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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, LV

To: Group 63 Staff

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The magnetic properties of ferrite materials have been studied in terms of the interaction parameters α, β, and n. On the basis of this study Néel was able to explain the non-linearity of the inverse susceptibility in the paramagnetic region (Fig. 106) and to predict various magnetization curves which have since been observed experimentally.

The next step is to relate the interaction parameters to the exchange integrals. In doing this, we shall start with Néels argument, but will shortly transfer the discussion to accord with a report recently written by Smart and Howard of the Naval Ordnance Laboratory* This report, which is based on the Néel paper, introduces some new ideas as well as a slightly different notation. We shall therefore go over some of the material covered in the previous lectures in the light of these new concepts.

Two neighboring ions A and B of resultant spins $\vec{S}_a$ and $\vec{S}_b$ (in units of $\hbar$) have a mutual magnetic energy.+

$$W_{ab} = -2J_{ab}\vec{S}_a \cdot \vec{S}_b \qquad \text{LV-1}$$

wherein J_{ab} is the exchange integral.

The molecular field approximation consists of replacing the instantaneous value of $\vec{S}_b$ by its time averaged value

$$\vec{S}_b = \frac{\vec{I}_b}{Ng\,\mu_B}$$

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* Smart, J.S. and Howard, L.S., "The Néel Theory of Ferromagnetism and the Ferrites," Internal Report, U.S. Naval Ordnance Laboratory (1952)

+ Van Vleck, J.H., Electric and Magnetic Susceptibilities, Oxford (1932)

where N is Avogadro's number, g is the Landé splitting factor, and μ_B is the Bohr magneton $\left(\frac{eh}{4\pi mc}\right)$.

The magnetic moment of an A ion is equal to $g\mu_B\vec{S}_a$. W_{ab} has the same value as if this ion were in a fictitious magnetic field $U_{ab}\vec{I}_b$; that is

$$W_{ab} = U_{ab}\vec{I}_b \cdot \vec{I}_a \qquad \text{LV-2}$$

Thus U_{ab} is defined by

$$U_{ab} = \frac{2J_{ab}}{Ng^2\mu_B^2} \qquad \text{LV-3}$$

Similarly

$$U_{aa} = \frac{2J_{aa}}{Ng^2\mu_B^2}$$

$$U_{bb} = \frac{2J_{bb}}{Ng^2\mu_B^2}$$

The U's are thus directly proportional to the exchange integrals. Let Z_{aa} and Z_{ab} represent respectively the number of A and B ions neighboring an A ion; and let Z_{ba} and Z_{bb} represent the respective number of A and B ions neighboring a B ion. Then the molecular field to which the A and B ions are subjected may be described by the equations

$$\left.\begin{aligned} \vec{h}_a &= Z_{aa}U_{aa}\vec{I}_a + Z_{ab}U_{ab}\vec{I}_b \\ \vec{h}_b &= Z_{ba}U_{ba}\vec{I}_a + Z_{bb}U_{bb}\vec{I}_b \end{aligned}\right\} \qquad \text{LV-4}$$

From meeting 49, equations 10 and 11,

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

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

Comparing this with the previous equation we find

$$U_{aa} = \frac{n\alpha\lambda}{Z_{aa}}; \quad U_{ab} = \frac{n\varepsilon\mu}{Z_{ab}}$$

$$U_{ba} = \frac{n\varepsilon\lambda}{Z_{ba}}; \quad U_{bb} = \frac{n\beta\mu}{Z_{bb}} \qquad \text{LV-5}$$

In order to evaluate the Z's, the value of λ and μ must be known. The distribution of ferrite ions amongst A and B sites are described in the following table.

	A	B	B
NORMAL	M	Fe	Fe
PARTIALLY INVERSE	2λFe, $(1-2\lambda)$M	$(1-2\lambda)$Fe, 2λM	Fe
INVERSE	Fe	M	Fe

Thus there are 2λ Fe ions per A site and $[(1-2\lambda) + 1]/2$ Fe ions per B site. That is, $(1-\lambda)$Fe or μ Fe ions per B site.

Each A site in a ferrite is surrounded by 4 A sites and 12 B sites, while each B site is surrounded by 6 A sites and 6 B sites. Therefore,

$$\left.\begin{aligned} Z_{aa} &= 8\lambda & Z_{ab} &= 12\mu \\ Z_{ba} &= 12\lambda & Z_{bb} &= 6\mu \end{aligned}\right\} \qquad \text{LV-6}$$

Substituting these values into equation LV-5, and recalling that $\varepsilon = -1$ for anti-parallel alignment, obtain

$$\left.\begin{aligned} U_{aa} &= \frac{n\alpha}{8} \\ U_{ab} &= U_{ba} = -\frac{n}{12} \\ U_{bb} &= \frac{n\beta}{6} \end{aligned}\right\} \qquad \text{LV-7}$$

The values of the U's for ferrites obtained from these equations have been found to be negative when comparison with metals shows they should be positive. In order to overcome this discrepancy Néel introduced the concept of super-exchange, with the magnetic interaction taking place through the oxygen ions. This phenomenon was discussed in some detail at meeting 38.

At this point we shall start our discussion of the Smart and Howard report. The above discussion of Néel's was necessary for a clearer understanding of the new notations to be introduced.

Smart and Howard define the Weiss molecular field by the equations

$$\left.\begin{aligned} h_{aa} &= \gamma_{aa} I_a & h_{ab} &= \gamma_{ab} I_b \\ h_{ba} &= \gamma_{ba} I_a & h_{bb} &= \gamma_{bb} I_b \end{aligned}\right\} \qquad \text{LV-8}$$

where h_{ab} is the effective field value acting on A site due to neighboring B site ions. The other molecular fields are similarly defined. In these equations,

$$\left.\begin{aligned} \gamma_{aa} &= \frac{2Z_{aa}J_{aa}}{\nu_a g^2 \mu_B^2}; & \gamma_{ab} &= \frac{2Z_{ab}J_{ab}}{\nu_b g^2 \mu_B^2} \\ \gamma_{ba} &= \frac{2Z_{ba}J_{ba}}{\nu_a g^2 \mu_B^2}; & \gamma_{bb} &= \frac{2Z_{bb}J_{bb}}{\nu_b g^2 \mu_B^2} \end{aligned}\right\} \qquad \text{LV-9}$$

where ν_a and ν_b are the number of magnetic ions on the A and B sites in the sample. Since

$\frac{Z_{ab}}{\nu_b} = \frac{Z_{ba}}{\nu_a}$ and $J_{ab} = J_{ba}$, we have $\gamma_{ab} = \gamma_{ba}$.

The factor γ_{ab} is defined as a positive quantity, with the preceding sign expressing parallel or anti-parallel alignment. γ_{aa} and γ_{bb} may be positive or negative, depending on the sign of J_{aa} and J_{bb}. Applying Néel's assumption of anti-parallel alignment of the A and B sites, and letting H_o represent the external magnetic field,

$$\left.\begin{aligned} \vec{h_a} &= \vec{H_o} + \gamma_{aa}\vec{I_a} - \gamma_{ab}\vec{I_b} \\ h_b &= \vec{H_o} - \gamma_{ab}\vec{I_a} + \gamma_{bb}I_b \end{aligned}\right\} \qquad \text{LV-10}$$

Then

$$\left.\begin{aligned} \vec{I_a} &= \lambda N g \mu_B S\, B_s \left[\frac{g\mu_B S h_a}{kT}\right] \\ \vec{I_b} &= \mu N g \mu_B S\, B_s \left[\frac{g\mu_B S h_b}{kT}\right] \end{aligned}\right\} \qquad \text{LV-11}$$

wherein B_s is the Brillouin function, $g\mu_B S$ is the magnetic moment of one atom, and N is Avogadro's number.

To find the susceptibility above the Curie point the Brillouin function may be expanded, as at meeting 49, to yield

$$I_a = \frac{\lambda C h_a}{T}$$

$$I_b = \frac{\mu C h_b}{T}$$

where $C = Ng^2\mu_B{}^2 S(S+1)/3k$. Substitution of the molecular field values of equations LV-10 yields

$$\left.\begin{aligned} I_a &= \frac{\lambda C}{T}\left[H_o + \gamma_{aa} I_a - \gamma_{ab} I_b\right] \\ I_b &= \frac{\mu C}{T}\left[H_o - \gamma_{ab} I_a + \gamma_{bb} I_b\right] \end{aligned}\right\} \quad \text{LV-12}$$

Rearranging terms,

$$\left.\begin{aligned} \left(1 - \frac{\lambda C \gamma_{aa}}{T}\right) I_a + \frac{\lambda C \gamma_{ab}}{T} I_b &= \frac{\lambda C}{T} H_o \\ \frac{\mu C \gamma_{ab}}{T} I_a + \left(1 - \frac{\mu C \gamma_{bb}}{T}\right) I_b &= \frac{\mu C}{T} H_o \end{aligned}\right\} \quad \text{LV-12a}$$

On solving for I_a and I_b to determine the susceptibility one finds

$$\chi = \frac{I_a + I_b}{H_o} = \frac{C\left[T - \lambda\mu C(\gamma_{aa} + 2\gamma_{ab} + \gamma_{bb})\right]}{T^2 - (\lambda C \gamma_{aa} + \mu C \gamma_{bb})T + \lambda\mu C^2(\gamma_{aa}\gamma_{bb} - \gamma_{ab}^2)} \quad \text{LV-13}$$

When $H_o \rightarrow 0$ equation LV-12a gives $I_a = I_b = 0$, which is consistent with paramagnetic behavior, unless the determinant of the coefficients of I_a and I_b vanishes; that is,

$$\left(1 - \frac{\lambda C \gamma_{aa}}{T}\right)\left(1 - \frac{\mu C \gamma_{bb}}{T}\right) = \frac{\lambda\mu C^2 \gamma_{ab}^2}{T^2}$$

This is a quadratic equation which leads to the solutions

$$\left.\begin{aligned} T_c &= \tfrac{1}{2} C\left(\lambda\gamma_{aa} + \mu\gamma_{bb} + \sqrt{(\lambda\gamma_{aa} + \mu\gamma_{bb})^2 + 4\lambda\mu\gamma_{ab}^2}\right) \\ T_c' &= \tfrac{1}{2} C\left(\lambda\gamma_{aa} + \mu\gamma_{bb} - \sqrt{(\lambda\gamma_{aa} + \mu\gamma_{bb})^2 + 4\lambda\mu\gamma_{ab}^2}\right) \end{aligned}\right\} \quad \text{LV-14}$$

Since remanent magnetism when the imposed field is made to vanish is characteristic of ferro and ferrimagnetism, one of these quantities must be the Curie temperature. In the original Néel paper, only the positive root was considered. However, Smart and Howard substituted both roots into equation LV-12a and solved for $\vec{I}_a$ and $\vec{I}_b$ at $T = T_c$. They found that in this case $\vec{I}_a$ and $\vec{I}_b$ are antiparallel. Solving for $\vec{I}_a$ and $\vec{I}_b$ at $T = T'_c$, $\vec{I}_a$ and $\vec{I}_b$ were found to be parallel.

The actual Curie temperature is T_c since $T_c > T'_c$, and so represents a state of lower interaction energy. For both T_c and T'_c negative, the material has no Curie point and is always paramagnetic.

Let us examine T_c and T'_c to see the conditions under which the denominator of equation LV-13 has positive roots.

From equation LV-14 we have

$$T_c + T'_c = \lambda C \gamma_{aa} + \mu C \gamma_{bb}$$

$$T_c T'_c = \lambda\mu C^2 (\gamma_{aa} \gamma_{bb} - \gamma_{ab}^2)$$

If γ_{aa} and γ_{bb} are both positive, the sum of the roots are positive, so at least one root is positive.

If $\gamma_{aa} \gamma_{bb} < \gamma_{ab}^2$ the product of the roots is negative, so one root must be positive.

If γ_{aa} and γ_{bb} are both negative but $\gamma_{aa} \gamma_{bb} > \gamma_{ab}^2$, then the sum of the roots is negative and their product is positive, so both roots must be negative.

Thus a positive root exists everywhere in the γ_{aa}- γ_{bb} plane except to the left of the lower branch of the hyperbola $\gamma_{aa} \gamma_{bb} = \gamma_{ab}^2$. (In the Néel notation this corresponds to the region to the left of the lower branch of the hyperbola $\alpha\beta = 1$ in the α-β plane).

It will be recalled (meeting 49) that Néel expressed the paramagnetic behavior of ferrites by an equation of the form

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T-\theta'} \qquad \text{XLIX-14}$$

In the notation introduced by Smart and Howard

$$\frac{1}{\chi_0} = -(\lambda^2 \gamma_{aa} - 2\lambda\mu\gamma_{ab} + \mu^2 \gamma_{bb})$$

$$\theta' = \lambda\mu C(\gamma_{aa} + 2\gamma_{ab} + \gamma_{bb}) \qquad \text{LV-15}$$

$$\sigma = \lambda\mu C\left[\lambda(\gamma_{aa} + \gamma_{ab}) - \mu(\gamma_{ab} + \gamma_{bb})\right]^2$$

Equations LV-15 can be solved for the γ's to yield

$$\gamma_{aa} = -\frac{\mu\theta'}{\lambda C} - \frac{1}{\chi_0} \pm 2\mu\sqrt{\frac{\sigma}{\lambda\mu C}} \qquad \text{LV-16}$$

$$\gamma_{bb} = \frac{\lambda\theta'}{\mu C} - \frac{1}{\chi_0} \pm 2\lambda\sqrt{\frac{\sigma}{\lambda\mu C}}$$

$$\gamma_{ab} = \frac{\theta'}{C} + \frac{1}{\chi_0} \pm (\lambda - \mu)\sqrt{\frac{\sigma}{\lambda\mu C}}$$

Equation XLIX-14 is the equation of a hyperbola, which is shown in Fig. 131. The geometrical interpretation of the constants C, T_c, T'_c, θ, θ', σ, and $1/\chi_0$ are also shown in this diagram.

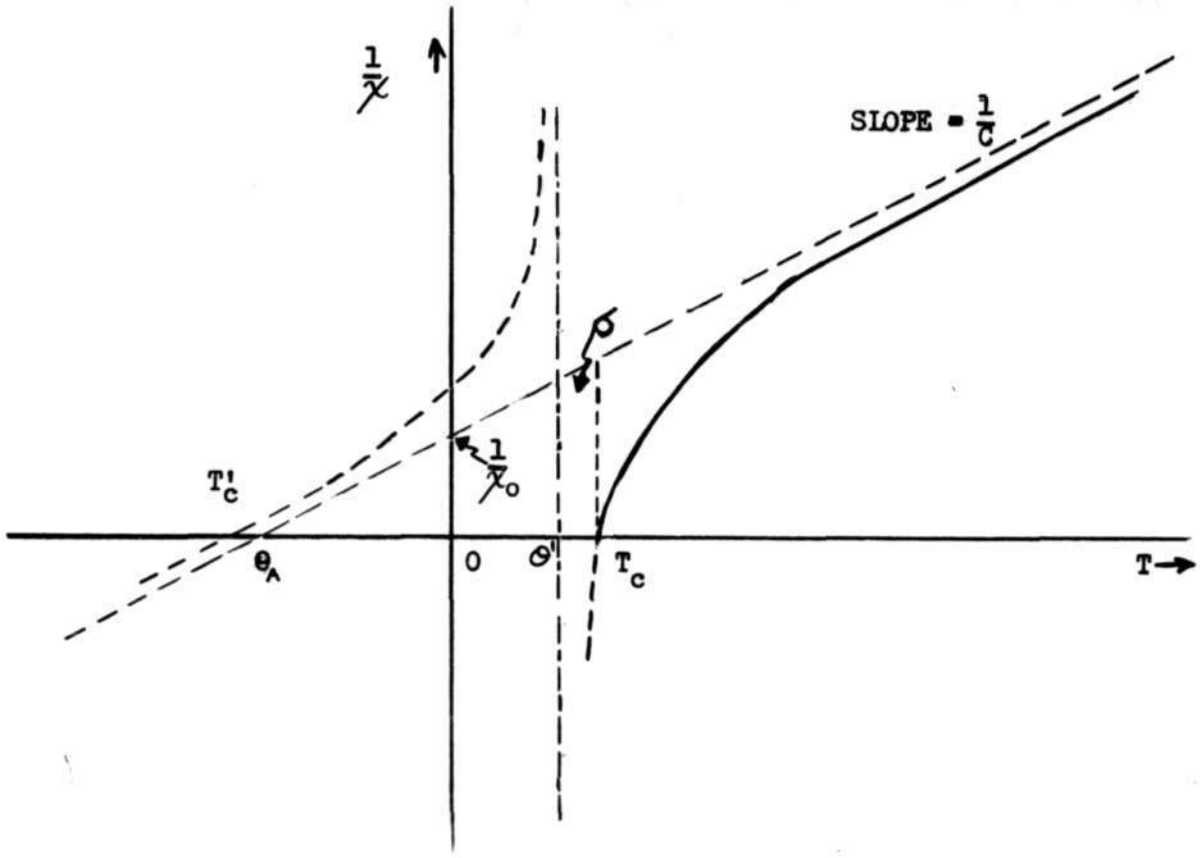

FIGURE 131

The asymptotes to the hyperbola are seen to be

$$T = \theta' \text{ and } \frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_o} \qquad \text{LV-17}$$

The value of χ_o can easily be determined experimentally, since it is the value of the asymptote

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_o} \text{ at } T = 0.$$

The experimental method of determining θ' and σ is not as simple, and requires further elaboration.

If T_a is the highest temperature at which a measurement is made, and χ_a is the corresponding susceptibility, then from equation XLIX-14

$$\frac{1}{\chi} - \frac{1}{\chi_a} = \frac{T-T_a}{C} - \sigma\left[\frac{1}{T-\theta'} - \frac{1}{T_a-\theta'}\right]$$

where T and χ are the temperature and susceptibility of another measurement at a lower temperature ($T < T_a$). This can be done for various values of T.

Dividing the above equation by $T-T_a$ and rearranging terms one obtains the relationship

$$\left[\frac{1/\chi_a - 1/\chi}{T_a-T} - \frac{1}{C}\right]^{-1} = \frac{1}{\sigma}\left[(T_a-\theta')^2 - (T_a-\theta')(T_a-T)\right] \qquad \text{LV-18}$$

If the left hand side of this equation is plotted against (T_a-T) a straight line should be obtained with the abscissa ordinate equal to $T_a-\theta'$ and an ordinate intercept equal to

$$\frac{(T_a-\theta')^2}{\sigma},$$

as shown in Fig. 132.

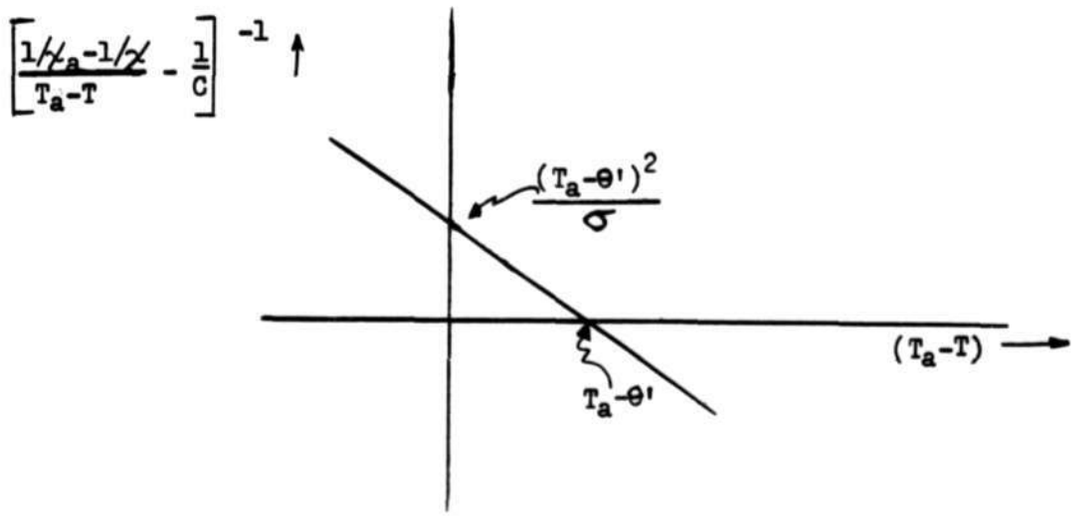

FIGURE 132

From these points σ and θ' can easily be determined. In practice it is found that the points of the curve indicated in Fig. 132 do not lie on a perfectly straight line but on a curve which is convex to the abscissa. However, this line is fairly straight for the middle values of (T_a-T). Drawing a straight line through this portion of the curve will give values of σ and θ' which approximate the experimental data reasonably well.

In the above work it has been assumed that the Curie Constant C is known accurately and is constant. However, this is only approximately true, and has led to some discrepancies. Néel has attempted to overcome these discrepancies by assuming the γ's are a function of temperature in accordance with the relationship

$$\gamma = \gamma_0 (1 + aT) \qquad \text{LV-19}$$

wherein the coefficient a has the same value for all three γ's. A new "Curie constant" C* is now defined by the relationship

$$\frac{1}{C^*} = \frac{1}{C} + \frac{a}{\chi_0} \qquad \text{LV-20}$$

where the Curie constant C is determined from theory or experiment.

The importance of these measurements above the Curie point should be emphasized. Equations LV-17 show that the exchange energies can be found from the parameters θ', χ_0 and σ obtained by measurements above the Curie point. These exchange energies in turn are used to predict the spontaneous magnetization below the Curie point.

The discussion by Smart and Howard of the spontaneous magnetization of ferrites below the Curie point is essentially the same as that of Néel and will not be repeated here. They obtain the various types of magnetic behavior shown in Fig. 133.

Comparison with experiment

Néels hypotheses are confirmed by the following experimental observations.

A) Guillaud* has shown that on substituting Zn^{++} for part of the divalent ions of a single ferrite there is an increase in saturation magnetization with increasing percentage of Zn^{++} up to about 40% Zn^{++} and then falls off, as shown in Fig. 133. Furthermore, the rate of increase at the beginning, if extrapolated, leads to a resultant magnetic moment of 10 Bohr magnetons for pure zinc ferrite.

This behavior is easily explained by the Néel model. Using nickel ferrite as an example, let us consider the substitutional process. The zinc ions tend to form a normal spinel, and go to the A sites, with Fe^{+++} replacing Ni^{++} in the B sites. Thus for a substituted Ni^{++} ion one loses $2.4\mu_B$ since Zn^{++} is non-magnetic. But there is a net increase of two Fe^{+++} ions aligned parallel for an increase of $10\mu_B$.

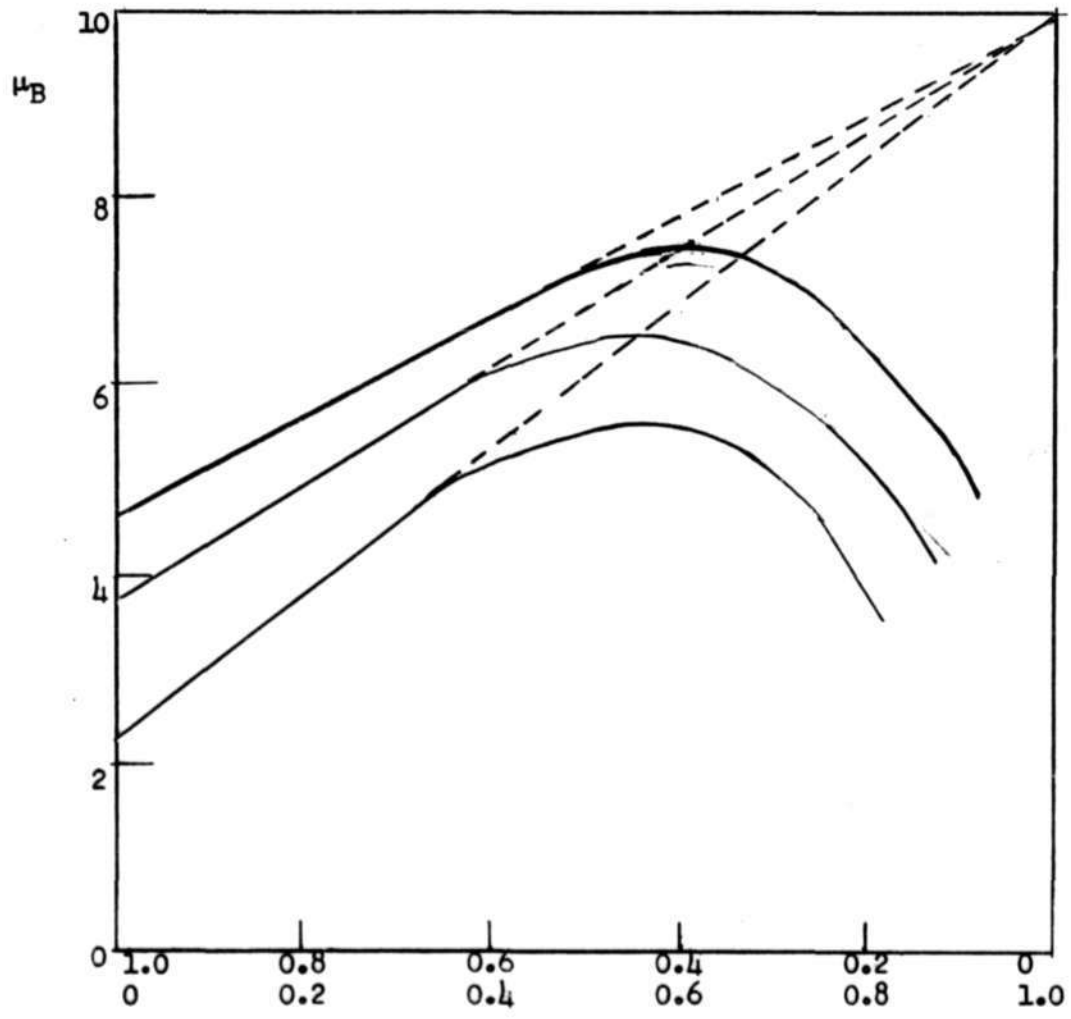

FIGURE 133

* Guillaud, C., Journal de Physique et le Radium, 12, 239 (1951).

The decrease in saturation magnetization which occurs with around 50% Zn^{++} can be explained by a fairly large negative B-B interaction. Then as the number of magnetic ions on A sites becomes small the B lattice sites will no longer saturate at low temperatures. Néel and Brochet* have calculated the value of β and shown that they are negative as predicted.

In addition, the magnetization curve has been found to change from a Q type curve to an R type curve (see Fig. 119) as the Zn^{++} content is increased. Néel+ has calculated the point (α,β) from the susceptibility data and shown that the point does move from region Q to region R (Fig. 118) in the proper manner.

B) The shape of the $1/\mu$ vs T curve in the paramagnetic region, as predicted by Néel (equation LXIX-14), is curved rather than straight. The Curie-Weiss relationship $1/\chi = C/T-\theta$ leads to a straight line relationship.

C) The saturation magnetization values of ferrites are much lower than the magnetic moments of the constituents would lead one to predict. However, the Néel hypothesis of antiparallel alignment of the ions on the A and B sites accurately predicts the lower values which are observed experimentally.

D) Specific Heat - Let us now examine the discontinuity in the specific heat of ferrites obtained from the Néel theory. The magnetic energy

$$W = -\frac{1}{2}\left[\vec{I}_a \cdot \vec{h}_a + \vec{I}_b \cdot \vec{h}_b\right].$$

Therefore, from equations LV-10

$$W = -\frac{1}{2}(Ng\mu_B S)^2\left[\gamma_{aa}\lambda^2 y_a^2 + 2\gamma_{ab}\lambda\mu|y_a y_b| + \gamma_{bb}\mu^2 y_b^2\right] \qquad \text{LV-21}$$

wherein y_a and y_b are the specific magnetizations of the A and B sites respectively; that is,

$$y_a = \frac{I_a}{\lambda Ng\mu_B S} \qquad y_b = \frac{I_b}{\mu Ng\mu_B S} \qquad \text{LV-22}$$

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* Néel, L. and Brochet, P., Comptes Rendus, 230, 280 (1950)

\+ Néel, L., Comptes Rendus, 230, 375 (1950)

For the region $T < T_c$ but near T_c

$$W = -\frac{1}{2}(Ng\mu_B S)^2 \frac{\phi_s}{\psi_s} \left(\frac{\lambda k_c + \mu/k_c}{\lambda k_c^2 + \mu/k_c^2}\right) \left[\gamma_{aa}\lambda^2 k_c - 2\gamma_{ab}\lambda\mu + \gamma_{bb}\frac{\mu^2}{k_c}\right] \frac{(T_c - T)}{T_c} \qquad \text{LV-23}$$

wherein

$$\phi_s = \frac{3S}{S+1}, \quad \psi_s = \frac{9}{10}\frac{\left[(S+1)^2 + S^2\right] S}{(S+1)^3}$$

and $k_c = \left[\frac{dy_a}{dy_b}\right]_{T=T_c}$

k_c may be determined from the quadratic equation

$$\lambda\gamma_{ab}k_c^2 + (\lambda\gamma_{aa} - \mu\gamma_{bb})\, k_c - \mu\gamma_{ab} = 0 \qquad \text{LV-24}$$

Equations LV-23 and LV-24 can be obtained by the method shown in detail in appendix VII, which was employed to arrive at analagous equations treated in Néel's original paper.

Differentiating equation LV-23 with respect to temperature gives the discontinuity in specific heat, which is

$$\Delta C = \frac{\partial W}{\partial T} = \frac{1}{2}\frac{(Ng\mu_B S)^2}{T_c}\frac{\phi_s}{\psi_s}\left(\frac{\lambda k_c + \mu/k_c}{\lambda k_c^2 + \mu/k_c^2}\right)\left[\gamma_{aa}\lambda^2 k_c - 2\gamma_{ab}\lambda\mu + \gamma_{bb}\mu/k_c\right]^2 \qquad \text{LV-25}$$

Various experimental determinations of the discontinuity of specific heat in magnetite, and the mean value of ΔC is about 0.075 cal/gm degree. Néel has calculated the value to be 0.068 cal/gm degree, which is in good agreement with experiment.

Experiments have also been performed on Ferroxcube III ($\sim$1/2MnO 1/2ZnO Fe_2O_3), and the specific heat discontinuity found to be 0.015 cal/gm degree. Theoretical calculations are off by a factor of about two, but this is not unusual for specific heat calculations based on the Weiss field theory.

Signed _____
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Approved _____
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ALL/NM:jrt

Group 62 (25)