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de Haas–van Alphen Effect in ReO_3†

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The de Haas–van Alphen effect in ReO_3 single crystals has been studied in detail using large impulsive magnetic fields. In addition to the three frequency branches reported by Graebner and Greiner and by Marcus, three new frequency branches have been detected. All of the frequencies observed are in good agreement with the augmented-plane-wave calculation of Mattheiss.

I. INTRODUCTION

The red transition-metal oxide ReO_3 has a cubic structure closely related to the perovskite structure observed in the tungsten bronzes.[1] In the unit cell of ReO_3 the Re atom is located at the origin while the O atoms occupy positions on the face centers. The space group for the ReO_3 structure is O_h^1.

Recently, Mattheiss[2] reported an extensive augmented-plane-wave (APW) band calculation for ReO_3 in which he describes the probable Fermi surface (FS) and the corresponding de Haas–van Alphen (dHvA) frequencies expected from his model. The present paper presents the results of a detailed experimental study of the FS using the dHvA effect (see Gold[3] for a recent review of the dHvA effect). Marcus[4] originally observed dHvA oscillations in ReO_3 and recently Graebner and Greiner[5] have presented precise measurements of magnetothermal oscillations in ReO_3. However, both of these investigators were unable to observe several frequencies belonging to the multiply-connected γ surface predicted by the APW calculations reported by Mattheiss.[2] The results to be presented here are in complete agreement with the earlier results and in addition three new frequency branches associated with the γ surface are presented.

II. EXPERIMENTAL

A. Sample Preparation and Characterization

Single crystals of ReO_3 were prepared for this investigation by an iodine vapor transport method similar to that reported by Ferretti *et al.*[6] and Graebner and Greiner.[5] The starting material for the crystal growth was a finely divided powder of ReO_3 purchased from City Chemical Corp. of New York.

A complete mass spectrographic analysis of the ReO_3 crystals was carried out. A total of 200 ppm impurities was found in the transported material with the main impurities being B, 40 ppm; Na, 30 ppm; Cl, 50 ppm; and Y, 40 ppm. No iodine was detected in the transported material. The lattice constant as obtained from the average of three independent determinations was 3.7455 ± 0.003 Å.

Electrical resistivity measurements were made on a rectangular single crystal using a standard four-probe method. A value of $(9.5 \pm 0.2) \times 10^{-6}\ \Omega/\text{cm}$ obtained at 300 K. Ferretti *et al.*[6] indicates a similar value for the room-temperature electrical resistivity. In the case of our measurements the error is due in large part of the uncertainty in the measurement of dimensions and probe separation on the small sample. Measurements on this crystal as a function of temperature are shown in Fig. 1. It can be seen that the resistivity increases rapidly with increasing temperature, as has been observed in the case of many transition metals[7,8]; however, the rapid increase (between T^2 and T^3) extends to much higher temperatures in ReO_3.

The resistivity ratio $\rho_{300}/\rho_{4.2\,\text{K}}$ was measured on several samples and found to be between about 500 and 700. Although the samples used for the de Haas–van Alphen measurements were too small for resistivity measurements, the ratios were probably of the same magnitude as those observed in the larger crystals.

B. dHvA Measurement Techniques

Two crystals were used in the present measurements. Both crystals were roughly cube shaped, one approximately $1 \times 1 \times \frac{1}{2}$ mm and the other $\frac{1}{3}$ mm on a side. It was found necessary to use the smaller sample to obtain sufficient dHvA signal at [110] and anywhere within about 30° of [100]. Presumably the eddy-current heating is particularly strong near [110] since the larger sample showed almost no signal here, although it gave very strong dHvA signals when between [111] and [001].

The samples were mounted on a glass capillary in a pick-up coil situated in a geared wheel[9] which could be turned from outside the cryostat so as to vary the orientation of the crystal with respect to the magnetic field. The sample could be oriented by means of x rays focused through the end of the pickup coil while the coil was mounted in the wheel, thereby permitting the plane of rotation to be set to better than 1° by adjusting the position of the sample in the capillary and rotating the capillary.

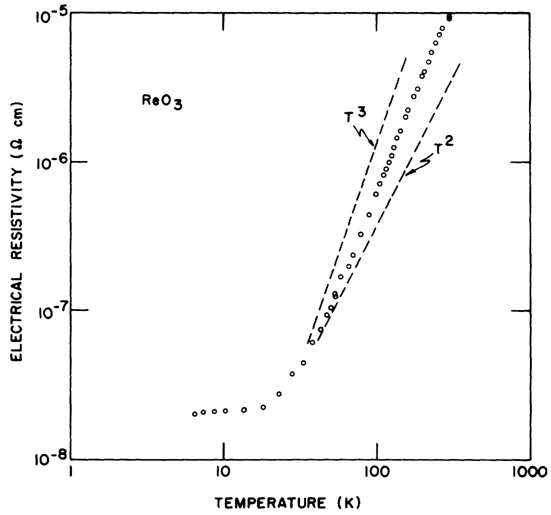


FIG. 1. The electrical resistivity of a single crystal of ReO_3 as a function of temperature. The resistivity increases rapidly with increasing temperature (between T^2 and T^3), as has been observed in many transition metals.

Because of some backlash in the gear assembly, the absolute values of the orientations in the plane of rotation were determined from the symmetries of the angular variations of the dHvA frequencies. Data were taken for field directions lying in the $(1\bar{1}0)$ and (010) planes.

The basic impulsive-field apparatus and high-speed digitizing and buffering system are essentially the same as those used by Girvan *et al.*[10] and Panousis and Gold.[11] As described earlier,[10] the entire system was calibrated using as a standard the [111] frequency of the ν oscillations in tungsten. Instead of the filter-periodogram approach used earler,[9,10] a fast Fourier transform method[12] was used to analyse the data since the saving in computer time was typically a factor of 20. A complete account of this technique can be found in work reported by Hoekstra.[13] It is estimated that the overall accuracy of the frequency results to be presented is 1% or 1°, whichever is greater.

III. RESULTS AND DISCUSSION

The angular dependence of the frequencies of the

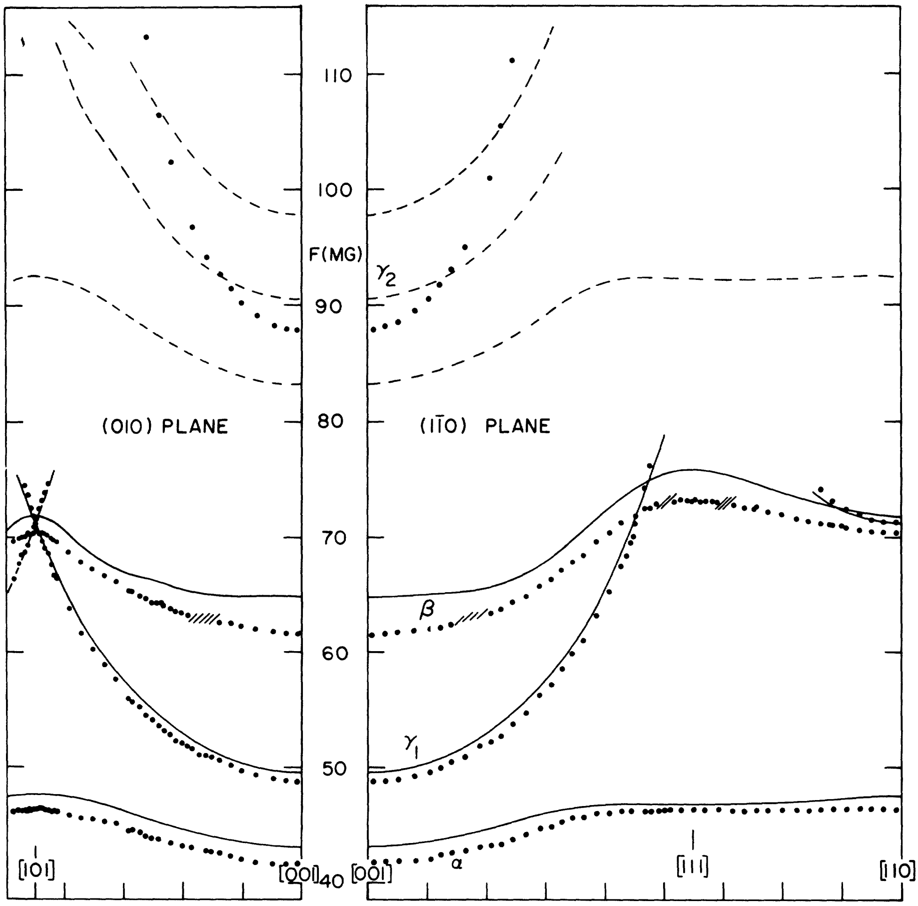


FIG. 2. Variations of the de Haas–van Alphen frequencies between 40 and 116 MG in ReO_3 for field directions in the $(1\bar{1}0)$ and (010) planes. Solid circles: fundamental terms; dashed lines: observed nonfundamental terms; hashed lines: regions in which the signal was too weak to be observed; solid lines: calculated frequencies expected from the APW FS in Fig. 4.

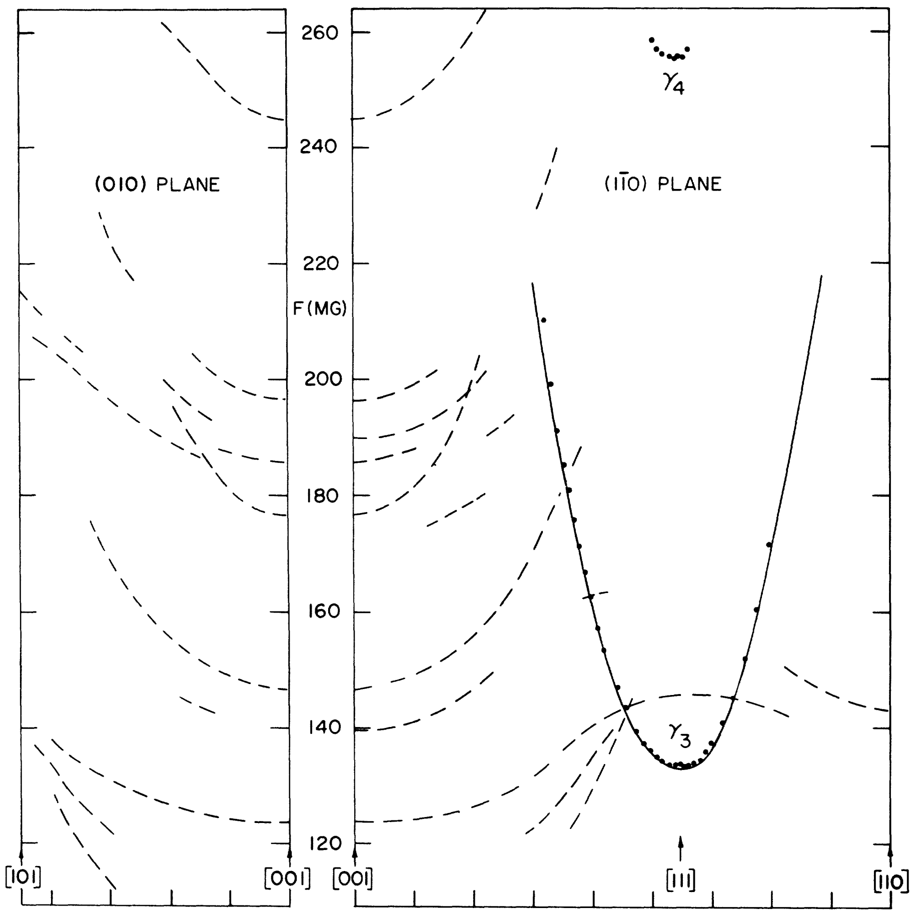
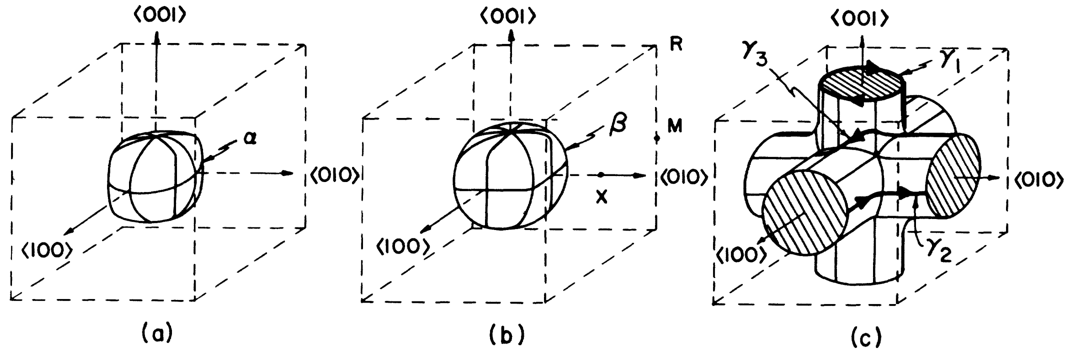


FIG. 3. Variations of the de Haas–van Alphen frequencies between 120 and 260 MG in ReO_3 for field directions in the (1$\bar{1}$0) and (010) planes. The symbols are the same as those used in Fig. 2.

fundamental dHvA terms for field directions lying in (010) and (1$\bar{1}$0) planes is shown in Figs. 2 and 3. The various branches have been labeled by the same Greek letters as in the APW FS reported by Mattheiss,[2] which is shown in Figs. 4(a), 4(b), and 4(c). This model gives rise to the frequency variations shown as solid curves in Figs. 2 and 3. The dashed curves in Figs. 2 and 3 indicate the experimentally observed variations for some of the nonfundamental terms and the hashed lines indicate regions in which the signal was too weak to be observed.

The α and β frequencies in Fig. 2 arise from the roughly spherical FS's shown in Figs. 4(a) and 4(b). The largest discrepancy (~5.5%) between experiment and theory for the β frequency branch



(a) (b) (c)

FIG. 4. Three-dimensional sketches of the three electron sheets of the APW FS in ReO_3 (after Mattheiss; we have added the γ_3 orbit to this figure).

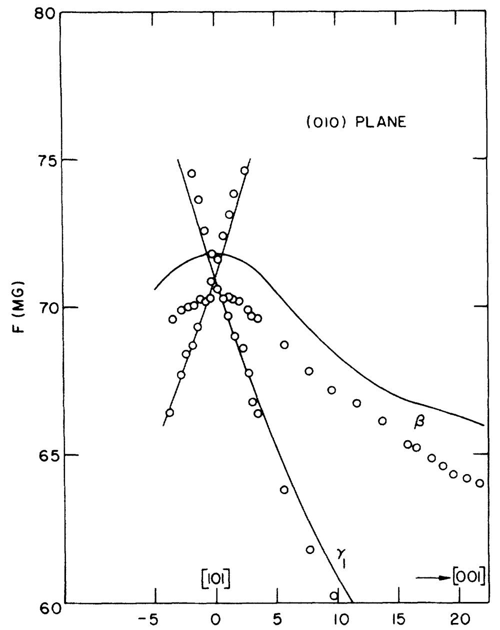


FIG. 5. Large-scale plot of the β and γ_1 frequencies (open circles) for field directions near [101] in the (010) plane. The solid lines are calculated frequencies expected from the APW FS in Fig. 4.

occurs at [001], as does the largest difference (~4%) for the α frequency branch. The effective mass of the carriers associated with the α oscillations at [111] and 25° from [111] toward [001] was measured (in units of the free-electron mass) and found to be 0.67 ± 0.02 and 0.63 ± 0.02, respectively. The value at [111] agrees well with the value quoted by Marcus[4] for this direction. The effective mass for the β oscillations 25° from [111] toward [001] was found to be 0.815 ± 0.02. These experimental masses lie some 5–11% higher than the values calculated by Mattheiss.[2]

The γ_1, γ_2, γ_3, and γ_4 frequencies shown in Figs. 2 and 3 arise from the multiply connected jungle-gym FS shown in Fig. 4(c). The agreement between experiment and Mattheiss's model is particularly good for this surface. The γ_1 frequency branch arises from an electronlike orbit associated with the arms of the jungle gym. The experimental value at [001] lies ~1.8% lower than the calculated value but agrees well with the calculated results at 45° from [001] in the $(1\bar{1}0)$ plane and also at [110]. As suggested by Graebner and Greiner,[5] this indicates that the arms of the APW model should be slightly tapered. Such a tapering will also increase the theoretical frequency value[2] of 84.0 MG for γ_2 at [001], which will improve the agreement with the experimental results to be discussed later. The γ_1 branch extends to about 48° in the $(1\bar{1}0)$ plane and acrosses the β branch at about 46°. In the (010) plane, the γ_1 branch crosses a symmetry-related branch at [110] and the upper branch extends 2.2°–2.4° beyond [110]. This crossing is shown in more detail in Fig. 5. The effective mass of the γ_1 oscillations was measured at 25° from [111] toward [001] and found to be 0.74 ± 0.02, which is ~10% higher than the calculated value.

The γ_2, γ_3, and γ_4 frequency branches represent new results which have not been reported before. The γ_2 frequency branch arises from holelike orbits centered about the point M in Fig. 4. This frequency has a minimum value of 87.8 MG at [001], which is ~4% higher than the theoretical prediction but is consistent with the suggested tapering of the arms mentioned above. The γ_2 branch extends to roughly 26°–27° in both the $(1\bar{1}0)$ plane and the (010) plane.

The γ_3 frequency branch arises from electronlike orbits centered about the intersection of the arms shown in Fig. 4(c). This orbit weaves in and out among the arms and we have attempted to indicate it in Fig. 4(c). The agreement between theory and experiment is better than $\frac{1}{3}\%$ for γ_3, as is shown in Fig. 3. How far γ_3 actually extends from [111] could not be determined since the signal became very weak as we rotated away from [111]. This loss in signal is probably due to the sharp increase in the effective mass of this orbit[2] away from [111].

The γ_4 oscillations are quite weak and could only be observed within 5° of [111]. We believe that this is a fundamental term and have tentatively assigned it to an holelike orbit centered at the point R in Fig. 4(b). This orbit is analogous to the γ_3 orbits and can be visualized by constructing a multiply commected hole surface similar to the γ surface but enclosing all space not inside the γ surface. The frequencies of all the fundamental branches for the symmetry directions [001], [110], and [111] are given in Table I.

TABLE I. de Haas–van Alphen frequencies in ReO_3 for high-symmetry directions.

Orientation	Branch	F(MG)
[001]	α	41.5
	γ_1	48.8
	β	61.6
	γ_2	87.8
[111]	α	46.3
	β	73.2
	γ_3	133.3
	γ_4	255.5
[110]	α	46.3
	β	70.3
	γ_1	71.1

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High-Resolution Specific Heat of $CoCl_2 \cdot 6H_2O$†

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The specific heat of a single crystal of $CoCl_2 \cdot 6H_2O$ has been measured with high resolution near $T_N = 2.29$ K. The data were fitted to the usual asymptotic form $C = A\epsilon^{-\alpha} + B$, where $\epsilon = |1 - T/T_N|$, using several different techniques. An examination of the gradient $\partial C/\partial T$ showed that the critical region was limited to $\epsilon \lesssim 7\times 10^{-2}$ and that for $\epsilon \lesssim 4\times 10^{-3}$ the specific heat was rounded. The data were found to fit the asymptotic form for $4\times 10^{-3} \lesssim \epsilon \lesssim 7\times 10^{-2}$ with $\alpha' = -0.19 \pm 0.04$ for $T < T_N$ and $\alpha = 0.34 \pm 0.05$ for $T > T_N$. It was also found that the observed rounding could be predicted by treating the sample as a system of microcrystals having a finite distribution of ordering temperatures. It was thus possible to produce a reasonable fit to all the data for $\epsilon < 7\times 10^{-2}$ using the above values of α' and α which were determined from the data in the "unrounded critical region." It was further found that the results of a previous experiment in another laboratory could also be fitted over the entire critical region using the above values of α' and α with a somewhat broader distribution of ordering temperatures.

I. INTRODUCTION

Recent theoretical advances[1] in the description of critical-point behavior of simple models have prompted numerous experimental studies of many different systems. Within the critical region, the specific heat of a system is expected to obey the asymptotic form

$$C/R = A\epsilon^{-\alpha} + B \ , \qquad (1)$$

where $\epsilon = |1 - T/T_N|$ and A', α', and B' below T_N (where T_N is the Néel temperature) may differ from the corresponding constants A, α, B above T_N. The values of α' and α which have been determined experimentally have shown a wide variation in magnitude.[2] In all cases the specific heat was observed to be "rounded" very near to the ordering temperature and in some cases[3,4] significant differences in the behavior of two different single crystals of the same material have raised questions concerning the possibilities of actually determining the intrinsic critical-point behavior.

The thermal and magnetic properties of $CoCl_2 \cdot 6H_2O$ have been investigated extensively,[5-16] and the nature of the magnetic interactions is fairly well known. At liquid-helium temperatures the Co^{2+} ions have an effective spin $S' = \frac{1}{2}$ with the nearest-neighbor interactions dominated by anisotropic exchange and with weaker exchange coupling between more distant neighbors. Dipolar interactions are not negligible but the ordered struc-