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Digital Computer Laboratory  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLVIII

To: Group 63 Engineers

From: Norman Menyuk

Date: April 7, 1953

Several pertinent papers given at the North Carolina Meeting of the American Physical Society were discussed at this meeting.

A paper presented by Berkowitz and Franklin\* was discussed first. They pressed samples consisting of carbonyl iron powders and silicic acid powders bonded in a resin. The iron grains have a diameter of approximately two microns, so there can be more than one domain within a grain.

They examined the approach to saturation for different samples and checked their results with Néel's<sup>†</sup> theory. Within an intermediate region of applied field (1000 oe. < H < 10000 oe.) the approach to magnetization has the form

$$I = I_s \left(1 - \frac{a}{H}\right)$$

XLVIII-1

where I = magnetization

$I_s$  = saturation magnetization

H = applied field

a = magnetic hardness

The magnetic hardness a is defined by the empirical equation given above. The larger the value of a the slower the approach to saturation. Néel correlated this quantity a with the porosity of magnetic material, and obtained a relationship shown approximately by the line in figure 101. Several experimental points obtained by Berkowitz and Franklin are shown on the same curve.

\* Berkowitz, A.E. and Franklin, A.D., "The Approach to Saturation in Dilute Ferromagnetic Powders."

† Néel, L., Journal de Physique et le Radium, 9, 84 (1948).

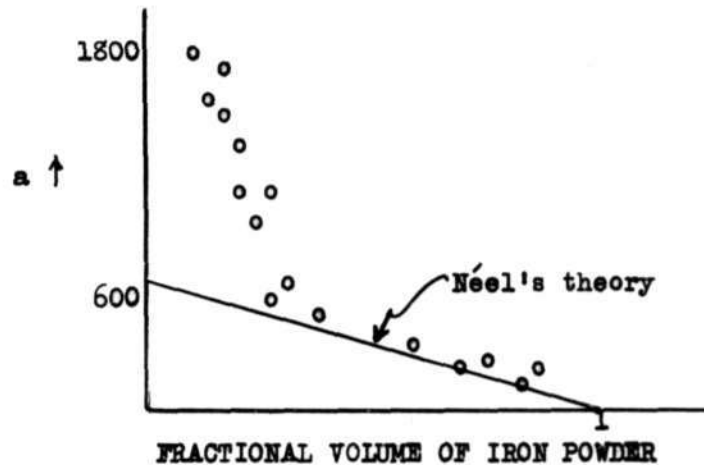


FIGURE 101

At high concentrations of iron powder the approach to saturation can be seen to agree quite well with Néel's theory. At low iron powder concentration there is a large deviation from his results. This deviation increases as the substance becomes more dilute. In the extremely dilute region the magnetization curves can be accounted for in terms of the domain theory for weakly interacting particles.

At very high field values ( $H > 10000$  oe.) the saturation curve no longer follows the form given in equation XLVIII-1, but goes over to the form

$$I = I_s \left( 1 - \frac{b}{H^2} \right) \quad \text{XLVIII-2}$$

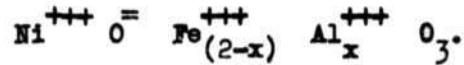
Néel has related the coefficient  $b$  with the anisotropy constant  $K$  by the equation

$$b = \frac{8}{105} \frac{K^2}{I_s^2} \quad \text{XLVIII-3}$$

The value of the anisotropy constant was obtained for several samples using Néel's method and by direct experimental techniques. In every case, the value obtained for  $K$  by Néel's method was considerably lower than the experimental value by a factor ranging from  $\frac{1}{10}$  to  $\frac{1}{100}$ . From this we can assume that

the value of  $K$  obtained by using equation XLVIII-3 cannot be accepted as valid.

The paper presented by Maxwell, Pickart, and Hall\* was discussed next. They prepared various samples of nickel ferrite-aluminate, which has the general form



These samples were prepared for various values of  $x$ . When  $x = 0$ , we have nickel ferrite ( $\text{Ni O Fe}_2 \text{O}_3$ ); and when  $x = 2$  we have nickel aluminate ( $\text{Ni O Al}_2 \text{O}_3$ ).

However, increasing  $x$  involves more than a simple substitution of trivalent aluminum ions for trivalent iron ions since nickel ferrite has an inverse spinel structure while nickel aluminate has a normal spinel structure. That is, in nickel ferrite the divalent nickel ions are in the octahedral (B) sites while half the trivalent iron ions are in the B sites and the other half are in the tetrahedral (A) sites. In nickel aluminate all the nickel ions are in the A sites and all the aluminum ions are in the B sites. (See meeting 42). For values of  $x$  greater than 0 and less than 2 the nickel ferrite-aluminate will therefore have a mixed spinel structure with some fraction of the ions in each site.

Maxwell, Pickart, and Hall investigated various properties of nickel ferrite-aluminate as a function of  $x$ . They found that the unit cell size decreased linearly as the trivalent aluminate was substituted for trivalent iron. This is shown in figure 102.

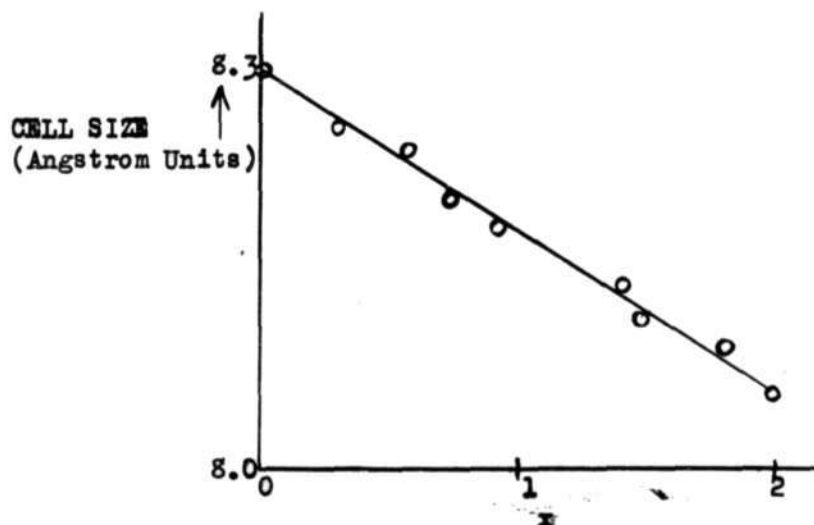


FIGURE 102

\* Maxwell, L.R., Pickart, S.J., Hall, R.W., "Thermomagnetic Investigations of Nickel Ferrite-Aluminates."

Increasing  $x$  decreases the saturation magnetization sharply, as is shown in figure 103. The exact shape of the curve depends upon the history of the sample. The magnetization of the fast annealed sample decreases almost linearly, going to zero at about  $x = 0.7$ . The absolute value of the magnetization then increases until  $x \approx 1.0$ , after which it goes to zero. In the upper portion of the curve the magnetization of the B sites predominates, while the magnetization of the A sites predominate in the lower half.

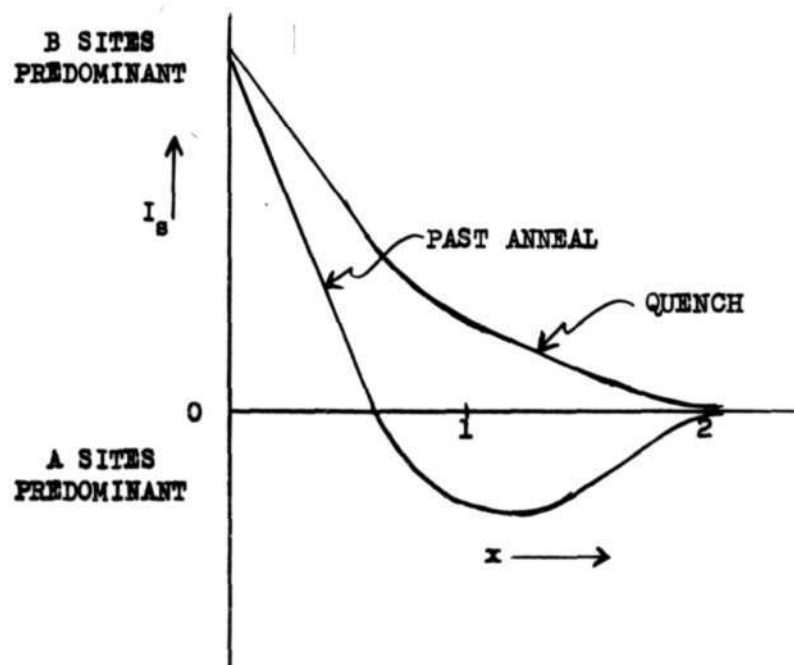


FIGURE 103

Increasing  $x$  also results in a decrease in the value of the Curie temperature  $T_c$ . The form of this decrease is indicated in figure 104.

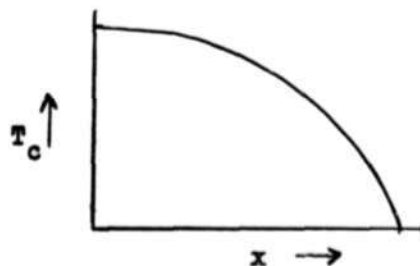


FIGURE 104

It is believed that the squareness ratio of the hysteresis loops of various ferrites can be increased by decreasing the value of  $I_s$ . To test this hypothesis, John Goodenough and Frank Vinal of the laboratory have prepared several samples in which  $I_s$  has been decreased by the substitution of aluminum for ferric ions.

In view of the relationship\*

$$(H - H_0) \tau \propto \frac{1}{I_s \sqrt{T_c}}$$

and the decrease of both  $I_s$  and  $T_c$  upon substitution of aluminum ions for ferric ions, a slower switching time  $\tau$  is to be expected for these samples. It would therefore appear that a compromise between the squareness ratio and the switching time will have to be reached.

Two other papers concerned with nickel ferrite-aluminate were presented at the meeting. The first of these† presented the experimental values of the  $g$ -factor obtained for the ferrite-aluminates for various values of  $x$ . The curve of these values is shown by the solid line in figure 105. The values shift from  $g > 2$  to  $g < 2$  at  $x$  approximately 0.7. This is the value at which the dominant magnetic moment shifts from the B sites to the A sites. The other paper‡ was concerned with a theoretical calculation of the  $g$ -values of nickel ferrite-aluminate as a function of  $x$ . The author calculated the resonance frequencies of a system containing two magnetic sublattices, each having different magneto-mechanical ratios. The values obtained are shown by the dashed line in figure 105 and are seen to give a semi-quantitative agreement with the experimental values.

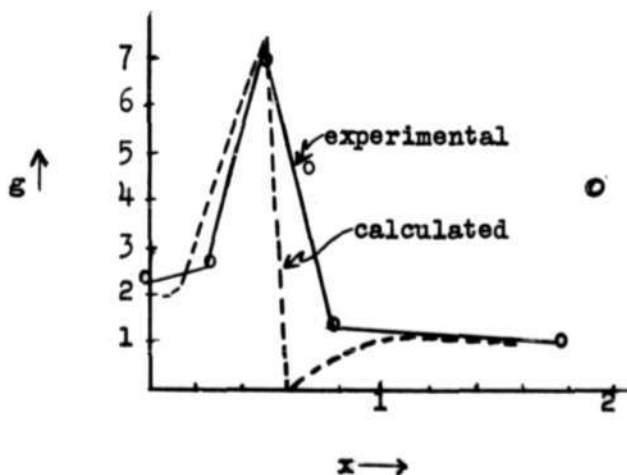


FIGURE 105

\* Goodenough, J. B. and Menyuk, N., Engineering Note E-532, Digital Computer Laboratory, 26 (1953).

† McGuire, T. R. "Magnetic Absorption in Nickel Ferrite-Aluminates".

‡ Wangness, R. K. "g Values of Nickel Ferrite-Aluminates".

A study of antiferroelectric  $\text{PbHfO}_3$  was presented by Shirane and Pepinsky.\* Phase changes are found to occur at  $160^\circ\text{C}$  and  $210^\circ\text{C}$ . At room temperature  $\text{PbHfO}_3$  has a tetragonal lattice of the perovskite type (see figure 66, meeting XXXVII) and a  $c/a$  ratio of 0.991. Between  $160^\circ\text{C}$  and  $210^\circ\text{C}$  the structure is still tetragonal, but the  $c/a$  ratio is 0.998. Both of these phases are antiferroelectric. Above  $210^\circ\text{C}$  the  $c/a$  ratio increases to 1.063 and the material is paraelectric.

Shirane noted that all antiferroelectric materials with which he is familiar have the ratio  $c/a < 1$ , while  $c/a > 1$  for paraelectric and ferroelectric materials.

In another paper A. de Bretteville Jr.\*\* discussed the antiferroelectric-ferroelectric phase transition in lead zirconate ( $\text{Pb Zr O}_3$ ). The hysteresis loop for this material is approximately as shown in figure 106, wherein  $E_T$  is the threshold field; that is, the field required to change the antiferroelectric to the ferroelectric phase below the Curie temperature.

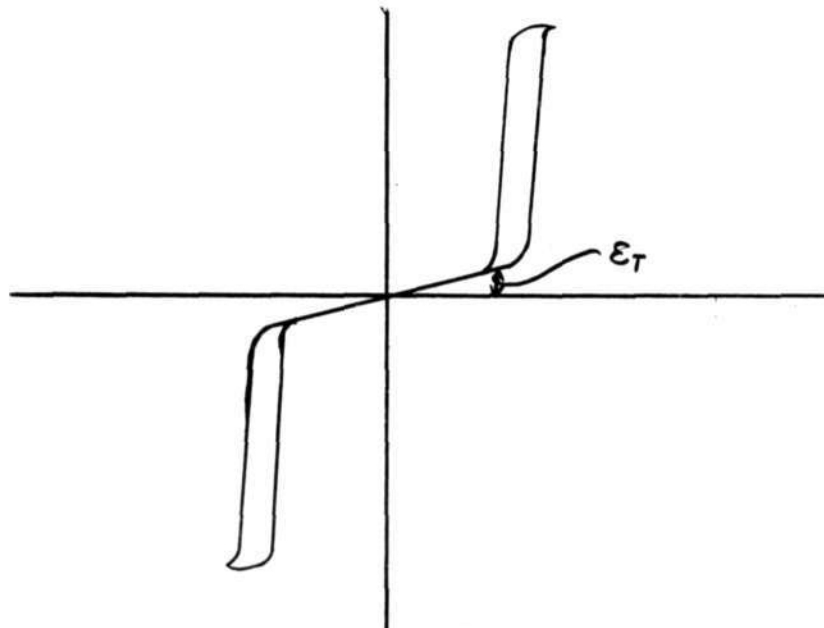


FIGURE 106

de Bretteville calculated the free energy difference between the two phases and found it to be small ( $\approx 3$  calories/mole at 25 kw/cm).

\* Shirane, G. and Pepinsky, R. "Phase Transitions in Antiferroelectric  $\text{Pb Hf O}_3$ ".

\*\* de Bretteville Jr., A. "Threshold Field and Free Energy for the Antiferroelectric-Ferroelectric Phase Transition in Lead Zirconate."

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He remarked that, to his knowledge, no pure barium titanate crystals have been obtained which display ferroelectric properties. All barium titanate crystals which are ferroelectric contain some impurities.

Signed Norman Menyuk  
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Approved DRB  
David R. Brown

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