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Self-Consistent Energy Bands of Silver by an Augmented-Plane-Wave Method*

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The band structures, Fermi surfaces, and density of states from two self-consistent augmented-plane-wave calculations of silver are presented and compared with previously reported results. The full Slater exchange term was used in one of these calculations, and $\frac{5}{6}$ of the Slater term was used in the other. Comparison with experimentally obtained data indicates that the calculation having the exchange reduced to $\frac{5}{6}$ yields the better results.

1. INTRODUCTION

APPARENTLY, only a few calculations of the band structure of silver have been made. In 1961, Segall[1] reported the results of two calculations by the Green's-function method. The potentials used in his calculations were generated from both Hartree and Hartree-Fock free-ion functions. He found that the general shapes of the bands were the same for both types of potentials, but that details of the Fermi-surface geometry and the density of states differed significantly. In 1966 and 1967, Chatterjee and Sen[2] reported results for a few high-symmetry points at Γ, X, and L, determined by the orthogonalized-plane-wave method and by the composite wave variational method. None of these calculations, however, was carried to self-consistency.

The Fermi surface and density of states of silver have also been studied by several experimenters who have used a variety of methods. In 1960, Shoenberg[3] reported a value for the "neck" radius of the Fermi surface obtained from de Haas–van Alphen (dHvA) studies. In 1962, Bohm and Esterling[4] reported corresponding results obtained from magnetoacoustic measurements. They also gave values for the "belly" radii. Other work on the geometry of the Fermi surface of silver includes the magnetoresistance studies of Coleman, Funes, Plastkett, and Tapp[5]; studies of the optical properties of silver by Cooper and Ehrenreich[6]; the dHvA studies of Joseph and Thorsen[7] and of Jan and Templeton[8]; and the cyclotron-resonance experiments of Howard.[9] The density of states for silver has been reported by Berglund and Spicer,[10] and by Krolikowski[11] as a result of their photoemission experiments. The basic conclusion drawn from all these studies is that silver has a Fermi surface and a density of states that are quite similar to those of copper.

A self-consistent augmented-plane-wave (APW) method was used in making the two calculations reported here. These calculations differ in that the full Slater exchange was used in one (hereafter referred to as "Slater$=1$") while $\frac{5}{6}$ of the Slater exchange was used in the other (hereafter referred to as "Slater$=\frac{5}{6}$"). The "Slater$=\frac{5}{6}$" term was chosen because earlier work on copper by Snow and Waber[12] and by Snow,[13] had shown that reducing the exchange to $\frac{5}{6}$ resulted in better agreement with experimental results. It was thought that the calculations for silver might be similarly improved. The method of calculation used was the same as that recently reported by Snow[13] and will not be described here.

2. RESULTS

A. Potentials

The starting potentials and fixed core charge densities were generated from a superposition of Herman and Skillman[14] wave functions. The final self-consistent potentials for "Slater$=1$" and "Slater$=\frac{5}{6}$" are available from the author on request. The value assigned to the lattice constant was 4.0779*kx* units, and the APW sphere radius R_s, assumed to be half the distance to the first nearest neighbors, was found to be 2.7302 Bohr units. Both potentials are on a logarithmic mesh and start at $R_1=1.23948\times10^{-4}$ Bohr units.

The starting values needed for the numerical integration of the radial Schrödinger equation were assumed to be approximately $R^{(l+1)}$, and, as used for the numerical integration on a logarithmic mesh, are given in Table I. These starting values were used for both

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Table I. Starting values used in the numerical integration of the radial Schrödinger equation. $R_1=1.23948\times10^{-4}$ and $R_2=1.30563\times10^{-4}$ (Bohr units).

l	$U(R_1)$	$U(R_2)$
0	1.2394758×10^{-4}	1.2721248×10^{-4}
1	1.3799301×10^{-6}	1.4918737×10^{-6}
2	1.5363004×10^{-8}	1.7495824×10^{-8}
3	1.7103901×10^{-10}	2.0518081×10^{-10}
4	1.9042072×10^{-12}	2.4062408×10^{-12}
5	2.1199872×10^{-14}	2.8218988×10^{-14}
6	2.3602188×10^{-16}	3.3093582×10^{-16}
7	2.6276729×10^{-18}	3.8810221×10^{-18}
8	2.9254342×10^{-20}	4.5514362×10^{-20}
9	3.2569371×10^{-22}	5.3376587×10^{-22}
10	3.6260051×10^{-24}	6.2596945×10^{-24}
11	4.0368949×10^{-26}	7.3410044×10^{-26}
12	4.4943457×10^{-28}	8.6091014×10^{-28}

present calculations, since they depend only on R, and since the same R values were used in both calculations. On the logarithmic mesh, the starting values, as described by Snow,[13] are given by

$$U(R_1)=R_1^{(l/2+1)}$$

and

$$U(R_2)=U(R_1)e^h(l+\tfrac{1}{2}).$$

B. Energy-Band Structure and Fermi Surface

The eigenvalues calculated for all the points in 1/48 of the Brillouin zone are also available from the author on request. Both calculations covered 2048 equally spaced points in the full Brillouin zone. The self-consistency criterion used in both of these calculations was that $|\Delta E(\mathbf{k})|$ for every point in the zone be less than 0.002 Ry between successive iterations.

Figure 1 shows for both calculations, the resulting $E(\mathbf{k})$ curves in the directions of high symmetry. The d band is narrower and lower in energy with respect to the sp band for the "Slater = 1" calculation than it is for the "Slater = $\frac{5}{6}$" case.

Energy differences that give the widths of the sp band and d band and indicate their relative locations with respect to each other and to the Fermi level are listed in Table II. The experimental results included in this table are from the photoemission studies of Berglund and Spicer.[10] The previous calculations are the Green's-function calculations of Segall,[1] which include results from two potentials as mentioned above. The values listed for Segall's[1] work were taken from his two $E(\mathbf{k})$ curves and are only approximate. The energy differences $\Gamma_{25'}$-Γ_1 and X_5-Γ_1 indicate the location of the d band with respect to the bottom of the sp band. X_5-X_1 and X_4-Γ_1 give the widths of the d band and sp band, respectively. The values E_f-X_5 and E_f-L_3 locate the top of the d band with respect to the Fermi level. The energy difference E_f-$L_{2'}$ locates the high symmetry point nearest the Fermi level. This point is included because it has been determined by Berglund and Spicer[10] and by Krolikowski[11] for both direct and indirect transitions.

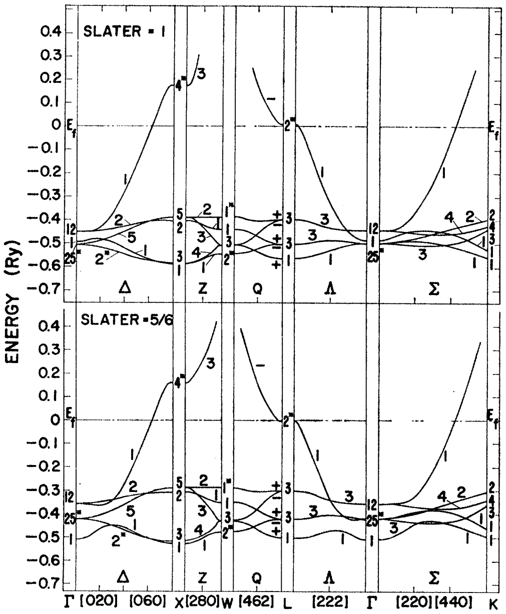

Fig. 1. $E(k)$ curves for self-consistent silver in directions of high symmetry, for "Slater = 1" and "Slater = $\frac{5}{6}$," shifted so that $E_f=0.0$ Ry.

The energy at $L_{2'}$ is above the Fermi energy for the "Slater = 1" calculation but is below it for "Slater = $\frac{5}{6}$." This indicates that the Fermi surface of silver for the "Slater = 1" calculation does not contact the Brillouin-zone boundary in the [111] direction. On the other hand, the indication for the "Slater = $\frac{5}{6}$" calculation is that the Fermi surface does contact the zone boundary

Table II. Energy-state differences that indicate position and width of the sp and d bands (in Ry).

	$\Gamma_{25'}$-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:							
Berglund and Spicer[a]	···	···	≃0.26	···	≃0.28	≃0.28	0.022
Previous calcs:							
Segall[b]							
Hartree-Fock	0.07	0.19	0.24	0.73	0.23	0.29	−0.09
Hartree	0.26	0.40	0.27	0.66	0.14	0.16	0.03
Present calcs:							
Slater = 1	−0.011	0.105	0.198	0.665	0.387	0.400	−0.013
Slater = $\frac{5}{6}$	0.090	0.221	0.235	0.667	0.290	0.304	0.007

[a] Reference 10.

[b] Reference 1.

TABLE III. Present and previously published values for the neck and belly radii of the Fermi surface for silver (in units of free-electron sphere radii).

	R_n	$R_{(100)}$	$R_{(110)}$	$R_{(100)}/R_{(110)}$
Experimental:				
Shoenberg[a]	0.14	...	...	...
Bohm and Easterling[b]	0.142	1.072	0.955	1.13
Morse[c]	...	1.006	0.975	1.03
Present calcs:				
Slater=1	(does not exist)	1.007	0.975	1.03
Slater=$\frac{5}{6}$	0.095	1.015	0.940	1.08

[a] Reference 3. [b] Reference 4. [c] Given in Ref. 4.

at L, thus forming necks similar to those found for copper. Values for the neck and belly radii are given in Table III, both for experiment and for the present calculations. These radii values are given in units of the free-electron sphere radius. The experimental values listed are from the dHvA studies of Shoenberg[3] and the magnetoacoustic studies of Bohm and Esterling[4] and of Morse.[4] The ratio of the belly radii in the [100] and the [110] directions, $R_{[100]}/R_{[110]}$, is a measure of the asphericity of the Fermi surface.

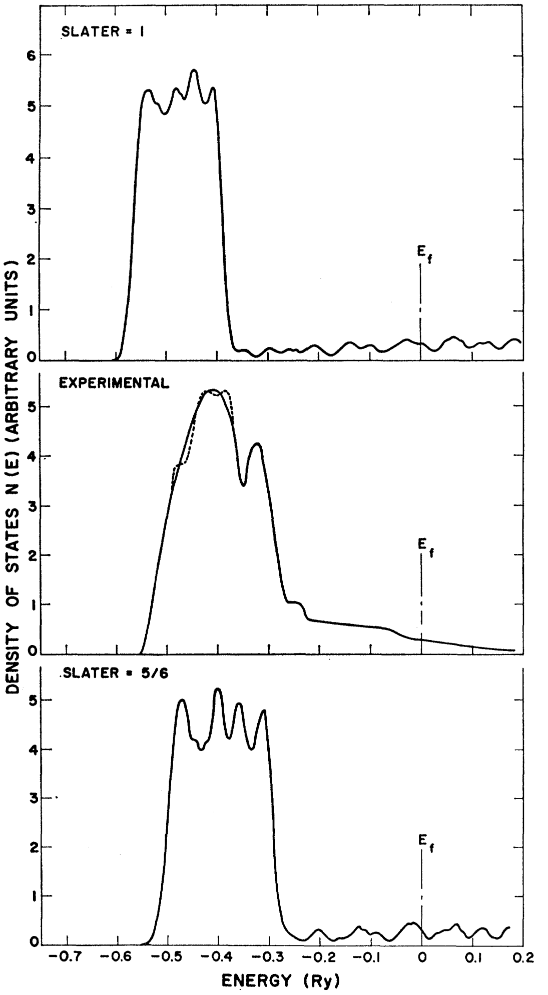

FIG. 2. Density-of-states curves from the two present self-consistent calculations and from photoemission studies by Krolikowski (Ref. 11).

C. Density of States

In Fig. 2, the averaged density-of-states curves for the two present calculations may be compared with Krolikowski's[11] experimental results. The averaging of the density of states has been described by Snow and Waber.[12] The dashed portion of the experimental curve suggests the presence of some possible fine structure in the d band observed by Krolikowski[11] and indicates that there are four peaks in the d band, which is consistent with the results of the two present calculations. The four strong peaks in the d band for the present results are also probably indicative of fine structure. However, most of the smaller variations in the curves above the d band are very likely due to statistical inaccuracies resulting from sampling significantly fewer states in this energy range.

3. DISCUSSION

In general, the results of both present calculations are in reasonably good agreement with experimentally obtained data and with previous calculations of Segall.[1] The general shapes of the bands and of the Fermi surface for silver are very similar to those found for copper, as would be expected from the similarity of the electronic structures of those two elements.

As in the copper work, the "Slater=$\frac{5}{6}$" calculation for silver agreed more closely with experiment than did the "Slater=1" calculation. In Table II, the d-band width and its relative location with respect to the Fermi level for the "Slater=$\frac{5}{6}$" calculation are in very good agreement with the experimental results given by Berglund and Spicer.[10] The location of the $L_{2'}$ point with respect to the Fermi energy for this calculation is also in good agreement with experiment.

In Table III, the neck radius for the present "Slater=$\frac{5}{6}$" calculation is somewhat smaller than that found experimentally. However, it can be seen in Fig. 1, at the $E(\mathbf{k})$ curves near $L_{2'}$ for "Slater=$\frac{5}{6}$," that the neck radius is very sensitive to small changes in the Fermi level and to statistical inaccuracies. In any event, the

"Slater$=\frac{5}{6}$" calculation does show a neck, while the "Slater$=1$" calculation does not.

Unlike the neck radius, the belly radii are far less sensitive to the location of the Fermi level, and the "Slater$=\frac{5}{6}$" results for the belly radii are in good agreement with those reported by Bohm and Esterling.[4]

The four peaks in the *d* band observed by Krolikowski are also present in the "Slater$=\frac{5}{6}$" curve (see Fig. 2). Since the experimental curve is based on an optical density of states, the relative heights of the peaks are not necessarily expected to agree with the density of states from the present calculations. However, the locations of the peaks with respect to the Fermi level should be, and are, in agreement.

4. CONCLUSION

It is concluded that although the self-consistent APW method of calculating the energy band structure of silver yields results that, in general, are in reasonable agreement with experimental findings, that agreement is improved when the Slater exchange term is reduced to $\frac{5}{6}$ of its original value.

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Knight Shift in Single-Crystal Mercury*

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The Knight shift of the Hg^{199} nucleus in oriented single crystals of mercury has been measured at $T=1.2°K$. The isotropic shift given in terms of ν_{Hg}, the resonant frequency of the Hg^{199} nucleus in the metal, and ν_D, the resonant frequency of the deuterium nucleus, is $(\nu_D)_{293°K}/(\nu_{Hg})_{1.2°K}=0.83856\pm0.00003$. The anisotropic Knight shift was measured and led to the result $(K_\perp-K_{\parallel})/K_{iso}=7.8\pm0.3\%$. Field-dependent oscillations of the Knight shift were not seen. Theoretical equations for the oscillation amplitude are discussed for particular oscillation frequencies in Hg and Sn.

I. INTRODUCTION

It was demonstrated in 1962 by Sagalyn and Hofman[1] that with proper attention to the relevant considerations, nuclear resonance signals can be seen without great difficulty in single crystals of metals. Since their original work on Cu and Al, work has been reported on the noncubic metals tin,[2] cadmium,[3] and thallium,[4] and recently on an oscillatory Knight shift in tin[5] and cadmium.[6] We have added to the list the nuclear resonance of the 16.9% abundant isotope Hg^{199} in single-crystal mercury.

Our original intention had been to search for a field-dependent Knight shift such as has been successfully seen in tin[5] and cadmium[6] subsequent to the beginnings of our work. We will report the negative results of our effort in Sec. III of this paper. In addition, we have measured both the isotropic and anisotropic Knight shifts at liquid-helium temperatures. The isotropic shift of Hg^{199} has been measured[7] accurately by observation of the resonance frequency and field in the liquid state (room temperature). The isotropic shift has also been measured,[8] with a relatively large uncertainty of 2%, at helium temperature in polycrystalline mercury. The anisotropic shift has previously only been inferred in Ref. 8 from the linewidth and line shape in polycrystalline samples at relatively low fields and temperatures.

Problems involving experimental technique played a significant role in the conduct of the experiment. We had to overcome a variety of interconnected difficulties brought about by the low abundance of the only spin-$\frac{1}{2}$ isotope, Hg^{199}, the nuclear-resonance techniques required when working with oriented single crystals, and the highly inconvenient fact that mercury is liquid at room temperature. These questions will be discussed briefly in Sec. II of this paper; for many of the details we

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