considerable promise. Such a representation is certainly desirable from the standpoints of simplicity and calculational accuracy. Moreover, the generalization of the methods of Sec. II to other d-band metals is quite straightforward. The major qualitative difference we foresee is that the core states will be affected by changes in the d states in cases where the latter are partially or fully occupied.

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Magnetoacoustic Evidence for the Existence of the L-Centered Pocket of Fermi Surface in Palladium*

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Quantum oscillations in ultrasonic attenuation have been observed in Pd. We report a new frequency which is attributed to small hole pockets at the L symmetry points. Such pockets were predicted by theory but have not been seen in de Haas–van Alphen experiments. Measurements have been made of the angular variation of the extremal area of these pockets and of their cyclotron effective masses in the (100) plane.

I. INTRODUCTION

Relativistic-augmented-plane-wave (RAPW) band calculations for palladium by both Mueller *et al.*[1] and Andersen[2] have predicted small pockets of holes around the symmetry points L, but oscillations corresponding to such carriers were not observed in the detailed de Haas–van Alphen (dHvA) studies of Windmiller *et al.*[3] We report here the frequencies of magnetoacoustic quantum oscillations in Pd, which we relate to the hole pockets at L. Our measurements yield cyclotron masses $m_c^* \simeq 1.1 m_0$, consistent with the theoretical predictions[1,2] of low velocities for these holes. The low effective masses usually associated with small pockets normally assure adequate amplitudes for the various oscillatory effects; the absence of dHvA signals from the holes at L in Pd is probably a consequence of the unusually high m_c^*.

Quantum oscillations in ultrasonic attenuation and velocity can offer the following important advantage over the dHvA effect in the investigation of the Fermi surfaces of small pockets of carriers: The amplitude of the oscillations due to such a small pocket, relative to the amplitudes of oscillations corresponding to large pieces of Fermi surface, may be enhanced in the magnetoacoustic case. We have observed this effect in Pd, where the acoustic-attenuation oscillations of lowest frequency, corresponding to the smallest extremal area of the Fermi surface, are the dominant feature, as illustrated in Fig. 1. A similar effect has been observed by Fletcher *et al.*[4] in Pt. We may see qualitatively how this arises by referring to the work of Mertsching[5] and of Testardi and Condon.[6] Consider extremal areas on two different pieces of Fermi surface, having (constant) relaxation time τ_1 and τ_2 and average deformation potentials appropriate to the longitudinal ultrasonic strain $\bar{\Lambda}_1$ and $\bar{\Lambda}_2$ (in Mertsching's notation). Then it follows from his equations (5.87) and (5.91) that the amplitudes of attenuation oscillations, $\delta\alpha_i$, and those of the velocity oscillations, δv_i, are related by

$$\frac{\delta\alpha_1}{\delta\alpha_2}=\frac{\tau_1}{\tau_2}\left(\frac{\delta v_1}{\delta v_2}\right) . \qquad (1)$$

This relation applies to both fundamental and harmonics, but it does not imply that the harmonic contents of $\delta\alpha_i$ and δv_i are identical. On the other hand, Testardi and Condon derive relations between the elastic constants (and thus the ultrasonic velocities) and the differential magnetic susceptibility dI_B/dB in terms of deformation parameters $D=\partial(lnA)/\partial\epsilon$, where A is the extremal Fermi surface area and ϵ is the strain relevant to the ultrasonic wave. It follows from their equation (13) and our equation (1) that oscillations from two different areas are related by

$$\frac{\delta\alpha_1}{\delta\alpha_2}=\frac{\tau_1(D_1+1)^2}{\tau_2(D_2+1)^2}\left[\left(\frac{dI}{dB}\right)_1\Big/\left(\frac{dI}{dB}\right)_2\right], \qquad (2a)$$

when longitudinal sound waves propagate perpendicular to the magnetic field, and from their (15) and our (1) it follows that

$$\frac{\delta\alpha_1}{\delta\alpha_2}=\frac{\tau_1D_1^2}{\tau_2D_2^2}\left[\left(\frac{dI}{dB}\right)_1\Big/\left(\frac{dI}{dB}\right)_2\right], \qquad (2b)$$

when longitudinal sound waves propagate parallel to the magnetic field. For a large piece of Fermi surface D is of order unity, but for very small cross sections (small relative to Brillouin-zone dimensions) D can be much larger, of the order of 20 or more (see for example, the experimental results of Testardi and Condon[6] on the coronet necks of Be, or those of Perz *et al.*[7] on the dumbbell waists of Sn). For such small areas, Eqs. (2a) and (2b) imply a great enhancement of the ultrasonic-attenuation oscillations (relative to dHvA), assuming the corresponding relaxation times are not anomalously low. In particular, the large amplitude of the oscillations corresponding to the small hole pockets at L in Pd which we have observed becomes understandable.

II. EXPERIMENT

The measurements were made on a single crystal[8] of Pd of resistivity ratio 80, spark machined into the form of a cylinder with flat parallel faces, approximately 8 mm in diameter by 8 mm long. The cylinder axis was oriented within 1° of a ⟨100⟩ crystal axis. Longitudinally polarized sound waves at 20, 60, and 140 MHz were propagated along the cylinder axis and their attenuation was measured by a pulse-echo technique to be described elsewhere.[9]

The sample was mounted in one of two sample holders. In one of these the cylinder axis (and hence ultrasonic wave vector) was oriented accurately parallel to the magnetic field. In the other the sample was placed in a rotatable copper collet oriented perpendicular to the field, to enable the field to be varied in a {100} plane, with an angular

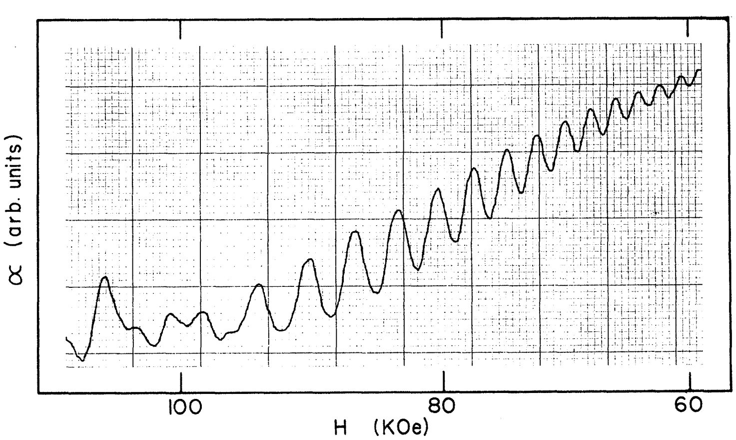

FIG. 1. Recorder tracing illustrating ultrasonic-attenuation (α) oscillations as a function of magnetic field H, for $\vec{H}$ near ⟨100⟩.

TABLE I. Frequencies of quantum oscillations in Pd with $\vec{H} \parallel \langle 100\rangle$.

	F (This work) (MG)	F (dHvA)[a] (MG)
Hole pocket at L	2.24	...
Hole pocket	5.78	5.73
at X	8.97	8.91
Open-hole surface	27.2	26.9
Γ-centered electrons	280	275

[a]See Ref. 3.

TABLE II. Cyclotron masses for pockets at L in Pd.

Field orientation	F (MG)	m_c^*/m_0
⟨110⟩	2.08 ± 0.04	1.15 ± 0.10
⟨110⟩	3.23 ± 0.06	1.10 ± 0.05
⟨100⟩	2.24 ± 0.04	1.10 ± 0.05

resolution of 1°. The collet permitted a limited (3°) adjustment of the sample axis with respect to the collet axis, so that the sample could be oriented accurately by Laue back-reflection x-ray techniques with its crystal axis parallel to the collet axis and hence perpendicular to the field.

The magnetic field was provided by a 109-kOe Nb_3Sn solenoid and measured by means of a copper magnetoresistance probe which was calibrated from 60 to 109 kOe by counting dHvA belly oscillations from an accurately oriented ⟨111⟩ Au sample, using Jan and Templeton's[10] frequency value. The magnetoresistance-probe current supply had long- and short-term stabilities of better than one part in 10^4 and one part in 10^6, respectively, while the voltage was measured to two parts in 10^5. The corresponding long-term uncertainty and short-term noise in the magnetic field measurement was approximately 10 and 1/10 Oe at 100 kOe. The main sources of uncertainty in the field measurements were the quoted error in Jan and Templeton's frequency value (± 0.1%) and hysteresis effects, which were observed during the calibration to be as high as 0.1% (the number of oscillations observed between a pair of magnetoresistance-probe voltages with field swept up did not agree exactly with the number observed when the field was swept down). We believe that the magnet homogeneity is changed, as part of the trapped flux is progressively released on decreasing the magnet current; the magnetoresistance probe is located just inside the 2-in.-i.d. windings, and the field there need not change in proportion to the field in the magnet center where the sample is located if the homogeneity is altered. We estimate our over-all uncertainty in reciprocal field to be not more than 0.2%. Measurements of the frequencies ascribed to the holes at L were taken from field sweeps between 60 and 109 kOe, although in some orientations oscillations were still observed at 45 kOe. Oscillations due to the hole pockets at X and the open-hole surface were only resolved above 80 kOe, and the oscillations due to the Γ-centered electron surface were only detectable above 105 kOe.

To verify that the oscillations arose from extremal orbits of the dHvA type[11] ($ql \ll 1$)[12] rather than those of the nonextremal resonance type, i.e., giant quantum oscillations[13] ($ql > 1$), field sweeps were made with $\vec{H}$ parallel as well as perpendicular and nearly perpendicular[14] to $\vec{q}$. These sweeps yielded the same frequencies of oscillation and so confirm that our measurements are of extremal areas of the Fermi surface, with area A (cm^{-2}) related to frequency F (G) by $A = 2\pi eF/\hbar c$. These observations are consistent with our estimates of ql based on the above ultrasonic frequencies and resistivity ratio, which give a range of ql from 0.01 to 0.08. In addition, the oscillations have a sinusoidal line shape characteristic of the $ql \ll 1$ regime (see Fig. 1).

III. RESULTS AND DISCUSSION

In Table I we present the frequencies observed with $\vec{H} \parallel \langle 100\rangle$. Our results for the known portions of the Fermi surface agree with those of Windmiller *et al.*[3] within our experimental error.[15] In

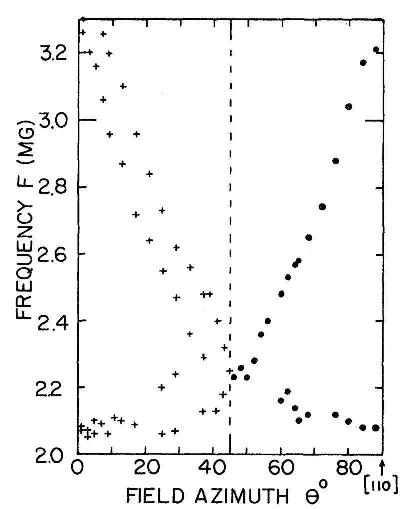

FIG. 2. Angular variation of frequency, with $\vec{H}$ in the (001) plane (●); also (+) with H in a plane tipped about 3° away from (001).

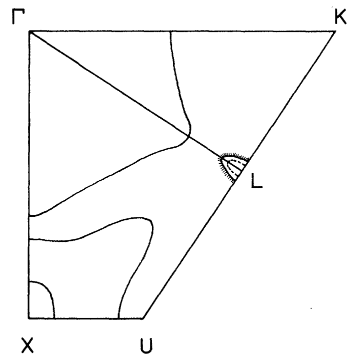

FIG. 3. {110} projection of proposed surface at L (shaded), in relation to the surfaces of Mueller *et al.*, Ref. 1.

addition we find a low frequency which we assign to the hole pockets at L predicted by RAPW calculations. Figure 2 shows the angular dependence of the new frequency as the field direction is varied in a {100} plane. The data in Fig. 2 were obtained from individual field sweeps at a series of orientations at a temperature of 1.1 K. The angular dependence shown in Fig. 2 has the symmetry expected for pockets of carriers at L. This symmetry was confirmed by a field-rotation diagram, but the latter method was not used to measure the angular dependence of the frequencies because the phase-number variation is very low (from ~21 to ~32 at 100 kOe) and because oscillations arising from two different cross sections of the pockets are superimposed. From symmetry we would expect these pockets to be approximately figures of revolution about ⟨111⟩ centered at L. A detailed examination of the data of Fig. 2 shows that an ellipsoid cannot be adequately fitted. We deduce that, in comparison with the best-fit ellipsoid (semiaxes $a = 0.067$ a.u., $b = 0.037$ a.u.), the pockets are extended along ⟨111⟩ directions about 15%; a section of the proposed surface is shown in Fig. 3.

The amplitudes of the low-frequency oscillations were measured as a function of temperature over the range 1.1–2.1 K and were observed to have a temperature dependence characteristic of dHvA oscillations. The cyclotron effective masses m_c^*, obtained from these measurements are given in Table II. These masses are unusually high for such small pockets and are approximately ten times larger than those measured for similar pockets in Rh.[16,17] A possible explanation for the high m_c^* in Pd may be the saddlepoint in $E(\vec{k})$ near L noted by Andersen,[2] which leads to low velocities in some directions and which could also account for the deviation of the pocket from an ellipsoidal shape. Mueller *et al.*[1] have estimated values for the unenhanced m_c^* of the L pockets, viz., $0.56m_0$ for $\vec{H} \parallel \langle 111\rangle$ and $0.95m_0$ for $\vec{H} \parallel \langle\bar{1}\bar{1}2\rangle$. The effective-mass measurements of Windmiller *et al.*[3] indicate an average mass-enhancement factor of 1.6 for other orbits in Pd. An enhancement factor of this order achieves consistency between the estimates of Mueller *et al.* and our effective-mass measurements.

In view of the relatively low resistivity ratio of our sample, we must consider the possibility that the pockets of carriers which we have detected arise from a shift in the Fermi level produced by impurities. For a resistivity ratio of 80 we expect no more than 0.1 at.% impurities, an estimate which is in accord with Hörnfeldt's[18] data on Pd-Co alloys. Using a rigid-band approximation, we calculate that a concentration of about 10% of impurities, of valence one less than that of Pd, would be required to create the L pockets by a shift of the Fermi level; if there were exchange-splitting effects, such as those Windmiller *et al.*[3] have seen by introducing Co into Pd, we estimate that over 1% of ferromagnetic impurities would still be required. Neutron-activation analyses[19] on a specimen taken from the same ingot as our sample revealed impurity concentrations totaling less than 40 ppm; in particular, the maximum concentrations of Fe (14 ppm) and Co (0.5 ppm) found are far too small to account for the presence of the L pockets. Moreover, in the same rigid-band approximation, a level of impurities sufficient to create the hole surfaces at L would also alter the areas and frequencies of the hole pockets at X by about 6%. This is clearly not the case in our sample, for which the frequencies associated with the holes at X show no splitting within our 1% resolution, and agree with those given by Windmiller *et al.*[3] to within 1% (see Table I). We conclude that the pockets of holes at L are a feature of pure Pd.

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[15]The internal consistency of our frequency values is about ±1%. Because of the increased importance of inhomogeneous-flux-trapping effects in the short field sweep used to determine the highest frequency and the small number of cycles of the very low frequency, the error for these may be as high as ±2%. The effects of the large variation in the background attenuation, which could not be completely eliminated, also contributed to the above errors.

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Accurate Resistivity and Thermoelectric-Power Calculations for Liquid Na and Liquid K[†]

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Calculations for the resistivity of pure liquid Na and K have been performed using the experimental structure factors of Greenfield, Wellendorf, and Wiser and the Shaw optimum model potential with the many-electron effects included via the Toigo and Woodruff dielectric function. We find good agreement with experiment for the resistivity and the temperature dependence of the resistivity. The thermoelectric-power results are somewhat less satisfactory. Exchange and correlation effects are seen to play an even larger role than heretofore estimated.

It is generally believed[1] that the electrical resistivity of simple liquid metals can adequately be determined with the use of the Ziman[2] formula

$$\rho = \frac{3\pi m^2 \Omega_0}{4 e^2 \hbar^3 k_F^6} \int_0^{2k_F} |w_q(k_F)|^2 a(q)\, q^3\, dq \;. \qquad (1)$$

(Here we have used the usual notation: Ω_0 is the volume per ion, m is the effective mass of the electrons, $a(q)$ is the structure factor of the liquid, and $w_q(k_F)$ is the matrix element of the screened electron-ion interaction for Fermi-surface scattering.) The limitations of this formula are well known and have been discussed elsewhere.[3,4] Essentially the Ziman formula describes the resistivity to first order in the scattering probability. As such it should yield an accuracy of about 10% for free-electron-like metals. To date, though, calculations of ρ using Eq. (1) have not approached this accuracy because the functions $a(q)$ and $w_q(k_F)$ themselves had not been determined with sufficient accuracy. We have based our calculations on the most accurate and unparametrized forms of these functions which are now available, at least for the cases of liquid Na and K. Since these functions also appear in calculations for the thermoelectric power Q, both ρ and Q can now be determined in a satisfactory fashion.

Previously the forms used for $a(q)$ had been determined from either neutron-diffraction experiments[5] or from a solution of the Percus–Yevick[6] equation for a liquid consisting of hard spheres.[7] This latter form for $a(q)$ depends only on a single parameter η, the hard-sphere packing fraction. Because the ions are not simply hard spheres, η cannot be a real physical quantity. Hence, choosing a rigorous value for it is not possible. But by comparing the long-wavelength limit of this model $a(q)$ to the compressibility measurements, a value of $\eta = 0.45$ was found by Ashcroft and Lekner[7] (AL) to be consistent for most liquid metals near their melting points. This is the value that has been used most often in resistivity calculations. Re-