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Structure Dependence of d Bands in Transition Metals

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The object is to provide a simple scheme for calculating the dependence of the d-band structure on the position of the atoms in the crystal. The Korringa-Kohn-Rostoker method in the narrow-band approximation has been used to calculate the nonhybridizing d bands for different crystal structures and for various values of volume/atom, in terms of the position and width of the d-scattering resonance. These bands have been fitted by near-neighbor linear combination of atomic orbitals (LCAO) parameters, as in the interpolation schemes of Hodges, Ehrenreich, and Lang, and of Mueller. It is shown that the dependence of the LCAO parameters on structure and volume can be described to a good approximation by simple structure-independent functions. The accuracy of the description for the d bands of the fcc and bcc phases of Fe is about 0.01 Ry. The results are discussed in relation to recent developments in transition-metal band theory.

1. INTRODUCTION

IT has recently been demonstrated[1,2] that the band structures of fcc transition metals can be accurately parametrized in terms of a nearly-free-electron (NFE) band, described by pseudopotential theory, interacting with a set of d bands, described by near-neighbor linear combination of atomic orbitals (LCAO) parameters. In symmetry directions of the Brillouin zone some d bands do not hybridize with the NFE band; these "nonhybridizing" bands depend only on the LCAO parameters, and can be used to study the d bands independently.

Here we parametrize the d bands of a transition metal in terms of the position E_d and the width W of the d scattering resonance. These two parameters depend only on the potential and are independent of the particular lattice arrangement (insofar as the potential in each cell is independent of the structure). It is shown that the near-neighbor LCAO parameters which describe the bands can then be determined as a function of the structure in a simple way.

Heine's[3] resonance form of the Korringa-Kohn-Rostoker (KKR) secular equation in the narrow band approximation is first summarized, and its useful features are discussed. This secular equation is used, with the tabulated KKR structure constants,[4] to determine the nonhybridizing d bands in the principal symmetry directions, in terms of E_d and W, for various values of lattice constant, for the fcc and bcc structures. First and second-neighbor LCAO parameters to fit these bands are then determined by minimizing the rms deviation, as in Mueller's[2] interpolation scheme, giving the parameters as a function of volume and structure. It is then shown empirically that these LCAO parameters can be expressed to a good approximation as simple functions of volume and nearest-neighbor distance, where the functions are structure-independent. The accuracy of this description is demonstrated by choosing E_d and W to fit the d bands of fcc Fe, and then predicting the LCAO parameters which describe the d bands of both the fcc and bcc phases of Fe. Finally, the scheme is discussed in relation to recent developments in transition-metal band theory by Heine,[3] by Hubbard,[5] and by Jacobs[6]; it is shown that the tight-binding integrals of the resonance orbitals[3] in the narrow-band KKR theory should not be identified with the near-neighbor LCAO parameters.

2. NARROW-BAND APPROXIMATION

In KKR theory,[7] the energies $E(\mathbf{k})$ of the nonhybridizing d bands are contained in the solutions of the $l=2$ block of the KKR secular equation. In terms of the structure constants $B_{lm,l'm'}$ defined by Segall and Ham[4,8] with respect to real angular wave functions, the $l=2$ block is (for a structure with one atom per unit cell)

$$\det\|B_{2m,2m'}(\mathbf{k},K)+K\delta_{mm'}\cot\eta_2\|=0. \qquad (2.1)$$

Here $K=E^{1/2}$, η_2 is the $l=2$ phase shift, and m designates the five d-real angular wavefunctions. The d-scattering resonance leads to the following form for η_2 in the energy range of the d bands[9]:

$$\tan\eta_2=\tfrac{1}{2}W/(E_d-E), \qquad (2.2)$$

where E_d and W are the position (relative to the muffin-tin constant) and width, respectively, of the d resonance. Heine's narrow-band approximation is to substitute (2.2) into (2.1) and evaluate the structure constants at $K=K_d\equiv E_d^{1/2}$, giving [Eq. (40) of Ref. 3]

$$\det\left\|\frac{aB_{2m,2m'}}{2K_d a}-\frac{(E-E_d)}{W}\delta_{mm'}\right\|=0, \qquad (2.3)$$

where a is the lattice constant. For several bands in symmetry directions only one diagonal element of (2.3)

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[1] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

[2] F. M. Mueller, Phys. Rev. **153**, 659 (1967).

[3] V. Heine, Phys. Rev. **153**, 673 (1967).

[4] B. Segall and F. S. Ham (unpublished). A copy of this report may be obtained as described in F. S. Ham, Phys. Rev. **128**, 82 (1962).

[5] J. Hubbard, Proc. Phys. Soc. (London) **92**, 921 (1967).

[6] R. L. Jacobs, Proc. Phys. Soc. (London) **1**, 492 (1968).

[7] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[8] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

[9] J. M. Ziman, Proc. Phys. Soc. (London) **86**, 337 (1965).

need be considered. Equation (2.3) is particularly convenient because, for a given structure, $aB_{2m,2m'}$ depends on K_d and a only through the product K_da, so the bands, in units of W, depend on the single variable K_da. (Segall and Ham[4] have tabulated the structure constants as a function of K_da for **k** values in the principal symmetry directions of the fcc and bcc structures.)

This narrow-band limit (evaluating the structure constants at $K=K_d$) can be considered correct to first order in W.[3] Heine[3] has shown that if W is estimated from the potential for Cu the solutions of (2.3) for the nonhybridizing bands agree well with the calculated Cu bands, demonstrating the accuracy of the narrow-band approximation. In particular, the bands have the correct shape to a very good approximation. It will be shown that if we choose E_d and W as parameters to fit the position and width of the d bands of a transition metal, then Eq. (2.3) will describe the bands accurately; the results of Sec. 4 indicate that the rms error involved in doing this for bcc or fcc Fe is about 0.01 Ry.

3. STRUCTURE DEPENDENCE OF *d* BANDS

A. LCAO Parametrization

Equation (2.3) provides a convenient tool to study the dependence of the d bands on the crystal structure and volume of the metal. We have calculated[10] the nonhybridizing d bands of (2.3) in the principal symmetry directions, at the values of **k** for which the KKR structure constants have been tabulated,[4] for $\epsilon=0.37$, 0.47, 0.57, and 0.67 for the fcc structure and $\epsilon=0.25$ and 0.35 for the bcc structure, where $\epsilon\equiv K_d^2a^2/4\pi^2$. [To decide which bands are nonhybridizing it is necessary to know the value of k beyond which the hybridization function vanishes. For bcc this has been assumed to be approximately the same as for Mueller's[2] $g(k)$. The choice is not critical.] This covers the range of values of K_da for most transition and noble metals. In each case the energies have been calculated at more than 20 d-band points. The bands have then been fitted by the first- and second-neighbor LCAO parameters of Slater and Koster's[11] two-center approximation d_0, $dd\sigma(s)$, $dd\pi(s)$, and $dd\delta(s)$, for the first- and second-neighbor distances s by minimizing the rms deviation between the calculated bands and the LCAO bands, as in Mueller's[2] scheme. (We have omitted the three-center parameter γ having found that it has only a small effect on the accuracy of the fit.[2]) The values of the parameters and the corresponding rms deviations are listed in Table I.

As shown in Sec. 4, these rms deviations are of the order of 0.01 Ry for a transition metal. We have found, as Mueller did, that the second-neighbor parameters for the fcc structure are negligibly small. However, the second-neighbor bcc parameters are sizeable, and cannot be ignored. (Fitting the bcc bands with first-neighbor parameters only was found to increase the rms deviation by a factor of 4.)

Table I. LCAO parametrization of the nonhybridizing d bands of the KKR secular equation in the narrow-band approximation.

LCAO parameters (units of W)	fcc				bcc	
	$\epsilon=0.37$	0.47	0.57	0.67	$\epsilon=0.25$	0.35
d_0-E_d	0.930	0.615	0.421	0.283	0.940	0.515
$dd\sigma(1)$	−1.520	−0.950	−0.666	−0.510	−1.420	−0.738
$dd\pi(1)$	0.704	0.456	0.334	0.265	0.842	0.610
$dd\delta(1)$	−0.008	−0.007	−0.007	−0.006	−0.114	−0.137
$dd\sigma(2)$	−0.038	−0.031	−0.028	−0.027	−0.734	−0.533
$dd\pi(2)$	0.005	0.006	0.005	0.006	0.314	0.203
$dd\delta(2)$	0.113	0.073	0.053	0.042	−0.048	−0.098
rms error	0.33	0.21	0.16	0.13	0.04	0.16

B. Analysis of LCAO Parameters

If the values $dd\lambda(s)$ (where $\lambda=\sigma$, π, δ) of the LCAO secular equation were determined by calculating overlap integrals of the potential between localized orbitals centered on different lattice sites, $dd\lambda$ would depend solely on the interatomic distance s and would not depend on the structure. It is of interest to determine whether the near-neighbor LCAO parameters which have been varied arbitrarily to fit calculated d bands are also simply functions of s. For a fixed d resonance, i.e., for fixed values of E_d and W, Table I gives ddλ for 12 values of s. As an example, $dd\pi$ is plotted versus s in Fig. 1. It is clear that the parameters cannot be expressed as functions of s to any useful accuracy. The reason is clear from Fig. 1; the d bandwidth does not decrease so rapidly with increasing lattice constant that it would be of negligible width if, for example, the fcc crystal were expanded so that the new first-neighbor distance were equal to the former second-neighbor distance.

It is now shown that the results of Table I are, to a good approximation, consistent with a relation of the form

$$dd\lambda=\Delta(\Omega)F_\lambda(s/r_0)\,, \qquad (3.1)$$

where $\Omega=$volume/atom, r_0 is the Wigner-Seitz sphere radius, and the functions Δ and F_λ are *independent* of structure. Equation (3.1) requires that the d bands remain the same shape, changing only in width, as the volume is changed for a fixed structure. [The shape of the fcc bands, for example, is determined by the ratio $dd\sigma(1){:}dd\pi(1){:}dd\delta(1)$.] It also requires that the dependence of the d bandwidth on volume be the same for each structure. Equation (2.3) has been used to determine the volume dependence of the bandwidth. For the fcc structure, the difference $E(X_2)-E(X_3)$ has been taken as a measure of the bandwidth, and is shown as a function of Ω in Fig. 2. We have also plotted

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[10] I am indebted to Roy Jacobs for his table of the appropriate Clebsch-Gordan coefficients of Eq. (5.4).

[11] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

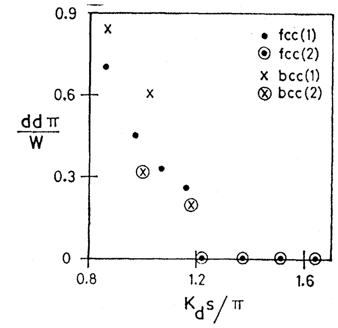

FIG. 1. The parameter $dd\pi$, determined by fitting bands of the KKR narrow-band approximation, is plotted against interatomic distance s to demonstrate that the LCAO parameters cannot be considered as functions solely of s to useful accuracy.

$c_2[E(H_{25'})-E(H_{12})]$ for the bcc structure and $c_3[E(\Gamma_5^-)-E(\Gamma_6^+)]$ for hcp,[12] where c_2 and c_3 are chosen to normalize the bandwidths to the fcc case ($c_2=0.748$, $c_3=4.44$). Figure 2 shows that the volume dependence of the bandwidth is approximately the same for each structure. The mean (solid line) curve of Fig. 2 is taken as the definition of the function $\Delta(\Omega)$ of (3.1), which can be considered as a canonical bandwidth. The values in Table I are used to plot $dd\lambda/\Delta$ versus s/r_0 in Fig. 3. The mean curves can be considered as definitions of the functions F_λ of (3.1). The errors corresponding to the scatter of the points from the mean curves are reasonably small for actual transition metals (see Sec. 4).

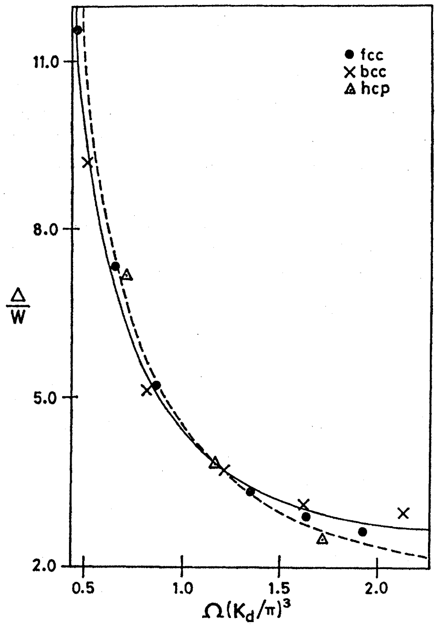

FIG. 2. The bcc and hcp d bandwidths have been normalized to that of the fcc structure. It is seen that the dependence of the d bandwidth on volume can be described accurately by a single structure-independent function Δ, defined by the solid line curve. The dashed curve is the prediction of the simple cellular model of Sec. 5 A.

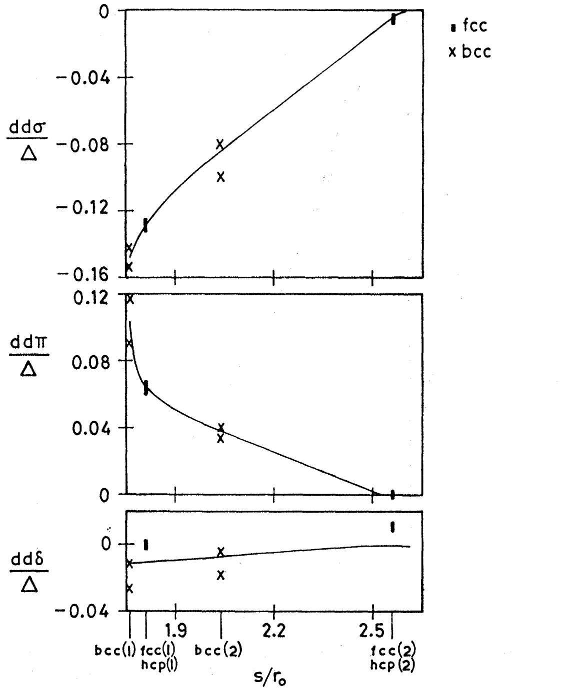

FIG. 3. It is shown that the results of Table I can be described by Eq. (3.1). Each rectangle indicates the spread of four values for the fcc structure. The solid-line curves can be considered as definitions of the functions F_λ.

Now consider the dependence of d_0 on structure and volume. Define

$$d_0' \equiv d_0 - E_d. \tag{3.2}$$

In Fig. 4, the values d_0' of Table I are plotted versus first-neighbor distance $s(1)$; they are consistent with a structure-independent description of d_0' as a function solely of $s(1)$.

If the bands have a fixed shape for each structure [Eq. (3.1)], the position of d_0 relative to the top and bottom of the band must also be fixed; this is demonstrated for the fcc structure in Table II.

Because of the accuracy of the narrow-band approximation, Figs. 2–4 should provide a good description of the d bands for the fcc and bcc structures, in terms of the two resonance parameters. It is now verified that the bands in the hcp structure are also consistent with this description, giving evidence that these functions describe properties of the bands that are approximately independent of structure.

C. Validity for hcp Structures

The first- and second-neighbor interatomic distances in the hcp structure are the same as in an fcc structure of the same volume/atom. If the above description is correct then the LCAO parameters should also be approximately the same in the two cases.

Figures 2–4 are used to predict the LCAO parameters

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[12] I am indebted to H. L. Davis and J. S. Faulkner for making available some KKR constants for the hcp structure.

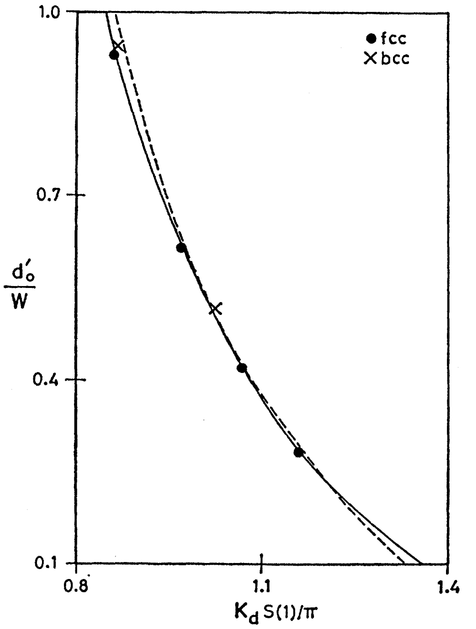

FIG. 4. The values of Table I are seen to be consistent with a description of d_0' ($\equiv d_0 - E_d$) as a function solely of first neighbor distance $s(1)$, given by the solid line curve. The dashed curve is the prediction of the simple cellular model of Sec. 5 A.

d_0, $dd\sigma(1)$, $dd\pi(1)$, and $dd\delta(1)$, in units of W, to correspond to the narrow-band approximation for the hcp structure, for the ideal c/a ratio, for $K_d a = \pi$ (where a is the usual hcp lattice constant). The matrix elements of the LCAO secular equation for the hcp structure[13] have been used with these values of the parameters to calculate the energies at two d-band points, Γ_5^- and Γ_6^+; the values are given in Table III. For comparison, the equivalent of Eq. (2.3) for the hcp structure[14] has been used with the KKR structure constants for hcp[12] to calculate the energies at Γ_5^- and Γ_6^+ in the narrow-band approximation for this Ka value. The deviations of the predicted values are given in Table III. For a d bandwidth equal to that of Cu, these deviations are 0.01 Ry.

4. ACCURACY OF DESCRIPTION

An example is now presented to estimate the magnitude of the errors involved when the description of Figs. 2–4 is applied to actual transition metals.

Wood[15] has calculated the band structures of the bcc and fcc phases of Fe by the augmented-plane-wave (APW) method. The same cellular potential was used for both calculations. (This potential was terminated at half the nearest-neighbor distance, which is a slightly different radius for the two phases, to form the muffin-tin potentials of Wood's calculations.) We choose E_d and W to fit the fcc Fe d bands, and then use Figs. 2–4 to predict the values of the LCAO parameters for both the fcc and bcc phases; these values will then be used in the LCAO secular equation to calculate the nonhybridizing bands for both phases, to compare with the APW calculations.

TABLE II. Constant position of d_0 relative to the top and bottom of the band for the fcc structure.

ϵ	$\frac{E(X_2)-d_0}{E(X_2)-E(X_3)}$
0.37	0.349
0.47	0.349
0.57	0.349
0.67	0.348

Since the d bands for the fcc structure are considered to have a fixed shape, determined by Fig. 3, the only variables are the position and width of the bands (given by E_d and W). Any two energy values on the nonhybridizing bands are sufficient to determine these two parameters. For convenience we choose $E(X_2)$ and $E(X_3)$ for Wood's fcc Fe bands. Then,

$$\Delta = E(X_2) - E(X_3)$$

and d_0 is determined by (Table II):

$$[E(X_2)-d_0]/[E(X_2)-E(X_3)] = 0.349 .$$

From d_0, Δ, and Eq. (3.2), the values of K_d and W for Fe are determined from Figs. 2 and 4 by trial and error or iteration ($E_d = 0.641$ Ry, $W = 0.105$ Ry). The corresponding LCAO parameters for both phases of Fe (taking into account the different volume of the bcc phase) follow from Figs. 2–4, and are listed in Table IV as the "predicted" values. (In each case d_0 is tabulated relative to Wood's muffin-tin constant, which is 0.040 Ry lower for the bcc calculation.) More than 20 energies on the nonhybridizing d bands for each phase have then been calculated from these parameters and the LCAO secular equation, and compared with Wood's APW bands to calculate the rms errors of Table IV. The APW d bands have also been fitted directly by varying the LCAO parameters arbitrarily to minimize the rms error, as in Mueller's scheme, and these "fitted" parameters are listed in Table IV for comparison. Finally, the error in the *shape* of the predicted bcc bands has been estimated by choosing d_0 as the value determined by fitting the APW bands, but using the predicted values of the $dd\lambda$ parameters.

TABLE III. Comparison of predicted and calculated energies for hcp.

hcp energies	Prediction (units of W)	KKR (units of W)	Deviation (units of W)	Deviation (Ry, for Cu)
$E(\Gamma_5^-)-E_d$	2.34	2.70	−0.36	−0.01
$E(\Gamma_6^+)-E_d$	0.76	1.08	−0.32	−0.01

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[13] M. Miasek, Phys. Rev. **107**, 92 (1957).

[14] J. Treusch and R. Sandrock, Phys. Status Solidi **16**, 487 (1966).

[15] J. H. Wood, Phys. Rev. **126**, 517 (1962).

TABLE IV. Comparison of predicted values of the LCAO parameters for fcc and bcc Fe, with the optimum values obtained by fitting Wood's APW bands.

LCAO parameters (Ry)	fcc (predicted)	fcc (fitted)	bcc (predicted)	bcc (fitted)	bcc (shape)
d_0	0.662	0.659	0.707	0.696	0.696
$dd\sigma(1)$	−0.0463	−0.0485	−0.0538	−0.0530	−0.0538
$dd\pi(1)$	0.0228	0.0198	0.0377	0.0348	0.0377
$dd\delta(1)$	−0.0036	−0.0008	−0.0044	−0.0052	−0.0044
$dd\sigma(2)$	0	0	−0.0305	−0.0307	−0.0305
$dd\pi(2)$	0	0	0.0138	0.0127	0.0138
$dd\delta(2)$	0	0	−0.0025	−0.0038	−0.0025
rms error	0.015	0.010	0.020	0.007	0.012

On the basis of a simple cellular model (see Sec. 5 A) the mean position of the *d* bands, d_0, is expected to be higher for a bcc structure than for an fcc structure of the same volume/atom if the same cellular potential is used, in agreement with Fig. 4. Table IV shows that d_0 for bcc Fe, as determined by fitting the APW bands, is 0.003 Ry lower than fcc (when compared relative to the same zero of energy); this is probably the result of terminating the cellular potential at a smaller muffin-tin sphere radius for the bcc calculation. The fcc (predicted) and bcc (shape) cases of Table IV show that the description of Figs. 2–4 predicts the fcc and bcc bands of Fe to within an rms error which is only 0.005 Ry greater than that of the optimum LCAO fits.

5. RELATION TO RECENT *d*-BAND THEORY

This description of *d* bands is now discussed in relation to recent theoretical work in this field by Heine,[3] by Hubbard,[5] and by Jacobs.[6]

A. Volume Dependence of Δ and d_0

Heine has considered the dependence on volume of the *d* bandwidth in terms of a simple cellular model. In this model the wave functions satisfying the antibonding and bonding conditions at half the nearest-neighbor distance *R* have energies $E_{\max}$ and $E_{\min}$, respectively, given by [Eq. (52) of Ref. 3];

$$\begin{aligned} E_{\max}-E_d&=-\tfrac{1}{2}W[n_2(K_dR)/j_2(K_dR)],\\ E_{\min}-E_d&=-\tfrac{1}{2}W[n_2'(K_dR)/j_2'(K_dR)], \end{aligned} \tag{5.1}$$

where j_2 and n_2 are the spherical Bessel and Neumann functions, and the primes denote differentiation with respect to *R*. The difference

$$E_{\max}-E_{\min}=-\tfrac{1}{2}W[n_2(K_dR)/j_2(K_dR) -n_2'(K_dR)/j_2'(K_dR)] \tag{5.2}$$

is taken as the *d* bandwidth. Heine has evaluated the Bessel functions by retaining only the leading term in the limit of small K_dR, and has shown that this gives the bandwidth proportional to R^{-5}.

It can readily be shown that this approximation to the Bessel functions introduces large errors (30–60%) into the difference $(E_{\max}-E_{\min})$ for the range of values of KR which are of interest. If the Bessel functions are evaluated exactly, Eq. (5.2) gives the volume dependence of the bandwidth shown by the dashed-line curve of Fig. 2. [We have plotted c_4 $(E_{\max}-E_{\min})$, where c_4 has been chosen to normalize the curve to the function $\Delta(\Omega)$ ($c_4=0.659$), versus the volume/atom Ω of an fcc crystal having half the nearest-neighbor distance *R*.]

This cellular model can be used to explain also the dependence of d_0' on lattice constant. For a given structure, the relative position of d_0 within the *d* band is independent of volume (as in Table II), so that

$$(E_{\max}-d_0)/\Delta=c,$$

where *c* is a constant. Using (3.2),

$$d_0'/W=(E_{\max}-E_d)/W-c\Delta/W. \tag{5.3}$$

$(E_{\max}-E_d)/W$ is given as a function of *R* by (5.1), and Δ/W can be determined as a function of *R* for the fcc structure from Fig. 2. If *c* is chosen to fit one point on the solid-line curve of Fig. 4 ($c=0.568$ fixes the relative position of d_0 within the fcc bands), then (5.3) gives the dashed-line curve of Fig. 4.

Hence, qualitatively, the shape of the functions $\Delta(\Omega)$ and $d_0'(s)$ of Figs. 2 and 4 follow from the volume dependence of the top and bottom of the *d* band in this simple cellular model.

B. Resonance Orbitals

Heine has shown that if the LCAO method is used with tightbinding combinations of resonance orbitals in place of the atomic orbitals, the LCAO secular equation reduces to (2.3) in the two-center approximation. [A resonance orbital is defined as the *d* function resulting from the integration of Schrödinger's equation outwards from the origin for $E=E_d$, for the spherical potential $V(r)$ on a single lattice site; $V(r)$ is taken to be zero beyond the muffin-tin sphere. Since $E_d>0$, the resonance orbital has a long-range oscillatory tail outside the sphere radius.] The implication of Heine's derivation is that the corresponding energy integrals (the matrix elements of the potential between resonance orbitals centered on different sites) are to be identified with the LCAO parameters of the interpolation schemes, and that therefore resonance orbitals on near neighbors only must contribute significantly; also, it would follow that the LCAO parameters depend only on interatomic distance, independent of the structure. We now derive expressions for these integrals and show that the near-neighbor contributions are not dominant, but rather the integrals decrease slowly with distance. This demonstrates that the energy integrals of resonance orbitals are *not* to be identified with the LCAO parameters of a near-neighbor interpolation scheme; rather, the resonance orbitals on distant sites contribute to an effective-near neighbor representation.

By Eq. (2.19) of Ref. 8,

$$B_{2m,2m'}=4\pi\sum_{LM} D_{LM}C_{2m,2m'}{}^{LM}, \tag{5.4}$$

where the C's are Clebsch-Gordan coefficients. D_{LM} can be expressed as a summation over the direct lattice vectors of the crystal, as shown for the Kohn-Rostoker definition of the structure constants in Eq. (A2.22) of Ref. 7. For the Ham-Segall[4,8] definition of the structure constants, the corresponding expansion can be derived is a similar way, giving

$$D_{LM}=\frac{-i}{(4\pi)^{1/2}}K\delta_{L0}\delta_{M0}+Ki^{-L}\sum_{\mathbf{s}\neq0}\exp(i\mathbf{k}\cdot\mathbf{s}) \times[n_L(Ks)-ij_L(Ks)]\mathcal{Y}_{LM}(\mathbf{s}), \tag{5.5}$$

where $\mathbf{s}$ denotes the direct lattice vectors of the crystal and $\mathcal{Y}_{LM}$ denotes the real angular wave functions, as defined by Eqs. (2.9) of Ref. 16. For simplicity, consider the special case for which (1) L is even [in (5.4) C vanishes unless $L=0,2$, or 4], (2) $E>0$, and (3) the crystal has a center of inversion. By using the fact that D_{LM} is then real,[8] (5.5) becomes, for this case,

$$D_{LM}=K(-1)^{L/2}\sum_{\mathbf{s}\neq0}\exp(i\mathbf{k}\cdot\mathbf{s})n_L(Ks)\mathcal{Y}_{LM}(\mathbf{s}). \tag{5.6}$$

From (5.4) and (5.6),

$$B_{2m,2m'}=4\pi K\sum_{\mathbf{s}\neq0}\exp(i\mathbf{k}\cdot\mathbf{s}) \times\Big[\sum_{LM}(-1)^{L/2}C_{2m,2m'}{}^{LM}n_L(Ks)\mathcal{Y}_{LM}(\mathbf{s})\Big]. \tag{5.7}$$

But, from Eqs. (A6) and (A10) of Ref. 3,

$$B_{2m,2m'}(\mathbf{k},K_d)=\frac{2K}{W}\sum_{\mathbf{s}\neq0}\exp(i\mathbf{k}\cdot\mathbf{s}) \times\langle\Phi_m(0)|V(0)|\Phi_{m'}(\mathbf{s})\rangle, \tag{5.8}$$

where $\Phi_m(\mathbf{s})$ denotes the resonance orbital centered on site $\mathbf{s}$. By the uniqueness of the Fourier expansion, (5.7) and (5.8) give, for $\mathbf{s}\neq0$,

$$\langle\Phi_m(0)|V(0)|\Phi_{m'}(\mathbf{s})\rangle =2\pi W\sum_{LM}(-1)^{L/2}C_{2m,2m'}{}^{LM}n_L(K_ds)\mathcal{Y}_{LM}(\mathbf{s}). \tag{5.9}$$

It can readily be verified for a specific case that terms other than those of near neighbors contribute significantly for values of K_d corresponding to transition metals, because of the slow decrease of $n_L(K_ds)$ as a function of s for $L=0$, 2, and 4.

The energies of some bands in symmetry directions are given by a single diagonal element of (2.3). By approximating such a band by a near-neighbor LCAO parametrization, and comparing with (5.7), it can be seen explicitly that the distant-neighbor integrals of the resonance orbital description contribute to the near-neighbor LCAO parameters.

C. Relation to Hubbard's and Jacobs's Hybrid Schemes

Hubbard[5] and Jacobs[6] have independently transformed the KKR secular equation into forms similar to the hybrid secular equation of the interpolation schemes, by splitting the $l=2$ structure constants into a sum in direct space plus a sum in reciprocal space; the former enters the *d-d* block of the hybrid secular equation, while the latter is transformed into the *c-c* and *c-d* blocks. Each method has an optimization parameter which is chosen to achieve rapid covergence of both summations, and the optimum value of the parameter depends on the lattice constant.[5] Our empirical description suggests that (1) the optimum value of the parameter is such that the summation in direct space converges as a function of s/r_0 in the distance indicated by Fig. 3; (2) the volume dependence of the optimization parameter enters the *d-d* block in a way which affects the bandwidth as in Fig. 2. It should be possible to derive the description of Figs. 2–4 as an approximation to these hybrid schemes.

6. SUMMARY AND DISCUSSION

The *d* bands of a transition metal depend on the potential through two parameters, the position and width of the *d* scattering resonance. For a fixed resonance, the *d*-band structure is determined by geometrical considerations, and this information is contained in the KKR structure constants. We have shown that, to a useful approximation, this dependence of the bands on the lattice arrangement can be described in a simple way. This should be of use, for example, in calculating compressibility and shear strength, and for interpreting experimental measurements of the optical properties and Fermi surfaces of transition metals as a function of hydrostatic pressure and uniaxial strain. It has been used[17] in discussing the observed crystal structures of the transition elements. It can be employed directly in Mueller's[2] interpolation scheme, reducing the number of parameters in the *d-d* block to two (compared with seven LCAO parameters for the bcc structure), with only a small decrease in the accuracy of the scheme.

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