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Pressure dependence of the Fermi surface of hcp Yb

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The pressure dependence of Fermi-surface cross sections for principal symmetry directions has been investigated using solid He pressure generation techniques. Careful searches for de Haas–van Alphen signals were conducted from 2 to 9 kbar in both virgin fcc crystals and samples transformed from hcp to fcc. No sign of the frequency reported by Ribault was detected. Results are discussed in terms of theoretically calculated pressure-induced changes in the band structure and Fermi surface of the hcp phase of Yb.

I. INTRODUCTION

Ytterbium metal has been the subject of a great deal of attention because of the metal-to-semiconductor transition[1] that has been shown to occur near 13 kbar nearly independently of temperature below 300 K. After some initial confusion because of the occurrence of a hcp phase in the region below room temperature[2] and 2 kbar,[3] a reasonable picture of the band structure and electronic properties seemed to be emerging. The Fermi surface determined by Tanuma *et al.*[4] appears to be well accounted for by the calculations of Jepsen and Andersen.[5] The situation in the fcc structure however is less clear. Slavin and Datars[6] were unable to observe any de Haas–van Alphen (dHvA) signals in fcc crystals transformed by pressure from hcp samples. Ribault[7] on the other hand, reported a single de Haas–van Alphen (dHvA) frequency in the fcc phase which decreased in magnitude rapidly extrapolating to zero near 13 kbar, in tempting agreement with the expected low-temperature metal-insulator transition pressure.

The availability of extremely high-purity Yb single crystals prompted us to try to obtain dHvA data in the fcc phase in virgin samples which had never been subjected to a crossing of the fcc ↔ hcp phase boundary.

In Sec. II we describe briefly the sample preparation and our experimental techniques. Our results are presented and discussed in Sec. III.

II. EXPERIMENTAL: CRYSTAL PREPARATION

The Yb metal used for the crystal preparation was prepared by the misch metal reduction-distillation technique as described by Beaudry and Gschneidner.[8] The metal was resublimed to further purify it, then put into a $3.2 \times 10\text{-cm}^2$ tantalum crucible and a lid welded in place under a helium atmosphere. The crucible and contents were heated to 1000 °C for 24 h in a 10^{-8}-Torr vacuum to quantitatively remove hydrogen. The lid was removed from the crucible and two disks each with a 6-mm hole were hung from a new lid, each 1 cm apart. The lid was again welded in place under a helium atmosphere. The bottom of the crucible was heated to 820 °C for 3 days in a thermal gradient of 4°/cm. The top of the crucible was thus about 780 °C. Yb crystals were formed on the lid and on the two disks. The crystals were cut by spark erosion and oriented by Laue back-reflection techniques.

A chemical analysis of the crystals was not obtained. However, the major impurities in the starting metal were O, N, H, and C. The H was removed quantitatively by the vacuum heat treatment and the double sublimation should have lowered the O, N, and C to less than 10 ppm by weight resulting in greater than 99.999% purity. Great care was taken that these crystals were never cooled significantly below room temperature so as to preclude transformation into the hcp phase.

De Haas–van Alphen (dHvA) frequencies were determined using the standard field modulation method[9] in a 55-kOe superconducting solenoid and in a rotatable split 100-kOe superconducting magnet. Pressures to 9 kbar were generated[10] in solid He. Pressure derivatives were determined as appropriate in one or more of three complementary techniques: (1) direct frequency measurement at various pressures, (2) phase shifting of a single dHvA oscillation in fluid He, (3) phase shifting[11] in solid He. In the

phase-shift methods the pressure derivative of the frequency, F, is given by $d\ln F/dP = B^{-1}\Delta H/\Delta P$, where B is the magnetic field and ΔH is the shift in position of the oscillation with an increment of pressure ΔP.

For studies in the fcc phase, care was taken to increase the pressure at room temperature so as to stay above the fcc-to-hcp transition. Samples of the hcp phase were formed by very slow cooling (<0.5 K/min through region of transition). Pressure then was applied at low temperatures (below 77 K) and never exceeding 2 kbar, so as to always remain in the hcp phase once it was formed.

III. RESULTS AND DISCUSSION

A. hcp Yb

Our results for the pressure dependence of the Fermi-surface cross sections are shown in Table I. The orbit assignments are taken from the band calculations of Jepsen and Andersen.[5] The earlier pressure results of Slavin and Datars[6] for $\vec{H}||[0001]$ are included for comparison; our results where they overlap are in excellent agreement.

The pressure results are surprising in the sense that there are so many negative pressure derivatives. The zeroth-order effect is given by $\frac{2}{3}K_T$ where K_T is the bulk compressibility (assuming isotropy). This scaling effect stems from the increase in the Brillouin-zone dimensions and the corresponding increase in the Fermi surface to maintain the same fraction of zone occupancy. At this writing the linear compressibilities or elastic constants of hcp Yb are not known but the nearly ideal c/a ratio indicates that the anisotropy should be small.

We can make some comparison with the behavior of the Fermi surface of Mg which also has a nearly ideal c/a ratio. There is a rough correspondence of the sheets of the Fermi surface of these two materials as pointed out by Jepsen and Andersen.[5] The γ sheet which corresponds to the cigars of Mg is observed to increase in size with pressure as do the cigars. The μ sheets which are related to the monster in Mg decrease in Yb as they do in Mg. The λ sheet corresponds to the lens in Mg which increases in size with pressure. In Yb this lens has a hole in the center so it resembles a lifesaver. We were unable to determine the pressure dependence of this sheet for $\vec{H}||[11\bar{2}0]$ due to the great inherent difficulty in observation of the frequency in most crystals. Jepsen and Andersen find this sheet to be purely d-like with no correspondence to the nearly free-electron situation appropriate for Mg.

The lowest-frequency sheet α is also of d character and has enormous pressure derivative of about -15%/kbar for $\vec{H}||[11\bar{2}0]$ and at 46° from [0001] in $(11\bar{2}0)$. We have calculated the band structure and Fermi surfaces of hcp Yb for various atomic volumes. The calculations were performed by exactly the same procedure which has given accurate descriptions of the Fermi surfaces of the hcp transition metals,[12] i.e., using a muffin-tin potential constructed from overlapping relativistic charge densities, with the Slater $\rho^{1/3}$ approximation for the exchange and correlation and employing the linear muffin-tin-orbital method[13] for the evaluation of the eigenvalues. The Fermi surfaces were calculated with a uniform $\vec{k}$ mesh consisting of 2541 points in the irreducible part of the Brillouin zone. Since hcp Yb is essentially a semimetal and the overlap of the bands is small, the Fermi surface is very sensitive to the value of the lattice parameter used. Furthermore the volume or pressure derivatives of the λ and μ sheets turn out to vary substantially, in fact changing sign, over a small range of lattice parameters (±1.3%) near the best estimate of the normal volume value at 0 K. Therefore it is not possible to quote a meaningful calculated pressure derivative for the λ and μ sheets on

TABLE I. Pressure dependence of cross sections of the Fermi surface of hcp Yb.

Cross section	Field direction	Frequency in 10^6 G	m^*	$d\ln F/dP$ in %/kbar Experiment	Calculated (Ref. 12)
α	[0001]	0.35		−3.4[a]	−2
α	$[11\bar{2}0]$	0.18	0.11	−14	−7
α	45° from [0001] in $(11\bar{2}0)$	0.18		−16	−11
γ	[0001]	1.42		0.2[a]	
μ	[0001]	1.56		−0.5[a]	
μ(?)	45° from [0001] in $(11\bar{2}0)$	7.70	0.52	−1.2	
λ	$[11\bar{2}0]$	1.80	0.18	· · ·	· · ·

[a] Reference 6.

the basis of this calculation. The α sheet was found to decrease substantially in size over this range of lattice parameters and the calculated values are shown in Table I and are in semiquantitative agreement with observation. These differences could, however, be attributed to inaccuracies in the calculated extremal areas since α is extremely small and therefore described by a small number of $\vec{k}$ points.

B. fcc Yb

We have searched unsuccessfully for dHvA signals between 2 and 9 kbar at 1 K to fields of 100 kG as a function of applied field direction in six carefully selected fcc single crystals of Yb. These crystals were never allowed to enter the hcp phase during these investigations. However, after exhausting the variables listed above, several of the samples were transformed by slow cooling into the hcp phase and showed large-amplitude dHvA signals. This is further evidence that the material is of extremely high quality.

We are then in agreement with the findings of Slavin and Datars who investigated crystals transformed from hcp to the fcc phase. These results are in contrast with those of Ribault who reported a single frequency of about 6×10^6 G at 4 kbar which extrapolated to zero frequency around 12 kbar. While there are frequencies in hcp Yb near this magnitude they do not have this large a negative pressure derivative, nor do they have the effective-mass ratio of $\sim$1 reported by Ribault.

We have no explanation for this serious disparity in our results with those of Ribault. We note that the accepted models for the phase change from hcp to fcc in Yb involve transformation of a small fraction (1–2%) of the Yb^{2+}, which constitutes hcp, to Yb^{3+} in the fcc phase. This accounts nicely for the volume change, for the change from diamagnetic to paramagnetic and for the increase in resistivity. If this picture is valid one might expect grave difficulties in observing dHvA oscillations in the fcc phase because of the large scattering introduced by the magnetic Yb^{3+} impurity. A possible explanation for the disagreement in our results with Ribault's might be that his samples were less pure in a way that lessened the number of magnetic scatterers while retaining the fcc phase. Studies to explore this possibility are under way.

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