

Calculation of the Static Properties of Local Moment Systems by the Mean Field Method

A. M. Stewart

School of Physics, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

Abstract

It is demonstrated that two different methods which have been used in the past to calculate the static properties of local moment systems in the mean field approximation are incomplete. A proof is given of the correctness of another method that the author has used in several previous calculations. It is found that some exact and very general relationships exist between the conduction electron magnetization and the local moment magnetization even when it is not valid to treat the interactions between the magnetic atoms by mean field theory.

1. Introduction to the Problem

The purpose of this paper is to discuss the calculation of the static susceptibility of a metal which contains local moments, such as a rare earth metal or intermetallic compound, that may be described by the s-d (or s-f) interaction. Even though this interaction has been known to us for several decades (Vonsovskii 1946; Zener 1951; Ruderman and Kittel 1954; Kasuya 1956; Yosida 1957) there has been in the past, as we shall show, ambiguity and confusion in regard to the correct form of the mean field that acts upon the magnetic ions in a concentrated magnetic material. We make the assumption throughout this paper that the temperature is sufficiently high for Kondo (1969) effects to be neglected.

The first theory of the susceptibility was proposed by Owen *et al.* (1956) who postulated that the mean field H_s that acted upon the conduction electron (s) system was

$$H_s = H + \lambda_{sd} M_d, \quad (1)$$

and that the mean field H_d that acted on the local moment (d) system was

$$H_d = H + \lambda_{sd} M_s + \lambda_{dd} M_d, \quad (2)$$

where H is the external magnetic field, M_s and M_d are the magnetizations of the s and d systems, and λ_{sd} and λ_{dd} are mean field coefficients that describe the exchange interaction between the s and d systems and the exchange within the d system respectively. Owen *et al.* (1956) attributed λ_{dd} to direct exchange and superexchange, such as occurs in transition element insulators, and their theory was criticized by Hasegawa (1959) on the grounds that the term in equation (2) with λ_{sd} took account of only the diagonal matrix elements of the s-d interaction and ignored the off-diagonal elements, which had been shown by Yosida (1957) to be of equal importance.

Equations (1) and (2) have also been used by Cottet *et al.* (1968) and Bloch and Lemaire (1970) to interpret the static magnetic properties of rare earth ions in a highly exchange-enhanced metallic host. These authors did not specify the precise mechanism to which they attributed λ_{dd} , but if it is considered to be due to the other ions acting through the indirect exchange interaction, as calculated, for example, by De Gennes (1962) using a method which takes account of both the diagonal and the off-diagonal matrix elements of the s-d interaction, then it would seem that terms in λ_{sd}^2 (which contain the square of the diagonal matrix element) appear twice, once in the term associated with M_s and then again in λ_{dd} (see equation (4) below). Any contribution to λ_{dd} from direct or superexchange would appear to be ruled out as being of insufficient magnitude in rare earth materials with their compact and well-shielded 4f shells.

On the other hand, in calculations that the author has made of various static properties of local moment systems (Stewart 1972a, 1972b, 1972c, 1973a, 1973b, 1974), instead of equation (2) the following equation, which was deduced from Yosida's (1957) effective Hamiltonian, was used:

$$H_d = H + \lambda_{sd} \chi(0) H + \lambda_{dd} M_d, \quad (3)$$

where $\chi(0)$ is the uniform Pauli susceptibility of the s system and λ_{dd} is explicitly stated to be given by a generalization of De Gennes's (1962) method. The difference between equations (2) and (3) is that the latter does not contain, in the term multiplied by λ_{sd} , the component of the conduction electron magnetization that is induced by the magnetic atoms upon which H_d acts.

Now Gomes and Guimarães (1974) have pointed out that if λ_{dd} is treated as an adjustable parameter which is varied to give the best agreement with experiment then it does not matter whether equation (2) or (3) is used. This is because equation (2) may be written in the same form as equation (3) but with $\tilde{\lambda}_{dd}$ in it instead of λ_{dd} , where

$$\tilde{\lambda}_{dd} = \lambda_{dd} + \lambda_{sd}^2 \chi(0). \quad (4)$$

However, it is clearly of interest to determine which of the equations (2) or (3) is correct in principle so as to be able to relate calculations of the susceptibility that take account of the conduction electron magnetization to those, such as De Gennes's (1962), that do not.

It is important to do this because the effects associated with the magnetization of the conduction electrons can make a contribution of up to 15% to the susceptibility of normal rare earth compounds; however, in those that contain samarium the effect can be very much larger. In fact, de Wijn *et al.* (1974) were not able to explain the measured magnetic form factor of samarium metal by means of conventional crystal field theory, but found it necessary to invoke the very large conduction electron polarization effects (about 50% of the total moment) that had been predicted to exist in samarium (Stewart 1972a, 1972b), in order to obtain reasonable agreement with experiment.

In Section 2 of this paper we show, by explicitly calculating each spatial Fourier component of the conduction electron magnetization, that equation (3) (or its trivial generalization to take account of the fact that what is important is the spin of the d system rather than the magnetization) is correct and that equation (2) is incorrect. In Section 3 we deduce that some exact and general relationships exist between the ionic

magnetization and the conduction electron magnetization of a local moment system even when a mean field treatment of the interactions between the magnetic atoms is not appropriate; for example, near a phase transition.

2. Mean Field Theory of the s-d Interaction

We consider a metal of volume V which contains a total of N atoms. Of these N atoms a certain number cN^* ($c \leq 1$) are magnetic with spin operators S_n and are randomly distributed at positions R_n over N^* possible sites. The Hamiltonian \mathcal{H}_d for the local moments is (Kasuya 1956)

$$\mathcal{H}_d = g_d \mu_B \sum_n S_n \cdot H + \frac{2}{g_s \mu_B N} \sum_n \sum_q J(q) \exp(iq \cdot R_n) S_n \cdot m(q), \quad (5)$$

where g_d and g_s are the gyromagnetic ratios of the local moments and the conduction electrons respectively; μ_B is the magnitude of the electronic Bohr magneton; k and q are allowed vectors in reciprocal space; $J(q)$ is the exchange integral; and $m(q)$, which is the operator for the Fourier transform of the conduction electron magnetization, is given by

$$m(q) = -\frac{1}{2} g_s \mu_B \sum_k \sum_{s,s'} \langle s' | \sigma | s \rangle C_{k-q,s'}^\dagger C_{k,s}. \quad (6)$$

In the above equation C^\dagger and C are Fermion operators, s and s' refer to spin states and σ is the Pauli spin operator.

We obtain the Heisenberg equation of motion for S_i by commuting it with \mathcal{H}_d :

$$\frac{\hbar}{g_d \mu_B} \frac{dS_i}{dt} = \left(H + \frac{2}{g_s g_d \mu_B^2 N} \sum_q J(q) \exp(iq \cdot R_i) m(q) \right) \times S_i, \quad (7)$$

and we identify the mean field H_i which acts on spin S_i as

$$H_i = H + \frac{2}{g_s g_d \mu_B^2 N} \sum_q J(q) \exp(iq \cdot R_i) \langle m(q) \rangle, \quad (8)$$

where the angular brackets denote an ensemble average. However, we note that we must omit from equation (8) that part of $\langle m(q) \rangle$ which is induced by S_i because, from the vector cross product, it can exert no torque on S_i as it is parallel to it. We next use the relation $\langle m(q) \rangle = \chi(q) H(q)$ to calculate $\langle m(q) \rangle$. Here, $H(q)$ is the Fourier transform of the effective field $H_c(r)$ that acts upon the conduction electrons in real space,

$$H(q) = \int \exp(-iq \cdot r) H_c(r) dr, \quad (9)$$

and $\chi(q)$ is the time-independent generalized susceptibility of the conduction electrons. For the particular case of non-interacting conduction electrons, it is well known that

$$\chi(q) = -\frac{\mu_B^2 g_s^2}{2V} \sum_k \frac{\langle n(k+q) \rangle - \langle n(k) \rangle}{\varepsilon(k+q) - \varepsilon(k)}, \quad (10)$$

where $n(k)$ is the occupation number and $\varepsilon(k)$ the band energy of the conduction state k in the extended zone scheme.

Now, by noting that any magnetic Hamiltonian

$$\mathcal{H} = - \int \mathbf{H}_e(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r}) \, d\mathbf{r}$$

may be expressed in the form

$$\mathcal{H} = -V^{-1} \sum_{\mathbf{q}} \mathbf{H}(\mathbf{q}) \cdot \mathbf{m}(-\mathbf{q}),$$

we can deduce from equation (5) that the q th Fourier component $\mathbf{H}(\mathbf{q})$ of the effective field that acts upon the conduction electrons is

$$\mathbf{H}(\mathbf{q}) = V\mathbf{H}\delta_{\mathbf{q},0} - \frac{2V}{g_s \mu_B N} \sum_n \mathbf{J}(-\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{R}_n) \langle \mathbf{S}_n \rangle, \quad (11)$$

and so $\langle \mathbf{m}(\mathbf{q}) \rangle$ is obtained merely by multiplying this by $\chi(\mathbf{q})$. In particular the uniform magnetization $\mathbf{M}_s = \langle \mathbf{m}(\mathbf{0}) \rangle V^{-1}$ of the conduction electrons is given by

$$\mathbf{M}_s = \chi(\mathbf{0}) \mathbf{H} + \chi(\mathbf{0}) \lambda_{sd} \mathbf{M}_d, \quad (12)$$

where

$$\lambda_{sd} = (2V/g_s g_d \mu_B^2 N) \mathbf{J}(\mathbf{0}), \quad \mathbf{M}_d = -g_d \mu_B V^{-1} \sum_n \langle \mathbf{S}_n \rangle, \quad (13)$$

thereby justifying equation (1).

This, of course, is a well-known result, and of more interest is the effective field \mathbf{H}_i of equation (8) that is produced when $\langle \mathbf{m}(\mathbf{q}) \rangle$ is obtained by multiplying equation (11) by $\chi(\mathbf{q})$. This is:

$$\begin{aligned} \mathbf{H}_i = \mathbf{H} \{ 1 + \lambda_{sd} \chi(\mathbf{0}) \} + \left(\frac{2V}{g_s g_d \mu_B^2 N} \right)^2 \sum_{\mathbf{q}} \mathbf{J}(\mathbf{q}) \mathbf{J}(-\mathbf{q}) \chi(\mathbf{q}) \\ \times \sum'_n \exp\{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_n)\} (-g_d \mu_B V^{-1} \langle \mathbf{S}_n \rangle). \end{aligned} \quad (14)$$

In this equation the prime on the sum over n means that the term $n = i$ must be omitted because spin i cannot exert a field on itself.

In the paramagnetic region, the validity of equation (3) may be confirmed by letting $\langle \mathbf{S}_n \rangle$ be independent of n . We then obtain

$$\lambda_{dd} = \left(\frac{2V}{g_s g_d \mu_B^2 N} \right)^2 \left(\sum_{\mathbf{G}} |J(\mathbf{G})|^2 \chi(\mathbf{G}) - (N^*)^{-1} \sum_{\mathbf{q}} |J(\mathbf{q})|^2 \chi(\mathbf{q}) \right), \quad (15)$$

an expression obtained by Yosida (1964) in a calculation that used $g_s = 0$ (note from equation (10) that λ_{dd} is independent of g_s). To derive equation (15) we have used the exact relation $J(-\mathbf{q}) = J^*(\mathbf{q})$ (Kasuya 1956); we have also assumed that the cN^* magnetic atoms are randomly distributed over a Bravais lattice of N^* sites whose reciprocal lattice has basis vectors \mathbf{G} . The two terms in equation (15) arise from the expression

$$\sum'_n \exp\{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_n)\} = c(N^* \delta_{\mathbf{q},\mathbf{G}} - 1), \quad (16)$$

where the sum is averaged over an ensemble of systems with all possible distributions

of the magnetic atoms, and the second term is necessary in order to subtract the $n = i$ term from the sum.

We note that $\chi(\mathbf{q})$ is positive definite because each term in the sum over \mathbf{k} in equation (10) is positive definite ($\langle n(\mathbf{k}) \rangle$ being a function of $\varepsilon(\mathbf{k})$ only), so that the only way for the mean field parameter λ_{dd} to be negative is for the second term in equation (15) to exceed the first. In fact both terms diverge in the approximation in which $J(\mathbf{q})$ is a constant and the electrons are free, and this can cause difficulty in the evaluation of the sums (but see Sakuri *et al.* 1973).

The quantity λ_{dd} is seen to be independent of c and, if the magnetic atoms have a Curie law susceptibility α/T per atom, the paramagnetic Curie temperature comes out to be proportional to c (in fact it is $cN^*\alpha\lambda_{dd}$), a result that is physically reasonable.

If the generalized susceptibility were of the extremely improbable form $\chi(\mathbf{q}) = \chi(\mathbf{0})\delta_{\mathbf{q},\mathbf{0}}$, then the effective field which acts on the ions would indeed be $H_d = H + \lambda_{sd}M_s$. It might be thought that this situation could occur for a conduction electron system with a small Fermi wavevector, resulting in a $\chi(\mathbf{q})$ that was large only for small \mathbf{q} . However, this is not necessarily the case because there would still be the divergences of both of the terms in equation (15) to be taken into account. We conclude, therefore, that the only physical situation in which equation (2) can be valid is the one in which the conduction electron magnetization induced by the magnetic ions is negligible compared with that induced by the external field; in other words, the dilute limit, and in this regime λ_{dd} will necessarily be zero.

3. Conduction Electron Contributions to the Magnetization

Equation (14) would be obtained if the following effective Hamiltonian \mathcal{H}_e were treated in the mean field approximation:

$$\mathcal{H}_e = \mu_B g_d \{1 + \lambda_{sd} \chi(\mathbf{0})\} \sum_i \mathbf{S}_i \cdot \mathbf{H} - \sum'_{i,j} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (17)$$

where

$$A_{ij} = \frac{2V}{(g_s \mu_B^2 N)^2} \sum_{\mathbf{q}} |J(\mathbf{q})|^2 \chi(\mathbf{q}) \exp\{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)\}. \quad (18)$$

This effective Hamiltonian, which Yosida (1957) obtained by treating equation (5) as a perturbation upon the conduction electron system (using \mathbf{S}_n as a fixed classical vector and not, as purported, as a quantum mechanical operator), is, in consequence, an approximation that leaves out any description of the time-dependent effects due to the retarded nature of the interactions between the ions (Barnes 1974). However, for static properties it should give an adequate description of the magnetic behaviour.

In fact, from the Hamiltonian (17) an exact and very general result can be obtained which describes the relation between the conduction electron magnetization and the ionic magnetization of a local moment system under all conditions of temperature (excluding Kondo effects), magnetic concentration and magnetic order. The primary objective is to obtain the quantities A_{ij} , or various combinations of them, from magnetization measurements so that they can be compared with theoretical calculations (see e.g. Freeman 1972; Sakuri *et al.* 1973).

To do this we first assume that the effective Hamiltonian of equation (17) can be solved *exactly* for the case where $\lambda_{sd} \chi(\mathbf{0}) = \alpha$ is zero (α can be made to approach zero without affecting anything else by letting g_s tend to zero). We can then calculate an

expression for the magnetization m_n^i of the ion n as a function of the external field H :

$$m_n^i = \sum_{r=0}^{\infty} {}_n a_r(T) H^r, \quad (19)$$

where the coefficients ${}_n a_r(T)$ depend on the temperature T and on the A_{ij} . The coefficients ${}_n a_r(T)$ can at present be calculated explicitly only in a few limiting cases because our understanding of the thermodynamic properties of the Heisenberg magnet is incomplete.

It may be seen from equation (17) that the effect of nonzero g_s is, by multiplying H by a factor of $(1+\alpha)$, to change equation (19) to

$$m_n^i = \sum_{r=0}^{\infty} {}_n a_r(T) H^r (1+\alpha)^r. \quad (20)$$

Next, using equation (12), we get

$$m_n^e = \sum_{r=0}^{\infty} {}_n a_r(T) H^r (1+\alpha)^r \alpha, \quad (21)$$

where m_n^e is the conduction electron magnetization induced by ion n . Although equation (12) was obtained in this paper by treating the interaction between the conduction electrons and the magnetic atoms by the mean field method, the result appears to be an exact one (Langreth and Wilkins 1972), at least in the absence of exchange enhancement of the conduction electrons. Finally, for the total magnetization $m_n = m_n^i + m_n^e$ that is associated with ion n we have

$$m_n = \sum_{r=0}^{\infty} {}_n a_r(T) H^r (1+\alpha)^{r+1}. \quad (22)$$

We see then that, due to conduction electron polarization effects, the spontaneous magnetization associated with each ion (the $r = 0$ term) is enhanced by a factor of $(1+\alpha)$ and the incremental susceptibility (the $r = 1$ term) by a factor of $(1+\alpha)^2$ over the values that would exist if these conduction electron effects were absent.*

It is well known that the results that we have obtained here apply to non-interacting ions (Kondo 1969), and it has also been shown that some of them apply to paramagnetic (Stewart 1972*a*) and ferromagnetic (Stewart 1974) systems in which the interionic interactions are treated by the mean field method. It was also conjectured but not proved by Wang and Cooper (1970) that the magnetic susceptibility of an antiferromagnet would be enhanced by a factor of $(1+\alpha)^2$. However, it has been demonstrated in the present section of this paper that the results apply to local moment systems in the paramagnetic, critical and magnetically ordered regions regardless of the nature of the magnetically ordered state. The importance of this result is that, by making allowance for the factor of $(1+\alpha)^{r+1}$, it permits the coefficients ${}_n a_r(T)$ to be deduced from magnetization data and so to be compared with theoretical calculations that have been made for the case of $g_s = 0$.

* These relations are exact only to order α because the s - d interaction, acting in second order, will mix other states of the local spin into the unperturbed state (Kondo 1969).

For rare earth atoms α is given by

$$\alpha = g_s J(\mathbf{0}) \rho (g - 1) / g, \quad (23)$$

where ρ , the Pauli susceptibility in units of density of states per spin atom, is

$$\rho = 2\chi(\mathbf{0}) V / g_s^2 \mu_B^2 N \quad (24)$$

and g is the Landé factor of the rare earth. The s-f interaction will also shift the gyromagnetic (or magnetomechanical) ratio g' of a rare earth material away from the Landé value. It can easily be shown that

$$g' = g \{ 1 + J(\mathbf{0}) \rho (g_s - g) (g - 1) / g \}; \quad (25)$$

once again this result is valid for all temperatures and for any type of magnetic order. The result had been obtained previously for the paramagnetic state only and $g_s = 2$ (Stewart 1973a). In two papers (Stewart 1972a, 1973a) some properties of metallic samarium compounds in the paramagnetic phase have been calculated for $g_s = 2$ (for samarium there are significant contributions to the magnetic properties from different angular momentum levels of the ion so that a unique g_d cannot be defined). These calculations can be extended to the case of $g_s \neq 2$ by means of the following prescription: (a) where $2J(\mathbf{0})\rho$ appears explicitly replace it by $g_s J(\mathbf{0})\rho$; (b) where $J(\mathbf{0})\rho$ appears explicitly leave it unchanged. However, it is likely that a value of g_s close to 2 will be suitable for calculating the properties of rare earth metals because the induced orbital magnetic moment (Kubo and Obata 1956), which shifts the gyromagnetic ratios of the paramagnetic transition metals away from 2, acts upon the spin polarization only indirectly through the spin-orbit interaction. This conclusion might need to be altered, though, if a significant interaction between the rare earth ion and the orbital moment of the conduction electrons were found to exist.

4. Discussion

The major result of this paper has been to obtain an explicit expression for the mean field that acts upon a magnetic ion in a metal and, in particular, to have proved that it is given by equation (3) and not by the expression (2) that has been used by other authors in previous calculations. It is emphasized that the mean field that we have obtained in this paper is in agreement with the mean field deduced from Yosida's (1957) effective Hamiltonian and used by the author (Stewart 1972a, 1972b, 1972c, 1973a, 1973b, 1974) in calculations of various static properties of local moment systems. The present paper therefore provides a full justification for the method of calculation used in these latter papers.

The results of this paper have provided a bridge between the two methods of calculating the static properties of local moment systems that have been used in the past. In the first method (see e.g. Cottet *et al.* 1968 and references therein), which was essentially aimed at calculating the dynamic response of the magnetizations of the local moment and conduction electron systems to applied fields, a mean field method (equations (1) and (2)), which is valid only in the dilute limit where the conduction electron magnetization induced by the magnetic ions is negligibly small compared with that induced by the external magnetic field, has been applied in an unwarranted

manner to situations in which concentration effects are important. In the second method (see e.g. De Gennes 1962; Freeman 1972; Sakuri *et al.* 1973), quantities like the coefficient λ_{ad} (which is proportional to the paramagnetic Curie temperature) have been obtained from free electron values of $\chi(\mathbf{q})$ or from values deduced from band structure computations, but no account has been taken of the effect of the external magnetic field upon the conduction electrons; in other words, it has been assumed that g_s is zero. The results of the present paper provide a unified method of calculating static properties which corrects the defects of both these previous schemes. In a recent paper, Barnes (1974) has begun the task of analysing the dynamical properties of concentrated local moment systems using the correct mean field but the free electron approximation for the conduction electron response functions.

Finally, it has been pointed out that some exact, concise and very general relations may be obtained that describe the effect of a nonzero conduction electron gyromagnetic ratio upon the magnetization of a local moment system.

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