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Localized Magnetic States in Metals

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The conditions necessary in metals for the presence or absence of localized moments on solute ions containing inner shell electrons are analyzed. A self-consistent Hartree-Fock treatment shows that there is a sharp transition between the magnetic state and the nonmagnetic state, depending on the density of states of free electrons, the *s-d* admixture matrix elements, and the Coulomb correlation integral in the *d* shell; that in the magnetic state the *d* polarization can be reduced rather severely to nonintegral values, without appreciable free electron polarization because of a compensation effect; and that in the nonmagnetic state the virtual localized *d* level tends to lie near the Fermi surface. It is emphasized that the condition for the magnetic state depends on the Coulomb (i.e., exchange self-energy) integral, and that the usual type of exchange alone is not large enough in *d*-shell ions to allow magnetic moments to be present. We show that the susceptibility and specific heat due to the inner shell electrons show strongly contrasting behavior even in the nonmagnetic state. A calculation including degenerate *d* orbitals and *d-d* exchange shows that the orbital angular momentum can be quenched, even when localized spin moments exist, and even on an isolated magnetic atom, by kinetic energy effects.

I. INTRODUCTION

RECENT experimental results[1] have shown that the occurrence of localized magnetic moments on iron-group ions dissolved in nonmagnetic metals is a more widespread, more systematic, but at the same time, more complicated phenomenon than previously suspected. In dilute solutions of iron, cobalt, and to a lesser extent, nickel, the appearance of such moments seems to be a function mainly of the host metal, although the moments observed differ greatly from one solute to another. As a function of the Matthias "electron concentration" parameter, one finds sharply defined regions where localized moments are strictly absent, interspersed with regions at the edges of which the moments appear almost discontinuously.

The regions of localized moments have a noticeable negative correlation with the superconducting transition temperature, and a rather less strong correlation with low density of states as measured by the low-temperature specific heat γT.

Such localized moments in metals have been often accepted as an experimental fact without examination of their meaning or of the conditions for their occurrence. Friedel and collaborators have made a start at an understanding of the phenomenon[2]; extending their work and some of the concepts set forth by us earlier,[3,4] we will here attempt to describe formally, in a highly simplified model, a quantum state of the metal in which such a moment exists, and to discuss the conditions required for its stability.

The fundamental conceptual difficulty here is that such a localized moment cannot be satisfactorily described within the usual type of one-electron theory which is adequate for the properties of nonmagnetic solids. The first problem is that in polyvalent metals the bandwidths are so great that the energies of the one-electron states which might contain the magnetic electrons are certainly coincident with a free-electron band. One-electron theory does not permit localization of such a state; the best one can do is to use a virtual state,[2] a state which, left to its own devices, would decay into one of the continuum of free-electron states.

The second problem is that it is very difficult to understand how, in a usual Hartree-Fock theory, the states of opposite spin on the ion can be empty while the parallel spin states are full. For instance, in solutions of Fe in Mo-Nb alloys, the Fe ion changes from being nonmagnetic to having a moment corresponding to about two electrons when the concentration is varied by only a few percent. This is impossible to credit as gradual filling up on one-electron energy states, even if we accept exchange as strongly favoring the parallel-spin states. There must in fact be a nearly discontinuous change in the quantum state of the many-electron problem.

The picture we suggest is founded on the same type of concept which is valuable in insulating magnetic materials[5] and which has been suggested as being essential in magnetic metals[6]: That the magnetic state is characterized by being the state in which the Coulomb correlation integral of electrons in inner shell states is a major parameter of the problem and must be included in the Hartree-Fock treatment from the first. Under these circumstances, the Hartree-Fock fields for electrons of different spins differ not only by exchange in-

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[1] B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960); B. T. Matthias and A. M. Clogston (to be published). There is, of course, a large literature on specific examples of localized moments, for which the reader is referred to extensive bibliographies in the papers of Friedel. (See reference 2.) The cited papers, however, are the first to bring out clearly the nature of the phenomenon of appearance and disappearance of localized moments as a function of the continuous variation of the nature of the solvent metal.

[2] P. de Faget de Casteljau and J. Friedel, J. phys. radium **17**, 27 (1956); J. Friedel, Can. J. Phys. **34**, 1190 (1956); J. phys. radium **19**, 573 (1958); Suppl. Nuovo cimento **VII**, 287 (1958); A. Blandin and J. Friedel, J. phys. radium **19**, 573 (1958).

[3] P. W. Anderson, Oxford Discussion on Magnetism, 1959 (unpublished).

[4] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **6**, 124 (1961).

[5] P. W. Anderson, Phys. Rev. **115**, 2 (1959).

[6] J. H. Van Vleck, Revs. Modern Phys. **25**, 223 (1953); reference 3.

tegrals but by true Coulomb integrals, and only this circumstance makes localized moments possible in the iron group.

The essence of what we do is a self-consistent calculation of whether this localized moment exists. The principle of the method is this: Assuming that the localized moment exists, this means that a d-shell state φ_d on the impurity atom of spin up is full; of spin down, empty. If we are to include the repulsive energy within the d shell in our Hartree field, an electron of spin down will see the repulsion of the extra spin-up electron, while the electrons of spin up will not, since they can have no exchange self-energy. Thus if the unperturbed energy of the spin-up state lies a distance E below the Fermi surface, the energy of the spin-down localized state will by $-E+U$, where U is the repulsive d-d interaction; this must lie above the Fermi level because we assumed this state empty.

Now we have shown[4] (it is in fact obvious) that the effect of covalent admixture of free-electron states with the d states is to reduce the number of electrons in the spin-up state and to increase the number in the spin-down state; thus there is a reduction in the total moment. We concentrate our attention here, however, on the changes in number of d electrons. These changes are such as to decrease the difference U between the spin-up and spin-down energies; $-E$ moves up to $-E+\delta nU$, $-E+U$ down to $-E+U(1-\delta n)$. δn is larger the larger the density of free electrons, the larger the d to free-electron admixture matrix element, and the smaller the energy difference between up and down states. If, by a change of one of these parameters, δn is increased, the energy difference decreases. We will show that eventually the situation breaks down cooperatively and becomes completely unstable, and it is no longer possible to maintain a localized moment.

When it is not possible to maintain the moment, the up- and down-spin d functions are equally occupied; we give here a self-consistent discussion of this state of affairs which shows that the highest partially occupied d level in this case tends to lie near the Fermi surface. We will give a brief discussion of susceptibility, specific heat, and other properties of such a state, and show that in it correlation effects can be of great significance to these properties of the metal; in particular, there may be a large, slightly temperature-dependent susceptibility which does not come from localized, orientable spins and is not reflected in the specific heat.

Before giving a detailed account of the theory and going on to discuss the possibilities of further extension, we will emphasize a few aspects of the results.

First, in the "localized" state it is irrelevant whether or not one speaks of a real or virtual level. Even in the virtual case, the moment is made up of the sum of contributions from actual stationary states of the full one-electron problem and cannot decay in time. We do expect that the state will usually be virtual in Friedel's sense[2] and that it can contain any nonintegral number of spins. Nevertheless, in many other ways the results—but not the methods—are best described in terms of a model with actual localized electrons rather than in terms of a many-electron band type of model.

Second it will be worthwhile to emphasize the comparisons and distinctions with respect to the earlier work of Friedel.[2] (See especially the paper of Friedel and Blandin.) Friedel has foreshadowed qualitatively some aspects of our ideas, most particularly in the fact that the only logical description of localized magnetic electrons on impurities in metals is in terms of virtual states. His discussion of these virtual states in terms of scattering theory, however, is considerably different, because he does not identify them closely with localized atomic states, as we find strong physical reasons to do. (In some of his work this connection has been foreshadowed.)

On the other hand, there are several vital differences. The most important is that he uses as the term which splits the spin up-spin down energies not the Coulomb integral

$$U=\int |\varphi_{\text{loc}}(1)|^2 e^2 r_{12}^{-1} |\varphi_{\text{loc}}(2)|^2 d\tau,$$

but true atomic exchange integrals. In a sense U is an exchange integral—the exchange self-energy of φ_{loc}, in fact—and in the general formulation of the Hartree-Fock method one can consider it so, but in fact the exchange self-energy term is usually—and incorrectly—ignored (see reference 7). However, the formal theory is much more straightforward if one includes U in the manner in which we do it, as a repulsion of opposite-spin electrons in φ_{loc}, not as an attraction of parallel ones. Quantitatively, U is very much larger than ordinary exchange integrals, and we will see that the size of U is actually necessary to explain the magnetic state. Exchange of the usual type is, as we shall see, a helpful influence where more than one d electron is involved, but not a major factor.

The other major difference is our use of a formal, self-consistent theory to derive the behavior in terms of the model parameters, and particularly the criterion for magnetism, which we find to be considerably more severe quantitatively than Friedel's, although it is of similar form. In general, we have constructed a much more explicit picture of the actual state of affairs.

A less central difference is our discussion of screening effects and their absence in the localized magnetic states as opposed to normal impurity states. We ascribe a considerably greater role to this feature than to the width of the virtual states in determining which solute ion states can show magnetism.

We will not make any attempt at detailed applications

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[7] One can trace the neglect of this term back to early papers in the theory of magnetic metals, e.g., J. C. Slater, Phys. Rev. **49**, 537 (1936), where the formal expressions given actually do include this term, but the evaluation from atomic energy levels drops it out again.

of our results but merely set out a rather schematized model to show the principles which we believe apply in practice. In a last section of this paper we will discuss possible further extensions and applications.

II. THE HAMILTONIAN; APPROXIMATIONS OF THE MODEL

The model we use can best be summarized by writing down the Hamiltonian:

$$H=H_{0f}+H_{0d}+H_{\text{corr}}+H_{sd}. \tag{1}$$

Here H_{0f} is the unperturbed energy of the free-electron system in second-quantized notation:

$$H_{0f}=\sum_{\mathbf{k},\sigma}\epsilon_k n_{\mathbf{k}\sigma},$$
$$n_{\mathbf{k}\sigma}=c_{\mathbf{k}\sigma}^{*}c_{\mathbf{k}\sigma}. \tag{2}$$

ϵ_k is the energy of the free-electron state of momentum k, $n_{\mathbf{k}\sigma}$ the number operator for momentum k and spin σ, and $c_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}^{*}$ the destruction and creation operators. The continuum of free-electron states has a density $\rho(\epsilon)$, which we normally assume constant, although it may easily be verified that a reasonable energy variation of $\rho(\epsilon)$ has little effect on the results.

In a real metal the "free-electron states" may be assumed to consist of the usual s and p free-electron shells for which quasi-free electrons are a good approximation, as well as in some cases—certainly Sc and Y and, we suspect, as far into the d shell as V or Mo—the "free" d electrons. As Slater and Wood have pointed out,[8] near the bottom of the band the d states are almost as extended as s and p states. Still farther into the transition series, only a portion of the d electrons could reasonably be taken free in our sense. (The essential criteria will appear in discussing H_{corr}.)

The second term, H_{0d}, is the unperturbed energy of the "d" states on the impurity atom. In the discussion in the body of the paper, we assume the physically unrealistic case of a single nondegenerate level, because the principle of the method is easily extended to the more complicated many-level d or f shell. In an Appendix we give the extension to a many-level shell; the only new feature there is internal exchange, which is a favorable effect. The term in the Hamiltonian is

$$H_{0d}=E(n_{d+}+n_{d-}). \tag{3}$$

A real question with respect to Eq. (3) is the precise definition of the localized eigenfunction φ_d; and in fact why we treat the effect of the solute atom entirely as that of a separate localized state φ_d and not purely as an impurity potential acting on the free electron gas, as is done by Friedel[2] and in many impurity problems not involving transition metals. The main reason will become clear shortly: that the correlation effects in φ_d, which is visualized as an inner shell level, are larger than for the free electrons because of the inner shell character of φ_d.

On the other hand, this separation and our theory are only easily applicable if φ_d is, in fact, orthogonal to the Wannier functions belonging to all of the free-electron band or bands. This allows us to distinguish the "d" state clearly from the free-electron states, and makes it plausible to leave out of our model Hamiltonian (1) the direct perturbation in the energy of the band functions caused by the impurity, as being irrelevant to the magnetic problem. We can in fact make —if we like—φ_d orthogonal to Wannier functions on all centers, but this will not be essential.[9]

The assumption of a d state distinct from the free electron band is not essential in order to form a virtual state; as Wolff[10] has pointed out, even in the Slater-Koster one-band theory virtual states can appear. On the other hand, in physical fact a localized d state has no resemblance to the band states near it in energy. In spite of the fact that because of completeness it can of course be built up out of a superposition of plane waves, the requisite plane waves are primarily in bands far from the Fermi level and thus need not be included in the free-electron Hamiltonian (2).

The third term, H_{corr}, is the repulsive energy among the d functions, which we schematize as

$$H_{\text{corr}}=Un_{d\uparrow}n_{d\downarrow},$$
$$U=\int|\varphi_d(\mathbf{r}_1)|^2|\varphi_d(\mathbf{r}_2)|^2e^2|\mathbf{r}_1-\mathbf{r}_2|^{-1}d\tau_1d\tau_2. \tag{4}$$

We have here neglected the correlation energy of the electrons in "free-electron" states and the d-free repulsion. The free states, even if, as in such metals as Y or Sc, they are partially d states, are very much more extended throughout the unit cell than are the localizable states near the top of the d band[8,9]; for this reason, and particularly because the free electrons experience a much more effective screening than the inner shells do, it is reasonable that U, in effect, might be ~10 v for inner-shell d functions but only a few volts for free functions. Energy-level tables even for free atoms show that s-s and s-d repulsive energies are 2–3 v smaller than d-d energies; but we rely mainly on the fact that the free electrons in the metal are much more spread out and much better screened than in the atom. It has

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[8] J. H. Wood, Phys. Rev. **117**, 714 (1960).

[9] In cases like Sc, Ti, and other lower d-shell ions, it may be most convenient to treat the free-electron states as orthogonalized plane waves, which is in fact a fair approximation. On the Sc or Ti site, the plane waves are orthogonalized to 1, 2, and 3 s and p but not $3d$ states; therefore, they have considerable $3d$ character even though they are basically free states. On the Fe or other magnetic type site, however, they must be orthogonalized to all $3d$ levels also; as demonstrated by M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961) this minimizes the perturbation of the free electron potential by the Fe atom. We are suggesting, then, that the two types of d states often postulated [see reference 8] are those which are essentially orthogonalized plane waves, and those which are made up primarily of atomic d wave functions.

[10] P. A. Wolff (to be published). Wolff shows that similar phenomena to those we describe occur even when the Freidel type of virtual state is used; this is reassuring but we believe the present approach is simpler and more physical.

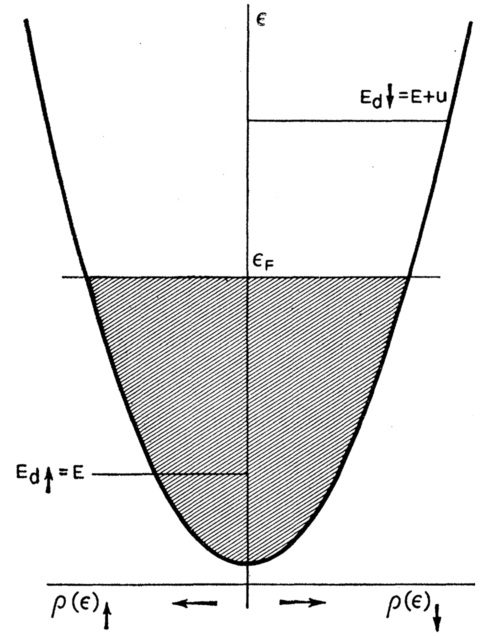

FIG. 1. Unperturbed energy levels in the absence of s-d admixture.

been suggested in the past[11] that the d-d repulsion might be to some extent screened out by s electrons; we think that such screening would require a kinetic energy loss to the s electrons as great as or greater than the correlation energy gained, and would be quite ineffective.

As we mentioned earlier, U is formally the exchange self-energy of the state φ_d as well as the Coulomb integral of that state. Thus, formally, we could write the exchange and correlation terms

$$\tfrac{1}{2}K(n_\uparrow+n_\downarrow)(n_\uparrow+n_\downarrow)-\tfrac{1}{2}J(n_\downarrow n_\downarrow+n_\uparrow n_\uparrow),$$

where both K and J are U; this shows the parallelism with normal exchange, but also shows why the term is often dropped, because the J part is really only a one-electron energy $n_\uparrow+n_\downarrow$.[7]

A sound argument from experiment that U must be large is the observation that in some cases Hund's rule is obeyed, so that intra-atomic exchange is clearly not screened in the d shell; and mechanisms which screen U would also tend to screen the exchange integrals.

The fourth essential part of the Hamiltonian is the s-d interaction term

$$H_{sd}=\sum_{\mathbf{k},\sigma} V_{d\mathbf{k}}(c_{\mathbf{k}\sigma}{}^*c_{d\sigma}+c_{d\sigma}{}^*c_{\mathbf{k}\sigma}). \tag{5}$$

This type of s-d interaction is a purely one-electron energy, entirely different from the s-d exchange interaction which enters the Zener type of theory. The d function usually has a symmetry different from the Wannier functions on the atom it occupies, so that matrix elements with the Wannier functions of the band on the same atom vanish; this is why such effects as we discuss do not usually appear in a one-atom theory. But there is no reason whatever for the matrix elements with Wannier functions on neighboring atoms to vanish. These matrix elements may be estimated to be of the order 2–3 ev or even more, from various sources—for instance, the lowering of the binding energy of Cu and other noble metals relative to the alkalies can be ascribed to s-d interaction.[12]

The effect of symmetry allows us to write down a useful expression for $V_{d\mathbf{k}}$ in terns of Wannier functions $a(\mathbf{r}-\mathbf{R}_n)$ belonging to the band:

$$\begin{aligned} V_{d\mathbf{k}} &= \frac{1}{\sqrt{N}}\int \varphi_d{}^*(\mathbf{r})\mathcal{H}_{\mathrm{H-F}}(\mathbf{r})\sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n}a(\mathbf{r}-\mathbf{R}_n) \\ &= \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_n\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}_n}V_d(\mathbf{R}_n). \end{aligned} \tag{6}$$

This has been used[4] to evaluate some of the perturbation theory results for polarization and other parameters. It will not be necessary in this paper, however, to simplify $V_{d\mathbf{k}}$ except to assume that the mean-square matrix element, averaged over a surface of constant energy ϵ_k, does not vary radically as we vary ϵ_k.

We treat the Hamiltonian (1) entirely in the Hartree-Fock approximation. That and the approximations already made in setting up the Hamiltonian are the only essential approximations; the one-electron problem posed by Eq. (5) as a perturbation will be completely solved later, in principle, although in much of what we do we could, for simplicity, treat Eq. (5) in perturbation theory.

III. SOME SIMPLE LIMITS

Let us first, however, exhibit the two simple limiting cases, so that we can see the alternatives available. Let us imagine first that V is very small and U very large; for simplicity, place E a certain distance below the unperturbed Fermi surface, $E+U$ above it. (See Fig. 1.) It is clear what will happen in this case: one electron, whether of spin up or down, will fall into the d shell state, since it is below the Fermi surface. Now because of the term H_{corr}, the effective one-electron energy in Hartree-Fock approximation for the other d shell state is now $E+U$, so that that state will remain empty. Thus one electron and one only is in the d shell, and this electron has a mean spin $s=\frac{1}{2}$, not zero as it would be if it really were half an electron apiece in spin-up and spin-down states. This state, then, is the magnetic state. It is interesting to note that in this state there is a large spin-dependence of the

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[11] C. Herring, see reference 6.

[12] A second source for this estimate is the size of the similar matrix elements between d functions and ligand s and p functions in magnetic insulators, as estimated from covalency effects or superexchange integrals (see reference 5).

Hartree field—if we occupy $\sigma=+$, for instance, the Hartree field for spin-up electrons differs by U from that for spin-down electrons. As we discussed earlier, this is not the usual atomic exchange effect, but a kind of correlation effect, which however appears within the unrestricted Hartree-Fock formalism. This type of exchange (or correlation) has been applied extensively in molecular theory[13] and in the theory of antiferromagnetism[5] but not previously in metals.

A second simple type of assumption is to ignore the possibility of unequal spin occupation and to suggest that equal numbers of d electrons appear with $+$ and $-$ spins. Again neglecting V as an approximation, we run into an interesting situation. If we assumed both d states empty, then clearly both have energies E, below the Fermi surface, and they must be filled. If, however, we fill them, that too is not allowed because then both have energy $E+U$ far above the Fermi surface. Clearly, a rough approximation is that each d state be filled just so that $E+\langle n\rangle U\simeq\epsilon_F$: the state adjusts itself so that it automatically lies near the Fermi surface. We shall see that the more complete theory tends to do this also.

IV. HARTREE-FOCK THEORY

In order to give a reasonably accurate discussion of the Hamiltonian (1), it must be treated in Hartree-Fock approximation. That means that we assume the wave function to be the (antisymmetrized) product function

$$\Phi_0=\prod_{\epsilon_n<\epsilon_F} c_n{}^*\Phi_{\text{vac}}, \tag{7}$$

where the one-electron state creation operators $c_n{}^*$ and energies ϵ_n are solutions of

$$[H,c_{n\sigma}{}^*]|_{\text{av}}\Phi_0=\epsilon_{n\sigma}c_{n\sigma}{}^*\Phi_0, \tag{8}$$

the "av" meaning that three fermion terms in the commutator are to be evaluated in terms of average values for the state Φ_0.

In the case of our simple Hamiltonian (1) these equations are very easy to solve. Let us set

$$c_{n\sigma}{}^*=\sum_{\mathbf{k}}(n|\mathbf{k})_\sigma c_{\mathbf{k}\sigma}{}^*+(n|d)_\sigma c_{d\sigma}{}^*; \tag{9}$$

and the equations for the various unperturbed operators are

$$[H,c_{\mathbf{k}\sigma}{}^*]|_{\text{av}}=\epsilon_k c_{\mathbf{k}\sigma}{}^*+V_{\mathbf{k}d}c_{d\sigma}{}^*; \tag{10}$$

and

$$[H,c_{d\sigma}{}^*]|_{\text{av}}=[E+U\langle n_{d,-\sigma}\rangle]c_{d\sigma}{}^*+\sum_{\mathbf{k}} V_{d\mathbf{k}}c_{\mathbf{k}\sigma}{}^*. \tag{11}$$

The resulting "equations of motion" for the relevant coefficients $(n|\mathbf{k})$ and $(n|d)$ are obtained by substitution of Eqs. (9), (10), and (11) into Eq. (8):

$$\epsilon_{n\sigma}(n|\mathbf{k})_\sigma=\epsilon_k(n|\mathbf{k})_\sigma+V_{\mathbf{k}d}(n|d)_\sigma, \tag{12a}$$

$$\epsilon_{n\sigma}(n|d)_\sigma=[E+U\langle n_{d,-\sigma}\rangle](n|d)_\sigma+\sum_{\mathbf{k}} V_{d\mathbf{k}}(n|\mathbf{k})_\sigma. \tag{12b}$$

V. GREEN'S FUNCTION SOLUTION OF ONE-ELECTRON EQUATIONS

Since these equations can, for practical purposes, be solved exactly by Green's function methods, we shall not stop to give the perturbation theory answers, even though they suffice under many circumstances for qualitative results.

The results we want to use are never actually the individual quantities $(n|\mathbf{k})_\sigma$ or the actual continuum level energies ϵ_n, but certain averages over these such as, for instance, the mean density of admixture of the $d\sigma$ state into the continuum levels of energy ϵ, i.e.,

$$\rho_{d\sigma}(\epsilon)=\sum_n \delta(\epsilon_n-\epsilon)|(n|d)_\sigma|^2.$$

This will be the most important quantity because it determines the d-function occupation number. This and all other quantities of interest may be obtained most directly by studying the Green's function:

$$G(\epsilon+is)=1/(\epsilon+is-H). \tag{13}$$

In the representation n of exact eigenstates, G is diagonal:

$$G_{nn}{}^\sigma(\epsilon+is)=1/(\epsilon+is-\epsilon_{n\sigma}), \tag{13a}$$

but in the unperturbed state representation, its matrix elements give the required densities; for instance,

$$\begin{aligned}\rho_{d\sigma}(\epsilon)&=\frac{1}{\pi}\sum_n |(d|n)_\sigma|^2 \lim_{s\to0}\frac{s}{s^2+(\epsilon-\epsilon_{n\sigma})^2}\\&=-(1/\pi)\text{Im}[G_{dd}{}^\sigma(\epsilon)];\end{aligned} \tag{14}$$

while the total modified density of states is

$$\rho_\sigma(\epsilon)=(1/\pi)\text{Im}[\text{Tr}G^\sigma(\epsilon)],$$

etc.

The equations for G are derived from Eq. (12), using

$$\sum_\nu(\epsilon+is-H)_{\mu\nu}G_{\nu\kappa}=\delta_{\mu\kappa}.$$

They are, making use of the abbreviations

$$E_\sigma=E+U\langle n_{d,-\sigma}\rangle, \tag{15}$$

and

$$\mathcal{E}=\epsilon+is, \tag{16}$$

$$(\mathcal{E}-E_\sigma)G_{dd}{}^\sigma-\sum_{\mathbf{k}} V_{d\mathbf{k}}G_{\mathbf{k}d}{}^\sigma=1; \tag{17a}$$

$$(\mathcal{E}-\epsilon_k)G_{\mathbf{k}d}{}^\sigma-V_{\mathbf{k}d}G_{dd}{}^\sigma=0; \tag{17b}$$

$$(\mathcal{E}-E_\sigma)G_{d\mathbf{k}}{}^\sigma-\sum_{\mathbf{k}'} V_{d\mathbf{k}'}G_{\mathbf{k}'\mathbf{k}}{}^\sigma=0; \tag{17c}$$

and

$$(\mathcal{E}-\epsilon_{\mathbf{k}'})G_{\mathbf{k}'\mathbf{k}}{}^\sigma-V_{\mathbf{k}'d}G_{d\mathbf{k}}{}^\sigma=\delta_{\mathbf{k}'\mathbf{k}}. \tag{17d}$$

From Eqs. (17a) and (17b) we may immediately solve for G_{dd}:

$$G_{dd}{}^\sigma(\mathcal{E})=[\mathcal{E}-E_\sigma-\sum_{\mathbf{k}}|V_{d\mathbf{k}}|^2(\mathcal{E}-\epsilon_k)^{-1}]^{-1}. \tag{18}$$

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[13] P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

The sum in Eq. (18) may be evaluated:

$$\lim_{s\to 0}\sum_{\mathbf{k}}(V_{d\mathbf{k}})^2\frac{(\epsilon-\epsilon_k)-is}{(\epsilon-\epsilon_k)^2+s^2}=-i\pi\langle V_{d\mathbf{k}}^2\rangle_{\mathrm{av}}\rho(\epsilon). \qquad (19)$$

Here we have neglected the effective energy shift of the d state,

$$\Delta E_d=P\left\{\sum_{\mathbf{k}}\frac{|V_{d\mathbf{k}}|^2}{\epsilon-\epsilon_{\mathbf{k}}}\right\}, \qquad (20)$$

because it may be taken into account simply by shifting the assumed unperturbed energy E. If the density of states is reasonably constant ΔE_d will not change very radically as E_σ changes. Thus we see that, except for the energy shift, G_{dd} behaves exactly as if there were an energy state—the "virtual state"—at

$$\mathcal{E}=E_\sigma+i\Delta,$$

where the "width parameter" Δ of the virtual state is defined by

$$\Delta=\pi\langle V^2\rangle_{\mathrm{av}}\rho(\epsilon). \qquad (21)$$

We usually assume that Δ is a constant parameter, roughly independent of E_σ. The density distribution (14) of the d state is

$$\rho_{d\sigma}(\epsilon)=\frac{1}{\pi}\frac{\Delta}{(\epsilon-E_\sigma)^2+\Delta^2}. \qquad (22)$$

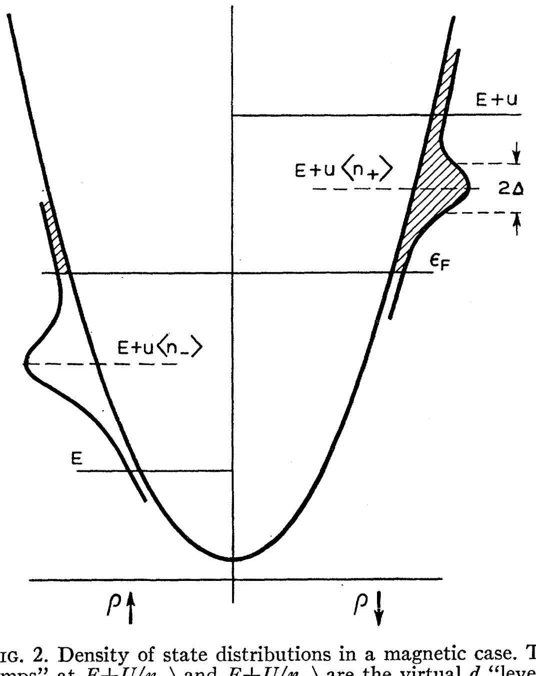


FIG. 2. Density of state distributions in a magnetic case. The "humps" at $E+U\langle n_-\rangle$ and $E+U\langle n_+\rangle$ are the virtual d "levels" of width 2Δ, for up and down spins, respectively. The numbers of electrons $\langle n_+\rangle$ and $\langle n_-\rangle$ occupying them are to be computed from the area of the unshaded portion, below the Fermi surface.

Equation (22) is the most important formula for our self-consistent treatment, but it will be of interest in the problem of polarization in the free-electron bands to work out the remainder of the elements of G. Starting with the off-diagonal elements of Eq. (17d), we obtain

$$G_{\mathbf{k}'\mathbf{k}}^{\sigma}=\frac{V_{\mathbf{k}'d}G_{d\mathbf{k}}^{\sigma}}{\mathcal{E}-\epsilon_{k'}}, \quad (\mathbf{k}'\neq\mathbf{k}).$$

This may then be substituted into Eq. (17c) to give

$$\Big[\mathcal{E}-E_\sigma-\sum_{\mathbf{k}'\neq\mathbf{k}}|V_{d\mathbf{k}'}|^2(\mathcal{E}-\epsilon_{\mathbf{k}'})^{-1}\Big]G_{d\mathbf{k}}^{\sigma}=V_{d\mathbf{k}}G_{\mathbf{kk}}^{\sigma},$$

which, using Eq. (19), is

$$\big[\mathcal{E}-E_\sigma+i\Delta+|V_{d\mathbf{k}}|^2(\mathcal{E}-\epsilon_k)^{-1}\big]G_{d\mathbf{k}}^{\sigma}=V_{d\mathbf{k}}G_{\mathbf{kk}}^{\sigma}. \qquad (23)$$

Now, the diagonal element of Eq. (17d) gives us

$$\begin{aligned}G_{\mathbf{kk}}^{\sigma}&=\left[\mathcal{E}-\epsilon_k-\frac{|V_{d\mathbf{k}}|^2}{\mathcal{E}-E_\sigma+i\Delta+|V_{d\mathbf{k}}|^2(\mathcal{E}-\epsilon_k)^{-1}}\right]^{-1}\\&=(\mathcal{E}-\epsilon_k)^{-1}+\big[|V_{d\mathbf{k}}|^2/(\mathcal{E}-\epsilon_k)^2(\mathcal{E}-E_\sigma+i\Delta)\big].\end{aligned} \qquad (24)$$

This can be interpreted to say that, although each $G_{\mathbf{kk}}$ has a pole at precisely the same energy, so that its perturbed energy is unshifted, nonetheless a certain amount of its density is to be found in the region of the virtual state—the admixture effect.[4] This is given by

$$-\frac{1}{\pi}\mathrm{Im}G_{\mathbf{kk}}(\epsilon)\simeq\frac{|V_{d\mathbf{k}}|^2}{(\epsilon-\epsilon_k)^2}\rho_d(\epsilon), \qquad (25)$$

near the virtual state. There are also shifts near the pole in the density, which correspond to the polarization effect computed in perturbation theory in reference 4. We shall see later that the compensation theorem of that reference may be derived directly from (24).

VI. SELF-CONSISTENCY CONDITIONS FOR LOCALIZED MOMENTS

In the preceding section we obtained the expression (22) for the density of d admixture in the continuum states of energy ϵ. In order to determine the number of d electrons of a given spin σ, we integrate this up to the Fermi energy ϵ_F, since all states ϵ_n below ϵ_F are full (at least at absolute zero). Thus

$$\begin{aligned}\langle n_{d\sigma}\rangle&=\frac{1}{\pi}\int_{-\infty}^{\epsilon_F}\frac{\Delta d\epsilon}{(\epsilon-E_\sigma)^2+\Delta^2}\\&=\frac{1}{\pi}\cot^{-1}\left(\frac{E_\sigma-\epsilon_F}{\Delta}\right).\end{aligned} \qquad (26)$$

Now we must make this equation self-consistent, which involves solving simultaneously the two equations (15) and (26).

$$\begin{aligned}\langle n_{d+}\rangle&=\frac{1}{\pi}\cot^{-1}\left(\frac{E-\epsilon_F+U\langle n_{d-}\rangle}{\Delta}\right),\\ \langle n_{d-}\rangle&=\frac{1}{\pi}\cot^{-1}\left(\frac{E-\epsilon_F+U\langle n_{d+}\rangle}{\Delta}\right).\end{aligned} \qquad (27)$$

Equation (27) is the fundamental equation of our self-consistent method.

To show its meaning, we have plotted out in Fig. 2 a typical magnetic case. We show the two virtual states in terms of their distributions $\rho_{d\sigma}(\epsilon)$ from Eq. (22) centered around the self-consistent energies E_σ from Eq. (15). The empty portions of the two distributions are shaded.

To show the possibilities inherent in Eq. (27), let us plot out $\langle n_{d+}\rangle$ vs $\langle n_{d-}\rangle$ in two cases. (See Fig. 3.) For simplicity we have chosen $\epsilon_F - E = U/2$, and values of U/Δ of 1 and 5. We see that when U/Δ is rather small, such as the case $U/\Delta = 1$, there is only one place where Eq. (27) is consistent, at $\langle n_+\rangle = \langle n_-\rangle = \frac{1}{2}$. But as U becomes larger, the maximum slope of the $\cot^{-1}$ curve becomes steeper and at $U/\Delta = 5$ we find the "localized" case in which there are three possible solutions, one at $\langle n_+\rangle = \langle n_-\rangle = \frac{1}{2}$ but another pair at $\langle n_+\rangle = 1 - \langle n_-\rangle = 0.822$, while $\langle n_+ - n_-\rangle = m = 0.644$, the moment in Bohr magnetons. The magnetic solutions are the stable ones energetically (this is obvious because the Hartree-Fock equations are variational; thus all three solutions must be extrema, and since the end points of the range are clearly not minima, this means that the two outside solutions must be minima, the center one a maximum).

Before giving a physical discussion of these localized moment states, let us work out some of the numerical consequences of Eq. (27). Let us introduce the dimensionless parameter

$$y = U/\Delta, \tag{28}$$

the ratio of the Coulomb integral to the width of the virtual state. When y is large, correlation is large and localization is easy, while y small represents the "normal", nonmagnetic situation. The parameter

$$x = (\epsilon_F - E)/U \tag{29}$$

is also useful; $x = 0$ means the empty d state is right at the Fermi level, while $x = 1$ puts $E + U$ at the Fermi level. $x = \frac{1}{2}$, where E and $E + U$ are symmetrically disposed about the Fermi level, is the most favorable case for magnetism. We shall find that $0 \leq x \leq 1$ is the only magnetic range, but in the nonmagnetic cases x can be outside this range.

Inserting Eqs. (28) and (29) into Eq. (27), and dropping angular brackets, we rewrite that equation

$$\pi n_{d\pm} = \cot^{-1}[y(n_{d\mp} - x)]. \tag{27'}$$

Let us investigate some special cases.

A. Magnetic limit: $y \gg 1$, x not small or too near 1. Then the $\cot^{-1}$ is either close to zero or to π, and $n_{d\pm}$ is near zero or one. Assume $n_{d+} \sim 1$, $n_{d-} \sim 0$. Then

$$\pi n_{d+} \cong \pi - \frac{1}{y(x - n_{d-})},$$

$$\pi n_{d-} \cong -\frac{1}{y(x - n_{d+})} = \frac{1}{y(n_{d+} - x)}.$$

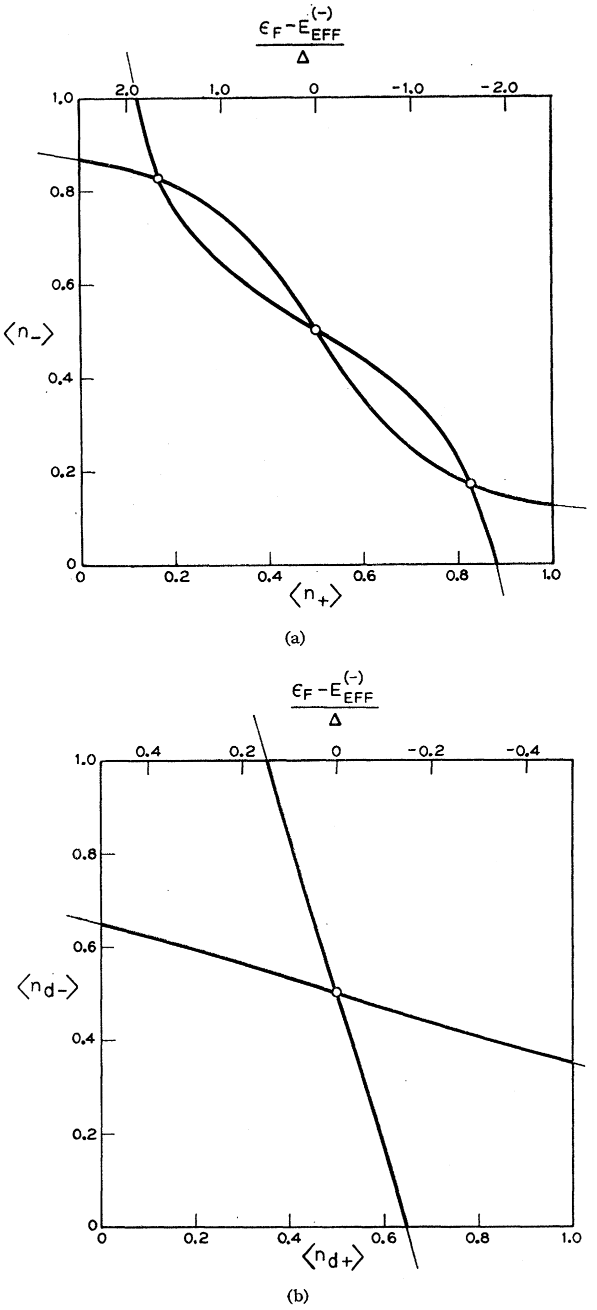


FIG. 3. (a) Self-consistency plot of $\langle n_+\rangle$ vs $\langle n_-\rangle$ for a typical magnetic case. $y = U/\Delta = 5$, $x = (\epsilon_F - E)/U = \frac{1}{2}$. Note three possible solutions. (b) A typical nonmagnetic case. $y = 1$, while $x = \frac{1}{2}$. The width is five times greater and only one intersection appears.

These may be approximately solved to obtain:

$$x(1 - n_{d+}) = (1 - x)n_{d-}$$

$$\simeq 1 \bigg/ \left[\pi y\left(1 - \frac{1}{\pi y x(1-x)}\right)\right], \tag{30}$$

$$m = n_{d+} - n_{d-} \cong 1 - 1/[\pi y x(1-x) - 1].$$

B. Nonmagnetic cases. Here we may assume $n_{d+}=n_{d-}=n$. Then Eq. (27) becomes

$$\cot\pi n=y(n-x). \tag{31}$$

In the simplest subcase, n will not be far from $\frac{1}{2}$—the final virtual state lying within a width of the Fermi level—so that

$$\cot\pi n\simeq\pi(\tfrac{1}{2}-n), \tag{32}$$

and

$$n\simeq\tfrac{1}{2}\left[\frac{(1+2xy/\pi)}{(1+y/\pi)}\right]. \tag{33}$$

We see that n tends to take on the value of $\frac{1}{2}$, meaning that the effective energy level stays near the Fermi level. The effective energy of the d state relative to the Fermi level is

$$E_{\text{eff}}=U(n-x)=U\frac{1-2x}{1+y/\pi}=\Delta y\frac{1-2x}{1+y/\pi}. \tag{34}$$

Thus this is a very good approximation when y is small or, when x is even reasonably close to $\frac{1}{2}$, for all relevant y.

In the opposite limit (y largish, x near 1 or 0); the most interesting region is x near 0 (results for $x\simeq1$ are symmetric), y quite large. Here

$$\cot\pi n\simeq1/\pi n,$$

and we have

$$y(n-x)\simeq1/\pi n. \tag{35}$$

Solving by successive approximations, we get

$$n\simeq1/(xy)^{\frac{1}{2}}+\tfrac{1}{2}x+\dots. \tag{36}$$

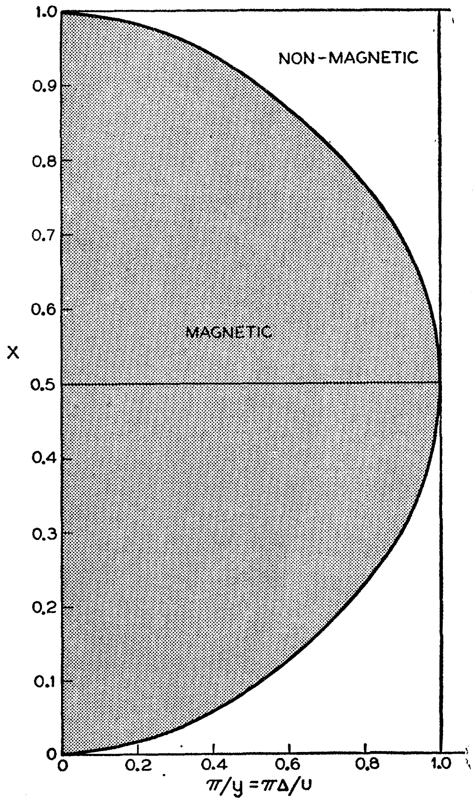


FIG. 4. Regions of magnetic and nonmagnetic behavior. Curve gives x_c vs $\pi/y_c=\pi\Delta/U$.

C. The Transition Curve. Next it is interesting to trace out the transition curve from magnetic to nonmagnetic behavior. Clearly, on the transition curve $n_{d+}=n_{d-}$, so that Eq. (31) is one condition on the curve.

The second may be obtained by differencing Eq. (27). The result is

$$\pi/\sin^2\pi n_c=y_c. \tag{37}$$

Here the subscript c refers to the values on the critical curve of transition into the magnetic case. Equations (37) and (31) cannot be solved in simple form for y_c vs x, but can be expressed simply in terms of n_c and x:

$$y_c=\frac{\pi}{\sin^2\pi n_c}=\frac{\cot\pi n_c}{n_c-x},$$

or

$$\sin2\pi n_c=2\pi(n_c-x). \tag{38}$$

From Eqs. (38) and (37) we can obtain the following approximations for $x\simeq\frac{1}{2}$ and $x\simeq0$ (symmetrical in $x=\frac{1}{2}$):

$$y_c\simeq\pi+\tfrac{1}{4}\pi^3(x-\tfrac{1}{2})^2+\dots,\quad x\simeq\tfrac{1}{2}; \tag{39a}$$

and

$$y_c^3\simeq4\pi/9x_c^2+\dots,\quad (x\simeq0). \tag{39b}$$

These results are summarized in Fig. 4, which gives the transition curve as a function of x and π/y, and in Fig. 5, which plots n and, where they are different, $\langle n_{d+}\rangle$ and $\langle n_{d-}\rangle$ as functions of π/y for two typical cases, $x=\frac{1}{4}$ and $x=\frac{1}{2}$. The plot vs π/y is essentially a plot vs Δ, the width of the virtual state.

In order to get a feeling for orders of magnitude, in the iron group U is expected to be about 10 ev. The density of states is fairly widely variable; in an s band as in Cu it might be of the order $\frac{1}{10}$ (ev)$^{-1}$, while some of the d-band metals might have densities twice to three times that. The least well-known parameter is $\langle V^2\rangle_{\text{av}}$. If one ascribes a fair fraction of the binding energy surplus of iron-group metals, such as Cu, as compared to non-d-band cases, such as K, to s-d coupling, V_{av} may well be $\sim$2–3 ev. This would also be borne out by the band displacements in Cu which perturb the Fermi surface. Thus $\Delta=\pi\langle V^2\rangle\rho(\epsilon)$ runs of the order 2–5 ev. This shows that the transition $U/\Delta=y=\pi$ occurs right in the interesting region, and that it is perfectly possible that the transitions from magnetic to nonmagnetic localized states observed by Matthias *et al.*[1] could be caused either by changes in the density of states or by motion of the Fermi level (changes in x). Note, however, that the shape of Fig. 3 indicates some insensitivity to x.

For rare-earth solutes, on the other hand, $U \sim 15$ ev and $V_{\mathrm{av}} \sim 1$ ev at most, so that magnetic cases are to be expected almost exclusively.

In Appendix I, we discuss the somewhat more realistic case of an orbitally degenerate localized level, as is usually expected to be present in d or f bands on high symmetry sites. In such a case, one must take into account the repulsion of the electrons with parallel spins but different orbits, as well as the fact that this repulsion is decreased by the atomic exchange integral J ($\sim$1-2 ev in the iron group). This is the usual "exchange" effect.

It turns out that the condition for "splitting" of the Hartree field is less stringent when we include J: The condition analogous to Eq. (37) is

$$\frac{U}{\Delta}=y_c \geq \frac{\pi}{\sin^2 \pi n_c}-\frac{J}{2\Delta}, \tag{40}$$

which shows that the required U is *decreased* by the presence of J. Note, however, that in the absence of U, we require $J>2\pi\Delta$. If our quantitative estimate of Δ is even approximately right, this shows that exchange of the usual sort is utterly incapable of causing magnetism in the d shell.

It is interesting that there is a second condition,

$$y_c' \geq \frac{\pi}{\sin^2 \pi n_c'}+\frac{J}{2\Delta}, \tag{41}$$

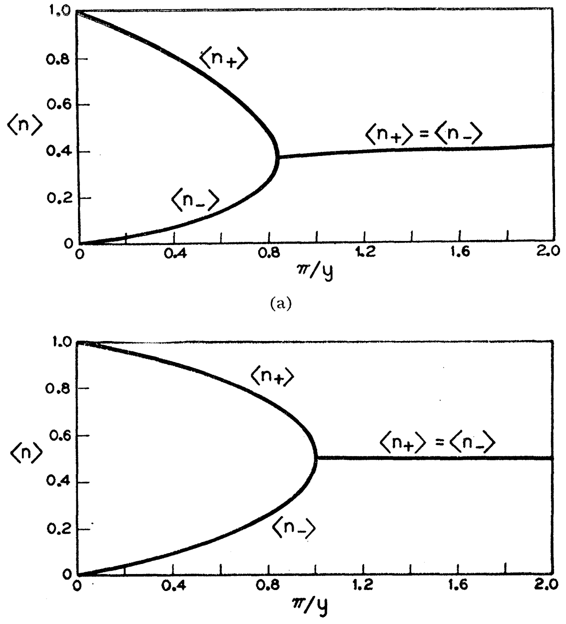
which expresses the requirement that the Hartree fields for the two *orbitally* degenerate states become different. Where Eq. (40) is satisfied, but not Eq. (41), we will observe "quenching" of the orbital magnetic moment by the kinetic energy of interaction with the band, but no quenching of the spin. As far as I know, this is actually the behavior of the iron group solutes in most cases; the fact that such behavior is not simply explained from the usual point of view has not been remarked before.

VI. POLARIZATION OF FREE ELECTRONS; THE COMPENSATION THEOREM

The "compensation theorem,"[4] which shows that the net free electron polarization roughly cancels between the admixture and antiferromagnetic effects, may be derived very easily from the diagonal elements $G_{\mathbf{kk}}$ of the Green's function from Eq. (24). That equation gives

$$G_{\mathbf{kk}}{}^{\sigma}(\epsilon)=(\epsilon-\epsilon_k)^{-1}+\frac{|V_{d\mathbf{k}}|^2}{(\epsilon-\epsilon_k)^2(\epsilon-E_\sigma+i\Delta)}. \tag{24}$$

Now the total density in energy of free-electron states is given by summing this over all k, which is very simple since the dependence of (24) on ϵ_k is so simple.



(a)

(b)

FIG. 5. Two typical plots of $\langle n_+\rangle$ and $\langle n_-\rangle$ as a function of $\pi/y=\pi\Delta/U$. $\langle n_+\rangle-\langle n_-\rangle$ gives the net number of spins, and vanishes at the transition y_c for the given x. (a) $x=\frac{1}{2}$; (b) $x=\frac{1}{4}$.

$$\begin{aligned}\rho_{\mathrm{free}}(\epsilon)&=\frac{1}{\pi}\int dk\,\mathrm{Im}G_{\mathbf{kk}}(\epsilon)\\&=-\frac{1}{\pi}\,\mathrm{Im}\int_{\infty}^{\infty}\rho(\epsilon_k)d\epsilon_k(\epsilon-\epsilon_k)^{-1}\\&\qquad\times\left\{1+\frac{|V_{d\mathbf{k}}|^2[(\epsilon-E_\sigma)+i\Delta]}{(\epsilon-\epsilon_k)[(\epsilon-E_\sigma)^2+\Delta^2]}\right\}.\end{aligned} \tag{42}$$

Introduce

$$\rho(\epsilon_k)=\rho(\epsilon)-(\epsilon_k-\epsilon)(d\rho/d\epsilon)|_{\epsilon_k}+\ldots, \tag{43}$$

and by a simple contour integration we obtain

$$\rho_{\mathrm{free}}(\epsilon)=\rho(\epsilon)+\frac{d\rho(\epsilon)}{d\epsilon_k}\,\frac{|V_{d\mathbf{k}}|^2(\epsilon-E_\sigma)}{(\epsilon-E_\sigma)^2+\Delta^2}. \tag{44}$$

The most interesting thing about this result is that if $\rho(\epsilon_k)$, the density of states, is constant in the first place, the presence of a virtual state anywhere in the spectrum fails to affect the free electron density at all; only the d state itself modifies the total density of states.

Since we can obtain the total number of free electrons of a given spin simply by integrating Eq. (44) up to the Fermi surface:

$$n_{\mathrm{free}}{}^{\sigma}=\int_{-\infty}^{\epsilon_F}\rho_{\mathrm{free}}{}^{\sigma}(\epsilon)d\epsilon, \tag{45}$$

this will be entirely unchanged, and there will be no net polarization of free electrons, if $\rho(\epsilon_k)$ is rigorously constant. Otherwise, there will be a change:

$$\Delta n_{\text{free}}{}^{\sigma} = |V^2| \int_{-\infty}^{\epsilon_F} d\epsilon \frac{d\rho(\epsilon)}{d\epsilon} \frac{\epsilon - E_\sigma}{(\epsilon - E_\sigma)^2 + \Delta^2}. \tag{46}$$

If we assume for simplicity that $d\rho/d\epsilon$ is roughly constant in the region of interest it turns out that even the first-order corrections tend to cancel in the polarization:

$$\Delta n_f{}^{+} - \Delta n_f{}^{-} = (\Delta m)_f \simeq \frac{|V|^2}{2} \frac{d\rho}{d\epsilon} \ln\left[\frac{(\epsilon_F - E_+)^2 + \Delta^2}{(E_- - \epsilon_F)^2 + \Delta^2}\right]. \tag{47}$$

(For this observation I am indebted to conversations with A. M. Clogston.)

This cancellation appears to be more or less fortuitous. There are two contributions physically:

(1) The *d* function becomes mixed with free electron wave functions and vice versa. Clearly, this leads to no net *total* polarization, since it is merely a unitary transformation of the wave function. However, it has the effect of reducing the *d* polarization, because some of the free functions above ϵ_F become partially *d*. At this stage, however, there is still a net spin of precisely one electron; and to compensate the *d* polarization, some previously unpolarized free electrons are polarized.

(2) The free electron functions also have an energy shift

$$\Delta E_{k\sigma} = |V_{dk}|^2 (\epsilon_k - E_\sigma)/[(\epsilon_k - E_\sigma)^2 + \Delta^2],$$

which leads to a *negative* first-order free electron polarization. This polarization is a true polarization rather than an admixture, similar in nature to a Zener-Nabarro-Kittel-Ruderman-Yosida polarization. In particular, this polarization requires a relaxation process in order to follow the time dependence of the localized spin in the presence of a variable external field, where the admixture polarization, being a high-frequency effect, will follow immediately. Thus, any *g* shifts caused by free electron polarization will tend to have antiferromagnetic sign. (We leave out of account here the true *s-d exchange* polarization which results from the relatively small *s-d* exchange integral. That has a definitely ferromagnetic sign. In the rare-earth group, this ferromagnetic effect may be relatively larger.)

The spacial distribution of the polarization is not as directly obtainable from the Green's functions. For this reason and for the sake of brevity, we leave this for a later publication.

VII. SUSCEPTIBILITY AND SPECIFIC HEAT

In the region of localized magnetic states, the susceptibility and specific heat—at least those caused by the solute—are probably controlled, near absolute zero, by the interaction of the solute moments. These moments, although they are not integral numbers of Bohr magnetons, are both localized and free to rotate, like ordinary ionic moments in insulators[14]; and they can exhibit ferromagnetic or antiferromagnetic behavior depending on their interactions. We will make no attempt here to explore the complexities of this situation.

In the nonmagnetic region, however, the localized virtual *d* states can have a very considerable effect on the metallic properties, such as spin susceptibility and specific heat; and in particular, these two measurements, which are often considered as both measuring the density of states at the Fermi surface, vary quite differently, and do not measure the same quantity. We have, thus, a simple model to exemplify the effects which exchange and correlation can have upon these properties. In this section we compute these quantities near absolute zero and in the nonmagnetic case only.

The effect of an external magnetic field is to shift the + spin Fermi level relatively to the − spin level by an amount 2 μH. This shift will change the occupations of the virtual levels, leading to relative shifts of these levels themselves.

In the preceding section, we proved that at least if the density of states $\rho(\epsilon_k)$ in the band was reasonably constant, any motion of the virtual levels could not affect the *net* polarization of the free electrons. That theorem is still valid here, so that the free-electron band will contribute its unperturbed susceptibility χ_0.

The motions of the *d* electron density are simply computed as follows: The shifts of the effective positions of the virtual levels are

$$\begin{aligned} \delta E_+ &= -\mu H + U\langle \delta n_- \rangle, \\ \delta E_- &= \mu H + U\langle \delta n_+ \rangle. \end{aligned} \tag{48}$$

The resulting changes in population may be obtained by differentiating Eq. (27):

$$\begin{aligned} (\pi/\sin^2\pi n)\langle \delta n_+ \rangle &= -\delta E_+/\Delta, \\ (\pi/\sin^2\pi n)\langle \delta n_- \rangle &= -\delta E_-/\Delta, \end{aligned} \tag{49}$$

or, subtracting the two equations of Eq. (49),

$$(\pi/\sin^2\pi n)\langle \delta n_+ - \delta n_- \rangle = y\langle \delta n_+ - \delta n_- \rangle + 2\mu H/\Delta.$$

Thus, the susceptibility is

$$\begin{aligned} \chi = \frac{M}{H} &= \frac{\mu\langle \delta n_+ - \delta n_- \rangle}{H} \\ &= \frac{2\mu^2}{\Delta(\pi/\sin^2\pi n - y)} = \frac{2\mu^2}{(\pi\Delta/\sin^2\pi n) - U}. \qquad 50) \end{aligned}$$

Equation (50) shows that as the system approaches the critical condition, Eq. (37), for magnetism, the absolute zero susceptibility per impurity increases, becoming infinite at the critical density of states. This is quite reasonable physically.

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[14] We have not demonstrated this explicitly, but it is reasonably obvious from the symmetries of the problem. It is interesting that, as in the similar case of nonspherical nuclei, the entity which rotates is effectively the Hartree field, not the individual electrons' moments.

The behavior of the added specific heat is quite different. Again, the result is extremely simple although the argument is rather long-winded. The standard formulas for the number of electrons and mean energy[15] are, if the density of states is $\rho_d+\rho_f$,

$$\bar{n}=\int_0^{\epsilon_F}(\rho_d+\rho_f)d\epsilon+\frac{\pi^2}{6}k^2T^2\frac{d\rho_d}{d\epsilon}, \tag{51}$$

since ρ_f is assumed constant for simplicity; and

$$\bar{\epsilon}=\int_0^{\epsilon_F}\epsilon(\rho_d+\rho_f)d\epsilon+\frac{\pi^2(kT)^2}{6}\left(\epsilon_F\frac{d\rho_d}{d\epsilon}+\rho_d+\rho_f\right). \tag{52}$$

In this case, not only ϵ_F can change with temperature, but also ρ_d, because if there is a shift δn_d in the occupation of the d states, the virtual state energy E_d shifts:

$$\delta E_d=U\delta n_d. \tag{53}$$

First, we express the conservation of n (neglecting ρ_d relative to ρ_f where possible, and keeping only lowest-order terms in T):

$$\frac{dn}{dT}=0=\frac{d\epsilon_F}{dT}\rho_f+\int_0^{\epsilon_F}\frac{d\rho_d}{dT}d\epsilon+\frac{\pi^2}{3}k^2T\frac{d\rho_d}{d\epsilon}.$$

Now

$$\frac{d\rho_d}{dT}=\frac{d\rho_d}{dE_d}\frac{dE_d}{dT}=-\frac{d\rho_d}{d\epsilon}\frac{dE_d}{dT}, \tag{54}$$

so

$$0=\frac{d\epsilon_F}{dT}\rho_f-\rho_d\frac{dE_d}{dT}+\frac{\pi^2}{3}k^2T\frac{d\rho_d}{d\epsilon}. \tag{55}$$

The net change in number of d electrons is

$$\delta n_d=-\delta n_f=-\delta\epsilon_F\rho_f,$$

so we get

$$0=-\frac{dn_d}{dT}-\rho_dU\frac{dn_d}{dT}+\frac{\pi^2}{3}k^2T\frac{d\rho_d}{d\epsilon},$$

or

$$\frac{dn_d}{dT}=\frac{(\pi^2/3)k^2T(d\rho_d/d\epsilon)}{1+U\rho_d}. \tag{56}$$

Now we return to Eq. (52), which we differentiate, again only to first order in T, in order to get C_{sp}:

$$C=\frac{d\bar{\epsilon}}{dT}=\frac{d\epsilon_F}{dT}\epsilon_F\rho_f+\int_0^{\epsilon_F}\epsilon\frac{d\rho_d}{dT}d\epsilon+\frac{\pi^2}{3}k^2T\left(\epsilon_F\frac{d\rho_d}{d\epsilon}+\rho_d+\rho_f\right).$$

From Eq. (55), we can combine the first and third terms; we also use Eq. (54) and get

$$C=\epsilon_F\left(\rho_d\frac{dE_d}{dT}\right)-\int_0^{\epsilon_F}\epsilon\frac{d\rho_d}{d\epsilon}d\epsilon\frac{dE_d}{dT}+\frac{\pi^2}{3}k^2T(\rho_d+\rho_f).$$

Finally, the second term may be integrated by parts; the result is

$$C=\frac{dE_d}{dT}\int_0^{\epsilon_F}\rho_dd\epsilon+\frac{\pi^2}{3}k^2T(\rho_d+\rho_f)$$

$$=n_d\frac{dE_d}{dT}+\frac{\pi^2}{3}k^2T(\rho). \tag{57}$$

The new term is almost obvious; it says that the virtual level's energy just shifts by δE_d as a whole. Using Eq. (56), we get explicitly:

$$C=\frac{\pi^2}{3}k^2T\left\{\frac{U(d\rho_d/d\epsilon)|_{\epsilon_F}}{1+U\rho_d}+\rho_d\right\}, \tag{58}$$

where ρ_d is the energy density of the impurity state,

$$\rho_d(\epsilon)=\frac{\pi\Delta}{(\epsilon-E_d)^2+\Delta^2}=\frac{\pi\Delta}{\sin^2\pi n};$$

$$\frac{d\rho_d}{d\epsilon}=\frac{2\pi\Delta(E_d-\epsilon)}{[(\epsilon-E_d)^2+\Delta^2]^2}. \tag{59}$$

Note that in Eq. (58) the sign in the denominator is +; there is no tendency whatever towards a singularity. This is because the instability refers only to opposite motions of the two Fermi levels. At best, the specific heat from the anomalous term will be 20–30% of the density of states term ρ_d. Thus, the specific heat is a much more accurate measure of density of states than is the susceptibility.

CONCLUSIONS AND DISCUSSION

A rather schematized model of the electronic structure of a metal containing a solute atom with one or more inner-shell orbitals available has been worked out in the preceding pages. While the schematic character of the model should not be ignored, we feel that nonetheless it contains the essential physics of the phenomena for such solutions as Mn, Fe, or other iron-group elements in Cu, Ag, and Au; for the same elements in early members of the transition series such as Sc, Y, Ti, Zr, and possibly V, Nb, and Mo; and many rare-earth solutions.

The essential criteria for our model's more-or-less literal validity are twofold: The "inner shell" orbital must be very different from the Wannier functions for the free electron bands in the solvent, so that a distinct localized orbital can be defined apart from band functions; and it must be sufficiently sharply localized that its Coulomb self-energy integral is not strongly screened out, while those of the band electrons are.

Under these circumstances, the competition between this Coulomb integral and the matrix elements—essentially kinetic energy—connecting the local state with the

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[15] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 150.

band states is undoubtedly the determining element as to whether or not a magnetic state is established. The parts of the problem which we have schematized out will have subsidiary importance.

Some of the things we have left out, with a brief discussion of their importance, are:

(1) True *s-d* exchange of the type normally postulated in *s-d* exchange theories. This will undoubtedly be present to a limited extent. Even in the free atoms, *s-d* exchange is a relatively small effect—1–2 ev. We may expect an appreciable screening of the Coulomb interactions for *s* electrons which may further reduce the effect. The primary result of *s-d* exchange will be to induce a more or less positive polarization of the free electrons, of the same order of magnitude, perhaps, as the terms ignored in the compensation theorem.

(2) *s-d* Coulomb repulsion. We have discussed this to some degree; as Herring[10] has pointed out, this may be expected to reduce the effective U by compensating for missing *d* charge with *s* charge, but we believe the magnetic case to be the situation in which this effect is small.

There would appear to be two distinct situations for impurities in metals. In such a case as Zn in Cu, the impurity may be considered simply as an extra positive charge, which is to be screened out by a deformation and modification of the free-electron band itself. But in the type of situation we envisage—for instance, Mn in Cu—the charge is expected to be compensated not by a deformation of the Cu *s* band, but by emptying levels approximating to the orbitals of the free atom—because these orbitals are of an entirely different symmetry and size from the functions available in the band. In other words, in such cases, it is far better to use as a starting approximation the neutral impurity atom itself, added to the, say, Cu matrix. This type of situation, in which the atomic properties of the solute are not strongly affected by solution, is probably the more widespread, especially when solvent and solute are widely different. It is in this case that one does not expect the free bands to be strongly perturbed, or to compensate effectively Coulomb effects in the inner shell.

Finally, free-electron correlation and exchange have been explicitly ignored; this is probably well justified in that we think of the free electrons as "quasi-particles," for which these effects are taken into account in the ϵ_k and the screened interactions.

A final question is whether a real many-body theory would give answers radically different from the Hartree-Fock results. Since our theory is exact in both limits ($U \to 0$ or ∞), we expect only numerical modifications; in particular, the spin-up and spin-down electrons can probably correlate the times at which they occupy the localized state to some extent, reducing the effect of U and making the magnetic criterion even more severe.

Having justified the model in the cases to which it does apply, what of situations in which it does not? One is led to suspect that the philosophy and some of the results may still be applicable. For example, in Co in Pd[16] one has no right to assume that the Co *d* shell function is any more local than the Pd one. On the other hand, the philosophy suggests to us that the large Pd susceptibility indicates that Pd is very close to entering the "magnetic state" on its own hook. In this case, it is reasonable that the perturbation due to Co could localize moments on neighboring Pd atoms; this might explain the observations qualitatively. In general, in such cases, one does not expect merely the decrease in *d* magnetization we have discussed here; generally, there will be larger polarization effects, which we emphatically have *not* studied, on the solvent *d* electrons themselves.

In general, we have not attempted to discuss the complex subject of interactions of *d* electrons on different atoms. It is the great conceptual simplification of the impurity problem that it is possible to separate the question of the existence of the "magnetic state" entirely from the actually irrelevant question of whether the final state is ferromagnetic, antiferromagnetic, or paramagnetic. We would suggest that it is this concept of separating these two problems which will be of the greatest value in the far more difficult problem of the ferro- and antiferromagnetic metals.

One result that can be carried over without much alteration into even the pure band theory of ferromagnetism has to do with the polarization of free electrons by the *d* electrons. There, as in the impurity case, the positions of the *d* levels of the two separate spins will be radically different, leading to precisely the same two contributions to the polarization: a positive admixture, and a negative true polarization, for precisely the same reason. These two contributions will tend to cancel and the net result will be that the *d* polarization will be reduced relative to that in the absence of such interaction. This reduction may be fairly large, leading to the interesting possibility that the 0.6 and 1.7 Bohr magnetons of Ni and Co may represent an "unperturbed" *d*-band polarization much closer to 1 and 2, respectively.

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[16] R. M. Bozorth, P. Z. Wolff, D. D. Davis, V. B. Compton, and J. H. Wernick, Phys. Rev. **122**, 1157 (1961).

APPENDIX A

Self-Consistent Theory for a Degenerate *d* Level

Let us generalize the Hamiltonian (1) in such a way as to include two degenerate *d* levels φ_1 and φ_2:

$$H=E(n_{1+}+n_{2+}+n_{1-}+n_{2-})$$
$$+\sum_{\mathbf{k},\sigma}\epsilon_k n_{\mathbf{k}\sigma}+\sum_{\mathbf{k},j,\sigma}V_{j\mathbf{k}}(c_{j\sigma}{}^*c_{\mathbf{k}\sigma}+c_{\mathbf{k}\sigma}{}^*c_{j\sigma})$$
$$+(U-J)(n_{1+}n_{2+}+n_{1-}n_{2-})+U(n_+n_-). \quad \text{(A.1)}$$

Here $j=1$ or 2 and the new parameter J, the exchange integral proper, is

$$J=\int\varphi_1{}^*(1)\varphi_2{}^*(2)\frac{e^2}{r_{12}}\varphi_1(2)\varphi_2(1)d\tau_1 d\tau_2. \quad \text{(A.2)}$$

E is again the unperturbed position of the two *d* levels, assumed degenerate as they might be in a cubic crystal. The $V_{j\mathbf{k}}$ must be different—in fact, different functions belonging to the same symmetry under the group of the Brillouin zone—for the two different j, but we can expect the widths and shifts of the two virtual levels to be the same, nonetheless, because of the symmetry.

By precisely the same techniques as in Sec. IV of the main body of the paper, we spread each effective *d* level out into a virtual level of width Δ. The effective Hartree field for each level depends on the occupation of all the other levels through the terms in U and J in Eq. (A.1):

$$E_{\text{eff}}(1+)=E+U(\langle n_{1-}\rangle+\langle n_{2-}\rangle+\langle n_{2+}\rangle)-J\langle n_{2+}\rangle, \quad \text{(A.3)}$$

etc. With these equations and Eq. (26) of the text, we arrive at the fundamental equations:

$$\cot(\pi n_{1+})=[E_{\text{eff}}(1+)-\epsilon_F]/\Delta, \quad \text{(A.4)}$$

etc. We introduce the parameters

$$y=U/\Delta;\quad x=(\epsilon_F-E)/U;\quad j=J/\Delta, \quad \text{(A.5)}$$

and Eq. (A.4) becomes

$$\left.\begin{aligned}\cot\pi n_{1+}&=y(n_{1-}+n_{2-}+n_{2+})-jn_{2+}-xy,\\ \cot\pi n_{2+}&=y(n_{1-}+n_{2-}+n_{1+})-jn_{1+}-xy,\\ \cot\pi n_{1-}&=y(n_{1+}+n_{2+}+n_{2-})-jn_{2-}-xy,\\ \cot\pi n_{2-}&=y(n_{1+}+n_{2+}+n_{1-})-jn_{1-}-xy.\end{aligned}\right\} \quad \text{(A.6)}$$

We will not work out all the details of the various results based on Eq. (A.6) but simply give a few general formulas. First, in the nonmagnetic state, clearly all the n's are equal,

$$n_{j\sigma}=n,$$

and the state is determined by

$$\cot\pi n=(3y-j)n-xy. \quad \text{(A.7)}$$

This has the same form as the nonmagnetic case in the text, and a fair approximation is often

$$n\simeq\frac{1}{2}\left(\frac{1+2xy/\pi}{1+(3y-j)/\pi}\right),$$

which will be valid when $x\sim 1$.

Second, we can study the condition that magnetic moments just appear by differentiating Eq. (A.6), obtaining a set of linear equations in the δn's which have a nonvanishing solution only on the transition curves:

$$\left.\begin{aligned}-\frac{\pi}{\sin^2\pi n}\delta n_{1+}&=y(\delta n_{1-}+\delta n_{2-})+(y-j)\delta n_{2+},\\ -\frac{\pi}{\sin^2\pi n}\delta n_{2+}&=y(\delta n_{1-}+\delta n_{2-})+(y-j)\delta n_{1+},\end{aligned}\right\} \quad \text{(A.8)}$$

and symmetrically for the n_-'s. Letting

$$\delta n_+=\delta n_{1+}+\delta n_{2+};\quad \delta n_-=\delta n_{1-}+\delta n_{2-}, \quad \text{(A.9)}$$

we may add these pairs of equations together, and subtract the two sums, to obtain:

$$(\pi/\sin^2\pi n)(\delta n_+-\delta n_-)=(y+j)(\delta n_+-\delta n_-),$$

or

$$\pi/\sin^2\pi n_c=y_c+j_c. \quad \text{(A.10)}$$

Equations (A.10) and (A.7) must be solved simultaneously to obtain the critical concentration for a given x, y, and j. Note, however, that the most favorable possible condition occurs when $n_c=\frac{1}{2}$, and that then

$$y_{\max}=\pi-j. \quad \text{(A.11)}$$

Thus j makes it easier to form the localized state, in general at least.

It is also possible that the Hartree field for orbital state φ_1, for instance, may differ from that for orbital φ_2. The critical condition for such a case to occur is obtained when we take the *difference* of the pair (A.8):

$$\frac{\pi(\delta n_{1+}-\delta n_{2+})}{\sin^2[\pi(n_{1+}+n_{2+})/2]}=(y-j)(\delta n_{1+}-\delta n_{2+}),$$

or

$$\frac{\pi}{\sin^2\pi(n_{1+})_c{}'}=y_c{}'-j_c{}'. \quad \text{(A.12)}$$

Since j is positive, this condition is always less easily satisfied than Eq. (A.10). It is, however, entirely possible for both to be satisfied, especially if *after* polarization of the spins $n_{1+}+n_{2+}$ is roughly unity.

As discussed in the text, this latter situation represents the closest approach to a truly localized magnetic state, with both an orbital and spin magnetic moment. The former case, in which $E_{1+}{}^{\text{eff}}=E_{2+}{}^{\text{eff}}$, is probably more often encountered. We have here in miniature, as it were, a model of the Van Vleck-Brooks orbital quenching mechanism in the magnetic metals..