Chapter 1
Introduction

1.1 Historical Overview

The beginning of theoretical studies on itinerant electron magnets goes back to the theory by Stoner [1]. It associates the magnetism in metals with the band splitting of the conduction electron states. Temperature and external field dependence of various magnetic properties are understood in terms of the change in the occupation number of conduction electrons. Since then the development along this line has been carried through by Wohlfarth and co-workers. In the following, the theoretical framework on this line is called the Stoner-Wohlfarth (SW) theory. An introductory review is presented in the book by Mohn [2].

In 1973, two papers were published by Moriya and Kawabata [3, 4] on the effects of collective magnetic excitations, called spin fluctuations. The theory is now well known as the self-consistent renormalization (SCR) spin fluctuation theory. In contrast to the SW theory, rolls of thermal magnetic fluctuations are particularly emphasized in this theory in deriving the Curie–Weiss (CW) law temperature dependence of magnetic susceptibility, observed generally in itinerant electron ferromagnets. Since then intensive theoretical and experimental investigations have been done on various magnetic, thermal, and transport properties of itinerant electron magnets [5].

The SCR theory draws an exact line between properties in the ground state and those at finite temperatures. In the ground state, the SW theory is assumed to be justified. It means that the applicability of the theory is restricted to properties at finite temperatures. Only the effects of thermal spin fluctuations have been their main concerns. For instance, the magnetic isotherm, i.e., the relation between the magnetization M and the external magnetic field H, is generally given as

$$H = a(T)M + b(T)M^3 + \cdots , \qquad (1.1)$$

where the coefficients, $a(T)$, $b(T)$, $\cdots$, on the right-hand side are functions of absolute temperature T. Their T-dependence is predominantly determined by the

effect of nonlinear couplings among thermal fluctuation amplitudes. The first coefficient $a(T)$ corresponds to the inverse of the magnetic susceptibility.

The theory assumes that the relative importance of the effect is mainly restricted to the first coefficient $a(T)$, since its magnitude is very small for magnets and paramagnets close to their magnetic instability points. On the other hand, the T-dependence of higher coefficients has been usually neglected for simplicity. Their values are assumed to be well evaluated by band theoretical calculations. Particularly the coefficient $b(T)$, as a lowest order nonlinear coupling constant, has a significant role in deriving the temperature dependence of the first coefficient $a(T)$.

The theory seemed to be very successful in predicting various magnetic, thermal, and transport properties even quantitatively [5]. Nevertheless, subtle difficulties are involved in the theory as shown below.

1. Temperature dependence of spontaneous magnetization always discontinuously drops to zero at the critical temperature T_C.
2. Nonlinear relation between M^2 and H/M was sometimes observed in the magnetization curve for the compound MnSi [6]. It implies that higher order coefficient, $b(T)$, for instance, in (1.1) is also temperature dependent.
3. The temperature dependence of the specific heat shows a spurious negative peak just above the critical temperature [7].

No satisfactory treatments were, therefore, possible for properties in the magnetically ordered phase as well as effects of external magnetic field.

From the efforts to overcome the above difficulties, a new framework of the spin fluctuation theory was proposed by Takahashi [8]. In contrast to the SCR theory, it explicitly takes into account the effect of zero-point spin fluctuations. It follows that properties of the ground state have become the targets of the theory. The theory has the following characteristic features:

- Magnetic isotherm, i.e., to find the M dependence of H in (1.1), becomes our main theoretical concern.
- Both effects of temperature and external magnetic field can be treated consistently from a unified point of view.

These theoretical developments of the spin fluctuation theory starting from around 1985 are reviewed in this book. The basic ideas necessary to understand the various magnetic properties of itinerant electron magnetism are also presented in detail.

Later in this section, a brief introduction to the theory of magnetism is presented. Then band theoretical treatment of itinerant electron ferromagnetism is explained for the comparison with spin fluctuation theories in later chapters.

1.2 Localized Heisenberg Magnets

When localized moments are defined for atoms in an insulating crystal, interactions of these moments are sometimes described by the following Heisenberg Hamiltonian:

$$\mathscr{H} = -J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \tag{1.2}$$

where $\boldsymbol{S}_i$ is the spin operator on i-th atom and $\langle i, j \rangle$ means that the summation is over the nearest neighbor pairs of i-th and j-th atoms. The coupling constant J, of the order of magnitude t_{ij}^2/U, is called the exchange interaction. Inter-atomic hopping energy and repulsive intra-atomic coulomb energy between electrons are denoted by t_{ij} and U, respectively. Owing to the presence of the above interactions, magnetic transition occurs at some critical temperature T_c. In the ordered phase below T_c, the spontaneous magnetization with some wave vector $\boldsymbol{q}$ appears in the absence of external magnetic field. To grasp a rough picture of magnetic phase transition derived from the above model, simple approximation methods are presented below.

1.2.1 Mean Field Approximation

Curie Law of the Isolated Single Atom System To begin with, let us deal with the single atom system with a finite total angular momentum $\boldsymbol{J}$ under the presence of the external magnetic field $\boldsymbol{H} = (0, 0, H)$ along the z-direction. The Hamiltonian is given by the following Zeeman energy:

$$\mathscr{H} = -\boldsymbol{\mu} \cdot \boldsymbol{H}. \tag{1.3}$$

In the presence of the spin–orbit interaction, only the total angular moment $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is a conserved quantity, rather than the spin moment $\boldsymbol{S}$ in (1.3), and the magnetic moment $\boldsymbol{\mu}$ is effectively proportional to $\boldsymbol{J}$, i.e., $\boldsymbol{\mu} = -g\mu_{\mathrm{B}} \boldsymbol{J}$. The constant g is known as the gyro-magnetic ratio. The Hamiltonian (1.3) is therefore represented as

$$\mathscr{H}_z = g\mu_{\mathrm{B}} \boldsymbol{J} \cdot \boldsymbol{H}. \tag{1.4}$$

Although the thermal average of $\boldsymbol{\mu}$ is zero in equilibrium state, the finite magnetic moment m, proportional to the external magnetic field H, is induced.

$$m = \langle \mu_z \rangle = \chi(T) H. \tag{1.5}$$

According to the conventional method of statistical mechanics, the thermal average of the above moment can be evaluated. In the presence of the magnetic field H along the z-axis, the eigenenergies of (1.3) split into the equidistant $(2J + 1)$ levels. Thermodynamic properties of the system are derived from the free energy $F(H, T) = -k_{\mathrm{B}} T \log Z$, and therefore from the following partition function Z:

$$Z = \sum_{m=-J}^{J} e^{g\mu_B m H/k_B T} = \frac{e^{-g\mu_B J H/k_B T}[1 - e^{g\mu_B(2J+1)H/k_B T}]}{1 - e^{g\mu_B J H/k_B T}}$$

$$= \frac{\sinh[(2J+1)g\mu_B H/2k_B T]}{\sinh(g\mu_B H/2k_B T)} \tag{1.6}$$

$$F(H,T) = -k_B\{\log\sinh[(2J+1)g\mu_B H/2k_B T] - \log\sinh(g\mu_B H/2k_B T)\}$$

The magnetic moment is then derived from the free energy, as given by

$$m = g\mu_B\langle J_z\rangle = -\frac{\partial F}{\partial H} = g\mu_B B_J(x)$$

$$B_J(x) = \{(1 + 1/2J)\coth[(1 + 1/2J)x] - (1/2J)\coth(x/2J)\}, \tag{1.7}$$

where $x = g\mu_B J H/k_B T$, and $B_J(x)$ is known as the Brillouin function.

Depending on the magnitude of x, the following expansion is satisfied for $\coth x$ in (1.7):

$$\coth x = \begin{cases} \dfrac{1}{x} + \dfrac{x}{3} + \cdots, & \text{for } |x| \ll 1 \\ 1 + 2e^{-2x} + \cdots, & \text{for } |x| \gg 1 \end{cases} \tag{1.8}$$

At high temperatures, since $x \ll 1$ is satisfied, the first line of (1.7) is approximated by

$$m \simeq \frac{(g\mu_B)^2 J(J+1)}{3k_B T} H = \chi(T)H. \tag{1.9}$$

Even if the system consists of a large number of atoms, e.g., N atoms, its magnetic susceptibility becomes N times larger than that in the case of a single atom, as far as inter-atomic interactions are negligible like systems of dilute gas. The magnetic susceptibility is then given as

$$\chi(T) = \frac{C}{T}, \quad C = \frac{N(g\mu_B)^2 J(J+1)}{3k_B}. \tag{1.10}$$

The above temperature dependence is known as the Curie law, and the constant C is the Curie constant.

The total magnetic moment squared, $\mu^2 = \boldsymbol{\mu}\cdot\boldsymbol{\mu}$, is a conserved quantity of the system, for the commutation relation, $[J^2, \mathscr{H}] = 0$, is satisfied. Equation (1.10) means that the following relation is satisfied between the conserved amplitude squared, $J^2 = J_x^2 + J_y^2 + J_z^2$, and the magnetic susceptibility $\chi(T)$.

$$\frac{1}{3}\boldsymbol{\mu}\cdot\boldsymbol{\mu} = (g\mu_B)^2 J(J+1) = \frac{1}{N}k_B T\chi(T) \tag{1.11}$$

The above relation is a special case of the fluctuation–dissipation theorem of non-equilibrium statistical mechanics, i.e., the case where the high temperature

approximation is justified. A brief explanation of the theorem will be given in Chap. 2. The Curie law temperature dependence of the magnetic susceptibility is closely related to the basic principle of the statistical mechanics. If we know the above relation (1.11) from the beginning, we will be able to derive the Curie law behavior of $\chi(T)$ straightforwardly.

Mean Field Approximation Let us next deal with a system, in which a large number of localized moments are included. Mutual interactions among them are described by the Heisenberg Hamiltonian of (1.2). By decreasing the temperature of such a system, the magnetic phase transition occurs at some critical temperature T_c. Below T_c, a finite spontaneous magnetization with some spatial modulation appears. As a simple approximate method for phase transitions, we will show below a treatment based on the molecular field approximation. We assume that the interaction in (1.2) is ferromagnetic, i.e., J is positive, for simplicity of the treatment.

In this approximation, interactions between a spin S_i on ith site with neighboring spins S_j on jth sites is approximated by an effective static external field.

$$H_m = \frac{J}{g\mu_B} \sum_j {}'\langle S_j \rangle \tag{1.12}$$

If the spontaneous moment is in the z-axis direction, it becomes equivalent to the problem in the presence of the following effective magnetic field H_{eff}:

$$H_{\text{eff}} = H + H_m = H + \frac{\zeta J}{N(g\mu_B)^2} M, \quad M = \frac{g\mu_B N}{\zeta} \sum_j {}'\langle S_j^z \rangle \tag{1.13}$$

where j represents the summation over the nearest neighbor ζ magnetic ions. The magnetization is denoted by M in this treatment. If we put the effective field H_{eff} of (1.13) into the external magnetic field of the single spin problem, the magnetic susceptibility (1.9) at high temperatures is written as

$$M \simeq \frac{N(g\mu_B)^2 S(S+1)}{3k_B T} H_{\text{eff}} = \frac{S(S+1)}{3k_B T} [N(g\mu_B)^2 H + \zeta J M]. \tag{1.14}$$

Now, from the definition of $\chi(T) = M/H$, the temperature dependence of the magnetic susceptibility is given as

$$\chi(T) = \frac{N(g\mu_B)^2 S(S+1)}{3k_B(T - T_C)}, \quad T_C = \frac{S(S+1)\zeta J}{3k_B} \tag{1.15}$$

It is called Curie–Weiss law temperature dependence. It diverges at the critical temperature T_c, called Curie temperature for ferromagnets. Below T_c, the spontaneous magnetization appears even in the absence of external magnetic field.

The temperature dependence of the magnetization in the ordered phase is obtained by solving the following equation:

$$M = N(g\mu_{\mathrm{B}})B_J(x), \quad x = \frac{\zeta J M}{N(g\mu_{\mathrm{B}})k_{\mathrm{B}}T}. \tag{1.16}$$

It is the same equation as (1.7), if H in x is replaced by H_{eff} for $H = 0$. At low temperatures, the following exponential temperature dependence, characteristic of systems with finite energy gap, is derived:

$$
\begin{aligned}
M &\simeq \frac{N}{2}g\mu_{\mathrm{B}}\left[(2S+1)(1+2\mathrm{e}^{-g\mu_{\mathrm{B}}(2S+1)H_{\mathrm{eff}}/k_{\mathrm{B}}T}) - (1+2\mathrm{e}^{-g\mu_{\mathrm{B}}H_{\mathrm{eff}}/k_{\mathrm{B}}T})\right] \\
&= Ng\mu_{\mathrm{B}}S\left(1 - \frac{1}{S}\mathrm{e}^{-g\mu_{\mathrm{B}}H_{\mathrm{eff}}/k_{\mathrm{B}}T} + \cdots\right),
\end{aligned}
\tag{1.17}
$$

the same expansion as (1.8) justified for $1 \ll |x|$. In order to derive the more reasonable dependence, the effect of spin waves has to be included.

Note that in the above treatment of the magnetic susceptibility, the magnetization M is directly estimated by using the thermodynamic relation (1.7). The approximate free energy is first evaluated in this example. Then the magnetic susceptibility is obtained from its second derivative with respect to the magnetization M. Similar treatments are also employed by the SW and SCR theories.

1.2.2 Phase Transitions of Heisenberg Magnets and Spin Amplitude Conservation

We show in this section another different approach based on the spin amplitude conservation. Only the case of ferromagnetism is treated as well for simplicity. The spin operator S_j on a jth magnetic ion site commutes with the squared spin amplitude S_i^2 on any ith site. The following commutation relation is then satisfied for each operator S_i^2:

$$[S_i^2, \mathscr{H}] = 0 \tag{1.18}$$

It implies that S_i^2 is a constant of motion and its expectation value is always conserved. The following spin amplitude conservation is satisfied:

$$\sum_i \langle S_i \cdot S_i \rangle = \sum_q \langle S_{\mathbf{q}} \cdot S_{-\mathbf{q}} \rangle = NS(S+1) \tag{1.19}$$

A number of magnetic ions in the crystal is denoted by N. In the case where a finite static magnetization is present, it is written as a sum of the mean spin amplitude squared and the average of squared fluctuation amplitudes.

$$|\langle S_0 \rangle|^2 + \sum_q \langle \delta S_{\mathbf{q}} \cdot \delta S_{-\mathbf{q}} \rangle = NS(S+1), \quad \delta S_{\mathbf{q}} = S_{\mathbf{q}} - \delta_{q,0}\langle S_0 \rangle. \tag{1.20}$$

In Eqs. (1.19) and (1.20), fourier components of spin operators are defined as

$$S_q = \sum_i e^{-iq \cdot R_i} S_i, \quad S_i = \frac{1}{N} \sum_q e^{iq \cdot R_i} S_q. \tag{1.21}$$

The Hamiltonian in (1.2) is also expressed in the wave number representation as

$$\mathcal{H} = -\frac{J}{2N^2} \sum_{ij} \sum_{qp} e^{i(q \cdot R_i - p \cdot R_j)} S_q \cdot S_{-p}$$

$$= -\frac{J}{2N^2} \sum_{ij} \sum_{qp} e^{iq \cdot (R_i - R_j) + i(q-p) \cdot R_j} S_q \cdot S_{-p} = -\frac{1}{2N} \sum_q J(q) S_q \cdot S_{-q} \tag{1.22}$$

where $J(q)$ is defined as a following sum of nearest neighbor sites j, as given by

$$J(q) = J \sum_j {}' e^{iq \cdot R_{ij}}, \quad (R_{ij} = R_i - R_j)$$

We show below that the magnetic properties of this model are derived from the above amplitude conservation (1.19). Note that the following fluctuation dissipation theorem is satisfied at high temperatures:

$$(g\mu_B)^2 \frac{1}{3} \langle S_q \cdot S_{-q} \rangle = k_B T \chi(q). \tag{1.23}$$

Equation (1.13) is then regarded as the condition that the wave vector dependence magnetic susceptibility $\chi(q)$ has to satisfy. What we have to do next is to find the wave vector dependence of $\chi(q)$.

Let us next deal with an effect of externally applied magnetic field H_q along z-axis with spatial modulation of a wave vector q. The Zeeman energy of this effect is given as

$$\mathcal{H}_1 = \frac{1}{2} g\mu_B (H_{-q} S_q^z + H_q S_{-q}^z)$$

$$= -g\mu_B \sum_i [H_q' \cos(q \cdot R_i) + H_q'' \sin(q \cdot R_i)] S_i^z, \tag{1.24}$$

$$H_q = H_q' - i H_q''$$

As an effect of this term, we expect the magnetic moments are induced in the system, that are proportional to H_q and H_{-q} with the same wave vectors $\pm q$. The magnetic susceptibilities $\chi(q)$ and $\chi(-q)$ are obtained as their coefficients. Each spin operator with wave vector q or $-q$ is then defined as a sum of the mean value and the fluctuation.

$$S_q = \langle S_q \rangle + \delta S_q, \quad S_{-q} = \langle S_{-q} \rangle + \delta S_{-q} \tag{1.25}$$

For other operators with different wave vectors, $p \neq \pm q$, their mean values are assumed to be zero ($\langle S_{\pm p} \rangle = 0$).

In the mean field approximation, only the linear terms with respect to fluctuations are retained, whereas the rest are neglected. The Hamiltonian is then written as follows:

$$\mathcal{H}_{MF} = -\frac{1}{N} J(q) \left(\langle S_q \rangle \cdot S_{-q} + \langle S_{-q} \rangle \cdot S_q \right) + \frac{1}{2} g\mu_B (H_{-q} S_q^z + H_q S_{-q}^z) \tag{1.26}$$

It is easy to see that the above Hamiltonian is effectively equivalent with the model in the absence of the magnetic field, provided that the external magnetic field H_q is replaced by

$$H_q \rightarrow H_{\text{eff},q} = H_q - \frac{2}{N g\mu_B} J(q) \langle S_q^z \rangle \tag{1.27}$$

The magnetic moment induced by the above spatially modulated effective magnetic field is given then by

$$M_q = -g\mu_B \langle S_q \rangle = \frac{1}{2} \chi_{\text{loc}}(T) H_{\text{eff},q}, \tag{1.28}$$

where $\chi_{\text{loc}}(T)$ represents a local magnetic susceptibility defined against the local magnetic field acting on each atomic site in the crystal.

Substituting the effective field (1.27) into the right-hand side of (1.28), we are led to the expression

$$M_q = \frac{\chi_{\text{loc}}(T)}{1 - \chi_{\text{loc}}(T) J(q)/N(g\mu_B)^2} \frac{1}{2} H_q = \chi(q) \frac{H_q}{2}, \tag{1.29}$$

where the wave vector-dependent magnetic susceptibility $\chi(q)$ is defined as a coefficient of $H_q/2$, given as

$$\begin{aligned}
\chi(q) &= \frac{\chi_{\text{loc}}(T)}{1 - \chi_{\text{loc}}(T) J(q)/N(g\mu_B)^2} \\
&= \frac{N(g\mu_B)^2}{[N(g\mu_B)^2/\chi_{\text{loc}}(T) - J(0)] + J(0) - J(q)}.
\end{aligned} \tag{1.30}$$

From the condition that both sides agree with each other for $q = 0$, (1.30) is also rewritten in the form

$$\chi(q) = \frac{1}{1/\chi(0) + [J(0) - J(q)]/N(g\mu_B)^2}, \tag{1.31}$$

where $\chi(0)$ is given by

$$\frac{1}{\chi(0)} = \frac{1}{\chi_{\text{loc}}(T)} - \frac{J(0)}{N_0(g\mu_B)^2}. \tag{1.32}$$

By putting the above (1.31) into (1.23), the spin amplitude conservation (1.19) is finally given as

$$\frac{T}{N} \sum_q \frac{1}{N/\chi(0) + [J(0) - J(q)]/(g\mu_B)^2} = \frac{1}{3} S(S+1). \tag{1.33}$$

Magnetic properties derived from the above equation are shown below.

- The critical temperature lower than that derived in the mean field approximation. In this formalism, T_c is determined by the condition,

$$k_B T_c \frac{1}{N} \sum_q \frac{1}{J(0) - J(q)} = \frac{1}{3} S(S+1). \tag{1.34}$$

It is derived by assuming $\chi^{-1}(0) = 0$ at $T = T_c$ in (1.33). To compare the result with (1.15) for T_c in the mean field approximation, note that the following properties are satisfied for $J(q)$:

$$\sum_q J(q) = 0, \quad J(0) = \zeta J, \quad \therefore \quad \frac{1}{N} \sum_q [J(0) - J(q)] = \zeta J \tag{1.35}$$

Mathematically, it is also known that the following inequality is generally satisfied, as far as all the a_i are positive.

$$\frac{1}{n} \left(\frac{1}{a_1} + \frac{1}{a_2} + \cdots + \frac{1}{a_n} \right) \geq \frac{n}{(a_1 + a_2 + \cdots + a_n)} \tag{1.36}$$

If we let $J(0) - J(q)$ and N correspond to a_i and n, we are led to the inequality

$$\frac{S(S+1)}{3k_B T_c} = \frac{1}{N} \sum_q \frac{1}{J(0) - J(q)} \geq \frac{N}{\sum_q [J(0) - J(q)]} = \frac{1}{\zeta J} = \frac{S(S+1)}{3k_B T_c^{\text{MF}}},$$

where the critical temperature in the mean field approximation is denoted by T_c^{MF}. Owing to the effect of fluctuations, the critical temperature T_c is obtained lower than T_c^{MF}, i.e., $T_c \leq T_c^{\text{MF}}$ is satisfied.

- Temperature dependence of magnetic susceptibility $\chi(T)$ around the critical point. The temperature dependence of the magnetic susceptibility is evaluated by solving (1.33) for $\chi(0)$ as a function of temperature. At high temperatures, its inverse, $\chi^{-1}(0)$, has to increase proportional to T, because the right-hand side is constant.

To find the temperature dependence around the critical temperature, $T_c \lesssim T$, let us rewrite (1.33) as

$$\frac{T}{N} \sum_{q} \frac{1}{N/\chi(0) + [J(0) - J(q)]/(g\mu_B)^2} = \frac{T_c}{N} \sum_{q} \frac{1}{[J(0) - J(q)]/(g\mu_B)^2},$$
(1.37)

where the right-hand side is replaced by the left-hand side of (1.34). By subtraction of the same value, $(T/N)\sum_{q}\{[J(0) - J(q)]/(g\mu_B)^2\}^{-1}$, from both the sides, (1.37) is further written in the form

$$\frac{T}{N} \sum_{q} \left(\frac{1}{N/\chi(0) + [J(0) - J(q)]/(g\mu_B)^2} - \frac{1}{[J(0) - J(q)]/(g\mu_B)^2} \right)$$

$$= \frac{(T_c - T)}{N} \sum_{q} \frac{1}{[J(0) - J(q)]/(g\mu_B)^2} \equiv c(T_c - T) \qquad (1.38)$$

where the constant c is defined as the summation over q on the right-hand side. The wave vector summation of the above left-hand side is easily evaluated by assuming the quadratic dependence, $[J(0) - J(q)]/(g\mu_B)^2 = Aq^2$, around the origin. The result is given as

$$T \frac{4\pi V}{(2\pi)^3 N} \int_0^{q_B} dq\, q^2 \left(\frac{1}{y + Aq^2} - \frac{1}{Aq^2} \right) = -\frac{T v_0}{2\pi^2 A} y \int_0^{q_B} dq\, \frac{1}{y + Aq^2}$$

$$= -\frac{T v_0}{2\pi^2 A} \sqrt{\frac{y}{A}} \tan^{-1}\left(\sqrt{\frac{A}{y}} q_B \right) \simeq -\frac{T v_0}{4\pi A} \sqrt{\frac{y}{A}} = c(T_c - T),$$
(1.39)

where we have defined $y = N/\chi(0)$ and $v_0 = V/N$ for volume per magnetic ion. The following $(T - T_c)^2$-linear temperature dependence of $y \propto 1/\chi(0)$ is finally derived in this region.

$$y = \left(\frac{4\pi c}{v_0} \right)^2 \frac{A^3}{T^2} (T - T_c)^2 \qquad (1.40)$$

The behavior different from the result of the mean field theory is characteristic of the critical phenomena.

We have shown two different treatments of magnetic properties of localized Heisenberg magnets. The first treatment is particularly concerned only with the order parameter induced in the system. In the second approach, the effects of fluctuations are explicitly taken into account. As a result, the critical temperature is lowered and more reasonable temperature dependence of the magnetic susceptibility can be derived around $T = T_c$.

1.3 Band Theoretical Approach

In this section, we give a brief overview of the Stoner-Wohlfarth (SW) theory of itinerant electron magnetism. It is essentially an application of the electron theory of metals in solid state physics. The theory is based on the following theoretical model known as the Hubbard Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + U \sum_i n_{i\uparrow}n_{i\downarrow}, \quad \mathcal{H}_0 = \sum_{i,j,\sigma} t_{ij}c_{i\sigma}^\dagger c_{j\sigma} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma}, \qquad (1.41)$$

where $\mathcal{H}_0$ represents the single electron hopping between magnetic ions in a crystal. Symbols $c_{i\sigma}^\dagger$ and $c_{j\sigma}$ of this term are the creation and the annihilation operators, respectively, for conduction electrons of ith and jth sites with spin direction σ. Among them the following anti-commutation relations are satisfied:

$$\{c_{j\sigma}, c_{j\sigma'}^\dagger\} = \delta_{ij}\delta_{\sigma,\sigma'}, \quad \{c_{i\sigma}, c_{j\sigma'}\} = \{c_{i\sigma}^\dagger, c_{j\sigma}^\dagger\} = 0 \qquad (1.42)$$

Operators and the single electron energy for the Bloch state with the wave number $\boldsymbol{k}$ are denoted by $c_{k\sigma}^\dagger$, $c_{k\sigma}$, and ε_k. The second term, responsible for the origin of magnetism, is the repulsive Coulomb interaction between electrons with different spin directions on the same atomic site.

In the SW theory, the appearance of itinerant electron magnetism and its various properties are understood associated with the changes of occupation numbers of conduction electrons around the Fermi energy. The substantial difficulty of the theory stems from this idea. The difference in the numbers of conduction electrons with up and down spin directions is regarded as the origin of the magnetism. The magnetization and the total number of electrons are therefore given as

$$M = -\frac{1}{2}\sum_k \langle n_{k\uparrow} - n_{k\downarrow}\rangle = -\frac{N_0}{2}\langle n_\uparrow - n_\downarrow\rangle$$
$$N = \sum_k \langle n_{k\uparrow} + n_{k\downarrow}\rangle = N_0 \langle n_\uparrow + n_\downarrow\rangle, \qquad (1.43)$$

where we have defined M as a difference of the average numbers of electrons with up and down electrons. The magnetization is given by $2\mu_B M$. In terms of M and N, the average numbers of $\langle n_\uparrow\rangle$ and $\langle n_\downarrow\rangle$ are defined by

$$\langle n_\uparrow\rangle = \frac{1}{2N_0}(N - 2M)$$

$$\langle n_\downarrow\rangle = \frac{1}{2N_0}(N + 2M) \qquad (1.44)$$

1.3.1 Hartree–Fock Approximation

It is generally very difficult to deal with the system described by the Hubbard Hamiltonian with a huge number of mutually interacting electrons. In the SW theory, the second interaction term in (1.41) is approximated by an effective magnetic field as given by

$$
\begin{aligned}
U \sum_i n_{i\uparrow} n_{i\downarrow} \Longrightarrow \ & U \sum_i (n_{i\uparrow} \langle n_\downarrow \rangle + n_{i\downarrow} \langle n_\uparrow \rangle - \langle n_\downarrow \rangle \langle n_\uparrow \rangle) \\
= \ & U \sum_{k\sigma} n_{k\sigma} \langle n_{-\sigma} \rangle - N_0 U \langle n_\downarrow \rangle \langle n_\uparrow \rangle \\
= \ & I \sum_{k\sigma} \left(\frac{N}{2} - \sigma M \right) c_{k\sigma}^\dagger c_{k\sigma} - I \left(\frac{N^2}{4} - M^2 \right), \quad (I = U/N_0)
\end{aligned}
$$
(1.45)

On the other hand, in the presence of a uniform external magnetic field H, the Zeeman energy is written in the form

$$
- M^z H = - \sum_k \frac{h}{2} (c_{i\uparrow}^\dagger c_{i\uparrow} - c_{i\downarrow}^\dagger c_{i\downarrow}) = - \sum_{k\sigma} \sigma \frac{h}{2} c_{k\sigma}^\dagger c_{k\sigma}, \quad (h = 2\mu_B H) \quad (1.46)
$$

Comparing (1.45) with (1.46), the effect of the repulsive Coulomb interaction is regarded as the presence of extra magnetic field, $2IM$. The following effective Hamiltonian is derived, with substitution of (1.45) for (1.41), in the presence of the external magnetic field.

$$
\begin{aligned}
\mathscr{H} &= \sum_{k\sigma} (\varepsilon_{k\sigma} - \mu) c_{k\sigma}^\dagger c_{k\sigma} - I \left(\frac{N^2}{4} - M^2 \right) \\
\varepsilon_{k\sigma} &= \varepsilon_k + \frac{IN}{2} - \sigma \Delta, \quad \Delta = IM + \frac{h}{2}
\end{aligned}
$$
(1.47)

Thermodynamic properties of this system are now evaluated according to the conventional procedure of statistical mechanics.

The free energy of our system of non-interacting Fermions is given as

$$
F(h, \mu, T) = IM^2 + F_0, \quad F_0(h, \mu, T) = -k_B T \sum_{k\sigma} \ln(1 + e^{-(\varepsilon_{k\sigma} - \mu)/k_B T})
$$
(1.48)

The total electron number N and the magnetization M are related to the chemical potential μ and the external magnetic field h, respectively, by the following thermodynamic relations:

$$-\frac{\partial F}{\partial \mu} = N(h, \mu, T) = \sum_{k\sigma} f(\varepsilon_{k\sigma})$$

$$= \int d\varepsilon \rho(\varepsilon)[f(\varepsilon + \Delta) + f(\varepsilon - \Delta)]$$

$$-\frac{\partial F}{\partial h} = M(h, \mu, T) = -\frac{1}{2} \sum_{k\sigma} \sigma f(\varepsilon_{k\sigma}) \tag{1.49}$$

$$= -\frac{1}{2} \int d\varepsilon \rho(\varepsilon)[f(\varepsilon + \Delta) - f(\varepsilon - \Delta)]$$

where the Fermi distribution function is defined as

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}. \tag{1.50}$$

1.3.2 Free Energy of Stoner-Wohlfarth Theory

In our treatment of systems showing magnetic phase transitions at some finite temperature, it is convenient to introduce the free energy $F(M, N)$, in place of $F(h, \mu, T)$, with respect to variables M and N. It is useful for our intuitive understanding of magnetic phase transitions. For example, the free energy then becomes minimum at finite spontaneous magnetization M for ferromagnet. These two free energies are related by the Legendre transformation,

$$F(M, N, T) = F(h, \mu, T) + hM + \mu N, \tag{1.51}$$

where variables h and μ on the right-hand side are eliminated by using (1.49) as functions of M and N. Then the following new thermodynamic relations are satisfied for new variables:

$$\frac{\partial F(M, N, T)}{\partial N} = \mu + \left[\frac{\partial F(h, \mu, T)}{\partial \mu} + N \right] \frac{\partial \mu}{\partial N}$$

$$+ \left[\frac{\partial F(h, \mu, T)}{\partial h} + M \right] \frac{\partial h}{\partial N} = \mu$$

$$\frac{\partial F(M, N, T)}{\partial M} = h + \left[\frac{\partial F(h, \mu, T)}{\partial \mu} + N \right] \frac{\partial \mu}{\partial M} \tag{1.52}$$

$$+ \left[\frac{\partial F(h, \mu, T)}{\partial h} + M \right] \frac{\partial h}{\partial M} = h$$

As will be shown later, the new free energy can be expanded in powers of M as far as the M dependence of the free energy in (1.51) is concerned.

$$F(M, T) = F(0, T) + \frac{1}{2}a(T)M^2 + \frac{1}{4}b(T)M^4 + \cdots \tag{1.53}$$

The first term on the right-hand side is the free energy at $M = 0$. In the SW theory, the free energy is expanded in powers of M and temperature T by regarding them as small parameters. As for the temperature dependence, the Sommerfeld expansion is applied to the following integral:

$$\int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) + \sum_{n=1} a_n (k_B T)^{2n} g^{(2n-1)}(\mu), \qquad (1.54)$$

where the integrand consists of a product of the Fermi distribution function $f(\varepsilon)$ and an arbitrary function $g(\varepsilon)$. Precise values of expansion coefficients a_n are known, e.g., $a_1 = \pi^2/6$, in the second term.

For the derivation of the free energy (1.53), we need to evaluate (1.49) expanded in terms of small parameters, T, Δ, and $\delta\mu \equiv \mu - \varepsilon_F$. The chemical potential in the non-magnetic ground state is denoted by ε_F. The energy of conduction electrons in the Fermi distribution function is then written as

$$\varepsilon_{k\sigma} - \mu = (\varepsilon_k - \sigma\Delta - \delta\mu) - \varepsilon_F = \varepsilon_k - (\delta\mu + \sigma\Delta).$$

If we always use the Fermi distribution function with fixed $\mu = \varepsilon_F$, (1.49) is rewritten as follows:

$$\begin{aligned}
N &= \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon)[f(\varepsilon - \Delta - \delta\mu) + f(\varepsilon + \Delta - \delta\mu)] \\
2M &= \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon)[f(\varepsilon - \Delta - \delta\mu) - f(\varepsilon + \Delta - \delta\mu)]
\end{aligned} \qquad (1.55)$$

It is better to use the following equation, in place of the above first equation, being derived by subtracting both sides of the first line of (1.55) and the same but with $\Delta = 0$ and $\delta\mu = 0$.

$$\sum_{\sigma=\pm 1} \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon)[f(\varepsilon - \sigma\Delta - \delta\mu) - f(\varepsilon)] = 0. \qquad (1.56)$$

Now the above (1.56) and the second equation of (1.55) are expanded in powers of $\delta\mu$, Δ, and $(k_B T)^2$, as given by

$$\begin{aligned}
2\rho\delta\mu &+ \frac{2\pi^2}{3}\rho'(k_B T)^2 + \rho'\Delta^2 + \cdots = 0 \\
2M &= 2\Delta\left[\rho + \frac{\pi^2}{3}\rho''(k_B T)^2 + \cdots\right] + 2\rho'\Delta\delta\mu + \frac{1}{3}\rho''\Delta^3 + \cdots \\
&= 2\rho\Delta\left[1 - \frac{\pi^2}{3}\left(\frac{\rho''}{\rho} - \frac{\rho'^2}{\rho^2}\right)(k_B T)^2 + \cdots\right] + \left(\frac{\rho''}{3} - \frac{\rho'^2}{\rho}\right)\Delta^3 + \cdots
\end{aligned} \qquad (1.57)$$

The last line is obtained by putting $\delta\mu$ in terms of Δ^2 and $(k_B T)^2$ into the right-hand side of the second line. With the use of $\Delta = IM + h/2$, the last expression is finally converted in the form

$$h = \frac{\partial F}{\partial M} = a(T)M + b(T)M^3 + \cdots , \tag{1.58}$$

where the coefficients $a(T)$ and $b(T)$ are given by

$$a(T) = \frac{2}{\rho} - 2I + \frac{\pi^2}{3} \left(\frac{\rho''}{\rho} - \frac{\rho'^2}{\rho^2} \right) (k_B T)^2 + \cdots ,$$
$$b(T) = \frac{1}{\rho^3} \left(\frac{\rho'^2}{\rho^2} - \frac{\rho''}{3\rho} \right) + \cdots . \tag{1.59}$$

The M dependence of the free energy in (1.52) is obtained by integrating the thermodynamic relation (1.52) with respect to M.

   The free energy (1.52) of the SW theory is given as a sum of two competitive contributions, i.e., the band energy resulting from the hopping of conduction electrons from an atomic site to site and the on-site repulsive Coulomb energy between electrons with opposite spin directions. The thermodynamic state is determined by its stability condition with respect to its variables. If it becomes stable for a state with finite magnetization M, ferromagnetism appears in the system. Since the variation of occupation numbers of conduction electrons is usually restricted within around the Fermi energy ε_F, magnetic properties are characterized in the form of the density of states around ε_F. The magnetic properties of the SW theory are therefore derived by the free energy (1.53) with coefficients $a(T)$ and $b(T)$ given by (1.59).

1.4 Magnetic Properties Derived from the SW Theory

Typical magnetic properties derived from the free energy (1.53) of the SW theory are summarized as follows:

- The condition of appearance of the spontaneous magnetization in the ground state is given as
$$a(0) < 0, \quad \text{or} \quad I\rho > 0. \tag{1.60}$$

  It is usually called the Stoner condition. When it is satisfied, the magnetism develops as the result of spin splitting of the conduction electron bands.
- Temperature dependence of the magnetic susceptibility is given as

$$\frac{1}{\chi_0(T)} \equiv \frac{\partial h}{\partial M} = \frac{1}{\chi_P(T)} - 2I, \tag{1.61}$$

where $\chi_P(T)$ is magnetic susceptibility for Pauli paramagnets with $I = 0$, given as

$$\chi_P(T) = \frac{\rho}{2}\left\{1 - \frac{\pi^2}{6}R(k_B T)^2 + \cdots\right\}, \quad R = \frac{\rho''}{\rho} - \frac{\rho'^2}{\rho^2}. \tag{1.62}$$

The coefficient $a(T)$ in (1.58) corresponds to the inverse of magnetic susceptibility.
- The Curie temperature T_c is given as

$$kBT_c = \left[\frac{6(I\rho - 1)}{\pi^2 R}\right]^{1/2}. \tag{1.63}$$

It is given by the condition, $a(T_c) = 0$. The magnetic susceptibility shows divergence at $T = T_c$. With this T_c, the temperature dependence of the first coefficient $a(T)$ is written as

$$a(T) = a(0)\left(1 - \frac{T^2}{T_c^2}\right). \tag{1.64}$$

- The spontaneous magnetic moment in the ground state is given as

$$a(0)M + b(0)M^3 = 0, \quad \therefore \; M_0 = \left[\frac{-a(0)}{b(0)}\right]^{1/2} = \left[\frac{2(I\rho - 1)}{\rho b(0)}\right]^{1/2} \propto T_c \tag{1.65}$$

It is determined by the magnetic isotherm (1.58) in the ground state for $h = 0$ by assuming $T = 0$. Comparing the result with (1.63) gives the relation $M_0 \propto T_c$.
- The temperature dependence of the spontaneous moment is given as

$$M(T) = \left[\frac{-a(T)}{b(T)}\right]^{1/2} \simeq \left[\frac{-a(0)}{b(0)}\right]^{1/2}\left[\frac{a(T)}{a(0)}\right]^{1/2} = M_0\left(1 - \frac{T^2}{T_c^2}\right)^{1/2} \tag{1.66}$$

Spontaneous magnetic moment at finite temperatures is also determined by the magnetic isotherm (1.58) for $h = 0$. The temperature dependence of the second coefficient $b(T)$ is assumed to be weak and is neglected here. It implies that the good linearity between M^2 and T^2 is satisfied in the wide range of temperature below T_c.
- Magnetic isotherm is given as

$$M^2(H, T) = -\frac{a(T)}{b(T)} + \frac{1}{b(T)}\frac{h}{M(H, T)}. \tag{1.67}$$

Therefore, the good linear relation between M^2 and H/M is satisfied in the case of small magnetic moment M. Observed results of M^2 from magnetization measurements are often plotted against H/M, called Arrott plot at present. It is also written in the form

Fig. 1.1 Observed tempera-
ture dependence of the spon-
taneous magnetization square
$M^2(0, T)$ of $ZrZn_2$, plotted
against T^2, by Ogawa [9]
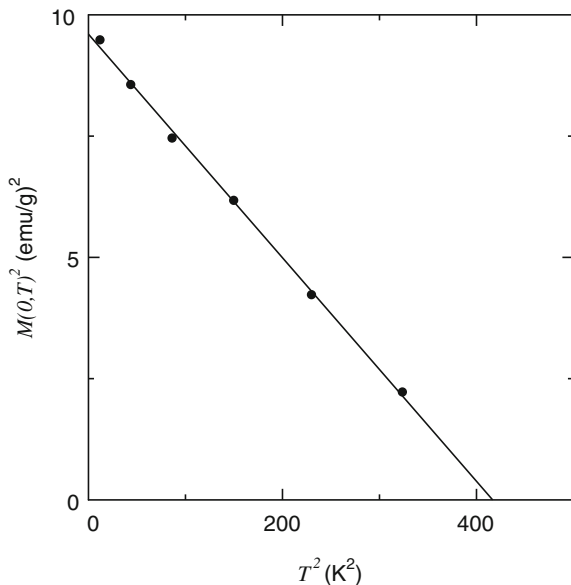
$$M^2(H, T) = M^2(0, 0) \left(1 - \frac{T^2}{T_c^2}\right) + M^2(0, 0) \frac{2\chi_0 H}{M(H, T)}, \qquad (1.68)$$

where $\chi_0 = 1/[2b(T)M^2(0, 0)]$ is called differential magnetic susceptibility.

Stimulated by these theoretical investigations, a number of experimental studies were made around 1970 on itinerant electron ferromagnets with small induced magnetic moments such as $ZrZn_2$, Sc_3In, Ni_3Al, and MnSi. Good linearity of their Arrott plots have been actually confirmed for most of them except for MnSi. Typical T^2-linear dependence is also observed for spontaneous magnetic moments and fourth expansion coefficients $b(T)$ of the free energy in powers of M. As an example, the temperature dependence of the spontaneous magnetic moment of $ZrZn_2$ observed by Ogawa [9] is shown in Fig. 1.1, in agreement with the prediction of the SW theory. The T^2-linear behavior of $b(T)$ is also confirmed for $ZrTiZn_2$ and $ZrZn_{1.9}$ by Wohlfarth and de Chatel [10] and for Ni–Pt alloys by Beille et al. [11].

1.5 Summary

In Table 1.1, typical magnetic properties of itinerant ferromagnets predicted by the SW theory are compared with those of localized moment models. Differences in these properties are summarized as below.

Table 1.1 Characteristic magnetic properties of itinerant electron ferromagnets in comparison with local moment magnets

Magnetic properties	Local moment systems	Itinerant ferromagnets
$M/(N_0\mu_B)$	Integer	$\ll 1$
$M(H, T)$ versus H for $T/T_c \ll 1$	Saturated	Unsaturated
Arrott plot	Nonlinear	Linear
$M^2(0) - M^2(T)$	$\propto T^{3/2}$	$\propto T^2$
$\chi(T)$	Curie–Weiss law	Curie–Weiss law
p_{eff}/p_s	~ 1	$\gg 1$

1. The magnitude of magnetic moment per magnetic atom
   For insulator magnets in which the spin–orbit coupling is negligible, magnitude of atomic magnetic moment takes an integer or a half-integer in units of μ_B, because of the quantization of the angular momentum. For itinerant electron magnets, on the other hand, it can take any value, because it is determined by the spin splitting of conduction electron bands.
2. Magnetic isotherm in the ground state
   For localized moment magnets, magnetization is almost saturated at low temperatures. Therefore, it is little affected by external magnetic field. In the case of itinerant ferromagnets, it still shows increase with increase in the external magnetic field strength. It results from the increasing spin splitting, according to the SW theory.
3. Temperature dependence of spontaneous magnetization at low temperatures
   Spontaneous magnetization shows the $T^{3/2}$-linear decrease for localized moment ferromagnets at low temperatures, resulting from thermal spin-wave excitations. On the contrary, for weak itinerant ferromagnets, T^2-linear decreases are rather well observed, seeming to be in agreement with the SW theory.
4. Temperature dependence of magnetic susceptibility
   Curie–Weiss law temperature dependence is generally observed for both these magnets. The ratios of two magnetic moments, i.e., the effective moment p_{eff} estimated from the Curie constant of magnetic susceptibility and the spontaneous moment p_s, are of about 1 for localized moment magnets, while for itinerant ferromagnets, considerably larger values are obtained. In the SW theory, the different dependence proportional to $(T^2 - T_c^2)^{-1}$ is derived in disagreement with experiments.

To conclude, most magnetic properties seem to be well accounted by the SW theory, as long as they are in the ground state or in the magnetically ordered phase. An exceptional difficulty has been the Curie–Weiss law dependence of magnetic susceptibility. Efforts to overcome the difficulty have brought about a new theoretical development.

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