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THE ROLE OF PRESSURE IN THE STUDY OF THE FERMI SURFACE*

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ABSTRACT

Pressure studies of the Fermi surface are providing critical tests for the physical significance of model descriptions for the electron structure of metals. Work since the most recent reviews is cited. The solid and fluid He pressure techniques used in on-going studies on Gd, U and Th are described briefly and results on these materials are discussed.

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I. INTRODUCTION

Pressure studies of the Fermi surfaces of metals have proven to be critical in evaluating various theoretical models and descriptions of the metal. The philosophy involved is to make whatever approximations and parametrizations necessary to achieve the best fit to the available normal volume data and then redo the model calculation at a reduced volume. A physically significant model should account for the observed variations with pressure of Fermi surface cross sections and should reflect properties related to corresponding changes in the density of states. Most of the studies to date have been on elemental metals but an increasing effort is being mounted in the area of intermetallic compounds.

It is probably fair to say that most of the easily obtainable single crystal elemental metals have been subjected to some level of investigation as a function of pressure. The bulk of these studies has been reviewed by Schirber¹ and by Brandt, Itskevich and Minina.² The effects of pressure on the electronic structure of d-band transition metals was reviewed by Svecharev and Panfilov.³ Therefore, only the most recent work will be cited here. We will also confine our comments to pressure studies and not discuss in the interest of brevity the similarly useful information obtained from uniaxial stress⁴ and magnetostriction techniques.⁵

Summarizing first recent work on the elements, Cs has been studied by dHvA measurements in both fluid He and in solid He to nearly 10 kbar.⁶ Templeton⁷ has substantially reduced the uncertainty in the pressure derivatives of Fermi surface cross sections along symmetry directions for the noble metals Cu, Ag and Au. Bryant and Vuillemin⁸ have reported fluid He phase

shift measurements in Cd which extend and complement the earlier work of Schirber and O'Sullivan.⁹ Beardsley, et al.¹⁰ have completed a rather complete experimental study of the Fermi surface of Mg which points out dramatically the importance of convergence in using local pseudopotential descriptions. There has been recent work¹¹ on In which extends and appears to be in quantitative disagreement with the earlier studies.¹² Brandt et al.¹³ reported studies of the Fermi surface of Sn to 10 kbar by measuring the oscillatory surface impedance. Anderson, et al.¹⁴ report comparison of Nb Fermi surface derivatives with a self-consistent APW band structure at normal and reduced lattice spacings. Fermi surface cross sections of both the hole and electron sheets of As were measured as a function of pressure and analyzed in terms of the Lin and Falicov pseudopotential model by Schirber and Van Dyke.¹⁵

The first direct Fermi surface studies under pressure on a rare earth material was the work of Slavins and Datars¹⁶ on hcp Yb. They measured the pressure derivatives of three dHvA frequencies for $H \parallel [0001]$ and could see no oscillations in the fcc phase. Ribault,¹⁶ on the other hand, reports a single frequency for the fcc phase which extrapolates to a magnitude of zero near 12 kbar.

Studies of the ferromagnetic d-band material Fermi surfaces as a function of pressure have been initiated^{18,19} in Co and Ni. These data are as yet fragmentary but promise to be sensitive to the details of the model description chosen to represent a ferromagnetic metal.

An increasing number of compound metals are being studied

using high-field magnetoresistance and dHvA techniques. It is therefore expected that pressure studies will ultimately be conducted in these materials. Several sheets of the Fermi surface of ReO_3 have been studied as a function of pressure by Schirber, et al.²⁰ Reasonable agreement with these results was obtained by Myron, Gupta and Liu²¹ who performed a Korringa-Kohn-Rostoker band calculation as a function of interatomic spacing. To date the series AuGa_2 , AuIn_2 , AuAl_2 has received the most attention primarily because of anomalies in the magnetic and superconducting properties of AuGa_2 . These anomalies can be understood on the basis of a band structure-electron transition model involving pushing the second band at Γ through the Fermi level at 7 kbar and liquid He temperatures.²² Anomalies in elastic properties and nmr were explained in InBi by a similar band structure based argument which could account for the pressure dependence of the Fermi surface measured by Schirber and Van Dyke.²³

Section II will describe very briefly the experimental techniques which have been used in recent studies of Gd, U and Th. The results of these studies will be given and discussed in Section III. Section IV will summarize where we are in this field today and give an opinion as to where the emphasis should be in future studies.

II. EXPERIMENTAL

High-quality long electron mean-free-path single crystal specimens are typically required for detailed measurements of the Fermi surface. This means that measurements are usually performed in high magnetic fields and at temperatures near 1 K. Under these conditions all pressure media are of necessity solid above

a few bar making it difficult to maintain strain-free conditions particularly on anisotropic materials. Although isolated examples of pressure studies of the Fermi surface were reported over two decades ago, it was not until the development of the field modulation deHaas-vanAlphen (dHvA) technique²⁴ that comprehensive studies could be performed. The field modulation technique allowed highly accurate Fermi surface cross section determinations without the necessity of introducing leads into the high-pressure environment. A second impetus to this type of study was the demonstration²⁵ that extremely hydrostatic conditions to 10 kbar could be achieved by careful isobaric freezing of He even with the most fragile and anisotropic single crystal specimens.

The dHvA measurements further lend themselves to pressure studies in that the oscillatory property, for example the magnetization which is given by $M = M_0 \sin 2\pi F/B$, typically has a very high phase F/B . (Here F is the dHvA frequency and B is the magnetic induction.) Thus very small changes in the frequency or cross-sectional area of the Fermi surface are related to shifts in position ΔH of a given feature in the pattern by

$$d \ln F / dP = \frac{1}{B} \frac{\Delta H}{\Delta P}$$

In some situations^{26,27} the sensitivity is such that the pressure derivative of the frequency can be measured accurately in fluid He, i.e., at pressures <25 bar at 1 K. These phase shift techniques have also been applied to situations where F/B is not large and/or the pressure derivative is small using solid He to effect measurable shifts in the oscillation position.²⁸ Typically, it is possible to obtain useful information about the volume depend-

ence of most cross sections of the Fermi surface in a given material by either one or a combination of i) direct measurement of the frequency in solid He to 10 kbar, ii) phase shift determination of the pressure derivative in fluid He, iii) phase shift determination of the derivative in solid He to 10 kbar.

In the studies of 4f and 5f materials discussed below, the work was all done in a 55 kOe superconducting solenoid at temperatures in the 1 - 4 K range. All three pressure techniques described above were used as appropriate. The Gd sample was a 1/8 in. diameter sphere cut by spark erosion from a rod of residual resistance ratio ~ 260 prepared by an electrotransport process.²⁹

The Th was also purified by electrotransport and then heated 144 hours at 4×10^{-12} Torr. Crystals were formed by a temperature cycling technique³⁰ with residual resistance ratios of ~ 2000 . Samples were cut by spark erosion into 1 mm diam. x 3 mm long cylinders oriented along principal crystallographic directions.

The U samples were cut by spark erosion into ~ 1 mm diam. x ~ 3 mm long cylinders from single crystal material grown by recrystallization within the α phase.³¹ The residual resistance ratio as measured was about 30 but it is not clear what the significance of this ratio is in view of the numerous phase changes U undergoes below 50 K. It was found that pressures > 7.5 kbar quenched these transitions allowing retention of the α phase to 1 K.

A. Gadolinium

Our results³² for Gd are shown in Table I. These are the first studies thus far of the pressure dependence of the Fermi surface of a rare earth metal. Several of the cross sections

reported to date were measured by more than one of the three techniques outlined in the previous section for determination of pressure derivatives of dHvA frequencies. The agreement between the various techniques is excellent. These results show a surprising variation in both sign and magnitude. This is particularly striking in view of the near isotropy of the linear compressibilities of Gd. In such cases, the dominant effect (except for small cross sections) is typically given by the scaling of the Fermi surface with the Brillouin zone at the rate of $2/3 K_T$ where K_T is the bulk compressibility. For Gd this would correspond to a value of 0.0017 kbar^{-1} . Of particular interest is the large negative derivative observed for the $0.52 \times 10^6 \text{ G}$ frequency for H || $[11\bar{2}0]$. This result obtained in solid He to 4 kbar indicates that an electron transition will occur near 8 kbar at liquid He temperatures. To date there are not data in this pressure-temperature range to corroborate this prediction.

It has proven very difficult to obtain a satisfactory model description for the Fermi surface of Gd. The usual practice of rigidly splitting a paramagnetic band calculation cannot simultaneously account for the topology of the Fermi surface observed and correctly give the proper value for the magnetization.³² It appears that fully self-consistent relativistic ferromagnetic band calculations will be required.

B. Uranium

Results for pressure studies of the Fermi surface of α -U are summarized³³ in Table II. Previous attempts to obtain information pertaining to the Fermi surface of α -U have been thwarted by the occurrence of several crystallographic phase changes as α -U is cooled below 43 K. We found that cooling the specimen at

pressures above ~ 7.5 kbar permitted retention of the α -U phase allowing dHvA oscillations to be observed. The data as yet are very limited. One cross section was measured as a function of pressure using the solid He phase shift technique.²⁸

This work has inspired an attempt³⁴ to make a band calculation for α -U. Heretofore only high-temperature cubic structures had been treated. This is a formidable challenge because α -U crystallizes in an orthorhombic lattice with 4 atoms/cell. In addition a relativistic calculation is necessary.

C. Thorium

The results³⁵ for pressure derivatives of all three sheets of the Fermi surface of Th are given in Table III. Again many of the cross section derivatives were obtained by more than one technique and found to be in good agreement. The striking result is that all of the cross-sectional areas decrease as the inter-atomic spacing is reduced. This behavior is completely unprecedented for a cubic material.

Th begins the 5f series. Although it is tempting to view the 5f series by analogy with the 4f rare earth metals, considerable experimental evidence points to itinerant character for the 5f electrons for the early part of the series. Koelling and Freeman³⁶ showed that treatment of the 5f electrons as itinerant substantially improved the agreement between their relativistic band structure description and experiment over earlier treatments in which the 5f electrons were considered to be very localized. They also made several predictions as to the way the Fermi surface would change with pressure. In particular they predicted that the superegg would decrease in size compensated by an increase in size of the dumbbell. The electron sheet (the lung) was expected

to more or less scale with the Brillouin zone. The results in Table III do not agree with these predictions in that all the sheets are observed to decrease.

Further attempts to account for these results using RAPW band descriptions as a function of interatomic spacing with and without the presence of the f resonance indicate that the unexpected behavior of the Fermi surface of Th with volume is probably due to changes in s-d hybridization.³⁵ It is likely that the actinides will also require self-consistent calculations in order to account in detail for the observed volume dependence.

V. CONCLUSIONS

This update of recent studies of the effect of pressure on the Fermi surface of metals and a brief look at ongoing work on Gd, U and Th should indicate that this field is still very active. The experimental studies continue to prompt new theoretical endeavors and may in the case of the 4f and 5 f metals lead to new insight into the way these materials must be treated from a band theoretical point of view.

Future work will probably center on the increasingly more available rare earth materials and on intermetallic compounds. The latter area is very active at normal volumes with high field magnetoresistance, dHvA, Schubnikov-deHaas, magnetoacoustic and magnetothermal oscillations and cyclotron resonance techniques all being employed to map out experimentally the electronic structure. Pressure studies should, as they have in the elemental metals, provide critical tests for the model description. The compounds have the advantage that an enormous diversity exists permitting detailed examination of properties through an iso-

structural or isoelectronic series, a flexibility just not usually available with elements.

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Table I. de Haas-van Alphen frequencies and their pressure derivatives $d \ln F / dP \equiv [F(P) - F(0)] / F(0) \Delta P$ for Gd, in units of kbar^{-1} . The frequencies were determined using 19 kG for $8\pi M_s / 3$ and are in units of 10^{-6} G. For spherical samples, $B = H + 4 \pi M_s / 3$ where M_s is the saturation magnetization. The uncertainties given are estimates corresponding to the most accurate determination when more than one method was employed.

<u>Field Direction</u>	<u>Frequency</u>	<u>$d \ln F / dP$</u>
[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

^b solid He phase shift

^c solid He frequency measurement

Table II. Frequency and mass data obtained at 9.3 kbar for α -uranium. The pressure derivative $d\ln F/dP$ is defined as $[F(P_1) - F(P_2)]/[P_1 - P_2]F$ and was determined between 8.5 and 9.3 kbar.

Direction	Frequency	Effective Mass	$d\ln F/dP$
[010]	$1.269 \times 10^7 \text{ G}$	0.91	$3.7 \times 10^{-3} \text{ kbar}^{-1}$
[100]	$1.39 \times 10^7 \text{ G}$	~ 0.9	-
[001]	-	-	-

Table III. Pressure Dependence of Fermi Surface
Cross Sections of Th

Cross Section	Orientation	Frequency (in 10^6 G)	$d\ln F/dP$ (in 10^{-4} kbar $^{-1}$)	
hole superegg (N)	[100]	22.1	-38(± 4)	a
			-40(± 1.0)	b
electron lung (L)	[100]	10	-4.4(± 0.4)	c
hole superegg (F)	[110]	24.7	-38(± 4)	a
electron lung (C)	[110]	9.6	-3.4(± 0.3)	c
electron lung (A)	[110]	2.014	-50(± 10)	a
			-60(± 10)	b
hole dumbbell (E)	[110]	19.8	-12(± 7)	a
			-11(± 2)	c
			-13(± 5)	b
hole dumbbell (H)	[111]	10.9×10^6	-39(± 5)	a
electron lung (I)	[111]	11.6×10^6	-14(± 6)	a

a - fluid He phase shift

b - direct frequency measurement in solid He

c - solid He phase shift

Orbit designation that of Boyle and Gold, Phys. Rev. Lett. 22, 461 (1969).