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Effect of pressure on the Fermi surface and band structure of ferromagnetic Gd. I. Experiment*

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We report measurements of the effect of pressure on eight cross sections of the Fermi surface of ferromagnetic Gd. Cross sections were obtained from de Haas–van Alphen effect measurements on a spherical crystal cut from a boule refined by electrotransport to a residual resistivity ratio of ~260. Pressure derivatives were determined using both fluid-He and solid-He techniques. The results show a surprising variation in both sign and magnitude in view of the near isotropy of the linear compressibilities of Gd. An electron transition involving the disappearance of a cross section of the Fermi surface near 8 kbar is indicated.

I. INTRODUCTION

There are very little data available on the Fermi surfaces of the trivalent rare-earth metals. Except for a single de Haas–van Alphen (dHvA) frequency reported for lutetium[1] and for terbium,[2] the only direct measurements until very recently were those of Young *et al.*[3] and ours[4] on Gd. The former investigation gives orientation data for several cross sections, but the absolute values of the frequencies are in error because of the use of an incorrect magnetization. This situation was discussed in Ref. 4 in which corrected data were compared with the results of a relativistic augmented-plane-wave (RAPW) calculation for paramagnetic Gd which was then split in a rigid-band fashion. While this comparison was somewhat more successful than that attempted by Young *et al.*[3] starting with an APW band structure of paramagnetic Tb, it was still not completely satisfactory in that the splitting of the paramagnetic bands required to preserve the Fermi-surface topology, led to much too large a conduction-electron moment. More recently Mattocks and Young[5] have reported further orientation data and two additional high frequencies for a higher-quality (resistance ratio of 500) specimen of Gd.

In this study we report measurements of the pressure dependence of the cross-sectional areas of the Fermi surface for fields along principal crystallographic directions. In the near future we will present a self-consistent relativistic ferromagnetic band-structure[6] calculation as a function of interatomic spacing. Such comparisons of pressure data and volume-dependent band calculations have proven useful in testing the applicability of models of the electronic structure of nonmagnetic material. It is of interest to ascertain the value of this approach to a ferromagnetic metal such as Gd.

II. EXPERIMENTAL

The sample used for the bulk of the study was a $\frac{1}{8}$-in.-diam sphere of Gd cut by spark erosion from a rod of material of residual resistivity ratio ~260. The material had been purified by an electrochemical process described by Peterson and Schmidt.[7] We obtained some data which was in good agreement with that presented here on cylindrical samples cut from "bamboo" stock grown by the same process. These latter data have more uncertainty due to the relatively unknown demagnetizing factors associated with their irregular shapes.

The dHvA frequencies were obtained by the now standard field modulation techniques[8] in a 55-kOe superconducting solenoid. It is not feasible to use the usual *in situ* field calibrations such as nmr or a known dHvA frequency[9] when dealing with a ferromagnetic sample because of the severe field distortion near the sample itself. We instead rechecked the current versus field calibration using a known dHvA frequency periodically during the investigation. It is our experience that this calibration is maintained for field above 10 kG to within 0.1–0.2% with our Nb-Zr–wound solenoid, the primary error being due to small residual fields locked in the magnetic windings.

In a ferromagnetic material such as Gd, the dHvA oscillations are periodic in B^{-1}, where B

is the magnetic induction. For a spherical sample as we have used $B = H_a + \frac{8}{3}\pi M_s$, where H_a is the applied field and M_s is the saturation magnetization. We determined our frequencies by fitting to straight-line plots of integers versus $(H_i + \frac{8}{3}\pi M_s)^{-1}$, where H_i are zero crossing (or peaks) of oscillations. A large body of data yielded $\frac{8}{3}\pi M_s = 18.6 \pm 0.7$ kG. This is in good agreement with recent determinations[10] of $(7.63 \pm 0.02)\mu_B$/atom which correspond to 18.1 kG. We have chosen *for convenience* to calculate all our frequencies using $\frac{8}{3}\pi M_s = 19$ kG. Except for the lowest frequencies where the number of oscillations observed dominate the uncertainty in the frequency completely, the data were typically taken between applied fields of 30 and 50 kOe. Thus the frequencies can be converted to magnetizations near 19 kG by multiplying by $1 + 0.035\epsilon$, where ϵ is the (small) difference in kG between the new M_s and 19 kG.

Pressure derivatives of the cross sections were obtained using three different techniques as appropriate. The higher frequencies could be phase shifted[11,12] in fluid He at pressures less than 25 bar at 1 K. Here advantage is taken of the high-phase F/B, where F is the dHvA frequency so that a shift in the position of the oscillation ΔH with a pressure change in fluid He can be observed. The pressure derivative is then given by

$$\frac{d\ln F}{dP} = B^{-1}\frac{\Delta H}{\Delta P}. \tag{1}$$

Direct measurements of the frequency versus pressure to 4 kbar (generated in solid He)[13] were made for those situations where a sufficient number of oscillations could be detected to determine the frequencies to high enough precision to see the change with pressure. The third method, the solid-He phase-shift technique,[14] was used on the very-low-frequency oscillations where the phase is not sufficiently high to use the fluid-He technique and the direct change of frequency with a few kilobars is too small to observe. This technique is very useful in these cases because it is often the smaller frequencies that are most sensitive to the details of the band structure and unless they have large pressure derivatives, their behavior is very difficult to determine. When possible, more than one technique was used as a check on consistency.

The periodicity of the dHvA oscillations in B^{-1} introduces an added complexity to the determination of pressure derivatives in a ferromagnetic metal because of the possibility of variation of M_s with pressure. In the phase-shift techniques an additional term is required which for a spherical specimen results in

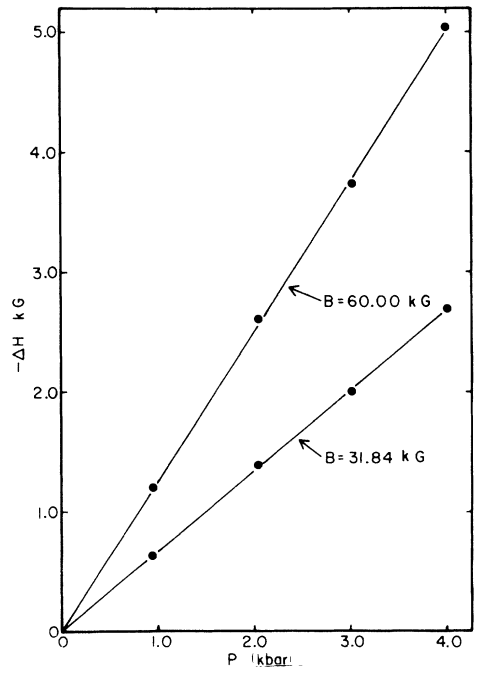

FIG. 1. Example of solid-He phase-shift measurements for the 1.96×10^6 G frequency for $\vec{H} \| [0001]$ in Gd. The minus sign associated with ΔH (the shift in field of a single oscillation) means that the feature is moving towards lower field with increasing pressure. This translates to a negative pressure derivative.

$$\frac{d\ln F}{dP} = \frac{1}{B}\frac{\Delta H}{\Delta P} + \frac{8\pi M_s}{3B}\frac{d\ln M_s}{dP}. \tag{2}$$

There is a similar contribution to the observed change in the number of cycles between two field markers in a direct determination of the frequency. Equation (2), in fact, provides a method for the determination of the pressure dependence of the magnetization which may in some cases be more accurate for low-temperature measurements than direct magnetization studies under pressure. To effect this, measurements are made at as widely differing fields as possible and $d\ln M_s/dP$ is determined from the difference in the observed phase shifts.

Using Eq. (2) and the solid-He phase-shift technique on the strongest set of oscillations we observed, the 1.96×10^6-G frequency for $\vec{H} \| [0001]$, we attempted to determine $d\ln M_s/dP$ (see Fig. 1). Measurements at $B \sim 32$ kG and $B \sim 60$ kG gave identical results of -0.0210 kbar^{-1} within our experimental uncertainty in our best runs of ± 0.0005 kbar^{-1} for the pressure derivative of this frequency. This results in a value for $d\ln M_s/dP < 0.001$ kbar.$^{-1}$ Fleming and Liu[15] calculated a lowering of the density of states by 0.26 states/(Ry atom kbar) which leads to a value of $d\ln M_s/dP \sim -0.0008$

kbar^{-1} which is below the limits of our sensitivity. Since this factor is always weighted by $8\pi M_s/3B$ it does not affect any of the determinations of $d\ln F/dP$ within our experimental uncertainties, so will be neglected in this context.

III. RESULTS AND DISCUSSION

Our experimental results are summarized in Table I. The frequencies were all determined using 19 kG for $\frac{8}{3}\pi M_s$. The pressure derivatives are surprisingly large and variable considering the near isotropy of the compressibilities[16] ($k_c = 0.849\times10^{-3}$ kbar^{-1}, $k_a = 0.809\times10^{-3}$ kbar^{-1}, where k_c and k_a are the linear compressibilities along the c and a axes, respectively). Our results predict an electron transition[17] corresponding to the destroying of a sheet of Fermi surface near 8 kbar as the 5.2×10^5-G frequency for $\vec{H}\|[11\bar{2}0]$ is pushed to zero. See Fig. 2. We would expect anomalies in electronic properties at low temperatures to reflect this electron transition, but there has apparently been no work reported in this pressure-low temperature regime.

In Ref. 4 we compared the corrected dHvA frequencies with a relativistic APW calculation for *paramagnetic* Gd. Only the larger frequencies could be tentatively identified. Furthermore, the splitting necessary to maintain the observed Fermi surface topology led to a spin moment of $0.78\mu_B$/atom which cannot be reconciled with the observed conduction-electron moment of $0.63\mu_B$/atom. Mattocks and Young[5] attempted to fit their dHvA frequency data which are in excellent agreement with ours (differing essentially only in slight differences in the magnetization used in calculation of the frequencies) with exchange splittings varying from 0.060 to 0.070 Ry over the Brillouin zone. Even with this additional degree of freedom they were unable to account for the eight lowest frequencies. Therefore it does not seem fruitful to make any detailed comparison with our experimental results of calculations of this type as a function of interatomic spacing.

A non-self-consistent, ferromagnetic, relativistic APW calculation using a local exchange approximation which gave the proper radial extent to the $4f$ orbitals[6,18] (as observed by neutron diffraction[19]) also overestimated the magnetic moment ($0.79\mu_B$). The problem with these calculations is the lack of self-consistency. In building a crystal potential from overlapping atomic charge densities there is a serious error made in approximating the occupied metallic d states with the atomic $5d$ orbitals. The atomic $5d$ orbitals are very localized compared to the bondinglike density associated with the occupied d states at the bottom of the d band. The $4f$-$5d$ overlap is very sensitive to the radial extent of the d orbitals,[20] and the atomic charge density approximation for creating the crystal potential results in too much localization and

TABLE I. de Haas–van Alphen frequencies and their pressure derivatives $d\ln F/dP \equiv [F(P) - F(0)]/F(0)\Delta P$. The frequencies were determined using 19 kG for $\frac{8}{3}\pi M_s$ and are in units of 10^6 G. The pressure derivatives are in units of kbar^{-1}. The uncertainties given are estimates corresponding to the most accurate determination when more than one method was employed.

Field direction	Frequency	$d\ln F/dP$
[0001]	0.28	0.025 ± 0.005 [b]
	1.96	-0.021 ± 0.001 [a,b,c]
	16.9	0.002 ± 0.001 [a]
	13.9	0.005 ± 0.002 [a]
	40.7	0.012 ± 0.003 [a]
[10$\bar{1}$0]	1.5	...
[11$\bar{2}$0]	0.52	-0.12 ± 0.01 [c]
	1.7	-0.04 ± 0.02 [a,c]
	2.8	...
	46.6	0.007 ± 0.001 [a,c]

[a] Fluid-He phase shift (0–25 bar).
[b] Solid-He phase shift (0–4 kbar).
[c] Solid-He frequency measurement (0–4 kbar). Free-electron scaling prediction is two-thirds the volume compressibility or 0.0025 kbar^{-1}, assuming isotropic compressibilities.

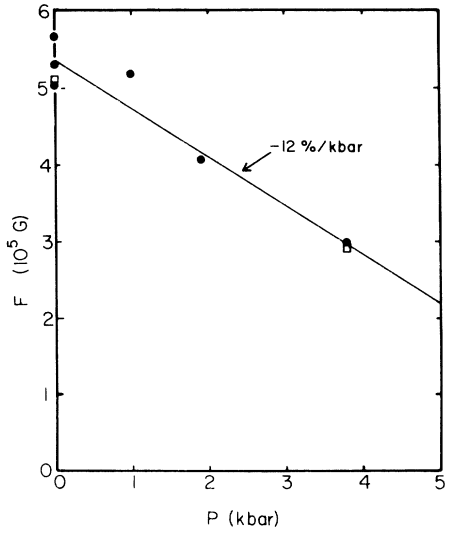

FIG. 2. Pressure dependence of the 5.2×10^5 G frequency for $\vec{H}\|[11\bar{2}0]$ vs pressure. Linear extrapolation to zero frequency is assumed. This assumption is not inconsistent with Lifshitz's treatment, but is difficult to verify directly.

hence gives too large a magnetization. We are presently finishing self-consistent calculations which promise better comparison with the experimental data presented in this paper.

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