TIGHT-BINDING INTERPOLATION SCHEMES APPLIED TO
MOLYBDENUM AND COPPER

M. S. Thesis Submitted to Iowa State University, May 1972

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Date of Manuscript: May 1972

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

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Tight-binding interpolation schemes applied
to molybdenum and copper

by

Randall Jay Iverson

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

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Major: Solid State Physics

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1972

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Tight-binding interpolation schemes applied
to molybdenum and copper

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Tight-binding interpolation schemes which represent transition and noble metal s, p, and d bands have been applied to molybdenum and copper. A tight-binding scheme for bcc metals has been used to fit first-principles calculations of the energy bands of Mo and obtain Fermi surfaces which have been compared to de Haas-van Alphen and radio-frequency size-effect experimental data. A spin-orbit parameter of 0.0075 Ry (equal to the atomic spin-orbit parameter) was found to give the proper cross-sectional areas for the electron lens on the Δ axis and the neck of the electron jack; this value also gave a separation of $0.012(\frac{2\pi}{a})$ between the hole octahedron and the electron jack along the Δ axis, in agreement with the de Haas-van Alphen data, but in disagreement with the radio-frequency size-effect data. A tight-binding interpolation scheme for fcc metals was developed, applied to Cu, and compared to the widely used LCAO-OPW interpolation scheme. It appears that the only significant differences appear above the top of the pure d bands, where the tight-binding scheme has too low a density of states and the LCAO-OPW scheme too high a density of states compared to the first-principles calculations.

INTRODUCTION

Electronic band structure calculations have proved extremely valuable in recent years in understanding a wide variety of experimental data obtained on noble and transition metals (1). In particular, the augmented-plane-wave (2) and Kohn-Korringa-Rostoker (3) methods applied to muffin-tin potentials have provided generally excellent first-principles bands for many of these metals.

For many applications, however, it has been necessary to resort to interpolation schemes (4-6) which permit 1) rapid calculations of the bands at many points in $\vec{k}$ space, 2) easy incorporation of the effects of ferromagnetic and spin-orbit coupling, and 3) minor adjustments in the bands to secure better agreement with experimental data.

Several such interpolation schemes have been developed. The LCAO-OPW scheme (4,5) which represents the d bands in the tight-binding approximation by linear combinations of atomic orbitals (LCAO's) (7) and the conduction (s and p) bands by orthogonalized plane waves (OPW's) has proved exceptionally suitable for face centered cubic (fcc) noble and transition metals. This scheme involves 9 basis functions (5 LCAO's, 4 OPW's) for each spin. The LCAO-OPW schemes have not proved as successful for body centered cubic (bcc) (8,9) and hexagonal close packed (hcp) (10) metals because of the need for many more OPW's, which makes the scheme unwieldy.

On the other hand, a pure tight-binding interpolation scheme representing s, p, and d bands by LCAO's has worked well for bcc transition

metals (6,9). This scheme requires the inclusion of first, second, and third nearest-neighbor interactions, and involves a rather large number of parameters. It is also physically less meaningful than the LCAO-OPW scheme since the conduction bands are clearly not tight-binding in origin. Nevertheless, it has proved to be a useful scheme. A pure tight-binding interpolation scheme based on s, p, and d LCAO's could also be set up for fcc and hcp metals, but this does not appear to have been attempted in the past.

The present thesis is divided into two parts. The first part applies the bcc tight-binding interpolation scheme to a recent band structure calculation for Mo; experimental data relating to the Fermi surface of Mo is analyzed and it is suggested that some of the data exhibits systematic errors. The second part develops an fcc tight-binding interpolation scheme which is used to interpolate existing APW calculations for copper; the new scheme is found to be comparable in accuracy to the LCAO-OPW scheme now widely used to interpolate fcc energy bands.

APPLICATION TO BCC MOLYBDENUM

In recent years a number of experiments (11-16) have been carried out yielding information about the Fermi surface of Mo. In the Ames Laboratory at Iowa State University the Fermi surface of Mo has been studied by the de Haas-van Alphen technique (16) and by the radio-frequency size-effect technique (15).

The Fermi surfaces of molybdenum are:

- I Hole ellipsoids centered at 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 axis.

Spin-orbit coupling separates surfaces II and III along the Δ axis and it separates the electron lens IV from the "neck" of the electron jack III.

The results of the Ames Laboratory Fermi surface experiments exhibit important discrepancies. The size-effect studies, which provide a direct measure of the extremal dimensions of the Fermi surfaces, yield a separation along the Δ axis between surfaces II and III of $(.075 \pm .02)(\frac{2\pi}{a})$ (15), which is estimated to require a spin-orbit parameter of 0.03 Ry (17), about four times larger than the atomic spin-orbit parameter of 0.0075 Ry of Herman and Skillman (18). The de Haas-van Alphen studies, on the other hand, suggest a much smaller separation and consequently a much smaller spin-orbit parameter.

Band calculations can shed light on these questions and provide yet another estimate of the spin-orbit parameter which suggests the radio-

frequency size-effect data are in error. One previous Mo band calculation was carried out by Loucks (19), who made an error in his unit cell size (20) and therefore had a somewhat inaccurate crystal potential.

New energy bands for Mo (see Figure 1) have been calculated using an interpolation scheme fit to the renormalized atom APW calculations of Hodges, et al. (21); Appendix A provides details of these calculations. From these energy bands it is possible to obtain Fermi surface cross-sections in the absence of spin-orbit coupling (see Figure 2).

These cross-sectional areas were compared with experimental data provided by Hoekstra (16) and are listed in Table 1. The cross-sections are qualitatively identical, but quantitative differences exist: the band structure gives a hole octahedron that is too small and hole ellipsoids, electron jack, and electron lens that are too big.

In order to get Fermi surfaces agreeing better with Hoekstra's data it was necessary to lower the Fermi level with respect to the d bands and raise it with respect to the s-p bands. This was accomplished very simply in the context of the interpolation scheme by adjusting the separation of the d bands and s-p bands by lowering the s-p bands 0.080 Ry relative to the d bands. This is not an unreasonable shift as it is well known that first principles band calculations cannot give accurate values of the s-d separation.

The results of the modified band structure are plotted in Figures 3 and 4 and the new cross-sections again compared to Hoekstra's data (see Table 1). The resulting Fermi surface cross-sectional areas are very close to the experimentally determined data except at the neck of

Figure 1. Energy bands along selected symmetry directions for bcc Mo, obtained by an APW calculation using renormalized atom potentials (21)

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Figure 2. Fermi surface cross-sections in (100), (110), and (111) planes for the bcc Mo bands shown in Figure 1. The Roman numerals identify the different sheets (see text). Spin-orbit coupling, which has been neglected here, has small effect, primarily producing small separations between surface III and surfaces II and IV

Figure 3. Energy bands for Mo modified by lowering the conduction bands with respect to the d bands by 0.08 Ry

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Figure 4. Fermi surface cross-sections in (100), (110), and (111) planes for the modified bcc Mo bands shown in Figure 3. The Roman numerals identify the different sheets (see text). Spin-orbit coupling, which has been neglected here, has small effect, primarily producing small separations between surface III and surfaces II and IV

the jack and the neck of the lens due to the fact that the spin-orbital coupling was not included.

Table 1. Comparison of the Fermi surfaces of Mo.

Surface	Field Direction	Area-Experimental	Theory	Theory (modified)
Lens	<110>	5.11		5.15
	<100>	5.18	8.2	5.3
	<100>	8.24	13.1 ^a	9.5 ^a
Ellipsoid	<100>	22.70	37.7	26.5
	<111>	24.00		22.9
	<111>	30.15		36.5
Octahedron	<110>	113.5		113
	<100>	150.7	140	146
	<111>	103.7		98
Jack	<100> (neck)	11.7	13.1 ^a	9.5 ^a
	<110> (ball)	31.6	37.2	32.1
	<111> (body)	84.7		68
	<110> (ball)	158		159
	<100> (ball)	231		242

^aWith zero spin-orbit parameter.

Now that the experimental and theoretical values were sufficiently close, various spin-orbit parameters were inserted and the resulting cross-sectional areas of the neck and lens were compared to the experimental data. The best fit was found by setting the spin-orbit parameter equal to 0.0075 Ry (see Figure 5), a value equal to that of the atomic

Figure 5. Enlargement of the part of the (100) plane near the intersection of surface III (the electron "jack") and surface IV (the electron lens), showing the effect of spin-orbit coupling. The solid lines correspond to a spin-orbit parameter $\bar{\xi} = 0$, while the dashed lines correspond to $\bar{\xi} = 0.0075$ Ry

spin-orbit parameter given by Herman and Skillman (18).

This spin-orbit parameter gives a separation of $0.012 \left(\frac{2\pi}{a}\right)$ between the hole octahedron and the electron jack along the Δ axis, in good agreement with information extracted from the de Haas-van Alphen studies (16) but in disagreement with Ames Laboratory radio-frequency size-effect data (15), which gave a separation over six times as large. It is not in disagreement with earlier size-effect data (14). As other transition metal studies have indicated that the crystal spin-orbit parameter is never much larger than the atomic value, and sometimes smaller (9,22), it appears that the Ames Laboratory size-effect data are in error and should be about six percent larger than the reported values.

APPLICATION TO FCC COPPER

Previous interpolation schemes for fcc structured metals such as those of Hodges, et al. (4) and Mueller (5) have used LCAO's to represent d bands and OPW's to represent conduction (s and p) bands. Pure LCAO interpolation schemes have already been used for bcc iron calculations by Cornwell, et al. (6), and Gold, et al. (9). This chapter discusses the development of a pure LCAO interpolation scheme for fcc metals; while being less realistic physically than the LCAO-OPW schemes, it appears to produce energy levels (see Table 3) and bands (see Figure 6) comparable to the other schemes.

The interpolation scheme is based on the simplified LCAO scheme of Slater and Koster (7), using a basis of five d functions, three p functions, and one s function for each spin direction. Only first nearest neighbor interactions are retained. The p orbitals are redefined with an extra factor of i relative to the Slater-Koster definitions so that all matrix elements are real (see Appendix B). It was necessary to derive one matrix element not included in Slater and Koster:

$$H_{x^2-y^2,z} = 4E_{x^2-y^2,z} (011) \sin \zeta (\cos \eta - \cos \xi)$$

The Hamiltonian energy matrix can be set up and diagonalized on a computer (see Appendix C) once values have been chosen for the three-center integrals of Slater and Koster.

The three-center integrals are treated as adjustable parameters and their values chosen to fit certain energy levels obtained from first-

Figure 6. Comparison of energy bands for Cu from Burdick's APW calculation (23) with tight-binding interpolation scheme fit

principles band calculations, such as those from the APW method. Appendix D indicates the method used to fit the copper bands of Burdick (23); the numerical values of the parameters fit to Burdick's bands are given in Table 2.

A band-by-band comparison between Burdick's energy levels and those of the present interpolation scheme is shown in Table 3. A comparison at all 89 points listed by Burdick shows a maximum deviation of 0.020 Ry when all bands up to 0.13 Ry above the Fermi level are considered; this may be compared to a maximum deviation of 0.027 Ry in the LCAO-OPW scheme. The average deviation for the pure LCAO scheme was 0.003 Ry, and the rms deviation was 0.006 Ry, compared to a rms deviation of 0.008 Ry for the LCAO-OPW scheme.

In a comparison of the energies below which there are exactly enough states to accommodate n electrons (of both spins) the two interpolation schemes give results quite similar to those obtained from Burdick's bands. These are compared in Table 4.

The only significant differences appear above the top of the pure d energy levels, where the pure LCAO scheme has too low a density of states and the LCAO-OPW scheme too high a density of states.

If desired, ferromagnetic splitting and spin-orbit coupling can be added to the pure LCAO interpolation scheme in exactly the same manner as was used in the LCAO-OPW scheme (24). However, the Hamiltonian matrix will then be complex rather than real.

Table 2. Parameter values for the fit to Burdick's bands

d Parameters		s-p Parameters		Hybridization Parameters	
$E_{xy,xy}$	(000) = 0.33075	$E_{x,x}$	(000) = 1.70000	$E_{xy,x}$	(110) = -0.0400
$E_{xy,xy}$	(110) = -0.02031	$E_{x,x}$	(110) = 0.10000	$E_{xy,x}$	(011) = 0.0100
$E_{xy,xy}$	(011) = 0.00619	$E_{x,x}$	(011) = -0.04900	$E_{xy,s}$	(110) = 0.0320
$E_{xy,yz}$	(011) = 0.01025	$E_{x,y}$	(110) = 0.14875	$E_{x^2-y^2,z}$	(011) = 0.0350
$E_{xy,3z^2-r^2}$	(110) = 0.00954	$E_{x,s}$	(110) = -0.08800	$E_{3z^2-r^2,z}$	(011) = 0.0055
$E_{x^2-y^2,x^2-y^2}$	(110) = 0.01295	$E_{s,s}$	(000) = 0.76025	$E_{3z^2-r^2,s}$	(110) = 0.0310
$E_{3z^2-r^2,3z^2-r^2}$	(000) = 0.32630	$E_{s,s}$	(110) = -0.07169		
$E_{3z^2-r^2,3z^2-r^2}$	(110) = -0.00781				

Table 3. Comparison of energy bands (in Ry)

$\vec{k}$	Band	LCAO	Burdick	Difference
(0,0,0)	Γ_1	-0.100	-0.10	.000
	Γ_{25}'	.299	.299	.000
$(0, \frac{2\pi}{a}, 0)$	Γ_{12}	.357	.357	.000
	X_1	.163	.163	.000
	X_3	.200	.200	.000
	X_2	.399	.399	.000
	X_5	.412	.412	.000
	X_4'	.704	.704	.000
$(\frac{3\pi}{2a}, \frac{3\pi}{2a}, 0)$	K_1	.187	.205	-0.018
	K_1	.241	.228	.013
	K_3	.314	.327	-0.013
	K_4	.359	.367	-0.008
	K_2	.404	.396	.008
$(\frac{\pi}{a}, \frac{2\pi}{a}, 0)$	W_2'	.228	.216	.012
	W_3	.267	.268	-0.001
	W_1	.334	.354	-0.020
	W_1'	.412	.412	.000
$(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$	L_1	.166	.164	.002
	L_3	.297	.297	.000
	L_3	.401	.401	.000
	L_2'	.510	.510	.000
$(0, \frac{\pi}{a}, 0)$	Δ_1	.078	.08	-0.002
	Δ_2'	.250	.243	.007
	Δ_1	.328	.328	.000
	Δ_5	.347	.342	.005
	Δ_2	.378	.371	.007
$(\frac{\pi}{2a}, \frac{\pi}{2a}, \frac{\pi}{2a})$	Λ_1	.043	.05	-0.007
	Λ_1	.269	.281	-0.012
	Λ_3	.313	.309	.004
	Λ_3	.362	.359	.003

Table 4. Total number of states

Number of Electrons (both spins)	LCAO	Burdick	LCAO-OPW
1	.191 Ry	.19 Ry	.189 Ry
2	.224	.22	.223
3	.253	.26	.255
4	.279	.28	.290
5	.304	.30	.309
6	.319	.32	.325
7	.336	.34	.347
8	.361	.36	.366
9	.386	.39	.389
10	.402	.40	.405
11	.571	.55	.534
12	.971	.91	.880

SUMMARY AND CONCLUSIONS

Tight-binding interpolation schemes which represent transition and noble metal s, p, and d bands have been applied to molybdenum and copper. A tight-binding scheme for bcc metals has been used to fit first-principles calculations of the energy bands of Mo and obtain Fermi surfaces which have been compared to de Haas-van Alphen and radio-frequency size-effect experimental data. A spin-orbit parameter of 0.0075 Ry (equal to the atomic spin-orbit parameter) was found to give the proper cross-sectional areas for the electron lens on the Δ axis and the neck of the electron jack. This value also gave a separation of $0.012 \left(\frac{2\pi}{a} \right)$ between the hole octahedron and the electron jack along the Δ axis, in agreement with the de Haas-van Alphen data, but in disagreement with the radio-frequency size-effect data. The theoretical calculations reported here suggest that the size-effect measurements were in error and should have been about 6 percent larger than reported.

A tight-binding interpolation scheme for fcc metals was developed, applied to Cu, and compared to the widely used LCAO-OPW interpolation scheme. It appears that the only significant differences appear above the top of the pure d bands, where the tight-binding scheme has too low a density of states and the LCAO-OPW scheme too high a density of states compared to the first-principles calculations. It appears that, on the whole, the pure LCAO scheme for fcc metals is as accurate as the LCAO-OPW scheme, and further experience will be needed to determine in which situations it is superior or inferior.

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ACKNOWLEDGEMENTS

The author is grateful to Professor Laurent Hodges for suggesting the interpolation scheme studies and for the many stimulating discussions concerning the thesis problem.

The author is also indebted to James Hoekstra for providing data on his de Haas-van Alphen studies of Molybdenum.

It is with the greatest appreciation that the author thanks his wife, June, for her patience and understanding during the years of graduate study and for typing the rough draft of this manuscript.

APPENDIX A: RESULTS OF RENORMALIZED ATOM BAND CALCULATIONS FOR BCC MOLYBDENUM

The Mo bands used in this thesis have been calculated using renormalized atom potentials (21). The energy levels at points of high symmetry and at midpoints of symmetry directions have the following values relative to the muffin-tin potential, which is 0.850 Ry below the vacuum level:

$\Gamma_1 = 0.404$	$N_1 = 0.433$	$H_{12} = 0.380$	$\Delta_1 = 0.597$	$\Lambda_1 = 0.606$
$\Gamma'_{25} = 0.729$	$N_2 = 0.566$	$H'_{25} = 1.145$	$\Delta_2 = 0.598$	$\Lambda_3 = 0.615$
$\Gamma_{12} = 0.940$	$N_1 = 0.963$	$F_3 = 0.581$	$\Delta_5 = 0.797$	$\Lambda_3 = 0.950$
$P_4 = 0.646$	$N_4 = 1.006$	$F_1 = 0.622$	$\Delta'_2 = 0.905$	$\Lambda_1 = 1.106$
$P_3 = 1.012$	$N'_1 = 1.017$	$F_3 = 1.019$	$\Delta_1 = 1.142$	
	$N_3 = 1.211$			

The interpolation scheme fit to these bands used the following parameters:

$E_{s,s}(000) = 1.468$	$E_{3z^2-r^2,s}(001) = 0.0280$
$E_{s,s}(111) = -0.1300$	$E_{xy,s}(110) = -0.002$
$E_{s,s}(100) = -0.024$	$E_{xy,x}(111) = -0.048$
$E_{s,s}(110) = 0.010$	$E_{yz,x}(111) = -0.045$
$E_{x,s}(111) = 0.080$	$E_{x^2-y^2,x}(111) = 0.031$
$E_{x,s}(100) = 0.080$	$E_{3z^2-r^2,z}(011) = -0.039$
$E_{x,x}(000) = 1.863$	$E_{xy,x}(010) = 0.024$
$E_{x,x}(111) = 0.0750$	$E_{xy,x}(110) = -0.005$
$E_{x,x}(111) = 0.062$	$E_{xy,x}(011) = 0.005$
$E_{x,y}(100) = 0.175$	$E_{x^2-y^2,z}(011) = 0.010$
$E_{y,y}(100) = 0.009$	$E_{xy,xy}(000) = 0.8731$

$$\begin{aligned}
 E_{xy,s}(111) &= -0.044 \\
 E_{xy,xy}(111) &= -0.026 \\
 E_{xy,zx}(111) &= -0.04031 \\
 E_{xy,xy}(100) &= 0.01619 \\
 E_{x^2-y^2, x^2-y^2}(001) &= 0.007 \\
 E_{xy,xy}(110) &= -0.00428 \\
 E_{3z^2-r^2, 3z^2-r^2}(110) &= 0.0035 \\
 E_{xy,zx}(011) &= -0.0012
 \end{aligned}$$

$$\begin{aligned}
 E_{3z^2-r^2, 3z^2-r^2}(000) &= 0.82585 \\
 E_{3z^2-r^2, 3z^2-r^2}(111) &= 0.035 \\
 E_{xy, 3z^2-r^2}(111) &= -0.029 \\
 E_{xy,xy}(011) &= 0.001 \\
 E_{3z^2-r^2, 3z^2-r^2}(001) &= -0.06567 \\
 E_{x^2-y^2, x^2-y^2}(110) &= -0.0018 \\
 E_{xy,xy}(011) &= 0.00178
 \end{aligned}$$

APPENDIX B: MATRIX ELEMENTS
OF THE FCC TIGHT-BINDING INTERPOLATION SCHEME

The basis functions 1 through 9 correspond to xy , yz , zx , $x^2 - y^2$, $3z^2 - r^2$, ix , iy , iz , and s in the Slater-Koster notations. The matrix elements in the three-center nearest-neighbor approximations for the fcc lattice are thus:

$$H(1,1) = E_{xy,xy}(000) + 4E_{xy,xy}(110) \cos \xi \cos \eta + 4E_{xy,xy}(011)(\cos \xi \cos \zeta + \cos \eta \cos \zeta)$$

$$H(2,2) = E_{xy,xy}(000) + 4E_{xy,xy}(110) \cos \eta \cos \zeta + 4E_{xy,xy}(011)(\cos \eta \cos \xi + \cos \zeta \cos \xi)$$

$$H(3,3) = E_{xy,xy}(000) + 4E_{xy,xy}(110) \cos \zeta \cos \xi + 4E_{xy,xy}(011)(\cos \zeta \cos \eta + \cos \xi \cos \eta)$$

$$H(4,4) = E_{3z^2-r^2, 3z^2-r^2}(000) + 3E_{3z^2-r^2, 3z^2-r^2}(110)(\cos \xi \cos \zeta + \cos \eta \cos \zeta) + 4E_{x^2-y^2, x^2-y^2}(110)(\cos \xi \cos \eta + \frac{1}{4} \cos \xi \cos \zeta + \frac{1}{4} \cos \eta \cos \zeta)$$

$$H(5,5) = E_{3z^2-r^2, 3z^2-r^2}(000) + 4E_{3z^2-r^2, 3z^2-r^2}(110)(\cos \xi \cos \eta + \frac{1}{4} \cos \xi \cos \zeta + \frac{1}{4} \cos \eta \cos \zeta) + 3E_{x^2-y^2, x^2-y^2}(110)(\cos \xi \cos \zeta + \cos \eta \cos \zeta)$$

$$H(6,6) = E_{x,x}(000) + 4E_{x,x}(110)(\cos \xi \cos \eta + \cos \xi \cos \zeta) + 4E_{x,x}(011) \cos \eta \cos \zeta$$

$$H(7,7) = E_{x,x}(000) + 4E_{x,x}(110)(\cos \eta \cos \zeta + \cos \eta \cos \xi) + 4E_{x,x}(011) \cos \zeta \cos \xi$$

$$H(8,8) = E_{x,x}(000) + 4E_{x,x}(110)(\cos \zeta \cos \xi + \cos \eta \cos \zeta) + 4E_{x,x}(011) \cos \xi \cos \eta$$

$$H(9,9) = E_{s,s}(000) + 4E_{s,s}(110)(\cos \xi \cos \eta + \cos \eta \cos \zeta + \cos \zeta \cos \xi)$$

$$H(1,2) = -4E_{xy,yz}(011) \sin \zeta \sin \xi$$

$$H(1,3) = -4E_{xy,yz}(011) \sin \eta \sin \zeta$$

$$H(1,4) = 0$$

$$H(1,5) = -4E_{xy,3z^2-r^2}(110) \sin \xi \sin \eta$$

$$H(1,6) = 4E_{xy,x}(110) \cos \xi \sin \eta + 4E_{xy,x}(011) \sin \eta \cos \zeta$$

$$H(1,7) = 4E_{xy,x}(110) \cos \eta \sin \xi + 4E_{xy,x}(011) \sin \xi \cos \zeta$$

$$H(1,8) = 0$$

$$H(1,9) = -4E_{xy,s}(110) \sin \xi \sin \eta$$

$$H(2,3) = -4E_{xy,yz}(011) \sin \xi \sin \eta$$

$$H(2,4) = -2\sqrt{3} E_{xy,3z^2-r^2}(110) \sin \eta \sin \zeta$$

$$H(2,5) = 2E_{xy,3z^2-r^2}(110) \sin \eta \sin \zeta$$

$$H(2,6) = 0$$

$$H(2,7) = 4E_{xy,x}(110) \cos \eta \sin \zeta + 4E_{xy,x}(011) \sin \zeta \cos \xi$$

$$H(2,8) = 4E_{xy,x}(110) \cos \zeta \sin \eta + 4E_{xy,x}(011) \sin \eta \cos \xi$$

$$H(2,9) = -4E_{xy,s}(110) \sin \eta \sin \zeta$$

$$H(3,4) = 2\sqrt{3} E_{xy,3z^2-r^2}(110) \sin \xi \sin \zeta$$

$$H(3,5) = 2E_{xy,3z^2-r^2} \sin \xi \sin \zeta$$

$$H(3,6) = 4E_{xy,x}(110) \cos \xi \sin \zeta + 4E_{xy,x}(011) \sin \zeta \cos \eta$$

$$H(3,7) = 0$$

$$H(3,8) = 4E_{xy,x}(110) \cos \zeta \sin \xi + 4E_{xy,x}(011) \sin \xi \cos \eta$$

$$H(3,9) = -4E_{xy,s}(110) \sin \zeta \sin \xi$$

$$H(4,5) = \sqrt{3} E_{3z^2-r^2,3z^2-r^2}(110)(\cos \xi \cos \zeta - \cos \eta \cos \zeta) -$$

$$\sqrt{3} E_{x^2-y^2,x^2-y^2}(110)(\cos \xi \cos \zeta - \cos \eta \cos \zeta)$$

$$H(4,6) = 2\sqrt{3} E_{3z^2-r^2,z}(011) \sin \xi (\cos \eta + \cos \zeta) +$$

$$2E_{x^2-y^2,z}(011) \sin \xi (\cos \eta - \cos \zeta)$$

$$H(4,7) = -2\sqrt{3} E_{3z^2-r^2,z}(011) \sin \eta (\cos \xi + \cos \zeta) -$$

$$2E_{x^2-y^2,z}(011) \sin \eta (\cos \xi - \cos \zeta)$$

$$H(4,8) = 4E_{x^2-y^2,z}(011) \sin \zeta (\cos \eta - \cos \xi)$$

$$H(4,9) = 2\sqrt{3} E_{3z^2-r^2,s}(110)(\cos \eta \cos \zeta - \cos \xi \cos \zeta)$$

$$H(5,6) = -2E_{3z^2-r^2,z}(011) \sin \xi (\cos \eta + \cos \zeta) +$$

$$2\sqrt{3} E_{x^2-y^2,z}(011) \sin \xi (\cos \eta - \cos \zeta)$$

$$H(5,7) = -2E_{3z^2-r^2,z}(011) \sin \eta (\cos \xi + \cos \zeta) +$$

$$2\sqrt{3} E_{x^2-y^2,z}(011) \sin \eta (\cos \xi - \cos \zeta)$$

$$H(5,8) = 4E_{3z^2-r^2,z}(011)(\cos \xi \sin \zeta + \cos \eta \sin \zeta)$$

$$H(5,9) = -2E_{3z^2-r^2,s}(110)(-2 \cos \xi \cos \eta + \cos \xi \cos \zeta + \cos \eta \cos \zeta)$$

$$H(6,7) = -4E_{x,y}(110) \sin \xi \sin \eta$$

$$H(6,8) = -4E_{x,y}(110) \sin \xi \sin \zeta$$

$$H(6,9) = -4E_{x,s}(110)(\sin \xi \cos \eta + \sin \xi \cos \zeta)$$

$$H(7,8) = -4E_{x,y}(110) \sin \eta \sin \zeta$$

$$H(7,9) = -4E_{x,s}(110)(\sin \eta \cos \xi + \sin \eta \cos \zeta)$$

$$H(8,9) = -4E_{x,s}(110)(\sin \zeta \cos \eta + \sin \zeta \cos \xi)$$

APPENDIX C: COMPUTER PROGRAM FOR THE FCC TIGHT-BINDING INTERPOLATION SCHEME

This program involves the following steps:

1. Reading in the parameter values and the $\vec{k}$ -points (in units of $\frac{\pi}{4a}$) for which energy levels are to be calculated.
2. For each $\vec{k}$ -point, calculating the Hamiltonian matrix elements, diagonalizing the matrix to obtain the energy eigenvalues and eigenfunction coefficients $U(M,N)$, and placing the results in the appropriate histograms for density of states, etc.

3. Printing out the following information for the full calculation, with results expressed per atom per spin:

ENERGY = energy

DENS = cumulative number of states for all energies
lower than ENERGY

DENST = cumulative number of states corresponding to
d bands of T_{2g} character (xy,yz,zx)

DENSE = cumulative number of states corresponding to
d bands of E_g character ($x^2-y^2, 3z^2-r^2$)

DENSP = cumulative number of states corresponding to
p bands

DENSS = cumulative number of states corresponding to
s bands

ETA = density of states at ENERGY computed using an
interval of 0.01 Ry

ETOTAL = sum of one-electron energies of all occupied
states below ENERGY

The program itself is given below:

```

      DIMENSION H(9,9),U(9,9),XXXX(9),DENS(1000)
      DIMENSION W(510),X(510),Y(510),Z(510),ETOTAL(1000)
      DIMENSION DENSE(1000),DENSS(1000),DENSP(1000),DENST(1000)
      WRITE (6,320)
320  FORMAT (1H1)
C    X(I), Y(I), AND Z(I) ARE VALUES OF KX,KY, AND KZ IN UNITS OF PI/8A
100  FORMAT (F7.5,2I3,F7.1)
150  FORMAT (6(1X,F2.0,3F3.2))
180  FORMAT (6F8.5)
      READ (5,100) RAP,NPTS,NDENS,BZWT
      READ (5,180) E11000,E11110,E11011,E44110,E55000,E55110
      READ (5,180) E12011,E15110,E16011,E16110,E19110
      READ (5,180) E48011,E58011
      READ (5,180) E59110,E66000,E66011,E66110,E67110,E69110
      READ (5,180) E99000,E99110
      READ (5,150) (W(I), X(I), Y(I), Z(I), I=1, NPTS )
120  FORMAT (6(3X,F8.5))
      WRITE (6,120) E11000,E11110,E11011,E44110,E55000,E55110
      WRITE (6,120) E12011,E15110,E16011,E16110,E19110
      WRITE (6,120) E48011,E58011
      WRITE (6,120) E59110,E66000,E66011,E66110,E67110,E69110
      WRITE (6,120) E99000,E99110
      ENERGY=-.1
      ETA=0.0
      IF(NDENS) 190,300,190
190  DO 250 I=1,900
      DENS(I) = 0.0
      DENSS(I)=0.0
      DENSP(I)=0.0
      DENSE(I)=0.0
      DENST(I)=0.0
      ETOTAL(I)=0.0
250  CONTINUE
300  DO 100 I=1, NPTS
      SX=SIN(0.392699*X(I))
      SY=SIN(0.392699*Y(I))
      SZ=SIN(0.392699*Z(I))
      CX=COS(0.392699*X(I))
      CY=COS(0.392699*Y(I))
      CZ=COS(0.392699*Z(I))

```


$H(1,1)=E11000+4.*E11110*CX*CY+4.*E11011*(CX*CZ+CY*CZ)$
 $H(2,2)=E11000+4.*E11110*CY*CZ+4.*E11011*(CY*CX+CZ*CX)$
 $H(3,3)=E11000+4.*E11110*CZ*CX+4.*E11011*(CZ*CY+CX*CY)$
 $H(4,4)=E55000+3.*E55110*(CX*CZ+CY*CZ)+4.*E44110*(CX*CY+CX*CZ/4.+CY$
 $X *CZ/4.)$
 $H(5,5)=E55000+4.*E55110*(CX*CY+CX*CZ/4.+CY*CZ/4.)+3.*E44110*(CX*CZ$
 $X +CY*CZ)$
 $H(6,6)=E66000+4.*E66110*(CX*CY+CX*CZ)+4.*E66011*CY*CZ$
 $H(7,7)=E66000+4.*E66110*(CY*CZ+CY*CX)+4.*E66011*CZ*CX$
 $H(8,8)=E66000+4.*E66110*(CZ*CX+CY*CZ)+4.*E66011*CX*CY$
 $H(9,9)=E99000+4.*E99110*(CX*CY+CY*CZ+CZ*CX)$
 $H(1,2)=-4.*E12011*SX*SY$
 $H(1,3)=-4.*E12011*SY*SZ$
 $H(1,4)=0.$
 $H(1,5)=-4.*E15110*SX*SY$
 $H(1,6)=4.*E16110*CX*SY+4.*E16011*SY*CZ$
 $H(1,7)=4.*E16110*CY*SX+4.*E16011*SX*CZ$
 $H(1,8)=0.$
 $H(1,9)=-4.*E19110*SX*SY$
 $H(2,3)=-4.*E12011*SX*SY$
 $H(2,4)=-2.*SQRT(3.)*E15110*SY*SZ$
 $H(2,5)=2.*E15110*SY*SZ$
 $H(2,6)=0.$
 $H(2,7)=4.*E16110*CY*SZ+4.*E16011*SZ*CX$
 $H(2,8)=4.*E16110*CZ*SY+4.*E16011*SY*CX$
 $H(2,9)=-4.*E19110*SY*SZ$
 $H(3,4)=2.*SQRT(3.)*E15110*SX*SZ$
 $H(3,5)=2.*E15110*SX*SZ$
 $H(3,6)=4.*E16110*CX*SZ+4.*E16011*SZ*CY$
 $H(3,7)=0.$
 $H(3,8)=4.*E16110*CZ*SX+4.*E16011*SX*CY$
 $H(3,9)=-4.*E19110*SZ*SX$
 $H(4,5)=SQRT(3.)*E55110*(CX*CZ-CY*CZ)-SQRT(3.)*E44110*(CX*CZ-CY*CZ)$
 $H(4,6)=2.*SQRT(3.)*E58011*SX*(CY+CZ)+2.*E48011*SX*(CY-CZ)$
 $H(4,7)=-2.*SQRT(3.)*E58011*SY*(CX+CZ)-2.*E48011*SY*(CX-CZ)$
 $H(4,8)=4.*E48011*SZ*(CY-CX)$
 $H(4,9)=2.*SQRT(3.)*E59110*(CY*CZ-CX*CZ)$
 $H(5,6)=-2.*E58011*SX*(CY+CZ)+2.*SQRT(3.)*E48011*SX*(CY-CZ)$
 $H(5,7)=-2.*E58011*SY*(CX+CZ)+2.*SQRT(3.)*E48011*SY*(CX-CZ)$
 $H(5,8)=4.*E58011*(CX*SZ+CY*SZ)$
 $H(5,9)=-2.*E59110*(-2.*CX*CY+CX*CZ+CY*CZ)$
 $H(6,7)=-4.*E67110*SX*SY$
 $H(6,8)=-4.*E67110*SX*SZ$
 $H(6,9)=-4.*E69110*(SX*CY+SX*CZ)$
 $H(7,8)=-4.*E67110*SY*SZ$
 $H(7,9)=-4.*E69110*(SY*CX+SY*CZ)$
 $H(8,9)=-4.*E69110*(SZ*CY+SZ*CX)$

C. MATRIX OF H'S IS DIAGONALIZED

```

N=9
IEGEN=0.
NR=0.
DO 500 K=1,9
500 H(K,K)=H(K,K)+2.
CALL HDIAG (H,N,IEGEN,U,NR,XXXX,IQ,RAP)
DO 505 J=1,9
505 H(J,J) = H(J,J) - 2.0
WRITE (6,200) X(I),Y(I),Z(I), (H(J,J),J=1,9)
200 FORMAT (2X, 3F6.2, 9F10.4)
IF (NDENS) 510,1000,510
510 DO 530 J=1,9
IF (H(J,J)-.800) 520,520,530
520 HJJ=1000.*(H(J,J)+.0005)
NHJJ=HJJ
NHJJ=NHJJ+101
DENS (NHJJ)=DENS (NHJJ)+W(I)/BZWT
DENSS (NHJJ)=DENSS (NHJJ)+W(I)*(U(9,J)**2)/BZWT
DENSP (NHJJ)=DENSP (NHJJ)+W(I)*(U(6,J)**2+U(7,J)**2+U(8,J)**2)/BZWT
DENSE (NHJJ)=DENSE (NHJJ)+W(I)*(U(4,J)**2+U(5,J)**2)/BZWT
DENST (NHJJ)=DENST (NHJJ)+W(I)*(U(1,J)**2+U(2,J)**2+U(3,J)**2)/BZWT
ETOTAL (NHJJ)=ETOTAL (NHJJ)+H(J,J)*W(I)/BZWT
530 CONTINUE
1000 CONTINUE
IF (NDENS) 700,850,700
700 WRITE (6,705)
750 FORMAT (1H1)
DO 710 N=2,900
DENSS (N)=DENSS (N)+DENSS (N-1)
DENSP (N)=DENSP (N)+DENSP (N-1)
DENSE (N)=DENSE (N)+DENSE (N-1)
DENST (N)=DENST (N)+DENST (N-1)
ETOTAL (N)=ETOTAL (N)+ETOTAL (N-1)
710 DENS (N)=DENS (N)+DENS (N-1)
ETA=100.*DENS (1)
WRITE (6,800) ENERGY,DENS (1),DENST (1),DENSE (1),DENSP (1),DENSS (1),E
XTA,ETOTAL (1)
DO 720 N=2,5
ENERGY=ENERGY+.001
ETA=100.*DENS (N+5)
720 WRITE (6,800) ENERGY,DENS (N),DENST (N),DENSE (N),DENSP (N),DENSS (N),E
XTA,ETOTAL (N)
DO 730 N=6,895
ENERGY=ENERGY+.001
ETA=100.*(DENS (N+5)-DENS (N-5))
730 WRITE (6,800) ENERGY,DENS (N),DENST (N),DENSE (N),DENSP (N),DENSS (N),E
XTA,ETOTAL (N)
DO 740 N=896,900

```

```
ENERGY=ENERGY+.001  
740 WRITE (6,800) ENERGY,DENS(N),DENST(N),DENSE(N),DENSEP(N),DENSS(N),E  
XTA,ETOTAL(N)  
800 FORMAT (3X,F5.3,7(5X,F10.7))  
850 STOP  
END
```

APPENDIX D: PARAMETER FITS

There are eight pure d parameters chosen by exact fits to the pure d levels Γ_{25}^1 , Γ_{12} , X_3 , X_2 , X_5 , L_{31} , L_{32} , and K_4 :

$$E_{xy,xy}(000) = \frac{1}{2} X_5 + \frac{1}{4} (\Gamma_{25}^1 + X_3)$$

$$E_{xy,xy}(110) = \frac{1}{16} (\Gamma_{25}^1 + X_3) - \frac{1}{8} X_5$$

$$E_{xy,xy}(011) = \frac{1}{16} (\Gamma_{25}^1 - X_3)$$

$$E_{xy,yz}(011) = \frac{1}{4} [L_{31} + L_{32} - \frac{1}{2} X_5 - \frac{1}{4} X_3 - \frac{1}{4} \Gamma_{25}^1 + \frac{1}{2} (\frac{1}{2} - \frac{1}{\sqrt{2}}) \Gamma_{12} + (\frac{1}{2} + \frac{1}{\sqrt{2}}) X_2 - 2K_4]$$

$$E_{xy,3z^2-r^2}(110) = \sqrt{\frac{1}{96} \{ (L_{32} - L_{31})^2 - [(\sqrt{2} - 1) \Gamma_{12} - (1 + \sqrt{2}) X_2 + 4K_4 - L_{31} - L_{32}]^2 \}}$$

$$E_{x^2-y^2, x^2-y^2}(110) = \frac{1}{8} [(2 - \sqrt{2}) \Gamma_{12} + (2 + \sqrt{2}) X_2 - 4K_4]$$

$$E_{3z^2-r^2, 3z^2-r^2}(000) = \frac{1}{2} (\sqrt{2} - 1) \Gamma_{12} - (\frac{1}{2} + \frac{1}{\sqrt{2}}) X_2 + 2K_4$$

$$E_{3z^2-r^2, 3z^2-r^2}(110) = \frac{1}{24} [\sqrt{2} \Gamma_{12} - (4 + \sqrt{2}) X_2 + 4K_4]$$

There are seven pure s-p parameters fit to the four levels Γ_1 , Γ_{15} (a high level well above the d bands), X_4^1 , and L_2^1 and to these sums of hybridizing levels: $L_{11} + L_{12}$, $\Lambda_{11} + \Lambda_{12}$ at $\Delta(0, \frac{\pi}{a}, 0)$, and $\Lambda_{11} + \Lambda_{12}$ at $\Delta(\frac{\pi}{2a}, \frac{\pi}{2a}, \frac{\pi}{2a})$

$$E_{s,s}(000) = L_{11} + L_{12} - E_{xy,xy}(000) + 8E_{xy,yz}(011)$$

$$E_{s,s}(110) = \frac{1}{12} (\Gamma_1 - E_{s,s}(000))$$

$$E_{x,x}(110) = \frac{1}{16} (\Gamma_{15} - X_4')$$

$$E_{x,x}(011) = \frac{1}{8} (\Gamma_{15} + X_4') - \frac{1}{4} E_{x,x}(000)$$

$$E_{x,y}(110) = \frac{1}{8} (E_{x,x}(000) - L_2')$$

where $E_{x,x}(000)$ and $E_{x,s}(110)$ are chosen to fit $\Delta_{11} + \Delta_{12}$ and $\Lambda_{11} + \Lambda_{12}$.

There are six hybridization parameters which mix the d bands with the s-p bands:

$E_{xy,s}(110)$ is chosen to fit L_{11} exactly

$E_{3z^2-r^2,s}(110)$ is chosen to fit X_{11} exactly

$E_{3z^2-r^2,z}(011)$ is chosen to fit Δ_{11} and Δ_{12} approximately

$E_{x^2-y^2,z}(011)$ is chosen to fit W_2' approximately

$E_{xy,x}(110)$ is chosen to fit W_3 approximately

$E_{xy,x}(011)$ is chosen to fit Λ_{11} , Λ_{12} , K_{11} , and K_{12} approximately.