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Accurate Resonance-Parameter Approach to Transition-Metal Band Structure

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The position E_d and width W of the d resonance are shown to be good physical parameters, in that the *same* pair of parameters ($E_d = 0.540$, $W = 0.088$ Ry) is capable of reproducing Wood's band structure of fcc and bcc iron to within a rms error of 0.006 Ry. The energy levels were obtained by diagonalizing an improved hybrid nearly-free-electron tight-binding model Hamiltonian that includes explicitly the nonorthogonality of the basis functions.

The band structure of all transition and noble metals is characterized by the presence of a fairly tightly bound d band, which overlaps and hybridizes with a broader nearly-free-electron s-p band. Hodges *et al.*[1] and Mueller[2] set up a model Hamiltonian based on this hybrid nearly-free-electron tight-binding (H-NFE-TB) picture and successfully fitted the first-principles band structure of copper[3] to within a rms error of 0.01 Ry. Subsequently, Heine,[4] Hubbard,[5] and Jacobs[5] derived from first-principles model Hamiltonians of essentially this H-NFE-TB form by manipulating the basic Korringa-Kohn-Rostoker (KKR)[6] equations. The numerous[1,2] TB overlap integrals and hybridization matrix elements could now be expressed[7] analytically in terms of only *two* fundamental parameters E_d and W,[8] which are, respectively, the position and width of the resonance associated with the $l = 2$ phase shift,[9] namely,

$$\tan\eta_2 = \tfrac{1}{2} W(E)/(E_d - E) \quad . \tag{1}$$

This phase shift is accurately represented over the entire width of the d band if the energy dependence of the resonance width is expressed explicitly in the form[7]

$$W(E) = \{[K j_2^2(K r_i)]/[K_d j_2^2(K_d r_i)]\} W \quad , \tag{2}$$

where $K^2 = E$ and r_i is the inscribed sphere radius. The width of the d band is proportional to W, whereas the hybridization is proportional to $W^{1/2}$. The latter is not unexpected,[4] since $W/\hbar$ gives the probability of a localized d-electron tunneling through the centrifugal barrier into plane-wave states, provided that the resonance energy E_d is measured with respect to the bottom of the conduction band.

In the present paper we shall substantiate our argument given previously[10] that E_d and W, *taken together*, are good constant parameters for describing the band-structure energy *about the absolute position* of the resonance under a change of volume or crystal structure. This very important property arises because they always appear in the TB and hybridization matrix elements *combined together* in a certain ratio[10] that remains invariant, to a high degree of accuracy, from one volume[10] or structure to the next, even though the resonance parameters themselves do change individually. It must be stressed, however, that they are *not* good physical parameters if E_d is measured with respect to the muffin-tin plateau[6] instead of the bottom of the conduction band. For example, in the former case E_d and W (measured in rydbergs) have the values (0.608, 0.108) and (0.649, 0.122)[11] for fcc and bcc iron,[12] respectively, whereas in the present paper we have reproduced the identical fcc and bcc band structure by using the same set of parameters (0.540, 0.088) in both cases.

Furthermore, we shall present an improved H-

NFE-TB model Hamiltonian that includes, in addition to the usual TB and hybridization matrix elements, the higher-order terms that arise from the nonorthogonality of the basis functions. Although Mueller's[2] interpolation scheme took explicit account of the nonorthogonality of the TB and conduction-block basis functions by introducing a further two parameters, it ignored the nonorthogonality of the TB basis functions with each other.[13] From a first-principles point of view, these two orthogonality terms are of equal importance and their neglect has lead in the past[14] to fairly considerably inaccuracies in those energy levels which lie far from the resonance. Fortunately, they too can be expressed in terms of the resonance parameters E_d and W.

We begin by considering the *energy-dependent*[15] H-NFE-TB model Hamiltonian. The corresponding first-principles wave functions have the expected form[16]: The d-block basis functions are TB Bloch waves (expanded about the origin atom in a manner similar to that developed by Löwdin[17]), whereas the conduction basis functions are essentially plane waves orthogonalized to the core states (not including the valence d states). Therefore, we can write the determinantal form of Schrodinger's equation as

$$\det\begin{vmatrix} K-EI & H_0-(E-E_d)B \\ H_0^\dagger-(E-E_d)B^\dagger & T-(E-E_d)(I+S) \end{vmatrix}=0, \quad (3)$$

where I is the unit matrix. B and S are the orthogonality matrices that arise from the nonorthogonality of the basis set wave functions mentioned above. Explicit expressions for K, T, and H_0 have been given previously.[7] K is the conduction block, which contains weakly energy-dependent pseudopotential matrix elements of the KKRZ[9] form. T is the usual Slater and Koster[18] TB block, whose overlap parameters d_0', $dd\sigma$, $dd\pi$, and $dd\delta$ are given by Eq. (45) of Ref. 7 in terms of E_d, W, the distance R between the neighbors considered, and an Ewald-type[19] splitting parameter β. The larger this value of β, the more rapidly[20] the overlap parameters fall off with R, so that *less* nearest-neighbor shells need be included in the TB summation. H_0 is the energy-independent part of the hybridization block and is given by Eq. (13) of Ref. 7 evaluated at the resonance energy E_d. It contains a Gaussian cutoff, whose exponential decay in reciprocal-lattice space depends on the splitting parameter. The larger β, the larger becomes the hybridization tail,[21] so that *more* reciprocal-lattice vectors need be included in the conduction-block basis set.

The orthogonality matrices can also be written explicitly. By expanding the energy-dependent TB and hybridization matrix elements[15] about the resonance energy E_d, we find that

$$S=-\left(\frac{d}{dE}\,[T(E)]\right)_{E=E_d}=-T' \quad (4)$$

and

$$B=-H_0/2\beta \quad , \quad (5)$$

which are valid to first order provided that

$$|E-E_d|/4\beta\ll 1. \quad (6)$$

S thus has the same form as T, except that the overlap parameters are replaced by their energy derivatives, which are easily calculable by slightly modifying the analytic expressions quoted above for the TB overlap parameters. Similarly, B has the same form as H_0.

The off-diagonal energy dependence of the determinantal Eq. (3) is now removed by working within the approximation (6). First, the d-block basis functions are orthogonalized with the help of the orthonormalizing matrix

$$N_d^{-1/2}=(I+S)^{-1/2}=I+\tfrac{1}{2}T' \quad . \quad (7)$$

Then the orthogonalized-plane-wave (OPW) basis functions are orthogonalized to this new TB basis set, and finally this new OPW basis is renormalized using

$$N_c^{-1/2}=(I-BB^\dagger)^{-1/2}=I+\tfrac{1}{2}(H_0H_0^\dagger/4\beta^2) \quad . \quad (8)$$

Our determinantal equation has now been transformed into the form

$$\det|H_m-(E-E_d)\,I|=0, \quad (9)$$

which can be solved by diagonalizing the *energy-independent* model Hamiltonian matrix

$$H_m=\begin{pmatrix} C & H_{cd}+\dfrac{1}{2\beta}H_{cd}D \\ H_{cd}^\dagger+\dfrac{1}{2\beta}DH_{cd}^\dagger & D \end{pmatrix} \quad , \quad (10)$$

where

$$D=T+\tfrac{1}{2}(TT'+T'T) \quad , \quad (11)$$

$$C=N_c^{-1/2}(K-E_dI)N_c^{-1/2}+\frac{1}{\beta}H_{cd}H_{cd}^\dagger+\frac{1}{4\beta^2}H_{cd}DH_{cd}^\dagger \quad , \quad (12)$$

$$H_{cd}=N_c^{-1/2}H_0N_d^{-1/2} \quad . \quad (13)$$

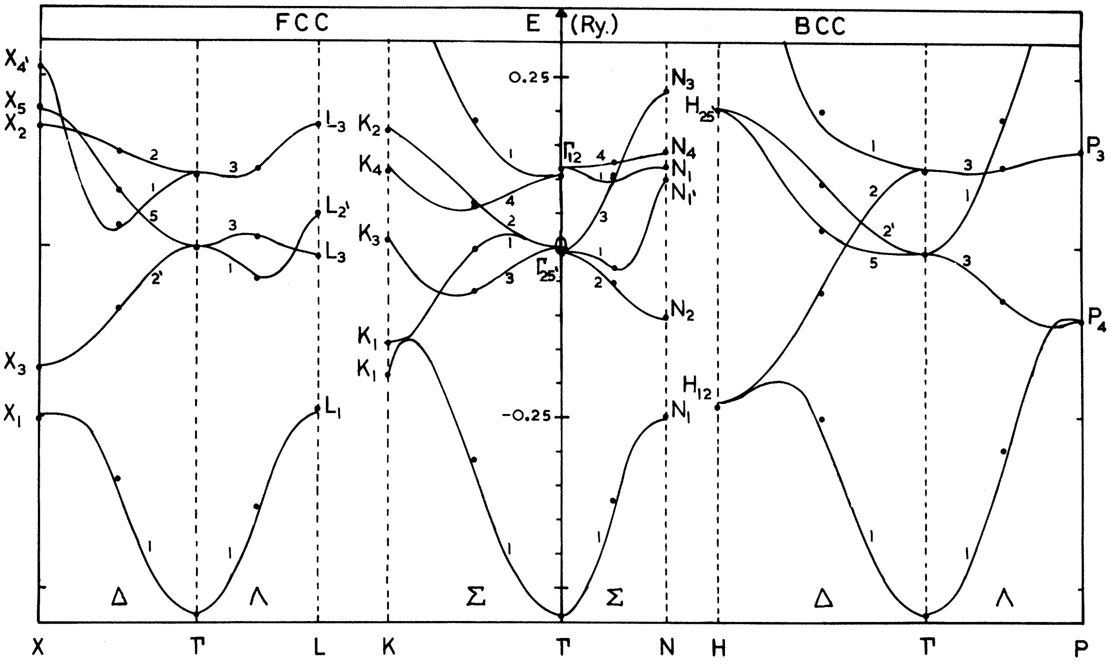

FIG. 1. The energy levels of fcc and bcc iron, obtained by diagonalizing our model Hamiltonian with resonance parameters $E_d = 0.540$ Ry and $W = 0.088$ Ry. The first-principles levels of Wood (Ref. 12) are represented by the solid circles, whose extent is a measure of his estimated accuracy.

Although this H-NFE-TB model Hamiltonian can be used to yield accurate first-principles energy levels by computing the phase shifts relative to the muffin-tin zero, in this paper we shall instead show how it can be used as a simple parametrization scheme. Wood's[12] augmented-plane-wave (APW) calculations on fcc and bcc iron provide a convenient test case, not only for demonstrating the accuracy of our model Hamiltonian, but also for illustrating that E_d and W are good physical parameters for calculating the band-structure energy with respect to the absolute position of the d resonance. Figure 1 shows the band structure of fcc and bcc iron obtained by diagonalizing H_m. We used Wood's[12] lattice parameters, namely, 6.892 and 5.406 a.u. for fcc and bcc, respectively, and we chose the same value of r_i in both cases, namely, 2.341 a.u., which is the inscribed sphere radius of bcc iron. The resonance parameters were chosen in the following way. E_d was taken to be the energy difference between the resonance position, as given by the first-principles $l = 2$ phase shifts[11], and the bottom of the conduction band at Γ.[12] We obtain $E_d = 0.540$ Ry to within 0.001 Ry for both structures. W was taken as 0.088 Ry to obtain the correct width of the pure d bands. The pseudopotential matrix elements were chosen to give correctly the bottom of the conduction band $\Gamma_1 (V_0 = 0.006$ Ry) and the pure p states $N_{1'} (V_{110} = 0.040$ Ry), $L_{2'} (V_{111} = 0.039$ Ry), and $X_{4'} (V_{200} = 0.034$ Ry). For iron, the width of the d band and hence W is sufficiently large for the hybridization tail (proportional to $W^{1/2}$) to bring in reciprocal-lattice vectors beyond the nearest neighbors. So that although we have fitted the band structure of fcc copper[3] which has a fairly narrow resonance ($W = 0.0284$ Ry) with only a 9×9 model Hamiltonian to within a rms error of 0.006 Ry, we require for the convergence of the wider iron band structure

TABLE I. The tight-binding overlap integrals and their energy derivatives corresponding to a value of the splitting parameter $\beta = 0.9$. Energies in rydbergs.

TB parameter	fcc			bcc			
d'_0	0.0722			0.0722			
e'_0	0.0549			0.0549			
Number of shell	1	2	3	1	2	3	4
$-dd\sigma$	0.0348	0.0023	0.0001	0.0429	0.0188	0.0006	0
$-ed\sigma$	0.0156	0.0019	0.0001	0.0166	0.0111	0.0005	0
$dd\pi$	0.0164	0.0005	0	0.0216	0.0073	0.0001	0
$ed\pi$	0.0098	0.0005	0	0.0121	0.0051	0.0001	0
$-dd\delta$	0.0021	0	0	0.0030	0.0008	0	0
$-ed\delta$	0.0015	0	0	0.0020	0.0006	0	0

the first 13 reciprocal-lattice vectors for fcc and 14 for bcc. The resulting energy levels are remarkably insensitive to the choice of splitting parameter.[16] Only the few levels near the bottom of the *d* band for which approximation (6) becomes important are noticeably β sensitive. However, these levels have converged to within about 0.002 Ry for the value of $\beta = 0.9$ used in the present calculations. Table I lists the resulting values of the TB overlap parameters and their energy derivatives. It is seen that we need only retain out to second nearest neighbors for fcc and third for bcc.

The model Hamiltonian reproduces the energy levels[12] below $X_{4'}$, to within a rms accuracy of 0.005 Ry for fcc (81 levels) and 0.006 Ry for bcc (74 levels). This success of the simple resonance parameter scheme should make it extremely useful in providing accurate transition-metal band structures and wave functions, under change of volume or structure,[10] once the good physical parameters E_d and W have been found.

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Influence of Surface Force-Constant Changes on Surface-Mode Frequencies

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Investigations of the dynamical properties of metallic crystals with free surfaces have been performed on the basis of a Born–von Karman model with atomic interactions up to second nearest neighbors including noncentral forces. The effect of a variation of the force constants near the surface on the surface-mode dispersion relations is analyzed. The calculations were based on a nonstandard Green's-function technique. Results are presented for the (100) surface of nickel. Surface modes are shown to exist below and above the cyclic frequency band as well as in a gap within the bulk region. The consequences of the fulfillment of the conditions of rotational invariance for the surface-mode dispersion relations are demonstrated.

I. INTRODUCTION

Within the last year several theoretical studies of surface vibrational modes of crystal lattices have been published. For example, Tong and Maradudin[1] have investigated a NaCl crystal slab using the rigid-ion model introduced by Kellermann. Allen *et al.*[2,3] have performed extended calculations for monatomic crystal slabs with atoms interacting through a Lennard-Jones (12, 6) potential, thus gaining a realistic description of noble gas crystals.

In investigating localized surface modes another topic has also been of great interest, namely, the effect of isotopic surfaces, i.e., of surface layers consisting of atoms with masses different from the mass of the bulk atoms, but with no changes in the forces between atoms near the surface.[2-5] It is