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Abstract. The energy band structure of metallic gold has been calculated by non-relativistic and relativistic augmented plane wave methods. The $E(k)$ against k curves are plotted for some directions of high symmetry. The conduction band is an s–d mixture. The density of states curves are plotted. The results are compared with available experimental and other theoretical data on the band structure of gold.

1. Introduction

The first elaborate band structure calculations using the augmented plane wave (a.p.w.) method proposed by Slater (1937) were made by Burdick (1963) for copper thereby establishing the power of this technique. Since then a large number of band structure calculations have been reported by others on different elements. Loucks (1967) has given a list of metals for which a.p.w. calculations have recently been made. Snow and Waber (1967) and Snow (1968 a, b) have recently made self-consistent non-relativistic a.p.w. energy band structure calculations on copper and silver. Loucks (1967) has maintained that for metals having atomic numbers greater than about 71, the relativistic effects become prominent. He has developed the relativistic augmented plane wave method (Loucks 1965 a, 1966) which he has applied to tungsten (Loucks 1965 b) and lead (Loucks 1965 a).

Even though much work has been reported on noble metals such as copper and silver, no *ab initio* complete band structure calculations have been made for gold. Cooper *et al.* (1965) have described the experimental results on optical properties of gold. Mande (1960) has described x-ray work on gold. Also extensive data are available on the shape and size of the Fermi surface of gold (Morse 1960, Shoenberg 1960). The present work describes two sets of complete energy band structure, Fermi energy and the density of states calculations for gold via non-relativistic and relativistic a.p.w. methods. A comparison is made with available data from experiments and other theoretical calculations.

2. Theory

The theory of both the relativistic as well as the non-relativistic a.p.w. method is given in detail by Loucks (1967). The calculations were made on a CDC-3600 computer. Programs were based on those given by Loucks (1967). The non-relativistic a.p.w. programs were tested by making energy band calculations for points along one symmetry axis in the

Brillouin zone for copper. These results coincided with the initial results of Snow and Waber (1967).

3. Potential

The potential used in the present calculations is the standard muffin-tin type, that is spherically symmetric inside the a.p.w. spheres and constant in space outside the spheres. The a.p.w. sphere radius was so chosen to be equal to one half the nearest-neighbour distance in the face-centred cubic lattice. The crystal potential was constructed by a superposition (Mattheiss 1964) of the atomic potentials from up to the 14th nearest neighbours in the face-centred cubic lattice. The atomic potentials used in calculating the crystal potential were from the self-consistent Dirac–Slater calculations made by Liberman *et al.* (1965). Snow and Waber (1967) and Snow (1968 a, b) have tried different exchange potentials and report that $\frac{5}{6}$ Slater exchange gives better results; however, the present calculations were done taking unit Slater exchange. The radial mesh employed was a logarithmic scale, the starting point of which was chosen to $-8.647\,523$ for the non-relativistic case and $-8.651\,114$ for the relativistic case (since the lattice constants for the two cases are different); an interval of mesh of 0.05 was used.

4. Non-relativistic calculation

Gold has a lattice constant equal to 4.0786 Å (American Society for Testing Materials, Philadelphia powder diffraction file). The a.p.w. sphere radius obtained is 2.725 a.u. The constant potential outside the a.p.w. sphere is found to be -1.0535 ryd. The muffin-tin potential is so adjusted as to make this constant potential zero.

Taking l values up to 6 the logarithmic derivatives $R'(l, E)/R(l, E)$ were found, where $R(l, E)$ is the solution of the radial Schrödinger equation for fixed l and E, l being the orbital quantum number and E the energy in ryd. As expected, these derivatives differ from the free-electron case in that there is no discontinuity for $l = 0$ when plotted against energy. However, the logarithmic derivative for gold resembles that of copper and has discontinuity for $l = 2$ at $E = 0.64$ ryd.

The energy eigenvalues were computed for 89 points in $\frac{1}{48}$ of the Brillouin zone. From these, the energy eigenvalues for 2048 uniformly distributed points of the Brillouin zone were obtained by the application of symmetry properties. The points in the Brillouin zone are labelled according to their symmetry in the standard BSW way (Bouchaert *et al.* 1936). The present calculations were up to 0.82 ryd for some points whereas for most points the lower limit was used. The aim was to locate the Fermi energy and so the region below and
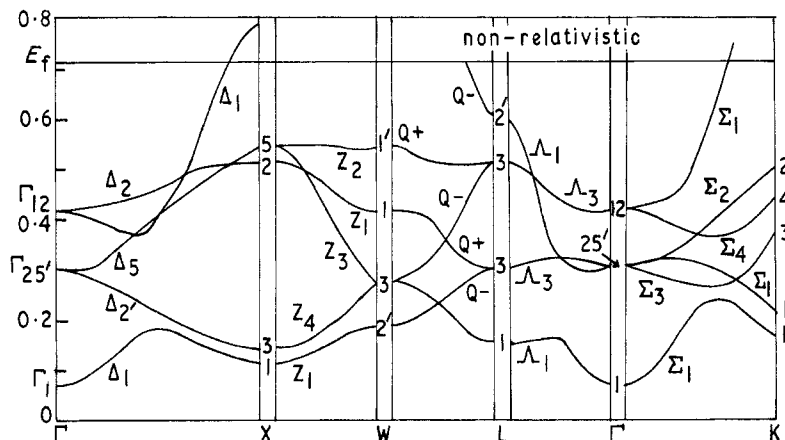

Figure 1. Non-relativistic energy bands for gold. Energies are in rydbergs and constant potential outside the a.p.w. spheres is zero.

immediately above it was carefully scanned. The eigenvalues were obtained by finding the zeros of the 32 × 32 determinant. Figure 1 gives the plot of energy curves in certain symmetric directions.

To locate the Fermi level, the energy eigenvalues for each point in the Brillouin zone were labelled in increasing order of magnitude. In the case of gold the states arising from up to 5p levels of the atom will be completely filled. Only 5d and 6s levels of the atom are expected to form the conduction band. Hence while finding the Fermi energy we take into account only the ten d electrons and one s electron per atom. Since each energy level can accommodate two electrons of opposite spin, the first 5·5 × 2048 = 11 264 energy levels will be occupied and all higher energies will be unoccupied. The Fermi energy is found to be 0·713 ryd. To this we should add the constant potential and we obtain

$$E_f = 0.713 - 1.0535 = -0.3405 \text{ ryd} = -4.638 \text{ eV}.$$

The density of states is defined as half the number of electrons per unit energy interval (in eV) per atom. The number of electrons per electron volt per atom is plotted against the energy (figure 2). The histogram has the bar width of 0·005 ryd and is an average of five different histograms of bar width 0·025 ryd.

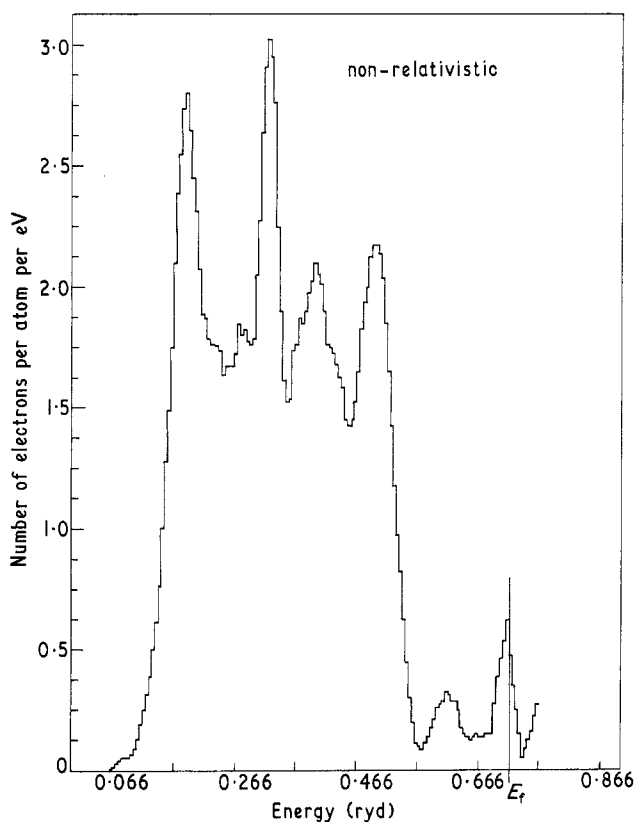Figure 2. Non-relativistic histogram for the number of electrons per atom per electron volt. Energies are in rydbergs.

5. Relativistic calculations

The relativistic calculations are made in accordance with Louck's (1967) theory. The lattice constant was chosen to be 7·6799 a.u. This lattice constant has been used by Jacobs (1968). The maximum value of κ (see Loucks 1967, chapter 4, equation 4.78) was taken to be

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Table 1. The relativistic energy eigenvalues for various points in the Brillouin zone

BSW symbol	k	Energy eigenvalues in rydbergs						
		Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
Γ	000	−0·157	0·134	0·134	0·231	0·300	0·300	
Δ	010	−0·143	0·132	0·137	0·233	0·303	0·310	
Δ	020	−0·105	0·125	0·148	0·242	0·292	0·319	
Δ	030	−0·047	0·110	0·161	0·261	0·286	0·334	
Δ	040	0·010	0·090	0·186	0·288	0·301	0·356	
Δ	050	0·031	0·069	0·249	0·318	0·344	0·386	
Δ	060	0·024	0·052	0·321	0·345	0·420	0·432	
Δ	070	0·013	0·041	0·359	0·371	0·451	0·562	
X	080	0·010	0·039	0·372	0·389	0·469	0·645	0·978
Σ	110	−0·130	0·133	0·138	0·236	0·295	0·303	
	120	−0·093	0·127	0·147	0·245	0·289	0·323	
	130	−0·037	0·113	0·158	0·265	0·283	0·343	
	140	0·019	0·094	0·176	0·291	0·298	0·372	
	150	0·040	0·074	0·224	0·323	0·340	0·415	
	160	0·032	0·058	0·284	0·353	0·396	0·490	
	170	0·021	0·048	0·329	0·374	0·436	—	
Z	180	0·018	0·046	0·354	0·381	0·455	—	
Σ	220	−0·058	0·127	0·148	0·255	0·280	0·339	
	230	−0·007	0·119	0·153	0·270	0·273	0·369	
	240	0·045	0·105	0·158	0·285	0·297	0·414	
	250	0·066	0·090	0·184	0·320	0·332	0·476	
	260	0·056	0·076	0·229	0·349	0·379	—	
	270	0·044	0·068	0·270	0·364	0·418	—	
	280	0·041	0·067	0·297	0·366	0·438	—	
Σ	330	0·035	0·121	0·154	0·259	0·283	0·414	
	340	0·077	0·118	0·155	0·265	0·304	0·472	
	350	0·098	0·110	0·159	0·299	0·334	0·548	
	360	0·087	0·104	0·183	0·331	0·372	—	
	370	0·073	0·101	0·214	0·342	0·410	—	
Z	380	0·069	0·102	0·234	0·342	0·429	—	
Σ	440	0·096	0·122	0·176	0·253	0·319	0·541	
	450	0·100	0·125	0·181	0·277	0·344	—	
	460	0·095	0·129	0·180	0·309	0·376	—	
	470	0·086	0·135	0·186	0·323	0·410	—	
W	480	0·085	0·140	0·192	0·329	0·429	—	
Σ	550	0·084	0·140	0·208	0·278	0·361	—	
	560	0·073	0·139	0·218	0·305	0·387	—	
	570	0·069	0·132	0·224	0·328	0·416	—	
K	660	0·053	0·128	0·258	0·322	0·404	—	
Δ	111	−0·118	0·135	0·138	0·240	0·297	0·315	
	121	−0·082	0·130	0·146	0·249	0·289	0·325	
	131	−0·028	0·118	0·155	0·261	0·291	0·347	
	141	0·025	0·102	0·169	0·275	0·322	0·379	
	151	0·045	0·083	0·211	0·300	0·370	0·428	
	161	0·038	0·066	0·268	0·331	0·412	0·518	
	171	0·028	0·056	0·314	0·358	0·438	—	

BSW symbol	k	Energy eigenvalues in rydbergs						
		Band 1	Band 2	Band 3	Band 4	Band 5	Band 6	Band 7
S	181	0·026	0·054	0·340	0·370	0·448	—	
	221	−0·051	0·134	0·147	0·254	0·288	0·339	
	231	−0·005	0·130	0·154	0·256	0·298	0·368	
	241	0·038	0·121	0·160	0·264	0·330	0·412	
	251	0·057	0·106	0·185	0·287	0·374	0·480	
	261	0·055	0·088	0·227	0·318	0·408	—	
	271	0·048	0·077	0·267	0·343	0·428	—	
	281	0·047	0·075	0·219	0·356	0·434	—	
	331	0·025	0·134	0·166	0·249	0·305	0·410	
	341	0·054	0·131	0·176	0·254	0·328	0·468	
	351	0·074	0·122	0·179	0·279	0·364	0·545	
	361	0·080	0·110	0·193	0·308	0·396	—	
	371	0·075	0·105	0·217	0·328	0·416	—	
	381	0·074	0·106	0·233	0·337	0·425	—	
	441	0·069	0·129	0·206	0·248	0·337	—	
	451	0·084	0·123	0·206	0·271	0·361	—	
	461	0·094	0·118	0·198	0·298	0·389	0·470	
Q	471	0·092	0·127	0·193	0·317	0·411	—	
	551	0·079	0·131	0·222	0·277	0·373	—	
	561	0·074	0·134	0·220	0·301	0·395	—	
Λ	222	−0·029	0·140	0·155	0·251	0·303	0·344	
	232	0·000	0·138	0·175	0·247	0·323	0·370	
	242	0·030	0·136	0·183	0·251	0·365	0·415	
	252	0·050	0·125	0·192	0·268	0·402	0·503	
	262	0·058	0·109	0·218	0·291	0·422	—	
	272	0·058	0·099	0·249	0·315	0·427	—	
U	282	0·060	0·097	0·267	0·335	0·422	—	
	332	0·012	0·136	0·214	0·244	0·338	0·399	
	342	0·029	0·134	0·219	0·258	0·367	0·459	
	352	0·049	0·129	0·212	0·270	0·400	0·556	
	362	0·068	0·121	0·213	0·284	0·416	—	
	372	0·078	0·118	0·221	0·301	0·418	—	
	442	0·037	0·132	0·225	0·284	0·368	0·576	
	452	0·053	0·128	0·225	0·287	0·390	—	
Q	462	0·076	0·121	0·220	0·286	0·405	—	
	552	0·060	0·128	0·230	0·290	0·395	—	
Λ	333	0·008	0·134	0·228	0·294	0·368	0·398	
	343	0·016	0·133	0·224	0·315	0·399	0·456	
	353	0·034	0·132	0·221	0·299	0·417	0·593	
	363	0·059	0·130	0·223	0·283	0·420	—	
	443	0·016	0·132	0·222	0·345	0·405	0·510	
Q	453	0·030	0·133	0·223	0·328	0·412	0·593	
L	444	0·010	0·134	0·224	0·386	0·437	0·482	0·776

In order to obtain the correct energy for a given k the value of constant potential between spheres ($-$ 1·0653 ryd) must be added to the listed value. For listed values of k see Burdick (1963).
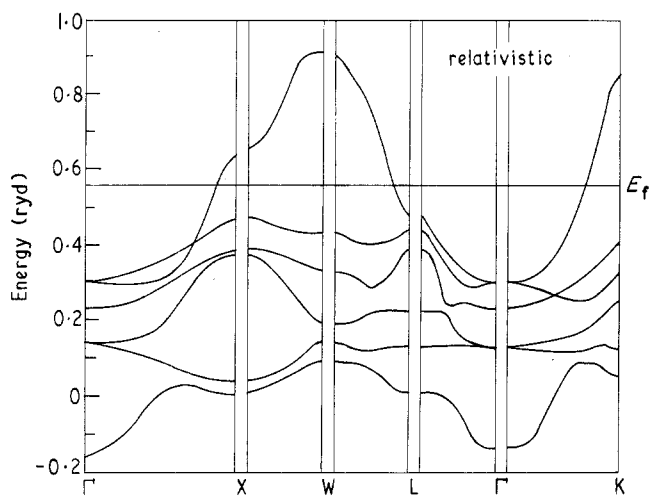
Figure 3. Relativistic energy bands for gold. Energies are in rydbergs with constant potential outside the a.p.w. sphere set equal to zero.
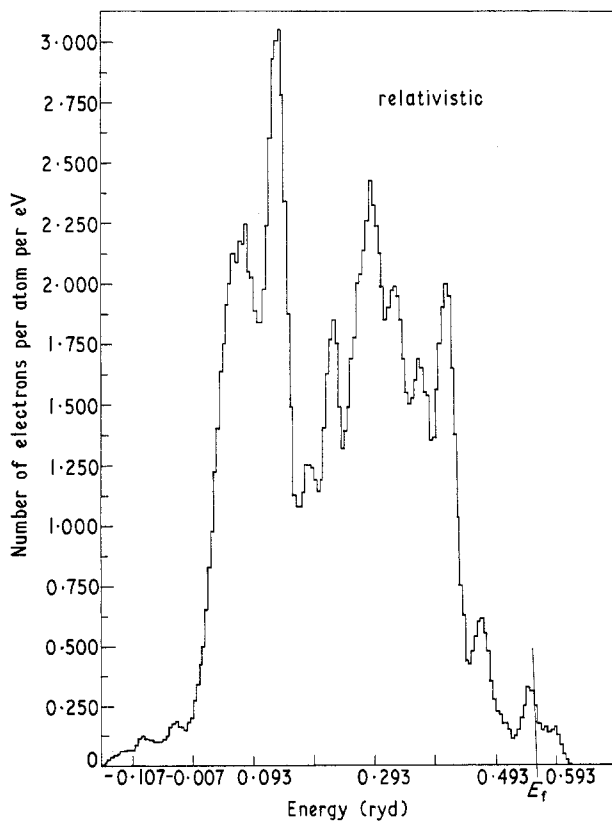

Figure 4. Relativistic histogram for the number of electrons per atom per electron volt. Energies are in rydbergs.

seven. As in the non-relativistic case a discontinuity is found in the logarithmic derivative when plotted against energy for both positive and negative κ. The energy eigenvalues are found by obtaining the zeros of a 24×24 determinant. The eigenvalues for different points of the Brillouin zone are tabulated in table 1 and plotted in some symmetry directions in figure 3. Fermi energy obtained is 6·92 eV as against the free-electron model value of 5·5 eV. The number of electrons per atom per electron volt is plotted against energy in figure 4.

6. Discussion

Chatterjee and Sen (1968) have calculated energy eigenvalues for gold at a few symmetry points of the Brillouin zone by the quantum-defect method. Table 2 provides a comparison between their values and the present calculations.

Jacobs (1968) has calculated the band structure for the noble metals using the Korringa–Kohn–Rostoker method. A comparison for some points for gold is given in table 3.

Table 2

Points	(1)	(2)	(3)
Γ_s	$-1\cdot0122$	$-0\cdot988$	$-1\cdot222$
X_s	$-0\cdot3278$	$-0\cdot507$	$-0\cdot596$
X_p	$-0\cdot3636$	$-0\cdot515$	$-0\cdot676$
L_s	$-0\cdot5857$	$-0\cdot542$	$-0\cdot679$
L_p	$-0\cdot4409$	$-0\cdot452$	$-0\cdot528$

(1) Chatterjee and Sen (1968); (2) present non-relativistic; (3) present relativistic. All energies are in ryd.

Table 3

	(1)	(2)	(3)
X'_4–X_5	0·348	0·240	0·176
$\Gamma_{25'}$–Γ_1	0·191	0·234	0·291
X'_4–Γ_1	0·703	0·721	0·802
X_5–Γ_1	0·355	0·481	0·626
X_5–X_3	0·271	0·405	0·430
X_1 upper–X_5	—	0·770	0·509
L_1 upper–L'_2	0·368	0·486	0·294

(1) Jacobs (1968); (2) present non-relativistic; (3) present relativistic. All energies are in ryd.

6.1. Fermi surface

Shoenberg (1962) has measured the size of the Fermi surface of gold. He reports that the Fermi surface touches the Brillouin zone on the hexagonal faces. The present calculations, both relativistic and non-relativistic, confirm this.

The Fermi surface is given explicitly by the equation

$$E(k) = E_f.$$

The Fermi energy was found as described earlier. E_f contours of constant energy have been found in three planes, namely $\langle 100 \rangle$, $\langle 110 \rangle$ and the hexagonal plane $\langle 111 \rangle$. This was done for both non-relativistic and relativistic cases. The contours for E_f are shown in figure 5 for the relativistic case. The contours for the non-relativistic case are almost similar. The striking features of the Fermi surface are (i) a neck on the hexagonal face and (ii) a deviation from spheres in the belly region.

The shape of the Fermi surface is in agreement with the experiments of Shoenberg (1962), Roaf (1962) and Morse (1960). Table 4 gives a comparison between experimental and calculated values of some of the Fermi surface parameters.

Table 4

	(1)	(2)	(3)	(4)
Belly radius along Γ–K	1·21	1·2	1·149	1·182
Belly radius along Γ–X	1·26	1·435	1·392	1·417
Neck radius	0·22	0·228	0·287	0·222

(1) Morse (1960); (2) Shoenberg (1962) and Roaf (1962); (3) present non-relativistic;
(4) present relativistic. All the values are in p units (10^{-19} gm cm s^{-1}).

6.2. Thermal data

The number of electrons per atom per electron volt (twice the density of states) at Fermi energy is found to be 0·620 for the non-relativistic case and 0·303 for the relativistic case. The electronic specific heat coefficient γ values for the two cases are $3·473 \times 10^{-4}$ and $1·697 \times 10^{-4}$ cal mol^{-1} deg C^{-2}. Martin (1964) and Du Chatenier and De Nobel (1962) have given experimental values of γ to be $1·74 \times 10^{-4}$ and $1·76 \times 10^{-4}$ cal mol^{-1} deg C^{-2}.

6.3. X-ray data

The x-ray absorption spectra reveal the nature of the unoccupied part of the conduction band while the emission spectra reveal the nature of the occupied part of the band. Mande (1960) has studied absorption and emission of x-rays for gold. The width of the occupied
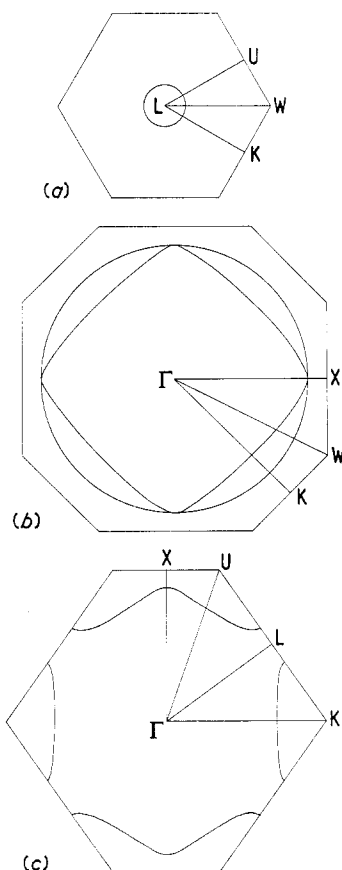

Figure 5. Intersection of Fermi surface with (a) hexogonal face $\langle 111 \rangle$, (b) $\langle 100 \rangle$ plane and (c) $\langle 110 \rangle$ plane. Relativistic calculations.

conduction band reported by him is 8·1 eV. The present non-relativistic calculations give this to be 8·798 eV (non-relativistic) and 9·696 eV (relativistic). While Mande reports the peak of the band to be 5·0 eV below the Fermi energy, in the present calculations the highest peak is found to be 5·3 eV below the Fermi energy in the non-relativistic case and 5·64 eV for the relativistic case.

Acknowledgments

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