PHYSICAL REVIEW VOLUME 117, NUMBER 3 FEBRUARY 1, 1960

Wave Functions for Iron *d* Band*

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(Received August 28, 1959; revised manuscript received September 23, 1959)

The one-electron wave functions for the *d* band of body-centered iron are examined and found to have significantly different character, depending on their energy location in the band. The bottom of the band is associated with diffuse wave functions, while the top is associated with more compact atomic-like functions. A smooth transition from one behavior to the other occurs as the energy is varied. This gives substantiation to recent descriptions of transition metals which have been based on "low *d*" assignments; here this is explained on the basis that a significant fraction of the *d* electrons in a solid do not "look" like atomic *d* electrons at all.

INTRODUCTION

THIS note describes features of the one-electron wave functions of angular momentum 2, obtained in the course of an energy band calculation for body-centered iron.[1] The method used for calculation has the advantage (for present purposes) of describing the wave function about the nuclei in terms of numerical integrations of the conventional radial Schrödinger equation. Thus one may, in large part, examine the behavior of the functions (whose eigenenergies define the energy bands) by looking at the solutions of the radial equation for appropriate values of the energy parameter.

Atomic iron has a ground configuration $3d^6 4s^2$ so that in crystalline iron the bands of interest will be those arising from the $3d$, $4s$, and perhaps $4p$ atomic functions. In transition metals the detailed structure of the $3d$ band is of great interest for many applications; in particular, the one-electron wave functions and associated one-electron charge densities as well as one electron-energy levels are of interest. We consider here just what these wave functions look like and how their behavior changes as we move from one portion of the band to another. We may briefly characterize our findings as follows.

The bottom (in energy) of the *d* band is characterized by one-electron *d* wave functions which are quite diffuse, being quite different from the conventional atomic *d* function, while at the top of the band we find the associated *d* wave function is quite contracted, much like an atomic function. As one moves upward in energy from the bottom to the top of the band, smooth transition from the diffuse to the contracted nature is observed. Thus it appears that in transition metals we may very well have "different kinds" of *d* electrons present, and pictures of these metals based on assumptions of completely localized *d* wave functions may need to be modified.

There will be recognized a similarity to the proposals of Pauling[2] who gave a description of the transition metals based on the assumption that there were two *d* bands—one described by diffuse functions (bonding) and the other by localized (antibonding) functions. More recently, Lomer and Marshall[3] have advanced a scheme for the transition metals based on the experimental results of Weiss and DeMarco[4] who find for some transition metals, including iron, a number of $3d$ electrons much lower than is expected from conventional band theory. Lomer and Marshall describe the *d* band as composed of localized *d* functions with an admixture of diffuse functions which they call $4c$, presumably derived from $4s$ and $4p$ (and perhaps higher) functions. In the present description it appears that the *d* functions themselves provide this diffuse part without the necessity of mixing in large quantities of $4s$ and $4p$.

CRYSTAL WAVE FUNCTIONS

To expand on the previous statements, we indicate briefly the construction of the one-electron energy band functions showing how the solutions of the radial Schrödinger equation enter. We used the augmented plane wave method (APW) of Slater[4] as developed and programmed by Saffren[5] for the Whirlwind computer. In this method the approximation to the self-consistent energy band potential is made as follows.

Around each nucleus of the crystal is drawn a sphere of radius R (which we took to be half the nearest neighbor distance). Inside these spheres the one-electron potential is taken to be a spherically symmetrical atomic-like potential $U(r)$ chosen appropriate to the particular crystal. In the region between these spheres the potential is taken as a constant. One then solves the one electron Schrödinger equation in this potential taking advantage of the crystalline symmetry. The resulting set of one-electron energies and wave functions then characterize the energy bands.

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* This work was supported in part by the Office of Naval Research, under contract with the Massachusetts Institute of Technology.

[1] J. H. Wood, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 28, April 15, 1958 and No. 31, January 15, 1959 (unpublished).

[2] L. Pauling, Phys. Rev. **54**, 899 (1938).

[3] W. M. Lomer and W. Marshall, Phil. Mag. **3**, 185 (1958). See also N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957).

[4] R. J. Weiss and J. J. DeMarco, Revs. Modern Phys. **30**, 59 (1958). Also B. W. Batterman, Phys. Rev. Letters **2**, 47 (1959); and R. J. Weiss and J. J. DeMarco, Phys. Rev. Letters **2**, 148 (1959).

[5] M. M. Saffren, Ph.D. thesis, Massachusetts Institute of Technology, 1959 (unpublished).

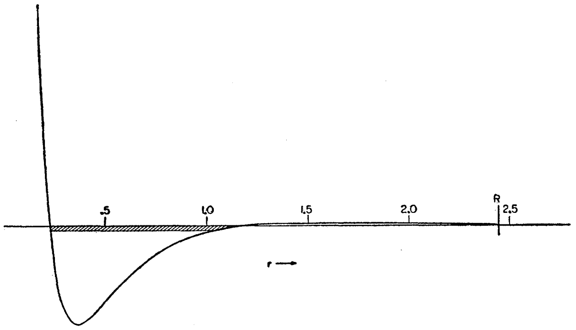

FIG. 1. Plot of the quantity $(6/r^2)-U(r)$ where $U(r)$ is that of reference 8. Atomic units.

If we pick a particular point $\mathbf{k}$ in the Brillouin zone for which the nth energy band has the value $E=E_n(\mathbf{k})$, then the associated wave function inside the sphere located at the origin can be written[6]

$$\psi_n(\mathbf{r};\mathbf{k},E)$$

$$=\sum_i A_i \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}(2l+1)i^l j_l(|k_iR|)\frac{u_l(r;E)}{u_l(R;E)}$$

$$\times\frac{(l-|m|)!}{(l+|m|)!}P_l^{|m|}(\cos\theta)P_l^{|m|}(\cos\theta_i)\exp m(\phi-\phi_i). \quad (1)$$

Outside the sphere we have

$$\psi_n(r;k,E)=\textstyle\sum_i A_i\exp(i\mathbf{k}_i\cdot\mathbf{r}).$$

The A_i are determined from a secular equation among the functions indexed by k_i. The set $\{\mathbf{k}_i\}$ is that generated from $\mathbf{k}$ by adding to it the vectors of the reciprocal lattice. θ and ϕ are polar coordinates about the origin; θ_i and ϕ_i are the polar coordinates of k_i.[7] The $u_l(r;E)$ are the solutions of the radial Schrödinger equation for angular momentum l and energy $E=E_n(\mathbf{k})$.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{du_l}{dr}\right)+\left(\frac{l(l+1)}{r^2}-U(r)\right)=Eu_l. \quad (2)$$

If, as in atomic self-consistent field calculations, we define $P(r)=ru(r)$ then $P(r)$ satisfies

$$\frac{d^2P_d}{dr^2}=g(r)P_l(r),$$
$$g(r)=\left[\frac{l(l+1)}{r^2}-U(r)-E\right]. \quad (3)$$

BEHAVIOR OF WAVE FUNCTIONS

Now it is clear that our energy band wave functions and energy levels will be strongly dependent on $U(r)$ inside the sphere. (This sphere, inscribed in the Wigner-Seitz unit cell, accounts for about 70% of the total volume of that cell.) Also, it is known from atomic calculations that $P(r)$ for $l=2$ is very sensitive to the value of the energy parameter E; small deviations from the energy which defines a $P(r)$ properly bounded at infinity lead to quite large deviations in $P(r)$.

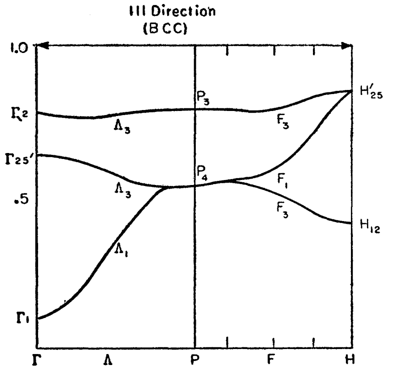

FIG. 2. Plot of energy bands $E_n(k)$ for bcc iron obtained via APW method (reference 3) using potential of reference 8. Energy in Rydbergs. Labeling that of Bouckaert, Smoluchowski, and Wigner.[9]

Consider what this might lead to in the case of the d band of a solid. The d band is described by functions $\psi_n(\mathbf{r};\mathbf{k},E)$ whose leading term in the expansion (1) will be $l=2$. Now if the spread in energy (bandwidth) of the d band is sizeable we may expect, in analogy with the atomic case, considerable changes in $u_2(r;E)$ which describes the radial behavior of this leading term, as we range from the bottom to the top of the band.

In Fig. 1 we have plotted the quantity $(6/r^2)-U(r)$ [see Eq. (3)], where the $U(r)$ is that of Manning[8] as used in the band structure calculation. This quantity is the effective potential energy for the determination of $u_2(r)$. In Fig. 2 we have plotted the band structure $E_n(\mathbf{k})$ along the [111] direction in k space.[9] As it turns out, the energy corresponding to H_{12} is the lowest energy in the d band while that corresponding to H_{25}' is almost at the top. All energies between are allowed and cover a range of a little more than 6 electron volts. We have indicated this range of the d band on Fig. 1 as a shaded band; the significant feature of this picture is that in the region beyond about 1 atomic unit any d band energy lies very close to the effective potential curve. A small change in energy can move the right hand classical turning point and thus the inflection point of $P_2(r)$ considerably [see Eq. (3)]. In Fig. 3 we show the results of integrating Eq. (3) for the lowest and highest energies in the band, as well as several intermediate energies.

These curves illustrate the greatly different characters of which we have spoken. At the bottom of the band we have a quite diffuse function retaining large

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[6] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[7] Such a function must, of course, have certain transformation properties under the operations of the group of the wave vector. The result of this demand is that certain k_i and l are absent from the sum; also obtained are sets of relations among the A_i.

[8] M. F. Manning, Phys. Rev. **63**, 190 (1943).

[9] The notation is that of Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

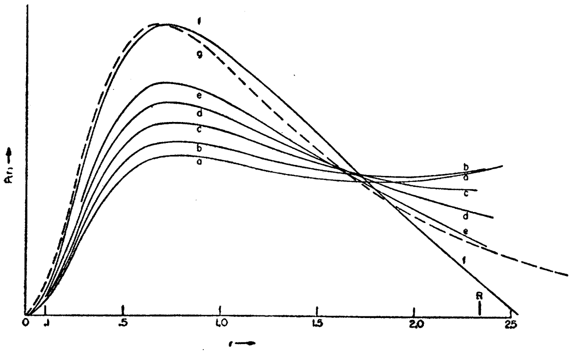

FIG. 3. Plot of radial wave functions $P_2(r)$ [see Eq. (3)] for d band energies. Functions are *not* normalized. (a) $E=E(H_{12})=0.41$ Rydberg (bottom of d band); (b) $E=0.45$ Rydberg; (c) $E=0.55$ Rydberg; (d) $E=0.65$ Rydberg; (e) $E=0.75$ Rydberg; (f) $E=E(N_3)=0.88$ Rydberg (top of d band); and (g) atomic $3d$ function [J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957)].

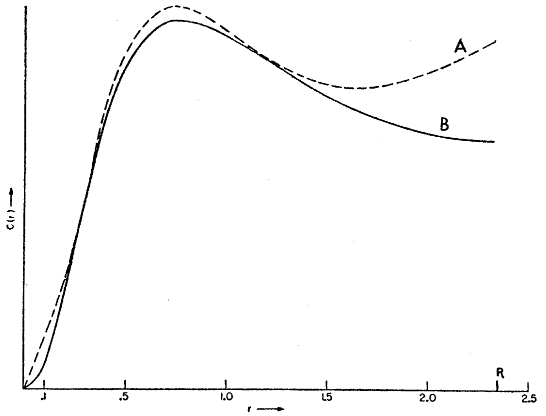

FIG. 4. Plot of $C(r)$ [see Eq. (4)] for the state P_4. A includes effect of p term in wave function; B includes only effect of d term.

amplitude right out to the sphere radius (half the nearest neighbor distance). At the top of the band we have switched over to a highly contracted functions; as a matter of fact, this function is more localized than a free atom d function (also plotted on Fig. 3). As we move up through the band we switch over smoothly from the diffuse to the contracted behavior. At an energy located halfway up in the band, we find the value of $P(r)$ at the sphere radius to be almost precisely half its maximum value.

Thus our one-electron energy band functions here written as sums of augmented plane waves, are going to describe quite different behaviors as we range across the d band. Now the expression (1) for the wave function inside the sphere involves a sum over angular momentum l. As we mentioned previously, for some states certain of the l are not present because of symmetry but this is not true in general—a general state in the d band will contain terms from all angular momenta. The question then arises as to whether the behavior of the other $u_l(r;E)$ might not seriously modify our description in terms of $l=2$ only. This does not seem to be the case although there are modifications of a quantitative nature for some states.

IMPORTANCE OF ANGULAR MOMENTA OTHER THAN TWO

The energy band calculation carried the sum on l through $l=12$. Our initial expectation is that if l other than $l=2$ is needed in expressing the wave function they will be $l=0$ and 1, corresponding to an admixture of $4s$ and $4p$. We have looked at this admixture in the following way, as suggested by M. M. Saffren.

From Eq. (1), one can form $\psi^*\psi$ giving us a one-electron charge density. If we integrate over angles and sum over the index i we are left with a charge density having the form[6]

$$\sum_l B_l\left[\frac{u_l(r;E)}{u_l(R;E)}\right]^2,$$

and if we wish we can define

$$C(r)=r\left(\sum_l B_l\left[\frac{u_l(r;E)}{u_l(R;E)}\right]^2\right)^{\frac{1}{2}}, \tag{4}$$

which is an analog of the $P(r)$ for atomic functions, the square of which gives the radial charge density.

We have examined $C(r)$ for several states in the d band where mixing of angular momenta is allowed by symmetry. The largest mixing we have found to date is for the function corresponding to the representation P_4, where pd mixing is allowed. Here the B for $l=1$ and $l=2$ turn out to be 1.108 and 1.131. In Fig. 4 we plot $C(r)$ for this case. The curve labeled A is that in which both $l=1$ and $l=2$ are included in computing $C(r)$ while that labeled B is that for $l=2$ alone. We see here that while there has been a substantial quantitative modification, qualitatively the picture is pretty much the same. Such has been the case for all those states so far examined; the behavior of the d radial wave function gives a rather good qualitative picture of the "radial wave function" $C(r)$.

The energy band calculation was also carried out for fcc iron[1] using again the Manning potential. Here too, we have examined the resulting wave functions and find a similar situation. Thus the present results do not seem to depend critically on the crystal structure, and, as is explained later, do not appear to be a result of using the particular numerical potential of Manning.

DISCUSSION

It is clear from the previous discussion that this picture of d electrons in a transition metal gives *some* substantiation to the Pauling and Lomer and Marshall descriptions. However, we need a good deal more information before we can have complete confidence in the picture. In particular, it is obvious that one should investigate the behavior of $\psi^*\psi$ for many more values of **k** and E. Here we have restricted ourselves to **k** for which symmetry makes computation of $C(r)$ a tractable job by hand. Next it would be useful to have a density of states function for the band structure. This will give information regarding the number of occupied states per unit energy range which together with the behavior of the one electron charge density can give us information about the total charge density.

There is, of course, the question as to whether this behavior is just a peculiarity of the numerical potential we have chosen for the problem. We do not believe this is so since in addition to the band calculation mentioned here we have also carried out another, using a quite different potential, and found the same situation with respect to the d wave functions in spite of the fact that the width of the d band nearly doubled. In order to see if this behavior will prevail across the series of transition metals, we have examined the wave functions of copper as calculated by Chodorow.[10] We find that he too obtains this behavior.

If, as appears at present, a sizeable fraction of the valence electrons are described by the "spread-out" d functions it is evident that the potential function $U(r)$ will be somewhat modified from the predominately atomic character which it has usually been assumed to have. Suppose we construct the crystal potential out of the argon cores centered on each of the iron nuclei plus the charge densities on each site arising from the valence electrons.[11] Then around any one site the potential may be looked upon as arising from the charge density located on that site plus contributions from all other sites (see reference 6). Now it is clear that if we have charge density "sticking out" to the very edges of the cells the contributions of the other sites will be very important in determining the local value of the potential. In particular, it would seem that the expansion of the local potential in terms of spherical harmonics will include contributions from other than $l=0$ terms; that is to say we will have a crystalline field present which might split the d band into two portions as Pauling has suggested. However, preliminary estimates of the changes in the d levels which may be expected upon inclusion of $l=4$ terms in the potential indicate that the d levels will not be modified by more than an electron volt. These estimates were made along the lines suggested by Leigh.[12] Reference to Fig. 2 shows that changes of this order of magnitude will not split the d band into two portions.

CONCLUSIONS

Now it is of interest to ask what the previous considerations indicate in the light of recent experimental work on the transition metals. If the wave functions in the self-consistent field description of the transition metals retain the characteristics we have described, then we would expect experimental analyses of the number of atomic d electrons in these metals would indicate a deficiency. The whole question is just how sizeable is this deficiency.

Weiss and DeMarco, in their investigations of electron charge density in the transition series metals, see only about two atomic d electrons per atom in iron. On the other hand, Batterman reports he obtains approximately a d^6 configuration. Very recently, Komura, Tomiie, and Nathans[13] have reported an investigation of Fe_3Al; they conclude on the basis of other evidence that the configuration of Fe in this alloy will not differ greatly from the configuration in the pure metal. Their results indicate a d^6 configuration, thus agreeing with Batterman.

Recently, Stern[14] has reported calculations of the energy bands and cohesive energy of bcc iron by a modified tight binding method. He reports the indicated configuration is d^7s. Stern also finds the sort of behavior we have found in the d wave functions [see his Fig. 1 where he plots $u(r)=P(r)/r$] and preliminary comparisons show a rather surprisingly good qualitative (and perhaps quantitative) agreement between the two calculations.

If we accept a configuration of d^7s, which seems reasonable from the energy band standpoint, then we must explain how it is that the x-ray experiments indicate a loss of one of these d's (if we accept the results of Batterman and Komura *et al.*) or of five d's (if we accept the results of Weiss and DeMarco).[15]

Although, as mentioned previously, we are not in a position to get an accurate density of states curve, we have been able to construct a very rough curve from the values of the energy at the nineteen values of **k** we have considered. This analysis indicates that there are about five d electron states per atom below an energy of 0.7 Rydberg. Now a glance at Fig. 3 will show that while we may expect smaller contributions from these states to the form factor than if they were atomic-like, it is also pretty clear that they cannot give a zero contribution as would be required by the Weiss and DeMarco picture. On the other hand, it is not unreasonable to suppose that they could account for the "vanishing" of one d electron as required by Komura and Batterman.

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[10] M. Chodorow, Ph.D. thesis, Massachusetts Institute of Technology, 1939 (unpublished).

[11] R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

[12] R. S. Leigh, Proc. Phys. Soc. (London) **71**, 33 (1958).

[13] Komura, Tomiie, and Nathans, Phys. Rev. Letters **3**, 268 (1959). See also Arp, Edmonds, and Petersen, Phys. Rev. Letters **3**, 212 (1959).

[14] F. Stern, Phys. Rev. **116**, 1399 (1959); and private communications.

[15] A complete discussion of the analysis of the x-ray and neutron diffraction results in iron and nickel is given by R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959).

Thus we feel at present that the energy band description can account for some reduction in the number of d electrons but it seems rather unlikely that this reduction can amount to more than one or two electrons.

ACKNOWLEDGMENTS

The writer thanks Professor J. C. Slater who suggested this problem. He is also indebted to members of the Solid-State and Molecular Theory Group at the Massachusetts Institute of Technology for many discussions. In particular, he would like to thank Dr. M. M. Saffren for the use of the computer programs for the augmented plane wave method without which the work would have been impossible, and for many discussions.

PHYSICAL REVIEW VOLUME 117, NUMBER 3 FEBRUARY 1, 1960

Ferromagnetic Anisotropy in Cubic Crystals*

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(Received August 21, 1959)

A re-evaluation has been made of Van Vleck's second-order perturbation theory of dipolar-type anisotropy in cubic ferromagnets. In the low-temperature limit of strong correlation between the direction of neighbor spins, the first anisotropy constant K_1 varies as the 10th power of the magnetization. The theory is somewhat analogous to a previous treatment of quadrupolar-type anisotropy in the strong-correlation limit. In both cases, the results are in agreement with the Akulov-Zener classical theory. For the dipolar case, complete agreement is also established between the Dyson-type spin-wave analysis of Charap and Weiss and the Holstein-Primakoff approach. Higher order terms in the latter are shown to lead to the Charap-Weiss correction from exchange interaction between spin waves, and this correction is extended to $S>\frac{1}{2}$. Essentially the same correction is obtained very easily from a simple modification of the Van Vleck formalism to take careful account of the average energy involved in simultaneous reversal of neighbor spins. It is shown that spin-wave theory, in agreement with classical theory, predicts identical values of dipolar-type anisotropy whether measured statically in a torque experiment or dynamically in a microwave resonance experiment.

I. INTRODUCTION

THE classical theory of ferromagnetic anisotropy in cubic crystals was formulated by Akulov.[1] He showed that if the anisotropy energy is expanded in powers of the direction cosines α_1, α_2, α_3 between the bulk magnetization vector and the three cubic axes, then the lowest nonvanishing term must be of the form

$$F_1=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)\equiv K_1\Gamma. \quad (1)$$

A rough estimate of the temperature dependence of K_1 was also given by Akulov. He considered the crystal to be composed of a number of small regions, and within each region he assumed that the magnetization vector makes a random small angle θ with respect to the average over-all direction of bulk magnetization. The anisotropy energy of each region is assumed to take the form (1). As the temperature increases the angle θ between regional and average magnetization becomes larger and larger, and the total anisotropy energy drops precipitously. The reason for the very rapid drop is illustrated in Fig. 1. When the average value of the angle θ is as shown in the figure, the total anisotropy energy will disappear; however, the sample magnetization $M(T)$, which is given by the average value of M_z, will be quite large. Akulov derived the expression

$$K_1(T)/K_1(0)\approx 1-10[M(0)-M(T)]/M(0). \quad (2)$$

Zener[2] has shown by a random-walk calculation of the average angle θ that a more precise formulation of (2) is a "10th power law."

$$K_1(T)/K_1(0)=[M(T)/M(0)]^{10}. \quad (3)$$

Furthermore, Zener has given a general expression for higher-order anisotropy. In particular, in the first term beyond (1),

$$F_2=K_2\alpha_1^2\alpha_2^2\alpha_3^2, \quad (4)$$

the temperature dependence of K_2 is as the 21st power of $M(T)$. If the solid curve in Fig. 1 were redrawn to represent F_2 it would cross the dotted curve at smaller θ, which accounts for the higher power. Zener has also shown that if $K_2(0)$ is of comparable magnitude to $K_1(0)$, the temperature falloff of K_1 increases. This is clear from Fig. 1 since, if the solid curve were to include both F_1 and a large F_2, it would have many wiggles and the total anisotropy would vanish as K_2.

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* This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

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