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SUBJECT: CONFERENCE ON FERRIMAGNETISM, 11-12 OCTOBER, 1954

To: Group 63 Staff

From: J. B. Goodenough, P. K. Baltzer, N. Menyuk, F. E. Vinal

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Approved: _____
            David R. Brown

Abstract:

The eighteen papers which were presented at the conference on ferrimagnetism at the U. S. Naval Ordnance Laboratory, 11-12 October 1954, are summarized. Pertinent discussions are also included.

The conference was opened by J. S. Smart with a discussion of the Neel theory of ferrimagnetism. This served as a background for the subsequent papers and contained nothing new. J. Smit of Philips, Eindhoven, showed the results of calculations for a modified Neel theory in which Yafet-Kittel type coupling is permitted.

In the second paper E. W. Gorter discussed the results which can be found in his thesis. In the first part of his talk he stressed eight factors which must be taken into account in interpreting the saturation data of ferrimagnetic spinels. These are listed below:

(1) Neel's hypothesis of preponderant negative AB interaction. e.g. $FeLi_{0.5}Fe_{1.5}O_4$ has m = 2.47, 2.6 μ_B as against a theoretical 2.5 μ_B.

(2) Cation distribution may be mixed and have a temperature dependence. e.g. $MgFe_2O_4$ and $CuFe_2O_4$.

(3) Ionic g factors may be greater than two. e.g. Fe $NiFe\ O_4$ has m = 2.2-2.4 μ_B whether slowly annealed or quenched. Also the g factor of Ni^{2+} in

A sites is different from that in B. Sites. He called attention to Wangsness' work which tells how the cation distribution can be determined from a knowledge of the g factor and I_s.

(4) Competing negative BB (or AA) interactions can cause the Yafet-Kittel type of triangulation of the magnetic moments. He employed this mechanism to explain the magnetization of $MnCr_2O_4$. (Yafet later pointed out that there can be angles in only one type of site at a time.)

(5) Valencies may vary which cannot be found by chemical analysis.

If there is one ion with three possible valencies, e.g. Mn_3O_4, or two ions each with two possible valencies, e.g. $Cu_{0.5}Fe_{2.5}O_4$, the valencies cannot be chemically determined.

(6) Insufficient knowledge of chemical composition, e.g. $MnFe_2O_4$, may give another spinel when fired in too much O_2, or a spinel plus a not easily detectable MeO phase when fired in too little O_2. Cooling in firing atmosphere may give reoxidation. ZnO, CdO, and Li_2O may volatilize even from their compounds. Therefore a chemical anlysis is necessary. Another example of insufficient knowledge of chemical composition is $\gamma\text{-}Fe_2O_3$. If $\gamma\text{-}Fe_2O_3$ contains no water, it is $Fe^{3+}\left[\square_{1/3}\ Fe^{3+}_{5/3}\right]O_4$, where $\square$ stands for a cation vacancy, with m = 3.3 μ_B whereas if it is saturated with water, it is $Fe^{3+}\left[H^+_{0.5}\ Fe^{3+}_{1.5}\right]O_4$ with m = 2.5 μ_B. Experimentally the saturation moment of $\gamma\text{-}Fe_2O_3$ is found to vary from 3.1 - 2.7 μ_B, the variation decreasing with increasing water content. However, an example where the above factors cannot account for the value found is $MnFe_2O_4$. (Guillaud found m = 4.6 μ_B instead of a theoretical value of 5 μ_B, and careful chemical analysis showed his sample was stoichiometric $MnFe_2O_4$.)

(7) Sign of the exchange interactions may not be as
     predicted by superexchange. In LiFeCr oxide spinels
     the superexchange interactions are negative, but in
     MnFeCr oxide spinels positive interactions cannot be
     excluded. The antiferromagnetism of CrO contradicts
     superexchange. (It was pointed out that although
     Zn^{2+} has strong preference for A sites and Cr^{3+} for
     B sites, low-temperature measurements show that
     $ZnCr_2O_4$ is not completely normal).

(8) In a mixed crystal series in which $(m_a - m_b)$ changes
     sign and the spins inside each sublattice are parallel,
     all Neel's anomalous saturation magnetization vs.
     temperature curves have been found. In those systems in
     which there are presumed to be angles inside one sub-
     lattice, no anomalies have been observed which could
     delineate a Yafet-Kittel type transition.

     If an antiferromagnetic material is composed of two
     antiparallel sublattices and if the cations of the two
     sublattices are on different types of anion interstices,
     the saturation magnetization vs. temperature curve will
     vary as shown in Fig. 1 because of the different tempera-
     ture dependence of the moment of the two sublattices.
     If, however, the cation distribution fluctuates within
     the material, the inhomogeneities will cause an observed
     spontaneous magnetization which, in the region of
     ideally low magnetization, is inaccurate. Gorter said
     (but did not show how) that remanence measurements can
     be used to obtain the correct Neel curve.

Gorter then went on to show how the angular dependence of the
superexchange is important. To illustrate this he showed why $BaFe_{12}O_{19}$
is ferromagnetic with 40 μ_B per unit cell while $KFe_{11}O_{17}$ is antiferro-
magnetic with 0 μ_B per unit cell.

Finally he discussed the mixed-crystal systems which appear in his thesis. He stressed particularly those systems which reverse their direction of magnetization on heating through a so-called compensation point.
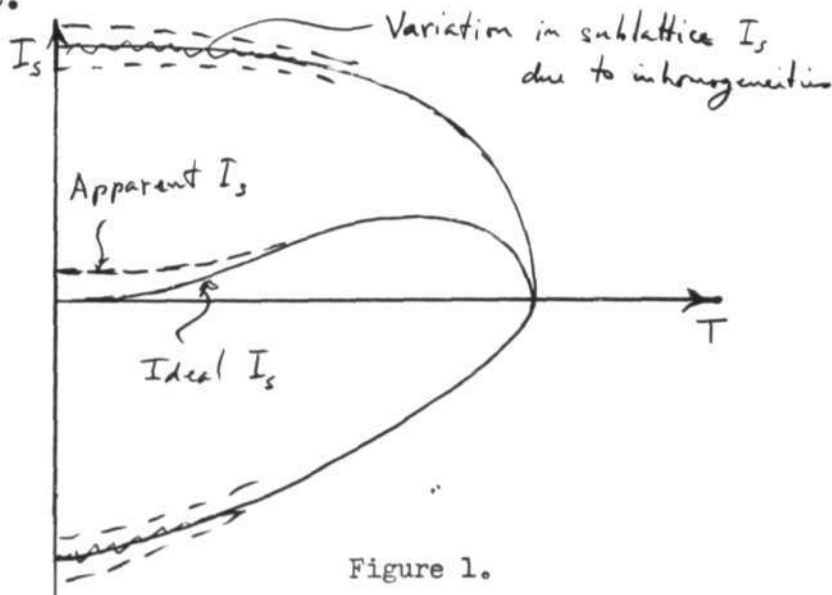

Figure 1.

Apparent and ideal magnetization vs. temperature curves for antiferromagnetic materials.

The third paper, by B. A. Calhoun, discussed the system $FeOGa_tFe_{2-t}O_3$. After this paper, which is reproduced in full as it was given, F. Vinal announced the results of our work on $GaFe_2O_4$. It is apparent that Calhoun was also trying to obtain a ferromagnetic spinel.

Magnetization and Cation Distribution
in Gallium-substituted Magnetics

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Abstract

A number of samples of different compositions in the system , magnetite-ferrous gallate (general formula $FeO\ Ga_tFe_{2-t}O_3$) have been prepared. The distribution of the cations among the octahedral and tetrahedral sites of the spinel lattice has been determined both from

the saturation magnetization and from the intensities of the x-ray
diffraction pattern. The effect of heat treatments in changing the cation
distribution will be discussed.

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We are presently studying the properties of mixed spinels
of magnetite and ferrous gallate, general formula $FeO\ Ga_tFe_{2-t}O_3$. We
have so far obtained data on samples having the following values of
t: 0.25, 0.50, and 1.20. Investigation of samples with other composi-
tions is currently under way, in addition to studies of other methods of
preparing these compounds. It is a pleasure to acknowledge the contribu-
tions made by several of my colleagues, in particular, Dr. L. Himmel who
did much of the work of preparing the samples and Miss E. Schilling who
carried out the magnetic measurements.

The samples were prepared by a two-stage sintering process. In
the first stage, iron, magnetite and gallium oxide were reacted to form
ferrous gallate and in the second stage, the appropriate amount of this
material was reacted with magnetite to yield the mixed ferrite. Prior
to sintering, the powders were mixed by grinding in a mortar and then
pressed into a pellet without the use of a binder. These pellets were
wrapped in platinum foil and then sealed in Vycor bulbs partially filled
with argon. During both sintering operations, the sample was held at
950 C for six days and then quenched into water. Powder patterns of the
ferrous gallate after the first sintering indicated that ca 95 percent
of the material had reacted. No iron or magnetite lines could be
detected and three very strong lines of gallium oxide were just observable.
After the second sintering, samples were examined with the Norelco
diffractometer and no evidence of a second phase could be detected.

Saturation magnetization was calculated from the change in
weight of a powdered sample in a non-uniform field. It was measured
from liquid nitrogen temperatures to the Curie point. Appreciable
oxidation of the samples occurred above 400 C so that the upper portions
of the magnetization-temperature curves and the Curie points contain
larger errors than the portion of the curves below 400 C. The x-ray

measurements of line intensities and unit cell edges were made with the
Norelco diffractometer using cobalt radiation and an iron filter. The
scattering power of iron atoms for cobalt radiation is low because of
the nearness of the iron K-absorption edge so that it is very easy to
determine the distribution of iron and gallium ions between the octahedral
and tetrahedral interstices of the spinel lattice from the intensities of
the diffraction peaks. In the sample containing 12.5 mol percent ferrous
gallate the ratio of the intensities of (220) to (111) varies from 2 for
all gallium in octahedral sites to 9 for all the gallium in tetrahedral
sites. For 60 mol percent ferrous gallate, the intensity ratio varies
from 2 to ca 350.

From the saturation magnetization, extrapolated to 0 K, and
the distribution of iron from the X-ray intensities, the distribution of
ferrous and ferric ions can be calculated. The results for samples
containing 12.5, 25, and 60 mol percent ferrous gallate indicated that
all the ferrous ions are in octahedral sites. For the two samples
with the small concentrations of gallium, approximately two-thirds of
the gallium is in tetrahedral sites. For the sample with the highest
gallium concentration, one-half of the gallium ions are in the tetra-
hedral sites.

The ionic distributions in these spinels appear to be
remarkably insensitive to temperature. The values above were obtained
after quenching from 950 C, but after annealing for five days at 400 C
and then quenching, the saturation magnetization increased very slightly,
indicating a shift of ca 1 percent of the gallium to the tetrahedral
sites.

The magnetization-temperature curves of the gallium-
substituted magnetites show a gradual change from the normal shape for
magnetite to an almost linear curve for 60 percent ferrous gallate.
This behavior is very similar to that found by Maxwell and Pickart
(L. R. Maxwell and I.J. Pickart, Phys. Rev. 92, 1120 (1953)) when they
substituted gallium in nickel ferrite. The change of the Curie point
with composition is, however, quite different from that observed in the

substituted nickel ferrites. The decrease of T_c with gallium concentration is much smaller in this case and appears to be non-linear.

Table I. Summary of Data
on Gallium Substituted Magnetite

Composition Fraction, t	Curie Temp. K	Saturation Mag. μB — 179 C
0 (Fe_3O_4)	850	4.1
.25	830	4.45
.50	720	4.83
1.00*	550*	2.67*
1.20	560	3.91

* DCL-8-12

In the fourth paper J. S. Kasper and C. P. Bean of General Electric discussed "The Magnetic Structure of Hausmannite, Mn_3O_4." They were embarrassed by their original abstract and came forward with the following results. Mn_3O_4 has become ferrimagnetic below about 50 to 60 K with a moment of $2\mu_B$ per molecule at 4 K. They were not able to interpret their neutron-diffraction data.

The fifth paper, by Goodenough and Loeb, is quoted in full below just as it was given. In connection with this paper there was a discussion the following day by H. Callen of the University of Pennsylvania on a mechanism called "degenerate superexchange." He claimed that buried within the formalism of Anderson's superexchange perturbation theory is the possibility of the admixture of degenerate excited states. Such a degeneracy could occur if identical atoms in identical lattice sites were being coupled magnetically through the O^{2-} ion. He suggested that where Anderson's theory predicts antiferromagnetic coupling through superexchange, degenerate superexchange would predict a parallel alignment because of the splitting of the degenerate excited level. Anderson then remarked that he had already considered this possibility and had found that the splitting of the degenerate level only gained back half of the energy difference between the energy levels of Anderson's

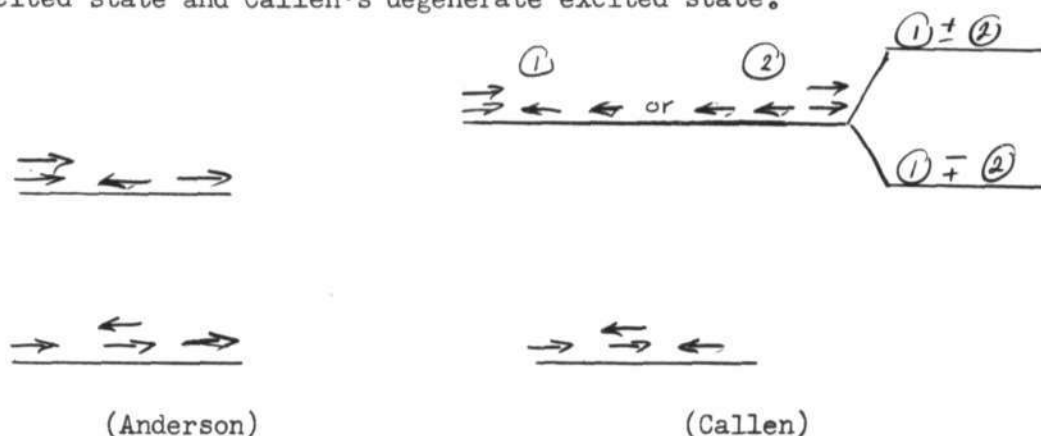excited state and Callen's degenerate excited state.

(Anderson)   (Callen)

Figure 2. Schematic energy-level diagram for superexchange
(Anderson) and degenerate superexchange (Callen).

Semicovalent Exchange

In the spinel lattice the cation magnetic moments are aligned
parallel or antiparallel by indirect exchange mechanisms. The first
model for these mechanisms was proposed by Kramers in 1934 and is known
as "superexchange." Superexchange is based on an ionic model for the
crystalline lattice; the stabilization of the magnetic-moment configura-
tion is attributed to the admixture of excited states with the ground
state of a system which contains two like transition-element cations
separated by an anion. The excited states are the result of removing
an electron from the anion and placing it in an empty or partially-filled
cation d orbital. If the cation d shell is less than half full, the
transferred electron aligns its spin parallel to the net spin already on
the cation in accordance with Hund's rule. If the d shell is already
half or more filled, the transferred electron is assumed to align its
spin antiparallel to the net spin already on the cation, the energy gap
between the d shell and next higher cation orbital being assumed larger
than any possible gain in Coulomb energy through parallel alignment.
Since the net spin on the anion of the excited system is antiparallel to
both the electron which was transferred from it and, through direct
exchange, to the spin on the cation on its opposite side, the two cations
are coupled ferromagnetically if the cation d-shell is less than half full,

antiferromagnetically if the cation d-shell is half, or more filled.

At the Washington meeting of the American Physical Society this spring, Dr. Loeb and I discussed briefly why an ionic model for the spinel lattice is inadequate. We indicated then how formation of partially homopolar bonds influence both lattice distortions and cation ordering between the A and B sites. We discussed in particular the lattice distortions to tetragonal symmetry in Mn_3O_4, $CuFe_2O_4$, and certain indates and suggested they were the result of the formation of square, quadricovalent bonds about cations in B sites which hybridize empty (dsp^2) orbitals. We shall now show that Kramer's model of super-exchange is inconsistent in two ways with a lattice in which homopolar bonding is significant.

First, it was assumed by Kramers that when a cation d shell is half, or more, filled, any additional electron aligns its spin antiparallel to the net spin already existing on the cation. Although this is true for the isolated atom, in a solid there may be empty lattice orbitals which are nearly degenerate with the atomic d orbitals. If the bonds of the lattice have considerable homopolar character, this is evidence that empty hybrid orbitals which are degenerate, or nearly degenerate, with the atomic d orbitals do indeed exist. The d shell is thereby extended so that an additional electron may align its spin parallel to the net spin of a cation which already has a half-filled d shell. In other words, the exchange forces, which favor a parallel alignment of the spins on an atom, may be greater than the energy gap between the d shell and the next higher lattice orbital.

Second, Kramers assumes the transferred electron retains its identity as an anion p electron and remains antiparallel to the net spin of the anion of the excited system. Without covalence, it is not at all clear why an electron should be simultaneously identified with both a cation and an anion.

Because of the apparent importance of covalence in the spinels, a new model, called semicovalent exchange, is proposed. Assume a cation

in an apparently electrovalent crystal has a net spin and hybridizes an empty lattice orbital which is degenerate, or nearly so, with the d orbitals and which overlaps a neighboring anion p orbital. Then Coulomb exchange energy is gained if that anion p electron which is parallel to the cation spin is excited to become part of the cation as well as part of the anion. Since only that anion electron which has its spin parallel to the net cation spin participates in this bond, the bond is called "semicovalent." "Semicovalence" is thus defined as a bond due to the coupling of a single anion electron to the net spin of a cation. Fe^{3+} and Mn^{2+}, which have been observed to favor A sites in the spinel lattice, are thought to be stabilized in these sites through semicovalence.

If an anion p orbital overlaps empty orbitals of two cations which are on opposite sides of it, semicovalent bonds may be found simultaneously with each of the cations. These cations will then be coupled antiferromagnetically since the spins of the two anion p electrons are antiparallel. This exchange mechanism is called "semicovalent exchange." Since its strength depends upon overlap of cation and anion orbitals, it has the same cation-anion-cation angular dependence as superexchange.

Further, semicovalent exchange can couple the moments of unlike atoms in different lattice sites. Therefore below 119 K, a temperature region in which double exchange is inhibited, the ferrous ions can still be coupled parallel to the other B-site cations and antiparallel to the ferric A-site cations through strong A-B semicovalent exchange, and the ferrimagnetism of Fe_3O_4 can be preserved.

Finally it should be noted that if normal covalent bonding occurs, both anion p electrons will be associated with only one of the cations, and there is no mechanism for coupling the spins of the two cations. Therefore cations which form coordinate covalent bonds with the lattice are magnetically isolated from the system. This can explain the surprisingly low Curie point in hausmannite.

R. M. Bozorth gave the sixth paper, which was entitled
"Anisotropy and Magnetostriction of Ferrites." He summarized the
published data and reported some new data for single crystals of the
ferrites of Mn, Fe, Co, Ni, Mn-Co and Co-Zn. Since the single crystals
were prepared by the method of Linde Air Products Co., they all
contained an excess of Fe over stoichiometry. The anisotropy constants
(K) of all these ferrites are negative at room temperature unless they
contain Co. The K of Cobalt ferrite is over 3×10^6 ergs/cm^3. In
cubic crystals the easy directions of magnetization are along the cube
diagonals for negative K and along the cube edges for positive K.

It should be pointed out at this point that Cobalt ferrite
possesses many very interesting properties. In fact the response of this
material to a magnetic anneal has been known but unexplained for years.
The magnetic moments throughout a polycrystalline sample of cobalt
ferrite can be aligned by means of cooling the material in a magnetic
field, without the aid of an alignment of the crystallites.

New data was presented concerning the effect of the magnetic
anneal on the anisotropy of a Co-Zn ferrite single crystal. These data
are thus pertinent to the understanding of the alignment phenomena in
the polycrystalline material. The anisotropy K of the Co-Zn ferrite
crystal was measured on a disc using the torque method. Magnetic
anneals were made at various temperatures. It was found that K is
affected by a magnetic anneal at temperatures as low as 150 C. When the
ln K is plotted versus the reciprocal of the absolute temperature at
which the ferrite was magnetically annealed, a relationship like that of
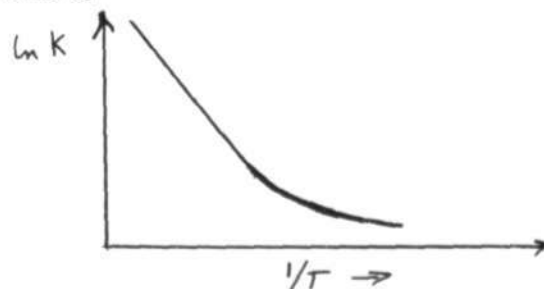Figure 3 is obtained.

Figure 3. Anisotropy vs. reciprocal of temperature at which a
Co-Zn ferrite was magnetically annealed.

The straight-line portion obtained for higher temperatures is indicative of an exponential relationship between the anisotropy and the temperature of anneal: $K = K_{(T = \infty)} e^{-E/kT}$, since $\ln K = - E/kT + \ln K_{(T = \infty)}$. Therefore the slope of the straight-line portion of the plot of $\ln k$ vs. $1/T$ is a measure of an activation energy E. E was found to be 0.9 electron volts. The mechanism of this phenomenon is under investigation.

The high magnetostriction (λ) of Co ferrite (up to 800×10^{-6}) is lowered and made more isotropic by addition of Zn. Mn ferrite is similarly affected. Addition of Zn to Mn ferrite lowers K markedly.

"Calculated Magnetic Anisotropy Constants of Ferrimagnetic Spinels," by R. S. Weisz of RCA, was the seventh paper. It was shown that, assuming that the initial permeability (μ_B) in ferrimagnetic spinels ($MeFe_2O_4$) is due predominately to rotation of electron spins, one can calculate the corresponding magnetic anisotropy constants. An empirical relation between initial permeability (μ_o) and the anisotropy (K) has been developed by Wijn of Philips for ferromagnetic materials, viz: $\mu_o - 1 = N I_s^2/K$. I_s is the saturation magnetic moment and N is an empirical constant taken as $4\pi/3$ or $8\pi/3$ by other workers in the past. In this work N is determined experimentally from data obtained on magnetite and is found to be N= 21. It was assumed that the ferrite single crystal grown by Smiltens of L.I.R. was stoichiometric. This value was then used to calculate K for various other ferrites from data on initial permeability and saturation moment. It was assumed that a very low strain density existed in the samples; this assumption was justified on the basis of the very gradual anneal which was given to the samples.

Table II. Calculated and Observed Anisotropy Constants
for three ferrites

Material	Calculated K	Observed K
$NiOFe_2O_3$	4×10^4 ergs/cc	5.1×10^4 ergs/cc
$CoOFe_2O_3$	3.4×10^6	1.7×10^6
$MnOFe_2O_3$	3.4×10^4	2×10^4

Good correlation was obtained between observed and calculated values of the anisotropy constant K, as indicated in the Table II. The values obtained for K were found to be a direct function of the orbital quantum number of the divalent cation Me.

In the eighth paper, "Motion of Individual Ferromagnetic Domain Walls" by J. K. Galt of Bell Telephone Laboratories, window frames cut from single crystals of nickel-iron ferrite $(NiO)_{0.75}(FeO)_{0.25}$ Fe_2O_3 were discussed. These frames were oriented so that the samples contained only one movable domain wall. The motion of this wall was then studied as a function of applied magnetic field at various temperatures.

At low field values the wall velocity was found to vary linearly with the applied field. However, at high field values, the velocity was found to increase at a faster rate than predicted by the linear relationship $v = G(H-Ho)$. In addition the output-voltage wave form, which is square at low fields, becomes similar to that from polycrystalline materials (i.e. has a maximum) at high field values.

The velocity of the domain wall at a given field value was found to decrease with decreasing temperature. The value of G changed from 26,150 cm/sec/oersted at room temperature to 160 cm/sec/oersted at T = 77 K. Most of this change occurred in the temperature interval between 77 K and 200 K.

Galt attempts to explain the sharp rise in the damping of domain-wall motion in terms of a relaxation associated with the transition occurring in magnetite at 115 K. In this case he arrives at the result that $v/H \sim 1/\tau$, where τ is the relaxation time and varies with temperature according to the relationship

$$\tau = \tau_{o} \, e^{\,\varepsilon/kt},$$

where ε is an activation energy. This activation energy can be obtained by measuring the imaginary part of the permeability, μ'', as a function of temperature for several values of frequency of a-c field.

While this explanation successfully predicts the sharp increase of wall-motion damping at low temperature, it still predicts a linear

relationship between velocity and applied field. Thus it does not explain the deviation from linearity observed at high fields. However, since the results are based on a first order calculation, Galt feels that a higher order calculation may account for the nonlinearity. This calculation has not been carried out.

In the ninth paper A. H. Morrish of the University of Minnesota discussed the dependence of H_c on compression for iron oxide powders that approach single-domain size. He and S. P. Yu had calculated the maximum particle size for a single-domain particle of Fe_3O_4 or $\gamma\text{-}Fe_2O_3$. The calculations were a straightforward extension of Kittel's calculations for metallic particles. They found that ellipsoidal particles with a large eccentricity were single-domain particles so that H_c varied with the change in the magnetostatic energy between the particles; the magnetostatic energy varies as the powder is compressed. They found, as predicted theoretically, that the highly acicular powders show a linear decrease of H_c with increasing density. Roughly spherical particles, on the other hand, are multidomain and show an almost constant H_c as a function of compression, a result expected for bulk material or for a very small magnetostatic energy between the multidomain particles. For a reference they quoted E. C. Stoner and E. P. Wohlfarth, Phil. Trans. Roy. Soc (London) A 240, 599 (1948).

In the tenth paper K. J. Sixtus discussed his observations of domain structure in hexagonal $BaFe_{12}O_{19}$. He found that the grains in this material consist of hexagonal platelets approximately 1 x 1 x 0.1 μ in size. The domains grow by jumping across the boundary between platelets, nucleation of reverse domains starting in scattered platelets. The coercive force was calculated as the average field necessary for a domain to jump across one of these boundaries, and the results checked out with the experiments.

R. K. Wangsness gave the eleventh paper, entitled "Ferrimagnetic Resonance and Some Related Effects," in which the semi-classical resonance theory was reviewed. In a system of particles the total torque is given by the time rate of change of the total angular momentum. In a magnetic

system the effect of the orbital angular momentum (L) is small, and that due to spin angular momentum (S) is large. Therefore:

$$\frac{d\vec{S}}{dt} = \text{Torque}$$

Since in a magnetic system the torque is equal to the cross product of the magnetization (M) and the field (H), we obtain:

$$\frac{d\vec{S}}{dt} = \vec{M} \times \vec{H}$$

which may also be written as:

$\vec{\omega} \times \vec{S} = \vec{M} \times \vec{H}$, where $\vec{\omega}$ is the angular velocity of the magnetic moment due to the torque applied. If $\vec{S}$ is parallel to $\vec{M}$, the vector notation may be dropped and the equation simplified to

$$\vec{\omega} = \frac{-M}{S} \vec{H} \text{ or } \vec{\omega} = -\gamma\vec{H},$$

where $\gamma = M/S$ is called the gyromagnetic ratio. This ratio is also expressed in the form $\gamma = eg/2mc$, where e is the charge and m the mass of an electron, c is the velocity of light and g is the Landé g-factor.

The apparent g-factor for nickel ferrite has been found to be frequency dependent. (See Table III). This effect is not understood.

Table III

Freq- Mc/sec	Apparent g of Nickel Ferrite
47,000	2.12
23,500	2.19
18,400	2.22

In a ferrimagnetic spinel magnetic ions are located on different kinds of lattice sites. Therefore the effective field H_{eff} at each site is:

$$H_{eff} = H_a + H_i, \text{ where}$$

the applied field H_a is the same for all sites but the internal field H_i is different for each kind of site. Since the magnetic ions form a coupled system, the precessional frequency $\vec{\omega}$ is the same for all ions. Therefore since $\vec{\omega} = -\gamma_{eff}(\vec{H}_a + \vec{H}_i)$, each kind of site must have a

different effective gyromagnetic ratio γ_{eff}. For each kind of site $S_i = M_i/\gamma_i$. The total spin $S = \sum_i S_i$ and the total magnetic moment $M = \sum_i \gamma_i S_i$ then interact to give a total $\gamma_{eff} = M/S$; the effective g-factor follows from $\gamma_{eff} = g_{eff} \, e/2mc$.

The above considerations become particularly significant for a spinel which has a compensation point (the point at which M changes sign). The curves of magnetization and spin vs. temperature for such a lattice and for the two component sublattices are shown in Fig. 4.
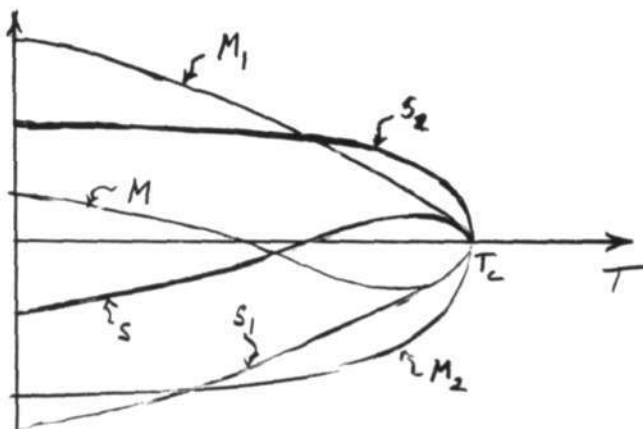
Figure 4.   Typical magnetization and spin vs. temperature
            curves for sublattices 1 and 2 and their resultant

Note that the compensation point for M occurs at a different temperature than the compensation point for S. This occurs if $\gamma_1 \neq \gamma_2$. In the temperature range between the two compensation points the total spin angular momentum and the total magnetic moment are parallel instead of antiparallel. This means that the sign of γ_{eff} changes sign at these points. Since $\gamma_{eff} = M/S$, γ_{eff} will be zero at the compensation point for M and theoretically infinite for the compensation point of S.

In the mixed ferrite system $NiFe_{(2-x)}Al_xO_4$ a compensation point for S is obtained at T = - 196 C for $x \approx 0.6$. This is indicated by the change in g as a function of x at T = -196 C (see Fig. 5).
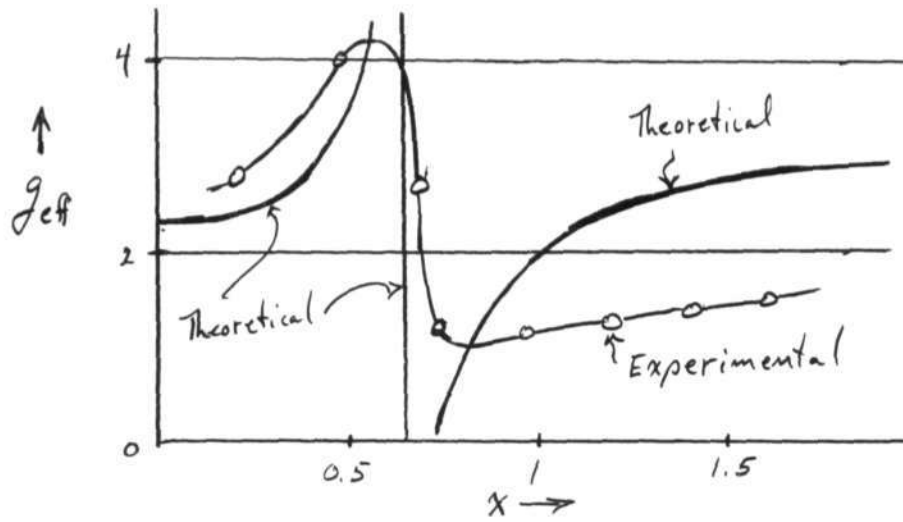
Figure 5 - Theoretical and experimental plots
for g_{eff} at T = - 196 C as a function
of x for the system $NiFe_{(2-x)}Al_xO_4$

Compensation points for M and S also occur in a heated
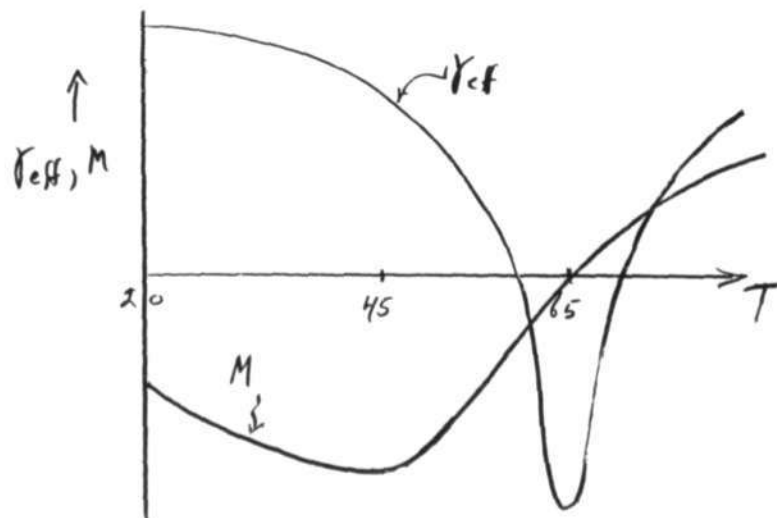LiCr ferrite, as shown in Figure 6.

Figure 6. Evidence of a compensation point in a
LiCr ferrite from measurements of γ_{eff} and
M as functions of temperature.

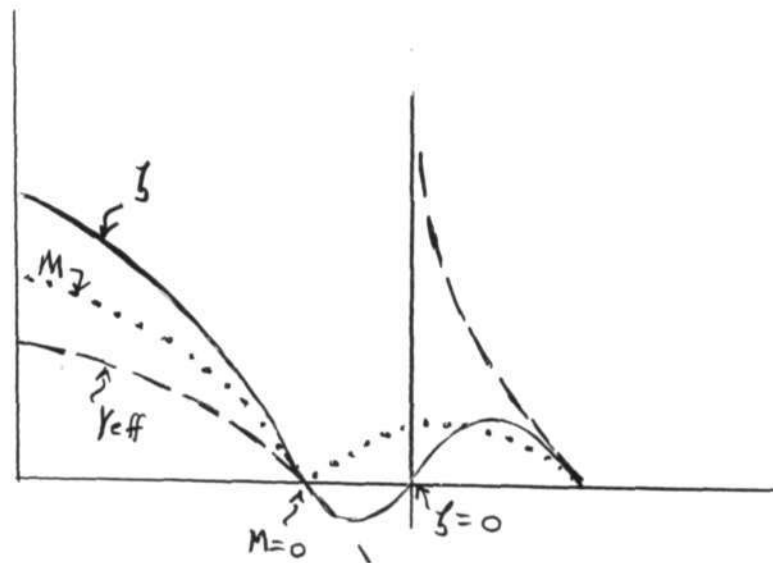A parameter related to the Faraday rotation effect is defined; viz. $\zeta = -\gamma_{eff} M$.

Figure 7.   Theoretical relationships between ζ, γ_{eff}, and M.

Since ζ changes sign near M = 0 and S = 0, the Faraday rotation should also reverse sign in the same temperature region, as shown in Figure 7.

F. Brown, C. L. Gravel, and D. Park of Sprague Electric and Williams College, respectively, gave the twelfth paper, "Direct Observation of Domain Rotations in Ferrites." A direct experimental observation of domain rotation in the initial permeability region of sintered nickel ferrite was reported. The technique used was similar to that originated by F. Bloch to observe nuclear precession.

A 0.5 cm. sphere of ferrite is surrounded by crossed transmitter and receiver loops adjusted for minimum rf signal when the sample is demagnetized. Application of a steady external field (as low as 5 oersteds) perpendicular to both loops causes a measurable receiver loop output which cannot be eliminated by readjustment of the loops. The induction is therefore due to a rotation of the magnetic moment. The field causing the rotation, or precession, in each magnetic domain

is supplied by the equivalent anisotropy fields associated with each domain. The external field is needed only to magnetize the sphere from its demagnetized state. A plot was made of the detector loop output (per unit applied field) vs. the frequency of the input to the transmitter loop. Since the applied steady field is much smaller than the effective anisotropy fields, this plot should delineate the rotational resonance spectrum of the polycrystalline sample.

Measurements were made from 20 Mc to 900 Mc. A maximum in the receiver output was found for about 200 Mc. It should be noted that from single-crystal measurements of the crystalline anisotropy, one would have expected a maximum response for about 2000 Mc, and not 200 Mc. This anomaly was not understood.

The thirteenth paper was "Neutron Diffraction Studies of Ferrimagnetic Spinels" by L. M. Corliss and J. M. Hastings of the Brookhaven National Laboratories. They first pointed out that neutron scattering is of two types: (1) a diffuse scattering which gives a background intensity commensurate with the paramagnetism of the material and (2) a coherent scattering which gives definite peaks or lines. These peaks are due to neutron scattering from (a) the nuclei and (b) the ordered, atomic magnetic moments, the atomic moments being due to the spin-coupled d-shell electrons.

They then reviewed the work of Shull and of Wollan and Koehler on magnetite, Fe_3O_4. One of the objectives of this work was to check the Neel hypothesis of ferrimagnetism which postulates the A-site atomic moments are antiparallel to the B-site atomic moments and the net magnetization of the material. Since only the A sites contribute to the (220) reflections, the (220) peak was carefully studied and found to be due to a magnetization which is opposite to an externally applied field. This work gives a direct confirmation for the Neel hypothesis for the case of Fe_3O_4. Attempts to find direct evidence for the Verwey hypothesis of electron ordering in the B sites of Fe_3O_4 below 120 K have been unsuccessful since powder methods have been the only techniques available. If a good single crystal of Fe_3O_4 were obtainable, this measurement could be done.

Corliss and Hastings have examined nickel ferrite, $NiOFe_2O_3$. They found no inconsistencies between their data and the Neel hypothesis. Corliss and Hastings also investigated a magnesium ferrite, $MgOFe_2O_3$, which was prepared by Brockman; since this sample is of interest because it had Mg^{2+} ions on both the A and B sites, they used this measurement to illustrate the neutron-diffraction techniques.

In order to interpret the coherent-scattering pattern, it is necessary to first separate those peak reflections which are due to nuclear scatter from those due to atomic-moment scatter. Those reflections which are due to the d-shell electrons can be removed from the composite pattern by orienting an external magnetic field to just cancel the effect of scattering by the atomic moments. The remaining peaks may be assumed to be those due to nuclear scatter. These and the background, which is due to diffuse scattering, are subtracted from the composite pattern to give the desired diffraction pattern due only to the spin-aligned d-shell electrons. This is illustrated schematically in Figure 8.
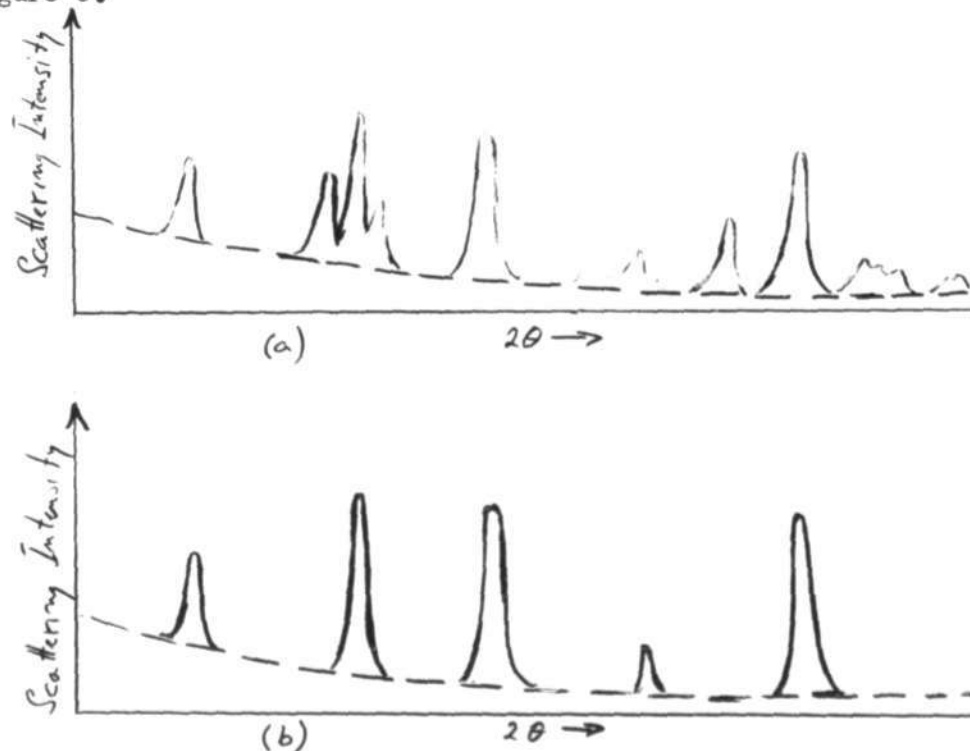

Figure 8. Neutron-diffraction patterns (a) without and
           (b) with an externally applied field to
           compensate for the atomic-moment scattering.

The diffraction peaks due to neutron scattering by the atomic
moments give the data necessary to calculate the following: (1) The
so-called u parameter which measures the packing of the oxygen ions
about the A sites, (2) the degree of inversion of $MgO \cdot Fe_2O_3$, (3) a
magnetic form factor, and (4) a measure of the radial distribution of
d electrons about the Fe^{3+} ions. These were found to be concentrated
about a mean radius of 0.5 Å from the center of the ion (see Fig. 9).

Corliss and Hastings then described their investigation of
$ZnOFe_2O_3$. This substance is a typical paramagnet at room temperature.
The neutron-scattering pattern indicates that it is a regular spinel
with no aligned magnetic moments. The only coherent scattering is from
the nuclei. Since $ZnFe_2O_4$ is known to contain 5 μ_B for each Fe^{3+} ion,
this material is especially suited for a study of the B-B magnetic-
exchange interactions as a function of temperature, the A-A and A-B
interactions being nonexistent. There was no apparent change in the
neutron-diffraction pattern down to 10 K. Below this temperature there
was a disappearance of diffuse (paramagnetic) scattering and the
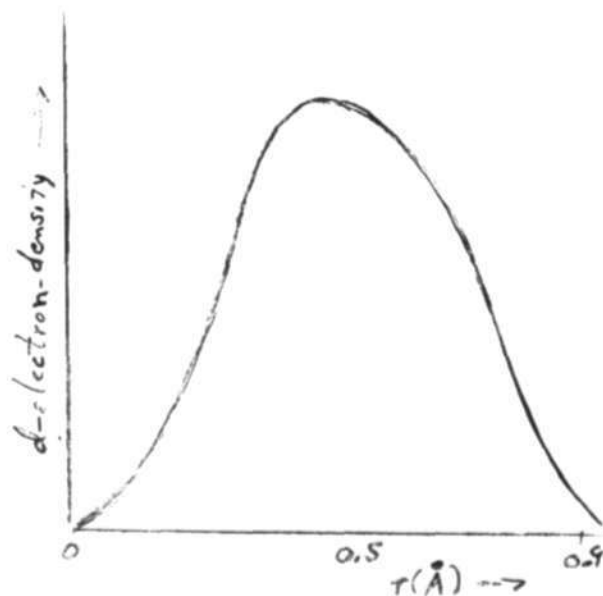appearance of new coherent-scattering peaks.

Figure 9.   Radial density distribution for the d
            electrons about Fe^{3+} in $MgOFe_2O_3$

These peaks are difficult to interpret. They indicate that the unit
cell must be doubled. A tentative structure was suggested which consists
of bands two magnetic atoms wide and parallel to the (210) direction
each of which is coupled antiferromagnetically to its two neighboring
bands. In this picture the ordered lattice is antiferromagnetic. There
is some mismatching at the boundaries between the bands.

Finally they discussed their measurements on a sample of
$ZnCr_2O_4$, the identical sample used by McGuire of N.O.L. for magnetic-
susceptibility measurements. Although the Cr^{3+} ions have a strong
preference for B sites, this specimen was found to be partially
inverted with some Mn^{2+} ions on the B sites. From a measurement of the
magnetic intensities of the (220) reflections, it was determined that
the average magnetic moment of an A-site cation was 3 μ_B. Since each
Mn^{2+} ion carries, presumably, an atomic moment of 5 μ_B, the small moment
which was observed is somewhat mysterious. It could be accounted for
by postulating Yaffet-Kittel coupling in the A sites, the A site moments
being ordered at angles relative to the B-site moment to give a reduced
net moment antiparallel to the B sites. Such a model, however, requires
a tripling of the unit cell, and there were no superstructure lines to
indicate that such a tripling of the unit cell exists in the crystal.

In Table IV there is a summary of some of the neutron-
diffraction data on spinels.

TABLE IV   Summary of Neutron-diffraction Studies on Spinels

Spinel	$M_x^{+2}Fe_{(1-x)}^{+3}Fe_{(x+1)}O_4$ Values of x	Values of "u" for lattice
Fe_3O_4	0	---
$ZnFe_2O_4$	1.00 ± 0.05	.385 ± .002
$NiFe_2O_4$	0	.381 ± .003
$MgFe_2O_4$ (1)	0.12 ± 0.01	.381 ± .001
(2)	0.10	.382 ± .002
$MgAl_2O_4$	1.00	.387 ± .001
$ZnCr_2O_4$	0.86 ± 0.03	.388 ± .001
$MnCr_2O_4$	1.00 ± 0.02	.388 (about)

J. S. Kouvel of Harvard gave the fourteenth paper, "Specific Heat of Ferrimagnetic Systems." This paper should be considered together with the two that followed, viz. "Low Temperature Heat Capacity Anomaly in Nickel Zinc Ferrite" by E. F. Westrum, Jr. and D.M. Grimes of the University of Michigan and "Specific Heats and Magnetic Susceptibilities of Normal Spinels at Low Temperatures" by S.A. Friedberg of Carnegie Tech.

About 25 years ago Millar measured c_p for Fe_3O_4 and found an anomaly at about 120 K. Recently Calhoun has shown that the amount of magnetic ordering in Fe_3O_4 increases gradually below the transition so that at low temperatures the ordering of magnetic moments is nearly complete. If the A-B exchange interactions are assumed to be the greatest, it follows that the change in entropy at low temperatures is due alone to an ordering of the spins, not to any change in direction.

McGuire and Howard have measured c_p in Ferroxcube III at the Curie temperature and found it has an anomaly which is similar to that in metals. Only the size and shape of the anomaly are affected by the ferrimagnetism, as against ferromagnetism, of the material.

Westrum and Grimes measured cp on five ferrite samples ranging in composition from $Ni_{0.1}Zn_{0.9}Fe_2O_4$ to $Ni_{0.4}Zn_{0.6}Fe_2O_4$. They found an interesting thermal anomaly near 9 K; the magnitude of the bump in the c_p vs. T curve increased with increasing Zn content (see Fig. 10). Friedberg also found this anomaly in $ZnFe_2O_4$, $ZnCr_2O_4$ and $CdFe_2O_4$. In all cases the transition to ferrimagnetic order occurred at about 10 K.

Because the electronic specific heat is small in the ferrites as compared with the metals, the ferrites are a good material for measuring c_s, the contribution to the specific heat due to the ordering of the spins. Kouvel performed a simple spin-wave treatment for the spinel to predict a temperature dependence for c_s at low temperatures. He assumed a long-range order of lattice spins which, just above T = 0 K, are subject to small perturbations which cause an increase in the entropy S.
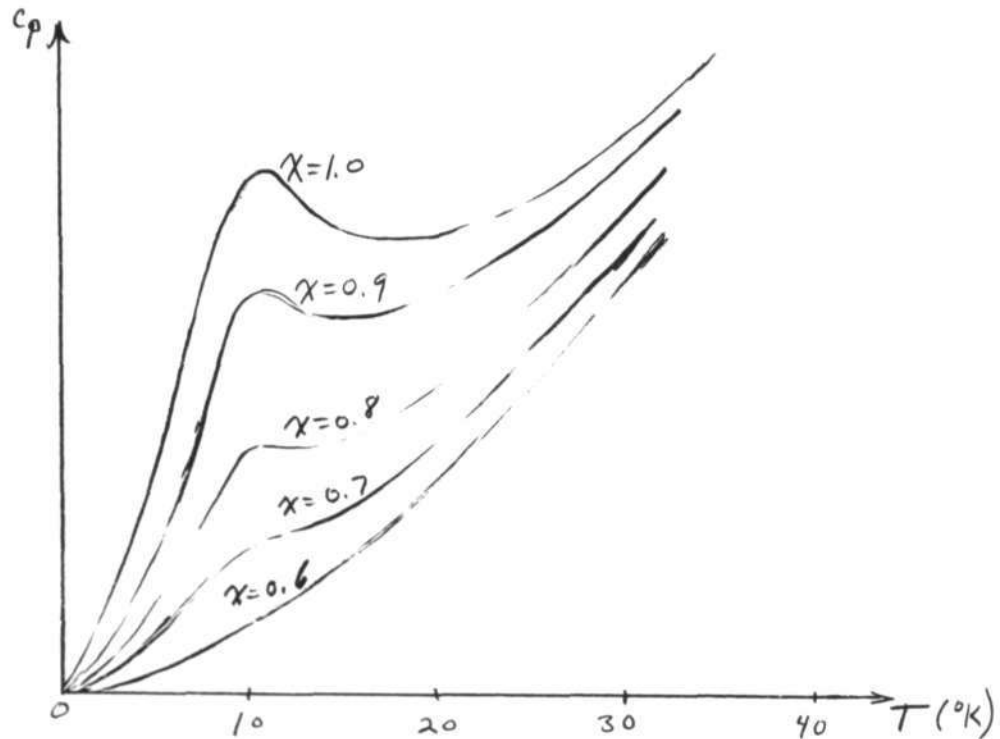
Figure 10.   Measurements of specific heat vs. temperature for $Ni_{(1-x)}Zn_xFe_2O_4$ for 0.6 x 0.9 by Westrum and Grimes and for $x = 1.0$ by Friedberg

Upon application of the Bloch spin-wave theory, for which this problem is particularly suited, Mott and Jones found for a ferromagnet $c_s \propto T^{3/2}$ with $(I_{so}-I_s)/I_{so} \propto T^{3/2}$, $\hbar\omega \propto p^2$ and for an antiferromagnetic $c_s \propto T^3$ with $\hbar\omega \propto p$. The electronic specific heat is proportional to T and masks this effect in metals. Kouvel and Brooks found that for a ferrimagnet $c_s \propto T^{3/2}$ and, because of the low electrical conductivity of the ferrites, are able to compare this theoretical result with experiment. In particular they found that for an inverse ferrite with S_1 the spin quantum number for the Fe^{3+} ions and S_2 that for the Me^{2+} ion,

$$c_s = 0.113 \, (kT/I)^{3/2}, \quad \Delta I_s/I_{so} = (0.117/S_1)(kT/I)^{3/2}$$

where $I = 4JS_2 (S_1+ S_2)/ S_1$ if J is the exchange constant given by $H = 2J \sum_{ij} \underline{S}_i \cdot \underline{S}_j$, or $k T_c = 4JA$ with T_c the Curie temperature and A a

constant. Calculations give the results in Table V as well as the fact that $c_s = c_p$ at about 2.7 K. These results were compared with the experimental data with fair success.

Table V. Calculation of $c_s/T^{3/2}$ for several ferrites

Ferrite	J/k	$c_s/T^{3/2}$ Joules/deg/mole
$NiFe_2O_4$	18	1.3×10^{-4}
$CoFe_2O_4$	13	3.6×10^{-4}
Fe_3O_4	14	3.3×10^{-4}
$MnFe_2O_4$	9	6.6×10^{-4}

After lunch P. W. Anderson brought up a point which he felt was being overlooked. He attributed the low Curie temperatures for BB interactions, i.e. about 10 K, to the fact that it was impossible to have a cooperative transition on the B sites since it is impossible to subdivide the B sites into antiferromagnetic coupling in any unique way. Each B-site cation has 6 near neighbor B-site cations which are arranged at corners of regular tetrahedra with the given cation as a common apex. At most 4 of these near-neighbor cations have spins antiparallel to that on the central cation. If N is the total number of B-site cations, there are $(3/2)^N$ possible arrangements which can give the very best possible short-range order. The short-range order has a finite entropy of $Nk \ln (3/2)$. This means there is no unique short-range order so that long-range order is alone important in the cooperative phenomena producing the specific heat anomaly at 10 K. He feels this explains the low temperature at which this anomaly occurs.

The seventeenth paper was "Neutron Diffraction Studies of Magnetic Compounds Having the Perovskite Structure," by W. C. Koehler and F. O. Wollan. After a brief review of the experimental techniques which are used in neutron diffraction work, a list of the perovskite-type structures which have been investigated by neutron diffraction was given (see Table VI). The perovskite-type compounds have the formula RMO_3, where R is a large cation such as La^{3+} or Ca^{2+} and M is a

smaller ion of the 3d transition group. The lattice structure is described by a b.c.c., CsCl configuration for the cations with octahedral coordination of O^{2-} ions about each of the small ions.

The interest in these structures as magnetic materials arises because, as has been shown by Jonker and van Santen (Physica 16, 337, 599 (1950); Physica 19, 120 (1953)), certain mixed oxides containing Mn or Co can be made ferromagnetic with Curie temperatures ranging from room temperature downwards, depending upon the composition. The system of particular interest is the $La_{1-x}Ca_x MnO_3$ system where $0 \leq x \leq 1$, since it has a complete range of solid solubility. The system $La_{1-x}Ba_x MnO_3$ and $La_{1-x}Sr_x MnO_3$ exhibit two-phase regions for $x > 0.5$. In the system $La_{1-x}Ca_x MnO_3$, I_s is a maximum for $x \approx 0.25$, and its magnitude suggests that in the small compositional region $0.25 \leq x \leq 0.40$ the magnetic moments associated with the manganese ions are aligned parallel. On either side of this maximum the saturation magnetization drops sharply so that for $x < 0.05$ and $x > 0.6$ it is very small or zero. This is illustrated in Figure 11.

The ferromagnetic properties of the manganites have been interpreted by Jonker and van Santen to be the result of a strong positive $Mn^{3+}-Mn^{4+}$ exchange combined with a weak $Mn^{3+}-Mn^{3+}$ interaction and a negative $Mn^{4+}-Mn^{4+}$ interaction. Since the neutron diffraction technique is suited to determining the magnitude and orientation of individual ionic moments below a Curie or Neel temperature, a number of preparations in the $La_{1-x}Ca_x MnO_3$ system were investigated by conventional neutron diffraction methods at room temperature and at one or more reduced temperatures. It was pointed out that great care was taken to obtain samples of the correct oxidation state. It was found that unless care was taken with firing atmospheres, a sample which was supposed to be $LaMnO_3$ could contain as much as 40 percent Mn^{4+}.

For pure $LaMnO_3$ (less than 5 percent Mn^{4+}) a transition to an ordered magnetic structure occurs at about 140 K. The magnetic structure of $LaMnO_3$ is built up of ferromagnetic layers, but adjacent layers have opposite spins so that the net magnetization is zero.
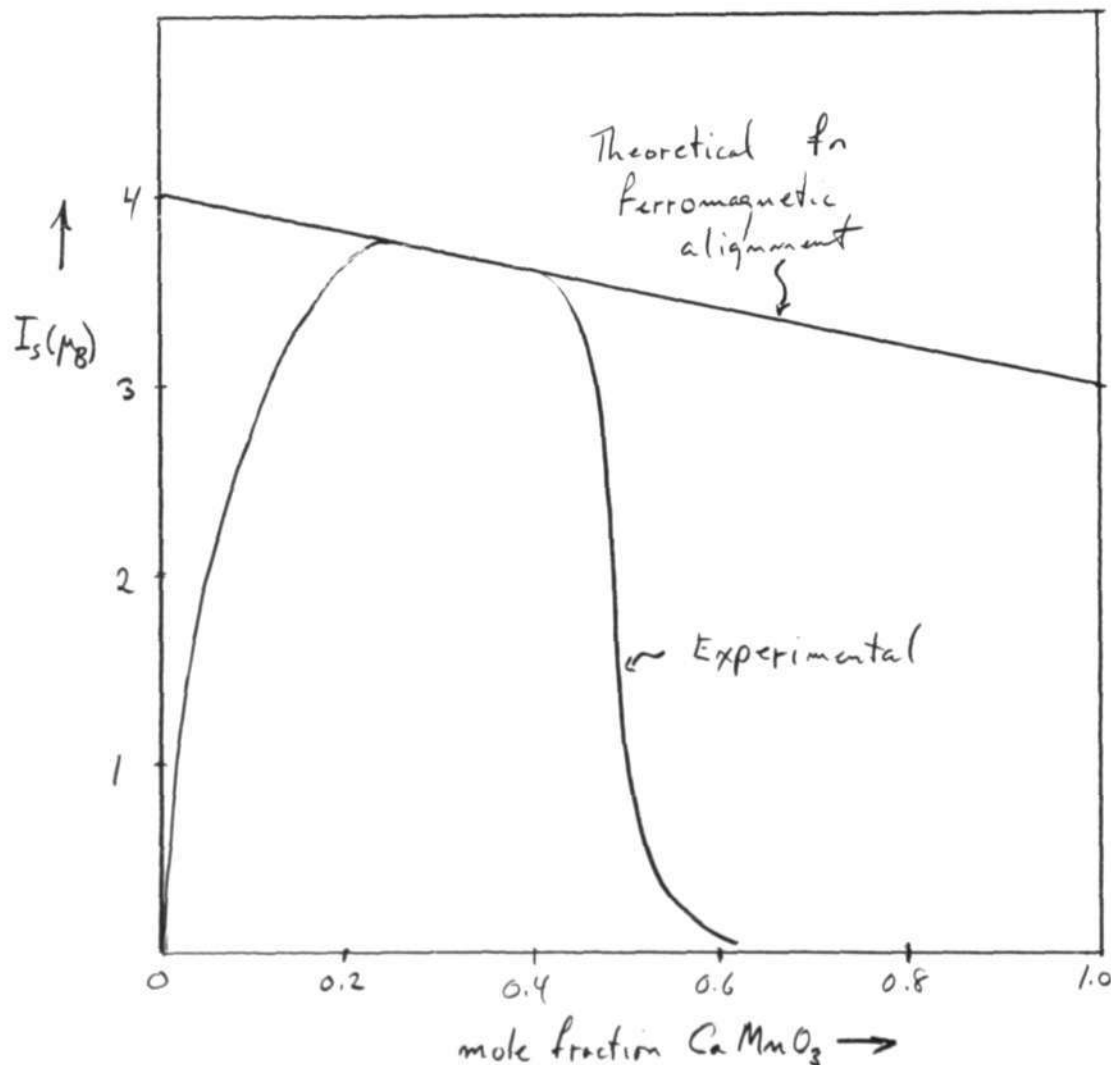
Figure 11. Saturation magnetic moment in $(La,Ca)MnO_3$ system as determined by Jonker and van Santen.

Thus each ion has four nearest neighbors of the same spin orientation, and two nearest neighbors with oppositely aligned spins. Dr. Harry Yakel, who supplemented the neutron diffraction work with a careful x-ray crystallographic investigation, reports that the structure is not cubic, but monoclinic with $a_1 = a_3 = 7.910$ A, $a_2 = 7.698$ A, and $\beta = 91°52'$. Presumably the ferromagnetic layers are perpendicular to

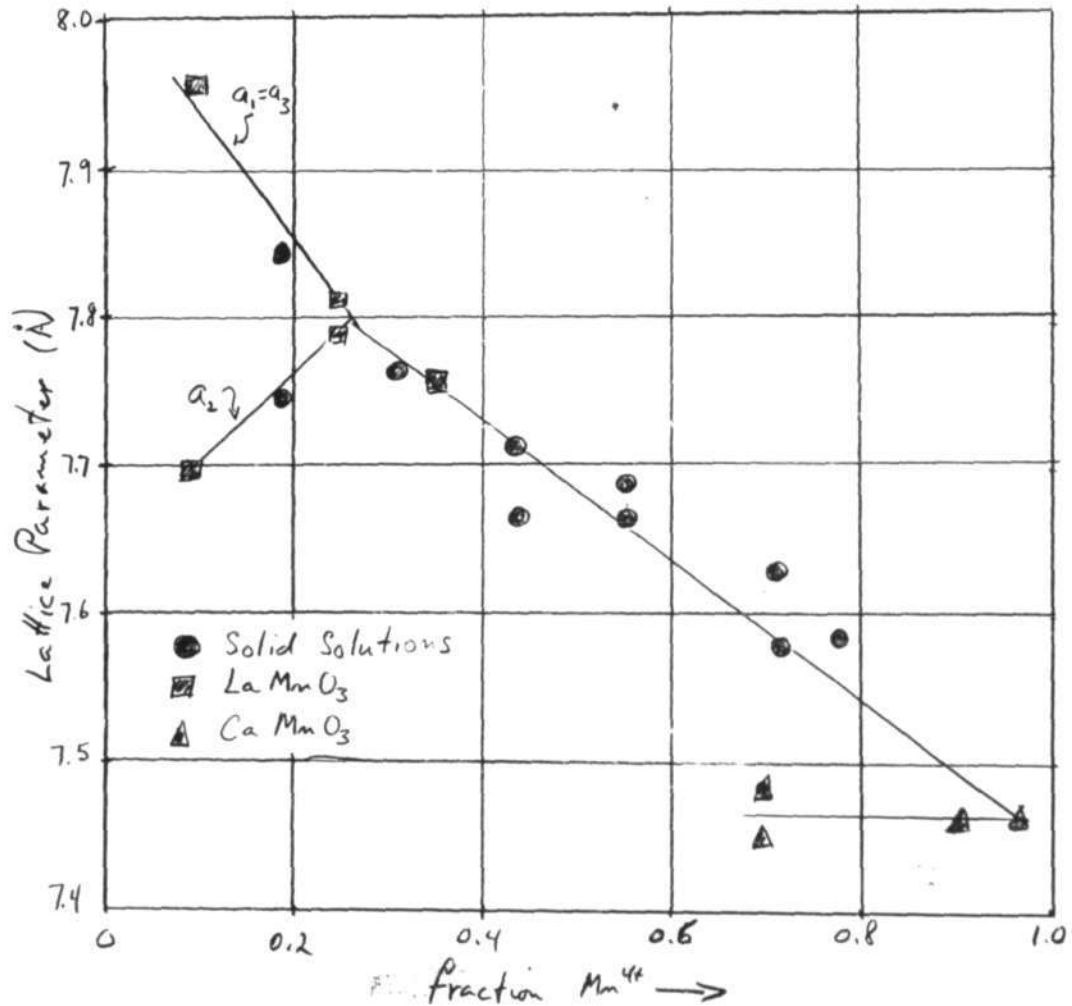the a_2 axis. (The crystallographic data is summarized in Fig. 12).

Figure 12. Crystallographic data for $(La,Ca)MnO_3$ system.

In the case of a sample of $CaMnO_3$ containing 96 percent Mn^{4+}, an antiferromagnetic structure transition was observed at approximately 110 K which may be imagined to consist of a rock-salt type structure of atomic moments with two sublattices; the spins on each sublattice are parallel to one another but antiparallel to the spins on the other so that each magnetic ion has six antiferromagnetic nearest neighbors. The x-ray data on samples with $0.4 \leq x \leq 0.7$ were not consistent. Some showed a nearly cubic symmetry while others showed tetragonal symmetry and others a monoclinic or rhombohedral symmetry.

For mixed compositions with $0.25 \leq x \leq 0.40$ the neutron diffraction patterns were essentially those characteristic of ferromagnetic materials, and the average magnetic moments per ion derived from these patterns are in good agreement with the values calculated on the assumption that all available 3d electrons contribute. The x-ray data indicates that in this compositional range the lattice is cubic. At the extreme end of this range, i.e., at $x = 0.4$, there was evidence of the beginnings of a new antiferromagnetic phase. This was a second magnetic phase, not a second crystallographic phase. Only one crystallographic phase was reported for the entire $La_{1-x}Ca_xMnO_3$ system.

For intermediate compositions, that is in the range between 10 percent and 25 percent Mn^{4+} and between 60 percent and 90 percent Mn^{4+}, the diffraction patterns are more complex. A specimen of $LaMnO_{3.1}$ containing 20 percent Mn^{4+} and a mixed oxide with $x = 0.15$ each exhibited magnetic scattering maxima at ferromagnetic line positions; but in addition there were observed comparable intensities at the angular positions characteristic of the $LaMnO_3$ antiferromagnetic structure. With apparatus recently put into operation, the diffraction pattern of $LaMnO_{3.1}$ (20 percent Mn^{4+}) in a magnetic field of 5000 oe. at 55 K was obtained. It was observed that only the reflections occurring at positions expected for a ferromagnet were affected by applied field. Those at the antiferromagnetic peak positions were unchanged. Thus it appears that for this specimen there exists a mixture of regions of antiferromagnetic ordering and of ferromagnetic ordering, both extensive enough that coherent neutron scattering is observed.

In the calcium-rich intermediate region a third type of anti-ferromagnetic structure was observed for a preparation with $x = 0.75$. This specimen appeared to contain a mixture of two antiferromagnetic phases. Generally, however, in this region the magnetic scattering patterns are complex and difficult to interpret. The x-ray data also shows structures with symmetry varying from cubic to tetragonal to rhombohedral.

In summary, there are three types of exchange interaction within the $La_{1-x}Ca_xMnO_3$ system. There are (1) $Mn^{3+}- Mn^{3+}$ interactions which are either positive or negative and have a strength given by the Neel temperature T_N = 140 K, (2) Mn^{4+} interactions which are positive with $T_N \approx 270$ K. He suggested that the strength of these interactions probably has a strong dependence on interatomic spacing.

There followed a discussion of the ionic ordering in different compositional regions. This work was not too conclusive, but he indicated that at x = 0.25 the Mn^{4+} tended to order across the cube diagonal of the elementary unit cell. It was postulated that somewhere between one and two Mn^{4+} ions in a unit cell must be sufficient to trigger the antiferromagnetic alignment of that cell to ferromagnetic alignment.

Some preliminary investigation of compounds involving other members of the 3d transition group indicated that $LaFeO_3$ and $LaCrO_3$ are antiferromagnetic at room temperature with the $CaMnO_3$ magnetic structure. The oxide $LaCoO_3$ shows no magnetic ordering down to 4.2 K. These results are summarized in Table VI. Studies are currently under way on the system $La_{1-x}Sr_xCoO_3$.

Table VI. Some Properties of Perovskite Investigated by Neutron Diffraction

Substance	Magnetic Structure	T_N	Crystallographic Structure
La VO_3	----	--	Cubic: a_1 = 7.842
La CrO_3	All near neighbors	300 K	Monoclinic: $a_1 = a_3$ = 7.777 Å, a_2 = 7.750 Å, β_2 = 90°15'
$LaMnO_3$	Ferromagnetic layers	140 K	Monoclinic: $a_1 = a_3$ = 7.910 Å, a_2 = 7.698 Å, β_2 = 91°52'
$LaFeO_3$	All near neighbors	375 K	Cubic: a_1 = 7.852 Å
$LaCoO_3$	---	---	Rhombohedral: a_1 = 7.651, β_1 = 90° 40'.

Discussion

It was learned that A. Gilleo of Bell Telephone and Jonker and van Santen of Philips have made mixed oxides in which they substituted for

the small rather than the large ions. They have obtained ferromagnetic
materials of low conductivity. If this is true, it is the first instance
of this phenomena.

The last paper, by J. Smit of Philips, was a discussion of
some physical properties of technical ferrimagnetics. The talk was split
into two parts, the first a discussion of ferroxcube materials, the
latter a discussion of ferroxdure materials.

From measurements of μ'', the imaginary part of the initial
permeability, it is evident that the losses in ferrites are caused by
at least two different mechanisms. The change in μ_o with applied
stress at very low stress levels shows that μ_o is caused by a rotation
of the spins in each Weiss domain. The same evidence is given by the
r.f. losses which can be explained quantitatively by the occurrence of
natural ferromagnetic resonances. This last phenomenon is influenced
strongly by the Weiss domain structure so that losses occur up to cm
waves. The cut-off frequency is given by $\omega = \gamma.4\pi \, I_s$, where I_s is the
spontaneous magnetization and γ the spectroscopic splitting factor.
This relation has been confirmed experimentally by temperature variation.

At low frequencies the residual losses are found to be caused
by a relaxation process due to the presence of ferrous next to ferric
ions. These ions also give rise to a ferrite electric conductivity:
The same energy of activation for the relaxation in the permeability and
the conductivity was found, i.e. $E_M = 0.30$ eV and $E_\rho = 0.29$ eV,
respectively, in one sample. For example $NiFe_2O_4$ with $\rho \approx 10^6 \, \Omega$ cm had
losses 10-20 times smaller than a $Ni_xZn_{1-x}Fe_2O_4$ sample in which $\rho \approx 10^2 \Omega$ cm.
The activation energies were 0.1 eV and 0.4 eV, respectively.
An exception to the generalization here is $CuFe_2O_4$ which had large losses
even though $\rho \approx 10^6 \, \Omega$ -cm. (A prior discussion with Smit on the presence
of covalent bonds about the Cu^{2+} ions in $CuFe_2O_4$ leads to the querie that
perhaps the covalent bonds are flipped from one plane to another in the
lattice as a result of the spin-orbit coupling with a resultant elastic
deformation on a microscopic scale and high losses.) Whereas Galt
believes that these losses are due to a transfer of an electron between

an Fe^{2+} and an Fe^{3+} ion in the B sites, Smit believes that the losses are mechanical losses which are due to a local magnetostriction about the Fe^{2+} ions.

The ferroxdure ceramic $BaFe_{12}O_{19}$ has a hexagonal structure and is characterized by a high value of the crystalline anisotropy ($\sim 3 \times 10^6$ erg/cm^3). The rotational permeability is very small, and therefore the permeability of about 5 in large crystals has to be attributed to domain-wall movements. At high frequencies (~ 1 Mc/sec.), resonance occurs which is a resonance of the Bloch walls, which have mass properties, oscillating ound their equilibrium positions.

Because of the high value of the anisotropy field (about 17000 gauss), ferromagnetic resonance cannot be excited in the preferred direction at 1.25 cm. Therefore the field has to be applied perpendicular to this direction. Resonance is then obtained at different values of the field, and from these resonance fields both the value of the anisotropy field and the g factor can be evaluated. This last factor is found to have the spin-only value. At values of the applied field lower than the anisotropy field, the Weiss-domain structure exists, and it was shown that, similar to the case for the ferrites, it has peculiar consequences for the resonance conditions.

From the measurements of the crystalline anisotropy and I_s at low temperature, together with the value of the g factor, it was concluded that the spin-orbit interaction is inactive in this material, as one should expect from the ionic structure. The crystalline anisotropy is presumably due to dipole interaction though preliminary calculations do not support this hypothesis.

Signed: *John B. Goodenough*
John B. Goodenough

JBG/md
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