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Total Energy of *d*-Band Metals: Alkaline-Earth and Noble Metals*

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We consider the sum of the one-electron energies of the occupied bands for a metal which has *d* bands interacting with nearly-free-electron bands. Using Hubbard's hybrid form of the Korringa-Kohn-Rostoker band-structure method, we consistently retain terms in the energy to first order in the width of the *d* scattering resonance. For the alkaline-earth and noble metals (the metals at each extreme of the transition series), it is shown that the lowest-order effect of the interaction between the *d* bands and the free-electron bands, and, in the case of a noble metal, also the effect of the finite width of the full *d* bands, results in a simple net contribution to the total energy given by $U_d=(10\Gamma/\pi)\ln(|\epsilon_0-\epsilon_F|/\epsilon_0)$, where ϵ_0 and Γ are the energy and width of the *d* scattering resonance, and ϵ_F is the Fermi energy for the unperturbed free-electron band. It is shown that this term is to be added to the usual pseudopotential contribution to the total energy, where, if the pseudopotential is expressed in Ziman's phase-shift formulation, the *d* phase shift is to be replaced by the residual phase shift which remains after the resonance part is extracted. It is also shown that the term U_d gives a negligibly small contribution to the cohesive energy and to the compressibility of Cu, indicating that the *d*-band contributions to these properties are to be found either in the volume dependence of the energy of the *d* resonance, or in contributions to the total energy of the metal other than that of the total band-structure energy.

1. INTRODUCTION

One of the major advantages of the pseudopotential formulation for the simple metals is that it has been possible to use perturbation theory starting from a free-electron gas to calculate the total energy of a metal and the dependence of the total energy on the lattice positions in the crystal. This has led, for example, to calculations of cohesive energy and the elastic constants, explanation of observed crystal structures, and the calculation of phonon frequencies for these materials.[1] The present work is intended as a step towards calculating such properties for transition metals, in which the presence of the *d* bands must be explicitly considered. Specifically, this paper is concerned with calculating an expression for the total band-structure energy (i.e., the sum of the one-electron energies of the occupied bands), which is the major contribution to the total energy. We consider the limiting cases of a transition metal in which, in zeroth order, the *d* bands are empty (alkaline-earth metals) or full (noble metals); for these materials the proximity of the *d* bands to the Fermi energy appreciably alters the nearly-free-electron (NFE) behavior.

Our starting point is the hybrid secular equation derived by Hubbard[2] and improved upon by Hubbard and Dalton,[3] based on an approximate transformation of the Korringa-Kohn-Rostoker (KKR) secular equation. In this hybrid theory, the energy bands of a transition metal are represented as the hybridization between NFE bands and *d* bands. In this formulation the width Γ of the *d* scattering resonance of the muffin-tin potential controls both the width of the *d* bands and the strength of the hybridization. We calculate the contributions to the total band-structure energy from the free-electron bands, the *d* bands, the hybridization interaction, and the pseudopotential interaction, consistently retaining lowest-order terms in Γ and the usual second-order terms in the pseudopotential. This can be considered as a perturbation treatment of this problem, where the zeroth-order state is a set of *d* bands of zero width located at ϵ_0, the energy of the *d* scattering resonance, crossing a free-electron band without hybridizing; the perturbation is concerned with the widening of the *d* bands and the hybridization, as well as the pseudopotential interaction. It is shown that there is a great deal of cancellation and combination among the various *d*-band contributions to the total band-structure energy, yielding a simple result for the net effect of the presence of the *d* bands.

2. SYNOPSIS OF KKR-HYBRID THEORY

Since much of this paper deals with mathematical manipulations of the KKR theory and, in particular, with Hubbard's transformation of the KKR equation to a hybrid form, this section is devoted to summarizing the aspects of this theory which will be used here.

In the KKR method,[4] the energy bands $\epsilon(\mathbf{k})$ for a crystal with one atom per unit cell are the roots of a determinant

$$|A_{LL'}(\mathbf{k},\epsilon)+\kappa\delta_{LL'}\cot\eta_l(\epsilon)|=0.$$

Here ϵ is measured relative to the zero of the muffin-tin potential, L stands for (l,m), $\kappa=\epsilon^{1/2}$, η_l is the l phase shift of the muffin-tin potential, and $A_{LL'}$ is a structure constant. In a transition metal the $l=2$ phase shift has a resonant form[5] (following Refs. 2 and 3, we use the symbol λ for the orbital angular momentum of the reso-

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[3] J. Hubbard and N. W. Dalton, J. Phys. **C1**, 1637 (1968).

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

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

nant state, which for a transition metal is $\lambda=2$):

$$t_\lambda(\epsilon)\equiv\tan\eta_\lambda=\Gamma/(\epsilon_0-\epsilon)+t_\lambda{}^s(\epsilon)\,, \tag{2.1}$$

where ϵ_0 and Γ are, respectively, the position and width of the λ scattering resonance, and $t_\lambda{}^s$ is a smooth residual phase shift. Apart from the resonance the phase shifts are considered to be small, and will be treated to low order.

Hubbard and Dalton[2,3] have transformed the KKR equation by splitting the phase shifts and the structure constants in the following way [see Eqs. (HD1) and (HD2); HD denotes equation numbers in Ref. 3]:

$$t_l(\epsilon)=t_l'(\epsilon)+\frac{\delta_{l\lambda}\Gamma}{\epsilon_0-\epsilon}\left(\frac{\epsilon}{\epsilon_0}\right)^{\lambda+1/2}\exp\left(\frac{\epsilon_0-\epsilon}{\beta}\right), \tag{2.2}$$

$$A_{LL'}=A_{LL'}{}'(\beta)+A_{LL'}{}''(\beta)\,. \tag{2.3}$$

Here β is an arbitrary positive constant, and $A_{LL}{}'$ and $A_{LL}{}''$ are defined in Ref. 3. This results in an approximate hybrid secular equation of the form

$$\begin{vmatrix}\mathbf{C} & \mathbf{H}^\dagger\\ \mathbf{H} & \mathbf{D}\end{vmatrix}=0\,, \tag{2.4}$$

where **C**, **D**, and **H** are matrices representing, respectively, the conduction (NFE) bands, the d bands, and the hybridization between them. The matrix elements are given by (HD30)–(HD33):

$$C_{\mathbf{KK}'}=(|\mathbf{k}+\mathbf{K}|^2-\epsilon)\delta_{\mathbf{KK}'}+v_{\mathbf{KK}'}(\mathbf{k})\,, \tag{2.5}$$

$$D_{mm'}=(\epsilon_0-\epsilon)\delta_{mm'}+\Gamma\hat{T}_{mm'}(\mathbf{k})-\Gamma t_\lambda'\sum_{m''}\hat{T}_{mm''}\hat{T}_{m''m'}\,, \tag{2.6}$$

$$H_{m\mathbf{K}}=\Gamma^{1/2}\hat{h}_m(\mathbf{k}+\mathbf{K})-\Gamma^{1/2}t_\lambda'\sum_{m'}\hat{T}_{mm'}\hat{h}_{m'}(\mathbf{k}+\mathbf{K})\,, \tag{2.7}$$

where **K** denotes the reciprocal-lattice vectors of the crystal and m denotes the magnetic quantum numbers of the d states; the functions $v_{\mathbf{KK}'}$, $\hat{T}_{mm'}$, and $\hat{h}_m$, all of which are β-dependent, are defined in Ref. 3.

Note that Γ determines both the width of the d bands and the strength of the hybridization. In the limit $\Gamma\to 0$, H vanishes and (2.4) gives a set of d bands of zero width at $\epsilon=\epsilon_0$ which do not hybridize with the NFE band. This limit will be taken as our zeroth-order model, and we will treat the corrections due to hybridization and d bandwidth to lowest order in Γ.

The approximations that have been made in Refs. 2 and 3 in deriving these equations are essentially a narrow-band approximation for the d bands and an NFE approximation for the remaining bands. These approximations will not introduce errors into our calculations to the order which we retain. The accuracy of the narrow-band approximation in describing the band structures of actual transition metals[3] is a justification of the procedure of retaining only lowest terms in Γ in our total energy calculations.

3. HYBRIDIZATION AND PSEUDOPOTENTIAL EFFECTS

In this section, we calculate the effect of hybridization and the pseudopotential on the lowest free-electron band. (Here it is assumed that the resonance occurs at an energy within the lowest free-electron band; if the resonance crosses the free-electron band $\mathbf{k}+\mathbf{K}$ for some nonzero reciprocal-lattice vector **K**, then replace **k** by $\mathbf{k}+\mathbf{K}$ in the following.) First, rewrite (2.4) as

$$\begin{vmatrix}k^2+v_{00}(\mathbf{k})-\epsilon & \mathbf{M}^\dagger\\ \mathbf{M} & \mathbf{N}\end{vmatrix}=0\,, \tag{3.1}$$

where we have explicitly written the first diagonal term in the NFE block, and the matrices **M** and **N** denote the remaining elements of the determinant of (2.4). Next, we follow a procedure employed by Heine[6] to obtain the effect of **M** and **N** on the lowest conduction band. By a matrix transformation of (3.1) [see Eq. (30) of Ref. 6] the root corresponding to the lowest NFE band is contained in the equation

$$k^2+v_{00}-\epsilon-\mathbf{M}^\dagger\mathbf{N}^{-1}\mathbf{M}=0$$

or

$$\epsilon=k^2+v_{00}-\mathbf{M}^\dagger\mathbf{N}^{-1}\mathbf{M}\,, \tag{3.2}$$

where the last term in (3.2) is a function of ϵ. Considering the last two terms on the right-hand side of (3.2) to be small corrections to the free-electron energy, we keep only contributions of order Γ and v^2 in $\mathbf{M}^\dagger\mathbf{N}^{-1}\mathbf{M}$, giving

$$\epsilon=k^2+v_{00}(\mathbf{k})-\sum_{\mathbf{K}\neq 0}\frac{v_{0\mathbf{K}}{}^2(\mathbf{k})}{|\mathbf{k}+\mathbf{K}|^2-k^2}-\Gamma\sum_m\frac{|\hat{h}_m(\mathbf{k})|^2}{\epsilon_0-k^2}\,. \tag{3.3}$$

[These lowest-order terms can be obtained by inspection from (2.5)–(2.7) by (a) replacing ϵ by k^2 in $\mathbf{M}^\dagger\mathbf{N}^{-1}\mathbf{M}$, (b) ignoring the last two terms on the right-hand side of (2.6), which contribute to order Γ^2, (c) ignoring the second term on the right-hand side of (2.7), which contributes to order Γv, since, from (HD21) and (HD12), t_λ' is of order v, and (d) also ignoring cross terms between v and $\hat{h}$, which contribute to orders $v^2\Gamma^{1/2}$ and $v\Gamma$.] The third term on the right-hand side of (3.3) is the familiar pseudopotential result of second-order perturbation theory, while the last term is the hybridization correction.

From (HD22) and (HD12), we have

$$v_{00}(\mathbf{k})=-\frac{4\pi}{k\tau}\sum_l\frac{(2l+1)t_l'(k^2)}{1+(1-\delta_{l\lambda})H_l(k^2)t_l'}\,, \tag{3.4}$$

where τ is the volume per atom, and $H_l(\epsilon)$ is defined in Ref. 3. It is useful to separate the terms in v_{00} which

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

depend on the *d*-resonance parameters from those due to the residual *d* phase shift. Equating (2.1) and (2.2), we obtain

$$t_\lambda' = t_\lambda^s + t_\lambda'', \tag{3.5}$$

where

$$t_\lambda'' = \frac{\Gamma}{\epsilon_0 - \epsilon}\left[1 - \left(\frac{\epsilon}{\epsilon_0}\right)^{\lambda+1/2} \exp\left(\frac{\epsilon_0 - \epsilon}{\beta}\right)\right]. \tag{3.6}$$

From (3.4), the contribution to v_{00} from t_λ'' is

$$v_{00}(t_\lambda'') = -(4\pi/k\tau)(2\lambda+1)t_\lambda''(k^2) \tag{3.7}$$

$$= -\frac{4\pi}{k\tau}\frac{(2\lambda+1)\Gamma}{(\epsilon_0 - k^2)}\left[1 - \left(\frac{k^2}{\epsilon_0}\right)^{\lambda+1/2} \exp\left(\frac{\epsilon_0 - k^2}{\beta}\right)\right]. \tag{3.8}$$

Finally, (3.3) can be rewritten as

$$\epsilon = k^2 + (\Delta\epsilon)_{ps} + \Gamma(\Delta\epsilon)_\lambda, \tag{3.9}$$

where

$$(\Delta\epsilon)_{ps} = v_{00}'(\mathbf{k}) - \sum_{\mathbf{K}\neq 0} \frac{v_{0\mathbf{K}}^2}{|\mathbf{k}+\mathbf{K}|^2 - k^2}, \tag{3.10}$$

with

$$v_{00}' = -\frac{4\pi}{k\tau}\sum_l (2l+1)\frac{t_l + \delta_{l\lambda}(t_\lambda^s - t_\lambda)}{1 + (1-\delta_{l\lambda})H_l t_l} \tag{3.11}$$

and

$$(\Delta\epsilon)_\lambda = \frac{v_{00}(t_\lambda'')}{\Gamma} - \sum_m \frac{|\hat{h}_m(\mathbf{k})|^2}{\epsilon_0 - k^2}. \tag{3.12}$$

From (HD19) the hybridization function is given by

$$\hat{h}_m(\mathbf{k}+\mathbf{K}) = F_{\lambda m}(\mathbf{k}+\mathbf{K}, \epsilon_0) = \frac{4\pi|\mathbf{k}+\mathbf{K}|^\lambda}{\tau^{1/2}\kappa_0^{\lambda+1/2}} \times Y_{\lambda m}^*(\mathbf{k}+\mathbf{K})\exp\left[\frac{\epsilon_0 - (\mathbf{k}+\mathbf{K})^2}{2\beta}\right], \tag{3.13}$$

where $\kappa_0 = (\epsilon_0)^{1/2}$. Then the second term on the right-hand side of (3.12) becomes, after simplification,

$$\sum_m \frac{|\hat{h}_m(\mathbf{k})|^2}{\epsilon_0 - k^2} = \frac{4\pi}{k\tau}\frac{(2\lambda+1)}{(\epsilon_0 - k^2)}\left(\frac{k^2}{\epsilon_0}\right)^{\lambda+1/2} \exp\left(\frac{\epsilon_0 - k^2}{\beta}\right). \tag{3.14}$$

By use of (3.8) and (3.14), Eq. (3.12) becomes simply

$$(\Delta\epsilon)_\lambda = -(4\pi/k\tau)(2\lambda+1)/(\epsilon_0 - k^2), \tag{3.15}$$

which for *d* bands ($\lambda = 2$) is

$$(\Delta\epsilon)_d = -20\pi/k\tau(\epsilon_0 - k^2). \tag{3.16}$$

The term $(\Delta\epsilon)_{ps}$ is to be interpreted as the NFE pseudopotential correction to the free-electron energy; this term vanishes if the *s*, *p*, and residual *d* phase shifts vanish. The last term on the right-hand side of (3.9) is the lowest-order correction to the free-electron energy due to the presence of the *d* bands, and vanishes as $\Gamma \to 0$.

4. TOTAL BAND-STRUCTURE ENERGY

Here we apply the results of Sec. 3 to calculate the effect of the *d* bands on the total band-structure energy of the alkaline-earth and noble metals. The effect of the pseudopotential contribution $(\Delta\epsilon)_{ps}$ is discussed in Sec. 5.

A. Alkaline-Earth Metals

An alkaline-earth metal in zeroth order consists of a free-electron band filled to a Fermi energy $\epsilon_F = k_F^2$, with an occupied set of *d* bands of zero width at an energy $\epsilon_0 > \epsilon_F$. The zeroth-order contribution to the total band-structure energy per atom is then

$$U_{FE} = \frac{2}{N}\sum_{\mathbf{k}<k_F} k^2, \tag{4.1}$$

where N is the number of atoms in the macroscopic crystal, and the factor 2 accounts for the two spin states corresponding to each **k** value. From Sec. 3 the resultant first-order contribution due to the presence of the *d* bands is

$$U_d = \frac{2\Gamma}{N}\sum_{\mathbf{k}<k_F} (\Delta\epsilon)_d.$$

From (3.16), we have

$$U_d = -\frac{20\Gamma}{\pi}\int_0^{k_F} \frac{k\,dk}{\epsilon_0 - k^2}$$

$$= (10\Gamma/\pi)\ln[(\epsilon_0 - \epsilon_F)/\epsilon_0]. \tag{4.2}$$

B. Noble Metals

A noble metal in zeroth order consists of a free-electron band filled to a Fermi energy $\epsilon_F = k_F^2$, with an occupied set of *d* bands of zero width at an energy $\epsilon_0 < \epsilon_F$. The zeroth-order contribution to the total band-structure energy is then

$$U_0 = \frac{2}{N}\sum_{\mathbf{k}<k_F} k^2 + 10\epsilon_0, \tag{4.3}$$

since there are 10 electrons per atom in a full *d* band. The first-order correction U_d, due to the nonzero width of the *d* bands and to the effects of hybridization and the *d*-resonance pseudopotential, consists of three contributions:

$$U_d = U_d^{(1)} + U_d^{(2)} + U_d^{(3)}, \tag{4.4}$$

where

$$U_d^{(1)} = \frac{2\Gamma}{N}\sum_{\mathbf{k}<k_F} (\Delta\epsilon)_d \tag{4.5}$$

is the net effect of the *d* bands on the occupied free-electron band, $U_d^{(2)}$ is the correction to the total energy of the *d* bands due to their nonzero width, and $U_d^{(3)}$ is the correction to the energy of the *d* bands due to their hybridization with the free-electron bands. It is now shown that $U_d^{(2)}+U_d^{(3)}=0$.

The total energy of the d bands of nonzero width, without hybridization, is obtained by summing the eigenvalues of the $\mathbf{D}$ block of (2.4) for all states $\mathbf{k}$ in the reduced Brillouin zone. For each value of $\mathbf{k}$, the sum of the eigenvalues of the matrix equals the trace of the matrix, so the total energy is

$$\frac{2}{N}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}(D_{mm}+\epsilon)\,, \tag{4.6}$$

where $\mathbf{k}_{\mathrm{BZ}}$ denotes a summation over all vectors $\mathbf{k}$ in the reduced Brillouin zone. The $\mathbf{D}$ matrix elements can be written in a tight-binding form (HD26)

$$\begin{aligned} D_{mm'}&=[\epsilon_0+\Gamma H_\lambda(\epsilon_0)-\epsilon]\delta_{mm'}\\ &\quad+\sum_{\mathbf{R}\neq 0}\mathcal{T}_{mm'}(\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{R}) \end{aligned} \tag{4.7}$$

by appropriate definition of $\mathcal{T}_{mm'}$. Then (4.6) reduces to

$$2(2\lambda+1)[\epsilon_0+\Gamma H_\lambda(\epsilon_0)]\,,$$

since the summation over $\mathbf{k}_{\mathrm{BZ}}$ causes the last term in (4.7) to contribute zero. The term $\Gamma H_\lambda(\epsilon_0)$ is a shift in the mean position of the d bands to an energy greater than ϵ_0, resulting from their nonzero width. (This can be identified with the volume-dependent quantity d_0' previously introduced by the author.[7])

From (4.6) and (2.6) the first-order correction to the energy can be written as

$$U_d^{(2)}=\frac{2\Gamma}{N}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}\hat{T}_{mm}.$$

However, from (HD25) we have

$$\hat{T}_{mm'}=\kappa_0^{-1}A_{\lambda m\lambda m'}''(\epsilon_0)\,,$$

so that

$$U_d^{(2)}=\frac{2\Gamma}{N\kappa_0}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}A_{2m2m}''(\epsilon_0)\,. \tag{4.8}$$

The total hybridization effect on the energy of the d bands at point $\mathbf{k}$ in the Brillouin Zone, due to interaction with a free-electron state of wave vector $\mathbf{k}+\mathbf{K}$, is equal and opposite to the hybridization effect of the d bands on this free-electron state. The latter was calculated to first order in Sec. 3, giving [see the last term on the right-hand side of (3.3)]

$$-\Gamma\sum_{m}\frac{|\hat{h}_m(\mathbf{k}+\mathbf{K})|^2}{\epsilon_0-|\mathbf{k}+\mathbf{K}|^2}\,.$$

Hence

$$U_d^{(3)}=\frac{2\Gamma}{N}\sum_{\mathbf{K}}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}\frac{|\hat{h}_m(\mathbf{k}+\mathbf{K})|^2}{\epsilon_0-|\mathbf{k}+\mathbf{K}|^2}\,.$$

Here the summation over the reciprocal-lattice vectors $\mathbf{K}$ (including $\mathbf{K}=0$) takes into account the hybridization effect on the d bands due to interaction with all the free-electron states. By use of (3.13) this becomes

$$U_d^{(3)}=\frac{2\Gamma}{N}\sum_{\mathbf{K}}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}\frac{|F_{2m}(\mathbf{k}+\mathbf{K},\,\epsilon_0)|^2}{\epsilon_0-|\mathbf{k}+\mathbf{K}|^2}\,.$$

However, from (HD6) we obtain

$$\frac{1}{\kappa}A_{LL'}'=-i^{l-l'}\sum_{\mathbf{K}}\frac{F_L(\mathbf{k}+\mathbf{K},\,\epsilon)F_{L'}^*(\mathbf{k}+\mathbf{K},\epsilon)}{|\mathbf{k}+\mathbf{K}|^2-\epsilon}\,,$$

so that

$$U_d^{(3)}=\frac{2\Gamma}{N\kappa_0}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}A_{2m2m}'(\epsilon_0)\,. \tag{4.9}$$

Combining (4.8) and (4.9), we have

$$U_d^{(2)}+U_d^{(3)}=\frac{2\Gamma}{N\kappa_0}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}(A_{2m2m}'+A_{2m2m}'')\,,$$

which, from (2.3), becomes

$$U_d^{(2)}+U_d^{(3)}=\frac{2\Gamma}{N\kappa_0}\sum_{\mathbf{k}_{\mathrm{BZ}}}\sum_{m}A_{2m2m}(\epsilon_0)\,. \tag{4.10}$$

However, from Eqs. (A2.14) and (A2.22) of Ref. 4, the structure factor can be written in the form

$$A_{2m2m}(\mathbf{k},\epsilon)\sim\sum_{\mathbf{R}\neq 0}e^{i\mathbf{k}\cdot\mathbf{R}}$$

as far as the $\mathbf{k}$ dependence is concerned, where the summation is over all the nonzero direct lattice vectors $\mathbf{R}$ of the crystal. Then, (4.10) becomes

$$U_d^{(2)}+U_d^{(3)}\sim\sum_{\mathbf{R}\neq 0}\sum_{\mathbf{k}_{\mathrm{BZ}}}\exp(i\mathbf{k}\cdot\mathbf{R})=0\,. \tag{4.11}$$

Finally, we have

$$\begin{aligned} U_d&=U_d^{(1)}\\ &=-\frac{20\Gamma}{\pi}\int_0^{k_F}\frac{k\,dk}{\epsilon_0-k^2}\,. \end{aligned}$$

Taking the principal part of the integral, we obtain

$$U_d=(10\Gamma/\pi)\ln[(\epsilon_F-\epsilon_0)/\epsilon_0]\,. \tag{4.12}$$

Equations (4.2) and (4.12) can be written in the single form,

$$U_d=(10\Gamma/\pi)\ln(|\epsilon_0-\epsilon_F|/\epsilon_0)\,, \tag{4.13}$$

for both the alkaline-earth and noble metals. Equations (3.16) and (4.13) are the principal results of this paper.

Note that (4.11) represents an exact cancellation between the raising in energy of the mean position of the d bands due to their nonzero width and their lowering in energy due to hybridization with the free-electron band.

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[7] R. A. Deegan, Phys. Rev. **171**, 659 (1968).

5. PSEUDOPOTENTIAL CONTRIBUTION

For both the alkaline-earth and noble metals there is also the following NFE pseudopotential contribution to the total energy:

$$U_{ps}=\frac{2}{N}\sum_{\mathbf{k}<k_F}(\Delta\epsilon)_{ps}\,, \tag{5.1}$$

where $(\Delta\epsilon)_{ps}$ is given by (3.10) and (3.11). From (HD21) and (HD12), the pseudopotential is

$$v_{\mathbf{K}\mathbf{K}'}(\mathbf{k})=-\frac{4\pi}{\tau}\sum_{l}\frac{(2l+1)t_l'(k^2)|\mathbf{k}+\mathbf{K}|^l|\mathbf{k}+\mathbf{K}'|^l}{k^{2l+1}[1+(1-\delta_{l\lambda})H_l(k^2)t_l']}$$
$$\times\exp\left(\frac{2k^2-|\mathbf{k}+\mathbf{K}|^2-|\mathbf{k}+\mathbf{K}'|^2}{2\beta}\right)$$
$$\times P_l\{\cos[(\mathbf{k}+\mathbf{K}),\,(\mathbf{k}+\mathbf{K}')]\}\,. \tag{5.2}$$

To low order in the phase shifts the square-bracketed terms in the denominators of (3.11) and (5.2) may be replaced by unity. Then $(\Delta\epsilon)_{ps}$ depends on the splitting parameter β, through the $v_{0\mathbf{K}}^2$ terms of (3.10), in two ways: (i) The phase shift t_λ' entering $v_{0\mathbf{K}}$ for $\mathbf{K}\neq 0$ contains a β dependence from t_λ'' [see (3.5) and (3.6)]; however, this is a term of order Γ^2 in $v_{0\mathbf{K}}^2$, which we neglect. Then, to lowest order, we replace t_λ' by t_λ^s in $v_{0\mathbf{K}}$. (ii) From (5.2), $v_{0\mathbf{K}}^2$ contains the following multiplicative factor:

$$\exp\left(\frac{\epsilon-k^2}{2\beta}\right)\times\exp\left(\frac{\epsilon-|\mathbf{k}+\mathbf{K}|^2}{2\beta}\right)\Bigg|_{\epsilon=k^2}$$
$$=\exp\left(\frac{k^2-|\mathbf{k}+\mathbf{K}|^2}{2\beta}\right). \tag{5.3}$$

This factor involves the approximation in Ref. 3 of replacing ϵ by k^2 in the pseudopotential terms, as explicitly demonstrated in (5.3). However, to the same order we can instead replace ϵ by $|\mathbf{k}+\mathbf{K}|^2$ in the second exponent of (5.3), since from the energy denominator in (3.10) this contribution will be sizable only for $k^2\simeq|\mathbf{k}+\mathbf{K}|^2$. Then the β dependence vanishes from $(\Delta\epsilon)_{ps}$, giving

$$(\Delta\epsilon)_{ps}=v_{00}{}^s(\mathbf{k})-\sum_{\mathbf{K}\neq 0}\frac{(v_{0\mathbf{K}}{}^s)^2}{|\mathbf{k}+\mathbf{K}|^2-k^2}\,, \tag{5.4}$$

where

$$v_{\mathbf{K}\mathbf{K}'}{}^s(\mathbf{k})=-\frac{4\pi}{\tau}\sum_{l}(2l+1)\frac{t_l+\delta_{l\lambda}(t_\lambda{}^s-t_l)}{k^{2l+1}}$$
$$\times|\mathbf{k}+\mathbf{K}|^l|\mathbf{k}+\mathbf{K}'|^lP_l\{\cos[(\mathbf{k}+\mathbf{K},\,\mathbf{k}+\mathbf{K}')]\}\,, \tag{5.5}$$

and the phase shifts t_l and $t_\lambda{}^s$ are evaluated at $\epsilon=k^2$. Note that this is precisely the Ziman form of the pseudopotential [Eq. (52) of Ref. 5], in the limit $r,\,r'\rightarrow 0$, with the d phase shift replaced by the residua, d phase shift $t_\lambda{}^s$. This also shows that in the limit $\Gamma\rightarrow 0$l for which the d-band term U_d disappears, we recover the usual NFE result for the total energy.

6. APPLICATION TO COPPER

Attempted calculations of the cohesive energy and, particularly, the compressibility of the noble metals which are based on an NFE approach are in serious disagreement with experiment. For example, Fuchs[8] calculated a value of 1.45 eV for the cohesive energy per atom of Cu, using a Wigner-Seitz method to obtain the bottom of a free-electron band, compared to an experimental heat of vaporization of 3.10 eV. The compressibility of Cu on a free-electron model is 2.6×10^{-6} cm^2/kg, compared[8] with an experimental value of 0.70×10^{-6}. The discrepancy between theory and experiment for these properties is ascribed to the effect of the d bands. In particular, the major contribution to the compressibility of the noble metals is usually attributed, on an atomic model, to an effective hard-core interaction between closed atomic d shells on adjacent atoms in the lattice. In this section, we calculate the effect of the d-band term of (4.13) on the cohesive energy and the compressibility of Cu.

A. Cohesive Energy

For Burdick's[9] potential for Cu the d-resonance parameters have been determined in Ref. 3 to be $\epsilon_0=0.306$ Ry and $\Gamma=0.008$ Ry. For the lattice constant of Cu ($a=6.8309$ a.u.) the free-electron Fermi energy for one electron is $\epsilon_F=0.518$ Ry. Then, from (4.13), we have

$$U_d=-0.0093\text{ Ry}=-0.126\text{ eV}\,,$$

which has very little effect on the cohesive energy. Thus the effect of hybridization and the d-resonance pseudopotential plus the shifting from ϵ_0 of the mean position of the d bands gives a very small net contribution to the binding energy. This indicates that the principal contribution of the d bands to the cohesive energy is due to either (i) the difference in energy between the free-atom d level $\epsilon_d{}^{\mathrm{at}}$ and the energy of the d resonance, which contributes a term equal to

$$10(\epsilon_d{}^{\mathrm{at}}-\epsilon_0-\epsilon_{\mathrm{mt}})\,, \tag{6.1}$$

where ϵ_{mt} is the position of the muffin-tin zero relative to the zero of the free-atom potential (recall that ϵ_0 was defined relative to ϵ_{mt}), or (ii) contributions to the total energy other than the total band-structure energy, such as correlation effects. In particular, note that it requires only a very small difference in (6.1) to contribute appreciably to the cohesive energy (which also shows that the energy of the d resonance must be within a few hundredths of a Ry of the free-atom d level). Either possibility is in agreement with the results for the compressibility described below.

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B. Compressibility

In the low-temperature limit the compressibility χ of a metal is given by [e.g., Eq. (8) of Ref. 8]

$$\frac{1}{\chi}=\frac{1}{12\pi R_0}\left.\frac{d^2U}{dr_0^2}\right|_{r_0=R_0}, \tag{6.2}$$

where U is the total energy per atom, r_0 is the radius of the Wigner-Seitz sphere, and $r_0=R_0$ for the equilibrium lattice spacing. From Sec. 4 B, the contribution to the total energy from the d bands (relative to the zero of the free-atom potential) is

$$10\epsilon_d+U_d, \tag{6.3}$$

where $\epsilon_d=\epsilon_0+\epsilon_{\mathrm{mt}}$, and U_d is given by (4.13). If we assume that Γ, ϵ_0, and ϵ_{mt} are independent of volume (physically, this means neglecting the self-consistent dependence of the potential on volume), the lowest-order d-band contribution to the compressibility of a noble metal would be

$$\frac{1}{\chi_d}=\frac{1}{12\pi R_0}\left.\frac{d^2U_d}{dr_0^2}\right|_{r_0=R_0}, \tag{6.4}$$

where the variable in U_d is

$$\epsilon_F=k_F^2=1/cr_0^2, \tag{6.5}$$

where $c=(4/9\pi)^{2/3}$ for a free-electron band containing one electron per atom. Substituting from (6.5) in (4.13), Eq. (6.4) becomes, after differentiating,

$$\frac{1}{\chi_d}=\frac{-5\Gamma}{3\pi^2R_0}\frac{(3c\epsilon_0-R_0^{-2})}{(1-c\epsilon_0R_0^2)^2}.$$

Using the values ϵ_F, ϵ_0, and Γ for Cu, as given in Sec. 6 A, we have

$$1/\chi_d=-3.28\times10^4\ \mathrm{Ry/(a.u.)^3}=-0.0483\times10^6\ \mathrm{kg/cm^2},$$

which is a very small contribution to the compressibility. Thus the effect of hybridization and the d-resonance pseudopotential plus the shifting of the mean position of the d bands gives a nearly vanishing net contribution to χ. This is in agreement with the results of Dalton and Deegan[10] on the structures of the transition metals, where a band-structure calculation which neglected the dependence of ϵ_d on the crystalline structure failed to give the effective hard-core repulsion required to favor the close-packed structure near the noble-metal end of the transition series. This result indicates that the effective hard-core interaction is to be found either in (i) a dependence of ϵ_d on volume, which could give a strong contribution to χ from the first term of (6.3), or (ii) a dependence on volume of those contributions to the total energy other than the sum of the one-electron energies.

7. SUMMARY AND DISCUSSION

It has been shown that, to lowest order, the energy of a free-electron state **k** is modified, because of interaction with d bands, by an amount $\Gamma(\Delta\epsilon)_d$, where $(\Delta\epsilon)_d$ is given by (3.16). This leads to a simple net d-band contribution U_d, given by (4.13), to the total band-structure energy of an alkaline-earth metal, and a d-band contribution of $10\epsilon_d+U_d$ to the energy of a noble metal, where ϵ_d is the energy of the d scattering resonance. This includes the hybridization and pseudopotential effects due to the d resonance and, in the case of a noble metal, also the shift in the mean energy of the d bands due to their nonzero width. It has been shown that these terms are to be added to the usual free-electron and NFE pseudopotential contributions, where the $l=2$ phase shift entering the pseudopotential in the KKR-Ziman[5] formulation is to contain only the residual, nonresonant part of the d phase shift.

As demonstrated for Cu, one of the most striking aspects of these results is the small size of the net contribution to the band-structure energy due to interaction with the d band. Hybridization contributions are frequently invoked to qualitatively explain various d-band effects, and it is hoped that one result of this work will be to focus attention, as in the case of the cohesive energy and compressibility of the noble metals, on the direction in which to look for explanations of such effects.

The method employed here cannot be directly extended to the case of transition metals with partially filled bands, since then in zeroth order $\epsilon_F=\epsilon_0$ and U_d will consequently diverge; also, the sum $U_d^{(2)}+U_d^{(3)}$ of Sec. 4 B will no longer vanish, but will give a more complex, structure-dependent contribution. (It appears at this time, however, that it is possible to devise a procedure to overcome the difficulties and thus provide a method for dealing with many of the so-far incalculable properties of the transition metals.)

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