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SUBJECT: Paramagnetic Behavior of Ferrites Containing Two Kinds of Magnetic Ions

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Abstract: The Néel theory of the paramagnetic behavior of susceptibility in ferrimagnetic ferrites is extended to include materials containing two kinds of magnetic ions. The equation of state is derived for the general case of an inverse spinel containing any kind of doubly ionized material in addition to the ferric ions. This equation is found to be considerably more complicated than the original equation of Néel. Additional calculations are made for the special case wherein the doubly ionized material is Mn^{2+}. This simplifies the numerical calculation without changing the general form of the solution. The final results indicate that the relationship between the exchange integrals and the paramagnetic susceptibility is too complicated to afford a satisfactory means of evaluating these integrals. A study is made of the assumptions implicit in the use of Néel's original equation for a ferrite with two kinds of magnetic ions. The results of this study indicate that these assumptions may be reasonably valid if the divalent ion is manganese, but they are not valid for any other divalent ion.

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In his classic article on the magnetic properties of ferrites,[1] Néel successfully explains the departure of the susceptibility from the Curie-Weiss law above the Curie temperature. According to this law, the susceptibility varies with temperature in the paramagnetic region in accordance with the equation

$$\chi = \frac{C}{T - \Theta} \tag{1}$$

where Θ is the Curie temperature, C is the Curie constant, and T is the temperature. However, instead of the straight-line relationship predicted by Eq. 1, the curve of $\frac{1}{\chi}$ vs T for ferrites is strongly concave toward the temperature axis.

Néel considered a ferrite with only one kind of magnetic ion, and on the basis of the ferrimagnetic properties of this material derived the equation

$$\frac{1}{\chi} = \frac{T}{C_j} + \frac{1}{\chi_o} - \frac{\sigma}{T - \Theta} \tag{2}$$

where χ_o, σ, and Θ are constants related to the exchange parameters. These relations are given in Appendix I. The significance of C_j is discussed below.

In addition to explaining the curvature of the $\frac{1}{\chi}$, T curve, Eq. 2, in conjunction with experimental results, affords a means of determining the relative values of the exchange interaction between ions on octahedral sites (B-B), ions on tetrahedral sites (A-A), and ions on different sites (A-B).

Since these interactions are important for an understanding of the magnetic properties of ferrites, it is of extreme interest to determine these values. However, as noted above, Eq. 2 was based on the assumption that only one kind of magnetic ion is present in the ferrite. Therefore, while this equation is valid for such materials as αFe_2O_3 and magnesium

1. L. Néel, Ann. de Physique, 12e Serie, 3, 137 (1948)

ferrite, it does not necessarily hold for ferrites of nickel, manganese, etc, which contain two kinds of magnetic ions. Nonetheless, this equation has been used by Fallot and Maroni[2] for the interpretation of the paramagnetic characteristics of iron, nickel, and cobalt ferrite; while Clark and Sucksmith[3] have used it to interpret results obtained with manganese ferrite.

In order to check the validity of their results, the behavior of the susceptibility above the Curie temperature has been calculated for a ferrite with two kinds of magnetic ions. This calculation, which constitutes the body of this report, indicates that Eq. 2 cannot be used in this case unless additional assumptions are made.

The Molecular Field

This calculation is limited to ferrites of the form $M^{2+}OFe^{3+}{}_2O_3$, where M^{2+} is a doubly ionized magnetic atom. The M^{2+} ion is assumed to lie exclusively in octahedral (B) sites of the spinel lattice, while the ferric ions are equally divided between octahedral and tetrahedral (A) sites. According to Néel's nomenclature[1], this means that $\lambda = \mu = 0.5$, where λ and μ are the fraction of Fe^{3+} ions on A and B sites respectively. This configuration is the accepted one for ferrites of nickel, manganese, iron, and cobalt. If λ' and μ' are taken as the fraction of M^{2+} ions on A and B sites respectively, then $\lambda' = 0$ and $\mu' = 1$.

The total magnetization I is therefore given by

$$\vec{I} = \lambda\vec{I}_a + \mu\vec{I}_b + \frac{1}{2}\mu'\vec{I}_b' \tag{3}$$

where $\vec{I}_a$ and $\vec{I}_b$ represent the magnetization of a gram-ion of ferric ions on the A and B sites respectively, and $\vec{I}_b'$ represents the magnetization of a gram-ion of M^{2+} ions. The factor $\frac{1}{2}$ is introduced to account for the fact that a ferrite containing a gram-ion of ferric ions will contain only a half gram-ion of M^{+2} ions.

2. M. Fallot and P. Maroni, J. Phys. et Rad., 12, 256 (1951)
3. C. A. Clark and W. Sucksmith, Proc. Roy. Soc., 225, 147 (1954)

Under the action of neighboring ions, each of the ions is subject to an internal molecular field. These fields are $\vec{h}_a$, $\vec{h}_b$, and $\vec{h}'_b$, respectively, at A and B sites containing ferric ions and B sites containing M^{2+} ions.

Each ion has neighbors of each kind, and the resultant molecular field acting upon an ion is the sum of the fields due to neighboring ions of each kind. In accordance with Néel's notation, the Fe^{3+} - Fe^{3+} interaction parameter is taken as n. For the case of two magnetic ions, we must introduce two additional interaction parameters n' and n'', representing Fe^{3+} - M^{2+} and M^{2+} - M^{2+} interactions respectively.[4] In addition, from geometrical considerations, it is apparent that A-B, B-B and A-A interactions are different from each other. If the absolute value of the A-B interaction factor is taken as unity, then α and β are defined by the equations

$$\alpha = \frac{\text{(A-A) interaction}}{|\text{(A-B) interaction}|} \; ; \quad \beta = \frac{\text{(B-B) interaction}}{|\text{(A-B) interaction}|} \tag{4}$$

The interactions between the various ions can therefore be summarized in the following table:

TABLE I

INTERACTIONS

$$\begin{tikzcd}[column sep=small]
\text{A site} & & \text{A site} & & \text{B site} & & \text{B site} \\
Fe^{3+} \arrow[r, dash] & n\alpha \arrow[r, dash] & Fe^{3+} \arrow[r, dash] \arrow[dr, dash] & n \arrow[r, dash] & Fe^{3+} \arrow[r, dash] \arrow[dr, dash] & n\beta \arrow[r, dash] & Fe^{3+} \\
 & & & n' \arrow[ur, dash] \arrow[dr, dash] & & n'\beta \arrow[ur, dash] \arrow[dl, dash] \arrow[dr, dash] & \\
 & & & & M^{2+} \arrow[r, dash] & n''\beta \arrow[r, dash] & M^{2+}
\end{tikzcd}$$

The molecular fields are therefore defined by the equations

$$\begin{aligned}
\vec{h}_a &= n\alpha\lambda\vec{I}_a + \varepsilon n\mu\vec{I}_b + 0.5\varepsilon n'\mu'\vec{I}'_b \\
\vec{h}_b &= \varepsilon n\lambda\vec{I}_a + n\beta\mu\vec{I}_b + 0.5n'\beta\mu'\vec{I}'_b \\
\vec{h}'_b &= \varepsilon n'\lambda\vec{I}_a + n'\beta\mu\vec{I}_b + 0.5n''\beta\mu'\vec{I}'_b
\end{aligned} \tag{5}$$

4. K. F. Niessen, Physica, 17, 1033 (1951)

where ε is a constant equal to -1 for materials with negative A-B exchange interaction.

Substituting $\lambda = \mu = 0.5$, $\varepsilon = -1$, and $\mu' = 1$ into Eqns. (3) and (5)

$$\vec{I} = 0.5\,(\vec{I}_a + \vec{I}_b + \vec{I}_b') \tag{6}$$

$$\begin{aligned} \vec{h}_a &= 0.5\,(n\alpha\vec{I}_a - n\vec{I}_b - n'\vec{I}_b') \\ \vec{h}_b &= 0.5\,(-n\vec{I}_a + n\beta\vec{I}_b + n'\beta\vec{I}_b') \\ \vec{h}_b' &= 0.5\,(-n'\vec{I}_a + n'\beta\vec{I}_b + n''\beta\vec{I}_b') \end{aligned} \tag{7}$$

The magnetization at each lattice site can be related to the molecular field at that site and to the external field vector $\vec{H}$ by the equations

$$\begin{aligned} \vec{I}_a &= I_o\, B_j\,(\vec{Z}_a) \\ \vec{I}_b &= I_o\, B_j\,(\vec{Z}_b) \\ \vec{I}_b' &= I_o'\, B_j\,(\vec{Z}_b') \end{aligned} \tag{8}$$

where $\vec{Z}_a = \dfrac{I_o(\vec{H} + \vec{h}_a)}{RT}$, $\vec{Z}_b = \dfrac{I_o(\vec{H}+\vec{h}_b)}{RT}$, $Z_b' = \dfrac{I_o'(\vec{H}+\vec{h}_b')}{RT}$

and where I_o and I_o' represent the molar magnetization at 0^oK. R is the universal gas constant. At high temperatures and moderate fields, the Brillouin function $B_j(\vec{Z})$ may be approximated by the equations

$$B_j(\vec{Z}_a) = \frac{j+1}{3j}\,\vec{Z}_a, \quad B_j(\vec{Z}_b) = \frac{(j+1)}{3j}\,\vec{Z}_b, \quad B_j(\vec{Z}_b') = \frac{j'+1}{3j'}\,\vec{Z}_b'$$

where j and j' are the total angular momentum quantum numbers of the Fe^{3+} and M^{2+} ions, respectively. Therefore, Eq. 8 may be rewritten in the form

$$\vec{I}_a = \frac{(j+1)}{3j}\,\frac{I_o^2}{R}\,\frac{(\vec{H}+\vec{h}_a)}{T} = \frac{C_j}{T}\,(\vec{H} + \vec{h}_a)$$

with similar equations for b and b$'$ sites, where $C_j = \dfrac{(j+1)}{3j}\,\dfrac{I_o^2}{R}$ and $C_j' = \dfrac{(j'+1)}{3j'}\,\dfrac{I_o'^2}{R}$. Then, substituting the molecular field values from Eq. 7

$$
\begin{aligned}
\vec{I}_a &= \frac{C_j}{T}\left[\vec{H} + 0.5\,(n\alpha\vec{I}_a - n\vec{I}_b - n'\vec{I}_b')\right] \\
\vec{I}_b &= \frac{C_j}{T}\left[\vec{H} + 0.5\,(-n\vec{I}_a + n\beta\vec{I}_b + n'\beta\vec{I}_b)\right] \qquad (9) \\
\vec{I}_b' &= \frac{C_j'}{T}\left[\vec{H} + 0.5\,(-n'\vec{I}_a + n'\beta\vec{I}_b + n''\beta\vec{I}_b')\right]
\end{aligned}
$$

Let us define two antiparallel unit vectors a and b such that $\vec{I}_a = I_a\,\hat{a}$, $\vec{I}_b = I_b\,\hat{b}$, $\vec{I}_b' = I_b\,\hat{b}$. Using this convention, I_a, I_b, I_b' are positive. In addition, let us assume that the external field is applied in such a direction that $\vec{H}\cdot\hat{a} = H$, $\vec{H}\cdot\hat{b} = -H$. Then Eq. 9 can be rewritten in scalar form as

$$
\begin{aligned}
I_a &= \vec{I}_a\cdot\hat{a} = \frac{C_j}{T}\left[H + 0.5\,(n\alpha I_a + nI_b + n'I_b')\right] \\
I_b &= \vec{I}_b\cdot\hat{b} = \frac{C_j}{T}\left[-H + 0.5\,(nI_a + n\beta I_b + n'\beta I_b')\right] \qquad (10) \\
I_b' &= \vec{I}_b'\cdot\hat{b} = \frac{C_j'}{T}\left[-H + 0.5\,(n'I_a + n'\beta I_b + n''\beta I_b')\right]
\end{aligned}
$$

Thus

$$
\begin{aligned}
&\left(\frac{2T}{C_j} - n\alpha\right) I_a - nI_b - n'I_b' - 2H = 0 \\
&-nI_a + \left(\frac{2T}{C_j} - n\beta\right) I_b - n'\beta I_b' + 2H = 0 \qquad (11) \\
&-n'I_a - n'\beta I_b + \left(\frac{2T}{C_j'} - n''\beta\right) I_b' + 2H = 0
\end{aligned}
$$

The above equations (11) can then be solved to determine I_a, I_b, and I_b'. The simplifying assumption $nn'' = n'^2$ is made[4]. Then, from Eq.6

$$
I = \vec{I}\cdot\hat{a} = 0.5\,(I_a - I_b - I_b'), \qquad (12)
$$

and the resultant value of I is found to be

$$I = \frac{H\left\{\frac{2T^2 n}{C_j}\left(\frac{2}{C_j'}+\frac{1}{C_j}\right) - T\left[\frac{2n'}{C_j}\{n(\beta-1)+n'\beta\}+n^2\left\{\frac{(2+\alpha+\beta)}{C_j'}+\frac{(\alpha+\beta)}{C_j}\right\}\right] + 0.5n(n'-n)^2(\alpha\beta-1)\right\}}{T\left[\frac{4T^2 n}{C_j^2 C_j'} - \frac{2T}{C_j}\left\{\frac{n'^2\beta}{C_j}+n^2\frac{(\alpha+\beta)}{C_j'}\right\} + n(\alpha\beta-1)\left\{\frac{n'^2}{C_j}+\frac{n^2}{C_j'}\right\}\right]} \tag{13}$$

Rearranging term and taking the inverse susceptibility $\frac{1}{\chi} = \frac{H}{I}$

$$\frac{1}{\chi} = \frac{T\left[4T^2 n - 2T\{C_j' n'^2\beta + C_j n^2(\alpha+\beta)\} + n(\alpha\beta-1)(C_j C_j' n'^2 + C_j^2 n^2)\right]}{2T^2 n(2C_j+C_j') - T\left[2C_j C_j' n'\{n(1-\beta)+n'\beta\}+n^2\{C_j^2(2+\alpha+\beta)+C_j C_j'(\alpha+\beta)\}\right]+0.5C_j^2 C_j'(n'-n)^2(\alpha\beta-1)} \tag{14}$$

As T increases indefinitely, $\frac{1}{\chi}$ approaches a straight line of slope $\frac{2}{2C_j+C_j'}$.

It should be noted that Néel's assumption of only one magnetic ion is equivalent to setting $n' = C' = 0$ in Eq. 14. In that case, Eq. 14 reduces to the original form derived by Néel for the case $\lambda = \mu = 0.5$.

Equation of State

In general, $C_j' = \text{constant} \times C_j$. For the special case of manganese ferrite ($M^{2+} = Mn^{2+}$), the constant is unity and $C_j' = C_j$. In view of the unwieldiness of Eq. 14, further calculations are limited to manganese ferrite. However, since the only difference between this and other ferrites lies in the numerical value of the constant, the resultant form of the solution is general, only the numerical factors are different. For $C_j = C_j'$, Eq. 14 reduces to

$$\frac{1}{\chi} = \frac{T\left[\frac{2T^2}{3C_j} - \frac{T}{3n}\{n'^2\beta+n^2(\alpha+\beta)\} + \frac{C_j}{6}(\alpha\beta-1)(n'^2+n^2)\right]}{T^2 - \frac{TC_j}{3n}\left[n'\{n(1-\beta)+n'\beta\}+n^2(1+\alpha+\beta)\right] + \frac{C_j^2}{12}(n'-n)^2(\alpha\beta-1)} \tag{15}$$

Eq. 15 can therefore be expressed in the form

$$\frac{1}{\chi} = \frac{2T}{3C_j} + \frac{1}{\chi_o} - \frac{(\sigma_o T + \sigma_1)}{(T - \Theta')(T - \Theta'')} \tag{16a}$$

or

$$\frac{1}{\chi} = \frac{2T}{3C_j} + \frac{1}{\chi_o} - \frac{\sigma_o}{(T-\Theta')} - \frac{(\sigma_o \Theta'' + \sigma_1)}{(T-\Theta')(T - \Theta'')} \tag{16b}$$

Thus the addition of a second magnetic ion into the spinel lattice leads to a new term in the susceptibility equation, and it changes the coefficient of the T/C_j term. In addition, the relationship of the constant and the exchange interactions are found to be radically altered.

The values of the constants in Eqn. 16 can be evaluated from experimental data. In order to obtain the exchange interactions n, n', α, β, these constants must be related to these interaction parameters. This is done as follows:

1) Θ' and Θ'' have been so defined that the denominator of Eq. 15 equals $(T-\Theta')(T - \Theta'')$. The values of Θ' and Θ'' follow directly. It can be seen that, in general, $\Theta'' < 0$ when $\alpha\beta < 1$.

2) $\frac{1}{\chi_o}$ is obtained from the relationship

$$\frac{1}{\chi_o} = \lim_{T\to\infty} \frac{1}{\chi} - \frac{2T}{3C_j} \tag{17}$$

3) σ_o and σ_1 are obtained from the relationships

$$\sigma_o T + \sigma_1 = \lim_{T\to\Theta'} - \frac{(T - \Theta')(T - \Theta'')}{\chi} \tag{18a}$$

$$\sigma_o T + \sigma_1 = \lim_{T\to\Theta''} - \frac{(T - \Theta')(T - \Theta'')}{\chi} \tag{18b}$$

The physical significance of $\frac{1}{\chi_o}$ can be seen from Fig. 1. It is the intercept on the $1/\chi$ axis of the asymptote $\frac{1}{\chi} = \frac{2T}{3C_j} + \frac{1}{\chi_o}$. In addition, the intercept of this line on the temperature axis is designated Θ_a, where $\Theta_a = -\frac{3C_j}{2\chi_o}$. The paramagnetic Curie temperature Θ_c is also shown. The determination of Θ_c requires the solution of the cubic equation

$$\Theta_c^3 - \frac{C_j}{2}\left[n(\alpha+\beta) + \frac{n'^2}{n}\beta\right]\Theta_c^2 + \frac{C_j^2}{4}(n^2+n'^2)(\alpha\beta-1)\,\Theta_c + \frac{C_j^3}{8}(n^3\alpha + \frac{n'^4}{n}\beta) = 0.$$

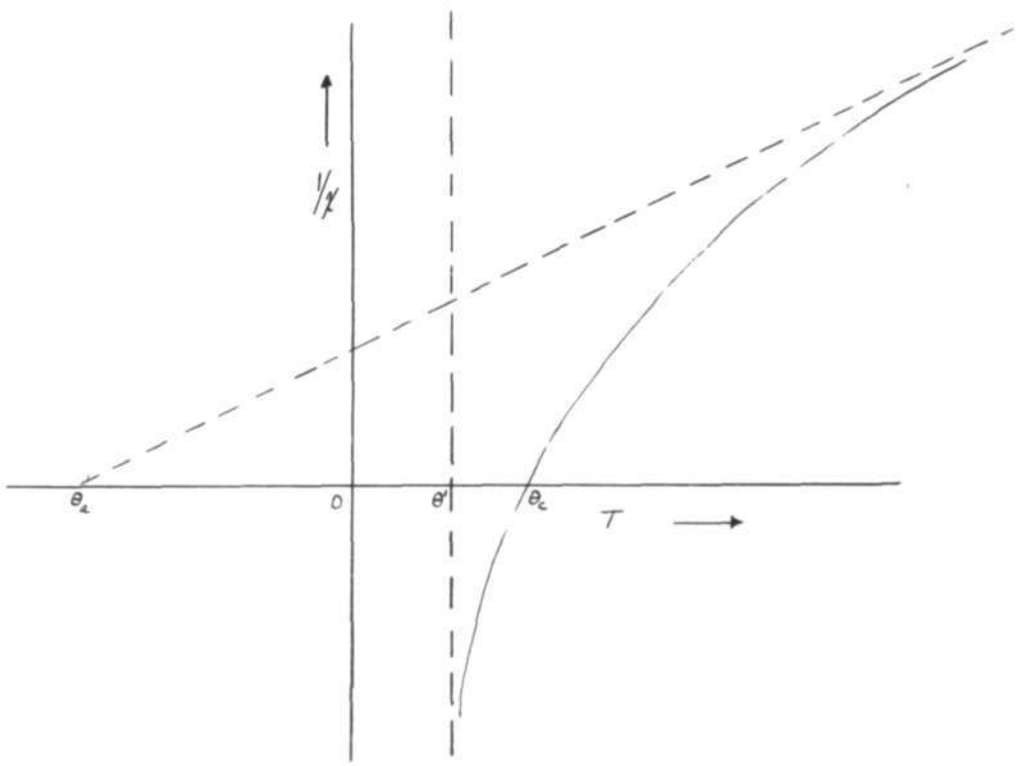

Figure 1.

The above equations, taken together with experimental data, theoretically provides sufficient information to solve for the interaction terms n, n', α, and β. The solution of the terms Θ', Θ'', $1/\chi_o$, σ_o, and σ_1 in terms of n, n', α, and β has been carried out and the results are given in Appendix II. These relationships, as can be seen, are extremely complicated, and in this respect differ radically from the simple solutions obtained by Néel for the case of one magnetic ion. As a result, it must be concluded that a study of the paramagnetic behavior of ferrites with two magnetic ions is not a practicable means of determining the exchange interactions of these ions.

<u>Special Case $n = n'$</u>

The problem can be simplified considerably by making the assumption $n = n'$. This is tantamount to the assumption that the exchange interaction is identical for M^{2+} ions and Fe^{3+} ions. In general, this is not a valid assumption. However, for the special case $M^{2+} = Mn^{2+}$, this appears to be fairly reasonable since the 3d electron configurations of Mn^{2+} and Fe^{3+} ions are identical and the ions are approximately of the same size. (Ionic radii of Fe^{3+} and Mn^{2+} are 0.64 and 0.80 Angstrom units respectively). In this case, Eq. 15 reduces to

$$\frac{1}{\chi} = \frac{\frac{2T^2}{3C_j} - \frac{Tn}{3}(\alpha+2\beta) + \frac{C_j n^2}{3}(\alpha\beta-1)}{T - \frac{C_j}{3}(2+\alpha+\beta)} \qquad (20)$$

Thus, $\frac{1}{\chi}$ can be expressed in a form identical with that obtained by Néel for the case of only one kind of magnetic ion. (Eqn. 2) The relationships between Θ', $\frac{1}{\chi_o}$, σ and α, β, n are:

$$\Theta' = \frac{C_j n}{3}\left[2+\alpha+\beta\right] \qquad (21)$$

$$\frac{1}{\chi_o} = \frac{n}{9}(4-4\beta-\alpha) \qquad (22)$$

$$\sigma = \frac{C_j n^2}{27}(1+2\beta-\alpha)^2 \qquad (23)$$

In this case, since the Mn^{2+} and Fe^{3+} ions are treated identically, the material may be considered a 'degenerate' material with only one magnetic ion. If this is so, then Eqs. (21),(22), and (23) should be identical with Eqs. (24),(25), and (26) of Appendix I for the particular case considered herein. In Appendix III this is shown to be the case.

Clark and Sucksmith[3] apparently used this method in their evaluation of α, β, and n, although this is not explicitly stated. The accuracy of their results is therefore limited to the accuracy of the assumption $n = n'$.

Signed: Norman Menyuk
Norman Menyuk

NM/md

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APPENDIX I

PARAMAGNETIC RELATIONS IN FERRITE CONTAINING ONE KIND OF MAGNETIC ION*

According to Eq. 2

$$\frac{1}{\chi} = \frac{T}{C_j} + \frac{1}{\chi_o} - \frac{\sigma}{T - \Theta}$$

the curve of $\frac{1}{\chi}$ vs. T is of the same general form as Fig. 1, with Θ of the above equation replacing Θ'. As T increases, $\frac{1}{\chi}$ asymptotically approaches a straight line of slope $\frac{1}{C_j}$.

The constants are related to the exchange parameters by the equations:

$$\Theta = nC_j \lambda \mu (2 + \alpha + \beta) \qquad (24)$$

$$\frac{1}{\chi_o} = n (2 \lambda \mu - \alpha \lambda^2 - \beta \mu^2) \qquad (25)$$

$$\sigma = n^2 C_j \lambda \mu \left[\lambda (1 + \alpha) - \mu (1 + \beta) \right]^2 \qquad (26)$$

Eqs. (20), (21), (22) lead to the relationships

$$\alpha = \frac{1}{n} \left(\frac{\mu \Theta}{\lambda C_j} - \frac{1}{\chi_o} \pm 2\mu \sqrt{\frac{\sigma}{C \lambda \mu}} \right) \qquad (27)$$

$$\beta = \frac{1}{n} \left(\frac{\lambda \Theta}{\mu C_j} - \frac{1}{\chi_o} \mp 2 \sqrt{\frac{\sigma}{C \lambda \mu}} \right) \qquad (28)$$

$$n = \frac{\Theta}{C_j} + \frac{1}{\chi_o} \mp (\mu - \lambda) \sqrt{\frac{\sigma}{C \lambda \mu}} \qquad (29)$$

The values of Θ, $\frac{1}{\chi_o}$, and σ can be determined experimentally from a study of the paramagnetic susceptibility. These quantities can then be used in conjunction with Eqs. (23), (24), and (25) to obtain α, β, and n. It should be noted that each set of values of Θ, $\frac{1}{\chi_o}$, and σ lead to two possible sets of values for α, β, and n. Spontaneous magnetization data, taken below the Curie temperature, is then required to determine which set is correct.

* A clear exposition of the Néel model of ferrimagnetism including the above information, is available in M.I.T. Lincoln Laboratory Memorandum M-2412 by Arthur L. Loeb.

APPENDIX II

PARAMAGNETIC RELATIONS IN MANGANESE FERRITE

$$\theta' = \frac{C_j}{6n}\left[\{\ \} + \sqrt{\ \ }\right]$$

$$\theta'' = \frac{C_j}{6n}\left[\{\ \} - \sqrt{\ \ }\right]$$

where

$$\{\ \} = \left\{n'\left[\beta\,(n' - n) + n\right] + n^2(1 + \alpha + \beta)\right\}$$

$$\sqrt{\ \ } = \Big\{n^4\left[(1+\alpha)^2 + (1+\beta)^2 + 2 - \alpha\beta\right] + n^2\left[4(n'-n) - \alpha\beta(n'-4n) + \beta^2(3n'-2n) + 2\alpha n\right] + n'^3\beta\left[2n(1-\beta) + n'\beta\right]\Big\}^{1/2}$$

$$\frac{1}{\chi_o} = \frac{1}{9n}\left[n^2(2-\alpha) + 2nn' - \beta\,(n+n')^2\right]$$

The values of σ_o and σ_1 given below have not been checked. Therefore, there may be errors present in some of the coefficients given below. However, the forms are correct, and the following equations are included only to show these forms and their complexity.

$$\sigma_o = \frac{C_j}{27n^2}\Big\{n^4\left[(\alpha-\beta)^2 + 1 - \alpha - \beta\right] + n^3n'\left[\beta(3+\beta-2\alpha) - 1 - \alpha\right] + n^2n'^2\left[1 + \beta(3 - 3\beta - 4\alpha)\right] + nn'^3\beta(1-\beta) + n'^4\beta^2\Big\}$$

$$\begin{aligned}\sigma_1 = -\frac{C_j^{\,2}}{324n^3}\Big\{ & n^6\left[7 + 24(\alpha^2+\beta^2) + 17(\alpha+\beta) + 18\alpha\beta(\alpha+2+\beta) + 13(\alpha^3+\beta^3)\right] \\ & + n^5n'\left[8 + \alpha\beta(18-\alpha-16\beta) + \beta(4+11\beta-13\beta^2) - 13\alpha\right] \\ & + n^4n'^2\left[-6 + 2\alpha\beta(4\alpha-3+4\beta) + 18\beta^2(1+2\beta) + 75\beta + 12\alpha\right] \\ & + n^3n'^3\left[7 + \beta(-9+15\beta-37\beta^2) + 3\alpha\beta(9-\beta)\right] \\ & + n^2n'^4\left[3\beta(9+\beta+8\beta^2+3\alpha\beta)\right] + nn'^5\left[24\beta^2(1-\beta)\right] + 13n'^6\beta^3\end{aligned}$$

The above equations indicate the difficulties involved in attempting to set up the counterparts of Eqs. (23),(24), and (25) for a ferrite with two magnetic ions.

APPENDIX III

If Mn^{2+} and Mn^{3+} are treated mathematically as "identical" ions, then 2/3 of the magnetic ions are on B sites, and 1/3 are on A sites. Therefore, in Eqs. (24), (25), and (26) $\lambda = 1/3$, $\mu = 2/3$. In addition, in one gram-molecule of $MnOFe_2O_3$ there are 3/2 gram-ions of magnetic ions. Therefore, C_j of Eqs. (24), (25) and(26) is numerically equivalent to 3/2 the value of C_j used in Eqs. (21),(22), and (23). When these substitutions are made, Eqs. (24),(25) and (26) are identical with Eqs. (21), (22), and (23), respectively.

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