

Theory of Localized Magnetic States in Metals

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(Received 15 November 1965)

The problem of determining the conditions for the occurrence of localized moments in dilute alloys on the basis of Anderson's model is re-examined. From a coupled set of Green's-function equations an approximate solution is found which includes the electron correlation in the impurity levels and which passes over to the exact solution in the limiting case of an isolated impurity. The Hartree-Fock theory is obtained only if the Coulomb repulsion U is relatively small. When U is large the correlation effects are important, and magnetic states are found only if the energy shift caused by the impurity-band electron scattering satisfies certain fairly restrictive conditions. Possible modifications when the degeneracy of the impurity levels, the intra-atomic exchange interactions, and the electron interactions in the host metal are taken into account are qualitatively discussed.

I. INTRODUCTION

A CONSIDERABLE amount of information has been amassed in recent years on the magnetic properties of dilute alloys. Much progress has been made since the susceptibility measurements of Matthias *et al.*¹ from which the presence of moments, localized around the impurity sites in some alloys, was originally deduced. Neutron-diffraction techniques² have enabled the moments to be observed directly and their distribution around the impurity to be calculated.

The theoretical problem of describing these magnetic states is exceedingly difficult. Calculations have so far been made in the Hartree-Fock theory and have been based on some simple model of an alloy which abstracts just those features that are essential for a description of a moment. One model, proposed by Wolff,³ describes electrons in a single band which are perturbed by a very short-range impurity potential. This is applicable when the states of the impurity are similar to those of the host metal as, for instance, is the case for iron impurities dissolved in palladium. An alternative model, used by Anderson,⁴ is for an alloy in which the impurity has an inner d level within the continuous energy spectrum of the conduction band for the host metal as, for example, nickel impurities dissolved in copper.

In an effort to overcome some of the limitations of the Hartree-Fock theory we consider an alternative approach to the problem which we shall base on Anderson's model.⁵ The total Hamiltonian is

$$H = H_b + H_d + H_{bd}. \quad (1)$$

H_b is the Hamiltonian for the conduction electrons of the host metal. In the wide-band limit it is the free-electron Hamiltonian.

$$H_b = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}} C_{\mathbf{k}\sigma}^\dagger C_{\mathbf{k}\sigma}, \quad (2)$$

where $C_{\mathbf{k}\sigma}^\dagger$ and $C_{\mathbf{k}\sigma}$ are the creation and annihilation operators for the free-electron states with momentum \mathbf{k} , energy $\epsilon_{\mathbf{k}}$, and spin σ .

The Hamiltonian describing the impurity is

$$H_d = T_0 \sum_{\sigma} C_{d\sigma}^\dagger C_{d\sigma} + U n_{d\uparrow} n_{d\downarrow}. \quad (3)$$

The first term is a nondegenerate level at T_0 (this is a restriction which we shall discuss later) and $C_{d\sigma}^\dagger$, $C_{d\sigma}$ are its creation and annihilation operators. The second term is the Coulomb repulsion between spin-up and spin-down electrons, where U is the Coulomb correlation integral,

$$U = \int \int \phi_d(\mathbf{r}_1)^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_d(\mathbf{r}_2)^2 d\mathbf{r}_1 d\mathbf{r}_2. \quad (4)$$

The scattering of the d and band electrons is assumed to be due to an interaction of the form

$$H_{bd} = \sum_{\mathbf{k}, \sigma} V_{d\mathbf{k}} (C_{\mathbf{k}\sigma}^\dagger C_{d\sigma} + C_{d\sigma}^\dagger C_{\mathbf{k}\sigma}). \quad (5)$$

To find the conditions for a moment at the impurity, the average values of $n_{d\uparrow}$ and $n_{d\downarrow}$ are calculated and then examined for a "magnetic" solution for which $\langle n_{d\uparrow} \rangle \neq \langle n_{d\downarrow} \rangle$.

In the Hartree-Fock theory the impurity electrons are effectively decoupled so that the average energy of the impurity $\langle H_d \rangle$ is written as

$$T_0 \langle n_{d\uparrow} \rangle + T_0 \langle n_{d\downarrow} \rangle + U \langle n_{d\uparrow} \rangle \langle n_{d\downarrow} \rangle. \quad (6)$$

A limitation of this approximation is that it does not fully allow for the fact that the spin-up and spin-down electrons can correlate the times at which they occupy the impurity levels. Consequently the energy of the nonmagnetic states in which $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle$ is overestimated by a factor which is proportional to the Coulomb repulsion U . However U must be relatively large for a moment to exist so that one of the impurity levels lies well above the Fermi level of the conduction band. This implies that the effects of the correlation could well be significant.

¹ B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. N. Corenzwit, and R. C. Sherwood, *Phys. Rev. Letters* **5**, 542 (1960).

² G. G. E. Low and M. F. Collins, *J. Appl. Phys.* **34**, 1195 (1963).
M. F. Collins and G. G. E. Low, *J. Phys. Radium* **25**, 596 (1964).

³ P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

⁴ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

⁵ A. C. Hewson, *Phys. Letters* **19**, 5 (1965).

To avoid these difficulties we propose to tackle the problem in two stages. First the system composed of the host metal plus isolated impurity described by the first two terms in Hamiltonian (1) is considered. The thermodynamic properties of this system, which includes the Coulomb repulsion between the impurity levels, can be calculated exactly. In the second stage, the band and d -electron scattering (5) is included, and is taken into account essentially as a perturbation.

The mathematical technique we shall use is the equation of motion method of calculating appropriately chosen double-time Green's functions. The Green's function⁶ $\langle\langle A(t):B(t')\rangle\rangle$ of two operators A and B in the Heisenberg representation is defined by

$$\langle\langle A(t):B(t')\rangle\rangle = -i\theta(t-t')\langle[A(t),B(t')]\rangle_{\pm}, \quad (7)$$

where $\theta(t-t')$ is the step function

$$\theta(t-t') = \begin{cases} 1 & t > t', \\ 0 & t < t'. \end{cases} \quad (8)$$

The square brackets represent either a commutator or anticommutator, and the pointed brackets an average over a canonical ensemble.

From the definition, the equation of motion can be derived and, if the Hamiltonian is time-independent, it can be expressed in terms of $\langle\langle A:B\rangle\rangle_E$, the Fourier transform of the Green's function with respect to the time difference $(t-t')$.

$$E\langle\langle A:B\rangle\rangle_E = (1/2\pi)\langle[A,B]\rangle_{\pm} + \langle\langle[A,H]_:B\rangle\rangle_E. \quad (9)$$

The quantities which are of direct physical interest are the correlation functions, and these are derived from the corresponding Green's function by the use of the relation

$$\begin{aligned} \langle B(t')A(t) \rangle \\ = \lim_{\epsilon \rightarrow +0} \int_{-\infty}^{+\infty} \frac{\{\langle\langle A:B\rangle\rangle_{E+i\epsilon} - \langle\langle A:B\rangle\rangle_{E-i\epsilon}\} e^{-iE(t-t')}}{(\epsilon^{\beta E \pm 1})} dE, \end{aligned} \quad (10)$$

where $\beta = 1/KT$.

II. AN ISOLATED IMPURITY

The thermodynamic behavior of the system described by the Hamiltonian

$$H = H_b + H_d \quad (11)$$

can be calculated from the equations of motion of the Green's functions

$$G_{dd}^{\sigma} = \langle\langle C_{d\sigma}:C_{d\sigma}^{\dagger}\rangle\rangle, \quad G_{kk'}^{\sigma} = \langle\langle C_{k\sigma}:C_{k'\sigma}^{\dagger}\rangle\rangle, \quad (12)$$

and

$$\Gamma_{dd}^{\sigma} = \langle\langle C_{d\sigma}n_{d,-\sigma}:C_{d\sigma}^{\dagger}\rangle\rangle.$$

The assumption of Anderson that the impurity d state is distinct from the conduction states of the metal

is used so that

$$[C_{d\sigma}, C_{k\sigma}^{\dagger}]_{\pm} = 0. \quad (13)$$

The equation of motion for $G_{kk'}^{\sigma}$ has the simple solution

$$G_{kk'}^{\sigma}(E) = (\delta_{kk'}/2\pi)(E - \epsilon_k)^{-1}. \quad (14)$$

The density of states of the band electrons $\rho_b^{\sigma}(E)$ is calculated from the imaginary part of the Green's function $G_{kk}^{\sigma}(E+i\epsilon)$ in the limit $\epsilon \rightarrow +0$. Using (14) we find

$$\rho_b^{\sigma}(E) = \sum_{\mathbf{k}} \delta(E - \epsilon_{\mathbf{k}}), \quad (15)$$

where the summation is over all the \mathbf{k} values of the band.

Hubbard⁷ has shown that the equations for G_{dd}^{σ} and Γ_{dd}^{σ} can be solved exactly, because they can be expressed in a closed form. The equation for G_{dd}^{σ} is

$$(E - T_0)G_{dd}^{\sigma} + U\Gamma_{dd}^{\sigma} = 1/2\pi \quad (16)$$

and for Γ_{dd}^{σ}

$$(E - T_0)\Gamma_{dd}^{\sigma} = \langle n_{d,-\sigma} \rangle / 2\pi + U \langle\langle n_{d,-\sigma}^2 C_{d\sigma}:C_{d\sigma}^{\dagger} \rangle\rangle. \quad (17)$$

Equation (17) is put into a closed form by use of the operator relation $n_{i\sigma}^2 = n_{i\sigma}$.

The solution for G_{dd}^{σ} is

$$G_{dd}^{\sigma} = \frac{1}{2\pi} \left(\frac{1 - \langle n_{d,-\sigma} \rangle}{E - T_0} + \frac{\langle n_{d\sigma} \rangle}{E - T_0 - U} \right). \quad (18)$$

The corresponding density of states is

$$\rho_d^{\sigma}(E) = (1 - \langle n_{d,-\sigma} \rangle) \delta(E - T_0) + \langle n_{d,-\sigma} \rangle \delta(E - T_0 - U). \quad (19)$$

There are two levels, T_0 and $T_0 + U$, containing $1 - \langle n_{d,-\sigma} \rangle$ and $\langle n_{d,-\sigma} \rangle$ states, respectively. For an isolated atom $\langle n_{d\sigma} \rangle$ can only have the values 0 or 1.

In the ground state of the combined system (11), the lowest energy levels are filled to the Fermi level E_F . The number of electrons in the d states, if T_0 is below E_F and $T_0 + U$ is above, is

$$\langle n_{d\sigma} \rangle = \int_{-\infty}^{E_F} \rho_d^{\sigma}(E) dE \quad (20)$$

which when integrated becomes

$$\langle n_{d\sigma} + n_{d,-\sigma} \rangle = 1. \quad (21)$$

This implies that either the spin-up or spin-down level is occupied. If a magnetic field is included in the z direction, the ambiguity of (21) is removed $\langle n_{d\uparrow} \rangle = 1$ and $\langle n_{d\downarrow} \rangle = 0$ so that the impurity has a moment and is in a "magnetic" state.

The form of these solutions are in contrast with the Hartree-Fock results which can be obtained, not by

⁶ D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [English transl.: Soviet Phys.—Usp. 3, 320 (1960)].

⁷ J. Hubbard, Proc. Roy. Soc. A276, 238 (1963); A281, 401 (1964).

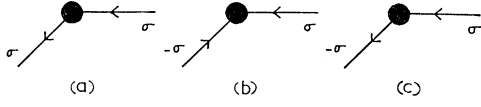


FIG. 1. The three types of scattering of a band electron.

solving the equation for Γ_{dd}^σ exactly, but by making the approximation

$$\Gamma_{dd}^\sigma = \langle n_{d,-\sigma} \rangle \langle \langle C_{d\sigma} : C_{d\sigma}^\dagger \rangle \rangle. \quad (22)$$

With this decoupling, the solution for G_{dd}^σ is

$$G_{dd}^\sigma = (2\pi)^{-1} (E - T_0 - U \langle n_{d,-\sigma} \rangle)^{-1} \quad (23)$$

with a corresponding density of states.

$$\rho_d^\sigma(E) = \delta(E - T_0 - U \langle n_{d,-\sigma} \rangle). \quad (24)$$

III. THE SCATTERING BETWEEN BAND AND d ELECTRONS

To predict the behavior of the system when the scattering (5) between the band and d electron is included we need the equations of motion of the Green's functions

$$G_{kd}^\sigma = \langle \langle C_{k\sigma} : C_{d\sigma}^\dagger \rangle \rangle, \quad G_{dk}^\sigma = \langle \langle C_{d\sigma} : C_{k\sigma}^\dagger \rangle \rangle, \quad (25)$$

and

$$\Gamma_{dk}^\sigma = \langle \langle C_{d\sigma} n_{d,-\sigma} : C_{k\sigma}^\dagger \rangle \rangle,$$

as well as those previously considered.

The commutation relations

$$[H, C_{k\sigma}]_- = \epsilon_k C_{k\sigma} + V_{kd} C_{d\sigma}, \quad (26)$$

and

$$[H, C_{d\sigma}]_- = T_0 C_{d\sigma} + U n_{d,-\sigma} C_{d\sigma} + \sum_{\mathbf{k}} V_{dk} C_{k\sigma} \quad (27)$$

are used to generate the following equations of motion

$$(E - T_0) G_{dd}^\sigma - U \Gamma_{dd}^\sigma - \sum_{\mathbf{k}} V_{dk} G_{kd}^\sigma = \frac{1}{2} \pi, \quad (28)$$

$$(E - \epsilon_k) G_{kd}^\sigma - V_{kd} G_{dd}^\sigma = 0, \quad (29)$$

$$(E - T_0) G_{dk}^\sigma - U \Gamma_{dk}^\sigma - \sum_{\mathbf{k}'} V_{dk'} G_{k'k}^\sigma = 0, \quad (30)$$

$$(E - \epsilon_{k'}) G_{k'k}^\sigma - V_{k'd} G_{dk}^\sigma = \delta_{k'k} / 2\pi, \quad (31)$$

$$\begin{aligned} (E - T_0 - U) \Gamma_{dd}^\sigma &= \langle n_{d,-\sigma} \rangle / 2\pi + \sum_{\mathbf{k}} V_{dk} \langle \langle C_{k\sigma} n_{d,-\sigma} : C_{d\sigma}^\dagger \rangle \rangle \\ &+ \sum_{\mathbf{k}} V_{dk} \{ \langle \langle C_{d,-\sigma}^\dagger C_{k,-\sigma} C_{d\sigma} : C_{d\sigma}^\dagger \rangle \rangle \\ &- \langle \langle C_{k,-\sigma}^\dagger C_{d,-\sigma} C_{d\sigma} : C_{d\sigma}^\dagger \rangle \rangle \}, \quad (32) \end{aligned}$$

and

$$\begin{aligned} (E - T_0 - U) \Gamma_{dk}^\sigma &= \sum_{\mathbf{k}'} V_{dk'} \langle \langle C_{k'\sigma} n_{-\sigma,d} : C_{k\sigma}^\dagger \rangle \rangle \\ &+ \sum_{\mathbf{k}'} V_{dk'} \{ \langle \langle C_{d,-\sigma}^\dagger C_{k',-\sigma} C_{d\sigma} : C_{k\sigma}^\dagger \rangle \rangle \\ &- \langle \langle C_{k',-\sigma}^\dagger C_{d,-\sigma} C_{d\sigma} : C_{k\sigma}^\dagger \rangle \rangle \}, \quad (33) \end{aligned}$$

where the operator relation $n_{i\sigma}^2 = n_{i\sigma}$ has again been used to simplify some of the terms in (32) and (33).

The higher order Green's function on the right-hand side of (32) and (33) cannot be expressed in terms of the lower order functions (12) and (25). Before we consider how to deal with them it will be useful to consider their physical interpretation (Fig. 1).

(a) $\langle \langle C_{k'\sigma}(t) n_{d,-\sigma}(t) : C_{k\sigma}^\dagger(t') \rangle \rangle$ describes the scattering of a band electron by the impurity. This term we describe as the normal scattering.

(b) $\langle \langle C_{k',-\sigma}^\dagger(t) C_{d,-\sigma}(t) C_{d\sigma}(t) : C_{k\sigma}^\dagger(t') \rangle \rangle$ represents the scattering of a band electron with spin σ into a hole with spin $-\sigma$, with a consequent excitation of two d levels. If U is large the probability that two d states are occupied at the same time is small and is zero in the limit $U \rightarrow \infty$.

(c) $\langle \langle C_{d,-\sigma}^\dagger(t) C_{k',-\sigma}(t) C_{d\sigma}(t) : C_{k\sigma}^\dagger(t') \rangle \rangle$ represents a spin-exchange scattering of a band electron. The spin on the impurity is flipped in the process.

We shall approximate to the Green's functions (a), (b), (c) and their counterparts in Eq. (32) by decoupling the d from the band electrons in a simple self-consistent way. The Green's function (a) for the normal scattering is replaced by $\langle n_{d,-\sigma} \rangle \langle \langle C_{k'\sigma} : C_{k\sigma}^\dagger \rangle \rangle$. There is no contribution from (b) as $\langle C_{d\sigma} C_{d,-\sigma} \rangle = 0$. The average $\langle C_{d\sigma}^\dagger C_{d,-\sigma} \rangle$ is related to the transverse components of the impurity spin. If we include a magnetic field in the z direction, this average will be zero so that there will also be no contribution from (c).

The method of approximation of the scattering terms is very similar to that used on the Hartree-Fock theory. The important difference is that we have preserved intact all Green's functions that involve the correlation of the spin-up and spin-down electrons in the impurity levels and which are multiplied by the factor U . For this reason the approximate equations are exact in the limit $V_{dk} \rightarrow 0$.

Equations (28)–(32) have been reduced to a closed form. The solution for $G_{dd}^\sigma(E)$ is

$$G_{dd}^\sigma(E) = \frac{1}{2\pi} \left[\frac{(E - T_0)(E - T_0 - U)}{E - T_0 - U(1 - \langle n_{d,-\sigma} \rangle)} - \sum_{\mathbf{k}} \frac{|V_{dk}|^2}{E - \epsilon_k} \right]^{-1}. \quad (34)$$

To calculate the density of states we use the relation

$$\lim_{\epsilon \rightarrow 0} \sum_{\mathbf{k}} \frac{|V_{dk}|^2}{E - \epsilon_k + i\epsilon} = P \sum_{\mathbf{k}} \frac{|V_{dk}|^2}{E - \epsilon_k} - i\pi \sum_{\mathbf{k}} |V_{dk}|^2 \delta(E - \epsilon_k). \quad (35)$$

For convenience we introduce the notation

$$\Delta(E) = \pi \sum_{\mathbf{k}} |V_{dk}|^2 \delta(E - \epsilon_k) \quad (36)$$

and

$$\Lambda(E) = P \sum_{\mathbf{k}} (|V_{dk}|^2 / (E - \epsilon_k)). \quad (37)$$

The density of states deduced from (33) is

$$\rho_d^\sigma(E) = \frac{\Delta(E)}{\pi} \left\{ \left[\frac{(E - T_0)(E - T_0 - U)}{E - T_0 - U(1 - \langle n_{d,-\sigma} \rangle)} - \Lambda(E) \right]^{-1} + \Delta^2(E) \right\}^{-1}. \quad (38)$$

This is a resonance-type formula with peaks at the values of E which satisfy the equation

$$(E-T_0)(E-T_0-U-\Lambda)-U\Lambda(1-\langle n_{d,-\sigma} \rangle)=0. \quad (39)$$

If $\Delta(E)$ and $\Lambda(E)$ are slowly varying functions of E over the band they can be treated as parameters. Equation (39) then has two solutions which, when Λ/U is small, are

$$E_{1\sigma}=T_0+\Lambda(1-\langle n_{d,-\sigma} \rangle) \quad (40)$$

$$E_{2\sigma}=T_0+U+\Lambda\langle n_{d,-\sigma} \rangle. \quad (41)$$

The widths of these levels are $\Delta(1-\langle n_{d,-\sigma} \rangle)$ and $\Delta\langle n_{d\sigma} \rangle$, respectively.

The scattering of the d and band electrons has caused the impurity level to be shifted and broadened. When U is comparable with Δ the two levels form an effective single level of width Δ with its center of gravity at $T_0+U\langle n_{d,-\sigma} \rangle$ as in the Hartree-Fock theory.⁷ When U is large the levels are distinct and like the atomic levels.

They are accessible either to spin-up or spin-down electrons. If the level E_1 is occupied part of the time by a spin-down electron, then the average probability that a spin-up electron is scattered into this state (which is proportional to the width of the level) is reduced by a factor $(1-\langle n_{d,-\sigma} \rangle)$. The energy shift, which depends on the degree to which scattering occurs, is proportional to the same factor.

The occupation number of the d states at absolute zero is found by integrating the density of states to the Fermi energy E_F .

$$\langle n_{d\sigma} \rangle = \frac{1}{\pi} \int_{-\infty}^{E_F} \Delta dE \left\{ \left[\frac{(E-T_0)(E-T_0-U)}{E-T_0-U(1-\langle n_{d,-\sigma} \rangle)} - \Lambda \right]^2 + \Delta^2 \right\}^{-1}. \quad (42)$$

This integral can be evaluated if Λ and Δ are treated as parameters. The result is

$$\begin{aligned} \langle n_{d\sigma} \rangle = & \frac{3}{4} + 1/2\pi \tan^{-1} \left[\frac{(E_F-T_0)(E_F-T_0-U+\Lambda)+U\Lambda(1-\langle n_{d,-\sigma} \rangle)}{\Delta(E_F-T_0-U(1-\langle n_{d,-\sigma} \rangle))} \right] \\ & - \frac{1}{4\pi} \left[\frac{L\{2\Lambda+U(2\langle n_{d,-\sigma} \rangle-1)+\Delta F\}}{L^2+F^2} \right] \left[\tan^{-1} \left\{ \frac{2T_0+2L+\Lambda-U-2E_F}{\Delta+2F} \right\} + \tan^{-1} \left\{ \frac{2E_F-2T_0-\Lambda-U+2L}{\Delta-2F} \right\} \right] \\ & + \frac{1}{4\pi} \left[\frac{\Delta L-F\{(2\langle n_{d,-\sigma} \rangle-1)U+2\Lambda\}}{L^2+F^2} \right] \ln \left[\frac{(2E_F-2T_0-U-2L)^2+(\Delta+2F)^2}{(2E_F-2T_0-\Lambda-U+2L)^2+(\Delta-2F)^2} \right], \quad (43) \end{aligned}$$

for $T_0+U+\Lambda > E_F$, where

$$L^2-F^2 = \frac{1}{4}[(U+\Lambda)^2-4U\Lambda(1-\langle n_{d,-\sigma} \rangle)-\Delta^2] \quad (44)$$

and

$$L^2+F^2 = \frac{1}{4}[\{(U+\Lambda)^2-4U\Lambda(1-\langle n_{d,-\sigma} \rangle)-\Delta^2\}^2 + \Delta^2\{2\Lambda+2\langle n_{d,-\sigma} \rangle-1\}U\}^{1/2}], \quad (45)$$

where $-\pi < \tan^{-1}(x/y) < \pi$ and the quadrant is determined as if x and y are proportional to $\sin\theta$ and $\cos\theta$, respectively.

For $E_F > T_0+U+\Lambda$, the first two terms in (43) are replaced by

$$\begin{aligned} & \frac{1}{4} + \frac{1}{2\pi} \tan^{-1} \\ & \times \left[\frac{(E_F-T_0)(T_0+U-E_F-\Lambda)-U\Lambda(1-\langle n_{d,-\sigma} \rangle)}{\Delta(T_0-E_F-U(1-\langle n_{d,-\sigma} \rangle))} \right]. \quad (46) \end{aligned}$$

Equation (43) generates two simultaneous equations for $\langle n_{d\uparrow} \rangle$ and $\langle n_{d\downarrow} \rangle$: the self-consistent solutions correspond to the points of intersection of the curves. For a moment to exist there must be solutions for which $\langle n_{d\uparrow} \rangle \neq \langle n_{d\downarrow} \rangle$.

When U is relatively small so that $U \ll E_F - T_0$ and $\Lambda \ll E_F - T_0$, (43) reduces to Anderson's expression.⁴ The effect of the correlations is negligible.

$$\langle N_{d\sigma} \rangle = (1/\pi) \cot^{-1}[(T_0+\Lambda-E_F+U\langle n_{d,-\sigma} \rangle)/\Delta]. \quad (47)$$

In this limit, however, the impurity levels E_1 and E_2 are below the Fermi level and only nonmagnetic states are possible.

In the other extreme $U \rightarrow \infty$, the density of states becomes

$$\rho_d^\sigma(E) = \frac{1}{\pi} \frac{\Delta(1-\langle n_{d,-\sigma} \rangle)^2}{[E-T_0-\Lambda(1-\langle n_{d,-\sigma} \rangle)]^2 + \Delta^2(1-\langle n_{d,-\sigma} \rangle)^2} \quad (48)$$

and the occupation number of the d levels is

$$\begin{aligned} \langle n_{d\sigma} \rangle = & \frac{1}{\pi} (1-\langle n_{d,-\sigma} \rangle) \\ & \times \left\{ \tan^{-1} \left[\frac{E_F-T_0-\Lambda(1-\langle n_{d,-\sigma} \rangle)}{\Delta(1-\langle n_{d,-\sigma} \rangle)} \right] + \frac{\pi}{2} \right\}. \quad (49) \end{aligned}$$

Before we continue and examine the solutions of (49), we must check that we have lost no magnetic solutions for which $U\langle n_{d,-\sigma} \rangle \rightarrow 0$ as $U \rightarrow \infty$. Let us

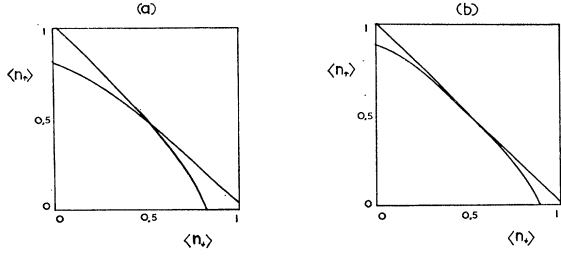


FIG. 2. (a) A self-consistent plot of $\langle n_{d\uparrow} \rangle$ versus $\langle n_{d\downarrow} \rangle$ for $(E_F - T_0)/\Delta = 2, \Lambda = 0$. There is only one self-consistent solution. (b) A plot with $(E_F - T_0)/\Delta = 4$.

calculate $\langle n_{d\sigma} \rangle$ on the assumption that $U\langle n_{d,-\sigma} \rangle \rightarrow 0$ as $U \rightarrow \infty$. We can then calculate $\langle n_{d,-\sigma} \rangle$ and examine whether there is a self-consistent solution of this form.

If

$$U\langle n_{d,-\sigma} \rangle \rightarrow 0$$

$$\langle n_{d\sigma} \rangle = \frac{1}{\pi} \int_{-\infty}^{E_F} \frac{\Delta dE}{(E - T_0 - \Lambda)^2 + \Delta^2} \quad (50)$$

in the limit $U \rightarrow \infty$. When Δ is finite and $T_0 + \Lambda$ is below the Fermi level, we see that $\langle n_{d\sigma} \rangle = 1 - \delta$, where δ is a finite quantity. Substituting this in the equation for $\langle n_{d,-\sigma} \rangle$,

$$\langle n_{d,-\sigma} \rangle = \frac{1}{\pi} \int_{-\infty}^{E_F} \frac{\Delta \delta^2 dE}{(E - T_0 - \Lambda \delta)^2 + \delta^2 \Delta^2}; \quad (51)$$

as this is not identically zero we cannot have missed any magnetic solutions on taking the limit $U \rightarrow \infty$ and obtaining Eq. (49).

A typical plot of $\langle n_{d\uparrow} \rangle$ and $\langle n_{d\downarrow} \rangle$ using (49) is shown in Fig. 2. There is only one solution, a nonmagnetic one: $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle \approx \frac{1}{2}$. As $\Delta \rightarrow 0$ and the lifetime of the impurity states becomes very large, the two curves move closer together and eventually coincide into the single curve

$$\langle n_{d\uparrow} + n_{d\downarrow} \rangle = 1. \quad (52)$$

If a magnetic field H is included and the limit $\Delta \rightarrow 0$ is taken before $H \rightarrow 0$, then the correct "magnetic" limit for an isolated atom is obtained:

$$\langle n_{d\uparrow} \rangle = 1, \quad \langle n_{d\downarrow} \rangle = 0. \quad (53)$$

In general, when Δ is finite the self-consistent solutions are nonmagnetic. The condition for three roots, i.e., magnetic solutions, is that $d\langle n_{d\uparrow} \rangle/d\langle n_{d\downarrow} \rangle < -1$. Using (49)

$$\begin{aligned} & \frac{d\langle n_{d\uparrow} \rangle}{d\langle n_{d\downarrow} \rangle} \\ &= -\frac{1}{2} - \frac{1}{\pi} \tan^{-1} \left[\frac{E_F - T_0 - \Lambda(1 - \langle n_{d\downarrow} \rangle)}{\Delta(1 - \langle n_{d\downarrow} \rangle)} \right] + \frac{(E_F - T_0)}{\pi} \\ & \times \frac{\Delta(1 - \langle n_{d\downarrow} \rangle)}{\{[E_F - T_0 - \Lambda(1 - \langle n_{d\downarrow} \rangle)]^2 + \Delta^2(1 - \langle n_{d\downarrow} \rangle)^2\}}. \quad (54) \end{aligned}$$

In the critical case at the onset of magnetic solutions $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = n_c$ where n_c satisfies the equations

$$\frac{3n_c - 1}{2(1 - n_c)} = \frac{1}{\pi} \tan^{-1} \left[\frac{E_F - T_0 - \Lambda(1 - n_c)}{\Delta(1 - n_c)} \right] \quad (55)$$

and

$$\begin{aligned} & \frac{2n_c - 1}{(1 - n_c)} = \frac{(E_F - T_0)}{\pi} \\ & \times \frac{\Delta(1 - n_c)}{[E_F - T_0 - \Lambda(1 - n_c)]^2 + \Delta^2(1 - n_c)^2}. \quad (56) \end{aligned}$$

When the width of the localized level is very small, according to (54) and (55), a magnetic state is possible if $T_0 > E_F$. In this case, $E_{1\uparrow} \approx T_0 + \Lambda$ is below the Fermi level and is occupied, while $E_{1\downarrow} \approx T_0$ is above the Fermi level and is almost empty.

The critical values of Λ/Δ and $(T_0 - E_F)/\Delta$ are plotted in Fig. 3. Only for a relatively small range of values do magnetic solutions exist: Λ/Δ must be negative and less than $-\pi/2$. This is in remarkable contrast to the Hartree-Fock results which, in the limit $U \rightarrow \infty$, only require that $E_F > T_0 - \Lambda$ for a magnetic solution. In the Hartree-Fock theory the average contribution to the energy from the impurity levels is

$$T_0 \langle n_{d\uparrow} \rangle + T_0 \langle n_{d\downarrow} \rangle + U \langle n_{d\uparrow} \rangle \langle n_{d\downarrow} \rangle. \quad (57)$$

The energy of a possible nonmagnetic state $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = n$ is $2T_0 n + U n^2$ and is proportional to U as $U \rightarrow \infty$.

When the correlation is included, the average energy is

$$T_0 \langle n_{d\uparrow} \rangle + T_0 \langle n_{d\downarrow} \rangle + U \langle n_{d\uparrow} n_{d\downarrow} \rangle. \quad (58)$$

For a nonmagnetic state, $U \langle n_{d\uparrow} n_{d\downarrow} \rangle$ is finite as $U \rightarrow \infty$ because no two electrons occupy the impurity levels at the same time and allow the Coulomb repulsion to come into play.

In the Hartree-Fock theory, the condition for a magnetic state can be written in a similar way to the Stoner-Wohlfarth condition for the ferromagnetism of a pure metal. The Hartree-Fock expression for the density of states is

$$\rho_d^\sigma(E) = (1/\pi) \Delta / [\{E - T_0 - \Lambda - U \langle n_{d,-\sigma} \rangle\}^2 + \Delta^2] \quad (59)$$

so

$$\frac{d\langle n_{d\sigma} \rangle}{d\langle n_{d,-\sigma} \rangle} = \frac{d}{d\langle n_{d,-\sigma} \rangle} \int_{-\infty}^{E_F} \rho_d^\sigma(E) dE, \quad (60)$$

or

$$\frac{d\langle n_{d\sigma} \rangle}{d\langle n_{d,-\sigma} \rangle} = -U \int_{-\infty}^{E_F} \frac{d\rho_d^\sigma(E)}{dE} dE \quad (61)$$

$$\frac{d\langle n_{d,+ \sigma} \rangle}{d\langle n_{d,- \sigma} \rangle} = -U \rho_d^\sigma(E_F). \quad (62)$$

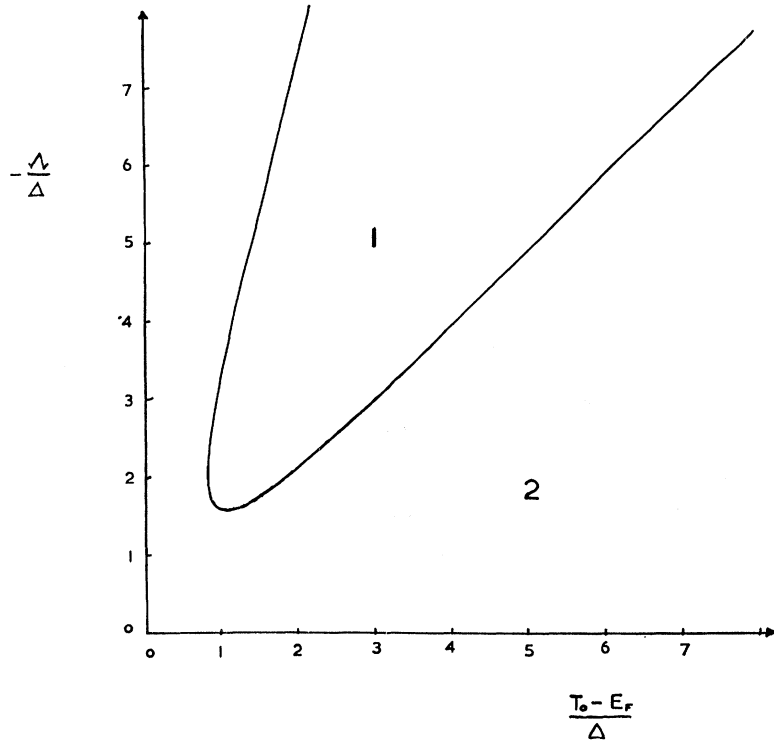


FIG. 3. The critical curve plotted from (55) and (56). In region (1) magnetic states are possible.

The condition for magnetic states that $d\langle n_{d\sigma} \rangle / d\langle n_{d,-\sigma} \rangle < -1$ becomes

$$U\rho_d^\sigma(E_F) > 1. \quad (63)$$

It is not possible to take the correlation effects into account simply as an energy shift. The modification of the widths is of equal importance and it is for this reason that we cannot switch the derivatives in Eq. (59) and present our results in a similar way to (62).

If for simplicity we make the assumption that the matrix elements for the d - and band-electron scattering are constant over the band, explicit expressions for $\Delta(E)$ and $\Lambda(E)$ can be derived. From (36)

$$\Delta(E) = \pi |V|^2 \rho_0(E), \quad (64)$$

where $\rho_0(E)$ is the density of states of the unperturbed conduction band.

For a parabolic density of states with a band width E_0 ,

$$\Delta(E) = \eta |V|^2 E^{1/2} \quad 0 < E < E_0 \quad (65)$$

and

$$\Lambda(E) = \Omega \eta |V|^2 \left\{ (E) \ln \left| \frac{\sqrt{E_0 + \sqrt{E}}}{\sqrt{E_0 - \sqrt{E}}} \right| - \sqrt{E_0} \right\}; \quad (66)$$

Ω is the atomic volume. Λ is negative only in the lower half of the band. The magnitude of the ratio Λ/Δ increases towards the bottom of the band.

A more symmetrical density of states that has been considered by Clogston⁸ is

$$\Delta(E) = \eta |V|^2 \{1 - (E/E_0)^2\} \quad (67)$$

⁸ A. M. Clogston, Phys. Rev. **125**, 439 (1962).

which has a band width $2E_0$,

$$\Lambda(E) = \Omega \eta |V|^2 \left\{ 2(E/E_0) + (E^2/E_0^2 - 1) \ln \left| \frac{E - E_0}{E + E_0} \right| \right\}. \quad (68)$$

Λ is negative in the lower half of the band and the ratio $\Lambda/\Delta \rightarrow -\infty$ as $E + E_0 \rightarrow +0$.

In general the type of band which will favor the occurrence of a magnetic state is one which has a dip in the region of the impurity level so that Δ is small, and is weighted in the lower region so that Λ is predominantly negative. If the impurity level falls either above or below the band, $\Delta \rightarrow 0$, and it becomes a discrete atomic level.

When U/Δ is large but finite, magnetic solutions are still possible but as U is reduced they eventually disappear. Using (42) a plot of $\langle n_{d\uparrow} \rangle$ and $\langle n_{d\downarrow} \rangle$ is shown in Fig. (4b) which gives a magnetic state. Equation (43)

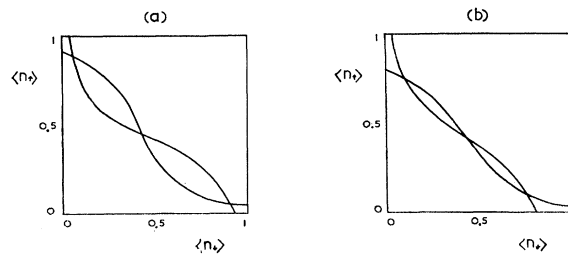


FIG. 4. (a) A plot for values $E_F - T_0/\Delta = -3$, $\Lambda/\Delta = -5$. There are three solutions. (b) The same plot with finite U , $U/\Delta = 8$.

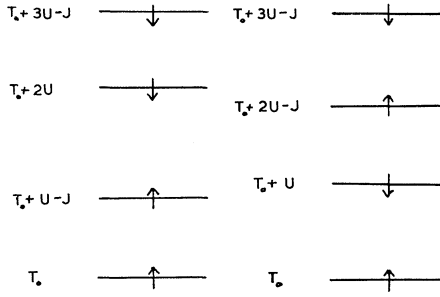


FIG. 5. The electron energy levels for an impurity with two orbital states.

is rather too complicated for an analytic expression to be derived for the value of U/Δ at which the magnetic solution disappears.

When the impurity state is magnetic there is a polarization of the band electrons. It is partly an apparent polarization due to the mixing of the states by the scattering, but there is also a contribution which is induced by the impurity. The total polarization can be calculated from $G_{kk^\sigma}(E)$. From Eqs. (28)–(33)

$$G_{kk^\sigma}(E) = \frac{1}{2\pi} \frac{1}{E - \epsilon_k} + |V_{dk}|^2 \left\{ (E - \epsilon_k)^2 \left[\frac{(E - T_0)(E - T_0 - U)}{E - T_0 - U(1 - \langle n_{d,-\sigma} \rangle)} - \sum_k \frac{|V_{dk}|^2}{E - \epsilon_k} \right]^{-1} \right\}. \quad (69)$$

To calculate the density of states of the band electrons $\rho_b^\sigma(E)$ we use the relation

$$\sum_k \frac{|V_{dk}|^2}{(E - \epsilon_k + i\epsilon)^2} = -\frac{d\Delta}{dE} - i\frac{d\Delta}{dE}, \quad \epsilon \rightarrow +0. \quad (70)$$

The density of states deduced from (69) and (70) is

$$\rho_b^\sigma(E) = \rho_0^\sigma(E) + \left\{ \frac{d\Delta}{dE} \left(\frac{(E - T_0)(E - T_0 - U)}{E - T_0 - U(1 - \langle n_{d,-\sigma} \rangle)} - \Delta \right) - \Delta \frac{d\Delta}{dE} \right\} \times \left[\left\{ \frac{(E - T_0)(E - T_0 - U)}{E - T_0 - U(1 - \langle n_{d,-\sigma} \rangle)} - \Delta \right\}^2 + \Delta^2 \right]^{-1}. \quad (71)$$

The polarization is

$$\int_{-\infty}^{E_F} \rho_b^\uparrow(E) - \rho_b^\downarrow(E) dE. \quad (72)$$

The “compensation theorem” of Anderson and Clogston,⁹ that the polarization is zero for a flat band, is no

⁹ P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. 6, 124 (1961).

longer true if the E dependence of the level shift is included. For a flat band the polarization is

$$\int_{-\infty}^{E_F} \frac{d\Delta}{dE} (\rho_a^\uparrow - \rho_a^\downarrow) dE. \quad (73)$$

From $G_{kk^\sigma}(E)$ it is also possible in principle to calculate the distribution of the polarization about the impurity.

IV. DISCUSSION

The results of the preceding calculation indicate that the correlation of the electrons in the impurity levels plays an important role in determining whether magnetic states are possible. If the energy shift Δ is negligible magnetic states do not occur. It is conceivable that in some dilute alloys that Δ/Δ is negative and large enough for a localized moment to be formed but in general this does not seem likely.

A dilute alloy of nickel impurities in copper falls within the scope of the model as the nickel atoms effectively supply only one d orbital to the conduction band of the copper. In this system localized moments have not been observed which indicates that our conclusions are correct.

Our Hamiltonian is inadequate as a description of dilute alloys in which localized moments have been observed. For example, to describe manganese ions in copper the full degeneracy of the d levels should be taken into account and the intra-atomic exchange between orthogonal orbitals included.

The Hamiltonian

$$H = T_0(n_{1\uparrow} + n_{1\downarrow} + n_{2\uparrow} + n_{2\downarrow}) + (U - J)(n_{1\uparrow}n_{2\uparrow} + n_{1\downarrow}n_{2\downarrow}) + U(U_{1\uparrow}n_{1\downarrow} + n_{1\uparrow}n_{2\downarrow} + n_{2\uparrow}n_{2\downarrow} + n_{2\uparrow}n_{2\downarrow})$$

can be used for an impurity with two degenerate levels φ_1 and φ_2 where J is the intra-atomic exchange coupling. If we assume that the lowest level is occupied by a spin-up electron in the state φ_1 , there are three ways in which a second electron can be added: (i) to the state φ_2 with its spin parallel to the original electron which requires an energy $T_0 + U - J$, (ii) to the state φ_2 with its spin anti-parallel to the original electron requiring an energy $T_0 + U$, (iii) to the spin-down φ_1 state with an energy $T_0 + U$. The energy of a third electron is $T_0 + 2U$ in case (i) and $T_0 + 2U - J$ for (ii) and (iii).

If the Fermi level of the conduction band lies between $T_0 + 2U - J$ and $T_0 + U - J$ then the levels of an isolated impurity will be occupied by two electrons with parallel spins and the impurity atom will have a spin one. The three-fold degeneracy of the level will be lifted by a magnetic field and the state $S_z = 1$ will be occupied.

When the impurity levels are weakly coupled to the band via an interaction of the form (5), the levels will be broadened and shifted but their relative positions will be the same. The “magnetic” state is likely to persist, for if one of the impurity electrons is scattered

into the band it is energetically more favorable for an electron in the same spin state to take its place. Only when both electrons are scattered into the band can the impurity spin be reversed. Nevertheless it is not clear whether there are magnetic states in the sense that $\langle n_{1\uparrow} + n_{2\uparrow} \rangle \approx 2$, $\langle n_{1\downarrow} + n_{2\downarrow} \rangle \approx 0$ or whether $\langle n_{1\uparrow} + n_{2\uparrow} \rangle = \langle n_{1\downarrow} + n_{2\downarrow} \rangle$ and the total spin changes from the up to the down state with a relatively long period. In this latter case, the impurity states cannot be separated by a magnetic field until the magnetic shift μH exceeds the widths of the levels Δ so that they can be resolved. If Δ is small the susceptibility might have a Curie-Weiss behavior at high temperatures and in large fields.

In other alloys, such as cobalt or iron in palladium, which are best described by Wolff's model, the interactions between the band electrons are important. In palladium these interactions cause the pure metal to have a high susceptibility and this is certainly the reason for the giant moments which have been observed by dissolving such impurities as iron in the metal.

Another effect which is likely to modify our results is the s - d exchange interaction

$$-\frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \left\{ \frac{1}{2} (c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}'\uparrow} - c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}'\downarrow}) (n_{d\uparrow} - n_{d\downarrow}) + c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}'\downarrow} c_{d\downarrow}^\dagger c_{d\uparrow} + c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}'\uparrow} c_{d\uparrow}^\dagger c_{d\downarrow} \right\}. \quad (74)$$

This interaction is more likely to increase the polarization of the band electrons than to help in forming a moment. Its effect on localized states has been considered in the Hartree-Fock approximation by Kim and Nagaoka.¹⁰

Finally we note the qualitative similarity of our conclusions and those of Hubbard⁷ and Kannamori¹¹ on the parallel problem of predicting the conditions for ferromagnetism in a pure metal. In both cases the correlation reduces the probability of magnetic states as the electrons avoid populating orbitals on the same atom resulting in an effective reduction of the Coulomb repulsion U . In the model of a pure metal there is a

¹⁰ D. Kim and Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **6**, 124 (1963).

¹¹ J. Kannamori, Progr. Theoret. Phys. (Kyoto) **30**, 275 (1963).

short-range interaction U associated with the orbitals of all the atoms so that the reduction due to correlation does not occur quite to the same degree as in an alloy.

When this work was completed we received a report of the work of Schrieffer and Mattis¹² who have also considered the correlation effects in Anderson's model. In our notation they have written the Green's function $G_{dd^\sigma}(E)$ in the form

$$G_{dd^\sigma}(E) = (E - T_0 - \Sigma_\sigma(E) + i\Delta E/|E|)^{-1}, \quad (75)$$

where $\Sigma_\sigma(E)$ is the proper self-energy and contains the correlation effects. An integral equation is set up for $\Sigma_\sigma(E)$ which is approximately evaluated in the low-density limit $\langle n_{d\sigma} \rangle < 0.3$ or $1 - \langle n_{d\sigma} \rangle < 0.3$ when the particle-particle t -matrix graphs give the dominant contribution.

This can be compared with our expression for $G_{dd^\sigma}(E)$ which was obtained without the low density restriction. It can be written in the form (75) with an explicit expression for $\Sigma_\sigma(E)$

$$\Sigma_\sigma(E) = U \langle n_{d,-\sigma} \rangle / [1 - U(1 - \langle n_{d,-\sigma} \rangle) / (E - T_0)]. \quad (76)$$

With a self-energy of this form, the assumption of Schrieffer and Mattis that the spectral weight or density of states obtained from $G_{dd^\sigma}(E)$ has a Lorentzian form

$$\frac{1}{\pi} |\text{Im} G_{dd^\sigma}(E)| = \frac{1}{\pi} \Delta / [(E - \epsilon)^2 + \Delta^2]$$

is too restrictive except for small or large U . In the latter case, by molding $G_{dd^\sigma}(E)$ to such a spectral density, the interesting width effects which we discuss following (46) are lost.

Despite these differences, our qualitative conclusion that a single-orbital impurity in a metal is unlikely to have a moment is the same.

ACKNOWLEDGMENTS

The author is indebted to Dr. S. Doniach, Dr. J. Hubbard, and Professor E. P. Wohlfarth for helpful discussions.

¹² J. R. Schrieffer and D. C. Mattis (to be published).