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The electronic structure of the noble metals I. The energy bands

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Abstract. Band structures for the noble metals have been calculated at twelve points in 1/48th of the Brillouin zone by the Korringa–Kohn–Rostoker method. The bands were calculated at two values of the lattice constant for copper and silver and at one value for gold. The potentials used in this calculation were constructed by a method akin to that used by Abarenkov and Heine and by Animalu and Heine for the nontransition metals. The results are presented and compared with experiment.

1. Introduction

This is the first of two papers on the electronic structure of the noble metals. The results presented here are energy bands for copper and silver calculated at two values of the lattice constant and for gold at one value. The bands are calculated by the Korringa-Kohn-Rostoker (KKR) method (Kohn and Rostoker 1954) at twelve points in 1/48th of the Brillouin zone of the face-centred cubic lattice. The bands at other points are obtained by an interpolation scheme based on the model Hamiltonian (Mueller 1967, Hodges *et al.* 1966, Jacobs 1968), which will be reported in the second paper of this series.

For a given crystalline potential it is now possible to calculate the corresponding band structure to any degree of accuracy. Both the KKR and augmented plane wave methods, for example, are well known to converge to the same answer. Thus for any substance it only remains to determine a suitable potential. This paper examines, in part, the problem of determining such a potential. In a calculation of the change in band structure due to a change in the lattice constant the most difficult problem is the self-consistent change in the potential. By setting up the potential for both lattice constants in a systematic and fundamental way we hope to obtain the correct answer for this change even if the band structures are not separately correct.

Band structure calculations for copper have previously been carried out by Segall (1962), Burdick (1963), Wakoh (1965) and Snow and Waber (1967), and for a large number of rare earth and transition metals by Mattheiss and Loucks (Loucks 1967). While the calculations for copper in general achieve good agreement with experiment, no systematic or uniform procedure for setting up the potential is used in these papers. On the other hand, Loucks and Mattheiss (Loucks 1967) have developed a systematic procedure based on Hartree-Fock-Slater calculations for free atoms which appears to give reasonably good results. Empirically this is a highly successful recipe, but it hardly does justice to many questions concerning exchange and correlation. Snow and Waber (1967) have carried out self-consistent augmented plane wave calculations of the energy bands of copper using the Slater $\rho^{1/3}$ approximation for the exchange potential and the modification of the Slater approximation by a factor of $\frac{2}{3}$ suggested by Kohn and Sham (1965). They did not include any correlation terms. Their object was to start from first principles and determine what value of the coefficient of Slater's approximate exchange potential gave the best agreement with experiment. What these many calculations do reveal is that reasonable band structures can be obtained but that certain features, in particular the position of the d bands relative to the conduction bands, are sensitive to the exact choice of the potential.

Our aim, in contrast with that of most of the previous workers, is to set up a potential by going back to fundamentals. To do this we shall take over the three main ideas which were used in setting up the model potential for non-transition metals (Abarenkov and Heine

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1965 a, Heine and Abarenkov 1964, Animalu and Heine 1965). Firstly, the potential seen by an electron is divided into two parts:

$$V = V_{\text{core}} + V_{\text{cond}}.$$

The first term contains the Hartree self-consistent potential of the core and all correlation and exchange effects of the core on the incident electrons. The second term includes all the effects due to the conduction electrons. Secondly, where convenient we represent $V_{\rm core}$ by a relatively weak pseudopotential $V_{\rm M}$ which is equivalent to dropping integral multiples of π from the phase shift producing, therefore, a radial pseudo-wave function without nodes. Thirdly, all the complications due to exchange and correlation with the core and self-consistency are taken into account exactly by fitting some parameters in $V_{\rm M}$ or $V_{\rm core}$ to the spectroscopic energy levels of a single electron in the field of an isolated ion core. For non-transition metals this procedure is almost trivial in its numerical simplicity and is probably better than some other methods because all the interactions with the core are fitted exactly. For the noble metals we shall show that it is possible to set up a reliable potential along similar lines, but more care and effort are needed. Also a certain degree of doubt is introduced in some of the levels in the bands by configurational interaction among the atomic energy levels. In §§ 2 and 3 we set up $V_{\rm core}$ and $V_{\rm cond}$ respectively. In §4 we give the resultant band structures and compare them with experiment.

In the second paper we shall discuss the description of these bands by a model Hamiltonian similar to that of Hodges *et al.* (1966) and Mueller (1967) with the intention of later applying this description to calculating band-structure-dependent experimental properties on the lines discussed by Jacobs (1968).

2. The potential for isolated atoms

We shall use a non-local potential for isolated atoms of the noble metals. For the l = 0 and 1 components of this potential it is possible to use a weak pseudopotential. The reason for this is that the highest l = 0 and 1 wave functions have several radial nodes at relatively large values of the radius. We set up this pseudopotential in exactly the fashion of Abarenkov and Heine (1965 a), i.e. we put the pseudopotential equal to an energy- and angular-momentum-dependent constant $-A_l(E)$ within a radius R_M and equal to -2/r outside R_M . The parameters $A_l(E)$ are treated as disposable constants. They have been evaluated at several energies for various values of R_M by Abarenkov and Heine (1965 b) from the atomic energy levels corresponding to the configurations $3d^{10}$ 4s, $3d^{10}$ 5s, $3d^{10}$ 6s, $3d^{10}$ 4p, $3d^{10}$ 5p and $3d^{10}$ 6p for copper and to similar configurations for the other metals. As we shall see in § 3 it is convenient to choose R_M equal to the radius of the inscribed sphere in the Wigner-Seitz cell of the metal. For values of R_M chosen in this way the constants $A_l(E)$ are easily obtained from the tables of Abarenkov and Heine. The values of R_M in each case are given in table 2.

To obtain the values of the parameters $A_l(E)$ at other energies we interpolate between the values obtained above using the best possible straight line. Unfortunately not all the values are reliable because the atomic energy levels of copper corresponding to the configurations $3d^{10}$ 5p and $3d^{10}$ 6p are heavily perturbed by interaction with the energy level corresponding to the configuration $3d^9$ 4s4p of the same symmetry (Whitelaw 1933). We shall take account of this in § 3 where we use more information obtained from the optical properties of the metal.

We require that our l = 2 potential should be adequate for electrons in the highest closed d shell which gives rise to the d bands in the metal. For copper these electrons have wave functions with no radial nodes. For gold and silver the nodes are at small values of the radius. It follows that the Abarenkov and Heine model potential is very energy dependent and therefore not very useful. We shall choose instead a model potential with an arbitrary parameter which is a good approximation to the true potential seen by the d electrons. Since we wish to avoid the difficult effects due to the relaxation of the outermost electron and to obtain a potential which includes interactions with the core electrons only, we aim at reproducing the energy levels of the singly ionized atom and choose our potential accordingly.

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We choose the analytic form of our potential to be in two parts. We provide the first part with an adjustable parameter and choose its functional form such that for some values of the adjustable parameter it is very close to the calculated atomic potential of Herman and Skillman (1963). A suitable functional form turned out to be given by the following equation:

$$V = \frac{-2\exp\{A(r-R_{\rm D})^2\}}{r}$$
(1)

where R_D is a fixed radius and A is the adjustable parameter whose value is determined from atomic energy levels as we shall see shortly. Since this part of our model potential was constructed to resemble the potential of Herman and Skillman it was taken to represent the potential seen by an electron outside the closed d shell of the free ion. Since we want our model potential to reproduce the energy eigenvalues of an electron in the d shell we need to add a term to this which is the self-exchange of an electron in the d shell. We calculate this self-exchange term using an analytic fit to the d wave functions of Herman and Skillman. For the sake of simplicity we take the spherical average of this as the second part of our model potential. This turns out to be

$$V_{\rm x,3d} = -\frac{2}{r} \left[\{1 - \exp(-\beta r)\} - \frac{\exp(-\beta r)}{n} \sum_{l=1}^{n} \frac{(n-l)(\beta r)^l}{l!} \right].$$
(2)

The values of β and n in this function were chosen to make the wave function from which $V_{x,3d}$ was calculated a good fit to the wave functions of Herman and Skillman. Our final model potential is merely the sum of these two parts. For the values of β and n chosen above and for a pre-chosen value of R_D we adjust the parameter A so that the first ionization energy (Moore 1949) of the free noble metal ion (e.g. Cu $3d^{10+}$) is reproduced exactly. The values of this parameter and of the various other constants for the three metals are presented in table 1.

Table 1. The parameters for the d potentials

	Copper	Silver	Gold
$R_{ m D}$ $(a_{ m B})$	2.7	3.0	3.0
$A (a_{\rm B}^{-2})$	0.4165	0.3957	0.4516
$B (a_{\rm B}^{-1})$	5.0	5.0	4.615
n	3	5	6

The form of the potential given by the sum of equations (1) and (2) was chosen with an eye to making the adjustable parameter a slowly varying function of the energy at least over the width of the d band and we shall in fact make the approximation that it is energy independent. This potential, while it accurately represents the situation in the d shell, can be expected to fail for electrons in higher d states for it will no longer have the correct exchange terms in it.

3. The potential in the metal

Our aim in this section is to construct effective single-particle potentials suitable for each metal from the potentials of § 2. These potentials are constructed for two values of the lattice constant for copper and silver and one value for gold. The normal lattice constants were obtained from Pearson (1958) and the lattice constants for the expanded materials were chosen large enough to give band structures in which the changes were significantly larger than the inherent numerical noise of the calculation.

We shall now assume that the electrons in the metal may be divided into two classes, viz. conduction electrons and core electrons including the d electrons. Then the potential seen by any electron may be written

$$V(\mathbf{r}) = V_{\mathrm{H core}}(\mathbf{r}) + V_{\mathrm{x core}}(\mathbf{r}) + V_{\mathrm{C core}}(\mathbf{r}) + V_{\mathrm{H cond}}(\mathbf{r}) + V_{\mathrm{x cond}}(\mathbf{r}) + V_{\mathrm{C cond}}(\mathbf{r})$$
(3)

where $V_{\rm H\ core}$, $V_{\rm x\ core}$ and $V_{\rm C\ core}$ are the Hartree, exchange and correlation potential operators due to interactions with the core electrons, and the remaining terms are the corrections to each of these terms due to the corresponding interactions with the conduction electrons in the metal. We shall now assume that at any point **r** the only contribution to each term comes from the electrons and the ion core within the same Wigner-Seitz cell. The first three terms in equation (3) may be replaced to a very good approximation by the model potentials of the previous section. We shall use local approximations for the remaining terms and discuss each of them and the final potential separately.

3.1. The Hartree term

To calculate $V_{\rm H\ cond}$ we need some model of the conduction electron charge density. The model we use will consist of a constant charge density outside spheres of radius $R_{\rm o}$ surrounding each atom and a charge density of half that value within the spheres due to orthogonalization. The radius $R_{\rm o}$ is the core radius for conduction electrons, i.e. in copper an approximate radius for 3s and 3p orbitals and similarly in the other metals. When we increase the lattice constant $R_{\rm o}$ does not change; we only have to take into account the change in the charge density which must still satisfy the condition $\int_{1\ cell} n\ d\tau = 1$. This model is clearly similar to various approximations used by Harrison (1966), Animalu and Heine (1965) and others. We estimate $R_{\rm o}$ from tables of wave functions (Herman and Skillman 1963). To obtain a spherically symmetric potential within each Wigner-Seitz cell we replace each cell by a sphere of radius $R_{\rm a}$ of the same volume. The potential we obtain is given by

$$V_{\rm H \ cond} = \frac{1+\alpha}{R_{\rm a}} \left\{ 3 - \left(\frac{r}{R_{\rm a}}\right)^2 \right\} - V_{\rm orth}$$

$$V_{\rm orth} = \frac{\alpha}{R_{\rm c}} \left\{ 3 - \left(\frac{r}{R_{\rm c}}\right)^2 \right\} \qquad \text{if } r < R_{\rm c}$$

$$= \frac{2\alpha}{r} \qquad \text{if } r > R_{\rm c}$$

$$(4)$$

where the values of the various constants are given in table 2 for each case.

Table 2. The lattice constants and parameters for $V_{\rm H \ cond}$

	Copper	Copper	Silver	Silver	Gold
а (ав)	6.8088	7.0710	7.6814	7.9195	7.6799
$R_{\rm M}$ $(a_{\rm B})$	2.4073	2.5000	2.7158	2.8000	2.7153
$R_{\rm a}$ $(a_{\rm B})$	2.6609	2.7630	3.0017	3.0948	3.0011
$R_{\rm c}$ $(a_{\rm B})$	1.6	1.6	1.9	1.9	1.95
α	0.11	0.10	0.15	0.15	0.16

3.2. The conduction term

We shall evaluate $V_{\rm x \ cond}$ using the effective potential approximation due to Kohn and Sham (1965)

$$V_{\rm x \ cond} = \frac{\rm d}{{\rm d}n} (nE_{\rm x \ cond})$$
⁽⁵⁾

where $E_{x \text{ cond}}(n)$ is the well-known Hartree-Fock exchange energy for a uniform electron gas of density n, and we obtain

$$V_{\rm x \ cond} = -\frac{1.224}{r_{\rm s}} \tag{6}$$

where r_s is the average distance between electrons. The conduction electrons are spread throughout the lattice in regions where there are few core electrons. Therefore for conduction electrons we can put r_s equal to the average distance between conduction electrons.

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The values we obtain are presented in table 3. Since the d electrons are concentrated in regions of high charge density the additional exchange with the conduction electrons is small. We may obtain a rough estimate from equation (6), which is -0.012 ryd in all cases.

Table 3. Average values for some of the terms in equation (3) suitable for constructing the total potentials

	Copper	Copper	Silver	Silver	Gold
$R_{\rm M}\left(a_{ m B} ight)$	2.4073	2.5000	2.7158	2.8000	2.7153
VH cond	0.885	0.852	0.784	0.761	0.783
$V_{\rm x \ cond} \ (l=0,1)$	-0.460	-0.443	-0.406	-0.396	-0.406
$V_{\rm x \ cond} \ (l=2)$	-0.012	-0.012	-0.012	-0.012	-0.012
$V_{\rm C \ cond}$ $(r < R_{\rm M})$	0	0	0	0	0
$V_{\rm C \ cond}$ $(r > R_{\rm M})$	-0.097	-0.095	-0.094	-0.093	-0.094
$V_0 = V_{x \text{ cond}} + V_{C \text{ cond}}$	-0.557	-0.538	-0.500	-0.489	-0.500
$(r > R_{\rm M}, l = 0, 1)$					

All potentials are in rydbergs.

3.3. The correlation term

The effective correlation potential saturates rapidly with increasing charge density. Therefore within the inscribed sphere in each Wigner-Seitz cell the total correlation is given to a good approximation by $V_{\rm C\ core}(\mathbf{r})$, i.e. $V_{\rm C\ cond}(\mathbf{r}) = 0$ in this region. In the interstices between these spheres $V_{\rm C\ cond}(\mathbf{r})$ may be obtained from the values of $E_{\rm C\ cond}$ calculated by Hubbard (1958) for a homogeneous electron gas. Animalu and Heine (1965) have tabulated $V_{\rm C\ cond}$ and the values we use are presented in table 3.

3.4. The total potential

We shall discuss the l = 0 and 1 potentials and the l = 2 potentials separately. When l = 0 and 1 the construction of the potential is very simple. We take the model potential of § 2 for the first three terms of equation (3). We add to this $V_{\rm H \ cond}$ from § 3.1 and $V_{\rm x \ cond}$ from § 3.2, $V_{\rm C \ cond}$ of course being zero from § 3.3. This gives a spherically symmetric potential for $r < R_{\rm M}$. In order to preserve the essential simplicity of the model potential for $r < R_{\rm M}$ we replace $V_{\rm H \ cond}$ and $V_{\rm x \ cond}$ by suitably weighted averages (Animalu and Heine 1965). This is valuable because the logarithmic derivatives for the KKR method can then be evaluated in terms of spherical Bessel functions and there is no need for numerical integrations.

When $r > R_{\rm M}$ (i.e. in the interstices between the inscribed sphere and the boundary of the Wigner-Seitz cell) the potential $V_{\rm H\ cond}$ is very nearly 2/r and the model potential is -2/r. Hence the sum of these terms is, to a good approximation, zero and the net potential between the inscribed spheres is

$$V_0 = V_{\rm x \ cond} + V_{\rm C \ cond} \tag{7}$$

which is easily evaluated from §§ 3.2 and 3.3 and is a constant, the muffin-tin constant.

For the KKR method we choose our energy zero at V_0 so that the final potential is obtained by adding V_0 to V from equation (3) and by evaluating the model potential at $E+V_0$. Thus our l = 0 and 1 potentials are finally in the form of square wells with energy- and *l*-dependent depths which are the values without asterisks given in table 4.

We now note that the l = 1 model potential for copper and gold is very uncertain except at the lowest energy value because the energy levels of the free atom from which the potential at other energy values is derived suffer heavily from configuration interaction (Whitelaw 1933). We can nevertheless obtain more information about the behaviour of the model potential in the metal from the optical data of Cooper *et al.* (1965) for the bulk metal. These data fix the highest d level at L relative to the lowest p level at L (i.e.

Table 4. The total potentials for l = 0 and 1

		Coppe	r	
	$R_{\rm M} = 2 \cdot$	4073 ав	$R_{\rm M}=2$	2·5000 ав
	E V	$V(E) (r < R_{\rm M})$	E	$V(E) (r < R_{\rm M})$
l = 0	0.4141	-0.1223	0.3794	-0.1389
	0.8072	0.0075	0.7725	-0.0208
	0.8957	0.0404	0.8610	0.0108
l = 1	0.6939	-0.4514	0.6592	-0.4202
	0.2250	-0.6150*	0.1952	-0.6116*
		Silver	•	
	$R_{\rm M} = 2 \cdot$	7158 а _в	$R_{\rm M} = 2$	2·8000 ав
	E = V($(E) (r < R_{\rm M})$	E i	$V(E) \ (r < R_{\rm M})$
l = 0	0.3196	-0.1494	0.2976	-0.1572
	0.7074	0.0004	0.6854	-0.0174
	0.7924	0.0407	0.7704	0.0214
l = 1	0.5945	-0.3319	0.5725	-0.3126
	0.7609	-0.2648	0.1420	-0.4868^{+}
	0.8125	-0.2492		
		Gold		
		$R_{\rm M}=2$	2·7153 а _в	
		E	$V(E) \ (r < R_{\rm M})$)
	l = 0	0.1978	-0.3526	
		0.6943	-0.1752	
		0.7878	-0.1281	
	l = 1	0.5614	-0.4719	
		0.0898	-0.7481*	
	All ene	rgies and poter	ntials are in rydb	ergs.

the level at the bottom of the conduction band gap). We may then adjust the model potential to give these levels correctly relative to each other provided of course that the d level is first corrected for spin-orbit coupling (Friedel *et al.* 1964).

This procedure gives us an l = 1 model potential for copper and gold with the normal lattice constant which is correct at the energy corresponding to the lowest p state of the free atom and which is also correct at an energy corresponding to that of the p conduction band state at L in the metal. The potential at other energy values is obtained by interpolation. A little care is needed to ensure that the potentials for expanded copper are consistent with these. This is done by requiring that when all the metallic corrections are removed the potentials for both values of $R_{\rm M}$ give the same logarithmic derivatives at a given energy and value of r. These corrected potentials for both values of the lattice constant are given in table 4 and are marked by asterisks. This same procedure is carried out for expanded silver and gives the value marked by a dagger.

For the l = 2 potential when $r < R_{\rm M}$ we take as before our model potential from § 2 and add to this $V_{\rm H\ cond}$, $V_{\rm x\ cond}$ and $V_{\rm C\ cond}$ as prescribed in §§ 3.1, 3.2 and 3.3. We are no longer allowed to approximate $V_{\rm H\ cond}$ by its average since the strongly peaked d wave functions sample $V_{\rm H\ cond}$ over a narrow range of values of r. We use equation (4) for $V_{\rm H\ cond}$. For $r > R_{\rm M}$ the potential is put equal to the muffin-tin constant obtained for the l = 0 and 1 potential. This is a good approximation because any electron in the interstices must see very nearly the same potential and because the strongly localized nature of the d wave functions makes the energy eigenvalues rather insensitive to the value of the muffin-tin constant for d electrons.

4. Calculation, results and discussion

The band structure was calculated at twelve points in 1/48th of the Brillouin zone by means of the KKR method using tables of the structure constants compiled by Ham and

Segall. At other points in the Brillouin zone the bands have been obtained from the model Hamiltonian (Mueller 1967, Hodges *et al.* 1966, Heine 1967) which will be discussed in the second paper of this series.

The calculated band structures for copper and silver are presented in figures 1 and 2 for the normal values of the lattice constant. The band structures for copper and silver at both normal and expanded lattice constants and for gold at the normal lattice constant are also presented in table 5.

We shall compare our calculated band structures for the noble metals with the following experimental evidence: (i) measurements of the Fermi surfaces of the noble metals by Shoenberg (1962) and Roaf (1962); (ii) measurements of the change in the Fermi surface when the metals are subjected to a uniform hydrostatic pressure (Templeton 1966);



Figure 1. The band structure of copper with the normal lattice constant. The full curve is the band structure interpolated between the KKR points using the model Hamiltonian.



Figure 2. The band structure of silver with the normal lattice constant. The full curve is the band structure interpolated between the KKR points using the model Hamiltonian.

(iii) the analysis by Cooper *et al* (1965) of the optical data on the noble metals; (iv) the measurements of the transverse neck effective mass by Koch *et al.* (1964) and Shoenberg (1962). In table 6 we present a comparison between the experimental quantities and the calculated quantities for a constant-energy surface corresponding to an energy E_c . This energy is chosen so that the gap $E_c - E(L_2')$ is equal to the experimental gap $E_F - E(L_2')$ obtained by Cooper *et al.* (1965). We also present for purposes of comparison the results of calculations carried out for copper by Snow and Waber (1967).

Firstly, we note that the experimental gap $E(L_2') - E(\dot{L}_{32})$ for silver is in reasonable agreement with the calculated gap when this is corrected for spin-orbit coupling (Friedel et al. 1964). The agreement is very good for copper and gold because the l = 1 potential

		Copper ($R_{\rm M} = 2.4073$	$Ba_{B}, a = 6$	·8088 а _в)		
k	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
0 0 0	-0.277	-0.004	-0.004	-0.004	0.060	0.060	
$\frac{1}{4}$ $\frac{1}{4}$ 0	-0.194	-0.030	0.008	0.017	0.038	0.076	
110	-0.048	-0.043	-0.026	0.036	0.068	0.307	
3 3 0	-0.102	-0.085	0.017	0.077	0.102	0.732	0.873
$\hat{0}$ $\frac{1}{2}$ 0	-0.238	-0.021	0.004	0.004	0.051	0.061	
0 1 0	-0.136	-0.059	0.051	0.051	0.060	0.085	
$0\frac{1}{2}0$			0.102	0.102	0.102	0.251	
010	-0.132	-0.110	0.111	0.128	0.128	0.468	0.960
111	-0.243	-0.008	0.008	0.008	0.060	0.060	_
1 1 1	-0.162	-0.008	-0.000	-0.000	0.068	0.068	
3 3 3		-0.000	-0.000	0.102	0.102	0.110	
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	-0.128	-0.004	-0.004	0.111	0.111	0.230	0.758
		Copper (1	$R_{\rm M} = 2.5000$	$a_{\rm B}, a = 7$	·0710 а _в)		
k	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
0 0 0	-0.243	-0.057	-0.057	-0.057	-0.008	-0.008	
14 I 0	-0.182	-0.076	-0.040	-0.040	-0.022	0.008	
$\frac{1}{2}$ $\frac{1}{2}$ 0	-0.102	-0.090	-0.055	-0.026	-0.001	0.229	
$\frac{3}{4}$ $\frac{3}{4}$ 0	-0.132	-0.118	-0.032	0.006	0.034	0.652	0.792
0 1 0	-0.213	-0.070	-0.045	-0.045	-0.016	0.002	
$0 \frac{1}{2} 0$	-0.146	-0.108	-0.014	-0.014	0.016	0.018	
$0 \frac{3}{4} 0$	—		0.026	0.034	0.034	0.197	
010	-0.162	-0.152	0.034	0.049	0.049	0.411	0.871
1 1 1 8 1 1	-0.221	-0.063	-0.053	-0.053	-0.006	-0.006	
\$ \$ \$	-0.158	-0.049	-0.049	-0.047	0.002	0.002	
3 3 3 8 8 8		-0.057	-0.057	0.026	0.026	0.055	
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	-0.146	-0.069	-0.069	0.034	0.034	0.181	0.640
		Silver (F	$R_{\rm M} = 2.7158$	$a_{\rm B}, a = 7 \cdot c$	6814 <i>а</i> в)		
k	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
0 0 0	-0.291	-0.277	-0.277	-0.277	-0.214	-0.214	
110	-0.288	-0.281	-0.254	-0.234	-0.231	-0.164	—
$\frac{1}{2}$ $\frac{1}{2}$ 0	-0.297	-0.294	-0.253	-0.236	-0.207	0.164	
³ ³ ² 0	-0.341	-0.321	-0.234	-0.201	-0.164	0.579	0.696
$0 \frac{1}{4} 0$			-0.261	-0.261	-0.218	-0.211	
$0\frac{1}{2}0$	-0.321	-0.298	-0.221	-0.221	-0.194	-0.089	
0 2 0						0.147	
010	-0.365	-0.361	-0.167	-0.149	-0.149	0.361	0.800
* * *	-0.290	-0.268	-0.268	-0.258	-0.215	-0.215	
4 4 4	-0.315	-0.265	-0.265	-0.207	-0.207	-0.151	
3 3 3 8 8 8						0.027	
* * *	-0.348	-0.278	-0.278	-0.161	-0.161	0.164	0.572

Table 5. The calculated band structures

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Table 5	(cont.)
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k		Band 1	Silver (R Band 2	$_{\rm M} = 2.8000$ Band 3	$a_{\rm B}, a = 7.9$ Band 4	Band 5 $a_{\rm B}$)	Band 6	Band 7
0 0	0	-0.302	-0.302	-0.302	-0.277	-0.258	-0.258	
1 1 1	0	-0.321	-0.308	-0.283	-0.260	-0.258	-0.183	
$\frac{1}{2}$ $\frac{1}{2}$	0	-0.318	-0.315	-0.272	-0.262	-0.243	0.126	
3 3 4 4	0	-0.356	-0.337	-0.265	-0.229	-0.207	0.527	0.648
$0\frac{1}{4}$	0		-0.292	-0.292	-0.280	-0.245	-0.227	
$0^{\frac{1}{2}}$	0	-0.340	-0.315	-0.253	-0.253	-0.227	-0.096	
$0^{\frac{3}{4}}$	0	<u></u>					0.126	
0 1	0	-0.384	-0.371	-0.208	-0.192	-0.192	0.331	0.721
1 1 8 8	18	-0.309	-0.296	-0.296	-0.252	-0.252	-0.246	
1 1	4	-0.327	-0.292	-0.292	-0.239	-0.239	-0.148	
3 3	3						0.006	
$\frac{1}{2}$ $\frac{1}{2}$	1/2	-0.359	-0.302	-0.302	-0.212	-0.212	0.151	0.501
			Gold (R _M	$= 2.7153 \ a_{\rm B}$	a = 7.67	99 а _в)		
k	:	Band 1	Gold $(R_{\rm M}$ Band 2	$= 2.7153 \ a_{\rm B}$ Band 3	a = 7.67 Band 4	99 а _в) Band 5	Band 6	Band 7
k 0 0	. 0	Band 1 0·442	Gold $(R_{\rm M}$ Band 2 -0.251	$= 2.7153 a_{\rm B}$ Band 3 -0.251	$a = 7.67^{\circ}$ Band 4 -0.251	99 a _в) Band 5 −0·171	Band 6 -0.171	Band 7
k 0 0 1 1	- 0 - 0	Band 1 	Gold $(R_{\rm M}$ Band 2 -0.251	$= 2.7153 \ a_{\rm B}$ Band 3 -0.251 -0.234	a, $a = 7.67^{\circ}$ Band 4 -0.251° -0.221°	99 a _B) Band 5 -0·171 -0·211	Band 6 -0.171 -0.137	Band 7
$ \begin{array}{c} \mathbf{k} \\ 0 \\ 0 \\ 1 \\ \mathbf$		Band 1 0.442 	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274	$= 2.7153 \ a_{\rm B}$ Band 3 -0.251 -0.234 -0.234	a = 7.679 Band 4 -0.251 -0.221 -0.198	$\begin{array}{l} \begin{array}{l} 29 & a_{\rm B} \ \\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	Band 6 -0.171 -0.137 0.107	Band 7
		Band 1 0.442 	Gold $(R_{\rm M} \\ \text{Band 2} \\ -0.251 \\ -0.274 \\ -0.308$	$= 2.7153 \ a_{\rm B}$ Band 3 -0.251 -0.234 -0.234 -0.234 -0.197	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152	$\begin{array}{l} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502	Band 7
$ \begin{array}{c} \mathbf{k} \\ 0 \\ 0 \\ 14 \\ 12 \\ 34 \\ 0 \\ 4 \\ 14 \\ 12 \\ 34 \\ 0 \\ 4 \\ 14 \\ 14 \\ 15 \\ 15 \\ 14 \\ 15$		Band 1 0.442 0.287 0.338	Gold $(R_{\rm M} \\ \text{Band } 2$ -0.251 -0.274 -0.308 -0.261	$= 2.7153 \ a_{\rm B}$ Band 3 -0.251 -0.234 -0.234 -0.197 -0.234	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234	$\begin{array}{l} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161	Band 7
k 0 4 12 2 2 2 0 4 12 2 2 4 14 0 12		Band 1 -0.442 -0.287 -0.338 -0.325	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305	$= 2.7153 \ a_{\rm B}$ Band 3 $= -0.251 \\ -0.234 \\ -0.234 \\ -0.197 \\ -0.234 \\ -0.181$	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181	$\begin{array}{l} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140	Band 7
$ \begin{array}{c} \mathbf{k} \\ 0 \\ 1 \\ 1 \\ 2 \\ 3 \\ 1 \\ 1 \\ 2 \\ 3 \\ 1 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 3 \\ 1 \\ \mathbf$	0 0 0 0 0 0 0 0 0	Band 1 -0.442 -0.287 -0.338 -0.325	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305 -0.305	$= 2.7153 \ a_{\rm B}$ Band 3 $= -0.251 \\ -0.234 \\ -0.234 \\ -0.197 \\ -0.234 \\ -0.181 \\ -0.181$	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181 -0.181	$\begin{array}{c} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \\ \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140 0.054	Band 7
$ \begin{array}{c} \mathbf{k} \\ 0 \\ 1 \\ 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 3 \\ 1 \\ \mathbf$	0 0 0 0 0 0 0 0 0 0 0	Band 1 -0.442 -0.287 -0.338 -0.325 -0.365	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305 -0.358	$= 2.7153 \ a_{\rm B}$ Band 3 $= -0.251 \\ -0.234 \\ -0.234 \\ -0.197 \\ -0.234 \\ -0.181 \\ -0.109$	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181 -0.087	$\begin{array}{c} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \\ \\ -0.087 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140 0.054 0.261	Band 7
k 0 1 1 2 2 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1		Band 1 -0.442 -0.287 -0.338 -0.325 -0.365	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305 -0.358 -0.271	$= 2.7153 \ a_{\rm B}$ Band 3 $= -0.251 \\ -0.234 \\ -0.234 \\ -0.197 \\ -0.234 \\ -0.181 \\ -0.109 \\ -0.248$	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181 -0.087 -0.248	$\begin{array}{c} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \\ \\ -0.087 \\ -0.174 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140 0.054 0.261 -0.174	Band 7
k 0 4 5 4 6 4 1 5 4 1 5 4		Band 1 -0.442 -0.287 -0.338 -0.325 -0.365 -0.351	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305 -0.358 -0.271 -0.234	$= 2.7153 \ a_{\rm B}$ Band 3 $= -0.251 \\ -0.234 \\ -0.234 \\ -0.197 \\ -0.234 \\ -0.181 \\ -0.109 \\ -0.248 \\ -0.234 $	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181 -0.087 -0.248 -0.224	$\begin{array}{c} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \\ \hline \\ -0.087 \\ -0.174 \\ -0.157 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140 0.054 0.261 -0.174 -0.174 -0.157	Band 7
k 0 4 2 2 4 4 2 3 1 8 3 8 3 8 4 8 8 8 8 8 8 8 8 8 8 8 8 8 8		Band 1 -0.442 -0.287 -0.338 -0.325 -0.365 -0.351	Gold $(R_{\rm M}$ Band 2 -0.251 -0.274 -0.308 -0.261 -0.305 -0.358 -0.271 -0.234	$= 2.7153 a_{\rm B}$ Band 3 = 0.251 $= 0.234$ $= 0.234$ $= 0.197$ $= 0.234$ $= 0.181$ $= -0.109$ $= 0.248$ $= 0.234$ $= -0.234$	$a = 7.67^{\circ}$ Band 4 -0.251 -0.221 -0.198 -0.152 -0.234 -0.181 -0.087 -0.248 -0.224 -0.224	$\begin{array}{c} 99 \ a_{\rm B}) \\ \text{Band 5} \\ -0.171 \\ -0.211 \\ -0.164 \\ -0.106 \\ -0.194 \\ -0.161 \\ -0.087 \\ -0.174 \\ -0.157 \\ -0.157 \\ -0.157 \end{array}$	Band 6 -0.171 -0.137 0.107 0.502 -0.161 -0.140 0.054 0.261 -0.174 -0.174 -0.157 -0.070	Band 7

The energies are in rydbergs and the **k** vectors in units of $2\pi/a$.

was adjusted to make this agreement good. This adjustment was not made for silver. We next note that all the features of the experimental Fermi surface of silver are in excellent agreement with those of the calculated constant-energy surfaces. In copper and gold the belly radii of our constant-energy surface are rather small compared with the experimental belly radii. Nevertheless, in copper the ratio of the belly radius in the ΓX direction to that in the ΓK direction is close to the experimental ratio. This is not true in gold, presumably because we have ignored spin-orbit coupling. The disagreement between the experimental and calculated belly radii for these two metals arises ultimately from the fact that the d band is too low relative to the conduction band. The values of the neck radii of our constant-energy surface are in moderately good agreement with the neck radii of the experimental Fermi surfaces. The agreement is closest in the case of silver.

The calculated transverse neck effective masses which are obtained from the interpolated band structures are not very close to the experimental values. Part of the disagreement may be due to the effects of the electron-phonon interaction. In table 6 we also present calculated values for copper and silver of $d(\lg A_n)/d(\lg A_s)$, the ratio of the relative change of the neck cross-sectional area to the relative change of the cross-sectional area of a nearly-free-electron Fermi surface when the metal is subjected to a uniform dilation or contraction. In calculating this we have made use of the band structures and the values of $m_{\perp}(L_2')$ for two values of the lattice constant for both metals and the experimentally determined quantities $d(\lg A_b)/d(\lg A_s)$. The calculated and experimental values of $d(\lg A_n)/d(\lg A_s)$ are in very reasonable agreement for both copper and silver.

We conclude that our method for calculating the band structures has worked well for silver, but that the band structures for copper and gold are not so reliable possibly because

		Copper	Silver	Gold
$E(L_2') - E(L_3)$ (ryd)	Experimental	0.109	0.270	0.144
	Calculated	0.119	0.325	0.203
	Calculated with	0.112	0.308	0.120
	spin–orbit coupling			
Belly radius of constant energy	Experimental	0.943	0.965	0.945
surface along ΓK in units of k_s		(0.872		
	Calculated	(0.939*)	0.938	0.926
		(0.8367		
Belly radius of constant energy	Experimental	1.076	1.029	1.129
surface along I'X in units of k_s	01111	0.982	1 01 2	1.046
	Calculated	₹ 0.998*	1.012	1.040
	D	(1.030)	0.14	0.19
Neck radius of constant energy	Experimental	0.20	0.14	0.18
surface along LK in units of R_s	Calculated	0.16*	0.12	0.14
	Calculated	0.28†	012	011
$m_{\rm e}(I_{\rm e})$ (A II)	Experimental	0.46	0.35	
for normal lattice constant	Calculated	0.29	0.28	
$m_{\rm c}(T_{\rm c})$ (A II)	Calculated	0.31	0.35	
for expanded lattice constant	Calculated	0.91	0.55	
$d(\log A)$				
$\frac{d(lgA_b)}{d(l=4)}$	Experimental	0.91 ± 0.01	$0{\cdot}84\pm0{\cdot}03$	$0{\cdot}78\pm0{\cdot}08$
d(lgA _s)				
$d(lgA_n)$	Experimental	4.2 ± 0.2	7.3 ± 0.7	5.4 ± 0.2
$d(lgA_s)$	Calculated	4.5	9.5	

Table 6. Comparison of the calculated band structures with experiment

All Fermi surface dimensions are given in units of $k_s = 4.912/a$, the radius of a one-electron free Fermi sphere. The calculated results marked with asterisks and daggers have been obtained from a self-consistent method using the Slater exchange potential with coefficients of 1 and § respectively (Snow and Waber 1967).

of the uncertainties due to configuration interaction discussed in § 3.4. It is notable that in copper we nevertheless obtain the correct answer for $d(\lg A_s)/d(\lg A_s)$ which depends only on the way in which the band structure changes when we change the lattice constant.

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