

Sublattice Effects in Magnetic Resonance*†

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(Received May 28, 1953)

The resonance frequencies of a system containing two or four magnetic sublattices with different gyromagnetic ratios are calculated. It is found that in many cases the results reduce to the standard formulas of ferromagnetic and antiferromagnetic resonance; they are stated, however, in terms of an effective gyromagnetic ratio equal to the quotient of the net magnetic moment and the net angular momentum of the system. Line splitting due to the existence of several normal modes of nearly equal frequencies, and the effect of the sublattice structure upon the anisotropy contribution to the line width are also discussed. The calculated values of effective g values and line widths as a function of composition are compared with the experimental results for the nickel ferrite-aluminates.

INTRODUCTION

THE interpretation of the static magnetic properties of antiferromagnetic and ferrimagnetic materials is generally based upon the possibility of dividing the magnetic ions into two or more groups such that the magnetic moments within each group are parallel.¹ The assumed interactions among the magnetizations of these groups, or sublattices, then results in a magnetic structure in which the magnetizations of a given pair of sublattices have a definite orientation with respect to each other—usually either parallel or antiparallel. The predominant interaction in these materials can be taken to be of an antiferromagnetic nature,¹ i.e., leading to an antiparallel orientation, but there are other possibilities involving combinations of ferromagnetic and antiferromagnetic interactions which lead to magnetic structures of varying degrees of complexity.²

In time dependent problems, such as the magnetic resonance experiments which we shall consider, the existence of sublattices gives rise to observable effects which are sometimes of a rather unexpected kind. Above the Curie temperature, the observed resonance absorption is much like that found in other paramagnetics although there are indications that the short-range magnetic order resulting from the interactions affects the magnitude of the absorption.³ Ferrimagnetic materials, such as the ferrites, have a macroscopic magnetization below the Curie temperature and resonance experiments on several of these⁴ have been interpreted very successfully on this basis by the use of the results of the usual theory of ferromagnetic resonance.⁵ The important role of the sublattices in the theory of antiferromagnetic resonance was first

pointed out by Nagamiya and Kittel.⁶ In essence, one regards the interacting sublattices as a coupled system whose normal modes and frequencies can be found by standard methods from the equations of motion. If \mathbf{M}_1 and \mathbf{M}_2 are the magnetizations of the sublattices, one finds in the simplest case that since the effective fields due to anisotropy have opposite signs for the two sublattices, the significant variables become $\mathbf{M}_1 \pm \mathbf{M}_2$ rather than the individual magnetizations. As a result, the effective field describing the interactions (the “exchange field”) no longer drops out as it ordinarily does in the ferromagnetic case,⁵ but usually forms the predominant part of the expression for the frequency. This method has since been generalized and applied to more complicated systems.⁷⁻⁹

A common feature of the above calculations is the assumption of the equality of the gyromagnetic ratios characteristic of the individual sublattices. Gyromagnetic ratios obtained from resonance experiments, however, are in general significantly different from the free electron spin value and the differences are primarily due to the varying contributions of the orbital angular momentum as determined by the crystalline potential.¹⁰ Since the grouping into sublattices is usually determined by the different crystallographic sites available to the magnetic ions, one should assume that the gyromagnetic ratios of the various sublattices are actually different. We then have the possibility that a shift of magnetic ions from one type of site to another can change the resultant magnetic moment and angular momentum of the sample as a whole by different factors and thus alter the “effective” value of the sample gyromagnetic ratio. One of the purposes of this paper is to demonstrate that these effects do occur and that very small differences in the gyromagnetic ratios can affect the resonance behavior of the material in a profound and sometimes striking manner.

We shall confine ourselves to the determination of the

* Supported in part by the U. S. Office of Naval Research.

† A brief report of part of this work was given at the North Carolina meeting of the American Physical Society. [Phys. Rev. **91**, 206 (1953).]

¹ L. Néel, *Ann. phys.* **3**, 137 (1948).

² P. W. Anderson, *Phys. Rev.* **79**, 705 (1950); J. H. Van Vleck, *J. phys. et radium* **12**, 262 (1951); J. S. Smart, *Phys. Rev.* **86**, 968 (1952).

³ R. K. Wangsness, *Phys. Rev.* **89**, 142 (1953).

⁴ See footnote 2 of reference 8 for a partial list of references.

⁵ C. Kittel, *Phys. Rev.* **73**, 155 (1948); J. H. Van Vleck, *Phys. Rev.* **78**, 266 (1950).

⁶ T. Nagamiya, *Prog. Theoret. Phys.* **6**, 350 (1951); C. Kittel, *Phys. Rev.* **82**, 565 (1951).

⁷ F. Keffer and C. Kittel, *Phys. Rev.* **85**, 329 (1952).

⁸ R. K. Wangsness, *Phys. Rev.* **86**, 146 (1952).

⁹ J. Ubbink, *Phys. Rev.* **86**, 567 (1952); *Physica* **19**, 9 (1953).

¹⁰ C. Kittel, *Phys. Rev.* **76**, 743 (1949).

normal frequencies ω of the system basing the calculations entirely upon the classical equations of motion,

$$d\mathbf{M}_i/dt = \gamma_i \mathbf{M}_i \times \mathbf{H}_i, \quad (1)$$

in which damping is neglected. In these equations, \mathbf{M}_i is the magnetization, γ_i the gyromagnetic ratio, and \mathbf{H}_i the effective field for the i th sublattice. By using (1), we are implicitly assuming the magnetic ordering to be sufficient to give \mathbf{M}_i a meaning. In principle, this would require the temperature to be nearly 0°K, but the results should be applicable as an approximation for higher temperatures provided that one recognizes that at a given finite temperature the approximation will be the poorer the lower the Curie temperature of the material. We shall first obtain the general result for a system comprising two magnetic sublattices and discuss a few of the important approximations and compare them with some interesting experimental data. Later, we extend our considerations to a system of four sublattices—a generalization which is found to increase the complexity of the possible resonance behavior.

TWO SUBLATTICES

The external static field H is assumed to be in the positive z direction. The molecular field coefficients describing the intra- and inter-sublattice interactions are λ_{11} , λ_{22} , and $\lambda_{12} = \lambda_{21} = \lambda$; they can be of either sign. We represent the common demagnetizing factors by N_x , N_y , N_z and the effective demagnetizing factors resulting from anisotropy⁵ by N_{1x} , N_{1y} , \dots , N_{2z} . The field on sublattice 1 can then be written as

$$\begin{aligned} \mathbf{H}_1 = & H\mathbf{k} + \lambda_{11}\mathbf{M}_1 + \lambda\mathbf{M}_2 - N_x(M_{1x} + M_{2x})\mathbf{i} \\ & - N_y(M_{1y} + M_{2y})\mathbf{j} - N_z(M_{1z} + M_{2z})\mathbf{k} \\ & - N_{1x}M_{1x}\mathbf{i} - N_{1y}M_{1y}\mathbf{j} - N_{1z}M_{1z}\mathbf{k}, \end{aligned} \quad (2)$$

with a similar expression for \mathbf{H}_2 .

Combining (1) and (2), we find as before⁸ that $M_{iz} \simeq \text{const} = M_i$. If we assume the other components to be proportional to $e^{i\omega t}$, we find from the secular equation that the normal frequencies are

$$\omega^2 = F \pm [F^2 - (A_x B_x - C_x D_x)(A_y B_y - C_y D_y)]^{1/2}, \quad (3)$$

where

$$\left. \begin{aligned} F &= \frac{1}{2}(A_x A_y + B_x B_y + C_x D_y + C_y D_x), \\ A_j &= \gamma P + E_{j+}, \\ B_j &= \gamma Q_j + \delta(N_j - \lambda)\Delta + E_{j+}, \\ C_j &= \delta P + E_{j-}, \\ D_j &= \delta Q_j + \gamma(N_j - \lambda)\Delta + E_{j-}, \\ E_{j\pm} &= \frac{1}{2}(N_{1j} - N_{1z})\gamma_1 M_1 \pm \frac{1}{2}(N_{2j} - N_{2z})\gamma_2 M_2, \\ P &= H + (\lambda - N_z)M, \\ Q_j &= H + (N_j - N_z)M, \quad j = x, y; \end{aligned} \right\} \quad (4)$$

and

$$M = M_1 + M_2, \quad \Delta = M_1 - M_2; \quad (5)$$

$$\gamma = \frac{1}{2}(\gamma_1 + \gamma_2), \quad \delta = \frac{1}{2}(\gamma_1 - \gamma_2). \quad (6)$$

As so often happens, this complicated general expression is not very helpful for understanding the effects due to the different gyromagnetic ratios, and we shall proceed at once to the consideration of several important cases of (3). We note first, however, that when $\gamma_1 = \gamma_2$ the result reduces to that previously found,⁸ and if δ is small, we can use the classifications introduced before as a guide for the simplification of (3). We shall further restrict ourselves for simplicity only to those cases of ordinary interest in which $\omega \approx \gamma H$ rather than to the range of very high frequencies in which the exchange field is predominant in determining the magnitude of ω .

THE FERROMAGNETIC FORMULA

For the present, we neglect the anisotropy fields by setting $E_j = 0$. We shall also assume that the Curie temperature is large enough so that the molecular fields whose magnitudes are of the order of $|\lambda M_i|$ are very great compared to the external field H and the demagnetizing fields, i.e., $|\lambda| \gg N_{x,y,z}$. We then find from (4) that $A_j = \gamma P$, $B_j \simeq \gamma Q_j - \lambda \delta \Delta$, $C_j = \delta P$, and $D_j \simeq \delta Q_j - \lambda \gamma \Delta$. Since we also have $P \simeq \lambda M$, we see that we can get a good approximation to F by keeping only those terms which are of the order of the square of the exchange field. We finally find that

$$F \simeq \frac{1}{2}(\gamma P - \delta \lambda \Delta)^2 \quad (7)$$

and

$$\begin{aligned} R &= (A_x B_x - C_x D_x)(A_y B_y - C_y D_y) \\ &= P^2(\gamma^2 - \delta^2)^2 Q_x Q_y. \end{aligned} \quad (8)$$

Upon comparing (7) and (8), we see that ordinarily we can expect that $R \ll F^2$. Thus we can get a good first approximation to ω^2 by expanding the radical in (3) in powers of R/F^2 ; we choose the minus sign in order that a result of the desired order of magnitude be obtained. We find that

$$\begin{aligned} \omega^2 &= R/2F \\ &= \gamma_{\text{eff}}^2 [H + (N_x - N_z)M][H + (N_y - N_z)M], \end{aligned} \quad (9)$$

where

$$\gamma_{\text{eff}} = P(\gamma^2 - \delta^2)/(\gamma P - \lambda \delta \Delta).$$

This becomes

$$\gamma_{\text{eff}} = (M_1 + M_2)[(M_1/\gamma_1) + (M_2/\gamma_2)]^{-1}, \quad (10)$$

if we use (5), (6), and the approximation $P = \lambda M$.

Equation (9) retains the form of the resonance condition suitable for a ferromagnetic but the existence of the sublattice structure is shown by the replacement of the electron spin gyromagnetic ratio by the effective ratio given by (10). Equation (10) has a simple physical interpretation as it expresses γ_{eff} as the ratio of the resultant magnetic moment and the resultant angular momentum of the system. This result can also be written in terms of the g values of the sublattices and their angular momenta S_i . Equation (10) then yields the

following expression for the effective value of g :

$$g_{\text{eff}} = (g_1 S_1 + g_2 S_2) / (S_1 + S_2). \quad (11)$$

Equations (9) and (11) have also been found by Tsuya¹¹ by means of the quantum-mechanical analog of our calculation.

Equation (9) was not obtained by using explicitly the physical conditions appropriate to the ferrimagnetic case, and also does not contain any direct reference to the anisotropy and exchange fields which are known to have an important influence on the resonance condition for this case. It turns out to be more suitable for further discussion to consider another approximation to (3) in order to see how these effects enter. This procedure will, in addition, enable us to get a better understanding of the mechanism by which the different gyromagnetic ratios affect the frequencies and the dependence of the line width upon the sublattice structure.

THE FERRIMAGNETIC CASE

We shall restrict ourselves in what follows to the case in which the sample is a sphere so that $N_{x,y,z} = N = 4\pi/3$. This corresponds to what is most often used experimentally, and also effects considerable simplification in the necessary algebra. Equation (4) shows that then N enters only in the combination λN which is approximately λ for materials with reasonable values of the Curie temperature.

In the ferrimagnetic case, the sublattices are antiparallel with M_1 , say, parallel to H . The simplest way of introducing the effect of anisotropy is to assume that the z direction is also nearly the direction of a preferred axis of the crystal, so that the anisotropy field can be written as H_a for M_1 and $-H_a$ for M_2 ; in the notation of (2), this means that we assume that⁸

$$-N_{1z}M_1 = N_{2z}M_2 = H_a; \quad N_{1x,y} = N_{2x,y} = 0. \quad (12)$$

Using these assumptions, we find from (4) that A_j , B_j , C_j , and D_j are all independent of j and equal, respectively, to

$$\left. \begin{aligned} A &= \gamma(H + \lambda M) + \delta H_a, \\ B &= \gamma H + \delta(H_a - \lambda \Delta), \\ C &= \delta(H + \lambda M) + \gamma H_a, \\ D &= \delta H + \gamma(H_a - \lambda \Delta). \end{aligned} \right\} \quad (13)$$

Since it is known¹² that in this case

$$\omega = \frac{1}{2}(A+B) \pm \left[\frac{1}{4}(A-B)^2 + CD \right]^{1/2},$$

we need only substitute the expressions given in (13) into the above equation to find that for a ferrimagnetic sphere we have

$$\begin{aligned} \omega &= \gamma H + \delta H_a + \frac{1}{2}\lambda(\gamma_2 M_1 + \gamma_1 M_2) \\ &\quad \pm \left\{ (\gamma H_a + \delta H) [\gamma H_a + \delta H - \lambda(\gamma_2 M_1 - \gamma_1 M_2)] \right. \\ &\quad \left. + \frac{1}{4}\lambda^2(\gamma_2 M_1 + \gamma_1 M_2)^2 \right\}^{1/2}. \end{aligned} \quad (14)$$

The effect of assuming different magnitudes H_{a1} and H_{a2} for the anisotropy fields is merely the replacement of H by $H + H_{a-}$ and H_a by H_{a+} where $H_{a\pm} = \frac{1}{2}(H_{a1} \pm H_{a2})$; we shall not consider this further.

Before we go on to consider other approximations to (14), let us temporarily assume that $H_a = 0$, so that (14) becomes

$$\begin{aligned} \omega &= \gamma H + \frac{1}{2}\lambda(\gamma_2 M_1 + \gamma_1 M_2) \\ &\quad \pm \left\{ \delta H [\delta H - \lambda(\gamma_2 M_1 - \gamma_1 M_2)] \right. \\ &\quad \left. + \frac{1}{4}\lambda^2(\gamma_2 M_1 + \gamma_1 M_2)^2 \right\}^{1/2}. \end{aligned} \quad (15)$$

A comparable result in which anisotropy is included but different values of γ_i are not is¹³

$$\begin{aligned} \omega/\gamma &= H + \frac{1}{2}\lambda(M_1 + M_2) \pm \left\{ H_a [H_a - \lambda(M_1 - M_2)] \right. \\ &\quad \left. + \frac{1}{4}\lambda^2(M_1 + M_2)^2 \right\}^{1/2}. \end{aligned} \quad (16)$$

If we now compare (15) and (16), we see that the effect of having $\gamma_1 \neq \gamma_2$ so that $\delta \neq 0$ is to introduce an apparent anisotropy field into the system even if none were naturally present. The magnitude of this field is $\delta H/\gamma$. The existence of this anisotropy can be seen most clearly from the equations of motion themselves rather than from results derived from them. Suppose in Eqs. (1), we assume that $\gamma_1 = \gamma_2 = \gamma$, use (7), and omit all other terms. The equations of motion for this case then become

$$\begin{aligned} d\mathbf{M}_1/dt &= \gamma \mathbf{M}_1 \times \mathbf{H} + \gamma \mathbf{M}_1 \times H_a \mathbf{k}, \\ d\mathbf{M}_2/dt &= \gamma \mathbf{M}_2 \times \mathbf{H} - \gamma \mathbf{M}_2 \times H_a \mathbf{k}. \end{aligned} \quad (17)$$

If, on the other hand, we assume that $\gamma_1 \neq \gamma_2$ and include only the external field \mathbf{H} , we find that we can write the equations of motion in the form

$$\begin{aligned} d\mathbf{M}_1/dt &= \gamma \mathbf{M}_1 \times \mathbf{H} + \mathbf{M}_1 \times \delta \mathbf{H}, \\ d\mathbf{M}_2/dt &= \gamma \mathbf{M}_2 \times \mathbf{H} - \mathbf{M}_2 \times \delta \mathbf{H}. \end{aligned} \quad (18)$$

Comparison of (17) and (18) clearly shows that if $\delta \neq 0$ the direction of the external field becomes in effect a preferred direction to which we can ascribe an anisotropy field of magnitude $\delta H/\gamma$. These results tend to blur the distinction between the effects on the single crystal resonance of anisotropy and differing gyromagnetic ratio and to increase the difficulty of making an unambiguous determination of anisotropy from resonance experiments especially since the term $\delta H/\gamma$ can be comparable in magnitude to H_a .

We can approximate (14) in general by expanding the radical in inverse powers of its last term. In so doing we get a result which is independent of λ and has the following form:

$$\omega = \gamma_{\text{eff}} \left\{ H + [(M_1 - M_2)/(M_1 + M_2)] H_a \right\}, \quad (19)$$

where γ_{eff} is again given by (10).

This result differs in an interesting way from the formula which is obtained for a sphere from the ferromagnetic formula; the term in the braces would be

¹¹ N. Tsuya, Prog. Theoret. Phys. 7, 263 (1952).

¹² Equation following (10) in reference 8.

¹³ Equation (11) of reference 8.

simply $H+H_a$ rather than the more complicated term in (19). Thus the sublattice structure not only alters the effective gyromagnetic ratio but makes the shift in resonance frequency due to anisotropy also depend upon the exact distribution of magnetic ions.

In a polycrystalline material or a powder, we would not expect the term involving H_a to result in a shift of the line, but rather in a contribution ΔH to the line width due to an orientational broadening. The resonance condition would be simply

$$\omega = \gamma_{\text{eff}} H, \quad (20)$$

and from (19) we see that the order of magnitude of ΔH could be expected to be given by

$$\frac{\Delta H}{H_a} = \frac{|M_1 - M_2|}{|M_1 + M_2|} = \frac{|g_1 S_1 - g_2 S_2|}{|g_1 S_1 + g_2 S_2|}. \quad (21)$$

Hence if M_1 and M_2 were to be altered by temperature variation or changes in composition this should be reflected in the behavior of the line width.

We now proceed to the consideration of the resonance conditions for two special situations which can occur in ferrimagnetics. The first corresponds to the vanishing of the resultant angular momentum, i.e., $S = S_1 + S_2 = 0$, or, equally well, $(M_1/\gamma_1) + (M_2/\gamma_2) = 0$. If $\gamma_1 \neq \gamma_2$, this does not mean the vanishing of the net magnetic moment. When $S = 0$, Eq. (10) would predict that γ_{eff} would be infinite; the expansion leading to (19), however, would no longer be legitimate and we must find the value of ω for this case from the exact expression (14). If we continue to write $\omega = \gamma_{\text{eff}} H$, we find that

$$\gamma_{\text{eff}}(S=0) = \gamma - (-2\delta\gamma_2\lambda M_1/H)^{1/2}, \quad (22)$$

where we have again chosen the minus sign, neglected the ratio H_a/H , and assumed that $|\lambda M_1| \gg H$.

For the other case in which $M = 0$, the first approximation for γ_{eff} as given by (10) predicts a value of zero. We find, however, that (14) becomes

$$\omega = \gamma H + \delta(H_a + H_E) \pm \{(\gamma H_a + \delta H) \times [\gamma(H_a + 2H_E) + \delta H] + (\delta H_E)^2\}^{1/2}, \quad (23)$$

where we have let $-\lambda M_1 = H_E$. We note in passing that if $\delta = 0$, this reduces to the well-known antiferromagnetic resonance condition $\omega/\gamma = H \pm [H_a(H_a + 2H_E)]^{1/2}$.⁶ Since, generally, $H_E \gg H$ and H_a , if $\delta \neq 0$, we can expand the radical in inverse powers of $(\delta H_E)^2$, and we find that (23) reduces to

$$\omega = \gamma_a H_a, \quad (24)$$

where

$$\frac{1}{\gamma_a} = \frac{1}{2} \left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right), \quad (25)$$

and where, as usual, the minus sign in (23) has been kept. This result, of course, also follows directly from (19). Equation (24) is independent of H , and since the frequency given by (24) will not ordinarily coincide

with the fixed applied frequency of the apparatus, no resonance will be observed, so that in the language of (20), we can say that in effect

$$\gamma_{\text{eff}}(M=0) = 0, \quad (26)$$

in agreement with the result given by (10).

If the plus sign before the radical of (14) is taken, the predominant term is $\frac{1}{2}\lambda(\gamma_2 M_1 + \gamma_1 M_2)$; this gives us the following result for the frequency of resonance in the exchange field:

$$\omega_e = \lambda(\gamma_2 M_1 + \gamma_1 M_2). \quad (27)$$

This agrees with the frequency found by Kaplan and Kittel¹⁴ by a more specialized calculation.

A COMPARISON WITH EXPERIMENT

In this section we shall discuss in detail only some of the results of resonance experiments which have been performed at the Naval Ordnance Laboratory on a series of compounds known as nickel ferrite-aluminates.¹⁵ These materials have the chemical formula $\text{NiOFe}_{2-x}\text{Al}_x\text{O}_3$, in which $0 \leq x \leq 2$. The resonance absorption was observed in small spheres of the sintered material; the frequency used was that corresponding to a wavelength of approximately 3 cm. Effective g values were found for each resonance by means of (20); the resulting values for liquid nitrogen temperature are shown in their dependence upon composition as open circles in Fig. 1.¹⁶

In order to calculate g_{eff} as a function of x from Eq. (11), it is necessary to know the distribution of the magnetic ions over the various lattice sites in order to find S_1 and S_2 . A reasonable, although not unique, distribution of this kind has been deduced for the nickel ferrite-aluminates by McGuire¹⁶ from measurements of

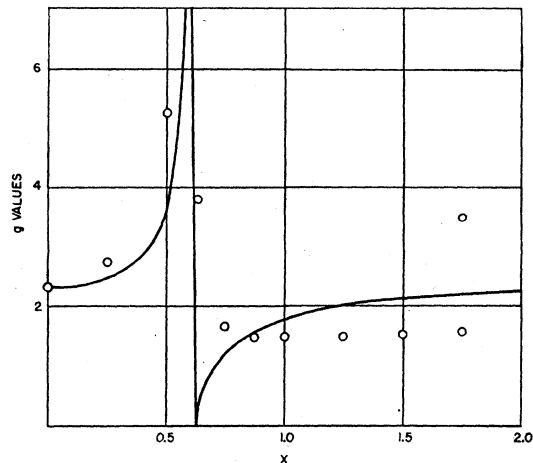


FIG. 1. g values vs composition for $\text{NiOFe}_{2-x}\text{Al}_x\text{O}_3$. Solid line is calculated values. Open circles are experimental points.

¹⁴ J. Kaplan and C. Kittel, *J. Chem. Phys.* **21**, 760 (1953).

¹⁵ Maxwell, Pickart, and Hall, *Phys. Rev.* **91**, 206 (1953); T. R. McGuire, *Phys. Rev.* **91**, 206 (1953).

¹⁶ T. R. McGuire (private communication).

the saturation magnetization. The theoretical curve shown in Fig. 1 was calculated from (11) by the use of this distribution. All of the nickel ions with spin 1 and $g_1=2.3$ were taken as comprising sublattice 1, while all of the iron ions with spin 2.5 and $g_2=2.0$ formed sublattice 2; the grouping was done in this way so that the two sublattice formulas could be used although both the nickel and the iron are apparently distributed on both A and B sites—this point will be considered in more detail in the next section. The large g values have an upper limit of about 10 for $x=0.6$ as given by the more exact formula (22).

The general agreement between the curves is fairly satisfactory. The disagreement at the two points $x=0.5$ and 0.65 is probably due to a small deviation in composition in this region of rapid change of g_{eff} . For $x>1$, the two curves really have in common only the tendency toward lower values, although the experimental results have a slight trend toward a value near 2.3 which would be expected for nickel aluminate provided that the resonance were observable. Other than the inadequacy of the formula (11), a more likely reason for the discrepancy for $x>1$ is that the distribution of magnetic ions used for the calculations is not quite correct since this distribution is especially hard to determine for $x>1$ and is also apparently very sensitive to the exact heat treatment given the sample.^{15, 16}

The composition dependent contribution to the line width as given by (21) has also been calculated with the use of the same distribution. These values are shown as the solid line in Fig. 2 along with the experimental results¹⁶ for the ratios $\Delta H(x)/\Delta H(0)$. The general agreement between the two curves is quite satisfactory especially in regard to the existence and location of the maximum and minimum. Better agreement than is observed can probably not be expected since no attempt has been made to allow for the contributions of the many other effects which can influence the line width; the remarks made above about the distribution for $x>1$ are equally applicable here.

A behavior which is qualitatively similar to that of Fig. 1 has been found for the variation of g with temperature in $\text{Li}_{0.5}\text{Fe}_{1.25}\text{Cr}_{1.25}\text{O}_4$ by van Wieringen.¹⁷ As discussed in the introduction, the present theory cannot be expected to give an exact account of temperature dependence, but the general aspect of van Wieringen's curve can be understood on the same basis, namely, that the magnetic moment and angular momentum vanish at two different points.

FOUR SUBLATTICES

In order to make the specific calculations of the last section, the atoms were grouped into sublattices by gyromagnetic ratio rather than by the orthodox grouping according to the type of crystallographic site

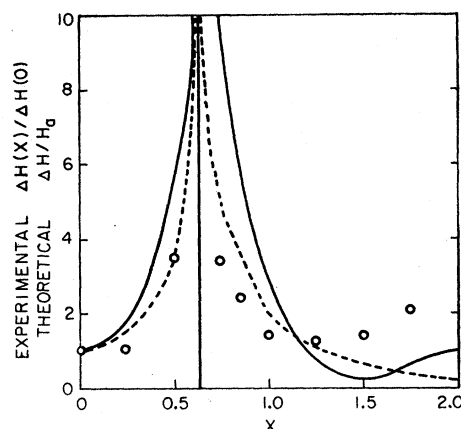


FIG. 2. Relative line widths vs composition for $\text{NiOFe}_{2-x}\text{Al}_x\text{O}_3$. Open circles are experimental points. Solid and dashed lines are values calculated from two- and four-sublattice formulas, respectively.

occupied. According to the distribution of ions which is indicated by the saturation magnetization, however, both the iron and nickel are distributed between the A and B sites of the spinel structure. As a result, in the specific case of the nickel ferrite-aluminates we are actually dealing with a system of four sublattices with the accompanying possibility of four different gyromagnetic ratios. The purpose of this section is to try to determine if our previous results are seriously affected by this situation.

One can proceed by using Eqs. (1) exactly as in the two sublattice case, but the secular determinant now has eight rows and columns and the complexity of the resulting expansion makes this method impractical. What we can do instead is to use a more approximate method whose utility has been demonstrated by Keffer and Kittel.⁷ The basic idea is that if the total change of the magnetization can be described in terms of an angular velocity ω then (1) can be written as

$$d\mathbf{M}_i/dt = \omega \times \mathbf{M}_i = \gamma_i \mathbf{H}_i \times \mathbf{M}_i, \quad (28)$$

where we have explicitly taken into account the fact that the electron gyromagnetic ratio is negative so that γ_i now stands for its magnitude.

The specific case to which we shall first apply (28) is shown in Fig. 3. The magnitudes of the magnetizations of the sublattices are A , B , C , and D with corresponding gyromagnetic ratios γ_A , γ_B , γ_C , and γ_D . The magnetizations are assumed to precess about the external field H with the same angular velocity ω ; we further assume the angles made by them with the direction of H to be small and, for definiteness, that $\phi_B > \phi_A > \phi_D > \phi_C$. The essential nature of the ferrimagnetic case has been included since A and B are assumed to be oppositely directed to C and D ; we now let λ be the magnitude of the molecular field coefficient describing the interaction between these two groups. The magnitudes of the coupling coefficient between A and B will be written as

¹⁷ J. S. van Wieringen, Phys. Rev. **90**, 488 (1953).

λ_1 and that for C and D as λ_2 ; we shall also explicitly assume that these couplings are of an antiferromagnetic nature.

If we neglect anisotropy and demagnetizing fields, the four equations obtained from (28) become

$$\begin{aligned}\omega A\phi_A &= \gamma_A A [H\phi_A + \lambda C(\phi_A - \phi_C) + \lambda D(\phi_A - \phi_D) + \lambda_1 B(\phi_B - \phi_A)], \\ \omega B\phi_B &= \gamma_B B [H\phi_B + \lambda C(\phi_B - \phi_C) + \lambda D(\phi_B - \phi_D) - \lambda_1 A(\phi_B - \phi_A)], \\ \omega C\phi_C &= \gamma_C C [H\phi_C + \lambda A(\phi_A - \phi_C) + \lambda B(\phi_B - \phi_C) - \lambda_2 D(\phi_D - \phi_C)], \\ \omega D\phi_D &= \gamma_D D [H\phi_D + \lambda A(\phi_A - \phi_D) + \lambda B(\phi_B - \phi_D) + \lambda_2 C(\phi_D - \phi_C)].\end{aligned}\quad (29)$$

The secular equation which results has the form

$$\omega^4 + a_1\omega^3 + a_2\omega^2 + a_3\omega + a_4H = 0, \quad (30)$$

where the coefficients a_i are rather long and involved functions of the external field, the molecular field coefficients, and the sublattice magnetizations.

The fact that we are looking for a solution of (30), however, such that $\omega \sim H$ enables us to obtain a suitable approximation from (30) rather easily. If we let H_E be the magnitude of the product of a molecular field coefficient and a magnetization, we can generally expect that $H_E \gg H$. If one then inspects the explicit expressions for the a_i , one finds that the order of magnitude of their largest terms are given by $a_1 \sim H_E$, $a_2 \sim H_E^2$, a_3 and $a_4 \sim H_E^3$. Then the order of the terms in (30) are H^4 , $H_E H^3$, $H_E^2 H^2$, $H_E^3 H$, and $H_E^3 H$, respectively. Since the ratio H/H_E is so small, we can then approximate (30) by the equation

$$a_3\omega + a_4H = 0 \quad (31)$$

and any fractional error made in finding ω from (31) will be of the order of the negligible term H/H_E .

Thus we have found that the four sublattice system also leads to an expression for ω of the form given in (20) where, of course,

$$\gamma_{\text{eff}} = -a_4/a_3.$$

Explicit evaluation of this expression, in which only terms of the order of H_E^3 are kept, yields the result that

$$\gamma_{\text{eff}} = \frac{A + B - C - D}{A/\gamma_A + B/\gamma_B - C/\gamma_C - D/\gamma_D}. \quad (32)$$

We see that to this approximation γ_{eff} is again independent of the λ 's and is equal to the quotient of the net magnetization and the net angular momentum. In

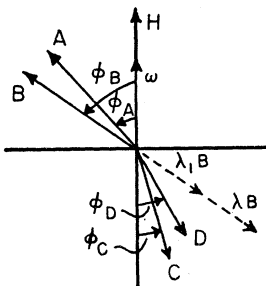


FIG. 3. Assumed normal mode for four sublattices. Dotted line indicates molecular fields ascribed to sublattice B.

terms of g values, (32) becomes

$$g_{\text{eff}} = \frac{g_A S_A + g_B S_B - g_C S_C - g_D S_D}{S_A + S_B - S_C - S_D}. \quad (33)$$

In the specific ferrimagnetic case exemplified by the nickel ferrite-aluminates we have assumed that $g_A = g_C = g_1$, and $g_B = g_D = g_2$. Equation (33) is then seen to reduce at once to (11) since $S_1 = S_A - S_C$ and $S_2 = S_B - S_D$ for this case.

Now we have assumed a specific form of the normal precession mode in order to obtain (29). As Keffer and Kittel have shown⁷ in the two sublattice case, we can assume that there are other possible modes which differ primarily in the sense of precession of the various sublattices. Such a possibility, analogous to that discussed by Keffer and Kittel, is shown in Fig. 4. Here we assume that A and B precess in phase as do C and D but that the sense of precession of these two groups is opposite. If one now writes down the equations similar to (29) as obtained from (28), one finds that the new equations are the same as (29) except that γ_C and γ_D are replaced by $-\gamma_C$ and $-\gamma_D$, respectively. The rest of the calculation would go as before with the net result that all of the algebraic signs in the denominator of (32) would be plus; the denominator of (33) would similarly have all plus signs, while the signs in both numerators would be unaltered.†

The same sort of considerations would be valid for other assumed modes so that the above results can be generalized and correlated with the assumed direction of the angular velocity of a given sublattice with respect to H . For if we treat $A, B, \dots, \gamma_C, \gamma_D$ as all positive numbers, all of the possibilities are contained in the following extension of (33), namely, that

$$g_{\text{eff}} = \frac{g_A S_A + g_B S_B - g_C S_C - g_D S_D}{S_A \pm S_B \mp S_C \mp S_D}. \quad (34)$$

Here we have assumed A and B to be "up," and C and

† Note added in proof.—Dr. J. Smit of the Philips Research Laboratories has kindly pointed out to me that the relative angles of the sublattices in the mode assumed in Fig. 4 are not constants of the motion so that the derivation of this paragraph is apparently vitiated. If one continues to use the small angle approximation, however, and evaluates Eqs. (28) for various phases of the assumed motion, the resulting frequency is still found to be that discussed in this paragraph. Actually, of course, the question of the reality of these modes can only be answered by considering the solutions of the exact equations of motion.

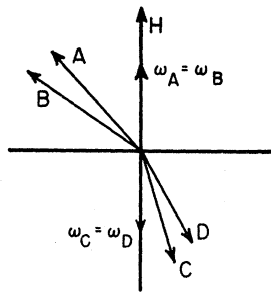


FIG. 4. Another assumed normal mode for four sublattices.

D "down." The signs in the denominator are chosen as follows: the upper sign applies if the assumed direction of the angular velocity of the sublattice is parallel to H (always the case for A since another choice will not lead to physically different values for g_{eff}), while the lower sign applies if the angular velocity is assumed to be antiparallel to H .

From (34), we see that if the angular momentum of one of the sublattices is small enough, then the frequencies of the two modes corresponding to different signs may be so close together that they both fall within the range of the apparatus. This is apparently the reason for the extra low-temperature peak observed in the nickel ferrite-aluminates with $x=1.75$. As shown in Fig. 1 the experimental value of g is 3.5; the value of g_{eff} calculated on this basis by using (11) with the denominator $S_1 - S_2$ is 3.8. The agreement is sufficiently good to show that these other modes very likely can give rise to an apparent splitting of the low-temperature resonance curve with values of g_{eff} given by the various formulas contained in (34).

Anisotropy and the Line Width

We shall briefly consider the result of including an anisotropy field in the mode pictured in Fig. 3. For simplicity we shall assume the anisotropy field to have the same magnitude H_a for all four sublattices and is directed parallel to H for A and B , and antiparallel to H for C and D .

When the equations of motion are written down from (28) for this case, they are found to be the same as (29) except that H is replaced by $H + H_a$ in the first two, and by $H - H_a$ in the last two. In accord with our previous method of approximation we need only find what the inclusion of H_a does to the last term of (30). This is a straightforward but lengthy calculation; the

result is that the frequency is given by

$$\omega = \gamma_{\text{eff}} \left\{ H + \frac{(A+B+C+D)}{(A+B-C-D)} H_a \right\}, \quad (35)$$

where γ_{eff} is again given by (32).

For a polycrystalline material or a powder, we can expect to find from this result a contribution ΔH to the line width of magnitude

$$\frac{\Delta H}{H_a} = \left| \frac{A+B+C+D}{A+B-C-D} \right|. \quad (36)$$

We see that in the interesting case in which $\gamma_A = \gamma_C = \gamma_1$ and $\gamma_B = \gamma_D = \gamma_2$, Eq. (36) does not reduce to the result (21) which was found for the two sublattice case since the numerator of (36) does not become $M_1 - M_2$. The relative line width calculated from (36) for the nickel ferrite-aluminates is shown as the dashed line in Fig. 2. The agreement with the experimental curve is definitely improved for values of x up to about 1.25, but the minimum which was previously found for $x > 1$ no longer appears. Very likely the disagreement with experiment for $x > 1$ is due to the use of a distribution for the ions which is not exact as we have previously discussed.

CONCLUSION

Both the theoretical considerations given above and the limited comparison with experiment indicate that the expressions for the effective gyromagnetic ratio given by (10) and (32) as well as their natural extension to more complex situations are accurately applicable to systems containing sublattices. If a system can be adequately described in terms of only two sublattices, then one has the possibility of actually being able to determine the magnetizations of the individual sublattices, and thence the ionic distribution by using both the measured values of the saturation magnetization and effective g values for the sample as a whole. For systems of more sublattices, these two values are not sufficient to determine the ion distributions completely, but comparison of experimental g values with those calculated from an assumed distribution will provide a useful check on the accuracy of the distribution. Equations (21) and (36) will be helpful when one is considering the contributions of other effects to the line width because their use will enable one to separate the contributions dependent upon the sublattice structure from the total observed widths.

I wish to thank Dr. L. R. Maxwell, Dr. T. R. McGuire, and Dr. J. S. Smart for some interesting discussions of this work.