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Fermi Surface of Mg under Hydrostatic Pressure*

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We report the effect of hydrostatic pressure on several cross-sectional areas of the Fermi surface of Mg. Pressure derivatives were obtained using the fluid-He phase-shift technique. The results differ significantly from the predictions of the free-electron model but are described quite well by a simple local-pseudopotential model.

I. INTRODUCTION

The Fermi surface of Mg has been studied in great detail by a variety of techniques including, in particular, magnetoacoustic[1] and de Haas–van Alphen[2,3] (dHvA) studies. The results are in general agreement with the free-electron construction[4] so that pseudopotential descriptions might be expected to be successful as model descriptions for Mg. Kimball, Stark, and Mueller[3] (KSM) fitted experimental data to pseudopotential models and concluded that a nonlocal description was required to achieve quantitative agreement with observation. Recent work[5,6] has shown that pressure studies of the Fermi surface can provide a fairly incisive test of a given pseudopotential model. The purpose of this paper is to report measurements of Fermi-surface cross sections as a function of hydrostatic pressure for comparison with the predictions of various model descriptions.

The Fermi surface of Mg consists of several sheets in the first four bands. Representations of these sheets have been presented many times in the literature so the reader is referred to the figures in Refs. 2 and 3. We have employed the nomenclature of KSM throughout. Here μ denotes cross sections associated with the second-band hole surface called the "monster," and λ and γ denote cross sections associated with the third-band electron sheets called the "lens" and "cigar," respectively. The subscripts 1 and 2 indicate whether the applied field is in the $(10\bar{1}0)$ or $(11\bar{2}0)$ plane. The superscripts number the cross sections in a given plane in order of increasing size. We will be concerned primarily with several of the second-band monster orbits and with third-band lens and cigar orbits. Although this is not a complete set of observable frequencies, we feel the six or seven orbits considered adequately represent both the normal volume and pressure behavior of the Fermi surface of Mg. Section II outlines briefly our experimental procedures. Section III describes a local-pseudopotential model that provides as satisfactory a fit to the normal-volume Fermi surface as does the nonlocal model described by KSM. This local model yields pressure derivatives for

Fermi-surface cross sections much more nearly in agreement with experiment than does the nearly-free-electron model, as discussed in Sec. IV.

II. EXPERIMENTAL

Samples were cut by spark erosion from single-crystal boules purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, Calif. These samples were right circular cylinders, typically $\frac{3}{16}$ in. diameter by $\frac{3}{8}$ in. long, with their axes aligned by standard back-reflection Laue techniques to within 1°–2° of principal crystallographic directions.

Cross-sectional areas of the Fermi surface were determined by measurement of dHvA frequencies using the field-modulation method[7] in either a 25-kOe Varian electromagnet or in a 55-kOe superconducting solenoid. Pressure derivatives were obtained by means of the fluid-He phase-shift technique.[6,8] Here the change of position of a single dHvA oscillation ΔH is measured with the application of a pressure increment $\Delta P \leq 25$ bars in fluid He at a magnetic field B. The large dHvA phase typically permits direct determination of the pressure derivative of the frequency $d\ln F/dP$ as given by the relation

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

In every case, proper choice of modulation amplitude, field magnitude, and direction and temperature allowed isolation of one or at most two frequencies. For example, for $H \| [11\bar{2}0]$, the lens frequency λ_1^1 is observed to beat with the sum frequency $\lambda_1^1 + \mu_1^5$ and to a lesser extent $\lambda_1^1 \pm 2\mu_1^5$. This was avoided by detecting at the 18th harmonic of the modulation frequency which suppresses μ_1^5 itself and by placing the field in such a direction that two monster waists destructively interfere for a particular field magnitude. This permitted adequate isolation of the λ_1^1 frequency to verify its somewhat unexpected pressure derivative (see Sec. IV).

III. PSEUDOPOTENTIAL MODEL

In the spirit of local-pseudopotential theory,[9] changes in the lattice can be included by assuming that the only change in the form factor $w(q)$ is that due to being inversely proportional to the atomic volume. (The values of q corresponding to reciprocal-lattice vectors, of course, change also.) The measured compressibilities[10] then complete a prescription for calculating the energy band structure as a function of pressure.

It is convenient to use an analytic expression for $w(q)$. We employ essentially the form used by Lin and Falicov in As,[11]

$$w(q) = (\Delta_0/\Delta)B_1(q^2 - B_2)\,(e^{B_3(q^2 - B_4)} + 1)^{-1} , \tag{2}$$

where Δ is the atomic volume, Δ_0 the atomic volume at zero pressure, and the B's are parameters chosen to yield a desired band structure.

Our fitting procedure was very similar to that described by KSM. Fourier coefficients were obtained by least-squares fitting energies at 12 points in the Brillouin zone. The energies at trial Fermi radii in the directions KSM chose were included,[12] plus the energy at the top of the hole band for the μ_1^1 orbit 28.7° from the hexad axis (0.010 Ry above the Fermi energy). As a separate step, the B parameters were determined such that Eq. (2) would reproduce the leading four Fourier coefficients.

In contrast to KSM, we found that a local pseudopotential would give a reasonable representation of the normal-volume Fermi surface. After a fairly detailed convergence study, we adopted a model employing in excess of 100 plane waves. All plane waves such that $k^2 < 7.25(2\pi/a)^2$ were included, where a is the basal-plane lattice constant. However, only the shortest 20 plane waves were treated exactly. The influence of the remaining plane waves was folded in by the Löwdin partitioning scheme.[13] This is significantly more plane waves than KSM used (no parameters have been added). Lack of convergence in the calculation of KSM does account for the fact that we could obtain a fit with a local model, whereas KSM could not. The convergence question, particularly as it bears on calculated pressure derivatives, will be dealt with in more detail in a separate publication.[14]

While the zero-pressure Fermi surface was quite sensitive to the first three Fourier coefficients ($V_{10\bar{1}0}$, V_{0002}, and $V_{10\bar{1}1}$) of the pseudopotential, the value of the fourth $V_{10\bar{1}2}$ was indeterminate. We agree with KSM that the signs of the pseudopotential coefficients (the first three) are uniquely determined by the zero-pressure data. Efforts to force the first coefficient negative significantly (0.005 Ry) degraded the fit.

We carried through complete calculations for two different choices of $V_{10\bar{1}2}$. Results for the model which was selected on the basis of pressure derivatives are shown in Table I. The calculated Fermi-surface areas of several orbits are listed. The experimental areas and those calculated by KSM using their nonlocal model are also included. In evaluating the fit it should be noted that for each orbit listed our deviation from experiment corresponds to less than 0.0005 Ry. The parameters used are tabulated in Table II. A significantly smaller value of $V_{10\bar{1}2}$ (0.014 Ry) led to a very comparable fit to the areas.[15] The zero-pressure fit based on this different choice of $V_{10\bar{1}2}$ led to slightly different values (~0.002 Ry) for the other coefficients.

To calculate pressure derivatives, the calculation is repeated at lattice parameters[16] correspond-

TABLE I. Comparison of calculated and observed Mg Fermi-surface areas and pressure derivatives of these areas.

Orbit[a]	θ[b]	Area (a.u.) Expt.[c]	This work	KSM[d]	$\frac{d\ln F}{dP}$ (%/kbar) Expt.	Theory
λ_1^1	0°	0.308	0.307	0.309		
λ_1^1	90°	0.0727	0.0732	0.0732	+0.05 ± 0.02	+0.09
μ_1^1	0°	0.00215		0.00216		
μ_1^1	28.7°	0.00183	0.00184		−0.9 ± 0.3	−0.78
μ_1^5	90°	0.00721	0.00725	0.00707	−0.17 ± 0.02	−0.19
μ_1^7	90°	0.0457	0.0461	(0.0448)[e]	+0.05 ± 0.02	+0.03
γ_1^1	0°	0.00598	0.00605	0.00612	+0.40 ± 0.04	+0.35
L_1^1	0°	0.0234	0.0235	0.0233		
C_1^1	90°	0.0208	0.0208	0.0206		
T_1^1	0°	0.00634			−0.8 ± (0.2)	
					Scaling = +0.18	

[a]Orbit nomenclature explained in text (L, C, and T are magnetic breakdown orbits).
[b]Angle measured from [0001].
[c]Reference 2.
[d]Nonlocal model, Ref. 3.
[e]Reference 3 lists this value for μ_2^7, but we interpret it to be μ_1^7.

ing to 20 kbar. The change in Fermi energy with pressure is estimated from the free-electron model[17] to be 0.264 eV. We determined a value for ΔE_F of 0.259 ± 0.001 eV by calculating the density of states for both zero-pressure and 20-kbar lattice constants using the linear-analytic method[18] with over 500 points in $\frac{1}{24}$ of the Brillouin zone. The zero-pressure calculation showed 2.002 ± 0.001 states/atom below E_F. This is a discrepancy of only 0.0003 Ry in E_F.

IV. DISCUSSION

Pressure derivatives for cross sections along principal crystallographic directions are given in Table I and are compared with the calculated value from the model described in Sec. III. The linear compressibilities[10] for Mg at liquid-He temperature are 9.20×10^{-4} kbar^{-1} parallel to the hexad axis and 8.95×10^{-4} kbar^{-1} in the basal plane. Since these values are so nearly isotropic and the Fermi surface of Mg so closely resembles the nearly-free-electron picture, it might be expected that cross sections would scale with the Brillouin zone. Then all cross sections would increase at a value of $\frac{2}{3}$ the volume compressibility or a rate of 0.18% per kbar (this assumes complete isotropy of the linear compressibilities). A perusal of the experimental results in Table I shows no correspondence with this simple model prediction.

The first-order correction to the scaling prediction for a nearly-free-electron metal would involve rounding off of the orbit corners by the pseudopotential Fourier coefficients. For any reasonable Mg pseudopotential form factor (ours, that due to either KSM or Animalu and Heine[19]), the first three Fourier coefficients will grow with increasing pressure (assuming $V_{10\bar{1}0}>0$), thus making orbits smaller and thus causing pressure derivatives to be *less* than the scaling prediction. The cigar orbit γ_1^1 in particular deviates widely from this anticipated behavior.

On the other hand, our volume-dependent pseudopotential model reproduces these deviations from scaling quite well. All calculated pressure derivatives are satisfactorily close to the experimental

TABLE II. Pseudopotential parameters used in the model description for the Fermi surface of Mg.

	This work	KSM[a]
$V_{10\bar{1}0}$	0.01501	0.014
V_{0002}	0.03077	0.026
$V_{10\bar{1}1}$	0.04198	0.036
$V_{10\bar{1}2}$	0.04000	0.058
E_F[b]	0.52554	0.522
B_1	0.2171	
B_2	1.302	(1.28)[c]
B_3	1.235	
B_4	1.3426	
Number of plane waves	~110[d]	10

[a]Reference 3, local model.
[b]With respect to Γ_1^+.
[c]This is zero crossing value [Eq. (2) is not used by KSM].
[d]See text.

value except λ_1^1. For λ_1^1 the model picks up only about $\frac{2}{3}$ of the deviation from free-electron scaling. Because of the difficulty associated with λ_1^1, the pressure derivative for this cross section was redetermined carefully in a more direct manner as indicated in Sec. II with identical results (within experimental uncertainty). Comparing this calculation with the model based on a different value of $V_{10\bar{1}2}$, there did not appear to be any way to adjust $V_{10\bar{1}2}$ to improve the fit to λ_1^1 without significantly degrading the fit to other orbits. This again points up the sensitiveness of model descriptions to pressure data.

In conclusion we find that a converged local-pseudopotential model fits the normal-volume Fermi surface at least as well as the nonlocal model described by KSM. In addition, our model adequately predicts the pressure derivatives of Fermi cross-sectional areas. We therefore feel that this is the simplest model yet presented for Mg possessing sufficient physical significance to account for detailed experimental data.

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[16]For 20-kbar lattice parameters we used $a = 5.9181$ a.u. and $c = 9.6040$ a.u. compared to $a = 6.0260$ a.u. and $c = 9.7811$ a.u. at zero pressure, which assumes volume-independent compressibilities.

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Experimental Charge Density of Copper*

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The first six charge-density form factors of crystalline copper have been measured by Bragg scattering of Cu$K\alpha$ and Mo$K\alpha$ x rays from copper-powder samples. Detailed studies of both the samples and the x-ray beam parameters have reliably established the experimental error at about 1%. The measured form factors are in best agreement with an augmented-plane-wave (APW) self-consistent-field calculation of Snow using $X\alpha$ Slater exchange for a value of α between 0.70 and 0.75. They are in poor agreement with an APW calculation using the Chodorow potential but agree well with a calculation by Wakoh using Slater exchange and a self-consistent procedure. It is concluded that form-factor measurements of high accuracy are a sensitive and useful test of band wave functions and crystalline potentials.

I. INTRODUCTION

The measurement of the intensity of elastic (Bragg) x-ray scattering from a solid directly determines the solid-state electron charge distribution. The experimental charge density, if found to sufficiently high accuracy, may be used to test the wave functions and charge density predicted by solid-state band computations. Since theoretical wave functions are very sensitive to the choice of