tion temperatures. Our theoretical results should be considered to be preliminary as some of the parameters used in the calculation (such as the effective mass) are not known accurately for $SrTiO_3$. However, both the concentration at which the maximum transition temperature occurs and the transition temperature itself are within the range of uncertainty of the parameters used in the calculations.

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*Present address: Xerox Corporation, Rochester, New York.

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DE HAAS–VAN ALPHEN EFFECT AND FERMI SURFACE IN PALLADIUM*

J. J. Vuillemin† and M. G. Priestley
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
(Received 28 January 1965)

Palladium is a particularly interesting transition metal for several reasons. The density of states at the Fermi level, as measured by the electronic specific heat,[1] is the highest for any pure metal, and the magnetic susceptibility is both very large and has an anomalous temperature dependence.[2,3] Attempts to explain this behavior[4,5] have used a model in which the Fermi level lies just above the peak in the density of states in a narrow d band, but there has been little detailed experimental information on the band structure. The galvanomagnetic data[6] indicate that Pd has an open Fermi surface.

An experimental determination of the Fermi surface of palladium also provides a test of Mattheiss's prediction[7] that isostructural transition metals have, except for shifts in the Fermi level, very similar band structures. We show that this model accounts for both our data and the galvanomagnetic data.

We have observed de Haas–van Alphen oscillations in palladium in the (110) plane and have found that the s band contains 0.36 ± 0.01 electron. It is inferred that the d band contains the same number of holes. By postulating a band structure for palladium similar to that for copper[8] and nonmagnetic nickel[9] (all are face-centered cubic), we place the s-band electrons at Γ and two groups of d-band holes at X.[10] The measurements were made using a modulation technique[11] with modulation frequencies of 600 and 2200 cps and phase-sensitive detection of the second harmonic. Data were taken at temperatures between 1.00 and 1.7°K in a 53-kG Varian superconducting magnet. The Pd single crystal had a resistance ratio 4.0×10^3.

Two distinct sets of periods were observed, one being about 30 times the other. The periods have been converted into extremal cross-sectional areas $\mathcal{A}_0$ of the Fermi surface by using the Onsager[12] relation

$$P = \frac{4\pi^2 e}{h \mathcal{A}_0} = \frac{2.673 \times 10^{-9}}{\mathcal{A}_0},$$

where the last form gives the period in reciprocal gauss if $\mathcal{A}_0$ is measured in atomic units. Figure 1 shows these areas as a function of θ, the angle from [100] in the (110) plane. Beats are observed in the fast period around [111], and these give rise to the double values of the extremal area shown in Fig. 1(a). Clearly these large areas arise from a closed surface which is centered at Γ because the area is single-valued over most of its range. It can easily be seen that the corresponding Fermi surface has "bumps" in the [111] directions, and consequently the smaller area at [111] is the central section through Γ, while the larger comes from a noncentral orbit around the bumps. There must also be smaller bumps in the [100] directions, because $\mathcal{A}_{100} > \mathcal{A}_{111}$.

An empirical interpolation scheme with circular [111] and [100] bumps of sinusoidal cross section was used in an attempt to deduce a consistent set of radius vectors at the symmetry

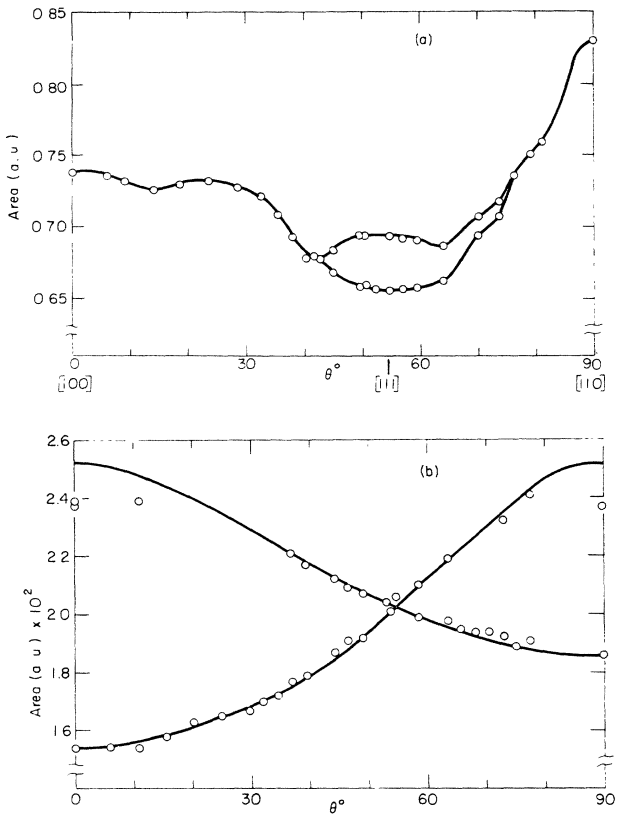

FIG. 1. The measured extremal cross-sectional areas of the Fermi surface for H in the (110) plane. The solid lines in (b) are from [100] ellipsoids with $a=b=0.070$, $c=0.115$ (in au).

directions. The best fit was obtained with

$$k_{111}=0.60 \text{ au}, \quad k_{110}=0.46, \quad k_{100}=0.54, \quad k_{211}=0.46.$$

For comparison, $\Gamma L=0.744$ au. This choice of parameters also accounts qualitatively for the beats at [111]. The measured areas are thought to be accurate to 1%, but the error in the radii is probably ±3%.

The above interpolation scheme leads to a volume for this surface of 0.36 ± 0.01 electron/atom. If, in the spirit of Mattheiss's rigid band model,[7] we now take Segall's[8] band structure for copper and shift the Fermi level downwards to just below X_5, we find that the s band centered on Γ_{12} has shrunk to approximately the observed volume and has an anisotropy similar to that observed. The reasons for locating the Fermi level just below X_5 are given below.

The observed areas for the second group of oscillations are shown in Fig. 1(b). The corresponding surfaces are approximately ellipsoids of revolution with their major axes along [100] directions. Within the framework of our model for the band structure these find a natural interpretation as d-band holes at X. The symmetry of the angular variation is consistent with a location at either X or W, but X is preferred for the following reason.

Pd, as a compensated metal, should contain 0.36 d-band holes to balance the s-band electrons. The observed volume per hole ellipsoid is only 1.8×10^{-3} electron/atom, so there must be another d-band Fermi surface, which is not observed in this experiment, and which contains nearly all the holes. In the absence of spin, X_5 is a doubly degenerate level which splits along XW and XK,[8] but not along $X\Gamma$, as is shown in Fig. 2. Hence, if X_5 is above the Fermi level, there are two pieces of Fermi surface at X, of which the one with the lighter mass has the appropriate anisotropy for the observed surface, as is seen from the sharp decrease in energy of one of the X_5 pair of levels as we move along XW (or along XK). The heavy-mass surface at X now will hold the missing d-band holes.

On the other hand, if we locate the observed holes at W, the band structure would have to be distorted considerably to accomodate the heavy holes elsewhere in the zone.

A measurement of the effective mass for the long period at [111] gave $(0.8\pm0.2)m_0$. Assuming an ellipsoidal parabolic band, we can now

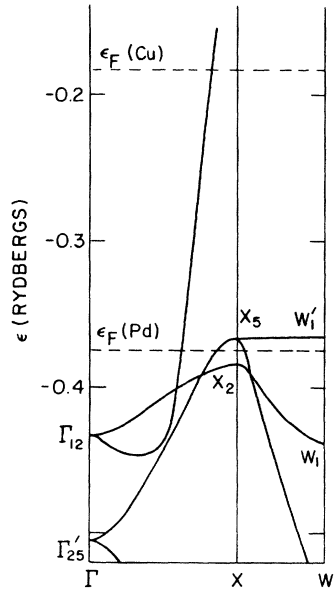

FIG. 2. The part of Segall's Cu band structure which is relevant to the interpretation of the palladium data. For palladium the zero of energy is arbitrary.

estimate the Fermi energy of the observed d-band holes to be about 0.11 ± 0.03 eV and, if spin-orbit coupling is neglected, this is also the Fermi energy for the heavy d-band holes. The temperature variation of the amplitude of the fast period (that from the s band) at $\theta = 14°$ gave $m^*/m_0 = 2.1 \pm 0.3$.

Using the observed effective masses to calculate the contribution of the s band and the light d holes to the electronic specific heat, we find that the observed surfaces account for less than 10% of the observed value[1] of 9.3 mJ deg^{-2} mole^{-1}. If we neglect many-body effects, the remainder is contributed by the heavy d holes. These must therefore have a very high effective mass, which makes them unobservable in the de Haas–van Alphen effect at 1°K.

There remains the question of whether any other d-band levels at symmetry points are above the Fermi level. Most d-band calculations[8,13] indicate that the energy separation of X_5 and W_1' is very small (~0.01 eV), whereas the other d levels are appreciably lower. Our experiments suggest that W_1' is above the Fermi level, because otherwise it is very difficult to accommodate the 0.36 hole per atom on the square faces of the Brillouin zone. However, it is the galvanomagnetic data[6] which provide conclusive evidence that W_1' is above the Fermi level and that the d-band levels at K and L lie below it. The heavy d-band holes then form a surface open in [100] directions which accounts for the observed stereogram. In addition, this model of the Pd band structure predicts correctly the sign and the approximate magnitude of the Hall constant[6] for H[100], the only direction in which geometric discompensation is observed.

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SUPERCONDUCTING SURFACE SHEATH OF A TYPE-II SUPERCONDUCTOR BELOW THE UPPER CRITICAL FIELD H_{c2}†

H. J. Fink
Atomics International Division of North American Aviation, Inc., Canoga Park, California
(Received 18 January 1965)

We have calculated the order parameter of a bulk type-II superconductor near its surface (bounded by a vacuum) for magnetic fields parallel to the surface and close to the upper critical field H_{c2} when the Ginzburg-Landau parameter $\kappa \gg 1$. We find that the energy gap near the surface is larger than about 70% of its zero-field value for fields just below H_{c2}. The maximum value of the order parameter is in general not at the surface but is field dependent and occurs within approximately one coherence length from the surface. The superconducting properties (order parameter, energy gap, superconducting electron concentration) of the metal near its surface do not show any abrupt changes near H_{c2}.

Consider a semi-infinite superconducting half-space with the boundary surface at $x = 0$ and vacuum for $x < 0$. The applied magnetic field H_0 is parallel to the z direction. Assume that the Ginzburg-Landau parameter $\kappa = \lambda/\xi \gg 1$ (λ is the penetration depth and ξ the coherence length) and also that $(H_{c2}-H_0)/H_{c2} \ll 1$. We know that to this approximation Abrikosov's normalized solution[1] for the magnetic field in the bulk of the material near the transition temperature is

$$H_B = H_0 - (1/2\kappa)|\Psi_B|^2, \qquad (1)$$

where the bulk order parameter Ψ_B is normalized with respect to the order parameter in