holes from one hole band to another. Contrary to Hall effect, the contributions of electrons and holes to conductivity are additive and a small number of new holes would make very little contribution to the temperature dependence of the electrical conductivity. The data in Figs. 2–5 indicate that the zero-field resistivity coefficients $\rho_{ii}{}^0$ are approximately proportional to $T^{1.9}$ and $T^{1.4}$ below and above 90°K, respectively, while most of the magnetoresistivity coefficients $\rho_{ijkl} \sim T^{-1.4}$. These variations are also in better agreement with the band-structure model of one conduction band overlapping with two valence bands as proposed above.

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Experimental Determination of the Effect of Hydrostatic Pressure on the Fermi Surface of Copper*

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We have measured the pressure derivatives of five cross-sectional areas of the Fermi surface of copper, using the fluid-He phase-shift method. The results are in excellent agreement with predictions of recent band-structure calculations by Davis, Faulkner, and Joy.

INTRODUCTION

A WEALTH of experimental data giving detailed information about the Fermi surface of copper is available in the literature. In particular, cross-sectional areas of the Fermi surface accurate to the order of 0.2% have been obtained recently from de Haas–van Alphen measurements.[1–3] Such Fermi-surface data constitute easily accessible experimental information of sufficient accuracy and quantity that it may be used to critically evaluate a band-structure calculation of a metal at least in the vicinity of the Fermi energy. However, most theoretical band-structure descriptions are in some sense parametrized to fit the experimental data, e.g., by the choice of the potential, adjustment of the exchange terms, or fitting pseudopotential coefficients. Pressure studies of the Fermi surface serve to add another dimension with which to test the physical significance of the theoretical description.

In a recent calculation,[4] using the Korringa-Kohn-Rostoker (KKR) formalism, Faulkner, Davis, and Joy have succeeded in obtaining essential agreement with the zero-pressure Fermi surface of Cu. In a subsequent paper,[5] these investigators calculated the band structure as a function of lattice parameter and gave values of the pressure derivatives of four cross-sectional areas of the Fermi surface. The pressure derivatives of two of these cross sections are available from the work of Templeton.[6] The purpose of this paper[7] is to present the pressure derivatives of the five cross-sectional areas (three additional cross sections plus the two given previously by Templeton) observable along the major symmetry axes [100], [110], and [111]. Because of the relative simplicity of the Fermi surface of the noble metals, these five experimental data constitute a rather complete description of the effect of pressure upon the Fermi surface of copper suitable for comparison with a theoretical description such as that of Davis *et al.*

The Fermi surface of copper consists of a spherical electron surface centered on Γ with interconnecting necks in the [111] directions.[3] With the magnetic field in the [111] direction, one observes a "belly" orbit and a "neck" orbit. In the [110] direction, the only extremal section gives rise to a hole orbit made up of the necks and spheres which resembles a "dogbone." A similar fourfold symmetric hole orbit known as the four-cornered "rosette" is observed in the [100] direction in addition to a "belly" orbit about the sphere. We have measured the pressure derivatives of the de Haas–van Alphen frequencies corresponding to these five cross-sectional areas.

EXPERIMENTAL

The samples were $\frac{3}{16}$-in.-diam×$\frac{5}{8}$-in.-long right circular cylinders cut by spark erosion from a boule whose residual-resistance ratio ($R_{300°K}/R_{4°K}$) was about 4000. These samples were etched down with dilute HNO_3 so as to slip into the $\frac{1}{8}$-in.-bore Be-Cu bomb and were oriented along the appropriate symmetry axes to within 2 deg by standard back reflection x-ray techniques.

The de Haas–van Alphen oscillations were detected

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using the low-frequency field-modulation technique[8,9] in fields to 55 kOe generated in a superconducting solenoid.[10] The pressure derivatives were determined with the phase-shift method first used by Shoenberg and Stiles[8] for orientation studies and by Templeton[6] for pressure studies. Except for the [111] direction, the patterns were sufficiently simple that judicious choice of the Bessel-function argument $\alpha=2\pi FH_{\rm mod}/B^2$ (where F is the dHvA frequency; $H_{\rm mod}$, the modulation amplitude and B, the magnetic induction) permits examination of a single frequency at a time.[11,12] Then the shift in field ΔH of a single oscillation is measured as the pressure is varied an amount ΔP.

If the magnetization M is given by

$$M=M_0\sin 2\pi F/B\,,$$

then

$$\left(\frac{dM}{dH}\right)_P=-\frac{2\pi FM_0}{B^2}\cos\frac{2\pi F}{B}\left[1+\frac{8\pi FM_0}{B^2}\cos\frac{2\pi F}{B}\right]^{-1}$$

and

$$\left(\frac{dM}{dP}\right)_H=\frac{2\pi FM_0}{B}\frac{d\ln F}{dP}\cos\frac{2\pi F}{B}\left[1+\frac{8\pi FM_0}{B^2}\cos\frac{2\pi F}{B}\right]^{-1}.$$

Equating $(dM/dH)_P\Delta H$ to $-(dM/dP)_H\Delta P$, the logarithmic pressure derivative of the frequency (and therefore of the cross-sectional area) is given by

$$d\ln F/dP=B^{-1}\Delta H/\Delta P\,. \quad (1)$$

It is noticed that the extra terms due to the periodicity of the magnetization in B^{-1}, rather than in H^{-1}, drop out.

With the field along [111], near 50 kOe, intermodulation between the neck and belly oscillations occurs so that a beating occurs between the belly frequency F_B and the difference frequency between the neck and belly, F_B-F_N. The individual pressure derivatives $d\ln F_B/dP$ and $d\ln(F_B-F_N)/dP$ are then obtained from[13]

$$\frac{\Delta H^{\pm}}{B\Delta P}=\frac{d\ln F_B}{dP}+\left[\frac{d\ln(F_B-F_N)}{dP}-\frac{d\ln F_B}{dP}\right]\times\left[1\pm F_B\mathcal{A}(F_B-F_N)^{-1}\mathcal{B}^{-1}\right]^{-1}, \quad (2)$$

where $\Delta H^{\pm}$ denotes the shift in field with the pressure change ΔP and $\mathcal{A}$ and $\mathcal{B}$ are the amplitudes of the F_B and (F_B-F_N) frequencies. The plus sign applies to beat maxima, the minus, to beat minima. As in Eq. (1), the periodicity of the magnetization in B^{-1} has been taken into account.

In our experiments, the superconducting solenoid was operated in the persistent mode and the field was swept over a range of about 25 G by means of a pair of coils wound in a Helmholz configuration outside the Dewars. It was noted that the direction and magnitude of the field generated by the Helmholz coils at the sample changed upon going into the persistent mode. Therefore, measurements were always made in terms of the fraction of the separation between oscillations. In cases where Eq. (2) was used, the error made by neglecting the difference between the instantaneous frequency and the dominant frequency could be calculated and was typically less than 1%. He gas pressure was read with a 0–3000 psi Heise gauge calibrated against a dead weight tester. Reproducibility to better than 0.01 of the separation between the oscillations was usually attained. Since the values of ΔH in the field ranges used were from 0.03 to 0.13 of this separation for the various frequencies, this reproducibility set the error in the pressure derivatives.

RESULTS AND DISCUSSION

Our pressure results are given in Table I together with the de Haas–van Alphen frequencies we observed.

TABLE I. Comparison of experimental and theoretical values of logarithmic pressure derivatives of cross-sectional areas of the Fermi surface of Cu in units of 10^{-4} kbar^{-1}. Our values for the particular de Haas–van Alphen frequencies are given in column 1 in units of G.

Cross section		This work	Templeton	Davis *et al.*
[111] belly	5.814(±0.006)×10⁸	4.25(±0.2)	4.29	4.35
[111] neck	2.177(±0.002)×10⁷	18 (±2)	19.7	15.3
[110] dogbone	2.520(±0.006)×10⁸	4.0 (±0.2)	···	4.04
[100] belly	6.046(±0.012)×10⁸	4.6 (0.2)	···	4.62
[100] rosette	2.470(±0.005)×10⁸	4.3 (±0.3)	···	···

The [111] frequencies were determined with *in situ* NMR as described earlier.[1] The other frequencies were obtained, using the NMR determined current-field ratio. Also listed in Table I are those experimental values found by Templeton.[6] We are in excellent agreement with Templeton's measurements for the necks and bellies in the [111] direction. The neck value was obtained both directly at low fields and from the two-frequency data mentioned above by use of Eq. (2). Although the two values agreed, the uncertainty in the latter determination was much larger. The uncertainty listed in Table I is from the direct phase shift near 28 kOe.

We can combine a portion of our results with those of Shoenberg and Watts[14] who examined the effect of tension on the dHvA frequencies for fields along [100] and [111] to obtain a measure of the effect of pure

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shear without change of volume. Using their notation, the dependence of the cross-sectional area A upon strain can be expressed as $d\ln A/d\ln A_s$, where A_s is the extremal cross-sectional area of a free electron sphere whose volume remains exactly half that of the Brillouin zone. Then,

$$\frac{d\ln A}{d\ln A_s}=\alpha+\frac{\frac{3}{4}\beta(C_{11}+2C_{12})}{C_{44}} \tag{3}$$

for tension along [111] and

$$\frac{d\ln A}{d\ln A_s}=\alpha+\frac{\frac{3}{2}\beta(C_{11}+2C_{12})}{(C_{11}-C_{12})} \tag{4}$$

for tension along [100], where α is the ratio of the change in cross section due to a pure volume change to that change given by the scaling of the Fermi surface with the Brillouin zone (in order to keep the zone precisely $\frac{1}{2}$ full). This scaling effect is equal in magnitude to $\frac{2}{3}$ the volume compressibility. The parameter β is the coefficient of the pure shear contribution to the relative change of the Fermi surface area.[14] Our measurements (and those of Templeton) give α directly so that we can calculate β for tension in the [100] direction for the belly and rosette cross sections. Table II gives the values of β calculated from our measured values of α. Except for the values of α derivable from Templeton's work with which we are in excellent agreement, there are no other experimental values for Cu for this quantity which is a measurement of the deviation from the free electron prediction of scaling for a cubic material. An earlier attempt by Caroline and Schirber[15] to measure α for the [111] necks using a magnetoresistance method was not sufficiently sensitive to see the deviation.

TABLE II. Experimental values of α and β (the latter calculated from combining this work with that of Shoenberg and Watts).[a]

	[111] Neck	[111] Belly	[100] Belly	[100] Rosette	[110] Dogbone
α	3.8±0.4	0.90±0.05	0.98±0.05	0.91±0.06	0.85±0.05
β	−12 ±3	−0.08±0.04	0.19±0.04	−0.24±0.06	···

[a] We have used the coefficients of Eqs. (3) and (4) given by Shoenberg and Watts (Ref. 14) to calculate β.

Davis, Faulkner, and Joy[5] have calculated the effect of a volume change on their Cu band structure using the same atomic charge densities from which they generated the normal lattice-spacing band structure. Thus, no additional parameters are introduced and the pressure effects stem entirely from summing the potential contributions from the neighboring sites at a new volume. Their predictions for the pressure derivatives of the cross sections are listed in Table I and are seen to be in substantial quantitative agreement with our results.[16] At the time of this writing, no calculations for comparison with uniaxial stress and pure shear information exist.

We would conclude that, as far as our results are concerned the band structure calculated by Davis, Faulkner, and Joy[16] is a physically significant description of the energy spectrum in the vicinity of the Fermi surface.

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[16] By adjusting the amount of the $\rho^{1/3}$ Slater exchange contribution in their potential, Davis and Faulkner have improved the value for the normal lattice-spacing neck cross section. The recalculated pressure derivative of the neck cross section is then larger and agrees within experimental uncertainty with our result and that of Templeton. H. L. Davis and J. S. Faulkner (private communication).