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Fermi-Surface Parameters and Band-Structures for the Noble Metals. I. Normal-Volume Results and Herman-Skillman Potentials*

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Using NMR field calibration, absolute values of de Haas–van Alphen frequencies for the noble metals were obtained with an error of about 0.1%. These and other experimental results are compared with results of energy-band calculations using the Korringa-Kohn-Rostoker method and potentials derived from Herman-Skillman atomic calculations. The theoretical and experimental results agree to within about 1% for copper and 1–10% for silver, and give reasonable (considering the nonrelativistic nature of the calculations) results for gold. The results indicate that it is possible to obtain meaningful results from Herman-Skillman potentials, contrary to the conclusions of others.

I. INTRODUCTION

THE Fermi surfaces of the noble metals are well known and are topologically simple. They consist of essentially spherical electron surfaces centered at the point Γ with interconnecting necks in the [111] directions. With the magnetic field in the [111] direction, a "belly" [$B(111)$] and "neck" [$N(111)$] orbit are observed. With the field along [110], a hole orbit made up of a combination of necks and spheres resembling a "dogbone" [$D(110)$] is seen. A similar fourfold symmetric hole orbit known as the "rosette" [$R(100)$] is observed for fields in a [100] direction in addition to another belly orbit about the spherical body of the surface [$B(100)$]. Two recent *ab initio* calculations of the band structures of Cu [1] and Ag [2] have demonstrated that such calculations can lead to values for Fermi-surface dimensions which are in surprisingly good agreement with experiment and compare favorably with the results of parametrized band calculations.[3,4]

Faulkner, Davis, and Joy[1] programmed the Korringa-Kohn-Rostoker (KKR) method for the calculation of constant energy surfaces. With this new technique they were able to calculate Fermi energies with a precision of about ±0.0002 Ry in comparison to uncertainties of about ±0.01 Ry which were typical of previous **k** search calculations. They investigated the Cu band structure for several crystal potentials. In particular, for the Chodorow potential[5,6] they found their band structure was in essential agreement with the results of Burdick's[6] augmented plane-wave (APW) calculation, with the important exception that Burdick's Fermi energy was too low by about 0.01 Ry. With the Chodorow potential Faulkner, Davis, and Joy calculated values for the areas of the large Fermi-surface cross sections for Cu, $B(100)$ and $D(110)$, which agreed with experiment to within 1% and a value for the "neck" cross-sectional area $N(111)$, which was less than the experimental value by only 8%. Faulkner, Davis, and Joy also constructed a crystal potential for Cu from wave functions taken from the Herman-Skillman tables.[7] In this case, however, their calculated Fermi surface did not provide even a qualitatively correct description, in that the Fermi surface calculated with this potential did not make contact with the (111) Brillouin-zone boundaries. This result would seem to be consistent with the results of KKR calculations by Ballinger and Marshall[8] who also decided that the Herman-Skillman potential was not suitable for application to the noble metals. Such a conclusion is not justifiable by the latter authors, since they did not generate a crystal potential by superposing neighboring atom contributions, but instead used a muffin-tin potential which included contributions from only one atom.

Christensen[2] has used the APW method to investigate several crystal potentials for Ag. With the APW method programmed for constant energy searching, he found that a potential constructed by superposing relativistic Dirac-Slater atomic charge densities[9] led to a band structure for Ag which agreed well with the photoemission results of Berglund and Spicer,[10] the Fermi-surface data,[11,12] and in most details with the self-consistent bands of Snow[13] for $\frac{5}{6}$ Slater exchange. Although the Fermi surfaces for Ag which resulted from Christensen's use of a Herman-Skillman potential did have necks, the calculated cross-section area of the necks for $H\|[111]$ was less than the experimental value by 40%.

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In the case of Cu, in particular, the inference has been drawn that the Herman-Skillman atomic wave functions do not lead to a valid energy band structure or Fermi surface. In lieu of evidence to the contrary, Gerhardt[14] was forced to take this position, and in addition, he concluded that only the Chodorow potential provided a band structure in quantitative agreement with his experimental results.

As an initial part of a program to develop a self-consistent parametrized band-structure scheme based on the KKR method,[15] we decided to reinvestigate the energy bands for the noble metals based on the atomic self-consistent field (SCF) Hartree-Fock-Slater charge densities calculated by Herman and Skillman. The advantage that the Herman-Skillman solutions had from our point of view was that one can vary the Slater exchange constant within the atomic SCF program so that it corresponds to the value in the exchange part of the crystal potential.

In this paper we report our results for the energy band structure and Fermi-surface properties of Cu, Ag, and Au. Section II consists of a short description of the experimental techniques used in measuring the de Haas–van Alphen (dHvA) frequencies with which we compare our calculated values. Section III outlines the KKR calculation, including a description of the methods used to generate the crystal potentials used in the calculations. In Sec. IV we compare the calculated band-structure and Fermi-surface results with the available experimental data and with the results of other calculations. The final section of the paper consists of a summary of results and conclusions.

II. EXPERIMENTAL PROCEDURES

The experimental setup and procedures have for the most part been discussed previously[16] so only a brief description will be given here. The samples were cut by spark erosion from large single-crystal boules grown by the Bridgman technique. The residual resistance ratios $[R(300°\text{K})/R(4°\text{K})]$ as determined by standard eddy current decay methods were ~ 4000, ~ 2000, and ~ 1600 for the Cu, Ag, and Au boules, respectively.

Cross-sectional areas were determined by measurement of dHvA frequencies detected using low-frequency field modulation techniques. Magnetic fields to 58 kG were obtained in a compensated (~ 2 parts in 10^5) superconducting solenoid. The magnetic-field values were measured to about ± 0.5 G by using an *in situ* NMR probe[17] which is an integral part of our experimental system. By direct NMR measurement of the field at our dHvA samples we are able to determine *absolute* dHvA frequencies for the noble metals with an error of about 0.1%; this limitation stemming primarily from orientation uncertainty.

III. KKR CALCULATIONS AND CRYSTAL POTENTIALS

We have programmed the KKR method for efficient calculation of constant energy surfaces and energy-band structures. Since whatever differences exist between our approach toward programming the KKR method and that used by Faulkner, Davis, and Joy[1] must be involved in details which are irrelevant to this paper, we will not attempt to give a description of the program itself. For a maximum angular momentum component of $2(l_{\max}=2)$, we require 8 min of CDC-3600 time to calculate an energy surface for the noble metals with a mesh density corresponding to 561 $\mathbf{k}$ vectors in 1/48 of the Brillouin zone. This represents the same mesh density used by Faulkner, Davis, and Joy and with it one can determine the Fermi energy to $\sim\pm 0.0002$ Ry. The running time is approximately 15 min for an energy surface when f-electron contributions $(l_{\max}=3)$ are included in the calculation. In the cases of Cu and Ag, the KKR energy bands were compared with energy bands calculated with the APW method using a potential which produced identical values for the $l=0$ to $l=3$ logarithmic derivatives over the energy range involved in these calculations. In general, the two sets of energy eigenvalues evaluated at the symmetry points Γ, X, and L agreed to within ± 0.0005 Ry. The energy-band and Fermi-surface results presented in this paper were calculated with the KKR method using a maximum angular momentum contribution $l_{\max}=3$.

The potentials used in these calculations were derived from Hartree-Fock-Slater atomic charge densities obtained from a slightly modified version of the Herman-Skillman program.[18] The superposition procedure described by Mattheiss[19] was used to obtain the spherically symmetric Coulomb and exchange potentials within the "muffin-tin" spheres. For both the atomic and crystal exchange potentials the unmodified Slater free-electron exchange approximation

$$V_{\text{exch}} = -6[3\rho(r)/8\pi]^{1/3} \tag{1}$$

was used. The superposition was carried out using four shells of neighbors in the fcc lattice. Including the next two shells changed the crystal potential by less than 5 mV and was felt to be negligible considering the *ad hoc* nature of the potential. The value of the constant potential in the region of the unit cell outside the touching spheres was obtained by averaging the superposed potential over the spherical shell between the radius corresponding to touching spheres and the radius of the Wigner-Seitz sphere. This procedure produces a

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TABLE I. Energy-level splittings for Cu in Ry. A value for the lattice parameter $a=6.83087$ a.u. was used in our calculation. Our value for $E(\Gamma_1)=-0.02112$ Ry.

	This work (Herman-Skillman)	Burdick[a] (Chodorow)	Snow[b] ($\frac{5}{6}$ Slater exchange)	Zornberg and Mueller[c] (Interpolation scheme)
$\Gamma_{25}'-\Gamma_1$	0.410	0.399	0.375	
$X_5-\Gamma_1$	0.514	0.512	0.477	
X_5-X_1	0.236	0.249	0.224	
$X_4'-\Gamma_1$	0.793	0.804	0.794	
E_F-L_3	0.148	0.154	0.159	0.14±0.02
E_F-X_5	0.137	0.143	0.149	
E_F-L_2'	0.062	0.045	0.029	
$E_F-\Gamma_1$	0.6514	0.655	0.626	

[a] Reference 6.
[b] Reference 20.
[c] Reference 3.

TABLE II. Energy-level splittings for Ag in Ry. A value for the lattice parameter $a=7.72056$ a.u. was used in our calculation. Our value for $E(\Gamma_1)=-0.01424$ Ry.

	This work (Herman-Skillman)	Christensen[a] (Dirac-Slater)	Christensen[a] (Herman-Skillman)	Snow[b] ($\frac{5}{6}$ Slater exchange)	Lewis and Lee[c] (Interpolation scheme)
$\Gamma_{25}'-\Gamma_1$	0.062	0.104	0.048	0.090	0.150
$X_5-\Gamma_1$	0.187	0.227	0.127	0.221	0.258
X_5-X_1	0.224	0.235	0.224	0.235	0.225
$X_4'-\Gamma_1$	0.664	0.671	0.667	0.667	0.700
E_F-L_3	0.340	0.302	0.373	0.304	0.318
E_F-X_5	0.327	0.304	0.393	0.290	0.302
E_F-L_2'	0.0168	0.022	0.017	0.007	0.03
$E_F-\Gamma_1$	0.5145	0.532	0.520	0.525	0.56

[a] Reference 2. Christensen estimated the Fermi energy in his Herman-Skillman calculation with a quoted uncertainty of ±0.01 Ry.
[b] Reference 13.
[c] Reference 4.

TABLE III. Herman-Skillman energy-level splittings for Au in Ry. A value for the lattice parameter $a=7.70658$ a.u. was used in our calculation. Our value for $E(\Gamma_1)=0.03248$.

$\Gamma_{25}'-\Gamma_1$	$X_5-\Gamma_1$	X_5-X_1	$X_4'-\Gamma_1$	E_F-L_3	E_F-X_5	E_F-L_2'	$E_F-\Gamma_1$
0.086	0.274	0.315	0.699	0.322	0.301	0.054	0.575

value of the constant potential that differs from more exact averages over the true unit cell by about 0.50 eV because it underestimates contributions from regions of the unit cell outside the Wigner-Seitz sphere. Comparing Christensen's results with ours, we estimate that this procedure changes the calculated $B(111)$, $B(100)$, and $D(110)$ frequencies by a percent or two and the neck radius by as much as 50%. Since we are claiming agreements better than this for copper, our results are in a sense "because of" rather than "in spite of" this procedure.

IV. RESULTS

A. Energy-Band Structures

In Tables I–III we present our calculated results for the noble metals for a set of energy eigenvalue differences which indicate the position and width of the *sp* and *d* bands. The energy differences relate to the location of the top of the *d* band with respect to the bottom of the *sp* band ($\Gamma_{25}'-\Gamma_1$ and $X_5-\Gamma_1$), the width of the *d* band (X_5-X_1), the width of the *sp* band ($X_4'-\Gamma_1$), the location of the top of the *d* band with respect to the Fermi energy (E_F-L_3 and E_F-X_5), and the location of the "neck band" L_2' with respect to the Fermi energy (E_F-L_2'). In Tables IV and V we compare our calculated values for several energy eigenvalue differences in Cu and Ag with the com-

TABLE IV. Calculated and experimental values for level splittings in Cu in Ry.

Transition	Herman-Skillman	Chodorow[a]	Experiment
$X_4'-X_5$	0.278	0.292	0.29±0.01[b]
X_5-X_1	0.236	0.249	0.26[c]
$E_F-L_3^{\text{upper}}$	0.148	0.154	0.15±0.01[b]
E_F-X_5	0.137	0.143	0.15[c,d]
E_F-L_2'	0.062	0.045	0.026[c]
L_1-E_F	0.292	0.290	0.30±0.01[b]

[a] Reference 6.
[b] Reference 14.
[c] Reference 10.
[d] A. H. Lettington, Phys. Letters 9, 98 (1964).

TABLE V. Calculated and experimental values for level splittings in Ag in Ry.

Transition	Herman-Skillman	Experiment[a]
X_5-X_1	0.224	0.26
$E_F-L_3^{\text{upper}}$	0.341	0.28
E_F-X_5	0.327	0.28
E_F-L_2'	0.0168	0.022
L_1-E_F	0.277	0.29

[a] Reference 10.

parable experimental values. (The italicized parts of the numerical results in the tables reflect our estimate of the various experimental and theoretical uncertainties. In the case of the calculated values the uncertainty results from the respective methods used to calculate the Fermi energy.)

In the case of Cu we see that the bands calculated without Herman-Skillman crystal potential including the full Slater exchange contribution are very similar to those calculated by Burdick[6] using the Chodorow potential and with the self-consistent bands calculated by Snow[20] with a $\frac{5}{6}$ Slater exchange contribution. The energy eigenvalue L_2' lies about 0.062 Ry *below* the Fermi energy, in contrast to the result of Faulkner, Davis, and Joy[1] who found this level at 0.019 Ry above the Fermi energy with their Herman-Skillman crystal potential. The agreement between the calculated and experimental values for the level splittings in Cu is excellent. In particular, the close agreement between our values and the experimental results of Gerhardt[14] is gratifying, since the experimental values have associated uncertainties of less than ±0.01 Ry.

Our Herman-Skillman bands for Ag seem to be improved relative to those of Christensen[2] in that the *d* bands have been raised relative to the *sp* band and the Fermi energy, and the *d* bandwidth is in better agreement with the values calculated by Snow,[13] Lewis and Lee,[4] and by Christensen for the Dirac-Slater potential with full Slater exchange. The comparison of the calculated level splittings for Ag and the photoemission results of Berglund and Spicer[10] seems to be consistent with the observation that our *d* bands are still too low in energy.

The energy band splittings for Au shown in Table III are presented without comment. Large relativistic contributions have been neglected in calculating the Au band structure and the results probably have only a qualitative significance.

B. Fermi-Surface Calculations

In Table VI we compare the calculated values for the $B(111)$, $N(111)$, $B(100)$, and $D(110)$ dHvA frequencies in Cu, Ag, and Au with our experimental values.[21] Our experimental results for the $N(111)$ and $B(111)$ agree within experimental uncertainties with Jan and Templeton[22] for all three metals. In the calculations we have used room-temperature values for the lattice constants which differ from the low temperature values[23] by 0.3, 0.4, and 0.3% for Cu, Ag, and Au, respectively. We can estimate the effect that the use of the slightly larger lattice constants has on the results in Table VI from our calculated pressure derivatives[24] of the Fermi-surface cross sections. We find that the calculated value for $N(111)$ in Cu will increase by ~0.5% and the value for $N(111)$ in Ag will increase by ~5%. The primary effect of using the 4.2K lattice parameters will be to improve the agreement between experiment and the calculated $N(111)$ frequency for Ag.

Our Herman-Skillman cross sections for Cu agree with experiment to about 1%, in general. The major improvement over the results of Faulkner, Davis, and Joy[1] for the Chodorow potential is that the difference between the experimental and calculated $N(111)$ frequencies has been reduced from about 8 to about 1%. Our Herman-Skillman cross sections for Ag differ from experiment by about 1% except in the case of $N(111)$ where the frequency calculated with the room-temperature lattice constant is about 10% smaller than the experimental value. In Table VI we also list the experimental and calculated values for the radius of the [111] neck orbits in units of the free-electron sphere

TABLE VI. Our experimental and calculated dHvA frequencies (frequency in 10^8 G) for Cu, Ag, and Au. The room-temperature lattice constant values used in the calculations were 6.83087, 7.7206, and 7.7066 a.u. for Cu, Ag, and Au, respectively. We also compare the calculated and experimental radii of the neck orbits for $H\|[111]$ in units of the free-electron sphere radius $K_F{}^0$. The experimental values for k_N are determined from $k_N=[N(111)/\text{free-electron sphere dHvA frequency}]^{1/2}$. This approximation for the necks is very good since they are essentially circular. The departure of the [111] neck cross sections from circular is given roughly by $(k_N{}^{\max}-k_N{}^{\min})/k_N{}^{\mathrm{av}}=6\times10^{-5}$, 2×10^{-4}, and 9×10^{-5} for Cu, Ag, and Au, respectively.

	Cu		Ag		Au	
Cross section	Observed	Calculated	Observed	Calculated	Observed	Calculated
$B(111)$	5.814(±0.006)	5.803	4.606(±0.005)	4.620	4.495(±0.005)	4.564
$N(111)$	0.2177(±0.0002)	0.2194	0.0893(±0.0001)	0.07*99*	0.1533(±0.0002)	0.1713
$B(100)$	5.998(±0.006)	5.933	4.746(±0.006)	4.667	4.850(±0.006)	4.649
$D(110)$	2.514(±0.003)	2.505	2.016(±0.003)	2.020	1.938(±0.003)	1.969
k_N	0.1887	0.1900	0.1365	0.130 [0.141][a]	0.1787	0.1893

[a] Reference 2.

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[20] E. C. Snow, Phys. Rev. **171**, 785 (1968).

[21] W. J. O'Sullivan and J. E. Schirber, Phys. Rev. **181**, 1367 (1969).

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TABLE VII. (110) Fermi radius vectors for the noble-metal Fermi surfaces in units of the free-electron sphere radius. The angle θ is measured from [001].

	Cu		Ag		Au	
θ°	Herman-Skillman	Halse	Herman-Skillman	Halse	Herman-Skillman	Halse
0	1.0490	1.0593[1.056][a]	1.0280	1.0469[1.036][b]	1.041	1.1306
15	1.0019	1.0057	0.9993	1.0070	0.9998	1.0217
30	0.9858	0.9855	0.9902	0.9875	0.9860	0.9812
45	1.1242	1.1173	1.0561	1.0580	1.1242	1.0939
75	0.9892	0.9872	0.9943	0.9896	0.9907	0.9794
90	0.9534	0.9508[0.976][a]	0.9713	0.9638[0.963][b]	0.956	0.942
$\dfrac{k(100)}{k(110)}$	1.100	1.114[1.082][a]	1.058	1.086[1.076][b]	1.089	1.1997

[a] Reference 3.
[b] Reference 2. These values are results for the Dirac-Slater potential with the full Slater exchange.

radius K_F^0. Our calculated k_N in Ag and Christensen's value differ about equally from the experimental value. While the Herman-Skillman potential reproduces the general features of the Au Fermi surface, the calculated cross-sectional areas differ from experiment by about 5 to 10%.

A more revealing critique of our Fermi-surface results can be drawn from a comparison between our calculated Fermi radius vectors at various orientations with those determined by Halse[23] who has found detailed Fourier expansion representations of the noble-metal Fermi surfaces. In Table VII we compare our values for k_F/K_F^0 at various orientations in a (110) plane with the values given by Halse. In our case we use the free-electron Fermi radius corresponding to the room-temperature lattice parameters while Halse's values for K_F^0 are determined from the lattice parameter values corresponding to $T=4.2$°K. The comparison between the two sets of results calculated for slightly different lattice parameters is valid except in the region of the necks where the Fermi-surface variation with lattice parameter change departs markedly from free-electron behavior. From our inspection of Table VII we see that the Herman-Skillman Fermi surfaces tend to be more spherical than the "experimental" Fermi surfaces determined by Halse. This tendency towards underestimating the anisotropy of the belly section is most marked in the case of Au.

In Table VIII we compare our calculated effective masses for the noble metals with experiment. We calculate a larger value for $m^*[B(111)]$ than for $m^*[B(100)]$ in Cu. This result is in agreement with the cyclotron resonance measurements of Koch, Stradling, and Kip[25] and contrary to the result of the calculation by Zornberg and Mueller.[3] The "enhancement factor" α is defined by

$$\alpha=(m^*_{\mathrm{exp}}/m^*_{\mathrm{calc}})-1\,. \tag{2}$$

The value for α in Cu of about 0.10 is in agreement with the results of Faulkner, Davis, and Joy,[1] and Dresselhaus.[26] The enhancement factor for Ag is about 0.03 in reasonable agreement with the calculation of Christensen.[2] Although the Au values for α are scattered, we would infer from the entries in Table VIII that α for Au is greater than 0.20.

V. DISCUSSION

In this paper we have demonstrated that our version of a crystal potential made up from Herman-Skillman SCF solutions leads to an energy band structure for Cu which is similar in detail to that calculated by Burdick with the Chodorow potential. This Herman-Skillman crystal potential also leads to values for the major Fermi-surface cross sections of Cu which are in good agreement with experiment. In particular the calculated $N(111)$ dHvA frequency agrees with the experimental value to ~1%. In the case of Ag the

TABLE VIII. A comparison between the calculated and experimental values of the effective masses for specific noble metal orbits.

Cu	m^*/m_0 (Calc)	m^*/m_0 (Exp)	α
$N(111)$	0.412	0.46 ±0.02[a]	0.12
$B(111)$	1.28	(1.410±0.05, 1.385±0.005)[a]	0.10
$B(100)$	1.24	1.370±0.005[a]	0.10
$D(110)$	1.11	1.290±0.005[a](1.225±0.005)[a]	0.15(0.10)
Ag			
$N(111)$	0.38	0.39±0.02[b]	0.03
$B(111)$	0.902	0.93±0.01[c]	0.03
$B(100)$	0.896	0.93±0.01[c]	0.03
$D(110)$	1.00	1.03±0.01[c]	0.03
Au			
$N(111)$	0.321	0.29[d](0.44)[e]	<0(0.37)
$B(111)$	0.844	1.14±0.03[f]	0.28
$B(110)$	0.842	1.08±0.03[f]	0.28
$D(110)$	0.830	1.00±0.03[f]	0.20

[a] Reference 25.
[b] A. S. Joseph and A. C. Thorsen, Phys. Rev. **138**, A1159 (1965).
[c] D. G. Howard, Phys. Rev. **140**, A1705 (1965).
[d] A. S. Joseph, A. C. Thorsen, and F. A. Blum, Phys. Rev. **140**, A2046 (1965).
[e] Reference 11.
[f] D. N. Langenberg and S. Marcus, Phys. Rev. **136**, A1383 (1964).

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[25] J. F. Koch, R. A. Stradling, and A. F. Kip, Phys. Rev. **133**, A240 (1964).

[26] G. Dresselhaus, Solid State Commun. **7**, 419 (1969).

calculated Fermi-surface cross-sectional areas agree with experiment to about 1% except for the neck cross section, where the calculated value is less than the experimental result by about 10%. The effective masses we calculate are consistent with enhancement factors of ~0.10 and ~0.03 for Cu and Ag, respectively.

In the preceding discussion we have stressed that the Herman-Skillman potentials are *ours*. While calculations such as the ones reported in this paper may be loosely referred to as *ab initio*, there remain factors implicit in such calculations which bear little relation to the intrinsic physics but which can have an important bearing on the details of the band structure. This is particularly true when we make comparison with Fermi-surface data where energy differences of a few thousandths of a Ry can be critical.

Our results for Cu and those of Faulkner, Davis, and Joy are significantly different, although both calculations used a Herman-Skillman crystal potential with full Slater exchange. These authors[27] generated their potential from the tabulated values of the radial functions for Cu appearing in the book by Herman and Skillman, rather than by using the Herman-Skillman computer program. Although we were unable to obtain the crystal potential they used for comparison purposes, use of truncated values of the atomic charge densities tabulated on a coarse radial mesh may account for differences between their calculation and ours.

The differences between our calculated Ag band structure and Fermi surface results and those determined by Christensen with a Herman-Skillman potential, probably arise from two sources. First, we estimated the value of the constant potential between the muffin-tin spheres by a spherical averaging of the superposed potential over the spherical shell between the muffin-tin radius and the radius of the Wigner-Seitz sphere. Christensen used the Ewald[28] procedure to determine the value of the constant potential; the discontinuity of the potential at the muffin-tin sphere radius he calculated is about 0.04 Ry greater than the value we find. As a result, his d bands are more tightly bound than ours relative to the Fermi energy and the sp bands. Since the Ewald method should come closer to predicting the true value of the average potential outside the spheres, our Herman-Skillman band structure for Ag agrees better with experiment than does Christensen's because we chose a poorer method for estimating the constant potential. Second, Christensen used a fairly crude technique for determining the Fermi energy in his calculation with the Herman-Skillman potential and the uncertainty he quotes in the Fermi energy is ±0.01 Ry. Because of this, his value for the $N(111)$ cross sectional area must be considered as an intelligent guess.

Our position can be summarized as follows: We have found that, by following a particular format, crystal potentials for Cu and Ag which do a surprisingly good job of fitting the available experimental band-structure and Fermi-surface data can be generated from the Herman-Skillman wave functions. These potentials have significant *ad hoc* characteristics. Nevertheless, these potentials are at least good model potentials for the conduction electrons in these metals, and the results of this paper suggest that the Herman-Skillman potentials can be used as starting potentials in a process leading to a self-consistent parametrized band structure scheme based on the KKR method.[14]

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[27] H. L. Davis (private communication).

[28] J. C. Slater, P. DeCicco, M.I.T. Solid State and Molecular Theory Group, Quarterly Progress Report 1963 (unpublished), No. 50, p. 46.