

Memorandum M-1980

Page 1 of 6

Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLIX

To: Group 63 Staff

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The normal and inverse structures of ferrites ($M^{++} O^= Fe_2^{+++} O_3^-$) were discussed at meeting XLVII, and were defined as shown below:

SITE	NORMAL STRUCTURE	INVERSE STRUCTURE
A (Tetrahedral)	M^{++}	Fe^{+++}
B (Octahedral)	$2Fe^{+++}$	$Fe^{+++} M^{++}$

Néel's fundamental article on ferrites* will be discussed in detail at this meeting and for several additional meetings. In this article Neel considers the more general case of the mixed spinel structure in which a certain fraction λ of the trivalent ions occupy the A sites while the remaining fraction μ of the trivalent ions occupy the B sites. By definition,

$$\lambda + \mu = 1$$

XLIX - 1

Normal structure therefore corresponds to $\lambda = 0$, inverse structure to $\lambda = 0.5$.

Néel first considers the case in which only the trivalent ions have a magnetic moment, and investigates the magnetic properties to be expected when these ions are apportioned between two crystallographically different sites in the same material. The saturation magnetization of a gram-ion at absolute zero M_j is given by the equation

$$M_j = N g_j \mu_B$$

* Néel, L. "Propriétés Magnétiques des Ferrites" Annales de Physique, 3, 137-198 (1948).

where N = Avogadro's number
 g = Landé factor
 j = angular momentum quantum number
 μ_B = Bohr magneton

For the case of negligible interaction the magnetic ions behave as free ions and the magnetization of a gram-ion I is given as a function of the magnetic field H and the temperature T by

$$I = M_j B_j (Z) \quad \text{XLIX - 3}$$

where B_j is the Brillouin function

$$B_j(Z) = \frac{2j+1}{2j} \coth \frac{(2j+1)Z}{2j} - \frac{1}{2j} \coth \frac{Z}{2j} \quad \text{XLIX - 4}$$

Z is the Langevin variable

$$Z = \frac{M_j H}{RT} \quad \text{XLIX - 5}$$

and R is the universal gas constant.

For the special case $j \rightarrow \infty$,

$$B_\infty(Z) = \coth Z - \frac{1}{Z}$$

This is just the result obtained in the classical derivation of paramagnetic theory (see lecture IV). Since the function $\coth Z - 1/Z$ was arrived at by Langevin before the advent of quantum theory, it is known as the Langevin function $L(Z)$. As can be seen, the Langevin function is just a special case of the Brillouin function.

Another special case of interest arises for $j = 1/2$. This was discussed in detail at lecture V, and led to the result

$$B_{\frac{1}{2}}(Z) = \tanh Z$$

When the temperature is 0°K , $B_j(Z) = 1$. For high temperatures $Z \ll 1$, and the Brillouin function can be approximated by

$$B_j(Z) \approx \frac{(j+1)Z}{3j} \quad \text{XLIX - 6}$$

For this case one obtains the Curie law

$$I = \frac{C_j H}{T} \quad \text{where} \quad C_j = \frac{j+1}{3j} \frac{M^2}{R}$$

When the interaction between ions is not negligible, the different crystallographic features of the A and B sites leads one to expect that the ions on the two sites will exhibit different magnetic properties. If the magnetization of a gram-ion of the ions on the A sites is defined by I_a , and those on the B sites by I_b , the average magnetization of a gram-ion is then given by

$$\vec{I} = \lambda \vec{I}_a + \mu \vec{I}_b \quad \text{XLIX - 7}$$

In order to account for the magnetic interaction between ions Neel uses the concept of the Weiss molecular field. Weiss supposed this field was due to the action of surrounding dipoles as well as the external field; we now know that this effect is due to the exchange interaction, but since the cause of this effect is not brought in as a factor this approach is valid.

It is assumed that the action of the neighbors of an ion on site A, defined as \vec{h}_a , is equal to the sum of the molecular field due to neighboring A ions, \vec{h}_{aa} , and the field due to neighboring B ions, \vec{h}_{ab} . Then

$$\vec{h}_a = \vec{h}_{aa} + \vec{h}_{ab} \quad \text{XLIX - 8}$$

Similarly

$$\vec{h}_b = \vec{h}_{bb} + \vec{h}_{ba} \quad \text{XLIX - 9}$$

We can then say

$$\vec{h}_a = n (\alpha \lambda \vec{I}_a + \epsilon \mu \vec{I}_b) \quad \text{XLIX - 10}$$

$$\vec{h}_b = n (\beta \mu \vec{I}_b + \epsilon \lambda \vec{I}_a) \quad \text{XLIX - 11}$$

where n , α , β , and \mathcal{E} are the parameters which characterize the interaction. \mathcal{E} is equal to either +1 or -1, corresponding to a parallel or anti-parallel alignment of the A and B sites respectively; and n , α , and β are related to the exchange integrals.

In order to calculate the magnetization of the A and B ions, they are assumed to be subject to a magnetic field equal to the vector sum of the applied field H and the molecular field, thus

$$\vec{I}_a = \frac{C}{T} (\vec{H} + \vec{h}_a)$$

$$\vec{I}_b = \frac{C}{T} (\vec{H} + \vec{h}_b)$$

XLIX - 12

Two assumptions are implicit in the preceding equations. The first is that the number of ions about each ion is equal to the average number. This assumption is bad when λ becomes very small. The second assumption is that the ions are distributed at random amongst the sites. Essentially this means there is no ordering of the ionic structure.

We will first investigate the magnetic properties of the ferrites for the case of negative interaction between the sublattices. That is, $\mathcal{E} = -1$.

For the case $\mathcal{E} = -1$, eliminating \vec{I}_a , \vec{I}_b , \vec{h}_a , and \vec{h}_b from equations XLIX - 7, 10, 11, and 12 yields the equation*

$$I = \frac{C [T - nC \lambda \mu (2 + \alpha + \beta)]}{T^2 - nC (\lambda \alpha + \mu \beta) T + n^2 C^2 \lambda \mu (\alpha \beta - 1)} \vec{H} \quad \text{XLIX - 13}$$

The atomic susceptibility $\chi = \vec{I}/\vec{H}$. The inverse susceptibility can be expressed in the form

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\mathcal{E}}{T - \mathcal{E}} \quad \text{XLIX - 14}$$

* The Néel article gives this equation as

$$I = \frac{T^2 - nC (\lambda \alpha + \mu \beta) T + n^2 C^2 \lambda \mu (\alpha \beta - 1)}{T - nC \mu (2 + \alpha + \beta)} \vec{H},$$

The form given by equation XLIX - 13 appears to be the correct form. A derivation of this equation through equation XLIX - 17 is given in Appendix VI.

where

$$\frac{1}{\chi_0} = n (2 \lambda \mu - \lambda^2 \alpha - \mu^2 \beta) \quad \text{XLIX - 15}$$

$$C = n^2 c \lambda \mu [\lambda (1 + \alpha) - \mu (1 + \beta)]^2 \quad \text{XLIX - 16}$$

$$Q = n c \lambda \mu (2 + \alpha + \beta) \quad \text{XLIX - 17}$$

Equation XLIX - 14 represents a hyperbola asymptotic to the line

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0}$$

This line can be extrapolated to cut the temperature axis at a point

$$Q_a = -\frac{C}{\chi_0}$$

where Q_a is known as the asymptotic Curie point.

The curve and the asymptote are shown in figure 106. The curve cuts the temperature axis at the paramagnetic Curie temperature Q_p . Q_p can be calculated from equations XLIX - 14, 15, 16 and 17 and is found to be

$$Q_p = \frac{n c}{2} [\lambda \alpha + \mu \beta + \sqrt{(\lambda \alpha - \mu \beta)^2 + 4 \lambda \mu}] \quad \text{XLIX - 18}$$

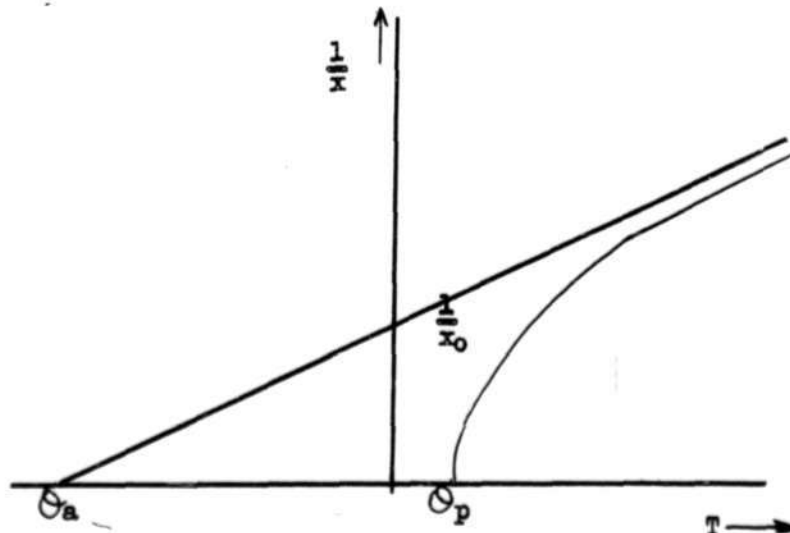


FIGURE 106

Equation XLIX - 14 differs from the classical Curie-Weiss law of paramagnetism because of the term $\frac{\sigma}{T-\theta}$.

The Curie-Weiss law holds for the special case $\sigma = 0$, and it can be seen from equation XLIX - 16 that $\sigma = 0$ when

$$\lambda(1 + \sigma) = \mu(1 + \beta)$$

XLIX - 19

Considering λ fixed and taking σ and β as rectangular coordinates with β measured along the ordinate and σ along the abscissa, equation XLIX-18 is the equation of a straight line. If we assume $\lambda < \mu$ the curve will appear as shown in figure 107.

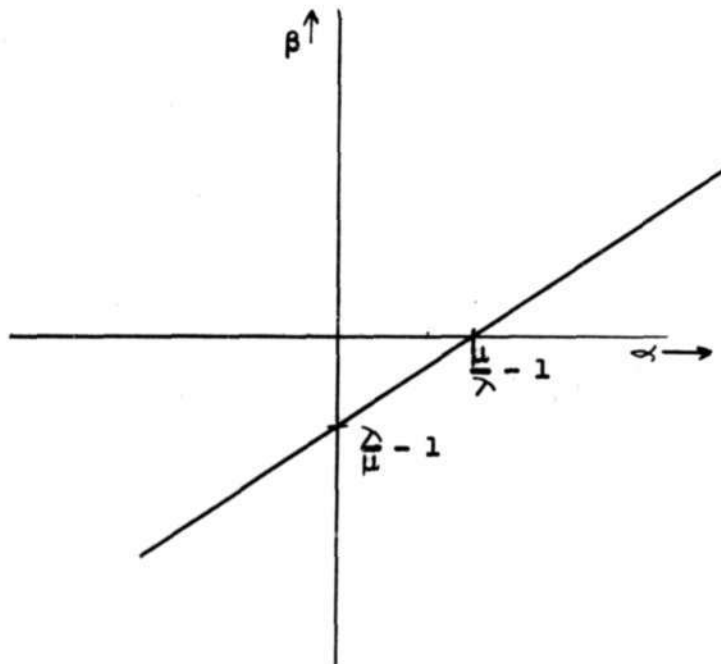


FIGURE 107

For any set of values of σ and β lying on the above curve the Curie-Weiss law holds.

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