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Molybdenum: Band Structure, Fermi Surface, and Spin-Orbit Interaction

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The nonrelativistic energy bands of bcc Mo are calculated by the renormalized-atom method and the Fermi surface is obtained using an interpolated band structure. The de Haas–van Alphen data for the neck orbit of the electron jack and the electron lens are used to derive, for the crystal, a spin-orbit parameter of 0.0075 Ry, approximately equal to the atomic spin-orbit parameter.

I. INTRODUCTION

The experimental data relating to the Fermi surface (FS) of bcc Mo have been reviewed by Hoekstra and Stanford in the preceding paper.[1] The FS of Mo has four sheets qualitatively similar to those of the minority-spin electrons in iron[2]: I, hole pockets ("ellipsoids") centered at the points N in the Brillouin zone; II, a hole octahedron centered at the point H; III, an electron "jack" centered at the point Γ; IV, electron lenses centered on the Δ symmetry lines.

In the absence of spin-orbit coupling the octahedron and jack would contact each other on the Δ symmetry line and each lens would contact a "neck" of the electron jack just off the Δ axis. The spin-orbit interaction in Mo produces separations between these pairs of surfaces.

The separation between the octahedron and the jack is of particular interest because reported experimental estimates of its value differ by more than the reported experimental errors. The radio-frequency-size-effect (RFSE) measurements of Boiko *et al.*[3] give a separation of $(2.5\pm2)\%$ of the ΓH dimension $2\pi/a$ while those of Cleveland and Stanford[4,5] give $(7.5\pm2)\%$.[5] The latter value is estimated to require a spin-orbit parameter of 0.03 Ry,[4] which is 4 times the atomic spin-orbit parameter of 0.0074 Ry calculated by Herman and Skillman.[6] The de Haas–van Alphen (dHvA) data of Hoekstra and Stanford[1] are consistent with the smaller value of the separation, that of Boiko *et al.*, but not consistent with that of Cleveland and Stanford.

The rest of this paper discusses the interpolated band structure of Mo, the resulting FS, and the value of the spin-orbit parameter obtained from a fit to the experimental dHvA data. The results indicate that the separation along the Δ axis between the octahedron and the jack is only about 1.2% of $2\pi/a$.

II. BAND STRUCTURE

Previous nonrelativistic band-structure calculations for Mo have been reported by Loucks[7] and Petroff and Viswanathan.[8] We originally intended

TABLE I. Nonrelativistic energy bands for bcc Mo at high-symmetry points calculated using the renormalized-atom method (Ref. 10). The $\vec{k}$ values are given in units of $\pi/4a$. Energies are in Ry relative to the muffin-tin potential, which is 0.850 Ry below the vacuum level.

$\vec{k}$	Symmetry	$E(\vec{k})$	$\vec{k}$	Symmetry	$E(\vec{k})$
(0, 0, 0)	Γ_1	0.404	(0, 4, 0)	Δ_1	0.597
(0, 0, 0)	Γ_{25}'	0.729	(0, 4, 0)	Δ_2	0.598
(0, 0, 0)	Γ_{12}	0.940	(0, 4, 0)	Δ_5	0.797
(0, 8, 0)	H_{12}	0.380	(0, 4, 0)	Δ_2'	0.905
(0, 8, 0)	H_{25}'	1.145	(0, 4, 0)	Δ_1	1.142
(4, 4, 4)	P_4	0.646	(2, 2, 2)	Λ_1	0.606
(4, 4, 4)	P_3	1.012	(2, 2, 2)	Λ_3	0.615
(4, 4, 0)	N_1	0.433	(2, 2, 2)	Λ_3	0.950
(4, 4, 0)	N_2	0.566	(2, 2, 2)	Λ_1	1.106
(4, 4, 0)	N_1	0.963	(2, 6, 2)	F_3	0.581
(4, 4, 0)	N_4	1.006	(2, 6, 2)	F_1	0.622
(4, 4, 0)	N_1'	1.017	(2, 6, 2)	F_3	1.019
(4, 4, 0)	N_3	1.211			

TABLE II. Interpolation scheme parameters (Refs. 2 and 11) for the fit to the bcc Mo bands of Table I.

$E_{s,s}(000) = 1.468$	$E_{xy,x}(110) = -0.005$
$E_{s,s}(111) = -0.1300$	$E_{xy,x}(011) = 0.005$
$E_{s,s}(100) = -0.024$	$E_{x^2-y^2,z}(011) = 0.010$
$E_{s,s}(110) = 0.010$	$E_{xy,xy}(000) = 0.8731$
$E_{x,s}(111) = 0.080$	$E_{3z^2-r^2,3z^2-r^2}(000) = 0.82585$
$E_{x,s}(100) = 0.080$	$E_{3z^2-r^2,3z^2-r^2}(111) = 0.035$
$E_{x,x}(000) = 1.863$	$E_{xy,3z^2-r^2}(111) = -0.029$
$E_{x,x}(111) = 0.0750$	$E_{xy,xy}(011) = 0.001$
$E_{x,y}(111) = 0.062$	$E_{3z^2-r^2,3z^2-r^2}(001) = -0.06567$
$E_{x,x}(100) = 0.175$	$E_{x^2-y^2,x^2-y^2}(110) = -0.0018$
$E_{y,y}(100) = 0.009$	$E_{xy,xy}(011) = 0.00178$
$E_{xy,s}(111) = 0.044$	$E_{xy,xy}(111) = -0.026$
$E_{3z^2-r^2,s}(001) = 0.0280$	$E_{xy,zx}(111) = -0.04031$
$E_{xy,s}(110) = -0.002$	$E_{xy,xy}(100) = 0.01619$
$E_{xy,x}(111) = -0.048$	$E_{x^2-y^2,x^2-y^2}(001) = 0.007$
$E_{yz,x}(111) = -0.045$	$E_{xy,xy}(110) = -0.00428$
$E_{x^2-y^2,x}(111) = 0.031$	$E_{3z^2-r^2,3z^2-r^2}(110) = 0.0035$
$E_{3z^2-r^2,z}(011) = -0.039$	$E_{xy,zx}(011) = -0.0012$
$E_{xy,x}(010) = 0.024$	

to use Loucks's bands making use of his computer decks available at Iowa State University, but it was discovered that Loucks had used an incorrect value of the unit-cell volume [194 (a.u.)^3 instead of 105 (a.u.)^3].[9]

A new nonrelativistic augmented-plane-wave (APW) calculation for Mo was subsequently carried out using the renormalized-atom approach.[10] We used a Wigner-Seitz radius of 2.928 a.u. and an APW sphere radius of 2.460 a.u., slightly smaller than half the nearest-neighbor distance. The energy levels at points of high symmetry are given in Table I.

The Mo energy bands were fit to the points listed in Table I using the Slater-Koster interpolation scheme for bcc transition metals.[2,11] The rms fit to the energy eigenvalues below 1.00 Ry was 0.005 Ry; the parameters are listed in Table II. The interpolated energy bands were computed at 285 equally spaced mesh points in $\frac{1}{48}$th of the Brillouin

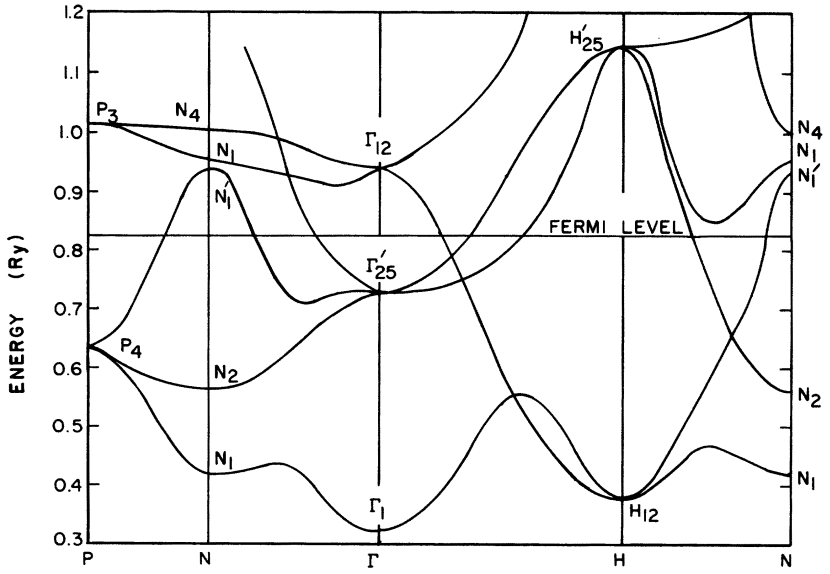

FIG. 1. Nonrelativistic energy bands for Mo modified by lowering the conduction bands with respect to the *d* bands by 0.08 Ry. The hole surfaces I (ellipsoids) and II (octahedron) arise from the third band at *N* and at *H*, respectively. The electron surfaces III (jack) and IV (lens) correspond to filled states in the fourth and fifth bands, respectively.

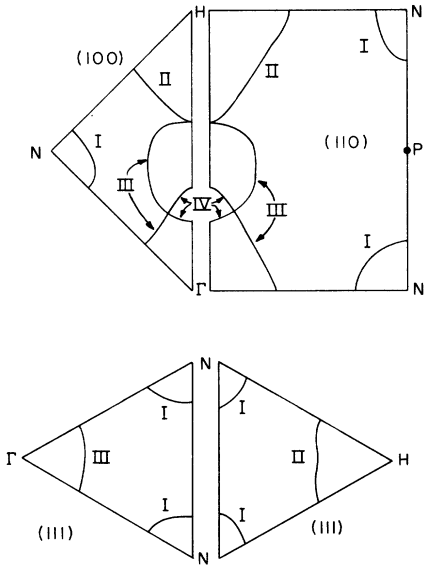

FIG. 2. FS cross sections in (100), (110), and (111) planes for the modified Mo bands shown in Fig. 1. The Roman numerals identify the different surfaces (see text). The correspondence with the dHvA frequencies of Hoekstra and Stanford (Ref. 1) is as follows: I gives rise to ρ orbits; II gives rise to ν orbits; III gives to π, σ, ξ, φ, ω, and τ orbits; IV gives rise to β orbits. Spin-orbit coupling, which has been neglected here, has the effect of producing small separations between surface III and surfaces II and IV in the (100) and (110) planes.

zone, and a density-of-states histogram was constructed to locate the Fermi level ($E_F = 0.839$ Ry).

The FS's for these bands proved to be qualitatively but not quantitatively correct; in particular, the hole octahedron was too small and the hole ellipsoids, electron jack, and electron lenses were too large.[12] This suggests that the band calculation placed the 4*d* bands too low with respect to the conduction (5*s*, 5*p*, ...) bands. The separation between the *d* bands and the conduction bands is known to be highly sensitive to the details of the crystal potential used in band calculations, and it is not uncommon to find that the separation inferred from experimental results differs by 1 or 2 eV from that given by the theoretical calculations.[2,13]

Therefore a new set of bands was constructed with the conduction bands lowered 0.08 Ry relative to the *d* bands; this was accomplished in the context of the interpolation scheme by using the values $E_{s,s}(000) = 1.388$ and $E_{x,x}(000) = 1.783$. Again, 285 points were used to determine the Fermi level ($E_F = 0.828$ Ry).

The modified bands are shown in Fig. 1 and the FS cross sections derived from them are shown in Fig. 2. Most of the FS cross-sectional areas are in good agreement (± 5%) with the dHvA data of Hoekstra and Stanford,[1] although the ellipsoid differences range up to 20%. No further attempt has been made to modify the band structure to secure better agreement.

III. SPIN-ORBIT INTERACTIONS

In the absence of spin-orbit interaction, the "neck" of the jack surface contacts the lens surface along a closed curve around the Δ axis, as indicated in Fig. 2. Spin-orbit interaction splits the two surfaces apart, as a result of which the ⟨100⟩ lens cross-sectional area is smaller than the ⟨100⟩ neck area; 8.24 MG compared to 11.7 MG.[1]

This fact can be used to determine the value of the spin-orbit parameter appropriate to the crystal. The interpolation scheme has previously been modified to incorporate spin-orbit coupling,[2,13,14] so it can be used to study the effect of spin-orbit coupling on the nonrelativistic band structure and FS. A single spin-orbit parameter, usually denoted $\bar{\xi}$, is involved in such a calculation.

The adjustment in the original band structure discussed in Sec. II was chosen to give ⟨100⟩ neck and lens areas intermediate between the experimental areas (in this case, 9.5 MG). The value of the spin-orbit parameter $\bar{\xi}$ required to give the correct difference between the ⟨100⟩ neck and lens areas is 0.0075 Ry, which is almost exactly the atomic spin-orbit parameter of Herman and Skillman.[6] The effect of the spin-orbit interaction on the FS is shown in Fig. 3.

This value of $\bar{\xi}$ splits the Δ_5 level of the nonrelativistic band structure to produce a separation of $0.012(2\pi/a)$, or 1.2% of the ΓH distance, between the hole octahedron and the electron jack. This

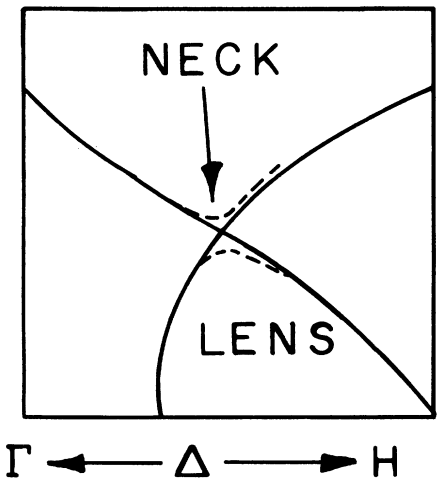

FIG. 3. Enlargement of the part of the (100) plane near the intersection of the jack surface III and the lens surface IV. The solid lines correspond to a spin-orbit parameter $\bar{\xi} = 0$ while the dashed lines correspond to $\bar{\xi} = 0.0075$ Ry.

agrees within experimental error with the RFSE data of Boiko *et al.*,[3] which gave a separation of $(2.5 \pm 2)\%$ of $2\pi/a$, and the dHvA data of Hoekstra and Stanford.[1] It is in disagreement with the RFSE data of Cleveland and Stanford,[5] which gave a separation of $(7.5 \pm 2)\%$ of the ΓH distance. A spin-orbit parameter which led to such a large separation would have a difference between the $\langle 100 \rangle$ neck and lens cross-sectional areas much larger than the experimental result.

We conclude that the spin-orbit parameter in Mo is probably about 0.0075 Ry and that the separation along the Δ axis between the octahedron and jack surfaces is about 1.2% of the ΓH distance.

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