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Edited by Peter Fulde

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Spin Fluctuations in Itinerant Electron Magnetism

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Springer-Verlag
Berlin Heidelberg New York Tokyo

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ISBN 3-540-15422-1 Springer-Verlag Berlin Heidelberg New York Tokyo
ISBN 0-387-15422-1 Springer-Verlag New York Heidelberg Berlin Tokyo

Library of Congress Cataloging in Publication Data. Moriya, Tôru. 1930–. Spin fluctuations in itinerant electron magnetism. (Springer series in solid-state sciences , 56). Bibliography: p. Includes index. 1. Magnetism, Band theory of. 2. Electron band theory of metals. 3. Nuclear magnetism. 4. Ferromagnetism. I. Title. II. Series. QC754.2.B35M67 1985 530.4'1 85-7926

Printed in Germany

Typesetting, offsetprinting and bookbinding: Graphischer Betrieb Konrad Triltsch, Würzburg
2153/3130-543210

56

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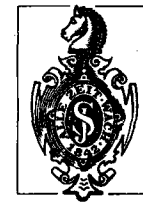

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Preface

Ferromagnetism of metallic systems, especially those including transition metals, has been a controversial subject of modern science for a long time. This controversy stems from the apparent dual character of the *d*-electrons responsible for magnetism in transition metals, i.e., they are itinerant electrons described by band theory in their ground state, while at finite temperatures they show various properties that have long been attributed to a system consisting of local magnetic moments. The most familiar example of these properties is the Curie-Weiss law of magnetic susceptibility obeyed by almost all ferromagnets above their Curie temperatures.

At first the problem seemed to be centered around whether the *d*-electrons themselves are localized or itinerant. This question was settled in the 1950s and early 1960s by various experimental investigations, in particular by observations of d-electron Fermi surfaces in ferromagnetic transition metals. These observations are generally consistent with the results of band calculations.

Theoretical investigations since then have concentrated on explaining this dual character of *d*-electron systems, taking account of the effects of electron-electron correlations in the itinerant electron model. The problem in physical terms is to study the spin density fluctuations, which are neglected in the mean-field or one-electron theory, and their influence on the physical properties.

There have been two main streams in the research in this direction. One has been to study the local moments in metals or the possibility for the itinerant electrons to exhibit spin density fluctuations that are described at least approximately as a set of local magnetic moments. This approach attained remarkable success in the 1960s from a qualitative point of view and has been extended further since then.

The other stream of research has been to improve the mean-field theory by taking into account the spatially extended spin density fluctuations in contrast with the local moment picture. This line of approach, represented by the random-phase approximation, was, however, not successful until the early 1970s when a self-consistent theory of coupled modes of extended spin fluctuations was advanced and the difficulties of the random-phase approximation were removed. This improved theory was remarkably successful when applied to weakly ferromagnetic metals where the long-wavelength components of spin fluctuations are the predominant thermal excitations.

For example, this theory postulates a new mechanism, without local magnetic moment, for the Curie-Weiss susceptibility. The theoretical and experimental investigations in this decade have well established the picture and theory of extended spin fluctuations in weakly ferro- and antiferromagnetic metals; there is now a new class of magnets at the opposite extreme to the quite familiar local moment systems.

This success has given a breakthrough to the theory of itinerant electron magnetism, since it is quite natural to expect that the properties of many metallic magnets are distributed between these mutually opposite extremes. Thus the latest investigations are focused on the intermediate regime between the extremes, to which most metallic magnets including Fe, Co, and Ni are considered to belong. The concept of spin fluctuations is now generalized to include both the local and extended moment limits and a theory of interpolation between them is expected to lead to a unified description of magnetism.

This monograph is intended to review the above-mentioned developments in the field of itinerant electron magnetism. The important steps in the theoretical developments in this area are treated, emphasizing recent theories including the latest attempts at a unified theory. We try to clarify as far as possible to what extent the subject is understood at present and what still has to be examined and clarified in future.

Since the emphasis is on the finite-temperature properties of magnets, important topics relating to the underlying electronic structures were largely omitted: the band-structure calculation, many-body effects in the ground state, and the experimental and theoretical investigations of photoemission which have marked significant progress in recent years. This specialization of topics seems reasonable in view of the size of the volume and of the author's knowledge. Also it is justifiable to discuss important concepts, giving a general picture of magnetism, without going into too fine details of the underlying electronic structure, as has actually been seen in the past theoretical developments.

I should like to thank Professors Y. Ishikawa, Y. Masuda, S. Ogawa, G. Shirane, H. Yasuoka, and K. R. A. Ziebeck for discussions and correspondence regarding the experimental results discussed here. I have benefited from many stimulating discussions with my colleagues who have taken part in the theoretical developments discussed here. My special thanks go to Dr. Y. Takahashi for critical reading of the manuscript and his resulting useful comments on it. I am greatly indebted to Mrs. K. Fujii for her constant help in typing and retyping the manuscript and drawing figures.

Tokyo, January 1985 *T. Moriya*

Contents

1. Introduction

Magnetism has been a subject of conspicuous interest and intensive research in the history of science. Modern theoretical research, which started with the advent of quantum mechanics, has enabled remarkable progress in our understanding of magnetism. The research efforts still continue at present, for example, in the area of metals with narrow d and/or f bands where the essential importance of the electron-electron correlation poses challenging problems to investigators.

This chapter briefly summarizes historical developments in the fundamental pictures and concepts in the modern theory of magnetism. Particular emphasis is placed on the magnetism of transition metals and their compounds, where the famous long-standing controversy between the itinerant and localized models has been resolved into a more general and well-defined problem of spin density fluctuations in a general sense, owing to the recent advance in the theory of itinerant electron magnetism, which is the main subject of this monograph.

1.1 Local Magnetic Moment and the Weiss Theory of Ferromagnetism

The modern theory of magnetism started with the concept of a local magnetic moment with a fixed size. Using this concept, *Langevin* [1.1] explained the Curie law of magnetic susceptibility. Let us now consider a set of atomic magnetic moments each with a fixed magnitude m under an external magnetic field H applied in the z direction. The statistical average of the magnetization is parallel to the external field and its value per atom at temperature T is given by

$$\begin{aligned}\langle m_z \rangle &= \int d\Omega\, m \cos\theta \exp(mH\cos\theta/k_B T)/\int d\Omega \exp(mH\cos\theta/k_B T)\\ &= mL(x),\\ L(x) &= \coth x - 1/x = x/3 - x^3/45 + \ldots,\\ x &= mH/k_B T,\end{aligned} \tag{1.1}$$

where $m\cos\theta$ is the z component of a magnetic moment, k_B the Boltzmann constant and the integrals are over the solid angle. Here $L(x)$ is called the

Langevin function. Using an expansion form of $L(x)$ in (1.1) gives the following expression for the magnetic susceptibility which is inversely proportional to T (the Curie law):

$$\chi = N_0 \lim_{H \to 0} \langle m_z \rangle / H = N_0 m^2 / 3 k_B T \equiv C/T, \tag{1.2}$$

where N_0 is the number of atoms in the crystal, and C is called the Curie constant.

Subsequently *Weiss* [1.2] introduced the notion of an interaction between atomic magnetic moments in solids and approximated its effect by a mean molecular field proportional to the average magnetization. Thus he added the molecular field term $\Gamma \langle m_z \rangle$ to the external field in the Langevin equation (1.1) and obtained

$$\begin{aligned} &\langle m_z \rangle = m L(y), \\ &y = m(H + \Gamma \langle m_z \rangle)/k_B T. \end{aligned} \tag{1.3}$$

Ferromagnetism is described by these equations when there is a solution with $\langle m_z \rangle > 0$ for $H = 0$. The condition for ferromagnetism is thus easily obtained by using the expansion form (1.1) of $L(y)$:

$$T < T_C = m^2 \Gamma / 3 k_B. \tag{1.4}$$

Here T_C is the Curie temperature below which ferromagnetism occurs. The susceptibility above the Curie temperature is calculated from (1.3) as

$$\chi = C/(T - T_C), \tag{1.5}$$

where the Curie constant C is given by (1.2). Equation (1.5) is called the Curie-Weiss law, abbreviated as the CW law from now on. The temperature dependence of the magnetization and that of the inverse susceptibility as obtained by the Weiss theory are shown in Fig. 1.1. Roughly speaking, these forms of $M - T$ and $1/\chi - T$ relations are commonly observed in almost all ferromagnets.

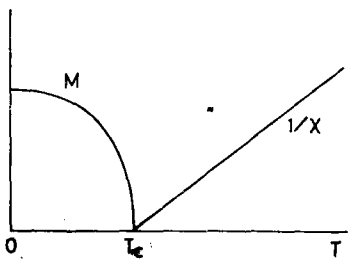

Fig. 1.1. Temperature dependence of magnetization and that of inverse magnetic susceptibility according to the Weiss theory

The Langevin-Weiss theory has explained quite successfully the essential properties of ferromagnets both below and above the Curie temperature. However, there were two difficulties intrinsic to the classical theory of physics. Firstly, it was difficult to justify the existence of an atomic magnetic moment of a constant magnitude. This is related with the Bohr-van Leewen theorem showing the absence of magnetism within purely classical statistics [1.3]. Secondly, the magnitude of the Weiss molecular field cannot be explained within classical physics; the magnetic dipole-dipole interaction gives a value for Γ which is about two or three orders of magnitude smaller than estimated from the observed value of T_C. These difficulties were resolved with the advent of quantum mechanics.

1.2 Magnetic Moments of Atoms

According to quantum mechanics, an electron in an atom goes into an eigenstate having quantized orbital and spin-angular momenta $\hbar \boldsymbol{l}$ and $\hbar \boldsymbol{s}$, where $h = 2\pi\hbar$ is the Planck constant, and each component of $\boldsymbol{l}$ and $\boldsymbol{s}$ is given by a well-known matrix. The magnetic moment of an electron is also quantized in units of $\mu_B = e\hbar/2mc$, the Bohr magneton, and is given by $\boldsymbol{m} = \mu_B(\boldsymbol{l} + 2\boldsymbol{s})$.

As for an atom as a whole, the total angular momentum is a good quantum number. Except for some heavy atoms the Russell-Saunders scheme is valid and the total orbital angular momentum $\boldsymbol{L} = \sum_i \boldsymbol{l}_i$ and the total spin $\boldsymbol{S} = \sum_i \boldsymbol{s}_i$ are also good quantum numbers. The total angular momentum and the total magnetic moment are given by $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ and $\boldsymbol{M} = \mu_B(\boldsymbol{L} + 2\boldsymbol{S}) = g_J \mu_B \boldsymbol{J}$, respectively, where g_J is the Lande g factor.

The eigenstates of atoms in the Russell-Saunders scheme are specified by the quantum numbers S, L, and J and their relative energies satisfy the Hund rules, i.e., the states with the largest value of S have the lowest energy and among these states the state with the largest L has the lowest energy. This lowest energy state has a degeneracy since J can take integral or half odd integral values between $L + S$ and $|L - S|$. This degeneracy is lifted by the spin-orbit coupling $\lambda \boldsymbol{L} \cdot \boldsymbol{S}$. The coupling constant is positive when a given (n, l) shell is less than half occupied and is negative when it is more than half occupied. Each state with a given J has a $(2J + 1)$-fold degeneracy which is lifted by the effect of an external magnetic field.

When the lowest energy state with given S, L and J is well separated from the other states, i.e., the energy separation ΔE is much larger than $k_B T$, we can regard the atom as having a fixed quantized angular momentum and a fixed magnetic moment. The Langevin equation (1.1) is

...ed into the following quantum-mechanical expression:

$$\begin{aligned}\langle m_z \rangle &= g_J \mu_B \langle J_z \rangle, \\ \langle J_z \rangle &= J B_J(x), \\ B_J(x) &= (1 + 1/2J) \coth(1 + 1/2J)\, x - (1/2J) \coth(x/2J), \\ x &= g_J \mu_B J H / k_B T, \end{aligned} \tag{1.6}$$

where $B_J(x)$ is the Brillouin function which reduces to the Langevin function in the limit of $J \to \infty$. The magnetic susceptibility is now given by

$$\chi = N_0 g_J^2 \mu_B^2 J(J+1)/3 k_B T. \tag{1.7}$$

In solids, a magnetic moment is exhibited only by an atom with a partially filled d or f shell. The s and p electrons usually take a principal part in bonding of solids and therefore their states in solids are quite different from those of free atoms, while the d and f electrons, having contracted orbitals compared with the s and p, are usually less important in bonding, and their orbitals are not much modified as the atom goes into a solid. In particular, the $4f$ electrons in rare-earth atoms usually keep almost the same states in solids as in free atoms; J is a good quantum number. For the d electrons, the influence of surroundings is more important and the orbital angular momentum is usually quenched by the effect of crystalline electric fields and the partial covalency. Only the total spin S then is a good quantum number. On the other hand, the d electrons in transition metals are usually itinerant electrons, transferring from atom to atom, and the atomic spin is no longer well defined.

1.3 Heisenberg Localized Electron Model

The origin of the Weiss molecular field was attributed by *Heisenberg* [1.4] to the quantum-mechanical exchange interaction between neighboring atoms. He developed a theory based on the Heitler-London model, conveniently expressed in terms of the atomic spin operators:

$$\mathcal{H} = -\sum_{j,l} J_{jl} (\boldsymbol{S}_j \cdot \boldsymbol{S}_l), \tag{1.8}$$

where j, l specify atomic sites in the crystal, and J_{jl}, the interatomic exchange interaction constant. The molecular field is simply given from this expression as

$$\boldsymbol{H}_{\text{mol}} = 2(g\mu_B)^{-1} \sum_l J_{jl} \langle \boldsymbol{S}_l \rangle, \tag{1.9}$$

where g is the gyromagnetic ratio or the g factor. Thus, from the Weiss molecular field theory

$$\begin{aligned} \langle S_z \rangle &= S B_s(x), \\ x &= [g\mu_B HS + 2J(0)\, S\langle S_z\rangle]/k_B T, \\ J(0) &= \sum_l J_{jl}. \end{aligned} \tag{1.10}$$

The Curie temperatures is given by

$$T_C = 2J(0)\, S(S+1)/3k_B, \tag{1.11}$$

and the magnetic susceptibility above T_C is given by

$$\chi = N_0 g^2 \mu_B^2 S(S+1)/3k_B(T - T_C). \tag{1.12}$$

Heisenberg assumed that $J(0)$ or the exchange constant J between neighboring atoms is positive and of an appropriate order of magnitude. Subsequent attempts to calculate J for ferromagnetic transition metals from realistic atomic orbitals, however, have failed to explain the sign and/or magnitude of J. As discussed shortly, we know at present that ferromagnetic transition metals are not described by the Heisenberg model in its naive form. However, the Heisenberg model as a phenomenological model of magnets and its various generalizations have been overwhelmingly important in elucidating various properties of magnetic materials. By generalizing the sign and range of J_{jl}, antiferro-, ferri- and helimagnetisms have been derived from it. It has led to the discovery of spin waves as elementary excitations, and to the statistical mechanical theory of phase transitions and critical phenomena. Furthermore, theories of magnetic resonances are also developed mainly on the basis of the localized moment model.

The Heisenberg model is actually justified from a microscopic point of view when well-defined local atomic moments exist. This is established to be the case in magnetic insulator compounds and in the majority of rare-earth metals. In the former, the mechanism of exchange interaction is the superexchange which is usually antiferromagnetic, while in the latter indirect exchange interaction via the conduction electrons dominates.

1.4 Itinerant Electron Model

Another main stream in the theory of magnetism induced by quantum mechanics is the itinerant electron theory of ferromagnetism. *Bloch* [1.5] first discussed the possibility of ferromagnetism of an electron gas by using the Hartree-Fock approximation (HFA), and *Wigner* [1.6] subsequently pointed out the importance of the electron-electron correlation which

suppress and eliminates the possibility of ferromagnetism in the electron gas. This conclusion has not been changed by more recent investigations based on modern many-body theories [1.7].

Thus the actual occurrence of ferromagnetism in transition metals is considered to be associated with the atomic character of d-band electrons around each atomic site and mainly intra-atomic exchange interactions; for the d bands the tight-binding model is more appropriate than the electron gas model. *Slater* [1.8] discussed the ferromagnetism of Ni by using HFA on the basis of the tight-binding d bands with intra-atomic exchange interaction only. According to this model the exchange energy I between the Bloch d-band electrons is independent of their wave vectors and is given by

$$I = J/N_0 , \tag{1.13}$$

J being the average of the intra-atomic exchange energy and N_0 the number of atoms in the crystal. The total exchange energy of the system with N electrons and magnetization M (in units of $2\mu_B$) is given by

$$E_{\text{exch}} = \tfrac{1}{4} IN^2 - IM^2 , \tag{1.14}$$

$$N = N_\downarrow + N_\uparrow , \quad M = \tfrac{1}{2}(N_\downarrow - N_\uparrow) , \tag{1.15}$$

where N_σ is the number of electrons with spin σ. *Stoner* [1.9] also developed an itinerant electron theory of ferromagnetism with an approximation of a molecular field which is independent of the wave vector of an electron. This approximation is equivalent to the above approximation of local exchange interactions.

The kinetic energy of an electron system increases with increasing magnetization, owing to splitting of the energy bands for up- and down-spin electrons as shown in Fig. 1.2. When the band splitting 2Δ is small

$$E_{\text{kin}} = \varrho\Delta^2 - \frac{3}{4}\varrho F_1 \Delta^4 + \ldots = \frac{1}{\varrho} M^2 + \frac{1}{4\varrho^3} F_1 M^4 + \ldots ,$$

$$F_1 = (\varrho'/\varrho)^2 - (\varrho''/3\varrho) , \tag{1.16}$$

where ϱ, ϱ' and ϱ'' are the density of states and its derivatives at the Fermi level for $M = 0$.

From (1.14, 16) the total energy is given by

$$E = \frac{1}{\varrho}(1 - I\varrho) M^2 + \frac{1}{4\varrho^3} F_1 M^4 + \ldots . \tag{1.17}$$

Thus a ferromagnetic state is realized for

$$\alpha_0 \equiv I\varrho(\varepsilon_F) > 1 . \tag{1.18}$$