Self-Consistent Band Structure of Aluminum by an Augmented-Plane-Wave Method*

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Two self-consistent band-structure calculations by the augmented-plane-wave method have been completed for metallic aluminum. In one, the rigid-core model was used. That is, only the conduction band $(3s,3p)$ functions were allowed to vary as self-consistency was achieved. In the second, the $(2s,2p)$-core as well as the conduction-band functions were allowed to vary. Though the differences in the core eigenvalues of these two calculations were about 0.03 Ry, differences between equivalent states in the two bands were less than 0.001 Ry. Both self-consistent-field calculations are in good agreement with previously reported theoretical results. The calculations indicate that the Fermi surface of the third zone is multiply connected at the zone corner W, but the calculations are not sufficiently precise to allow any definite conclusions to be drawn on this matter.

INTRODUCTION

SEVERAL theoretical and experimental studies of the electronic structure of aluminum have been made. Most of these are in reasonably good agreement as to the general shape of the bands and the Fermi surface, but there are differences of opinion about the topology of the Fermi surface near the point W in the Brillouin zone. Gunnersen[1] studied the de Haas–van Alphen effect in aluminum. His results indicated that there are pockets of electrons near the Brillouin-zone boundary, but he did not locate these well enough to describe the shape of the Fermi surface. About the same time, Heine[2-4] determined the band structure and Fermi surface of aluminum from experimental data on both the de Haas–van Alphen and the anomalous skin effects and also from low-temperature specific-heat data. In addition he calculated the band structure by the orthogonalized-plane-wave (OPW) method. Thus, he was able to describe the Fermi surface of aluminum as consisting of a first zone nearly full of electrons, except for small pockets of holes at the zone corners; a second zone nearly empty, except for pockets of electrons near the zone faces, but not including the zone corners; and a third zone with only a few electrons in small isolated regions along the zone edges. Harrison[5] reanalyzed the de Haas–van Alphen data of Gunnersen[1] and found it to be consistent with a free-electron model of the Fermi surface for aluminum. In this model, the first zone is completely full, the second zone contains a single closed Fermi surface near the zone boundary surrounding a nearly empty zone, the third zone contains along the zone edges regions of electrons which are multiply connected at the zone corners, and the fourth zone contains small pockets of electrons at the zone corners. The multiply connected regions in the

third zone form what is referred to as "Harrison's monster." Harrison[6] later extended Heine's OPW calculation and deduced a Fermi surface almost the same as that described above except for a rounding of the edges of the surface which occurs in the second zone. Segall[7] used the Green's-function method to determine the band structure of aluminum and obtained results consistent with those of Harrison. Moore and Spong[8] studied the cyclotron resonance of aluminum. Their results did not provide topological details of the Fermi surface but did indicate that the regions in the third zone were multiply connected as predicted by Harrison. However, recently, Ashcroft,[9] using de Hass–van Alphen data, proposed a new model of the Fermi surface of the third zone. In his model, the regions of electrons along the zone edges are only doubly connected near the zone corners at W about the square faces, forming isolated "square" regions instead of Harrison's multiply connected "monster." Several experimental results[10-15] have been reported since then for a variety of methods, with considerable disagreement as to details of the Fermi surface. Segall[16] pointed out in his report on the Green's-function calculation that a change in the Fermi level of about 0.01 Ry in band-structure calculations can cause the connected third zone to become completely disconnected. He also pointed out, however, that the Fermi level would have to be changed by more than 0.03 Ry if the corners of the second-zone surface were to contact the zone boundary. Though most of the reports on the second-zone Fermi surface since that of

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FIG. 1. Comparison of the initial and self-consistent potentials with the atomic potential.

Heine[2–4] agree with the Harrison[6] model, Balcome[17] recently found that his magnetoresistance results are consistent with a second-zone Fermi surface touching the zone boundary at the corners of the zone. With these differences of opinion still unresolved, it was felt that a self-consistent augmented-plane-wave (APW) calculation on the band structure of aluminum would be of significant value. The band structure, density of states, and Fermi surface resulting from such a calculation are reported here and compared with previously reported results.

In a recent Hartree-Fock-Slater self-consistent-field (SCF) atomic calculation on aluminum,[18] the effect that changes in the outer electron shells would have on the SCF $1s$ eigenvalue was studied. It was found that changing the electronic configuration of aluminum from $(3s^2 3p^1)$ to $(3s^1 3p^2)$ causes a shift of 0.13 Ry in the SCF $1s$ eigenvalue. Comparing the size of this shift with the self-consistency criterion of 0.002 Ry shows that the shift is not trivial and cannot be ignored in the self-consistent atomic calculations. Since the bands were changed in energy as the calculation was taken to self-consistency, there was no reason to believe that the core states were self-consistent in the resulting field or that the small effect on the resulting band structure could be ignored in taking these states to self-con-

sistency. In the case of aluminum, as was pointed out above, small changes in the bands can result in significant changes in the Fermi surface of the third zone near the zone corners at W.

For this reason, it was decided that the study should be extended to include the core states in the band calculation while self-consistency was being achieved, rather than "freezing" these states, as is usually done in band calculations.

An attempt was made to include all the core states during a self-consistent calculation. Unfortunately, the number of significant figures needed to specify the $1s$ eigenvalue, from which a usable wave function could be determined, exceeded the limits of the IBM 7094 computer used. It was possible, however, to complete such a calculation for aluminum in which the $(2s, 2p)$ states as well as the $(3s, 3p)$ states were included. Some of the results of this calculation are reported and compared with those obtained with the $(2s, 2p)$ states included in the "frozen" core.

METHOD OF CALCULATION

A self-consistent APW method was used in making the calculations. In this method, the crystal potential used was a "muffin-tin" type. That is, it was considered to be spherically symmetric about the center of the Wigner-Seitz cell, within the sphere of radius equal to half the distance to the first nearest-neighboring atom, and to be a constant elsewhere in the cell. This constant value is referred to as the constant potential V_c. The potential for the first iteration was obtained from a superpositioning of the atomic potentials of the first four nearest neighbors in the fcc lattice. The atomic potentials were obtained from nonrelativistic Hartree-Fock-Slater atomic SCF calculations as described by Herman and Skillman.[19] The potentials for the second and following iterations were generated from the charge density resulting from the band calculations of the previous iteration. This iterative process was continued until the self-consistency criterion was satisfied, i.e., $|\Delta E(\mathbf{k})|$ for every point in the zone was less than 0.002 Ry between successive iterations. A more detailed description of this self-consistent APW method and the methods of obtaining potentials are given by Snow and Waber.[20]

RESULTS

The results reported here are from the self-consistent calculation, covering 2048 points in the Brillouin zone, in which the $(2s, 2p)$ states were included in the rigid core.

The values of the self-consistent potential resulting from this calculation are listed in Table I for $0 < r < 2.78$ Bohr units. Figure 1 compares the free atomic potential,

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

TABLE I. Potential of self-consistent aluminum for $0 < r < 2.78$. [r in Bohr units and $V(r)$ in atomic units.] $V_c = -0.831054$ (uncorrected).

r	$-V(r)$	r	$-V(r)$	r	$-V(r)$
0.005	5141.218	0.400	28.075	1.280	3.116
0.010	2540.280	0.420	25.869	1.300	3.017
0.015	1672.913	0.440	23.905	1.320	2.924
0.020	1239.081	0.460	22.150	1.340	2.835
0.025	978.773	0.480	20.576	1.360	2.751
0.030	805.275	0.500	19.158	1.380	2.670
0.035	681.429	0.520	17.879	1.400	2.594
0.040	588.635	0.540	16.720	1.420	2.521
0.045	516.561	0.560	15.667	1.440	2.452
0.050	458.998	0.580	14.709	1.460	2.386
0.055	411.996	0.600	13.833	1.480	2.324
0.060	372.916	0.620	13.032	1.500[a]	2.264
0.065	339.930	0.640	12.296	1.540	2.152
0.070	311.733	0.660	11.620	1.580	2.049
0.075	287.365	0.680	10.996	1.620	1.955
0.080	266.107	0.700	10.419	1.660	1.868
0.085	247.408	0.720	9.884	1.700	1.787
0.090	230.841	0.740	9.388	1.740	1.712
0.095	216.066	0.760	8.927	1.780	1.643
0.100[a]	202.814	0.780	8.497	1.820	1.578
0.110	180.041	0.800	8.096	1.860	1.518
0.120	161.201	0.820	7.720	1.900	1.462
0.130	145.378	0.840	7.368	1.940	1.409
0.140	131.926	0.860	7.038	1.980	1.360
0.150	120.365	0.880	6.728	2.020	1.313
0.160	110.342	0.900	6.436	2.060	1.270
0.170	101.582	0.920	6.162	2.100	1.230
0.180	93.877	0.940	5.903	2.140	1.192
0.190	87.056	0.960	5.658	2.180	1.157
0.200	80.986	0.980	5.427	2.220	1.124
0.210	75.556	1.000	5.209	2.260	1.093
0.220	70.676	1.020	5.002	2.300	1.065
0.230	66.271	1.040	4.806	2.340	1.039
0.240	62.278	1.060	4.621	2.380	1.014
0.250	58.645	1.080	4.445	2.420	0.992
0.260	55.327	1.100	4.278	2.460	0.971
0.270	52.287	1.120	4.120	2.500	0.953
0.280	49.492	1.140	3.970	2.540	0.936
0.290	46.916	1.160	3.828	2.580	0.920
0.300[a]	44.534	1.180	3.693	2.620	0.906
0.320	40.279	1.200	3.565	2.660	0.895
0.340	36.595	1.220	3.444	2.700[b]	0.884
0.360	33.382	1.240	3.329	2.740	0.875
0.380	30.562	1.260	3.220	2.780	0.867

[a] Points where the mesh size is doubled.
[b] Radius of APW sphere (RS =2.7057).

the initial crystal-starting potential, and the self-consistent crystal potential.

The eigenvalues, relative to the constant potential set equal to zero, for the points in 1/48 of the Brillouin zone are given in Table II. The corrected value for the constant potential, found to be -1.22522 Ry in the manner described by Snow and Waber,[20] must be added to the values in the table to obtain the proper eigenvalues. Figure 2 is a plot of the corrected $E(\mathbf{k})$ curves in the directions of high symmetry. The dot-dash line labeled E_f indicates the location of the Fermi energy and the dashed line labeled V_c indicates the location of the corrected-constant potential. Table III compares the eigenvalues for the points of high symmetry reported by Heine,[4] Harrison,[6] and Segall[7] with those obtained in the present calculation. It should be noted that the original eigenvalues reported by Heine and
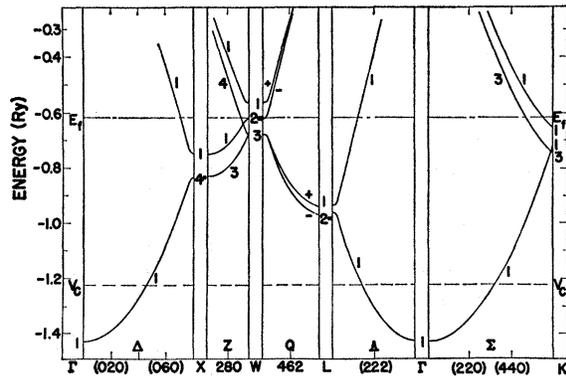
FIG. 2. $E(\mathbf{k})$ curves for self-consistent aluminum in the direction of high symmetry.

Harrison contained a Bohm and Pines[21] correction. For comparison, this correction has been removed from these two sets of eigenvalues reported here.

The Fermi energy from the self-consistent calculation was found to be -0.62297 Ry or -8.476 eV. The corresponding Fermi surface has the same general shape as that found by Harrison, except that the electron pockets of the fourth zone were not found in the present calculation. The intersections of the Fermi surfaces of the second and third zones with the (100) and (110) planes are shown in Fig. 3. In this figure, the area Γ, K, W, X, Γ is in the (100) plane, and the area Γ, K, L, U, X, Γ is in the (110) plane.

The density-of-states curve resulting from the present calculation, plotted with respect to $E_f = 0$, is shown as the solid line in Fig. 4. The dashed line in this figure represents the parabolic curve based on the free-electron model. It should be pointed out that most of the fluctuations in the solid curve are due to statistical inaccuracies resulting from sampling relatively few
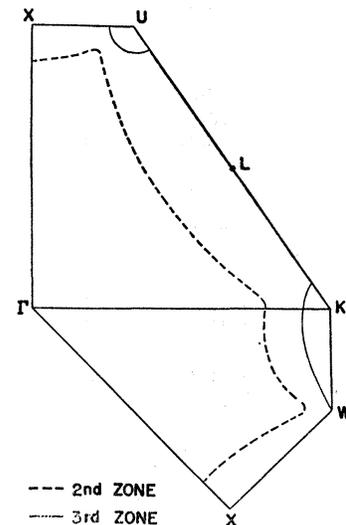
FIG. 3. Intersections of the (100) and (110) planes with the Fermi surface for the second and third zone of self-consistent aluminum.

--- 2nd ZONE
---- 3rd ZONE

[21] D. Pines, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. I, p. 368.

TABLE II. Eigenvalues of points of 1/48 of the Brillouin zone considering 2048 points in the entire zone, given with respect to $V_c=0$.

K			Band 1		Band 2		Band 3		Band 4
Γ	(000)/4	1	−0.20725						
X	(080)/4	4′	0.38974	1	0.47235				
L	(444)/4	2′	0.25958	1	0.28401				
K & U	(660)/4	3	0.46626	1	0.49760	1	0.55872		
Δ	(010)/4	1	−0.19711						
Δ	(020)/4	1	−0.16671						
Δ	(030)/4	1	−0.11620						
Δ	(040)/4	1	−0.04586						
Δ	(050)/4	1	0.04397						
Δ	(060)/4	1	0.15268	1	0.78146				
Δ	(070)/4	1	0.27860	1	0.60166				
Z	(180)/4	3	0.39931	1	0.48206	4	0.85882	1	0.92231
Z	(280)/4	3	0.42801	1	0.51089	4	0.73460	1	0.81764
Z	(380)/4	3	0.47585	1	0.55726	4	0.62923	1	0.72062
W	(480)/4	3	0.54287	3	0.54287	2′	0.60099	1	0.65940
Λ	(111)/4	1	−0.17684						
Λ	(222)/4	1	−0.08600	1	0.84781				
Λ	(333)/4	1	0.06396	1	0.53453				
Q	(471)/4	−	0.43303	+	0.45501	−	0.74939	+	0.78191
Q	(462)/4	−	0.33699	+	0.36175	−	0.95925		
Q	(453)/4	−	0.27896	+	0.30361				
Σ	(110)/4	1	−0.18697						
Σ	(220)/4	1	−0.12629						
Σ	(330)/4	1	−0.02580	3	0.86800	1	0.94766		
Σ	(440)/4	1	0.11355	3	0.69597	1	0.78268		
Σ	(550)/4	1	0.29029	3	0.56196	1	0.65013		
S	(181)/4	3	0.40887	1	0.49162	1	0.74986		
	(120)/4	+	−0.15660						
	(130)/4	+	−0.10613						
	(140)/4	+	−0.03584						
	(150)/4	+	0.05393	−	0.94436				
	(160)/4	+	0.16255	+	0.79046	−	0.89677	+	0.95886
	(170)/4	+	0.28835	+	0.61110	−	0.86832	+	0.93143
	(230)/4	+	−0.07595	−	0.97270				
	(240)/4	+	−0.00582	−	0.88709	+	0.96294		
	(250)/4	+	0.08374	−	0.82046	+	0.89794		
	(260)/4	+	0.19211	−	0.77278	+	0.81328	+	0.85971
	(270)/4	+	0.31756	+	0.63899	−	0.74415	+	0.82733
	(340)/4	+	0.04406	−	0.78215	+	0.86560		
	(350)/4	+	0.13327	−	0.71528	+	0.80016		
	(360)/4	+	0.24120	−	0.66748	+	0.75127	+	0.86962
	(370)/4	+	0.36604	−	0.63879	+	0.67920	+	0.73581
	(450)/4	+	0.20227	−	0.62912	+	0.71663		
	(460)/4	+	0.30952	−	0.58114	+	0.66839	+	0.93222
	(470)/4	+	0.43334	−	0.55244	+	0.63734	+	0.75964
	(560)/4	+	0.39642	−	0.51412	+	0.60240		
B	(570)/4	−	0.48542	+	0.51590	+	0.57644	+	0.84074
	(121)/4	+	−0.14648						
	(131)/4	+	−0.09607						
	(141)/4	+	−0.02582	+	0.90025				
	(151)/4	+	0.06387	+	0.83398				
	(161)/4	+	0.17241	+	0.78161	+	0.80608		
	(171)/4	+	0.29809	+	0.62022	+	0.75964		
	(221)/4	+	−0.11620	+	0.96792				
	(231)/4		−0.06621		0.86487				
	(241)/4		0.00418		0.77979				
	(251)/4		0.09366		0.71307				
	(261)/4		0.20194		0.66486		0.82941		0.97324
	(271)/4		0.32724		0.62860		0.65852		0.94550

TABLE II. (continued).

K	Band 1		Band 2		Band 3		Band 4
(281)/4	−	0.43757	+	0.51928	+	0.62998	+	0.93626
(331)/4	+	−0.01580	+	0.76126				
(341)/4		0.05402		0.67560				
(351)/4		0.14315		0.60853		0.92279		
(361)/4		0.25095		0.56037		0.86432		0.88916
(371)/4		0.37549		0.53112		0.69825		0.85045
(381)/4	−	0.48542	+	0.51590	+	0.57644	+	0.84074
(441)/4	+	0.12344	+	0.58951	+	0.90574		
(451)/4		0.21205		0.52222		0.84050		
(461)/4		0.31899		0.47423		0.79277		0.94169
(551)/4	+	0.29977	+	0.45502	+	0.77497		
(561)/4		0.39469		0.41818		0.72752		
(232)/4	+	−0.03581	+	0.74412				
(242)/4	+	0.03410	+	0.65838				
(252)/4	+	0.12337	+	0.59121				
(262)/4	+	0.23133	+	0.54297	+	0.85785		
(272)/4	+	0.35608	+	0.51360	+	0.68050		
(332)/4	+	0.01417	+	0.63968				
(342)/4		0.08382		0.55338				
(352)/4		0.17269		0.48588				
(362)/4		0.27996		0.43775		0.90408		
(372)/4		0.39469		0.41818		0.72752		
(442)/4	+	0.15304	+	0.46668				
(452)/4		0.24117		0.39917				
F (552)/4	+	0.31784	+	0.34258	+	0.95170		
(343)/4	+	0.13329	+	0.44770				
(353)/4	+	0.22156	+	0.38009				
F (363)/4	+	0.31766	+	0.34249	+	0.95065		
(443)/4	+	0.20199	+	0.36071				

states. Some, however, may be attributed to the fine structure of the bands. Two such fluctuations are the dips labeled as A and B in the figure. These dips are probably due to the band gaps near the zone boundary, between L_2^* and L_1 and between W_3 and W_2^*, respectively. On the other hand, two similar dips labeled as C and D do not correspond to any such gaps in any of the high-symmetry directions. It should be recognized, therefore, that the use of such a density-of-states curve to identify fine structure in the energy bands is quite limited. Of course, improved statistical accuracy could be attained by fitting a pseudopotential to the data and locating as many more states as desired. With a sufficiently large number of states, a density of states could be derived that would give a more complete picture of the fine structure of the bands.

DISCUSSION

The $E(\mathbf{k})$ curves given in Fig. 2, obtained from the present calculation, have the same general shape as

TABLE III. A comparison of energies (in Ry) for states of high symmetry, with respect to $\Gamma_1 = 0$.

	Heine[a]	Harrison[b]	Segall[c]	Present
$\Gamma_1(000)/4$	0.000	0.000	0.000	0.000
$X_4'(080)/4$	0.592	0.585	0.622	0.597
$X_1(080)/4$	0.717	0.693	0.698	0.679
$W_3(480)/4$	0.774	0.774	0.776	0.750
$W_2'(480)/4$	0.826	0.826	0.819	0.808
$W_1(480)/4$	0.949	0.949	0.923	0.866
$L_2'(444)/4$	...	...	0.483	0.467
$L_1(444)/4$	...	...	0.512	0.491
$K_3(660)/4$	0.699	0.679	0.699	0.673
$K_1(660)/4$	0.742	0.713	0.723	0.705
$K_1(660)/4$	1.075	0.810	0.802	0.766

[a] As listed by Segall (Ref. 7).
[b] Reference 6.
[c] Reference 7.
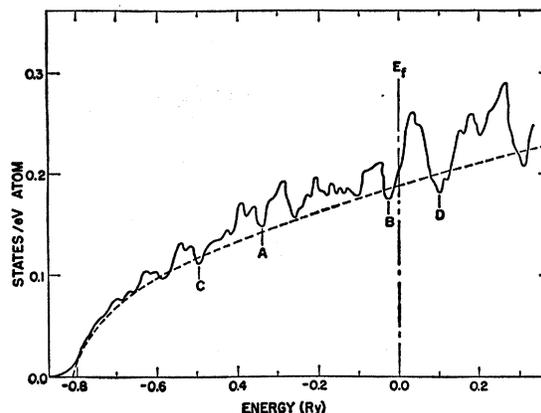
FIG. 4. Density-of-states curve for self-consistent aluminum.

those given by Harrison[6] and Segall.[7] The only difference that seems possibly significant among the three sets of results (see Table III) is that the bands resulting from the present calculation are, in general, slightly narrower than those reported by either Harrison or Segall. Figure 4 indicates that these narrower bands give a slightly higher density of states than is predicted by the free-electron model, but which is still in reasonably good agreement with that approximation.

The Fermi surface resulting from this calculation (see Fig. 3) is also in good agreement with those given by Harrison[5,6] and Segall.[16] The Fermi surface of the second zone is a single closed surface near the zone boundary, while the Fermi surface of the third zone consists of small pockets of electrons along the zone edges, multiply connected at the zone corners W. As was pointed out by Segall, a very small shift in the Fermi level with respect to W_2' could cause the Fermi surface of the third zone to become only doubly connected, as was indicated by Ashcroft,[9] or even completely disconnected at the corners of the zone. In the present calculation, the W_2' eigenvalue lies only 0.0013 Ry below the Fermi energy. Since the self-consistency criterion of the present calculation is on the order of 0.002 Ry, any definite conclusion about how the Fermi surface of the third zone is connected at the zone corners would not be justified.

As mentioned above, an attempt was made to include the core states in the self-consistent band-structure calculations. A calculation in which the $(2s, 2p)$ core states were considered to be part of the bands and the corresponding functions allowed to vary was converged to self-consistency. When the results of this calculation were compared with those obtained with these two states "frozen" in the core, very little effect could be attributed to the valence-band states, the maximum energy difference between equivalent states in the valence bands being on the order of 0.001 Ry. The energy difference between the equivalent $(2s, 2p)$ states, however, was on the order of 0.03 Ry. Though no significant change in the bands resulted from including the $(2s, 2p)$ states in the calculation, the changes in the eigenvalues of these core states could have a significant effect on the total binding energy.

CONCLUSIONS

From the work reported here, it was concluded that the self-consistent APW calculations for metallic aluminum yield results that are in reasonably good agreement with those previously reported. These calculations, however, are not sufficiently precise to allow drawing definite conclusions about how the Fermi surface of the third zone is connected at the zone corner W.

Allowing the core functions to vary as self-consistency is achieved was found to have very little effect on the resulting band states in the APW calculation on aluminum. However, it was noted that the resulting shifts in the eigenvalues of these core states could have a significant effect on the total binding energy.

ACKNOWLEDGMENTS