

Digital Computer Laboratory  
Massachusetts Institute of Technology  
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLVI, MARCH 26, 1953

To: Group 63 Engineers

From: Arthur L. Loeb, John B. Goodenough

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On March 26 Professor N. Bloembergen of the Department of Physics, Harvard University, was guest speaker at the seminar. He discussed mainly the ferrimagnetic properties of ferrites and the mechanism of spin reversal in domain wall motion.

The general formula of ferrites is written  $BO Fe_2O_3$ , where B may be any divalent ion, including the ferrous ion. Ferrites crystallize in a spinel structure. The metallic ions are distributed over two kinds of sites, VIZ.

- A, "Tetrahedral sites," in which each metal ion is surrounded by four oxygens, and
- B, "Octahedral sites," in which each metal ion is surrounded by six oxygens.

There are 8 occupied A-sites and 16 occupied B-sites per unit cell. In the normal spinels trivalent ions occupy B sites, divalent ions A sites. Ferrites frequently show "inverse spinel" structure with trivalent ions in the A sites. The B sites are occupied half by divalent and half by trivalent ions.

The magnetic interactions between neighboring d-shell electrons is predominantly "super-exchange," a mechanism which was discussed in Lecture 38. The direct exchange is weak because of the large separation of the metallic ions. Because of the lattice geometry, there are more A-B than B-B pairs coupled through oxygen by "super-exchange!" In the ferrites  $MO Fe_2O_3$ , where M is not  $Fe^{++}$ , the Fe ion has five electrons in the d-shell so that the super-exchange coupling causes an antiferromagnetic alignment of spins and there is poor electrical conductivity. (This latter property is the reason these materials are of importance in high frequency work and as memory cores). As a result the ions on the A sites align their spins parallel to one another but antiparallel to the spins on the B sites. There are four experimental facts which corroborate this picture.

- (1) Magnetite ( $\text{Fe}_3\text{O}_4$ ), which is the iron ferrite  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ , has a magnetic moment of  $4\mu_B$  per molecule. ( $\mu_B = 1$  Bohr magneton = the spin magnetic moment of one electron). If the material were ferro-magnetic, i.e. had all its spins aligned parallel, the magnetic moment per molecule would be  $14\mu_B$  since each  $\text{Fe}^{+++}$  ion has a spin of  $5\mu_B$  and each ferrous ion has a spin moment of  $4\mu_B$ .
- (2) Measured values of  $1/\chi$  vs.  $T$ , where  $\chi$  is the susceptibility and  $T$  the absolute temperature, show a departure from the Curie-Weiss paramagnetic straight line relationship at lower temperatures. If the straight line portion of the curve (at high temperatures where the paramagnetic law holds) is extrapolated to the temperature axis, the Curie temperature,  $T_C$ , is found to be negative. The actual curve is shown in Fig. 87. Fig. 87 (a) departs from the straight line law to intersect the temperature axis at a Néel temperature,  $T_N$ . [The Néel temperature is usually referred to as the Curie temperature in the literature]. This is typical of an antiferromagnetic material. The magnetization of the material is due to the unbalance of spin magnitude in the two antiferromagnetically aligned spin system. This type of magnetism is called ferrimagnetism.

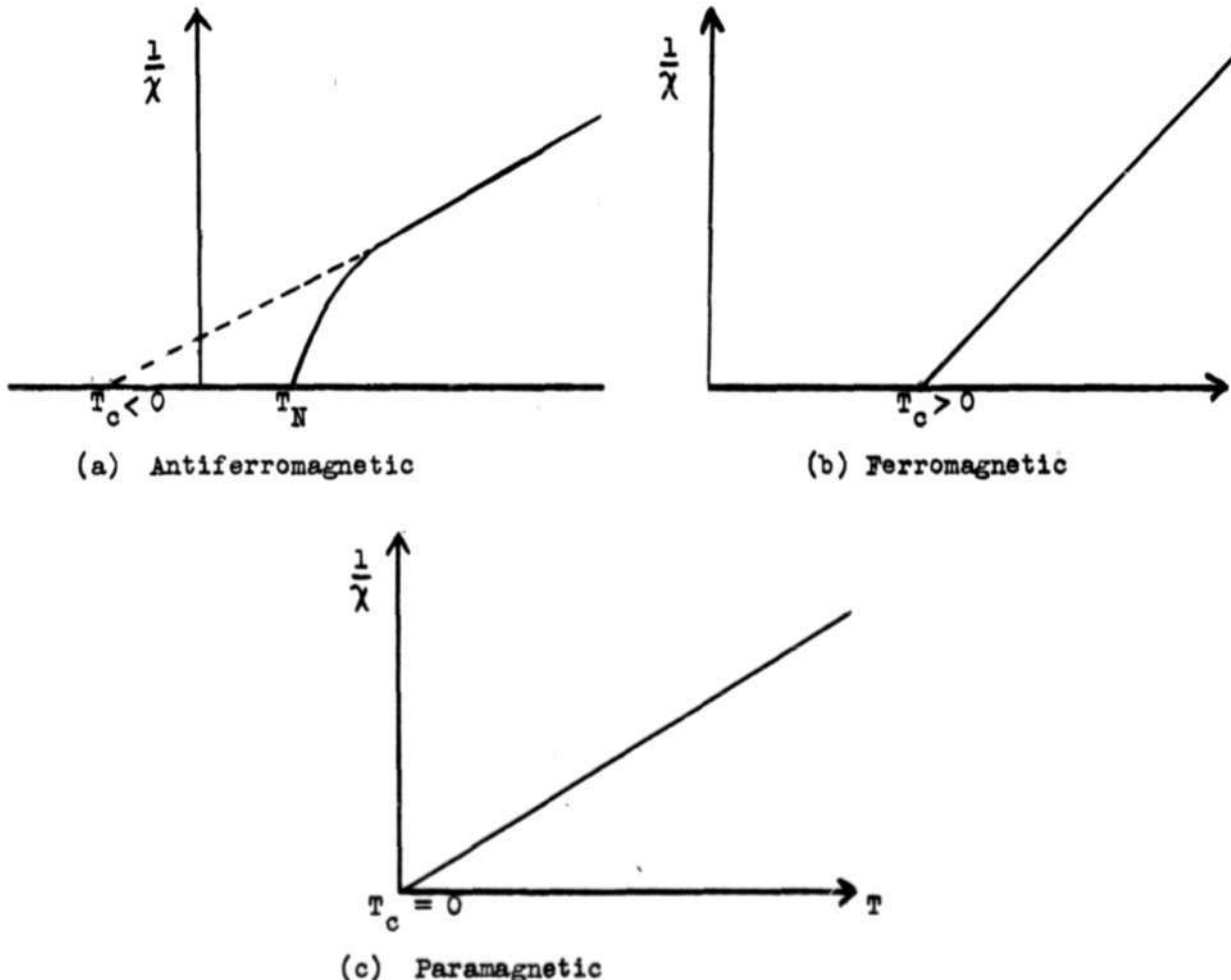


FIGURE 87 Typical  $1/\chi$  vs.  $T$  curves for magnetic materials.

- (3) Neutron diffraction by Smart and Shull and at Brookhaven has confirmed the alternating spin orientation in the crystal: the size of the unit crystal cell is twice as large for antiferromagnetic spin systems as for ferromagnetic systems (see Fig. 88).

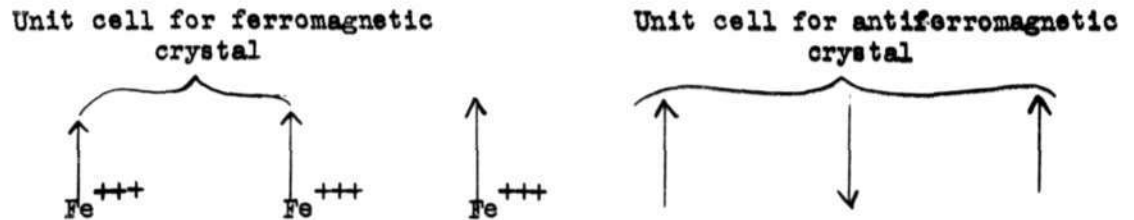
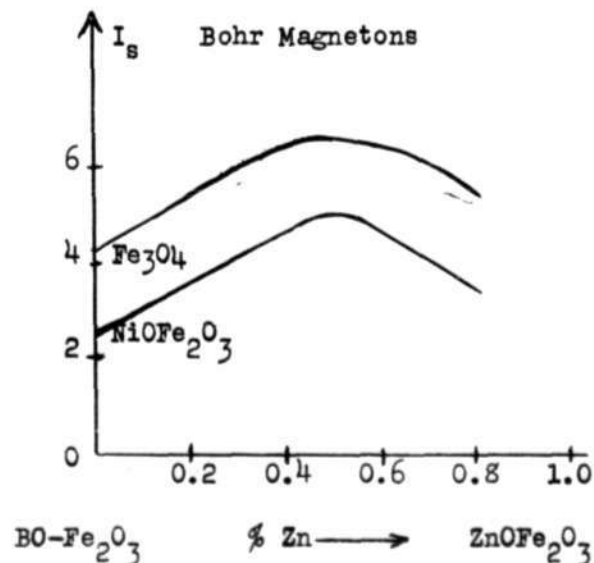


FIGURE 88

An analogy was pointed out between neutron diffraction of paramagnetic crystals and X-ray patterns of disordered alloys, as well as between neutron patterns of ferrimagnetic crystals and X-ray diffraction of ordered alloys. In paramagnetic and ferromagnetic materials the patterns are very similar, but ferrimagnetic orientation increases the size of the unit cell by a factor 2. Similarly in a disordered Cu-Au alloy there are enough Cu-Cu and Au-Au nearest neighbor pairs to account for certain lines in the X-ray diffraction pattern which cannot occur for the ordered alloy, in which all Cu-s are separated by Au, all Au-s by Cu.

- (4) An impressive proof of the ferrimagnetic character of the ferrites is a measurement of the change of magnetic moment per molecule with the addition of zinc. Zinc is a relatively large ion. It prefers, therefore, to go to the tetrahedral, or A sites. Although Zn<sup>++</sup> has a full d-shell with no spin magnetic moment, when the Zn<sup>++</sup> ions replace the Ni<sup>++</sup> or the Fe<sup>++</sup> ions in nickel ferrite or magnetite, the magnetic moment per molecule increases. This is shown in Fig. 89. The explanation of

FIGURE 89  
The saturation magnetization of mixed ferrites, plotted in Bohr Magnetons per molecule as a function of the zinc ferrite content, for different mixed ferrites.



this is Table I. The addition of  $Zn^{++}$  ions changes the imbalance of magnetic

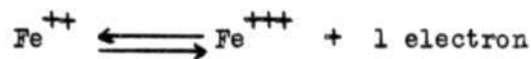
TABLE I

A-sites		B-sites	Magnetic Moment per molecule
8 Fe <sup>+++</sup>	↑	8 Fe <sup>+++</sup> ↓ 8 Ni ↓	2.3
1 Zn <sup>++</sup> 7 Fe <sup>+++</sup>	↑	9 Fe <sup>+++</sup> ↓ 7 Ni ↓	$(2.3)(\frac{7}{8}) + \frac{10}{8} = 3.25$

moment on the A and B-sites in favor of a higher net magnetization. When the material contains more than 50% zinc ferrite, the B-sites begin to couple antiferromagnetically with one another since there are now more B-B than B-A magnetic ion pairs. When there is 100% zinc ferrite, the  $Fe^{+++}$  ions on the B-sites couple antiferromagnetically and the  $Zn^{++}$  ions have no magnetic moment. The material has no net magnetic moment. The magnetization therefore goes through a maximum as a function of zinc content. Because of the decrease in the difference of the number of A-B and B-B magnetically coupled pairs, the net magnetic coupling decreases with the addition of zinc and the Néel temperature is depressed.

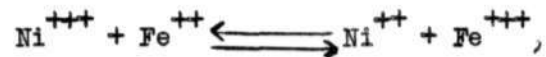
The conductivity of stoichiometrically pure  $NiO.Fe_2O_3$  is less than  $10^{-8}$  mho/cm. While it is very difficult to produce stoichiometrically pure crystals, it is nevertheless easy to prepare  $NiO.Fe_2O_3$  crystals with a conductivity less than  $10^{-6}$  mho/cm.

An exceptional material is magnetite,  $FeO.Fe_2O_3$ , which has the remarkably high conductivity of  $10^{-2}$  mho/cm. (Metals have a conductivity of about  $10^{+5}$  mho/cm). Verwey and Mott explain this on the basis of the resonance equilibrium:



The conductivity is then explained on the basis of the same model as that used by Zener for the perovskites, namely the double-well potential, with electron transfer between iron ions occurring via oxygen. This mechanism was explained as "Double Exchange" in Lecture XXXVII. It was pointed out there that "Double Exchange" gives rise to ferromagnetic spin alignment. Since the  $Fe^{++}$  and  $Fe^{+++}$  ions are both on B-sites in magnetite, the "Double Exchange" mechanism should occur between the ferromagnetically aligned B-site ions. In the case of

$\text{NiO} \cdot \text{Fe}_2\text{O}_3$  the corresponding equilibrium would be



a reaction which has a high excitation energy and which does not allow resonance between two identical potential wells.

The ferrites behave as semiconductors, i.e. the resistance decreases with increasing temperature. This indicates that electrons must be boosted across an energy gap in order to be free to conduct current. The magnitude of this energy gap, the excitation energy, is obtained when the logarithm of the resistivity is plotted vs. the reciprocal of the temperature. Fig. 90 shows curves for nickel ferrite and for magnetite, with the slopes representing excitation energies. It is clear that in nickel ferrite the excitation energy is greater than in magnetite.

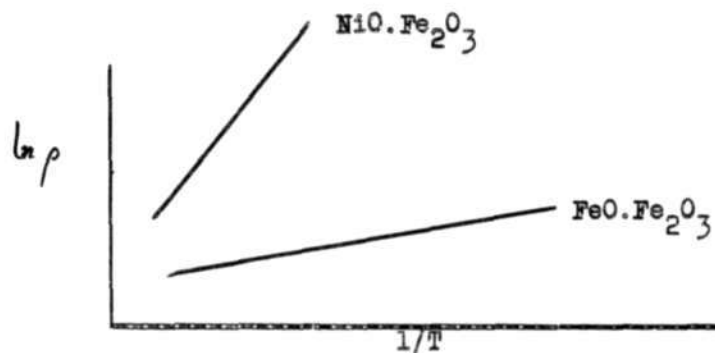
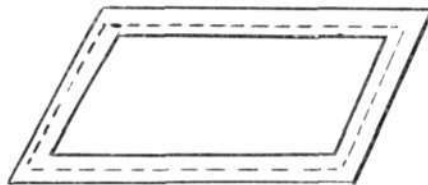


FIGURE 90

Impurities or deviations from the stoichiometric proportions in  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$  increase the conductivity and decrease the excitation energy. If there is a deficiency of nickel, for example, there will be lattice vacancies where nickel ions should be. For each  $\text{Ni}^{++}$  which is in deficiency there will have to be two  $\text{Ni}^{+++}$  ions created to bring about electrical neutrality in the lattice. The presence of both  $\text{Ni}^{++}$  and  $\text{Ni}^{+++}$  in the lattice permits conductivity by the "Double Exchange" mechanism since the nickel ions are all on B-sites with their spins parallel to one another. The reason the activation energy decreases with increase in nickel deficiency is thought to be a long range interaction between the lattice vacancies which are separated on the average by only 5 or 6 lattice sites with 1% nickel deficiency. The long range interaction is possible because of the high dielectric constant of the material.

Impedance to domain wall motion

Domain wall motion represents a progressive switching of electron spins. The speed of domain motion is limited by the speed with which an electron can reverse its spin. Domain wall motion actually represents a perturbation of equilibrium, and the time for establishment of a new equilibrium may be of the order of microseconds. Galt has measured the speed of domain wall motion for  $\text{Fe}_3\text{O}_4$  using a crystal grown by von Hippel. This crystal was diamond shaped, as shown in fig. 91. The window-frame edges were cut along the  $[111]$  directions, or along a direction of easy magnetization. The  $180^\circ$  domain walls formed parallel to the window frame edges.

FIGURE 91

A magnetic field pulse was imposed on this crystal, and the resulting change in magnetic flux density was measured as a function of time by means of the response in a sensing coil. He found for the domain wall speed

$$v = 1900 (H - H_c) \text{ cm/sec}$$

The time lag in the establishment of equilibrium can perhaps be more easily understood by magnetic resonance. As indicated in appendix II, electron spins precess around an external field. The electrons can be excited to higher energy states in which the angle between the spin and the external field is larger. This excitation can be accomplished by absorption of magnetic radiation energy of frequency equal to that of the precession of the electron spins. In an external field of 2000 gauss this frequency is  $\sim 10^{10}$  c.p.s., i.e. is in the radio frequency range.

Classically it can be said that the radio frequency magnetic field provides the torque necessary to bend the spin of the electron away from the external field. In order to be effective, this torque should always act in the direction of the spin rotation throughout the entire period of rotation. Unless the frequency of the r.f. field and the spin precession coincide, there will be an opposing torque imposed over part of the cycle. The direction in which the precessing spin rotates must match the r.f. field.

A  $180^\circ$  phase shift in the r.f. field will cause a counter torque over the entire cycle.

In order to obtain sufficient power in the r.f. field to obtain a sufficiently large change of precessional angle for accurate relaxation measurements, the r.f. field is turned on a sample for a microsecond. The sample is subjected to a square pulse. The time required for the sample to respond, i.e. the time required to reestablish equilibrium, is then a measure of the effective inertia of electron spin. Fig. 92 shows the experimental apparatus.

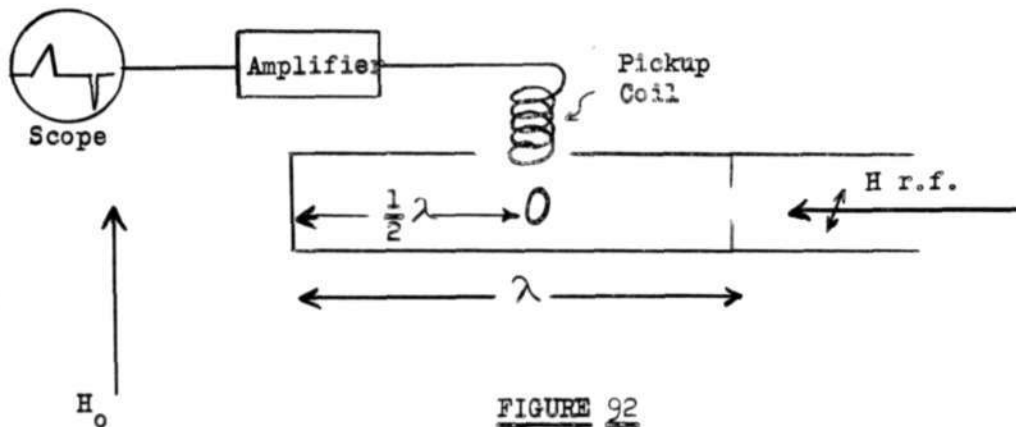


FIGURE 92

Figure 93 shows the response to a typical r.f. pulse which led to a measured relaxation time of less than  $10^{-7}$  sec.  $10^{-7}$  is the limit of their apparatus.

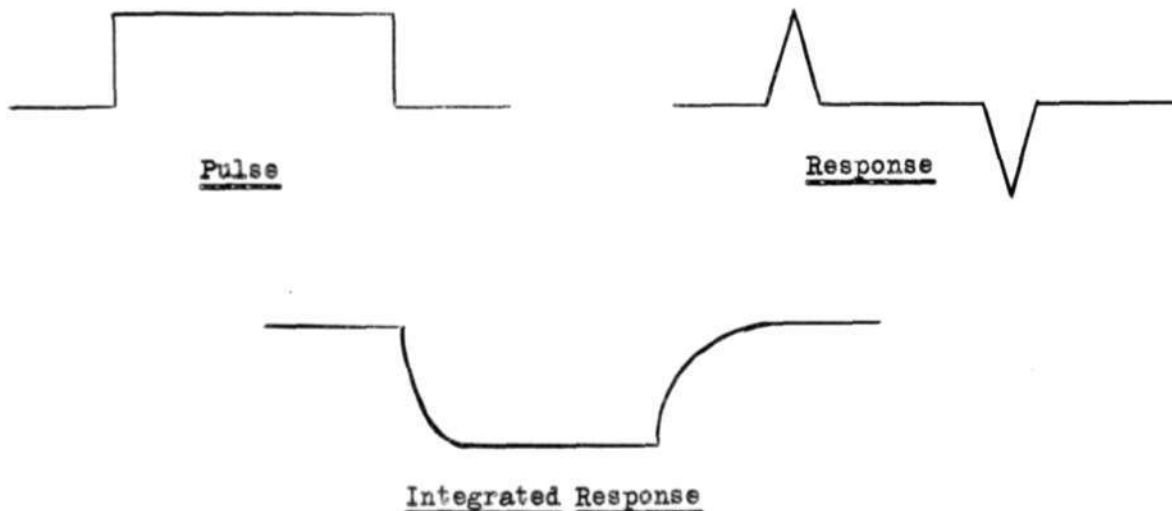


FIGURE 93

A short relaxation time indicates rapid response of electron spin to an external field, or small Bloch wall inertia. In lecture XIV resonance phenomena were discussed in general, and it was shown how the width of an absorption band is related to the relaxation time for the absorption mechanism. In radio frequencies a continuous range of absorption frequencies can be examined conveniently by varying the external "constant" field continuously. Thus by plotting the response to (absorption of) radiation vs. the intensity of the external field as shown in Fig. 94, the width of the absorption band can be measured. For a sample similar to the one used for the pulse response test the relaxation time was found to be  $\sim 10^{-9}$  sec. The two experiments give consistent results.

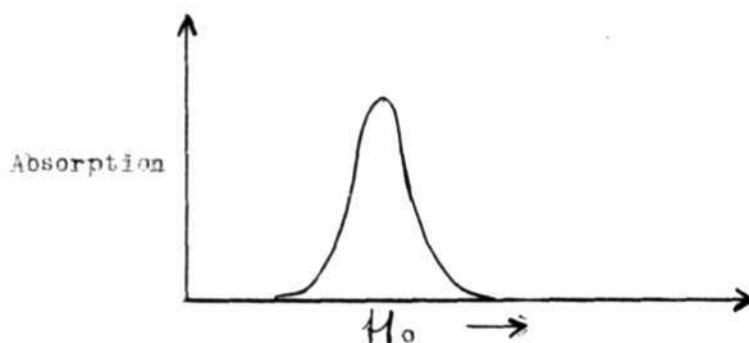


FIGURE 94

When ordinary conductivity was discussed, two mechanisms which inhibit the motion of electrons through a lattice were mentioned, namely their collisions with the lattice, and the thermal vibration of the atoms which disturb the lattice periodicity. A similar mechanism is responsible for the electron spin relaxation phenomenon.

The angle of precession of electron spins about a given external field direction is a measure of the magnetic energy of the system. A temperature  $T_m$  is characteristic of this energy when  $kT_m$ , where  $k$  is the Boltzmann constant, is equal to the average magnetic energy stored in the individual atoms and measured by the precession angle. (See Appendix II). There is, similarly, a characteristic temperature  $T_l$  for the vibrational energy of the atoms in the lattice, and  $T_e$  for the exchange energy between electron spins. At equilibrium  $T_m = T_l = T_e$ . When an r.f. field is applied so as to increase the precession angle, magnetic energy alone is introduced into the system. There is no increase in the thermal energy or the exchange energy of the lattice since the Hamiltonian for the r.f. field commutes with these energies. With the r.f. field on,  $T_m > T_l = T_e$ . When the r.f. field is removed, equilibrium must be reestablished between  $T_m$  and  $T_l = T_e$ . A change of energy from magnetic to vibrational and "exchange" occurs through a "collision" of the magnetic "spin-waves" with the phonons, or vibrational waves, of the lattice.




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The spin relaxation time is a measure of the time required to reestablish equilibrium in the lattice. At high temperatures the rate of "collision" between spin waves and phonons will be greater and equilibrium can be established more quickly. The spin relaxation time should, therefore, decrease with increasing temperature. This would result in faster wall motion with increasing temperature.

Signed

  
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