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Self-Consistent Energy Bands of Metallic Copper by the Augmented-Plane-Wave Method. II*

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The band structure, Fermi surface, and density of states from two self-consistent, augmented-plane-wave calculations of copper are presented and compared with previously reported results. These calculations differ from those reported in the first paper on copper by Snow and Waber in that Hartree-Fock-Slater wave functions given by Herman and Skillman were used in the present work in generating the starting potential and fixed-core charge density; improved starting values for the numerical integration of the radial Schrödinger equation, obtained from a logarithmic radial mesh, were also used; and the calculations were performed on a CDC 6600 computer, which retains about twice as many significant figures as does the IBM 7094 machine on which the original calculations were made. The present calculations differ in that the coefficients of the Slater exchange term are 1 and $\frac{5}{6}$.

1. INTRODUCTION

SINCE completion of the work presented in the first copper paper by Snow and Waber[1] (hereinafter referred to as SW-I), improvements in some of the methods of numerical calculation have been introduced into the augmented-plane-wave (APW) program. Of these, probably the most important is the use of a radial mesh that varies logarithmically. In this mesh, the value of the radius (R_n) for each point is given by

$$R_n = R_1 e^{(n-1)h},$$

where n is the mesh point number R_1 is the smallest value of the radius, and h is a constant that causes the mesh to cover the desired range. The value of h is determined by

$$h = \frac{1}{(N-1)} \ln \frac{R_N}{R_1},$$

where N is the total number of points to be used, and R_1 and R_N are the smallest and largest values, respectively. This type of mesh has two highly desirable features: (1) The radial points for small values of R are close together in the range where the functions tend to vary rapidly, and (2) the radial points for larger values of R are farther apart in the range where the functions tend to vary much more slowly. A further advantage of this type of mesh is that R_1 may be chosen to be as small as needed. If R_1 is small enough, $R_1^{(l+1)}$ and $R_2^{(l+1)}$ are good approximations to the starting values needed for the numerical integration of the radial Schrödinger equation by the Noumerov[2] method.

Another difference between the present calculations and those reported in SW-I is the use of nonrelativistic Hartree-Fock-Slater wave functions, given by Herman and Skillman,[3] to generate the crystal starting potentials and the "frozen" core charge densities in the present work. Since the band calculation is nonrelativistic, use of nonrelativistic core charge densities and wave functions should make the calculations more consistent.

Coefficients of 1 and $\frac{2}{3}$ for the Slater exchange term were used in the calculations reported in SW-I. In that paper, it was concluded that a coefficient between 1 and $\frac{2}{3}$ should yield results in better agreement with experimental findings. In the present work, coefficients of 1 and $\frac{5}{6}$, (hereinafter referred to as "Slater$=1$" and "Slater$=\frac{5}{6}$") were used. It was expected that the results of the calculation for Slater$=\frac{5}{6}$ would be in good agreement with experimental findings, as in fact they are.

Since SW-I was published, a CDC 6600 computer has become available. This machine carries about twice as many significant figures as does the IBM 7094 machine on which the original calculations were made. Use of the CDC 6600, therefore, reduces roundoff errors and improves the accuracy of the calculations.

2. METHOD OF CALCULATION

The same general method of calculation was used in both the present and the earlier work, except as mentioned above. That method was reported in SW-I and, therefore, will not be described in detail here. However, a few remarks about the Noumerov[2] integration method on a logarithmic mesh are in order.

On a linearly varying radial mesh, the radial function $P_n(l,E)$ at the point R_n is given by Pratt[4] as

$$\alpha P_n = [2P_{n-1}(\alpha - 5G_{n-1}) - P_{n-2}(\alpha + G_{n-2})]/(\alpha + G_n),$$

where

$$G_n = E + V_n - l(l+1)/R_n^2$$

and

$$\alpha = 12/(\Delta R)^2.$$

In these expressions, E is the energy, V_n is the potential at the point R_n, l is the orbital angular momentum quantum number, and ΔR is the linear mesh size given by

$$\Delta R = R_n - R_{n-1}.$$

On the logarithmic mesh we solve for $U_n(l,E)$, which is

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[1] E. C. Snow and J. T. Waber, Phys. Rev. **157**, 570 (1967).

[2] B. Noumerov, Monthly Notices Roy. Astron. Soc. **84**, 592 (1924).

[3] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[4] G. W. Pratt, Phys. Rev. **88**, 1217 (1952).

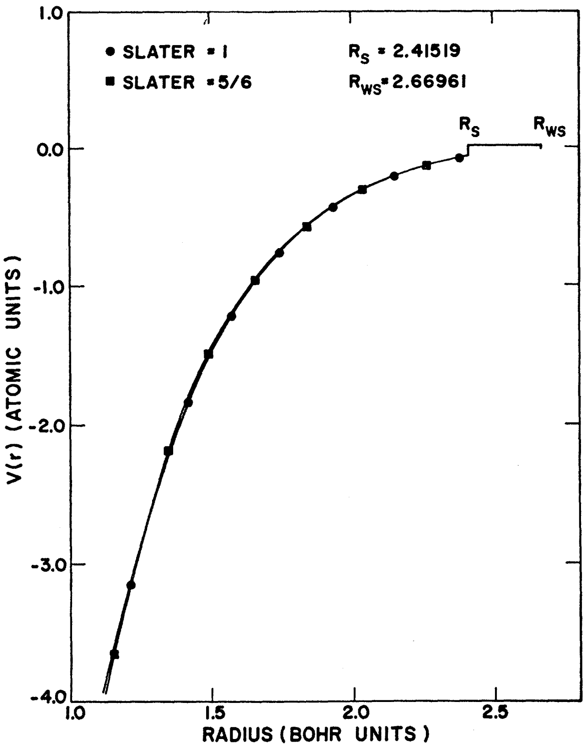

FIG. 1. Comparison of self-consistent potentials, for full and $\frac{5}{6}$ exchange, shifted so that $V_c=0.0$ Ry.

related to the $P_n(l,E)$ above by

$$U_n(l,E)=e^{-nh/2}P_n(l,E)$$

and is given by the expression above with P_n replaced by U_n. G_n is then given by

$$G_n=R_n^2(E+V_n)-l(l+1)-\tfrac{1}{4}$$

and α is given by

$$\alpha=12/h^2,$$

where h is the constant that determines the separation of the radial points on the logarithmic mesh, as described in the introduction. These are basically the same relationships as described in more detail by Loucks[5] in his recent book on the APW method.

Once U_n has been determined, P_n can be obtained from

$$P_n=e^{nh/2}U_n.$$

To solve the U_n equation, the values of U_1 and U_2 are needed. Since these correspond to very small values of the radius, R_1 and R_2, the approximation given by Hartree,[6]

$$P_n\simeq R_n^{(l+1)}[1-(z/l+1)R_n+\cdots],$$

was used. Also since R_1 is approximately 1×10^{-4} Bohr units for the present calculation, the second term was dropped. The starting values for the U_n equation are thus given by

$$U_1=e^{-h/2}R_1^{(l+1)} \quad\text{and}\quad U_2=e^{-h}R_2^{(l+1)}.$$

Thus U_1 and U_2 will become very small for large values of l, such as $l=12$, and may cause "under-flow" problems on the computer. Since the solution of these equations depends only on the ratio of P_1 to P_2, both P_1 and P_2 may be divided by a constant without affecting the results in the APW calculation. Therefore, the starting values given above were divided by $e^{-h/2}\times R_1^{l/2}$ to become

$$U_1=R_1^{(l/2+1)} \quad\text{and}\quad U_2=U_1\times e^{h(l+1/2)}.$$

TABLE I. Starting values used in the numerical integration of the radial Schrödinger equation. $R_1=1.10152\times10^{-4}$ Bohr units; $R_2=1.16031\times10^{-4}$ Bohr units.

l	$U(R_1)$	$U(R_2)$
0	1.1015205×10^{-4}	1.1305356×10^{-4}
1	1.1560827×10^{-6}	1.2498671×10^{-6}
2	1.2133475×10^{-8}	1.3817945×10^{-8}
3	1.2734488×10^{-10}	1.5276472×10^{-10}
4	1.3365271×10^{-12}	1.6888951×10^{-12}
5	1.4027300×10^{-14}	1.8671632×10^{-14}
6	1.4722121×10^{-16}	2.0642480×10^{-16}
7	1.5451358×10^{-18}	2.2821358×10^{-18}
8	1.6216718×10^{-20}	2.5230223×10^{-20}
9	1.7019988×10^{-22}	2.7893351×10^{-22}
10	1.7863048×10^{-24}	3.0837580×10^{-24}
11	1.8747867×10^{-26}	3.4092582×10^{-26}
12	1.9676514×10^{-28}	3.7691160×10^{-28}

3. RESULTS

A. Self-Consistent Potentials

The values for the final self-consistent potentials resulting from the calculations are available from the author on request. The APW sphere radius R_s used in these calculations was assumed to be half the distance to the first nearest neighbor, which was found to be 2.4152 Bohr units. Figure 1 shows the two self-consistent potentials as the APW program would "see" them, i.e., they have been shifted so that $V_c=0$. The starting values for the Noumerov numerical integration of the radial Schrödinger equation are listed in Table I and were used in both calculations, since they were both done on the same logarithmic radial mesh.

B. Energy-Band Structure and Fermi Surface

All the results presented here were obtained from self-consistent calculations covering 2048 equally spaced points in the Brillouin zone. The resulting eigenvalues for all the points in 1/48 of the zone are also available from the author on request.

Figure 2 shows the resulting $E(\mathbf{k})$ curves, in the directions of high symmetry, for both present calculations. These curves were plotted with respect to zero Fermi energy (E_F), as indicated in the figure by dot-

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[5] T. L. Loucks, *Augmented Plane Wave Method* (W.A.Benjamin, Inc., New York, 1967).

[6] D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York, 1957).

TABLE II. Energy differences for states which indicate position and width of the *sp* and *d* bands (in Rydbergs).

	$\Gamma_{25'}$-Γ_1	X_5-Γ_1	X_5-X_1	$X_{4'}$-Γ_1	E_F-X_5	E_F-L_3	E_F-$L_{2'}$
			Experimental				
Spicer[a]	...	...	0.205	...	0.147	...	0.026
Lettington[b]	...	...	...	...	0.147	0.162	...
			Previous calculations (not self-consistent)				
Segall[c]	0.331	0.470	0.300	0.807	0.183	0.197	0.064
Burdick[d]	0.399	0.512	0.249	0.804	0.143	0.154	0.045
Mattheiss[e]	0.463	0.570	0.252	0.794	...	...	...
Faulkner *et al.*[f]							
V_{I}	...	...	...	0.808	...	...	0.056
V_{II}	...	...	...	0.799	...	...	0.089
V_{III}	...	...	...	0.804	...	...	−0.019
			Previous calculations (self-consistent)				
Wakoh[g]	0.386	0.499	0.245	...	0.159	...	...
Snow and Waber (SW-I)[h]							
Slater = 1	0.216	0.308	0.191	0.717	0.228	0.240	0.020
Slater = $\frac{2}{3}$	0.392	0.508	0.262	0.720	0.111	0.123	0.102
			Present calculations				
Slater = 1	0.278	0.369	0.189	0.793	0.223	0.232	−0.005
Slater = $\frac{5}{6}$	0.375	0.477	0.224	0.794	0.149	0.159	0.029

[a] Reference 7.
[b] Reference 8.
[c] Reference 9.
[d] Reference 10.
[e] Reference 11.
[f] Reference 12.
[g] Reference 14.
[h] Reference 1.

dash lines labeled E_F. The *d* band for the Slater = 1 calculation is seen to be narrower and lower in energy with respect to the *sp* band then it is for the Slater = $\frac{5}{6}$ calculation. Energy differences for states, which indicate the positions and widths of the *sp* band and *d* band are given in Table II. The experimental results were taken from the photoemission studies of Berglund and Spicer[7] and Lettington.[8] Among the previous calculations that were not carried to self-consistency are the Green's-function calculation of Segall[9] and the APW calculations of Burdick[10] and Mattheiss.[11] Also included in Table II are some of the results from a set of Green's function calculations by Faulkner, Davis, and Joy.[12] In their calculations, they used three potentials; V_{I}, which is essentially the Chodorow potential described by Burdick[10]; V_{II}, generated from a superposition of atomic wave functions given by Watson[13]; and V_{III}, generated from a superposition of atomic wave functions given by Herman and Skillman.[2] The previous self-consistent calculations reported are the Green's-function calculation of Wakoh,[14] and the APW calculation of Snow and Waber.[1] In Table II, the energy differences Γ_{25}'-Γ_1 and X_5-Γ_1 indicate the location of the top of the *d* band with respect to the bottom of the *sp* band; X_5-X_1 and X_4'-Γ_1 give, respectively, the widths of the *d* band and *sp* band; and E_F-X_5 and E_F-L_3 give the location of the top of the *d* band with respect to the Fermi level. The energy difference E_F-L_2', which locates the first high-symmetry point with respect to the Fermi level, is included because it has been located by Berglund and Spicer[6] from both direct and indirect transitions.

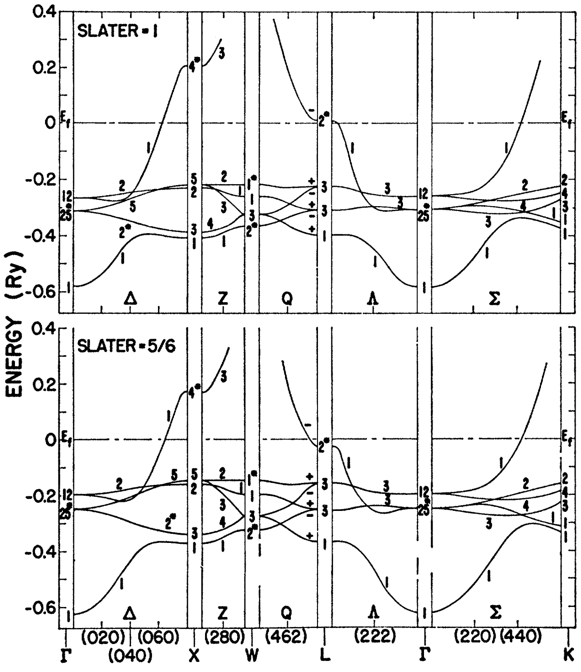

FIG. 2. $E(\mathbf{k})$ curves for self-consistent copper in directions of high symmetry, for full and $\frac{5}{6}$ exchange, shifted so that $E_F = 0.0$ Ry.

The "neck" and "belly" radii of the Fermi surface for copper from experimental results, previous calculations, and the two present self-consistent calculations are given in Table III. The tabulated experimental

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[7] C. W. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964).

[8] A. H. Lettington, Phys. Letters **9**, 98 (1964).

[9] B. Segall, Phys. Rev. **125**, 109 (1962).

[10] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[11] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

[12] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. **161**, 656 (1967).

[13] R. E. Watson, Phys. Rev. **119**, 1934 (1960).

[14] Shinya Wakoh, J. Phys. Soc. Japan **20**, 1894 (1965).

results are from the de Haas–van Alphen work of Shoenberg,[15] and the magnetoacoustic studies of Bohm and Easterling,[16] and Kamm.[17] Among the previous calculations are the Green's function calculations of Segall,[9] for his l-dependent potential and the Chodorow potential; the self-consistent APW calculations of Snow and Waber[1]; and the Green's-function calculations of Faulkner, Davis, and Joy,[12] for the three potentials described above.

The neck radius of the Fermi surface does not exist for the present Slater$=1$ calculation, because the Fermi surface does not contact the Brillouin zone boundary in the [111] direction for that calculation. It is interesting to note that a similar result was reported by Faulkner, Davis, and Joy,[12] for their V_{III} potential, which was generated from Herman and Skillman atomic wave functions. Their V_{III} potential should be similar to that used as a starting potential in the present Slater$=1$ calculation.

C. Density of States

Figure 3 shows the averaged density-of-states curves resulting from the present Slater$=1$ and Slater$=\frac{5}{6}$ self-consistent APW calculations, and also the experimental density-of-states curve resulting from the photoemission studies of Spicer.[18] All three of these curves are given with respect to the Fermi level at zero energy. The main points of comparison are the width and the location of the d band with respect to the Fermi level. The d band is described by that portion of the experimental curve between -0.16 and -0.39 Ry. Note that in all three curves there are three major peaks in the range of the d band.

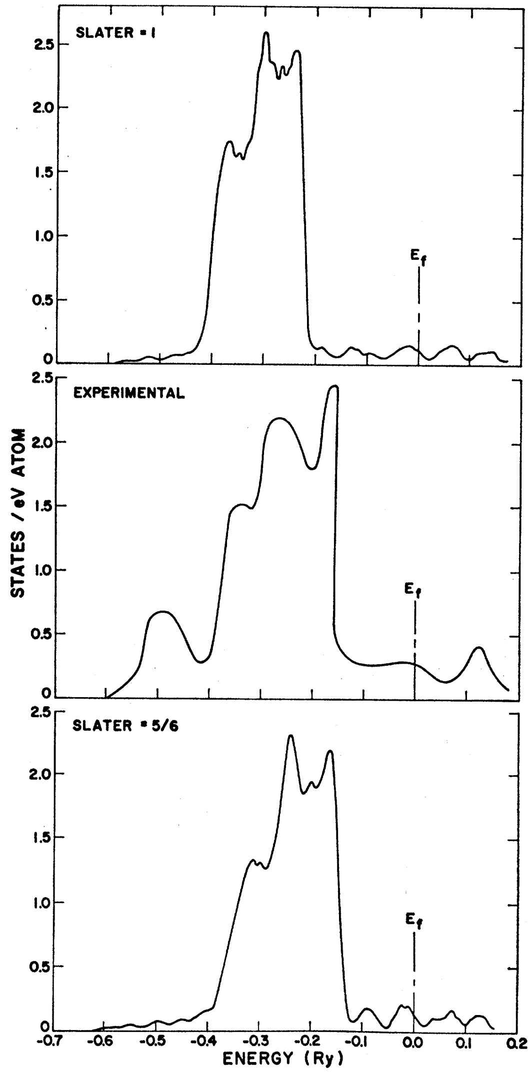

FIG. 3. Density-of-states curves from the two present self-consistent calculations and that obtained from photoemission studies by Spicer (see Ref. 18).

4. DISCUSSION

In general, both the Slater$=1$ and Slater$=\frac{5}{6}$ calculations give results that are in reasonably good agreement with those previously reported. However, as was predicted in SW-I, the results from the present Slater$=\frac{5}{6}$ calculation are in much better agreement with experimental findings than are the results from the present Slater$=1$ calculation. The values listed in Table II show that the bandwidths and relative locations with respect to the Fermi level for the Slater$=\frac{5}{6}$ calculation are in excellent agreement with the tabulated experimental results, except for the d-band widths. However, the d-band width given by Spicer has approximately the value that would be obtained if the d band at half-maximum on his experimental curve given in Fig. 3 were measured. On the other hand, the energy difference X_5-X_1 represents the width of the d-band nearer the base, which on Spicer's curve is about 0.23 Ry.

Further evidence of the excellent agreement of the Slater$=\frac{5}{6}$ results with experiment can be seen in the density-of-states curves given in Fig. 3. Not only are the d-band widths and locations in excellent agreement, but the three main peaks in the d band align very nicely with those in Spicer's experimental curve. The peak on Spicer's curve at -0.5 Ry does not appear in the calculated curve. However, Spicer's curve is an optical density of states and there is some question as

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[15] D. Shoenberg, Phil. Mag. **5**, 105 (1960).

[16] H. V. Bohm and V. J. Esterling, Phys. Rev. **128**, 1021 (1962).

[17] G. N. Kamm, Bull. Am. Phys. Soc. **11**, 446 (1966).

[18] W. E. Spicer, in *International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris 13–16 September 1965. Proceedings,* edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966).

TABLE III. Summary of the present and previously published values for the neck and belly radii of the Fermi surface for copper (in Å^{-1}).

	R_n	$R_{(100)}$	$R_{(110)}$	$R_{(100)}/R_{(110)}$
	Experimental			
Shoenberg[a]	0.28	1.40	1.38	1.014
Bohm and Esterling[b]	0.27	1.41	1.30	1.085
Kamm[c]	···	1.44	1.31	1.099
	Previous calculations			
Segall[d]				
l-dependent	0.28	1.39	1.26	1.10
Chodorow	0.20	1.43	1.29	1.11
Snow and Waber (SW-I)[e]				
Slater = 1	0.22	1.36	1.28	1.062
Slater = $\frac{2}{3}$	0.38	1.44	1.14	1.263
Faulkner *et al.*[f]				
V_{I}	0.25	1.43	1.30	1.100
V_{II}	0.29	1.45	1.28	1.133
	Present calculations			
Slater = 1	(does not exist)	1.36	1.30	1.044
Slater = $\frac{5}{6}$	0.31	1.39	1.29	1.077

[a] Reference 15.
[b] Reference 16.
[c] Reference 17.
[d] Reference 9; belly radii determined from Fig. 8 of Segall's paper.
[e] Reference 1.
[f] Reference 12.

to whether this peak should appear on the calculated curve.

The neck radius of the Fermi surface for the present Slater = $\frac{5}{6}$ calculation, as given in Table III, is slightly larger than has been reported from experimental studies. It is however, in much better agreement with experiment than either the nonexistent neck radius of the present Slater = 1 calculation or the neck radii reported in SW-I. The belly radii in both the (100) and (110) planes for the present Slater = $\frac{5}{6}$ calculation are in good agreement with the experimental results of Bohm and Easterling,[16] and Kamm.[17] The ratio of the two belly radii which is a measure of the asphericity of the Fermi surface, for the present Slater = $\frac{5}{6}$ calculation is also in good agreement with recent experimental findings.

5. CONCLUSIONS

It is concluded that the self-consistent APW method of calculating the energy-band structure of metallic copper, with the exchange reduced to $\frac{5}{6}$ of the Slater free-electron approximation, yields results that are in excellent agreement with experimental results, as was predicted by SW-I.

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