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# Magnetism in Transition Metals

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An attempt is made to distinguish "band-type magnetization" from "alignment-type magnetization" on the basis of whether the local moments associated with the Wannier functions on the atom sites are "induced" or "permanent." In general, the local moment is partially induced and partially permanent, and a criterion is suggested: A local moment is defined to be of the permanent variety if in the presence of magnetic forces (supposed characteristic of the crystal in a given circumstance) tending to produce a moment in one sense ($\hat{z}$, say) of a direction, it can maintain itself (perhaps altered in magnitude, however) in the opposite sense ($-\hat{z}$), as well as in $\hat{z}$. The internal mechanisms tending to produce permanent moments are simplified to just the $H_{\rm corr}$ of Anderson, and the external inducing mechanism are the Heisenberg interaction and a magnetic field, $H_{\rm spin}$, say. If $H_{\rm corr}$ dominates $H_{\rm spin}$, then it is shown that a local moment can maintain itself to the polarizing tendencies (whence an alignment type of magnetization calculation is appropriate), but if $H_{\rm spin}$ dominates $H_{\rm corr}$, then the local moment has only one sense possible in this environment (and a band type of calculation is appropriate). It is suggested that this distinction is relevant to transition metals.

## 1. INTRODUCTION

MAGNETISM in transition metals has many unanswered questions and curious phenomena associated with it. In this paper, we shall attempt to correlate theories which assume fixed permanent magnetic moments in the atoms, related to the $d$ electrons (primarily at least), and theories in which the atomic magnetic moment is not a consequence of internal forces, but of the influence of interactions with neighboring atoms.

If there are fixed magnetic moments, then they may show ferromagnetic behavior as a result of the alignment tendencies caused by the Heisenberg exchange interactions with neighboring atoms:

$$H_{\rm spin}=-2\sum A(\mathbf{f}-\mathbf{f}')\mathbf{S}_{\mathbf{f}}\cdot\mathbf{S}_{\mathbf{f}'}\,. \tag{1.1}$$

We shall use $\mathbf{f}$ to mean both the position of an atom, and (later on) a $d$-band Wannier function on it. $\mathbf{S}_{\mathbf{f}}$ here represents the spin on the $\mathbf{f}$ atom (see below for an explicit definition), and $A(\mathbf{f}-\mathbf{f}')$ is the exchange integral. The picture of fixed atomic spins being lined up by $H_{\rm spin}$ we shall call *alignment magnetization* (AM).

On the band theory of magnetization (Slater,[1] Stoner,[2] etc.), one envisages the $d$ band split into two parts, an up-spin part and a down-spin part. The lowest energy in each of these subbands is not the same, differing by an amount somehow related to the exchange integral. Each band electron has a spin associated with it; thus, this picture can preserve the half-integral electron spin yet account for the variety of fractional spins "per atom," a known property of transition metals. As just described, this version will be called *band magnetization* (BM). On the other hand, the theory could also be described in terms of Wannier functions (see Sec. 3 below), in which case exactly the same results occur, the only difference being that the spins are now associated with the Wannier functions on the atoms. We shall see that since these functions are not exact solutions of the one-electron problem they can be regarded as occupied to a fractional extent, in a manner exactly analogous to the filling up of the localized states in impurities.[3–5] This also gives, then, the result of fractional spins "per atom," but now the atom is understood in the sense of the Wannier functions on it. When band magnetization is rephrased in this manner, the interpretation of the effect of the exchange interaction, Eq. (1.1), is quite direct: It polarizes the electrons on the atoms (this is not an $sd$ polarization; it is entirely within the $d$ band). That is, in contrast to the AM picture, the redescribed band picture supposes that the exchange interaction between Wannier functions on different atoms does not simply align the local moments; it produces them in the first place, the alignment being taken for granted. Therefore we shall henceforth speak of this as *polarization magnetization* (PM).

Thus we interpret band magnetization in terms of local moments *induced* at the atom sites, and alignment magnetization in terms of *permanent* moments at the atom sites. The transition metals are of interest because they are in some sense midway between these two limiting cases. Now, although it may be possible to make a calculation which ignores the nature of the local moments and searches for the general solution to the problem, we should like in this paper to see if there can exist some criterion which would distinguish situations which are characterized by predominantly permanent local moments from situations which are characterized by predominantly induced local moments. In order to do this we have to have some model of what produces a local moment of the permanent type. Fortunately, in the recent literature[3–5] there has been a great deal of work on local moments on impurities that can be

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[1] J. C. Slater, Phys. Rev. **49**, 537 (1936).

[2] E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938).

[3] J. Friedel, Can. J. Phys. **34**, 1190 (1956). See also A. Blandin and J. Friedel, J. Phys. Radium **20**, 160 (1959).

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

[5] P. Wolff, Phys. Rev. **124**, 1030 (1961).

adapted. The model of the metal is simplified enormously by supposing that there is only one $d$ orbital. The other $d$ orbitals may have large effects[6,7] but to start we shall consider just one. Then Anderson's work[4] has indicated that local moments may be produced by the "correlation" term

$$H_{\mathrm{corr}}=\sum Un_{\mathbf{f}+}n_{\mathbf{f}-} \qquad (1.2)$$

in the Hamiltonian. This is one part of the $e^2/r$ interaction between the electrons (Wannier functions) of different spin on an atom. Here $n_{\mathbf{f}\pm}$ is the occupation number operator for the $d$-band Wannier functions of spin $\pm$ on the $\mathbf{f}$ site. The term has the effect that two electrons of different spin do not tend to be at the same atom, for if they are, an additional energy $U$ is formed. We shall regard all the internal mechanisms producing a local moment as being reduced to this simple mechanism. In the extreme case where there is no interaction between sites, the $U$ term will certainly produce a local moment, as follows directly from the work of Anderson. We shall call this the limit of *local magnetization* (LM).

One way to distinguish AM from PM, we have suggested above, is to decide whether the local moments at atom sites are permanent or induced. We now suggest that one way to distinguish whether the local moment is permanent or induced is to find out if the local moment can exist in, say, the $z$ direction if there are external torques tending to produce it in the $-z$ direction. That is, in the permanent case, a given local moment can *exist* both parallel to the crystal moment ($m$) and also antiparallel to it, for example. Thus, if we search for the stable moments relative to the $m$ direction, there will, in general, be *two* solutions (see Sec. 4), $M$ and $-M'$, say. On the other hand, if the local moment is induced by the environment, it can exist in only one direction (along $z$ but not $-z$, say). Thus we suggest that the problem of AM versus PM is to be reduced to whether there can exist two or one stable moments in the presence of a spin-polarizing moment coming from the environment. This environment will be adjusted to be as close as possible to what the real crystal presents. The heart of this argument is contained in the simple example explored in Sec. 4.

We shall select a Hamiltonian that exhibits the minimum number of terms required to exhibit AM, PM, and LM, namely

$$H=H_0+H_{\mathrm{spin}}+H_{\mathrm{corr}}, \qquad (1.3)$$

where $H_0$ contains all the one-electron terms. This is to be put in terms of the Wannier functions of the $d$ band, and the Bloch functions of the $s$ band. The one-electron problem

$$H_0(\mathbf{r}_i)\psi(\mathbf{r}_i)=E\psi(\mathbf{r}_i) \qquad (1.4)$$

is assumed to have solutions which are Bloch functions: $\psi_{\mathbf{k}}$, $E_{\mathbf{k}}$ for the $s$ band, and $\psi_\lambda$, $E_\lambda$ for the $d$ band. The $d$-band Wannier functions $a_{\mathbf{f}}(\mathbf{r})$ are then defined by

$$\psi_\lambda(r)=\sum_{\mathbf{f}} \exp(i\boldsymbol{\lambda}\cdot\mathbf{f})a_{\mathbf{f}}(\mathbf{r}). \qquad (1.5)$$

In second quantization, $H_0$ is diagonal in the Bloch states, but not so in the Wannier states. There appear the nondiagonal matrix elements

$$V_{\mathbf{f}'\mathbf{f}}\equiv\int a_{\mathbf{f}'}{}^*H_0a_{\mathbf{f}}d^3r. \qquad (1.6)$$

There is, however, no interaction between $s$ and $d$ bands in the one-electron terms since

$$V_{\mathbf{kf}}\equiv\int\psi_{\mathbf{k}}(\mathbf{r})^*H_0a_{\mathbf{f}}(\mathbf{r})d^3r=0. \qquad (1.7)$$

Thus, in second quantization, $H_0$ becomes

$$H_0=\sum E_{\mathbf{k}}n_{\mathbf{k}}+\sum V_{\mathbf{f}'\mathbf{f}}n_{\mathbf{f}'\mathbf{f}}, \qquad (1.8)$$

where we have defined a notation

$$\begin{aligned} n_{\mathbf{f}'\mathbf{f}}&=\sum_\sigma n_{\mathbf{f}'\mathbf{f}\sigma}=\sum_\sigma c_{\mathbf{f}'\sigma}{}^\dagger c_{\mathbf{f}\sigma}, \\ n_{\mathbf{f}}&=n_{\mathbf{ff}}, \end{aligned} \qquad (1.9)$$

using creation operators $c^\dagger$ and destruction operators $c$, and where $\sigma$ means ($\pm$), i.e., spin. For completeness, we add here the corresponding notation[8] that will be used when we come to spin-spin interactions

$$\begin{aligned} S_{\mathbf{f}'\mathbf{f}+}&=c_{\mathbf{f}'\mathbf{f}}{}^\dagger c_{\mathbf{f}-}, \\ S_{\mathbf{f}'\mathbf{f}-}&=c_{\mathbf{f}'-}{}^\dagger c_{\mathbf{f}+}, \\ S_{\mathbf{f}'\mathbf{f}z}&=\tfrac{1}{2}(n_{\mathbf{f}'\mathbf{f}+}-n_{\mathbf{f}'\mathbf{f}-}), \\ S_{\mathbf{f},i}&=S_{\mathbf{ff},i} \quad (i=+,-,z). \end{aligned} \qquad (1.10)$$

This latter is useful in writing a dot product:

$$\begin{aligned} 2S_{\mathbf{f}'\mathbf{f}}\cdot S_{\mathbf{g}'\mathbf{g}}&=2\sum_{xyz} S_{\mathbf{f}'\mathbf{f}x}S_{\mathbf{g}'\mathbf{g}x} \\ &=S_{\mathbf{f}'\mathbf{f}+}S_{\mathbf{g}'\mathbf{g}-}+S_{\mathbf{f}'\mathbf{f}-}S_{\mathbf{g}'\mathbf{g}+}+2S_{\mathbf{f}'\mathbf{f}z}S_{\mathbf{g}'\mathbf{g}z}. \end{aligned} \qquad (1.11)$$

The Hamiltonian[8a] in Eq. (1.3) has all the parts that go to make up AM, PM, and LM. In the first, only $H_{\mathrm{spin}}$ is needed; in the second $H_0+H_{\mathrm{spin}}$ is needed, and in the third, we need the diagonal part of $H_0$ (in terms of the Wannier basis) plus $H_{\mathrm{ccrr}}$. In Sec. 3 we demonstrate how these various sub-Hamiltonians lead to the designated types of magnetization. In Sec. 4, we link up the diagonal part of $H_0$, and $H_{\mathrm{spin}}$, and $H_{\mathrm{corr}}$, and show how the criterion mentioned above to distinguish AM from PM enters. In Sec. 5, we generalize the criterion calculation to the situation where the off-diagonal elements of $H_0$ are also included, and in Appendix A we consider a still more accurate approximation in solving this aspect of the problem. Section 6 is more or less

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[6] W. M. Lomer, Proc. Phys. Soc. (London) **82**, 156 (1963).

[7] D. C. Mattis, IBM research paper RC-1298, 1964 (to be published).

[8] M. Bailyn, Phys. Rev. **137**, A1914 (1965).

[8a] This Hamiltonian is essentially the one used by D. C. Mattis, Phys. Rev. **132**, A2521 (1963).

a digression to indicate what happens to an AM calculation once one tries to take into account off-diagonal terms in $H_0$.

The general method used in approaching all these problems is the Green's function method,[9] for which the appropriate definitions and equations are set down in Sec. 2, along with a discussion of moments and averages.

In the rest of this introductory section, we shall describe how the Wannier functions can come to be regarded as analogous to the resonant states of Friedel and Anderson, and in fact how each Wannier function can be imagined as a miniature replica of the whole *d* band. To do this, we shall consider the Hamiltonian to be just $H_0$, and ask for the probability of occupation of the *d*-band Wannier function $\mathbf{f}$, $\sigma$. We shall borrow from the $G$ formalism of Eqs. (2.12)–(2.15) of Sec. 2 to do this. The definitions used there will be assumed in what follows here. The probability of occupation of the $\mathbf{f}$, $\sigma$ state is simply related to the diagonal Green's function $G_\sigma(\mathbf{f},\mathbf{f}|E)$ [see Eq. (2.14)], and the equation for this $G$ using $H=H_0$ is from Eq. (2.15):

$$i\frac{\partial}{\partial t}G_\sigma(\mathbf{f},\mathbf{f}'|t-t')=-\delta(t-t')\delta_{\mathbf{f},\mathbf{f}'}+\sum_{\mathbf{f}''}V_{\mathbf{f}\mathbf{f}''}G_\sigma(\mathbf{f}''\mathbf{f}'|t-t') \qquad (1.12)$$

which can be solved using energy and lattice Fourier components such as

$$V(\boldsymbol{\nu})=\sum\exp[i\boldsymbol{\nu}\cdot(\mathbf{f}-\mathbf{f}')]V_{\mathbf{f}\mathbf{f}'}. \qquad (1.13)$$

The answer is easily [see Eq. (3.10)]

$$\langle n_{\mathbf{f}\sigma}\rangle=N^{-1}\sum_{\nu}f(V(\boldsymbol{\nu})),$$
$$\equiv\int dEA(E)f(E)\cdots E=V(\boldsymbol{\nu}), \qquad (1.14)$$

where $f(E)$ is the Fermi function containing the Fermi energy $E_F$. Thus, Eq. (1.14) has the interpretation that the spectral function $A(E)$ for the Wannier functions[10] is just the density of one-electron *d* band Bloch states. The description here is then quite similar to that of the localized resonant states (sometimes called "virtual bound" states) for impurities, as discussed by Friedel,[3] Anderson[4] (whose formulation was the pattern for our derivation), and Wolff.[5] The similarity to Ref. 4 comes from the fact that our $H_0$ plays the role that Anderson's *sd* interaction did. In the present paper we do not contemplate any *sd* interaction at all, and in any case there is rigorously, in transition metals, no *sd* interaction of the Anderson type (see Sec. 7).[10a]

In the result, Eq. (1.14), there is no dependence on spin on the right-hand side. For this reason, Wannier functions of both spins are filled to the same level $E_F$ starting from the same lowest energy. $E_F$ is itself determined by normalization of all the electrons, including the conduction electrons. If the latter are the main factor, then $E_F$ can at least approximately be regarded as a fixed parameter as far as filling up of the *d*-band Wannier function goes. This filling up is a miniature, in fact, of the crystal behavior: When the band description is used, it is the band that gets filled up; when the Wannier functions are used, it is they that get filled up in exactly the same way [$A(E)$ being the *d*-band density of states] and to exactly the same extent.

Thus when $H_{\text{corr}}$ is added we may expect unequal filling of the two Wannier functions (extrapolating from the work on impurity problems), and when $H_{\text{spin}}$ is added, we also expect an unequal filling, the latter equivalent to BM as shown in Sec. 3. Further, when the filling is unequal, we interpret the result as a local moment on the atom, since the Wannier functions are localized on (or near) the atom. Thus, if BM (or PM as we shall henceforth denote this type of magnetization) exhibits a Curie point,[2] our interpretation leads to the notion that above the Curie point there are no local moments while below there are both local moments and a moment for the crystal as a whole. The distinction between crystal and local moments is discussed in Sec. 2. Perhaps this interpretation has something to do with the hypothesis of Wilkinson *et al.*[11] concerning just this behavior of local moments in chromium.

There have been a number of papers on closely related problems using similar methods. Some of these are concerned with the problem of impurities in a metal, in which the *sd* interaction of Anderson plays an important role. Suhl and Fredkin[12] calculated the partition function directly starting from Anderson's Hamiltonian. One could do the same (or at least attempt it) starting from Eq. (1.3) above, but we wished to use Green's function theory, and further, we wished to be able to say something about local moments even when there is no crystal moment, something that cannot be done on Suhl and Fredkin's approach, as they point out.

Kim and Nagaoka[13] have considered the *sd* exchange interaction along with the Anderson *sd* mixing interaction, and have looked at the problem of many, randomly distributed, impurities interacting through such *sd* terms. It is known that the *sd* exchange interaction gives an effective ion-ion interaction of the $H_{\text{spin}}$-type between impurities, and that the *sd* mixing term

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[9] For Green's function methods, see V. L. Bonch-Bruevich and S. V. Tyablikov, ***The Green's Function Method in Statistical Mechanics*** (North-Holland Publishing Company, Amsterdam, 1962).

[10] See Ref. 9, pp. 13, 14 and Eq. (5.3). We call the numerator in Eq. (5.3) the "spectral function." This corresponds to the definition used in L. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin Company, Inc., New York, 1962), Eqs. (1)–(14).

[10a] If *approximate* *k*-state functions are used, then a mixing *sd* term does appear.

[11] M. K. Wilkinson, E. O. Wollan, W. C. Koehler, and J. W. Cable, Phys. Rev. **127**, 2080 (1962).

[12] H. Suhl and D. R. Fredkin, Phys. Rev. **131**, 1063 (1963).

[13] D. Kim and Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **30**, 743 (1963).

gives an effective $V_{\mathbf{f}'\mathbf{f}}$ term between impurities; hence their problem begins to resemble ours to some extent. They find in fact that the ordering of the moments has an effect on the local moment magnitude, just as we do. In a number of respects their paper bears a strong relevance to ours, although they were looking specifically at *sd* effects, which do not enter our model at all.

Alexander and Anderson[14] have considered the two-impurity problem, taking into account an *sd* mixing term and a term of the type in Eq. (1.6) above, as well as $H_{\text{corr}}$.

D. C. Mattis[8a] has considered the same Hamiltonian as ours and found a detailed spin-wave spectrum, comparable to the results in Sec. 6. His paper is thus closely related to ours.

In the next section, we shall define the moments, and the Green's functions appropriate to the calculation of them.

## 2. MOMENTS, AVERAGES, AND GREEN'S FUNCTIONS

The crystal moment $m_\sigma$ and the spin magnitude $\mathcal{S}$ are considered to arise from the properties of the *d*-band Wannier functions on the various atoms. We limit ourselves in this paper to just one *d* band, for which the Wannier states on the **f** site are called simply "**f**$\sigma$," ($\sigma=\pm$). Then

$$\begin{aligned} m_\sigma &= N^{-1}\sum_{\mathbf{f}}\langle n_{\mathbf{f}\sigma}-n_{\mathbf{f},-\sigma}\rangle \\ &= N^{-1}\sum\langle n_{\mathbf{f}\sigma}(1-n_{\mathbf{f},-\sigma})-n_{\mathbf{f},-\sigma}(1-n_{\mathbf{f},\sigma})\rangle, \end{aligned}\tag{2.1}$$

$$\mathcal{S}^2=\langle \mathbf{S}_\mathbf{f}\cdot\mathbf{S}_\mathbf{f}\rangle=3\langle S_{\mathbf{f}z}S_{\mathbf{f}z}\rangle,\tag{2.2}$$

where the grand canonical average is meant:

$$\langle X\rangle=\frac{\sum_{\mathfrak{N}}\langle\mathfrak{N}|\exp(-\beta H+\mu N)X|\mathfrak{N}\rangle}{\sum_{\mathfrak{N}}\langle\mathfrak{N}|\exp(-\beta H+\mu N)|\mathfrak{N}\rangle}.\tag{2.3}$$

The sums are over all configurations $\mathfrak{N}$ of the occupations of the $2N$ states $n_{\mathbf{f}_1+}n_{\mathbf{f}_1-}n_{\mathbf{f}_2+}\cdots$; $\beta=(kT)^{-1}$; and $\mu$ is the chemical potential.

These definitions can be rewritten using Eqs. (1.9) and (1.10) as follows:

$$m\equiv m_+=N^{-1}\sum\langle S_{\mathbf{f}+}S_{\mathbf{f}-}-S_{\mathbf{f}-}S_{\mathbf{f}+}\rangle,\tag{2.4}$$

$$S^2\equiv\tfrac{4}{3}\mathcal{S}^2=\langle(n_{\mathbf{f}+}-n_{\mathbf{f}-})^2\rangle=\langle S_{\mathbf{f}+}S_{\mathbf{f}-}+S_{\mathbf{f}-}S_{\mathbf{f}+}\rangle.\tag{2.5}$$

$S$ is introduced because of its convenient normalization. Notice the simple relation between the two types of moments, $S^2$ and $m$, as shown on the right in these last equations.

It follows immediately from the above that

$$m^2\leqslant S^2.\tag{2.6}$$

The proof follows from the inequalities

$$1\geqslant\langle n_{\mathbf{f}+}(1-n_{\mathbf{f}-})\rangle\equiv P=\langle S_{\mathbf{f}-}S_{\mathbf{f}+}\rangle=\langle S_{\mathbf{f}+}{}^\dagger S_{\mathbf{f}+}\rangle\geqslant0,\tag{2.7}$$

$$1\geqslant\langle n_{\mathbf{f}-}(1-n_{\mathbf{f}+})\rangle\equiv Q=\langle S_{\mathbf{f}-}{}^\dagger S_{\mathbf{f}-}\rangle\geqslant0,\tag{2.8}$$

valid since among other things all averages of the form $\langle L^\dagger L\rangle$ are non-negative. But, then

$$m_+{}^2=(P-Q)^2\leqslant|P-Q|\leqslant P+Q=S^2,\tag{2.9}$$

the first inequality occurring because $|P-Q|<1$, the second because both $P$ and $Q$ are positive. This completes the proof. From this it follows that if $S=0$, then $m_+=0$, and if $m_+\neq0$, then $S\neq0$. Or in words: If no moment exists on any atom, then no moment exists in the crystal; and, if there exists a crystal moment, then there must also exist local moments. These are certainly necessary conditions on the problem.

Again, because of the definitions in Eqs. (2.4) and (2.5), we can get an explicit relation between $m$ and $S$:

$$m_+=S^2-2\langle S_{\mathbf{f}-}S_{\mathbf{f}+}\rangle=2\langle S_{\mathbf{f}+}S_{\mathbf{f}-}\rangle-S^2.\tag{2.10}$$

In the standard calculation of the crystal moment $m$, the local moment is chosen so that either **f**+ is occupied, and not **f**−; or **f**− is occupied and not **f**+, whence $S=1$. In that case, which we call the case of "fixed spin," Eq. (2.10) becomes

$$m_+=2\langle S_{\mathbf{f}+}S_{\mathbf{f}-}\rangle-1.\tag{2.11}$$

The calculation of $m$ on this basis has been made by Green's function methods with great success.[9] It corresponds to the AM approximation defined in the Introduction. The method is, however, more general, provided one knows how to estimate $S$.

To evaluate the averages two types of Green's functions may be employed. First there are the functions that lead to a direct evaluation of $\langle n_{\mathbf{f}\pm}\rangle$, namely

$$\begin{aligned} G_\sigma{}^\pm(\mathbf{f},\mathbf{f}'|t-t')&\equiv\pm i\theta(\pm t\mp t')\langle[c_{\mathbf{f}\sigma}(t),c_{\mathbf{f}'\sigma}(t')^\dagger]_+\rangle \\ &\equiv\langle\langle c_{\mathbf{f}\sigma}(t)|c_{\mathbf{f}'\sigma}{}^\dagger(t')\rangle\rangle_{(+)}{}^\pm; \end{aligned}\tag{2.12}$$

$\theta$ being a step function, and the notation identical to that of Ref. 9. The subscripts $(\pm)$ refer to the type of commutator employed. The $\pm$ superscripts denote functions that have energy components analytic in different parts of the complex energy plane, but the combination

$$\begin{aligned} G_\sigma(\mathbf{f},\mathbf{f}'|E_0\pm iE_1)=(2\pi)^{-1}&\int_{-\infty}^{\infty}d(t-t')G_\sigma{}^\pm(\mathbf{f},\mathbf{f}'|t-t') \\ &\times\exp[i(E_0\pm iE_1)(t-t')]\cdots E_1\geqslant0 \end{aligned}\tag{2.13}$$

may be regarded as a single function defined over all $E$ space, with a discontinuity along the real axis. We henceforth leave superscripts off.

The desired $z$ component of the moment is then by standard arguments

$$\begin{aligned} M_f&\equiv\langle n_{\mathbf{f}+}\rangle-\langle n_{\mathbf{f}-}\rangle; \\ \langle n_{\mathbf{f}\sigma}\rangle&=\int_{-\infty}^{\infty}dEf(E)2\,\mathrm{Im}G_\sigma(\mathbf{f},\mathbf{f}|E+i0), \end{aligned}\tag{2.14}$$

where $f(E)$ is the Fermi function. This type of Green's function corresponds to what Anderson used to get local moments, as shown by Kim and Nagaoka.[13] We shall

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[14] S. Alexander and P. W. Anderson, Phys. Rev. **133**, A1594 (1964).

find also that it will be giving us information about the local moments. To determine $G$ itself, one solves the equation of motion

$$i(\partial/\partial t)G_\sigma(\mathbf{f},\mathbf{f}'|t-t')=-\delta(t-t')\delta_{\mathbf{f},\mathbf{f}'} -\langle\langle[H,c_{\mathbf{f}\sigma}(t)]_-|c_{\mathbf{f}'\sigma}(t')^\dagger\rangle\rangle_{(+)}. \qquad (2.15)$$

For the crystal moment, one usually computes directly the averages of the type in Eqs. (2.4) and (2.5). We shall have occasion to use the rather more general Green's functions

$$g^\pm(\mathbf{ff}'',\mathbf{f}'|t-t')\equiv\pm i\theta(\pm t\mp t')\langle[S_{\mathbf{ff}'',+}(t),S_{\mathbf{f}',-}(t')]_-\rangle \equiv\langle\langle S_{\mathbf{ff}'',+}(t)|S_{\mathbf{f}',-}(t')\rangle\rangle_{(-)}{}^\pm \qquad (2.16)$$

with energy components

$$g(\mathbf{f},\mathbf{f}'',\mathbf{f}'|E_0\pm iE_1)=\frac{1}{2\pi}\int d(t-t')g^\pm(\mathbf{ff}'',\mathbf{f}'|t-t') \times\exp[i(E_0\pm iE_1)(t-t')]\cdots E_1\geqslant 0, \qquad (2.17)$$

but for the purpose of the averages in Eqs. (2.4) and (2.5), all we need are

$$g(\mathbf{f},\mathbf{f}'|E)\equiv g(\mathbf{ff},\mathbf{f}'|E). \qquad (2.18)$$

Then, by standard arguments,

$$\langle S_{\mathbf{f}+}S_{\mathbf{f}-}\rangle=\int dE(1-e^{-\beta E})^{-1}2\,\mathrm{Im}g(\mathbf{f},\mathbf{f}|E). \qquad (2.19)$$

The other average $\langle S_{\mathbf{f}-}S_{\mathbf{f}+}\rangle$ differs from this by having an extra factor $\exp(-\beta E)$ in the integrand.[15] The averages in Eqs. (2.4) and (2.5) are then

$$m_+=\int_{-\infty}^{\infty} dE2\,\mathrm{Im}g(\mathbf{f},\mathbf{f}|E), \qquad (2.20)$$

$$S^2=\int_{-\infty}^{\infty} dE[2\,\mathrm{Im}g(\mathbf{f},\mathbf{f}|E)]\coth\tfrac{1}{2}\beta E. \qquad (2.21)$$

It would seem as if we could get both $m$ and $S$ from these results, but that is not so, for the Green's functions turn out to be functions of $m$ in such a way that Eq. (2.20) is nothing more than the identity $m=m$ (in the standard calculation: see Sec. 3). Further, although Eq. (2.21) looks like an expression for $S^2$, in fact the right-hand side is a function of $m$, and the relation is usually conceived as an equation for $m$ as a function of the temperature $T$, with $S^2$ as a parameter, as we indicated apropos of Eqs. (2.10) and (2.11).

To obtain the Green's function, one solves

$$i(\partial/\partial t)g(\mathbf{ff}'|t-t')=-\delta(t-t')\delta_{\mathbf{ff}'}m_+ -\langle\langle[H,S_{\mathbf{f}+}(t)]_-|S_{\mathbf{f}',-}(t')\rangle\rangle_{(-)}. \qquad (2.22)$$

This completes the outline of definitions and averages to be used.

## 3. STANDARD CALCULATIONS

In this section we shall discuss (1) the standard case of $d$-band magnetization, but handled here in terms of the Wannier functions; the PM situation of the Introduction; (2) the simplest local moment calculation; the LM situation of the Introduction; and (3) magnetism via the Heisenberg interaction and with fixed local spins, as worked in the basic Green's function literature; the AM situation of the Introduction.

For PM, we use

$$H=\sum V_{\mathbf{f}'\mathbf{f}}n_{\mathbf{f}'\mathbf{f}}-2\sum A(\mathbf{f}-\mathbf{f}')S_{\mathbf{f}}\cdot S_{\mathbf{f}'}, \qquad (3.1)$$

which corresponds to atoms interacting via Bloch terms and via a Heisenberg interaction. Equation (2.15) becomes

$$i(\partial/\partial t)G_\sigma(\mathbf{ff}'|t-t')=-\delta(t-t')\delta_{\mathbf{ff}'}+\sum V_{\mathbf{ff}''}G_\sigma(\mathbf{f}'',\mathbf{f}'|t-t') -\sum_{\mathbf{f}''\neq\mathbf{f}}A(\mathbf{f}-\mathbf{f}'')\langle\langle\tfrac{1}{2}(n_{\mathbf{f}''\sigma}-n_{\mathbf{f}'',-\sigma})c_{\mathbf{f},\sigma}+S_{\mathbf{f}'',-\sigma}c_{\mathbf{f},-\sigma}|c_{\mathbf{f}'\sigma}(t')^\dagger\rangle\rangle_{(+)}. \qquad (3.2)$$

We chain break according to the Hartree-Fock approximation:

$$\text{last term in Eq. (3.2)}\rightarrow-\tfrac{1}{2}[\sum A(\mathbf{f}-\mathbf{f}'')\langle n_{\mathbf{f}'',\sigma}-n_{\mathbf{f}'',-\sigma}\rangle]G_\sigma(\mathbf{ff}''|t-t') -[\sum_{\mathbf{f}''}A(\mathbf{f}-\mathbf{f}'')\langle S_{\mathbf{f}'',-\sigma}\rangle]G_{-\sigma,\sigma}(\mathbf{f},\mathbf{f}'|t-t'), \qquad (3.3)$$

where

$$G_{-\sigma,\sigma}(\mathbf{ff}'|t-t')=\langle\langle c_{\mathbf{f},-\sigma}(t)|c_{\mathbf{f}'}{}^\dagger{}_{,\sigma}(t')\rangle\rangle_{(+)}. \qquad (3.4)$$

We shall suppose that the second sum in Eq. (3.3) is zero, since we shall at the least assume that the magnetization of any neighbor shell is the same as that of the lattice as a whole, and we assume the crystal magnetization is in the $z$ direction. ($S_{\mathbf{f},\sigma}$ is a linear combination of the components in the $x$ and $y$ directions.) For the same reason we shall replace $\langle n_{\mathbf{f}\sigma}-n_{\mathbf{f},-\sigma}\rangle$ in the first sum in Eq. (3.3) by $m_\sigma$. Thus Eq. (3.2) reduces to

$$[E+\tfrac{1}{2}A'(0)m_\sigma]G_\sigma(\mathbf{ff}'|E) =-\frac{1}{2\pi}\delta_{\mathbf{f},\mathbf{f}'}+\sum V_{\mathbf{ff}''}G_\sigma(\mathbf{f}'',\mathbf{f}'|E), \qquad (3.5)$$

after the energy Fourier component is taken. Here

$$A'(\mathbf{v})=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]A(\mathbf{f}-\mathbf{f}'). \qquad (3.6)$$

Similarly, as in Eq. (1.13), we shall use

$$V(\mathbf{v})=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]V_{\mathbf{ff}'}. \qquad (3.7)$$

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[15] Reference 9, Eq. (2.8).

We solve Eq. (3.5) by taking the Fourier components

$$G_\sigma(\mathbf{v}|E)=\sum \exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma(\mathbf{ff}'|E). \quad (3.8)$$

The answer is

$$G_\sigma(\mathbf{v}|E)=-(2\pi)^{-1}[E-V(\mathbf{v})+\tfrac{1}{2}A'(0)m_\sigma]^{-1}. \quad (3.9)$$

Then, from Eq. (2.14),

$$\langle n_{\mathbf{f}\sigma}\rangle=N^{-1}\sum_{\nu} f(V(\mathbf{v})-\tfrac{1}{2}A'(0)m_\sigma). \quad (3.10)$$

Now, if we can treat $E_F$ as a given parameter in Eq. (3.10), and if we invoke a density $n(V)$ of states

$$N^{-1}\sum_{\nu}\rightarrow\int_0^{V_{\max}} n(V)dV, \quad (3.11)$$

then Eq. (3.10) provides

$$\begin{aligned}M_f&\equiv\langle n_{\mathbf{f}+}\rangle-\langle n_{\mathbf{f}-}\rangle\\&=\int dVn(V)[f(V-\tfrac{1}{2}A'(0)m_+)-f(V+\tfrac{1}{2}A'(0)m_+)],\end{aligned} \quad (3.12)$$

$$\begin{aligned}\langle n_{\mathbf{f}}\rangle&\equiv\langle n_{\mathbf{f}+}\rangle+\langle n_{\mathbf{f}-}\rangle\\&=\int dVn(V)[f(V-\tfrac{1}{2}A'(0)m_+)+f(V+\tfrac{1}{2}A'(0)m_+)].\end{aligned} \quad (3.13)$$

These two equations form the basis of Stoner's theory of magnetism [see Eqs. (2.10), (2.11) in Ref. 2]. The only difference is that we have the description in miniature as it were, in terms of the Wannier functions, whereas he talks in terms of the crystal as a whole.

The result, Eq. (3.10), corresponds to filling up a sub-band of particular spin to a certain extent; but, in our case, it corresponds to an identical filling up of the Wannier function of particular spin.

Note that there is always the solution $M=0$. If there is another solution $M'$, say, then there is also $-M'$ as a solution. Thus, the calculation does not distinguish between up and down magnetizations.

This completes the discussion of PM. We turn now to LM. For this we use the Hamiltonian

$$H=V_0(n_{\mathbf{f}+}+n_{\mathbf{f}-})+Un_{\mathbf{f}+}n_{\mathbf{f}-}, \quad (3.14)$$

corresponding to an isolated atom with internal electrostatic interaction between spin states. The Green's function equation, Eq. (2.15), becomes

$$\begin{aligned}[i(\partial/\partial t)-V_0]G_\sigma(\mathbf{ff}|t-t')=&-\delta(t-t')\\&-U\langle\langle n_{\mathbf{f},-\sigma}c_{\mathbf{f}\sigma}|c_{\mathbf{f}\sigma}(t')^\dagger\rangle\rangle_{(+)}.\end{aligned} \quad (3.15)$$

If we chain break according to

$$\langle\langle n_{\mathbf{f},-\sigma}c_{\mathbf{f}\sigma}|c_{\mathbf{f}\sigma}(t')^\dagger\rangle\rangle_{(+)}\cong\langle n_{\mathbf{f},-\sigma}\rangle G_\sigma(\mathbf{f},\mathbf{f}|t-t'), \quad (3.16)$$

where $\langle n_{\mathbf{f},-}\rangle$ is an average of the occupation of the $\mathbf{f}$, $-$ state, and take energy Fourier components, we get

$$G_\sigma(\mathbf{ff}|E)=-(2\pi)^{-1}[E-V_0-U\langle n_{\mathbf{f},-\sigma}\rangle]^{-1}. \quad (3.17)$$

Then from Eq. (2.14)

$$\langle n_{\mathbf{f},\sigma}\rangle=f(V_0+U\langle n_{\mathbf{f},-\sigma}\rangle). \quad (3.18)$$

We can write this in a form analogous to Eqs. (3.12), (3.13):

$$\begin{aligned}M_{\mathbf{f}}\equiv\langle n_{\mathbf{f}+}\rangle-\langle n_{\mathbf{f}-}\rangle=&f(V_0+\tfrac{1}{2}U\langle n_{\mathbf{f}}\rangle-\tfrac{1}{2}UM_{\mathbf{f}})\\&-f(V_0+\tfrac{1}{2}U\langle n_{\mathbf{f}}\rangle+\tfrac{1}{2}UM_{\mathbf{f}}),\end{aligned} \quad (3.19)$$

$$\begin{aligned}\langle n_{\mathbf{f}}\rangle\equiv\langle n_{\mathbf{f}+}\rangle+\langle n_{\mathbf{f}-}\rangle=&f(V_0+\tfrac{1}{2}U\langle n_{\mathbf{f}}\rangle-\tfrac{1}{2}UM_{\mathbf{f}})\\&+f(V_0+\tfrac{1}{2}U\langle n_{\mathbf{f}}\rangle+\tfrac{1}{2}UM_{\mathbf{f}}).\end{aligned} \quad (3.20)$$

These are again two equations in two unknowns. It is sometimes easier to regard Eq. (3.18) as the two equations, in which case the solutions can be exhibited as the intersections of the two curves $n_{\mathbf{f},+}(n_{\mathbf{f},-})$ and $n_{\mathbf{f},-}(n_{\mathbf{f},+})$, leaving off the average signs. These curves are just two Fermi functions.

It can easily be seen that for small $U$ there is one solution only, $M=0$, whereas, for larger $U$, there are three, $M=0$, $M=M'$, say, and $M=-M'$. Again, the calculation has not averaged over the orientations of the moment. For $U$ sufficiently large, the two extreme solutions $M'$ and $-M'$ are approximately $\pm1$ and fairly independent of whatever interactions exist *between* atoms. This then tells us nothing about the crystal moment, it tells that there is a local moment which is more or less fixed in magnitude. This is the LM limit, as discussed in the Introduction.

Finally, if the local moment magnitudes are in fact firmly fixed, there still is the problem of how to calculate the crystal magnetization resulting from the alignment of the local moments. For this problem the Hamiltonian is

$$H=H_{\text{spin}}=-2\sum A(\mathbf{f}-\mathbf{f}')\mathbf{S}_{\mathbf{f}}\cdot\mathbf{S}_{\mathbf{f}'}, \quad (3.21)$$

and the second Green's function formalism of Sec. 2 is utilized. From Eq. (2.22)

$$\begin{aligned}i(\partial/\partial t)g(\mathbf{ff}'|t-t')=&-\delta(t-t')\delta_{\mathbf{f},\mathbf{f}'}m_++2\sum A(\mathbf{f}-\mathbf{f}'')\\&\times\langle\langle(n_{\mathbf{f}+}-n_{\mathbf{f}-})(S_{\mathbf{f}+}-S_{\mathbf{f}''+})|S_{\mathbf{f}',-}(t')\rangle\rangle_{(-)}.\end{aligned} \quad (3.22)$$

Making the chain break according to

$$\begin{aligned}\langle\langle(n_{\mathbf{f}+}-n_{\mathbf{f}-})&(S_{\mathbf{f}+}-S_{\mathbf{f}''+})|S_{\mathbf{f}',-}(t')\rangle\rangle_{(-)}\\&\cong m_+[g(\mathbf{ff}'|t-t')-g(\mathbf{f}'',\mathbf{f}'|t-t')],\end{aligned} \quad (3.23)$$

and taking energy Fourier components, we find

$$\begin{aligned}Eg(\mathbf{ff}'|E)=&-(1/2\pi)\delta_{\mathbf{f},\mathbf{f}}m_+\\&+2m_+\sum_{\mathbf{f}''}A(\mathbf{f}-\mathbf{f}'')[g(\mathbf{ff}'|E)-g(\mathbf{f}''\mathbf{f}'|E)].\end{aligned} \quad (3.24)$$

Taking the lattice Fourier component

$$g(\mathbf{v}|E)=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]g(\mathbf{ff}'|E), \quad (3.25)$$

we can solve

$$g(\mathbf{v}|E)=-(2\pi)^{-1}m_+[E-2m_+(A'(0)\cdot A'(\mathbf{v}))]^{-1}. \quad (3.26)$$

Substitution into Eq. (2.21) gives

$$S^2 = N^{-1} \sum_{\nu} m_+ \coth(\beta m_+ [A'(0) - A'(\mathbf{\nu})]) . \quad (3.27)$$

And Eq. (2.20) is just $m = m$. These are the standard Green's function results. They constitute the AM limit of the Introduction. Notice that for every solution $m_+$ there is also a solution $-m_+$.

## 4. THE CRITERION CALCULATION I

In the previous section, the simplest versions of the basic types of magnetization calculations were reviewed. Band magnetization is usually not associated with local moments, but rather with itinerant electrons which carry the spins. However, when put in terms of Wannier functions, the magnetization can be reinterpreted as the spin polarizing of the Wannier functions on a given atom by interactions with neighboring atoms.[8a] If this interaction is turned off, there is no net moment associated with any atom. On the other hand, alignment magnetization is usually regarded as the effect of the permanent moments on neighbor atoms in attempting to line up the given atom's permanent moment. If the interaction is turned off, then there are still the local moments $M$ on the atoms, produced by interactions within each atom.

Thus we are led to distinguish PM from AM on the basis of whether the local moment is induced or permanent. To define a permanent local moment on atom $A$, say, we shall imagine that the moments of the other atoms of the crystal are "frozen" either parallel or antiparallel to the crystal moment $m$ in such a way that every neighbor shell of $A$ has an averaged moment equal to the true crystal moment $m$. (Alternatively, we could replace the Heisenberg interaction by an external magnetic field $\mathcal{H}$ designed to give the same molecular field at the atom $A$.) If, then, a calculation of the local moment on $A$ exhibits two stable states, one parallel to $m$, one antiparallel to $m$, the two not necessarily equal in magnitude, then we shall say that the moment on $A$ is "permanent." If only one stable moment (parallel) is possible, then the local moment at $A$ will be called "induced." (See below for an example.)

In this way, we propose a criterion between when PM is the appropriate type of magnetization and when AM is the appropriate type. As always, in such arguments, the extremes and situations close to the extremes are the situations best described by the criterion. Nevertheless, we shall propose that some idea of the transition can be obtained by continuing the distinction to more intermediate situations.

To indicate how this criterion appears, let us consider the following Hamiltonian:

$$H = \sum V_0 (n_{\mathbf{f}+} + n_{\mathbf{f}-}) + \sum U n_{\mathbf{f}+} n_{\mathbf{f}-} \\ -2 \sum A(\mathbf{f} - \mathbf{f}') \mathbf{S}_{\mathbf{f}} \cdot \mathbf{S}_{\mathbf{f}'} , \quad (4.1)$$

containing both a term trying to form a local moment through internal interactions (the $U$ term) and the usual Heisenberg term.

We search for the local moment by calculating drectly the averages for $n_{\mathbf{f}\sigma}$. Equation (2.15) becomes

$$\left( i \frac{\partial}{\partial t} - V_0 \right) G_\sigma (\mathbf{ff} | t - t') = -\delta(t - t') - U \langle\langle n_{\mathbf{f},-\sigma} c_{\mathbf{f}\sigma} | c_{\mathbf{f}\sigma}^\dagger (t') \rangle\rangle_+ \\ - \sum A(\mathbf{f} - \mathbf{f}'') \langle\langle [\tfrac{1}{2} (n_{\mathbf{f}'',\sigma} - n_{\mathbf{f}'',-\sigma}) c_{\mathbf{f}\sigma} + S_{\mathbf{f}'',\sigma} c_{\mathbf{f},-\sigma}] | c_{\mathbf{f}'\sigma}^\dagger (t') \rangle\rangle_+ . \quad (4.2)$$

Chain breaking as in Eq. (3.16) for the $U$ term, and as in Eq. (3.3) for the $A$ term, we get

$$G_\sigma (\mathbf{ff} | E) = -(2\pi)^{-1} [E - V_0 - U \langle n_{\mathbf{f},-\sigma} \rangle \\ + \tfrac{1}{2} A'(0) m_\sigma ]^{-1} , \quad (4.3)$$

where we used the stipulation that each shell has an averaged moment $m$. Thus

$$\langle n_{\mathbf{f}\sigma} \rangle = f(V_0 + U \langle n_{\mathbf{f},-\sigma} \rangle - \tfrac{1}{2} A'(0) m_\sigma) . \quad (4.4)$$

This is the mathematical result, whose physical implications we shall now try to assess.

Let us treat the Fermi function as a step function. Then $\langle n_{\mathbf{f}+} \rangle$ can be either 1 or 0 depending on whether the argument in the Fermi function, Eq. (4.4), is either less than $E_F$ or greater than $E_F$. Similarly for $\langle n_{\mathbf{f},-} \rangle$. We assume $m_+ > 0$. By then looking for when $M = \langle n_{\mathbf{f},+} \rangle - \langle n_{\mathbf{f},-} \rangle$ is 1, 0, $-1$ we get the diagram of Fig. 1, giving us possible $M$'s as functions of $m$. These are the stable solutions referred to above. Here we see that sometimes the atom can have two stable moments, oriented oppositely, and sometimes only one. If two moments are possible in an environment characterized by $m$, then, as stated above, we regard the local moment as sufficiently strong to be labeled "permanent," and conclude that an AM calculation is appropriate. If, however, only one stable moment is possible, then we conclude that production of the local moment depends entirely on the external interactions, and that the appropriate procedure is to set $M = m$, and look for the self-consistent solutions, i.e., to perform a PM calculation. In the former case, we still have the problem of determining $S^2$, but from Fig. 1 on our present model, it is quite simple: $S^2 = 1$. In general, however, this will be a more formidable problem (see Sec. 5).

It should be emphasized here that the attempt of this argument is not primarily to evaluate the magnetization, but to decide whether or not local moments exist in a "permanent" sense. We could call the argument a "criterion calculation." For example, the two stable states that the moment could have in the above model are not meant to describe what actually takes place in the real crystal. An atom could undergo spin waves and what not in an AM calculation starting from Eq. (4.1) that is well beyond what the two stable moments imply. All that is attempted by the criterion calculation is to see whether or not a moment on the atom could exist in say the $z$ direction if the environment tends to line it up in the $-z$ direction. This gives some idea of the strength of the internal interactions tending to produce the local moment, and is perhaps an arbitrary criterion. Nevertheless is seems plausible at the least, and is rather simple to handle. Once a distinction is made, then one performs a quite different calculation to find out what the magnetization is. For the PM case, the difference lies in the self-consistency condition $M=m$ imposed on the equations after which solutions are attempted. In the AM case, one has a different Green's function formalism altogether.

One could object to the whole procedure and say that if one identifies $M$ with $m$ in a PM type of calculation, and solves the problem to arbitrary accuracy, one has the crystal moment solved to arbitrary accuracy no matter how one wishes to think about the local moments. This is a valid argument, it seems to us, but irrelevant to the present purpose, which is to understand in some sense when permanent moments may be said to exist on atoms.

To finish this section, we shall make a few remarks concerning situations in which the external moment $m$ comes not from atoms of the same sort, but say from an impurity or a magnetic field. Suppose, for example, that a strongly magnetic impurity is placed in a nonmagnetic transition metal. Then we can appeal to Fig. 1 for a rough idea of what could happen. If $a<1$, then, before the impurity is placed in the metal, the moment of the neighbor shell of atom $A$ may be below $m_c$ (suppose only one shell is of importance). If, now, the impurity enters this shell, the moment of the shell may go effectively beyond $m_c$. Thus the moment of the atom under consideration could go from either $+1$ or $-1$ to *necessarily* $+1$. That is, the impurity could line up all its neighbors. On the other hand, if $a>1$, then it may be that initially there are no local moments on the metal atoms. Then when the impurity is introduced, an atom $A$ in a neighbor shell may see the moment of its neighbor shell (containing the impurity) increase enormously [go beyond $(a-1)/b$ effectively, that is] and set off the moment on $A$ itself. Thus the impurity could produce (or more dramatically: trigger) the moments on its neighbors. Such a view is quite consistent with experiments in which giant moments are found associated with magnetic impurities in nonmagnetic transition metals. This result could also be viewed as an extremely large band susceptibility, but it seems to us a much more natural description to regard it as a setting-off of large induced local moments.

## 5. THE CRITERION CALCULATION II

The remainder of this paper is devoted to an attempt to generalize the results of the previous section by using the more realistic Hamiltonian

$$H=\sum V_{\mathbf{f}'\mathbf{f}}n_{\mathbf{f}'\mathbf{f}}+\sum Un_{\mathbf{f}+}n_{\mathbf{f}-}-\sum 2A(\mathbf{f}'-\mathbf{f})\mathbf{S}_{\mathbf{f}'}\cdot\mathbf{S}_{\mathbf{f}}-\sum \mu_0\mathcal{H}S_{\mathbf{f}z}\,, \quad (5.1)$$

where at times we shall include the magnetic field term in $\mathcal{H}$. To start, we again search for the occupation number averages, and hence use the $G$ formalism of Eqs. (2.12)–(2.15). Equation (2.15) becomes

$$\left(i\frac{\partial}{\partial t}\pm\mu_0\mathcal{H}\right)G_\sigma(\mathbf{ff}'|t-t')=-\delta(t-t')\delta_{\mathbf{f},\mathbf{f}'}+U\langle\langle n_{\mathbf{f},-\sigma}c_{\mathbf{f}\sigma}|c_{\mathbf{f}'\sigma}{}^\dagger(t')\rangle\rangle_{+}+\sum V_{\mathbf{ff}''}G_\sigma(\mathbf{f}''\mathbf{f}'|t-t')$$
$$-\sum A(\mathbf{f}-\mathbf{f}'')\langle\langle[\tfrac{1}{2}(n_{\mathbf{f}'',\sigma}-n_{\mathbf{f}'',-\sigma})c_{\mathbf{f}\sigma}+S_{\mathbf{f}'',-\sigma}c_{\mathbf{f},-\sigma}]|c_{\mathbf{f}'\sigma}{}^\dagger(t')\rangle\rangle_{+}\,. \quad (5.2)$$

Following the ideas of Sec. 4, we use a Hartree chain-breaking approximation

$$\langle\langle n_{\mathbf{f},-\sigma}c_{\mathbf{f}\sigma}|c_{\mathbf{f}'\sigma}{}^\dagger(t')\rangle\rangle\cong\langle n_{\mathbf{f},-\sigma}\rangle G_\sigma(\mathbf{ff}'|t-t')\,, \quad (5.3\text{a})$$

$$\sum A(\mathbf{f}-\mathbf{f}'')\langle\langle[\ \ ]|c_{\mathbf{f}'\sigma}{}^\dagger(t')\rangle\rangle_{+}\cong\tfrac{1}{2}m_\sigma A'(0)G_\sigma(\mathbf{ff}'|t-t')\,. \quad (5.3\text{b})$$

The energy Fourier component of Eq. (5.2) is then simply

$$(E-\bar{E}_{\mathbf{f}\sigma})G_\sigma(\mathbf{ff}'|E)=-(2\pi)^{-1}\delta_{\mathbf{f},\mathbf{f}'}+\sum V_{\mathbf{ff}''}G_\sigma(\mathbf{f}'',\mathbf{f}'|E)\,, \quad (5.4)$$

where

$$\bar{E}_{\mathbf{f}\sigma}=U\langle n_{\mathbf{f},-\sigma}\rangle-\tfrac{1}{2}A'(0)\bar{m}_\sigma\,, \quad (5.5)$$

$$\bar{m}_\sigma=m_\sigma[1+\mu_0\mathcal{H}(\tfrac{1}{2}A'(0)|n_\sigma|)^{-1}]\,. \quad (5.6)$$

Equation (5.4) is the basic equation to solve. The environment of the $\mathbf{f}$ atom enters the equation in two places: in the $\bar{m}$ term of $\bar{E}$, and in the nondiagonal $V_{\mathbf{ff}''}$'s. In Sec. 4, only the diagonal $V_{\mathbf{ff}}=V_0$ term appeared. Thus Eq. (4.3) incorporates the approximation that as far as the Bloch energy terms are concerned, the atom under consideration does not see any neighbors. In the present section we shall go one step beyond this. We shall assume that as far as the Bloch energy terms are concerned, the atom under consideration sees neighbors which are replicas of itself; that is, in Eq. (5.4) we shall treat the $G$'s on the right-hand side as of the same type as the $G$ on the left-hand side. On this approximation, the solution can be obtained by taking the Fourier component

$$G_\sigma(\mathbf{v}|E)=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma(\mathbf{f},\mathbf{f}'|E) \quad (5.7)$$

whence Eq. (5.4) becomes

$$G_\sigma(\mathbf{v}|E)=-(2\pi)^{-1}[E-\bar{E}_{\cdot\sigma}-V(\mathbf{v})]^{-1} \quad (5.8)$$

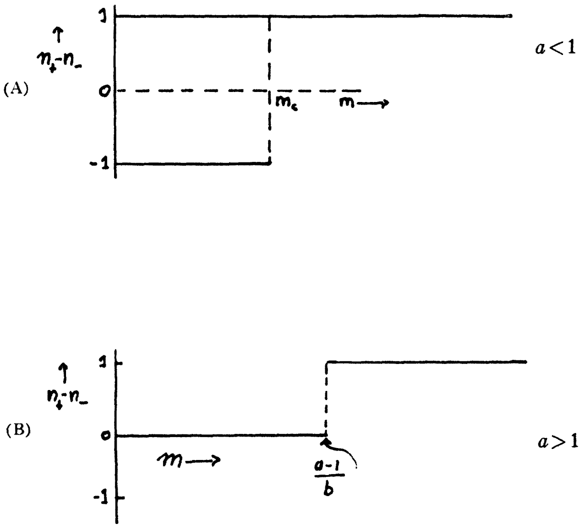

FIG. 1. Local moments as functions of an environment moment $m$, according to Eq. (4.4). [See the discussion following Eq. (4.4).] The notation is the following: $a=U^{-1}(E_F-V_0)$ and $b=\frac{1}{2}U^{-1}A'(0)$. Further, $m_c$ is the smaller of $(1-a)b^{-1}$ and $ab^{-1}$. In (A), for $m<m_c$, the possibility of the two local moments $+1$ and $-1$ implies that the local moment is "permanent." For larger $m$, the $-1$ solution is no longer possible; hence we describe the local moment as "induced." In (B), only the induced moment is possible.

and the average occupation number is

$$\langle n_{f\sigma}\rangle=N^{-1}\sum_{\nu} f(V(\nu)+U\langle n_{f,-\sigma}\rangle-\tfrac{1}{2}A'(0)\tilde{m}_\sigma). \quad (5.9)$$

Comparing this with Eq. (4.4) we see that the $V_0$ term has been replaced by $V(\boldsymbol{\nu})$, and a sum on $\boldsymbol{\nu}$ taken. This corresponds to the view adopted in Sec. 1 that the Wannier functions are miniatures of the $d$ bands containing a spectral function proportional to the $d$-band density of states. Thus the difference between Eq. (4.4) and Eq. (5.9) is that the former considers the atom isolated as far as the Bloch energies go, and hence the atom has a unique energy $V_0$, whereas the latter considers the atom to have a spectrum of energies corresponding to the $d$-band density of states. Equation (5.9) merges into Eq. (4.4) as the $d$-band width converges to the value $V_0$.

An approximation in which the effect of the rest of the crystal on a given atom is given more accurately is the following. At any instant, we may imagine the atom moments as participating in spin waves or what not, but providing nevertheless a crystal moment $m_+$ along some direction. Let us replace the effect of any atom by the effect of one of two averaged moments $M_{\parallel}$ and $M_{\mp}$, whose values are to be determined ultimately. Such a replacement will preserve the crystal moment $m_+$ if we stipulate that the fraction of atoms with $M_{\mp}$ is $x_{\mp}$ and the fraction with $M_{\parallel}$ is $x_{\parallel}$, with $x=x_{\parallel}-x_{\mp}$ determined by

$$m_+=\tfrac{1}{2}(1+x)M_{\parallel}-\tfrac{1}{2}(1-x)M_{\mp}. \quad (5.10)$$

By the same token an averaged $S^2$ may be estimated by[16]

$$S^2=\tfrac{1}{2}(1+x)M_{\parallel}^2+\tfrac{1}{2}(1-x)M_{\mp}^2, \quad (5.11)$$

or, using $x$ determined from Eq. (5.10)

$$S^2=m_+(M_{\parallel}-M_{\mp})+M_{\parallel}M_{\mp}. \quad (5.12)$$

The problem is then carried through by going back to Eq. (5.4) and considering Fourier components of the $G$'s that sum only over parallel atoms (or alternatively only over antiparallel atoms). In this way, the Bloch energy terms will reflect in a more realistic way the effect of the environment being characterized by a crystal moment $m_+$. The details are carried out in Appendix A. Sections 4 and 5 and Appendix A therefore represent a progression of approximations in how the Bloch energy terms are handled.

We shall now make some numerical estimates of Eq. (5.9). For variety, we shall allow here the Fermi level $E_F$ to be determined by the $d$ band alone (in Sec. 4, it was the $s$ band that determined it). Thus imposing one electron per atom, we get

$$\langle n_{f+}\rangle+\langle n_{f-}\rangle=1. \quad (5.13)$$

Next we shall use a free-electron or effective-mass approximation for the $d$-band energies

$$N^{-1}\sum_{\nu}=\tfrac{3}{2}C\int V^{1/2}dV,$$
$$\tfrac{3}{2}C=\tfrac{3}{4}E_F^{-3/2}. \quad (5.14)$$

If we integrate Eq. (5.9) allowing $f(E)$ to be a step function, and take the $\frac{2}{3}$ power of the result, we get (we call $n_{f+}$ by $n_+$ from now on)

$$n_{\pm}^{2/3}=C^{2/3}[E_F-Un_{\mp}\pm\tfrac{1}{2}\tilde{m}_+A'(0)], \quad (5.15)$$
$$=y[z/2-n_{\mp}\pm x\tilde{m}_+], \quad (5.16)$$

where we use the dimensionless abbreviations

$$x=(2U)^{-1}A'(0);\quad y=C^{2/3}U;\quad z=2E_FU^{-1}. \quad (5.17)$$

If, now, Eq. (5.13) is used, and we subtract the $-$ from the $+$ equation, we get

$$y=\frac{(1-n_+)^{2/3}-n_+^{2/3}}{1-2n_+-2x\tilde{m}_+}. \quad (5.18)$$

The solutions of this equation are portrayed in Figs. 2 and 3. In Fig. 2, we have fixed $2x\tilde{m}_+$ at some value and plotted the right-hand side of Eq. (5.18) as a function of $n_+$. The solutions of the equation are given by the intersection of these curves with $y=\text{const}$ [namely, the equation of the left-hand side of Eq. (5.18) as a function of $n_+$]. The case $y=y_c\cong0.84$ is a critical value. For if $y<y_c$, there are never two solutions for $n_+$, so that no matter what $m$ is, the only moments are induced ones

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[16] *Note added in proof.* Of course $S$ is really the average of the $z$ component squared [see Eq. (2.5)]. The above identification is only a crude estimate, the better the more "permanent" the local moment is. Even if $M_{\parallel}=M_{\mp}=0$, $S$ can still exist.

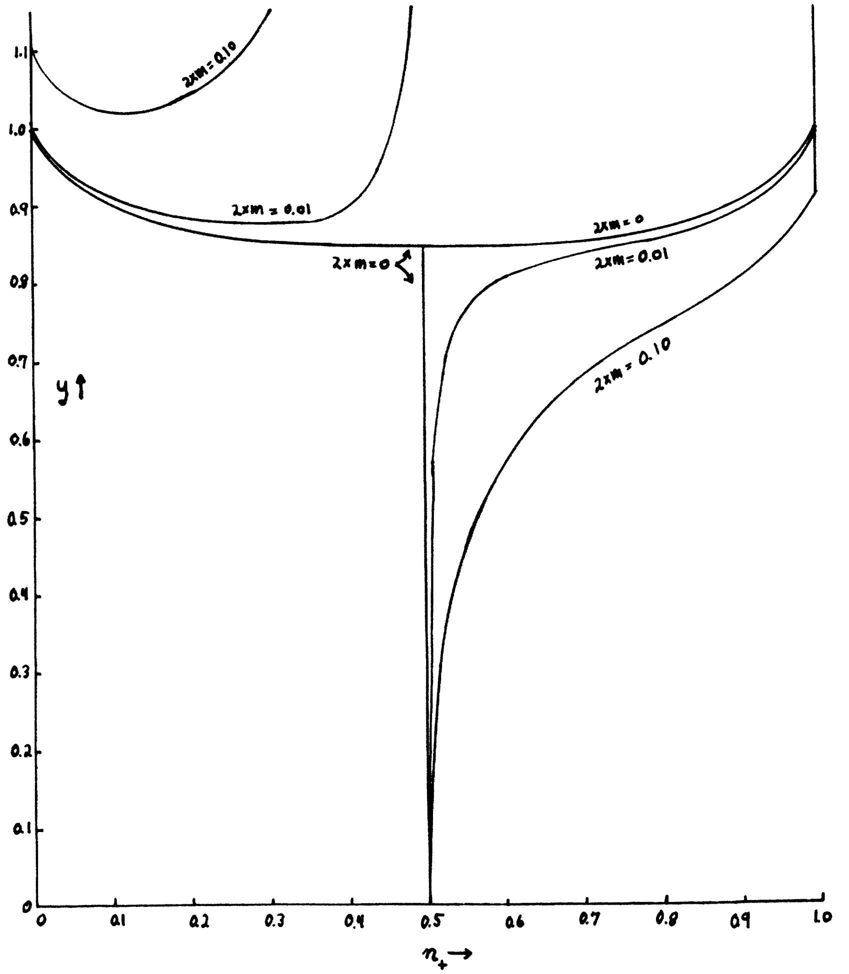

FIG. 2. Graphical solutions of Eq. (5.18). The solutions are obtained corresponding to the crystal parameters $x$ and $y$ by finding the intersections of the straight lines $y=\text{const}$ with the curves drawn in the figure. For $y<y_c=0.84$, there is always only one solution for $n_+$; hence, the moments on the atoms are of the induced variety. For $y>y_c$, there comes a situation (small enough $m$) when two solutions are possible (really three, the third unphysical) indicating that the moments are of the permanent variety.

by our criterion. For the limiting case $m=0$, we have that above $y_c$ there are always two solutions for $n_+$, whence the moments are "permanent." If $m>0$, then the induced region keeps up to $y$'s higher than $y_c$, but at some value for $y$, there suddenly becomes available three solutions. The intermediate one we shall regard as unphysical, following Anderson's interpretation of a similar solution in his paper. The other two solutions exhibit the parallel and antiparallel moments that are the analogs of those found in Sec. 4.

In Fig. 3, we have plotted the values of $M$ as a function of $2xm_+$, for particular values of $y$, assuming $A'(0)$ positive. These curves are the generalizations of those in Fig. 1. For $y<y_c$, the local moments are always induced, and $M\rightarrow 0$ as $m\rightarrow 0$. But for $y>y_c$, for the small $m$'s, there are two solutions for $M$, the antiparallel ones given by the negative ones at the lower end. The first case resembles the curves in Fig. 1(B), the second those in Fig. 1(A).

This completes the analysis of Eq. (5.9).

## 6. THE AM CALCULATION

In this section we shall discuss what happens to an AM calculation when we use more general Hamiltonians than just $H_{\text{spin}}$.[8a] There are two such to consider: Eqs. (4.1) and (5.1). In the former, there is no change at all over what we found in Sec. 3. The reason for this is that the commutator of $S_{f+}$ with the new $H$ is no different from that of just $H_{\text{spin}}$, since $S_{f+}$ commutes with $H_{\text{corr}}$ and with $n_{f+}+n_{f-}$. Thus the standard result can be regarded as coming from this $H$ of Eq. (4.1) in the region of Fig. 1(a) with $m<m_c$. Since in this region $S^2=1$, the result is in fact just the ordinary spin-wave expression.

For Eq. (5.1), however, a number of differences appear. First of all, from Secs. 5 or Appendix A, it is clear that the local moment itself is not simply equal to 1. If[16] we identify $S^2$ with an average of $M_{\parallel}$ and $M_{\mp}$ such as found in Eq. (5.12), then we have $S^2$ as a function of $m$. Thus the resulting equation of the Green's function calculation, Eq. (2.21), becomes considerably more complicated, and one is probably justified in turning to graphical solutions to the problem. In words the situation is this: Not only is the crystal moment a function of the local moment, as given directly by Eq. (2.21), but the local moment $S^2$ must also be a function of the crystal moment. The solution must therefore be a self-consistent one for these two relations.

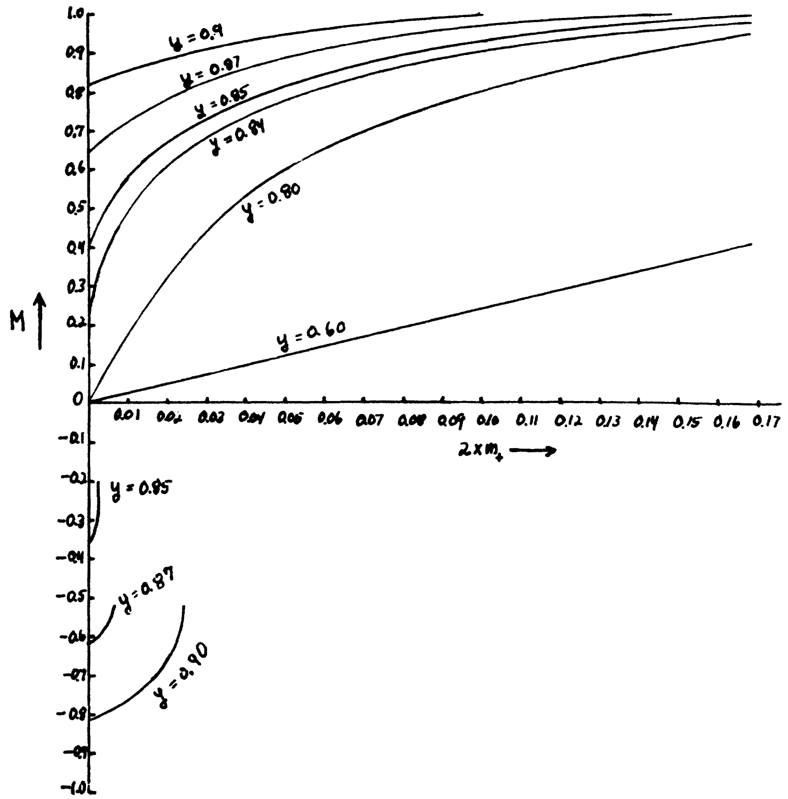

FIG. 3. Solutions of Eq. (5.18) for $M$ versus $2xm_+$ for particular crystal parameter values of $y$. This is the analogy of Fig. 1, but for a different criterion determining the Fermi level (from the $d$ band rather than the $s$ band) and based on an equation displaying the spectral function of the $d$-band Wannier functions.

The major difficulty with the AM calculation is not however with this aspect of the problem. It is with finding the $g$ functions to put into Eq. (2.21) in the first place. We shall in this section digress and make a reduction of the problem to some complicated expressions for $g$, but we will not be able to go the whole way and get explicit final results. Nevertheless, it was thought worthwhile to show what happens with the more general Hamiltonian of Eq. (5.1), and what sorts of difficulties arise.

Equation (2.22) with Eq. (5.1) for $H$ becomes the basic equation of motion:

$$i\frac{\partial}{\partial t}g(\mathbf{f}\mathbf{f}'',\mathbf{f}'|t-t')=-\delta(t-t')\{-\delta_{\mathbf{f},\mathbf{f}'}\langle n_{\mathbf{f}\mathbf{f}'',-}\rangle+\delta_{\mathbf{f}'',\mathbf{f}'}\langle n_{\mathbf{f}\mathbf{f}'',+}\rangle\}-\langle\langle[H,S_{\mathbf{f}\mathbf{f}'',+}(t)]_-|S_{\mathbf{f}',-}(t')\rangle\rangle_{(-)}. \tag{6.1}$$

Thus, the following commutators are needed:

$$[\sum_{\mathbf{f}'} Un_{\mathbf{f}'+}n_{\mathbf{f}'-},\, S_{\mathbf{f}\mathbf{f}'',+}]=U(n_{\mathbf{f},-}-n_{\mathbf{f}'',+})S_{\mathbf{f}\mathbf{f}'',+}\cdots\mathbf{f}''\neq\mathbf{f} \tag{6.2a}$$

$$=0\cdots\mathbf{f}''=\mathbf{f}. \tag{6.2b}$$

$$[\sum V_{\mathbf{l}'\mathbf{l}}n_{\mathbf{l}'\mathbf{l}},\, S_{\mathbf{f}\mathbf{f}'',+}]=\sum_{\mathbf{l}}(V_{\mathbf{l}\mathbf{f}}S_{\mathbf{l}\mathbf{f}'',+}-V_{\mathbf{f}''\mathbf{l}}S_{\mathbf{f}\mathbf{l},+}). \tag{6.3}$$

$$[\sum 2A(\mathbf{l}'-\mathbf{l})\mathbf{S}_{\mathbf{l}'}\cdot\mathbf{S}_{\mathbf{l}},\, S_{\mathbf{f}\mathbf{f}'',+}]=\sum_{\mathbf{l}}\{S_{\mathbf{l}+}[-A(\mathbf{l}-\mathbf{f}'')n_{\mathbf{f}\mathbf{f}'',+}+A(\mathbf{l}-\mathbf{f})n_{\mathbf{f}\mathbf{f}'',-}]+[-A(\mathbf{f}''-\mathbf{l})n_{\mathbf{f}\mathbf{f}'',+}+A(\mathbf{f}-\mathbf{l})n_{\mathbf{f}\mathbf{f}'',-}]S_{\mathbf{l}+}$$
$$+[A(\mathbf{f}-\mathbf{l})+A(\mathbf{f}''-\mathbf{l})]S_{\mathbf{f}\mathbf{f}'',+}S_{\mathbf{l}z}+[A(\mathbf{l}-\mathbf{f})+A(\mathbf{l}-\mathbf{f}'')]S_{\mathbf{l}z}S_{\mathbf{f}\mathbf{f}'',+}\}. \tag{6.4}$$

The chain-breaking approximations are as follows. First, the expression in Eq. (6.2a) is altered and decoupled taking into account the fact that, for example, $n_{\mathbf{f},-}$ in the product $n_{\mathbf{f},-}S_{\mathbf{f}\mathbf{f}'',+}$ contributes only when $\mathbf{f}+$ is present. Thus, one can write it as $n_{\mathbf{f},-}n_{\mathbf{f},+}S_{\mathbf{f}\mathbf{f}'',+}$ and then remove the product $n_{\mathbf{f},-}n_{\mathbf{f},+}$ at an average value, which then takes this effect into account. In sum, we get

$$\langle\langle(n_{\mathbf{f},-}-n_{\mathbf{f}'',+})S_{\mathbf{f}\mathbf{f}'',+}|S_{\mathbf{f}',-}\rangle\rangle=\langle\langle[n_{\mathbf{f},-}n_{\mathbf{f},+}-n_{\mathbf{f}'',+}(1-n_{\mathbf{f}'',-})]S_{\mathbf{f}\mathbf{f}'',+}|S_{\mathbf{f}',-}\rangle\rangle\cong-\mu_+g(\mathbf{f}\mathbf{f}'',\mathbf{f}'|E), \tag{6.5}$$

where we define

$$-\mu_+\equiv\langle n_{\mathbf{f},-}n_{\mathbf{f},+}-n_{\mathbf{f}'',+}(1-n_{\mathbf{f}'',-})\rangle=-\tfrac{1}{2}(S^2+m_+)+\tfrac{1}{2}(n_{\mathbf{f}}^2-n_{\mathbf{f}}), \tag{6.6}$$

where $S^2$ is defined by Eq. (2.5), and $n_{\mathbf{f}}^2$ is the average of $(n_{\mathbf{f}+}+n_{\mathbf{f}-})^2$.

In Eq. (6.4), quantities like $n_{\mathbf{ff}'',\pm}$ will be taken out at averaged values (unchanged in notation), as will $S_{1z}$ also. The result is then finally for the energy Fourier component [see Eq. (2.17)] of Eq. (6.1):

$$Eg(\mathbf{ff}'',\mathbf{f}'|E)=(2\pi)^{-1}\{\delta_{\mathbf{f},\mathbf{f}'}n_{\mathbf{ff}'',-}-\delta_{\mathbf{f}'',\mathbf{f}'}n_{\mathbf{ff}'',+}\}+U\mu_+g(\mathbf{ff}'',\mathbf{f}'|E)(1-\delta_{\mathbf{ff}''})-\sum_{\mathbf{l}}[V_{\mathbf{lf}}g(\mathbf{lf}'',\mathbf{f}'|E)-V_{\mathbf{f}''\mathbf{l}}g(\mathbf{fl},\mathbf{f}'|E)]$$
$$-\sum_{\mathbf{l}}[2\bar{A}(\mathbf{l}-\mathbf{f}'')n_{\mathbf{ff}'',+}-2\bar{A}(\mathbf{l}-\mathbf{f})n_{\mathbf{ff}'',-}]g(\mathbf{l},\mathbf{f}'|E)+2^{-1}m_+\sum_{\mathbf{l}}[2\bar{A}(\mathbf{f}-\mathbf{l})+2\bar{A}(\mathbf{f}''-\mathbf{l})]g(\mathbf{ff}'',\mathbf{f}'|E), \quad (6.7)$$

where

$$2\bar{A}(\mathbf{f}-\mathbf{l})=A(\mathbf{f}-\mathbf{l})+A(\mathbf{l}-\mathbf{f}). \quad (6.8)$$

The usual method for solving the standard $\mathbf{f}=\mathbf{f}''$ equation is to take the Fourier component

$$g(\mathbf{v}|E)=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]g(\mathbf{f},\mathbf{f}'|E). \quad (6.9)$$

Since there is a new type of Green's function in Eq. (6.6), we define also

$$g(\mathbf{v}',\mathbf{v}''|E)=\sum_{\mathbf{f}-\mathbf{f}'}\sum_{\mathbf{f}''-\mathbf{f}'}\exp[i\mathbf{v}'\cdot(\mathbf{f}-\mathbf{f}')-i\mathbf{v}''\cdot(\mathbf{f}''-\mathbf{f}')]g(\mathbf{ff}'',\mathbf{f}'|E). \quad (6.10)$$

The lattice Fourier component of Eq. (6.6) is then

$$[E-\mu_+U-2A'(0)m_++V(\mathbf{v}')-V(\mathbf{v}'')]g(\mathbf{v}',\mathbf{v}''|E)=-(2\pi)^{-1}[n_+(\mathbf{v}')-n_-(\mathbf{v}'')]$$
$$-\{[n_+(\mathbf{v}')-n_-(\mathbf{v}'')]2A'(\mathbf{v}'-\mathbf{v}'')+Um_+\}g(\mathbf{v}'-\mathbf{v}''|E), \quad (6.11)$$

where

$$n_\sigma(\mathbf{v})=\sum\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]n_{\mathbf{ff}',\sigma}. \quad (6.12)$$

The relationship between $g(\mathbf{v}|E)$ and $g(\mathbf{v}',\mathbf{v}''|E)$ can be seen from the definition

$$g(\mathbf{v}',\mathbf{v}''|E)=g(\mathbf{v}'-\mathbf{v}''|E)+\sum_{\mathbf{f}''\neq\mathbf{f}}\exp[i\mathbf{v}'\cdot(\mathbf{f}-\mathbf{f}')-i\mathbf{v}''\cdot(\mathbf{f}''-\mathbf{f}')]g(\mathbf{ff}'',\mathbf{f}'|E). \quad (6.13a)$$

If we introduce an average denoted by double angle brackets $\langle\langle\cdots\rangle\rangle_\nu$ such that $\mathbf{v}'$ roams over the first Brillouin zone, and $\mathbf{v}''$ is given by $\mathbf{v}'-\mathbf{v}''=\mathbf{v}$ [even if this means that $\mathbf{v}''$ goes beyond the first zone, in which case, the periodic nature of Eqs. (6.9) and (6.10) is implied], then operation by this average on Eq. (6.13a) gives

$$\langle\langle g(\mathbf{v}',\mathbf{v}''|E)\rangle\rangle_{\nu'-\nu''=\nu}=g(\mathbf{v}|E). \quad (6.13b)$$

Notice also

$$\langle\langle n_+(\mathbf{v}')-n_-(\mathbf{v}'')\rangle\rangle_\nu=m_+. \quad (6.13c)$$

Further, if we operate on Eq. (6.11) as it stands by this average, we obtain the component equation that would have come directly from Eq. (6.7) with $\mathbf{f}''=\mathbf{f}$.

If, however, we solve Eq. (6.11) for $g(\mathbf{v}',\mathbf{v}''|E)$ in terms of $g(\mathbf{v}'-\mathbf{v}''|E)$ and *then* average, we obtain an equation for $g(\mathbf{v}|E)$, namely

$$g(\mathbf{v}|E)=-\frac{1}{2\pi}\left[\left\langle\left\langle\frac{n_+(\mathbf{v}')-n_-(\mathbf{v}'')}{E-E'(\mathbf{v}',\mathbf{v}'')}\right\rangle\right\rangle_\nu\Big/\left\langle\left\langle\frac{E-E_\nu''(\mathbf{v}',\mathbf{v}'')}{E-E'(\mathbf{v}',\mathbf{v}'')}\right\rangle\right\rangle_\nu\right], \quad (6.14)$$

where

$$E'(\mathbf{v}',\mathbf{v}'')=\mu_+U+2A'(0)m_+-V(\mathbf{v}')+V(\mathbf{v}''), \quad (6.15)$$

$$E_\nu''(\mathbf{v}',\mathbf{v}'')=2m_+A'(0)-2[n_+(\mathbf{v}')-n_-(\mathbf{v}'')]A'(\mathbf{v})-V(\mathbf{v}')+V(\mathbf{v}''). \quad (6.16)$$

Equation (6.14) is the basic result of the present section. It is obviously extremely complicated, and we shall limit ourselves to rather simple observations. First of all, what enters Eq. (2.21) is the imaginary part of $g$ in the limit as $\epsilon$ goes to zero where the complex energy is written $E+i\epsilon$. In constructing the imaginary part of Eq. (6.14), we shall use the familiar relation $(x+i0)^{-1}=P(x)-i\pi\delta(x)$, and, for reasons that will appear later, we shall in addition keep along the $i\epsilon$ that goes with the $E-E''+i\epsilon$ in the numerator of the denominator. After a bit of rearranging and clearing imaginaries from denominators, we find

$$\mathrm{Im}g(\mathbf{v}|E)=\frac{1}{2\pi}\,\frac{-\gamma_+D+BC+\epsilon\gamma_1\gamma_+}{C^2+(D-\epsilon\gamma_1)^2}, \quad (6.17)$$

where we have made use of the following abbreviations $B$, $C$, and $D$:

$$B(\mathbf{v}|E)=\pi\langle\langle[n_+(\mathbf{v}')-n_-(\mathbf{v}'')]\delta(E-E'(\mathbf{v}',\mathbf{v}''))\rangle\rangle_\nu, \quad (6.18)$$

$$C(\mathbf{v}|E)=\langle\langle P(E-E'')/(E-E')\rangle\rangle_\nu, \quad (6.19)$$

$$D(\mathbf{v}|E)=\pi\langle\langle(E-E'')\delta(E-E')\rangle\rangle_\nu, \quad (6.20)$$

and the following averages

$$\gamma_1(\mathbf{v}|E)=\langle\langle[E-E'(\mathbf{v}',\mathbf{v}'')]^{-1}\rangle\rangle_\nu\,, \tag{6.21a}$$

$$\gamma_+(\mathbf{v}|E)=\langle\langle[n_+(\mathbf{v}')-n_-(\mathbf{v}'')][E-E'(\mathbf{v}',\mathbf{v}'')]^{-1}\rangle\rangle_\nu\,, \tag{6.21b}$$

$$\gamma_V(\mathbf{v}|E)=\langle\langle[V(\mathbf{v}')-V(\mathbf{v}'')][E-E'(\mathbf{v}',\mathbf{v}'')]^{-1}\rangle\rangle_\nu\,. \tag{6.21c}$$

The last one here is useful when we write out $C$ in detail

$$C(\mathbf{v}|E)=\gamma_1[E-2m_+A'(0)+2\gamma_+\gamma_1^{-1}A'(\mathbf{v})+\gamma_V\gamma_1^{-1}]\,. \tag{6.22}$$

The result in Eq. (6.17) can be separated into two parts, one involving the $\epsilon$ in the numerator, the other containing the rest:

$$\operatorname{Im}g(\mathbf{v}|E)=g_1(\mathbf{v}|E)+g_2(\mathbf{v}|E)\,, \tag{6.23}$$

$$g_1(\mathbf{v}|E)=(1/2\pi)\gamma_+[\epsilon\gamma_1/(C^2+D^2+\epsilon^2\gamma_1^2)]=\tfrac{1}{2}\gamma_+\delta[(C^2+D^2)^{1/2}]\,, \tag{6.24}$$

$$g_2(\mathbf{v}|E)=\frac{1}{2\pi}\,\frac{-\gamma_+D+BC}{C^2+D^2}=\frac{1}{2}\left\langle\!\!\left\langle\frac{-\gamma_+(\mathbf{v}|E)(E-E''(\mathbf{v}',\mathbf{v}''))+[n_+(\mathbf{v}')-n_-(\mathbf{v}'')]C(\mathbf{v}|E)}{C(\mathbf{v}|E)^2+D(\mathbf{v}|E)^2}\delta(E-E'(\mathbf{v}',\mathbf{v}''))\right\rangle\!\!\right\rangle_\nu\,. \tag{6.25}$$

The contribution from $g_1$ can be regarded as a generalized spin-wave contribution. For if, say, $U$ is very large and $\mu_+$ not zero, then $E'(\mathbf{v}',\mathbf{v}'')$ is large for all $\mathbf{v}'$, $\mathbf{v}''$. Thus, if $E$ is small, then the delta function $\delta(E-E')$ will not be satisfied and $D$ (and $B$) is zero. Then Eq. (6.24) is just

$$g_1(\mathbf{v}|E)=\tfrac{1}{2}(\gamma_+/\gamma_1)\times\delta(E-2m_+A'(0)+2\gamma_+\gamma_1^{-1}A'(\mathbf{v})+\gamma_V\gamma_1^{-1})\,, \tag{6.26}$$

which is a modified spin-wave spectrum.

The contribution from $g_2$ would seem to be quite complicated and difficult to interpret, but it may be surmised that it corresponds to the optical branches of Mattis' spectrum.[8a] We shall not pursue the calculation any further at this time.

We wish to conclude this section with two remarks. The first is that when the bandwidth reduces to zero, i.e., when $V(\mathbf{v}')$ becomes a constant, then $E'$ no longer depends on $\mathbf{v}'$ or $\mathbf{v}''$, and the denominator of the numerator in Eq. (6.12) cancels with the denominator of the denominator, and the result is the standard spin-wave solution.

The second remark is that in the approximation cited above Eq. (6.26), i.e., when $U$ is very large, the two parts of the spectrum, from $g_1$ and $g_2$, are well separated and distinct. However, as $U$ gets smaller and smaller, the two parts can begin to merge and it becomes meaningless to separate out the spin-wave part from the other. Since the size of $U$ is indicative of how "permanent" the local moment is, as discussed in earlier sections of this paper, it is clear that the distinguishability of the ordinary spin-wave spectrum depends explicitly on the existance of permanent moments. As the local moments become less and less "permanent" and more and more "induced," the spectrum starts to deviate from the standard spin-wave type and turns to a complicated mixture.

## 7. SUMMARY AND EXTENSIONS

In the preceding sections we have attempted to correlate different approaches to the magnetization in transition metals. The basic problem has been conceived as tying together internal effects, which tend to produce magnetic moments on the atoms through forces inside the atoms, external effects, which tend to produce magnetic moments on the atoms through forces between atoms, and realignment effects. We have classified the solutions of the local moment problem into two types: (1), where only one orientation of the local moment is possible, and (2) where two orientations are possible. In type 1, the problem is just a generalization of the band theory of magnetism. In type 2, the problem is twofold: first to calculate an average local moment (which turns out to depend in general on the environment, i.e., on the crystal moment and hence on the temperature), and second to calculate the crystal moment (which depends parametrically on the local moment), the two folds to be solved then simultaneously.

In order to improve the theory, a number of additional effects can be contemplated. First among these is the *sd* interaction. It is known that the conduction electrons get polarized by the local moments, and this is taken into account by the exchange term

$$H_{\mathrm{ex}}=-2\sum M_{\mathbf{k}'\mathbf{f}}{}^{\mathbf{fk}}S_{\mathbf{k}'\mathbf{k}}\cdot S_{\mathbf{f}}\,. \tag{7.1}$$

The effect of this term would be the first thing to look at. There is, however, another *sd* interaction term which we studied in a previous paper[8] on the impurity problem, namely

$$H^{(3)}=\sum M_{\mathbf{fk}}{}^{\mathbf{ff}}n_{\mathbf{fk}\sigma}n_{\mathbf{f},-\sigma}+\sum M_{\mathbf{kf}}{}^{\mathbf{ff}}n_{\mathbf{kf},\sigma}n_{\mathbf{f},-\sigma}\,. \tag{7.2}$$

This is a mixing term having similar characteristics to the *sd* interaction of Anderson. It is the *only* mixing term at work in the (pure) transition metal problem.[10a] Its influence is probably as significant as that of $H_{\mathrm{ex}}$.

A second improvement in the theory would be to take into account more $d$ orbitals. Mattis[7] has emphasized the view that a proper understanding of the magnetization problem in transition metals must ultimately depend on a kind of analogy with the atomic orbital situation, Hund rules and all. We agree that higher orbital effects will prove to be important considerations,[6] and should be incorporated in more complete theories.

Finally, we point to the fact that none of the problems[17] associated with the use of orthogonalized functions (the Wannier functions) have been dealt with here.

## ACKNOWLEDGMENTS

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## APPENDIX A: THE CRITERION CALCULATION

In Sec. 5 we outlined the various stages of approximation used in this paper. Above Eq. (5.10), a final calculation was indicated in which the crystal is approximated by atoms with fixed moments $M_\parallel$ or $M_\ddagger$ such that every neighbor shell has a resultant average moment $m_+$. In this Appendix, the details of the calculation are carried through.

The notation is similar to that of Sec. 5. An atom with a parallel moment $M_\parallel$ will have averaged occupation numbers $n_{\parallel,+}$ and $n_{\parallel,-}$, and similarly for the antiparallel case. The $\bar{E}$'s of Eq. (5.5) will then take on four possible values corresponding to $f$ being $\parallel$ or $\ddagger$, and $\sigma$ being $+$ or $-$. Thus

$$E_{\parallel,\sigma}=Un_{\parallel,-\sigma}+\tfrac{1}{2}A'(0)m_\sigma\,, \tag{A1}$$

$$E_{\ddagger,\sigma}=Un_{\ddagger,-\sigma}+\tfrac{1}{2}A'(0)m_\sigma\,, \tag{A2}$$

$$M_\parallel=n_{\parallel,+}-n_{\parallel,-}>0\,, \tag{A3}$$

$$-M_\ddagger=n_{\ddagger,+}-n_{\ddagger,-}<0\,. \tag{A4}$$

Now $x$ will characterize what we shall call an "arrangement." It is equivalent to stipulating a crystal magnetization. But this may occur with the distribution of moments $M_\parallel$ and $M_\ddagger$ in many ways among the sites. We shall call each one of these ways a "configuration." We shall consider Eq. (5.4) for every configuration consistent with a given arrangement and then average, the averaging of this type indicated by the symbol $\{\{\ \}\}$.

Finally, as regards notation, we shall rewrite $G_\sigma(\mathbf{f},\mathbf{f}'|E)$ as $G_\sigma{}^{(\parallel,\ddagger)}(\mathbf{f},\mathbf{f}'|E)$ for the case where $f$ is a parallel site and $f'$ an antiparallel one, and analogously for the other possibilities for $f$ and $f'$. We can then define a unique Fourier component of the $G$'s by summing $f$ over all parallel sites [the sum denoted by $\mathbf{f}(\|)$] with $\mathbf{f}'$ a parallel site and then averaging over configurations:

$$\begin{aligned} G_\sigma{}^{(\parallel,\parallel)}(\mathbf{v}|E)&=\{\{\sum_{\mathbf{f}(\parallel)}\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma{}^{(\parallel,\parallel)}(\mathbf{f},\mathbf{f}'|E)\}\}\\ &=x_\parallel\sum_{\text{all }\mathbf{f}}\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma{}^{\parallel,\parallel}(\mathbf{f},\mathbf{f}'|E) \end{aligned} \tag{A5}$$

and similarly for a sum over all antiparallel sites

$$G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{v}|E)=\{\{\sum_{\mathbf{f}(\ddagger)}\exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{f},\mathbf{f}'|E)\}\}\,. \tag{A6}$$

We are now in a position to solve Eq. (5.4) on this two-moment model. Let us choose $\mathbf{f}'$ to be a parallel site, and sum the equation over parallel $\mathbf{f}$'s:

$$(E-E_{\parallel,\sigma})G_\sigma{}^{(\parallel,\parallel)}(\mathbf{v}|E)=-\frac{1}{2\pi}+\sum_{\nu'}V(\mathbf{v}')N^{-1}\{\{\sum_{\mathbf{f}(\parallel)}\sum_{\mathbf{f}''}\exp[i(\mathbf{v}-\mathbf{v}')\cdot(\mathbf{f}-\mathbf{f}'')]\exp[i\mathbf{v}\cdot(\mathbf{f}''-\mathbf{f}')]G_\sigma(\mathbf{f}'',\mathbf{f}'|E)\}\}\,. \tag{A7}$$

Summing over antiparallel $\mathbf{f}$'s gives

$$(E-E_{\ddagger,\sigma})G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{v}|E)=\sum_{\nu'}V(\mathbf{v}')N^{-1}\{\{\sum_{\mathbf{f}(\ddagger)}\sum_{\mathbf{f}''}\exp[i(\mathbf{v}-\mathbf{v}')\cdot(\mathbf{f}-\mathbf{f}'')]\exp[i\mathbf{v}\cdot(\mathbf{f}''-\mathbf{f}')]G_\sigma(\mathbf{f}''\mathbf{f}'|E)\}\}\,. \tag{A8}$$

In both these equations, $\mathbf{f}''$ is summed over all sites.

To solve the equations we make one approximation, namely that the average of the product is the product of the averages. Thus, in Eq. (A7), there emerges

$$\{\{N^{-1}\sum_{\mathbf{f}(\parallel)}\exp[i\mathbf{f}\cdot(\mathbf{v}-\mathbf{v}')]\}\}=x_\parallel\delta_{\nu,\nu'}\,, \tag{A9}$$

and in Eq. (A8) there emerges

$$\{\{N^{-1}\sum_{\mathbf{f}(\ddagger)}\exp[i\mathbf{f}\cdot(\mathbf{v}-\mathbf{v}')]\}\}=x_\ddagger\delta_{\nu,\nu'}\,. \tag{A10}$$

The result is then

$$(E-E_{\parallel,\sigma})G_\sigma{}^{(\parallel,\parallel)}(\mathbf{v}|E)=-(2\pi)^{-1}+x_\parallel V(\mathbf{v})[G_\sigma{}^{(\parallel,\parallel)}(\mathbf{v}|E)+G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{v}|E)]\,, \tag{A11}$$

$$(E-E_{\ddagger,\sigma})G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{v}|E)=x_\ddagger V(\mathbf{v})[G_\sigma{}^{(\parallel,\parallel)}(\mathbf{v}|E)+G_\sigma{}^{(\ddagger,\parallel)}(\mathbf{v}|E)]\,. \tag{A12}$$

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[17] T. Arai, Phys. Rev. **134**, A824 (1964); **126**, 471 (1962).

The solutions are then easily obtained:

$$G_\sigma^{(\parallel,\parallel)}(\mathbf{v}|E)=-(2\pi)^{-1}[E-E_{\parallel,\sigma}-x_\parallel V-x_\parallel x_\ddagger V^2(E-E_{\ddagger,\sigma}-x_\ddagger V)^{-1}]^{-1}$$
$$=-(2\pi)^{-1}(E-E_{\ddagger,\sigma}-x_\ddagger V)(E-E_{1\sigma})^{-1}(E-E_{2\sigma})^{-1}, \qquad \text{(A13)}$$

where the roots $E_{1,2}$ are

$$E_{1\sigma,2\sigma}=2^{-1}\{[E_{\parallel,\sigma}+E_{\ddagger,\sigma}+V(\mathbf{v})]\pm[(E_{\parallel,\sigma}-E_{\ddagger,\sigma})^2+2xV(\mathbf{v})(E_{\parallel,\sigma}-E_{\ddagger,\sigma})+V(\mathbf{v})^2]^{1/2}\}. \qquad \text{(A14)}$$

The inverse is

$$G_\sigma^{(\parallel,\parallel)}(\mathbf{f},\mathbf{f}'|E)=N^{-1}\sum_\nu \exp[i\mathbf{v}\cdot(\mathbf{f}-\mathbf{f}')]G_\sigma^{\parallel,\parallel}(\mathbf{v}|E), \qquad \text{(A15)}$$

whence, from Eq. (2.14), the desired averages are

$$n_{\parallel,\sigma}=N^{-1}\sum_\nu\left[f(E_{1\sigma})\frac{E_{1\sigma}-E_{\ddagger,\sigma}-x_\ddagger V(\mathbf{v})}{E_{1\sigma}-E_{2\sigma}}+f(E_{2\sigma})\frac{E_{2\sigma}-E_{\ddagger,\sigma}-x_\ddagger V(\mathbf{v})}{E_{2\sigma}-E_{1\sigma}}\right]. \qquad \text{(A16)}$$

A similar equation exists for the antiparallel case. It is obtained from Eq. (A16) by interchanging $\parallel$ with $\ddagger$ everywhere (notice that $E_1$ and $E_2$ remain unaltered by this interchange). The coefficients of the Fermi functions in Eq. (A16) are essentially positive as can be verified by writing out $E_1$ and $E_2$ and noting that the square root in Eq. (A14) is always larger than $\{[(E_{\parallel,\sigma}-E_{\ddagger,\sigma})+xV]^2\}^{1/2}$.

This completes the derivation of the basic equations. The next step is to look for when the four equations in $n_{\parallel,+}$, $n_{\parallel,-}$, $n_{\ddagger,+}$, and $n_{\ddagger,-}$ have roots. We shall not do this in this paper. However, we can see in a simple way that the situation with vanishing small $U$ does not have any solutions for $M_\ddagger$. For in this limit

$$E_{\parallel,\sigma}=E_{\ddagger,\sigma}\equiv\tfrac{1}{2}A'(0)m_\sigma\equiv E_\sigma', \qquad \text{(A17)}$$

whence

$$E_{1\sigma}=E_\sigma'+V(\mathbf{v}),$$
$$E_{2\sigma}=E_\sigma', \qquad \text{(A18)}$$

and then

$$M_\parallel=x_\parallel A+x_\ddagger B,$$
$$-M_\ddagger=+[x_\ddagger A+x_\parallel B], \qquad \text{(A19)}$$

where

$$A=N^{-1}\sum_\nu(f(E_+'+V)-f(-E_+'+V)),$$
$$B=f(E_+')-f(-E_+'). \qquad \text{(A20)}$$

Now $E_+'$ is probably small compared to the Fermi level. If we accept this, then $B$ is negligible compared to $A$. Thus $M_\parallel$ and $-M_\ddagger$ will have the same sign, which contradicts the notion of $M_\ddagger$ [see Eq. (A4)]. The conclusion is that for small $U$ there is only one moment. This fits in with our previous results. We shall not pursue the consequences of these equations any further here.

To sum up this Appendix: We have shown that, if each atom is assumed to have one of two possible moments, oppositely oriented, and an environment characterized by $m$, then a set of equations can be developed for the local moments which may or may not have solutions with both $M_\parallel$ and $M_\ddagger$ the same sign. If there are solutions, then we conclude that the local moments are of the permanent variety and that an AM calculation is appropriate, with $M^2$ given by Eq. (5.12). If the only solutions have $M_\parallel$ of opposite sign to $M_+$, then we regard this as an inconsistency and conclude that only moments of the induced variety can exist, and that the PM calculation is the appropriate one. The difference between this Appendix and Sec. 5 is that here we have a somewhat better estimate of how the Bloch energy terms are altered by the presence of a magnetization in the crystal.