation was fitted to the dHvA data[4] for branch α. Those data exhibit considerable scatter and also lie generally higher than the present data, perhaps as a result of a difference in magnetic-field calibration.

In the APW calculation the Fermi level was determined by requiring one electron per unit cell. In Fig. 3 the calculated values are consistently larger than the observed areas. The discrepancies in area of α and β with the APW model indicate a difference of ~0.01 electron per unit cell. Such a slight discrepancy could be explained in a number of ways. A 1% deviation of the stoichiometry from ideal, for example, would not be unusual. Another explanation would be that the real Fermi surface is slightly larger at the intersection of the arms at Γ, so that orbit γ_3 about this intersection would be slightly larger than predicted. Unfortunately, γ_3 was not observed.

Orbit γ_2 and the extended orbits mentioned above, as well as γ_3, were not observed. Presumably the impurity or defect scattering of electrons was sufficient to damp these higher-frequency oscillations. The three sets of frequencies which were observed, however, provide quite good confirmation of the APW model.

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[12] Area (Å^{-2}) = 0.955 × frequency (10^8 G).