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[1] R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954); J. Smit, Physica 21, 877 (1955); S. H. Liu, Phys. Rev. 137, A1209 (1965).

[2] J. Kondo, Progr. Theoret. Phys. (Kyoto) 28, 846 (1962).

[3] F. E. Maranzana, Phys. Rev. 160, 421 (1967).

[4] R. E. Watson and A. J. Freeman, Phys. Rev. Letters 14, 695 (1965); 6, 277 (1961); J. O. Dimmock and A. J. Freeman, *ibid.* 13, 750 (1964).

[5] N. V. Volkenshtein and G. V. Fedorov, Fiz. Metal. i Metalloved. 18, 26 (1964).

[6] N. A. Babushkina, Fiz. Tverd. Tela 7, 3026 (1965) [Soviet Phys. Solid State 7, 2450 (1966)].

[7] F. J. Wald, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1969 (unpublished).

[8] W. G. Egan and H. J. Juretschke, J. Appl. Phys. 34, 1477 (1960).

[9] R. S. Lee and S. Legvold, Phys. Rev. 162, 431 (1967).

[10] H. J. Juretschke, J. Appl. Phys. 31, 1401 (1960).

[11] F. J. Weintraub, M.S. thesis, Polytechnic Institute of Brooklyn, 1964 (unpublished).

[12] W. Moller, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1968 (unpublished).

[13] W. Moller and H. J. Juretschke, Phys. Rev. B 2, 2651 (1970).

[14] A. F. Kip, Rev. Mod. Phys. 25, 229 (1953).

[15] D. S. Rodbell and T. W. Moore, General Electric Internal Report No. 64-RL-(3788M), 1964 (unpublished).

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Self-Consistent Warped-Muffin-Tin-Potential Energy Bands of γ-Fe with Various Exchange Approximations*

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Using a modified augmented-plane-wave expansion recently developed by us, we have calculated the energy bands and the binding energy of fcc γ-Fe. From a self-consistently calculated muffin-tin charge density, we obtained a warped-muffin-tin potential. We used the full, $\frac{7}{9}$, and $\frac{2}{3}$ Slater exchange potentials. All gave reasonable energy bands but when the "Koopmans corrections" recently suggested by Herman *et al.* were added, the *d* levels were driven below the *s* levels at all points in the Brillouin zone and an unphysical type of *s*-*d* hybridization was obtained.

I. INTRODUCTION

The purposes of this calculation are threefold: (i) to obtain self-consistent energy bands of γ-Fe, the fcc structure stable between 910 and 1400 °C, the only previous calculation being non-self-consistent[1]; (ii) to test the effect of various exchange potentials of the form

$$V_{ex}(\vec{r}) = -\alpha 3[3\rho(\vec{r})/\pi]^{1/3} \tag{1}$$

on both the energy bands and the binding energy of the crystal; also to test the so-called "Koopmans correction" of Herman *et al.*[2] to the one-electron energy levels; and (iii) to obtain crystal wave functions from which we can obtain the first iteration of a self-consistent true crystal potential as contrasted with the warped-muffin-tin potential used here. This will be the topic of a later paper.

The calculation is performed using the modified augmented-plane-wave expansion we have recently described.[3] In Sec. II, we explain how the warped self-consistent muffin-tin potential is obtained from a self-consistent muffin-tin charge density and calculate the energy bands for a $\alpha = 1$, $\frac{7}{9}$, and $\frac{2}{3}$. In Sec. III we discuss the physics behind the various choices for α and the so-called Koopmans correction. We calculate the Koopmans correction and find that it lowers everywhere the *d* band below the *s* band leaving a peculiar unphysical sort of *s*-*d* hybridization. In Sec. IV, we discuss the calculation of the binding energy of the crystal and compare it with the ionization energy of the atom calculated with the same exchange approximation. We find in no case is the crystal actually bound, i.e., its binding energy greater than the ionization energy of the atom, but that it is much more nearly bound for $\alpha = \frac{2}{3}$ than for $\alpha = 1$. In Sec. V, we speculate that although the Kohn-Sham (KS) ($\alpha = \frac{2}{3}$) potential gives better binding energies, the Slater ($\alpha = 1$) potential gives better energy bands.

II. SELF-CONSISTENT POTENTIAL AND ENERGY BANDS

The crystal wave function may be written as

$$\varphi_{n\vec{k}} = \sum_{\vec{\kappa}} a_{n\vec{k}\vec{\kappa}} \chi_{\vec{k}+\vec{\kappa}} , \tag{2}$$

where the modified augmented-plane-wave (APW) basis functions[3] are

$$\chi_{\vec{K}} = (N\Omega)^{-1/2} \Big(e^{i\vec{K}\cdot\vec{r}} - 4\pi \sum_{l=0}^{2} \sum_{m=-l}^{l} \sum_{j} i^l e^{i\vec{K}\cdot\vec{R}_j} \times [j_l(Kr_j) - f_l(r_j) j_l(Kr_0)/f_l(r_0)] \times Y^*_{lm}(\hat{K}) Y_{lm}(\hat{r}_j)\, \Theta(r_0 - r_j) \Big) ; \tag{3}$$

f_l is the solution of the Schrödinger equation within the inscribed sphere of radius r_0, j_l is a spherical Bessel function, $\vec{r}_j = \vec{r} - \vec{R}_j$, where $\vec{R}_j$ is a lattice vector, Θ is a unit step function, $\vec{k}$ is a wave vector within the Brillouin zone (BZ), and $\vec{\kappa}$ is a reciprocal-lattice vector. Between 41 and 52 reciprocal-lattice vectors were used at the various points in the BZ giving eigenvalues converged to within 0.0005 Ry. The BZ was sampled[4] at 64 points: $1\Gamma(0,0,0)$, $6\Delta(\frac{1}{2},0,0)$, $8\Lambda(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $12\Sigma(\frac{1}{2},\frac{1}{2},0)$, $24\Xi(\frac{3}{4},\frac{1}{4},\frac{1}{4})$,[5] $6W(1,\frac{1}{2},0)$, $3X(1,0,0)$, and $4L(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The muffin-tin charge density is obtained from

$$\rho_{n\vec{k}}(r) = \int |\varphi_{n\vec{k}}(r)|^2 \, d\omega , \tag{4}$$

where ω is the solid angle and $r < r_0$. Then

$$\rho(r) = \frac{1}{32} \sum_{n\vec{k}=1}^{256} \rho_{n\vec{k}}(r) , \tag{5}$$

for $r < r_0$. The sum is over the 256 lowest energy levels (neglecting spin degeneracy) and $\frac{256}{32} = 8$, the number of $3d$ and $4s$ conduction electrons. The number of levels of each type contributing to the sum is listed in the second column of Table I. This is just the number of points in the star of the wave vector (i.e., 6 for Δ, 8 for Λ, etc.) times the degeneracy of the particular level except for Σ_2, the highest occupied level, which only contributes two out of a possible 12 so that the sum will terminate exactly at 256. Defining

$$z = 8 - \int_0^{r_0} \rho(r)\, dr , \tag{6}$$

the total charge outside the inscribed sphere, we take the charge density outside the sphere to be constant,

$$\rho_{\text{out}} = z/\Omega_0 , \tag{7}$$

where $\Omega_0 = \Omega_1$, Ω is the volume of the unit cell, $\frac{1}{4}a^3$, and $\Omega_1 = 4/3\pi r_0^3$. We will at times need to divide the charge into two pieces, a constant density ρ_{out} existing everywhere plus a spherical distribution $\rho(r) - \rho_{\text{out}}$ existing within the inscribed sphere. The total charge contained in the constant density term is then

$$Z = (\Omega/\Omega_0) z . \tag{8}$$

To avoid confusion we will always specify whether we are talking about the $\rho(r)$ spherical distribution containing $26-z$ electrons (including core electrons) or the $\rho(r) - \rho_{\text{out}}$ spherical distribution containing $26-Z$ electrons. In Table II, we list z and Z for various α's.

The modified APW method[3] requires a knowledge of $V(\vec{\kappa})$, the κth Fourier transform of the crystal potential, and, in the warped-muffin-tin approximation, a knowledge of $V(r)$, the spherical average of the crystal potential within the inscribed spheres. To calculate the Coulomb contribution to the potential, we divide the charge into two neutral pieces, the $\rho(r) - \rho_{\text{out}}$ spherical electron distributions plus $26-Z$ protons centered at each lattice point and the everywhere constant ρ_{out} plus Z protons at each lattice point. Because the potentials of the neutral spherical distributions do not overlap, one can divide $V_{\text{Coul}}(r)$ into three contributions, that from the neutral spherical distribution on the particular site, $-2Z/r$ from the Z protons on that site, and a Madelung potential from ρ_{out} and the Z protons on all the remaining sites. The spherical average of the Madelung potential about a lattice site is[6]

$$V_{\text{Mad}}(r) = 3.58344\, Z/r_{ws} - \tfrac{4}{3}\pi Z \Omega^{-1} r^2 , \tag{9}$$

where r_{ws} is the radius of the equivalent atomic volume sphere. The Coulomb contribution to $V(\vec{\kappa})$ contains two contributions, the first of which is simply the Fourier transform of the contribution of a single neutral spherical distribution to $V_{\text{Coul}}(r)$. The second contribution is the Madelung potential due to ρ_{out} and the Z protons on all the lattice sites,

$$\begin{aligned} V_{\text{Mad}}(\vec{\kappa}) &= -8\pi/\kappa^2, \quad \kappa \neq 0 \\ V_{\text{Mad}}(\vec{\kappa} = 0) &= 0 . \end{aligned} \tag{10}$$

The exchange contribution to $V(r)$ is simply obtained by inserting $\rho(r)$ into Eq. (1). The Fourier transform of this is one of two contributions to $V_{\text{ex}}(\vec{\kappa})$. The second is obtained by inserting ρ_{out} in (1) yielding a constant V_{ex} for r outside r_0. The Fourier transform of this V_{ex} is obtained by writing it as the constant V_{ex} existing everywhere minus V_{ex} existing inside the inscribed sphere.

Using the potential just described we have calculated the energy bands, self-consistent to within an accuracy of 0.0005 Ry. In Table I, we compare our results for $\alpha = 1$, $\frac{7}{9}$, and $\frac{2}{3}$ with those obtained from the potential used by Wood.[1] The slight discrepancy between Wood's energy levels and ours is due to the choice of slightly different lattice constants. We took $a = 6.898$ (a.u.), the lattice constant at 1030 °C, in order to make r_0 commensurate with our integration mesh. In Figs. 1 and 2, we show the energy bands for $\alpha = 1$ and $\frac{2}{3}$. Aside from an over-all shift they are quite similar to the same states lying below the Fermi surface. The major difference is in the switch of the unoccupied L_3 and $L_{2'}$ levels and the broadening of the d bands as α decreases. The width of the s band as measured from Γ_1 to $X_{4'}$ is practically independent of α.

III. EXCHANGE APPROXIMATIONS

The exchange term in the expectation value of the Hamiltonian with an antisymmetrized product wave function is

$$\langle H_{\mathrm{ex}} \rangle = -\frac{1}{2} \sum_{\mu,\nu} \iint \varphi_\mu^*(\vec{r}_j)\, \varphi_\nu(r_j)\, (2/r_{ij})$$

TABLE I. Energy levels in Ry using Wood's potential, our potential with three different values of α, and $\alpha = \frac{2}{3}$ with Koopmans corrections. The second column lists the number of occupied levels of each type in the self-consistent potential.

State	Weight	Wood	$\alpha = 1$	$\alpha = \frac{7}{9}$	$\alpha = \frac{2}{3}$	Koopmans
Γ_1	1	−0.7176	−0.3291	−0.0593	0.0827	−0.3581
$\Gamma_{25'}$	3	−0.1719	0.0308	0.3879	0.5692	−0.4514
Γ_{12}	2	−0.0691	0.1037	0.4714	0.6582	−0.4362
X_1	3	−0.4226	−0.1229	0.2043	0.3703	−0.4182
X_3	3	−0.3476	−0.0934	0.2444	0.4158	−0.4697
X_2	0	0.0033	0.1553	0.5294	0.7195	−0.4191
X_5	0	0.0277	0.1719	0.5476	0.7385	−0.4125
X_4	0	0.0975	0.4456	0.7183	0.8621	0.3913
L_1	4	−0.4090	−0.1173	0.2034	0.3659	−0.3858
L_3	8	−0.1834	0.0258	0.3818	0.5624	−0.4473
L_3	0	0.0068	0.1576	0.5317	0.7217	−0.4172
$L_{2'}$	0	−0.1166	0.2551	0.5285	0.6727	0.2174
Δ_1	6	−0.5164	−0.1479	0.1332	0.2789	−0.2088
$\Delta_{2'}$	6	−0.2672	−0.0347	0.3115	0.4871	−0.4555
Δ_1	6	−0.1441	0.0774	0.4237	0.6015	−0.3656
Δ_5	12	−0.0913	0.0910	0.4545	0.6390	−0.4235
Δ_2	0	−0.0343	0.1288	0.4995	0.6879	−0.4275
Σ_1	12	−0.3697	−0.0473	0.2580	0.4122	−0.1950
Σ_3	12	−0.2435	−0.0085	0.3349	0.5088	−0.4035
Σ_1	12	−0.2301	0.0068	0.3529	0.5291	−0.4114
Σ_4	12	−0.1180	0.0746	0.4363	0.6199	−0.4273
Σ_2	2	−0.0671	0.1060	0.4727	0.6589	−0.4286
Σ_1	0	0.1094	0.3055	0.6498	0.8300	−0.1712
$W_{2'}$	6	−0.3412	−0.0629	0.2715	0.4409	−0.3936
W_3	12	−0.2447	−0.0066	0.3351	0.5078	−0.3860
W_1	6	−0.0835	0.1022	0.4661	0.6506	−0.4076
$W_{1'}$	0	0.0282	0.1723	0.5481	0.7390	−0.4122
W_3	0	0.5225	0.8019	1.1020	1.2603	0.5781
Λ_1	8	−0.5591	−0.1853	0.0911	0.2354	−0.2352
Λ_1	8	−0.2166	0.0181	0.3605	0.5352	−0.3899
Λ_3	16	−0.1559	0.0438	0.4024	0.5843	−0.4446
Λ_3	0	−0.0594	0.1122	0.4800	0.6668	−0.4274
Ξ_1	24	−0.3573	−0.0739	0.2553	0.4211	−0.3624
Ξ_1	24	−0.2939	−0.0349	0.3014	0.4716	−0.3800
Ξ_1	24	−0.1854	0.0473	0.3901	0.5635	−0.3368
Ξ_2	24	−0.0972	0.0884	0.4518	0.6362	−0.4238
Ξ_2	0	0.0133	0.1621	0.5366	0.7270	−0.4158
Ξ_1	0	0.1705	0.4120	0.7324	0.9021	0.0523
K_1	0	−0.3551	−0.0775	0.2575	0.4271	−0.4143
K_1	0	−0.3087	−0.0521	0.2831	0.4531	−0.4017
K_3	0	−0.1584	0.0654	0.4118	0.5861	−0.3210
K_4	0	−0.0569	0.1174	0.4847	0.6711	−0.4155
K_2	0	0.0063	0.1578	0.5277	0.7209	−0.4137
K_3	0	0.3913	0.6225	0.9641	1.1243	0.4103
K_1	0	0.5225	0.7690	1.0737	1.2337	0.5420

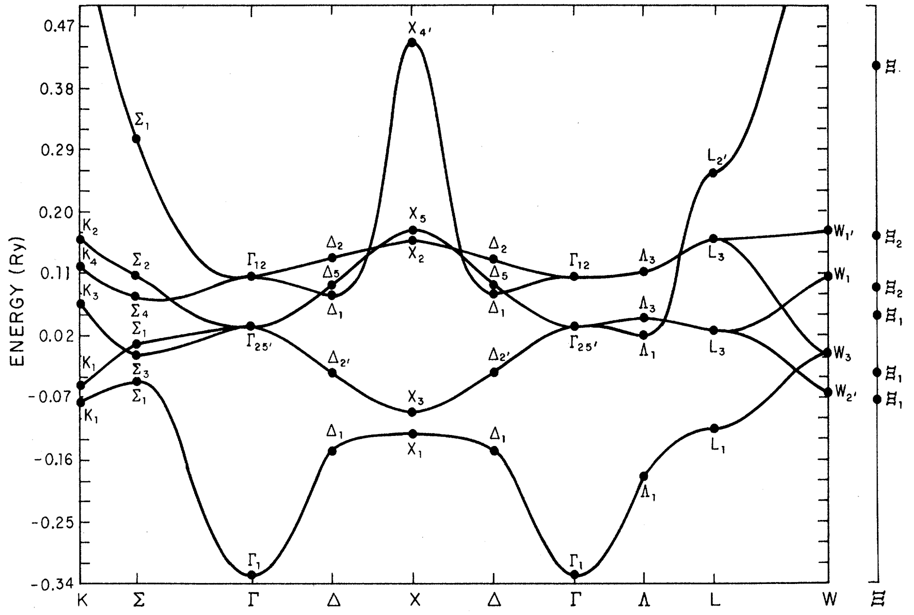

FIG. 1. Energy bands of fcc iron using the Slater exchange potential. The Fermi surface passes through the Σ_2 level.

$$\times\varphi_\mu(\vec{r}_i)\,\varphi_\nu^*(\vec{r}_j)\,d^3r_i\,d^3r_j\ . \qquad (11)$$

When the φ^*'s are varied to minimize the total energy, this term leads to the exchange potential in the one-electron Hartree-Fock (HF) Hamiltonian,[2]

$$V_{X\mathrm{HF}}(\mu,\vec{r}_j)=-\sum_\nu\int\varphi_\nu^*(\vec{r}_i)\varphi_\mu(\vec{r}_i)\,\frac{2}{r_{ij}}\,d^3r_i\,\frac{\varphi_\nu(\vec{r}_j)}{\varphi_\mu(\vec{r}_j)}\ . \qquad (12)$$

Slater[7] suggested that this could be approximated by the average exchange potential for a free electron gas,

$$V_{XS}(r)=-3\Big((3/\pi)\sum_\mu\varphi_\mu^*(\vec{r})\varphi_\mu(\vec{r})\Big)^{1/3}$$
$$=-3\,[3\rho(\vec{r})/\pi]^{1/3}\ , \qquad (13)$$

in which case $\langle H_{\mathrm{ex}}\rangle$ will be approximated by

$$\langle H_{XS}\rangle=\frac{1}{2}\sum_\nu\int\varphi_\nu^*(\vec{r})\,V_{XS}(\vec{r})\,\varphi_\nu(\vec{r})\,d^3r$$
$$=-\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}\int\rho^{4/3}(\vec{r})\,d^3r\ . \qquad (14)$$

Kohn and Sham (KS)[8] pointed out that if the variational procedure is applied directly to $\langle H_{XS}\rangle$ rather than to $\langle H_{\mathrm{ex}}\rangle$, one obtains an exchange potential in the one-electron Hamiltonian

$$V_{\mathrm{KS}}=\tfrac{2}{3}\,V_{XS}\ . \qquad (15)$$

They further pointed out that $\langle H_{XS}\rangle$ is the first term of an exact expansion of $\langle H_{\mathrm{ex}}\rangle$ in $\rho(\vec{r})$ and its derivatives[9] and thus so is V_{KS} for $V_{X\mathrm{HF}}$.

If Eq. (1) is used for the exchange potential in the one-electron Hamiltonian, then in some sense[10] the best value for α is that which yields wave functions which minimize the expectation value of the total HF Hamiltonian. A good approximation to this is to minimize the expectation value of the total Slater Hamiltonian whose exchange contribution is given by Eq. (14).[11] Using similar reasoning, Herman *et al.*[2] suggested calculating the one-electron binding energy from the one-electron Slater Hamiltonian

$$E_\mu^{\mathrm{binding}}\approx E_\mu+(1-\alpha)\int V_{XS}(\vec{r})\,|\varphi_\mu(r)|^2\,d^3r\ , \qquad (16)$$

where E_μ is the one-electron eigenvalue and the second term was called a Koopmans correction.[12] Because $\langle H_{XS}\rangle$ is the first term of an exact expansion of $\langle H_{\mathrm{ex}}\rangle$, whereas, V_{XS} is not the first term of an expansion for $V_{X\mathrm{HF}}$, the use of Eq. (14) does not violate the spirit of the KS theory, whereas Eq. (16) does. Furthermore, in any variational theory it is the lowest E_μ levels (not E_μ^{binding}) which are occupied to minimize the expectation value of the Hamiltonian. The physical interpretation of one-electron energies, the lowest of which are not in general occupied in the ground state, is not clear to us. Nevertheless, we have calculated the E_μ^{binding} energy bands from Eq. (16) for the KS $\alpha=\frac{2}{3}$ case. The results are given in the last column of Table I and in Fig. 3. We note that (i) the *d*

TABLE II. Total charge z outside inscribed sphere and charge in constant charge density, $Z=\Omega z/\Omega_0$ in units of electronic charge.

	$\alpha=1$	$\alpha=\frac{7}{9}$	$\alpha=\frac{2}{3}$
z	0.653	0.765	0.819
Z	2.278	2.670	2.859

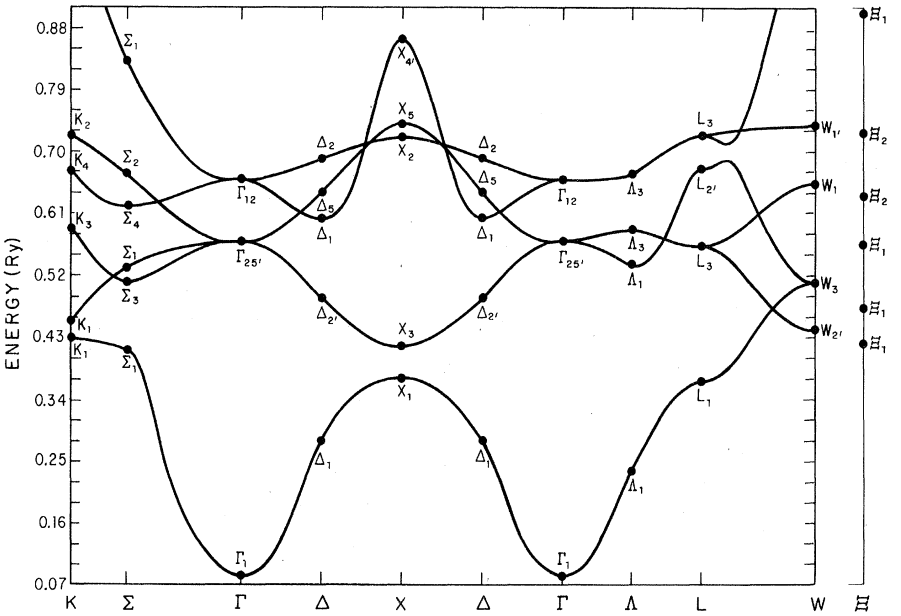

FIG. 2. Energy bands of fcc iron using the KS exchange potential. The Fermi surface passes through the Σ_2 level.

bands are very narrow, only 1 eV as measured from X_3 to W_2; (ii) the *d* bands have dropped everywhere below the *s* bands[13]; (iii) a peculiar unphysical sort of *s*-*d* hybridization occurs in which bands of the same symmetry cross. For example, because Γ_{12} drops below Γ_1, the Δ_1 band connecting Γ_{12} with X_4' must cross the Δ_1 band connecting Γ_1 with X_1. The *s*-*d* hybridization is of course built into the wave functions and not affected by the fact that pure *d* states have everywhere dropped below the pure *s* state. We are forced to conclude that the Koopmans correction is incorrect whenever strong hybridization occurs.[14]

IV. BINDING ENERGY

The binding energy per atom calculated with $\langle H_{XS}\rangle$ as an approximation for $\langle H_{ex}\rangle$ is

$$E=\left(\sum_{\mu=\text{core}}+\frac{1}{32}\sum_{\mu=n,k=1}^{256}\right)\left(E_\mu+\int_{\text{cell}}\varphi_\mu^*(r)\left[\left(\tfrac{1}{2}-\alpha\right)V_{XS}(\vec{r})-\tfrac{1}{2}V_{\text{el Coul}}(\vec{r})\right]\varphi_\mu(\vec{r})\,d^3r\right)-Z^2\,\frac{1.79172}{r_{ws}}-Z(26-Z)\,\frac{3.58344}{r_{ws}}\,, \qquad (17)$$

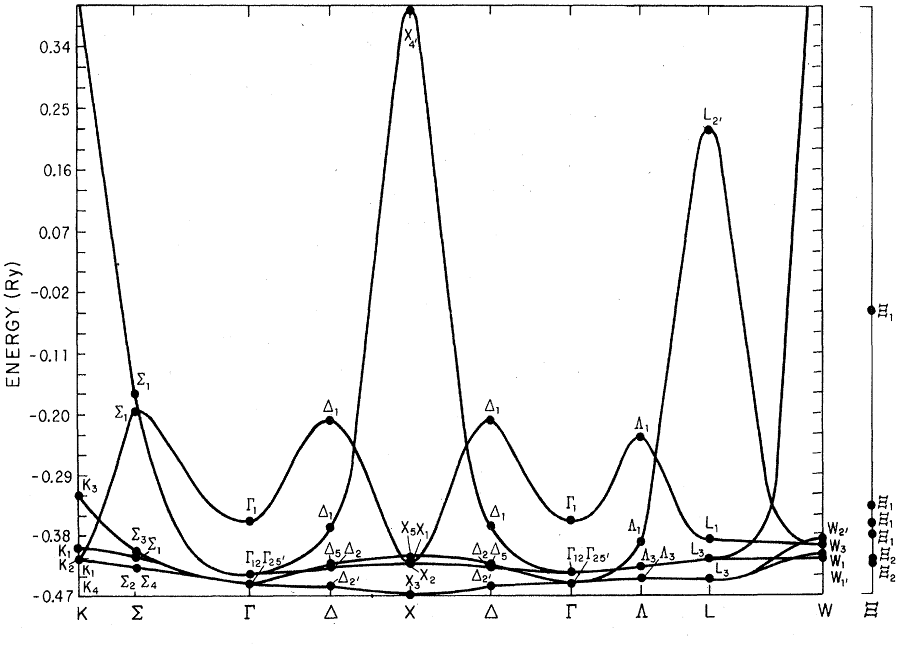

FIG. 3. Energy bands of fcc iron using the KS exchange potential with Koopmans corrections. Because some occupied levels lie above unoccupied levels, a Fermi surface cannot be defined.

where the φ_μ are eigenfunctions of the one-electron Hamiltonian with an exchange potential given by Eq. (1). Because of the cube root in the exchange, the core and conduction electrons must be considered on an equal footing. The product $\varphi^*_{nk}\,\varphi_{nk}$ contains two types of terms, those which exist only within the inscribed sphere and $e^{i\vec{k}\cdot\vec{r}}$ terms existing everywhere. For the former we use the spherically averaged potential in the integral in (17) for that is what was used in the calculation of E_μ, while for the latter we use the exact fourier transform $V(\vec{\kappa})$ of the potential obtained from the muffin-tin charge density. Note that $V_{\mathrm{el\,Coul}}$ contains two terms, that from the 26-Z spherical electronic charge distribution and that from the constant charge distribution of Z electrons per cell given by the r^2 term of Eq. (9). The latter contributes nothing to $V(\vec{\kappa})$, while the calculation of the contribution of the former to $V(\vec{\kappa})$ is straightforward.[15] The last term in (17) is the energy of the (26-Z) protons sitting in the Madelung potential of the constant part of the electronic charge density and the Z protons on all the other lattice sites. The preceding term is the energy of the Z protons in the same potential.[16]

In Table III, we list the binding energy of the crystal along with the binding (i.e., ionization) energy of the atom calculated for three different values of α. The lowest binding energy occurs at $\alpha=\frac{2}{3}$ as expected.[11] Indeed, in the atomic case we have calculated the binding energy for several values of α close to $\frac{2}{3}$ and found the minimum binding energy exactly at $\alpha=\frac{2}{3}$. One would expect some deviation from this exact result in the crystal because of errors introduced by the muffin-tin approximation as well as the 64 BZ point sampling. Because of our high degree of self-consistency, it requires about 10 h of CDC 6600 computer time to perform the calculation for each value of α. Therefore, we have not attempted to find that value of α which minimizes the binding energy of the crystal within the muffin-tin approximation.[11]

The binding energy minus the ionization energy is the cohesive energy which must be negative for the crystal to exist. We note that the cohesive energy is positive for any α but that it is much less positive for $\alpha=\frac{2}{3}$ than for $\alpha=1$. There are three improvements which can be made which should cause the cohesive energy to become negative. The exchange approximation can be improved to include terms in the gradient of the charge density. A correlation term, which ought to have a much larger effect in the crystal than in the atom, should be included. The true crystal charge density rather than the muffin tin should be used to calculate the crystal potential. The last of these improvements will be the topic of a later paper.

TABLE III. The binding energy of the crystal in Ry per atom and the ionization energy of the atom calculated using three values of α. The difference is the cohesive energy.

	$\alpha=1$	$\alpha=\frac{7}{9}$	$\alpha=\frac{2}{3}$
Binding	−2515.629	−2516.623	−2517.005
Ionization	−2517.260	−2517.698	−2517.788
Cohesive	1.631	1.075	0.783

TABLE IV. The $3d$-$4s$ energy separation and total binding energy (in Ry) of atomic krypton according to Ref. 2.

	$4s$-$3d$	Binding
HF	5.34	−5504.11
Slater	5.14	−5493.04
KS	4.49	−5493.73
Slater (HF)	4.55	−5503.47
KS (HF)	5.41	−5504.02
KS (Slater)	5.98	···

V. CONCLUSIONS

There are no experimental data with which to compare our calculated energy bands of γ-Fe. Even if there were, we could not conclude that exchange which yields the best energy bands is best; all we could conclude is that the errors in that exchange approximation were best cancelling the errors in the muffin-tin approximation. Therefore, we are forced to draw what conclusions we can from atomic calculations.

In the first column of Table IV, we list the $3d$-$4s$ energy separation calculated from atomic krypton.[2] We see that the Slater value is far closer to the HF than is the KS value. We also see that the KS wave functions are far better than the Slater, for when the expectation value of the HF Hamiltonian is calculated using these wave functions, the KS $3d$-$4s$ energy separation is much closer to the HF than is the Slater. When the expectation value of the Slater Hamiltonian is calculated with the KS wave function, we see that the Koopmans correction obtained is much too large. From this we conclude that the Γ_1 level must be raised relative to the $\Gamma_{25'}$ and Γ_{12} in the crystal. When the Slater potential is used this is a small correction, when the KS potential is used it is a large correction, however, it is never so large as the Koopmans correction tells us; in particular, we are quite certain that the Γ_1 level should not be raised above the $\Gamma_{25'}$ and Γ_{12} levels. If one had the computational facilities, one could get the levels at Γ very accurately by calculating the expectation value of the HF Hamiltonian with the KS wave functions. However, this would not be an appropriate method for calculating the energy bands throughout the BZ. Where hybridization can occur it must be calculated from the true s-d splitting and not from the KS. Where hybridization occurs the KS wave functions will be very poor and will lead to very poor HF energies.

In the second column of Table IV, we list the binding (total ionization) energy of atomic krypton. Since we have already concluded that the KS wave functions are better than the Slater (when there is no hybridization), it is not surprising that they give better binding energies when calculated from the expectation value of the HF Hamiltonian. Of course, from the variational theorem, they must give better binding energies when calculated directly from the Slater Hamiltonian. The fact that the KS binding energy eliminates only 6.3% of the error in the Slater binding energy indicates that the gradient terms in the KS expansion are important[17] and gives us hope that with them a negative cohesive energy will be obtained for the γ-Fe crystal.

We therefore conclude that the KS is the best of the $x\alpha$ exchange potentials for calculating binding energies and total charge densities and yields good one-electron wave functions when hybridization is not present but that a value of α close to one yields the best one-electron eigenvalues and when hybridization is present also the best one-electron wave functions.

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

[2] F. Herman, I. B. Ortenburger, and J. P. Van Dyke, Int. J. Quantum Chem. Symp. 3, 827 (1970).

[3] L. Kleinman and R. Shurtleff, Phys. Rev. 188, 1111 (1969).

[4] I. Goroff and L. Kleinman, Phys. Rev. B 1, 2574 (1970).

[5] This point lies on the reflection plane containing the (100) and (111) axes. We suggest the designation Ξ for these previously unnamed symmetry points.

[6] L. Kleinman, Phys. Rev. 146, 472 (1966).

[7] J. C. Slater, Phys. Rev. 81, 385 (1951).

[8] W. Kohn and L. J. Sham, Phys. Rev. 140, A 1133 (1965).

[9] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[10] In fact, the calculations on atomic krypton in Ref. 2 show that this α yields eigenvalues quite far from the HF eigenvalues. However the expectation value of HF one-electron Hamiltonian with these eigenfunctions was very close to the HF eigenvalue. This was the reason Herman *et al.* suggested making the Koopmans corrections.

[11] One should expect $\alpha = \frac{2}{3}$ to minimize the expectation value of the Slater Hamiltonian because the KS exchange potential is obtained variationally from the Slater Hamiltonian.

[12] We think this is a misnomer; Koopmans's theorem proves the equivalence of the one-electron eigenvalue and one-electron binding energy providing the wave functions are not localized so the removal of one electron is a negligible perturbation on the rest and providing the one-electron Hamiltonian is obtained variationally from the expectation value of the full Hamiltonian. This so-called Koopmans correction is an attempt to correct for errors introduced by the approximation for the exchange term in the full Hamiltonian whether or not the one-electron Hamiltonian was obtained variationally.

[13] This large drop of d relative to s levels was observed in Ref. 2 for atomic krypton.

[14] One might consider us naive to take the Koopmans correction to be the expectation value of the one-electron Slater Hamiltonian between KS wave functions as was done in the atomic case. By including off-diagonal matrix elements, we would prevent the various bands from crossing. However, because the KS wave functions form a complete set, if we carry this idea to convergence, we end up with the Slater eigenvalues and eigenfunctions. Therefore, we feel that the Koopmans correction concept is of very little utility in energy-band calculations.

[15] One must be careful of the sign of $V(0)$ which is negative while all other $V(\vec{k})$ are positive. Because the potential is arbitrary to within an additive constant, one is free to define the zeroth Fourier transform of the potential due to an electrically neutral system of point ions and a constant background of charge density to be zero. Thus, one may add the $26-Z$ protons to the spherical electron distribution when calculating $V(0)$ but not when calculating any other $V(\vec{k})$.

[16] Note the factor of $\frac{1}{2}$ in the first term relative to the second. The $(26-Z)$ protons are in an "external" potential $-Z(3.58344/r_{ws})$ due to the Z protons. The energy of the Z protons in this same potential (now a self-potential) must be multiplied by $\frac{1}{2}$ to avoid counting twice interactions between pairs of Z protons.

[17] In fact, in Ref. 2 the addition of small gradient terms in the KS exchange brought the binding energy of krypton below the HF value without making any change in the $3d$-$4s$ eigenvalue difference.