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SPONTANEOUS MAGNETIZATION OF AN INVERSE SPINEL FERRITE

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Summary

A molecular field theory is developed for the inverse spinel ferrite Fe_3O_4 which takes into account the disorder arising from the random arrangement of two types of magnetic ions in the B sublattice. It is shown that the perturbative expansion of the propagators can be partially summed. A diagrammatic interpretation of the summation is given. By numerically solving a set of nonlinear equations, the spontaneous magnetization curve for Fe_3O_4 is obtained.

Introduction

In the inverse spinel ferrites, the octahedrally coordinated sites, which form the B sublattice, are randomly occupied by an equal number of divalent and trivalent magnetic ions. Previous studies of these ferrites have not fully treated the disorder arising from the random arrangement. Kaplan[1] replaces the two different spins in the B sublattice with an "averaged" spin and than treats the system as a normal spinel ferrite. Mills, Kenan and Milford[2] assume that the two types of ions are arranged in an orderly fashion amoung the B sites. Klama and Ferchmin[3] treat the random arrangement of one type of ions in the B sublattice as being independent of the random arrangement of the other type of ion in the sublattice. Evans[4] and others[5] use the probability function for finding out of the six nearest neighbor sites occupied by a particular type of ion of find the statistical averages of various quantities which can interact with an ion located at a given site.

Magnetite[6,7] is an example of an inverse spinel ferrite. The divalent Fe^{2+} ions and the trivalent Fe^{3+} ions are randomly arranged in the B sublattice. The tetrahedrally coordinated sites, which form the A sublattice, are all occupied by the remaining Fe^{3+} ions. The superexchange interactions between the magnetic ions located on the nearest neighbor A and B sites, $J_{ij}\,(Fe^{3+}-Fe^{3+})$ and $J_{ij}\,(Fe^{3+}-Fe^{2+})$, should be the dominant interactions since the angle of the A–anion–B link is favorable for this type of interaction while the A–anion–A and the B–anion–B angles are not. Stephenson[8] has shown that a simple molecular field model gives an expression for the Curie points which can be fitted to the observed Curie points of most of the spinel ferrites. We shall also assume that the interlattice superexchange interactions are dominant and that the magnetites can be described by the following Heisenberg Hamiltonian

$$H = -\sum_{ij} J_{ij}\,(Fe^{3+}-Fe^{3+})\,\vec{A}_i\cdot\vec{B}_j\,b_j - \sum_{ij} J_{ij}\,(Fe^{3+}-Fe^{2+})\,\vec{A}_i\cdot\vec{C}_j\,c_j \qquad (1)$$

where A_i is the spin operator for a Fe^{3+} ion located at the i–th site in the A sublattice; B_j the spin operator for the Fe^{3+} ion located in the B sublattice; C_j spin operator for a Fe^{2+} ion; b_j is the site occupancy indicator for a Fe^{3+} ion and c_j is the site occupancy indicator[10] for the Fe^{2+} ion.

The purpose of this paper is to study the effects of the disorder arising from the random arrangement of the two magnetic ions in the B sublattice. In the next section, we obtain the effective molecular field acting on an A site. Because the effective field is the field inside a spinel ferrite having a definite arrangement of ions, an average over all possible configuration must be performed. This configuration averaging is done in the following section. It is seen that the random disorder gives rise to a local molecular field fluctuation acting on an A site. A diagram interpretation of the partial summation encountered in this section is then given, and finally the temperature behavior of the magnetization of Fe_3O_4 is presented.

Effective Molecular Fields

To obtain the effective molecular fields acting on the three types of magnetic ions in the inverse spinel ferrites, we introduce the following molecular field approximation

$$\sum_{ij} J_{ij}\,\vec{A}_i\cdot\vec{B}_j = \sum_i \vec{A}_i\cdot\sum_j J_{ij}\,\langle B^2\rangle + \sum_j \vec{B}_j \sum_i J_{ij}\,\langle A^2\rangle \qquad (2)$$

where $\langle\ \rangle$ denotes an ensemble average. Thus the effective fields acting on the $\vec{A}_i$, $\vec{B}_j$, and $\vec{C}_j$ spins are

$$H_{eff}\,(\vec{A}_i) = -\sum_j J_{ij}^{(1)}\,\langle B^2\rangle\,b_j - \sum_j J_{ij}^{(2)}\,\langle C^2\rangle\,c_j \qquad (3)$$

$$H_{eff}\,(\vec{B}_j) = -\sum_i J_{ij}^{(2)}\,\langle A^2\rangle \qquad (4)$$

and

$$H_{eff}\,(\vec{C}_j) = -\sum_i J_{ij}^{(2)}\,\langle A^2\rangle \qquad (5)$$

where $J^{(1)} = J\,(Fe^{3+}\text{–}Fe^{3+})$ and $J^{(2)} = J\,(Fe^{3+}\text{–}Fe^{2+})$. The site occupancy indicators b_j and c_j take on the values

$b_j = 1$ if the j-th site is occupied by a Fe^{3+} ion
$\quad = 0$ if it is not
$c_j = 1$ if the j–th site is occupied by a Fe^{2+} ion
$\quad = 0$ if it is not

Since a site can not be occupied by two ions simultaneously, the two site occupancy indicators must be related to each other, i.e., if the site is occupied by a Fe^{3+} ion, it can not be occupied by the Fe^{2+} ion. Thus we have $b_j = 1 - c_j$. Looking at the above fields, we see that only the field acting on the Fe^{3+} ion located on the i–th site in the A sublattice is directly dependent on the arrangement of the ions in the B sublattice.

It should be understood that the above effective field, $H_{eff}\,(\vec{A}_i)$, is the local field at the i–th site inside an inverse spinel ferrite having a definite arrangement of the Fe^{3+} and Fe^{2+} ions in the B sublattice. Since any arrangements of these ions is possible, the effective fields must be averaged over all possible configurations. The averaged effective fields are obtained by replacing the ensemble averaged spin $\langle A^z \rangle$ and the weighted ensemble average spins $\langle B^z \rangle\, b_j$ and $\langle C^z \rangle\, c_j$ by their configuration averaged value.

The configuration averages of the above spins can be calculated by using a trick introduced by Kaneyoshi[11]. He pointed out that the ensemble average of a spin S_i being upon by an effective field can be written as

$$\langle S_i \rangle = S \int B_s\,(\tfrac{1}{2}\beta E)\; \delta\,(E - H_{eff}\,(i))\; dE \tag{6}$$

where $B_S(\;)$ is the Brillouin function; S, the spin quantum number; $\delta(\;)$, the delta function and where $\beta = 1/k_BT$. The delta function can be written as the difference between two resolvents (or Green's functions), i.e.,

$$\delta\,(E - H_{eff}) = \frac{1}{2\pi} \lim_{e \to o} \left\{ \frac{i}{E - H_{eff} - ie} - \frac{1}{E - H_{eff} + ie} \right\}. \tag{7}$$

Substituting this into eqn. (6), we obtain

$$\langle S_i \rangle = S \lim_{e \to o} \frac{1}{2\pi} \int B_s\,(\tfrac{1}{2}\beta E)\; (G_{E-ie}\,(H_{eff}(i)) - G_{E+ie}\,(H_{eff}(i))\; dE \tag{8}$$

where $G_{E \pm ie}(H_{eff}(i))$ are the resolvents $1/(E - H_{eff} \pm ie)$. The configuration averages can be obtained by taking of configuration averages of the Green's function $G_{E \pm ie}(H_{eff}(i))$.

Configuration Averages

As was pointed out in the previous section, the effective field at the A site is the only ones which are directly dependent on the way the two types of ions are arranged in the B sublattice. Therefore, only the configuration average of the Green's function $G_{E \pm ie}(H_{eff}(A_i))$ has to be calculated. The configuration averaging of the other two Green's functions, $G_{E \pm ie}(H_{eff}(B_j))$ and $G_{E \pm ie}(H_{eff}(C_j))$, does not lead to any changes, i.e.,

$$G_{E\pm ie}(H_{eff}(B_j)) = \langle G_{E\pm ie}(H_{eff}(B_j))\rangle \tag{9}$$

and

$$G_{E\pm ie}(H_{eff}(C_j)) = \langle G_{E\pm ie}(H_{eff}(C_j))\rangle_c \,. \tag{10}$$

The resolvent or Green's function for the A spin located on the i–th site is

$$G_E\,(H_{eff}(A_i)) = \frac{1}{E + \sum\limits_j J_{ij}^{(1)}\langle B\rangle - \sum\limits_j (J_{ij}^{(1)}\langle B\rangle - J_{ij}^{(2)}\langle C\rangle)c_j} \tag{11}$$

where we have used the relationship $b_j = 1 - c_j$. By introducing the auxiliary Green's function

$$G_o(E) = (E + zJ^{(1)}\langle B\rangle)^{-1} \tag{12}$$

where z is the number of nearest neighbors of an A site and which is equal to six for the spinel structure ferrites, we can rewrite eqn. (11) as

$$G_z(H_{eff}(A_i)) = G_o(E)\ \frac{1}{1 - G_o(E)\sum\limits_i (J_{ij}^{(1)}\langle B^z\rangle - J_{ij}^{(2)}\langle C^z\rangle)c_j}\,. \tag{13}$$

Expanding the above equation via the geometric power expansion, we get

$$\begin{aligned} G_E(H_{eff}(A_i)) = G_o(E) \Big\{ & 1 + G_o(E) \sum_j h_{ij}c_j + G_o(E) \sum_{j_1} h_{ij_1}c_{j_1}G_o(E) \times \\ & \sum_{j_2} h_{ij_2}c_{j_2} + G_o(E) \sum_{j_1} h_{ij_1}c_{j_1}\ G_o(E) \sum_{j_2} h_{ij_2}c_{j_2}\ G_o(E) \times \\ & \sum_{j_3} h_{ij_3}c_{j_3} + \cdots\cdot + G_o^n(E) \sum_{j_1j_2\cdot\cdot j_n} h_{ij_1}\ h_{ij_2}\cdots\cdot h_{ij_n} \times \\ & c_{j_1}c_{j_2}\cdots\cdot c_{j_n} + \cdots\cdot \Big\} \end{aligned} \tag{14}$$

where $H_{jj} = J_{ij}^{(1)}\langle B^z - J_{ij}^{(2)}\langle C^z\rangle$. Introducing the following Fourier transforms

$$G_E(k) = \int G_E(H_{eff}(A_i))\ e^{ik_1r_i}\ dr_i$$

and

$$h_{ij} = \frac{1}{N} \sum_k h(k)\ e^{ik(r_j-r_i)},$$

the Fourier transform of eqn. (14) becomes

$$\begin{aligned} G_E(k) = G_o(E)\ \Big\{ & \delta(k) + G_o(E)\ \frac{1}{N} \sum_j \sum_{k_1} \delta(k-k_1)\ h(k_1)\ e^{ik_1r_j}\ c_j \\ & + G_o^2(E)\ \frac{1}{N}2 \sum_{j_1j_2} \sum_{k_1k_2} h(k_1)\ h(k_2)\,\delta(k-k_1-k_2)\ e^{ik_1r_1}\ e^{ik_2r_2} \\ & c_{j_1}\ c_{j_2} + \cdots\cdot + G_o^n(E)\ \frac{1}{N}n \sum_{j_1\cdot\cdot j_n} \sum_{k_1\cdot\cdot k_n} \Big(\prod_{i=1}^{n} h(k_i)\Big) \Big(\prod_{i=1}^{n} e^{ik_ir_i}\Big) \\ & \delta(k-k_1-k_2 \cdots -k_n)\ c_{j_1}c_{j_2}\cdots c_{j_n} + \cdots \Big\} \end{aligned} \tag{5}$$

where $r_i = r_j$.

The configuration of $G_E(k)$ is obtained by taking the comfiguration averages of the various products of the indicator operators, i.e., we need to known what the configuration averages of $\langle c_{j_1}\ c_{j_2}\rangle_c$, $\langle c_{j_1}\ c_{j_2}\ c_{j_3}\rangle_c$, ... $\langle c_{j_1}\ c_{j_2}\ c_{j_3}\rangle_c$, ... are. Leath and Goodman[10] have pointed out that the configuration average of a product of indicator operators is equivalent to a cumulant expansion of the product. Yonezawa and Matsubara[12] showed that the cumulant expansion could be expressed in terms of the site occupancy polynomial $P_n(c)$, e.g.,

$$\begin{aligned}
<c_j>_c &= P_1(c) \\
<c_{j_1}c_{j_2}>_c &= P_1^2(c) + P_2(c)\ \delta_{12} \\
<c_{j_1}c_{j_2}c_{j_3}>_c &= P_1^3(c) + P_1(c)P_2(c)\ (\delta_{12} + \delta_{13} + \delta_{23}) + P_3(c)\ \delta_{123} \\
<c_{j_1}c_{j_2}c_{j_3}c_{j_4}>_c &= P_1{}^4(c) + P_1{}^2(c)P_2(c)\ (\delta_{12} + \delta_{13} + \delta_{14} + \delta_{23} + \delta_{24} + \delta_{34}) \\
&\quad + P_2{}^2(c)\ (\delta_{12}\delta_{34} + \delta_{13}\delta_{24} + \delta_{14}\delta_{23}) + P_1(c)P_3(c)\ (\delta_{123} \\
&\quad + \delta_{124} + \delta_{134} + \delta_{234}) + P_4(c)\ \delta_{1234} \qquad (17)
\end{aligned}$$

where $\delta_{12} = \delta_{j_1 j_2}$. The first four site occupancy polynomials are

$$\begin{aligned}
P_1(c) &= c \\
P_2(c) &= c-c^2 \\
P_3(c) &= c-3c^2\ 2c^3 \\
P_4(c) &= c-7c^2\ 12c^3-6c^4 \qquad (18)
\end{aligned}$$

where c is the fraction of B sites which are occupied by the type C (Fe^{2+}) ion. The generating function for the P_n (c) polynomials is

$$\ln\ (1-c+ce^x) = \sum_{n=1}^{\infty} P_n(c)\ \frac{x^n}{n!} \qquad (19)$$

Substituting the configuration averages, eqn. (17), into eqn. (16), we get (up to the fourth order in the expansion)

$$\begin{aligned}
<G_E(k)>_c = G_o(E)\ \delta(k) \Big\{ & 1 + G_o(E)\ h(o)\ P_1(c) + G_o^2(E) \\
& \Big(h^2(o)\ P_1^2(c) + P_2(c)\ \frac{1}{N} \sum_{k_1} |h(k_1)|^2\Big) + G_o^3(E) \\
& \Big(h^3(o)\ P_1^3(c) + 3\ h(o)\ P_1(c)\ P_2(c)\ \frac{1}{N} \sum_{k_1} |h(k_1)|^2 \\
& + P_3(c)\ \frac{1}{N},\sum_{k_1k_2} h(k_1)\ h(k_2)\ h(-k_1-k_2)\Big) + G_o^4(E)\ \Big(h^4(o)\ P_1^4(c) + \\
& + G\ h^2(o)\ P_1^2(c)\ P_2(c)\ \frac{1}{N} \sum_{k_1} |h(k^1)|^2 + 3\ \Big(P_2(c)\ \frac{1}{N} \sum_{k_1} \\
& |h(k_1)|^2\Big)^2 + 4\ h(o)\ P_1(c)\ P_3(c)\ \frac{1}{N^2} \sum_{k_1k_2} h(k_1)\ h(k_2)\ h(-k_1-k_2) \\
& + P_4(c)\ \frac{1}{N^3} \sum_{k_1k_2k_3} h(k_1)\ h(k_2)\ h(k_3)\ h(-k_1-k_2-k_3)\Big) + \ldots \Big\} \qquad (20)
\end{aligned}$$

Neglecting terms containing $\frac{1}{N^2} \sum_{k_1k_2} h(k_1)\ h(k_2)\ h(-k_1-k_2)$, $\frac{1}{N^3} \sum_{k_1k_2k_3} h(k_1)\ h(k_2)$ $h(k_3)\ h(-k_1-k_2-k_3)$ and other higher order terms, part of the series can be summed to

$$<G_E(k)>_c = \cfrac{G_o(E)\ \delta(h)}{\cfrac{1 - G_o(E)P_1(c)h(c) - G_o^2(E)P_2(c)\frac{1}{N}\sum|h(k)|^2}{\cfrac{1 - G_o(E)P_1(c)h(o) - G_o^2(E)P_2(c)\frac{1}{N}\sum|h(k)|^2}{\cfrac{1 - G_o(E)P_1(c)h(o) - G_o^2(E)\cdots}{\ddots}}}} \qquad (21)$$

Expanding the above continued fraction by the geometric power expansion, we would have an agreement with eqn. (20) up to fourth order except for the coefficient in front of the $(P_2(c) \frac{1}{N} \sum |h(n)|^2)^2$ term. The coefficient in front of this term in the expansion of eqn. (21) would be a two instead of the three found in eqn. (20). Reasons for this difference will be given in the next section.

If we terminate the continued fraction in such a way that only terms up to second order appear in the denominator of equm. (21), the configuration averaged Green's function becomes

$$<G_E(k)>_c = \tfrac{1}{2}\, \partial(k) \left\{ \frac{1}{E-E_+} + \frac{1}{E-E_-} \right\} \tag{22}$$

where $$E_{\pm} = -\,(zJ^{(1)} <B^z>_c\, b + zJ^{(2)}\ <C^z>_c\, c) \pm \sqrt{(P_2(c) \frac{1}{N} \sum_{k_1} |J^{(1)}(k)\ <B^z>_c - J^{(2)}(k)\ <C^z>_c|^2} \tag{23}$$

Taking the inverse transformation of eqn. (23), we get

$$<G_E(H_{eff}(A_i))>_c = \tfrac{1}{2} \left\{ \frac{1}{E-E_+} + \frac{1}{E-E_-} \right\}. \tag{24}$$

Substituting this into eqn. (8), we obtain the following configuration average of the z component of the spin of a Fe^{3+} ion located in the A sublattice

$$<A^z>_c = \tfrac{1}{2}\, S_1 \left\{ B_{S_1}(\tfrac{1}{2}\beta E_+) + B_{S_1}(\tfrac{1}{2}\beta E_-) \right\} \tag{25}$$

where S_1 is the spin quantum number for the Fe^{3+} ion. The square root factor in $E_{\pm}$, $\left\{P_2(c)\ \frac{1}{N} \sum |\ J^{(1)}(k) <B^2>c - J^{(2)}(k)\ \ <C^2>c|^2\right\}^{\frac{1}{2}}$ can be thought of as being the local molcular field fluctuation which is acting on a Fe^{3+} ion located at a site in the A sublattice. This fluctuation is due to the fluctuations in the environment surrounding an A site caused by the random arrangement of the Fe^{3+} and Fe^{2+} ions in the B sublattice.

Diagram Summation

A better understanding of why the series, eqn. (20), sums to the continued fraction, eqn. (21), can be achieved if we examine the graphic representation[13] of eqn. (20). The diagrams shown in Figure 1 are the three diagrams present in the series of diagrams generated by the cumulant expansion of $<c_1c_2c_3>_c$, whose analytic forms are $G_0{}^3(E)P_1(c)\, h(O)\, P_2(c)\, (1/N) \sum |h(k)|^2$. The existance of three diagrams having the same analytic form accounts for the coefficient three in front of this term in eqn. (20). Figure 2 shows the six diagrams present in the diagram series generated by the expansion of $<c_1c_2c_3c_4>_c$ whose analytic forms are $G_0{}^4(E)\, P_1{}^2(c)\, h^2(O)\, P_2(c)\, (1/N) \sum |h(k)|^2$. The three diagrams shown in Figure 3 also appear in the series generated by the expansion of $<c_1c_2c_3c_4>_c$. These diagrams give rise to the $G_0{}^4(E) \left\{P_2(c)\, (1/N) \sum |h(k)|^2\right\}^2$ term in eqn. (2). Every term in eqn. (20) can be identified

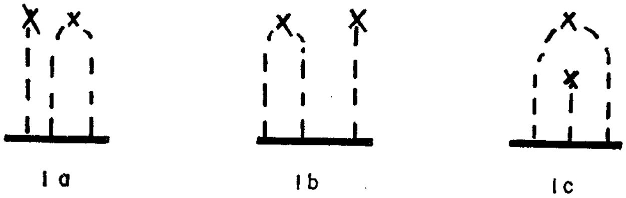
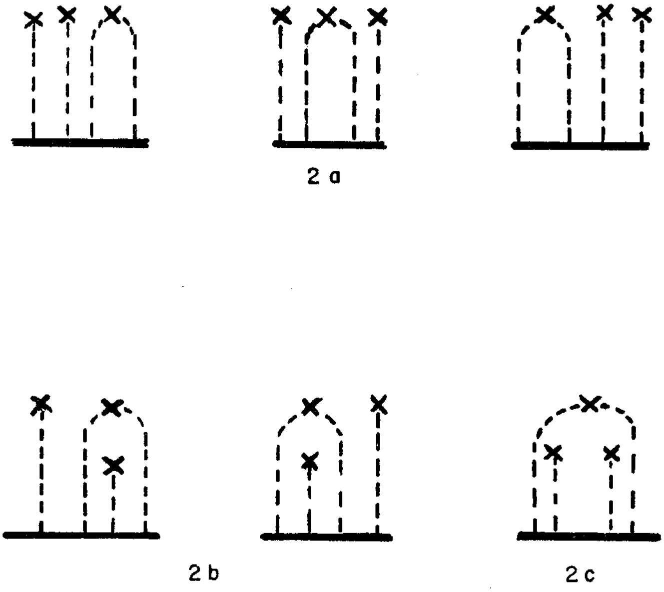


Fig. 1. Diagrams generated by the cumulant expansion of $\langle c_1\ c_2\ c_3 \rangle$, whose analyticel expressions are $G_o^3(E)P_1(c)P_2(c)h(O)(1/N)\sum|h(k)|^2$. 1a and 1b are reducible diagrams. 1c is an irreducible diagram.

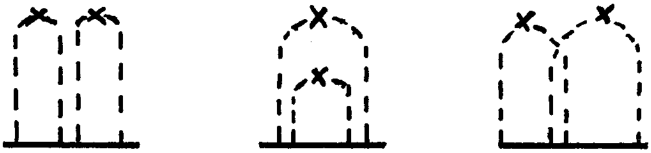


2 a

2 b

2 c

Fig. 2. Diagrams generated by the cumulant expansion of $\langle c_1\ c_2\ c_3\ c_4 \rangle$, whose analytical expressions are $G_o^4(E)P_1^2(c)P_2(c)h^2(O)(1/N)\sum|h(k)|^2$. 2a and 2b are reducible diagrams. 2c is an irreducible diagrams.



3 a 3 b 3 c

Fig. 3. Diagrams generated by the cumulant expansion of $\langle c_1\, c_2\, c_3\, c_4 \rangle$, whose analytical expressions are $G_o^4(E)\{P_2(c)(1/N)\sum|h(k)|^2\}^2$. 3a is a are reducible diagram. 3b is an irreducible diagram which is part of series which can be summed to give eqn. (26). 3c is an irreducible diagram which is not part of the series given in Fig. 4.

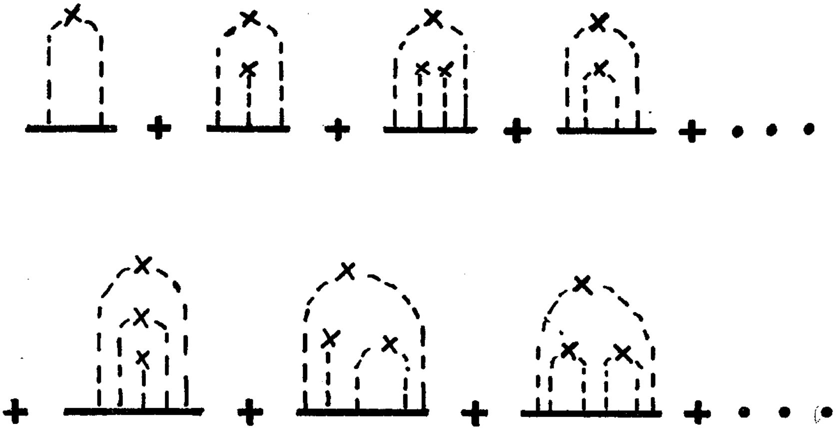


Fig. 4. Series of diagrams which can be summed to eqn. (26).

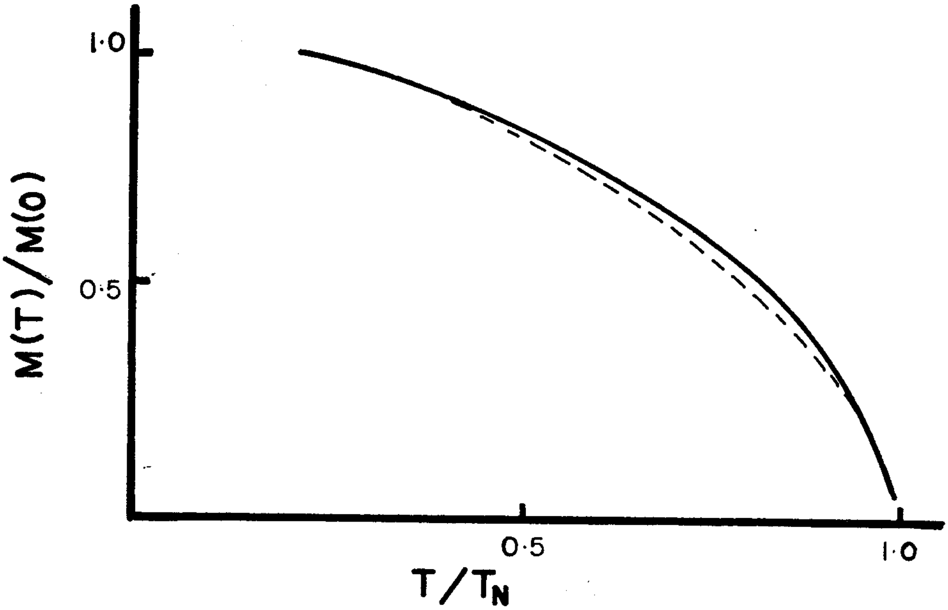


Fig. 5. Spontaneous magnetization curve for Fe_3O_4. Solid line indicate the curve predicted by our theory. Dotted line indicate the curve observed by Pauthenet and Bochirol[15].

with at least one diagram in the series of diagrams generated by the cumulant expansions. The coefficients in front of each term in eqn. (20) are just the number of diagrams whose analytic forms are the term in question.

Figures 1a, 1b, 2a, 2b and 3a show diagrams which can be separated into two diagrams by "cutting" one line in the diagram. These reducible diagrams can be considered as being the cross products resulting when a series of irreducible diagrams is squared, cubed, and so forth. The diagrams shown in Figures 1c, 2c and 3b are part of the series of irreducible diagrams shown in Figure 4. This series of diagrams can be summed to

$$G_0(E) \; <G_E'>_c \; P_2(c)\,(1/N)\sum|h(k)|^2 \tag{26}$$

where $<G_E'>_c$ is the configuration averaged Green's function. If we now neglect those diagrams containing three or higher order vertex interactions, the self energy of the configuration averaged Green's function becomes

$$P_1(c)h(O) + G_0(E) \; <G_E'>_c \; P_2(c)(1/N)\sum|h(k)|^2 + \text{ diagram of Fig. 3c} \tag{28}$$

If we drop the diagram shown in Figure 3c from the self energy $\sum$, the diagrammatic summation of the graphs of eqn. (20) would give

$$<G_E(k)>_c \; = \frac{G_c(E)\; S(k)}{1 - G_c(E)\; \sum'} \tag{29}$$

where $\sum' = P_1(c)h(O) + G_0(E) <G_E'>_c P_2(c)(1/N)\sum|h(k)|^2$. The diagrammatic expansion of eqn. (29) would contain the diagrams of Figures 1a, 1b, 1c, 2a. 2b, 2c, 3a and 3b but not the diagram of Figure 3c. Writing out the analytic expression for each of the diagrams in the expansion, we would get all of the coefficients in eqn. (20) except for the three in front of the term $G_0^4(E)\left\{P_2(c)(1/N)\sum|h(k)|^2\right\}^2$. The expansion of equation (29) would contain a two in front of this term since only the diagrams of Figures 3a and 3b would be present.

The discussion in this section would provide the basis for a Green's function description of the inverse spinel ferrites beyond the molecular field approximations used in the present paper. We shall return to this point in a later paper.

Spontaneous Magnetization

The values of the three types of spins in magnetite at different temperatures can be obtained by solving simultaneously the three non linear equations

$$<A^z> = \tfrac{1}{2}\, S_1 \left\{ B_{S_1}(\tfrac{1}{2}\beta E_+) + B_{S_1}(\tfrac{1}{2}\beta E_-) \right\}, \tag{25}$$

$$<B^z> = S_1\, B_{S_1}(\tfrac{1}{2}\beta z\, J^{(1)} < A^z >) \tag{26}$$

and

$$<C^z> = S_2\, B_{S_2}(\tfrac{1}{2}\,\beta z J^{(2)} < A^z >) \tag{27}$$

where $E_\pm$ are given by eqn. (23). The numerical values of $J^{(1)}$ and $J^{(2)}$ must be first obtained. One of the authors (IMT) has previously obtained an expression for the Curie temperature of a spinel ferrite which has two types of magnetic ions on both sublattices[14]. By fitting that expression to the Curie pointe of lithium ferrite (955° K) and to the Curie point of magnetite (851°K), we obtained the following values

$J^{(1)} = -20.7\ k_B$
and $J^{(2)} = -15.4\ k_B$

Substituting these values and the spin quantum numbers of Fe^{3+} and Fe^{2+} into eqns. (25) – (27), we were able to numerically solve the above equations using an IBM 360/138 computer.

Substituting the numerical values of the three spins at different temperatures into the following expression

$$M(T)/N = J_1\mu_8 < A^z > + J_1\mu_8 < B^z > + J^2\mu_B < C^z > , \qquad (28)$$

we were able to obtain the spontaneous magnetization curve shown in Figure 5. In the above equation, g_1 and g_2 are the Lande' g factor for Fe^{3+} and Fe^{2+}, respectively, and μ_B is the Bohr magneton. We have also plotted the experimental spontaneous magnetization curve for Fe_3O_4 obtained by Pauthenet and Bochirol[15]. The magnetization curve obtained from eqn. (28) is valid only in the temperature region above 119° K since a structural transition occurs at that temperature. Below 119° K, the structure of magnetite is orthorhombic while above, the structure is spinel. To obtain the magnetization curve below the transition temperature, we would have to rewrite all of the equations obtained in the previous sections so that they would reflect the orthorhombic structure of $Fe_3\ O_4$ instead of the spinel structure.

As is seen, the predicted curve lies slightly above the observed curve. Using a simple Weiss molecular field description, Neel[16] was able to obtain a curve which lied slightly below the observed curve. However, the excellent agreement could only be achieved if Neel assumed that the molecular field coefficients varied linearly with the temperature over the entire temperature range from O° K to 851° K. The numerical value of the linear coefficient term implied that the exchange interactions should vary as the inverse tenth power of the cation separation. Because the coefficient of linear expansion of magnetite is not the same over the entire temperature range, we felt that we were not in a position to incorporate a temperature variation of the superexchange interaction constants into our calculation.

References

1. Kaplan. H. (1952) *Phys. Rev.* **86**, 121.
2. Mills, R.E. Kenan, R.P. Milford, F.J. (1966) *Phys. Rev.* **145**, 704.
3. Klama, S. and Ferchmin, A.R. (1974) *Phys. Lett.* **48A**, 3.
4. Evans, B.J. (1968) in *Mossbaur Effect Methodology* Vol. 4, (Gruverman, I.J., ed.) Plenum Press, New York, p. 139.
5. Sawatzky. G.A. van der Wonde, F. and Morrish, A.H. (1969) *Phys. Rev.* **187**, 747.
6. Blasse, G. (1964) *Philips Res. Rep. Suppl.* **3**, 1.
7. Smit, J. and Wijn, H.P.J. (1959) *Ferrites*, Wiley, New York.
8. Stephenson, A. (1972) *Phil. Mag.* **25**, 1213.
9. Morrish, A.H. (1965) in *The Physical Principles of Magnetism*, Wiley, New York.
10. Leath, P.L. and Goodman, B. (1966) *Phys. Rev.* **148**, 968.
11. Kaneuoshi, T. (1970) *Prog. Theor. Phys.* **44**, 328.
12. Yonezawa, F. and Matsubara, T. (1966) *Prog. Theor Phys.* **35**, 357.
13. Edwards, S.F. and Jones, R.C. (1971) *J. Phys. Chem* **4**, 2109.

14. Tang, I.M. (1972) *Phys. Lett.* **42A**, 85.
15. Pauthenet, R. and Bochirol, L. (1951) *J. Phys. Radium* **12**, 249.
16. Neel, L. (1951) *J. Phys. Radium* **12**, 258.

บทคัดย่อ

ได้พัฒนาทฤษฎี molecular field เพื่อนำมาใช้กับ inverse spinel ferrite (Fe_3O_4) โดยได้คำนึงถึงความไม่เป็นระเบียบ (disorders) ซึ่งเกิดจากการเรียงตัวแบบสุ่ม (random) ของ magnetic ions สองแบบ ภายใน B sublattice. ทางทฤษฎีได้ให้ผลรวมบางส่วน (partial sum) การกระจายตัวแบบ perturbative ของ propagators และการตีความหมายแบบใช้แผนภูมิของผลรวมนี้ จากการแก้สมการ nonlinear ชุดหนึ่งก็ได้ spontaneous magnetization curve ของ Fe_3O_4.