

Cation Distributions in Mixed Ferrites

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In materials with the spinel structure, such as the ferrites, the cations are located on two different types of crystallographic sites. Expressions are derived for the equilibrium distribution of cations in mixed ferrites, which contain three different types of cations.

It is suggested that the cation distributions in such ferrites may be determined from the experimental values of magnetic moment and g factor. The method is applied to the nickel ferrite-aluminate series; the results agree reasonably well with x-ray diffraction data.

IN materials which have the chemical formula $MO \cdot N_2O_3$ and the spinel structure, two types of crystallographic sites are available to the cations. For each unit $MO \cdot N_2O_3$ there is one tetrahedrally coordinated, or A , site and two octahedrally coordinated, or B , sites. If the A sites contain only the divalent ions M^{++} , the crystal structure is said to be normal; if the A sites contain only trivalent ions N^{3+} , the structure is said to be inverted. Intermediate arrangements are, of course, possible.

The basic magnetic properties of the ferrites are very sensitive functions of the distribution of the metallic ions among the available A and B sites. For single ferrites, the distributions can be estimated by using a set of rules proposed by Verwey, Haayman, and Romeijn.¹ The gist of these rules is that the Fe^{3+} ion will occupy the A sites except when the divalent ion is Zn^{++} or Cd^{++} . Thus zinc and cadmium ferrites should be normal, and all other ferrites should be inverted. The Verwey rules obviously hold only in some approximation, since at any finite temperature at least some small fraction of the ions will be in "wrong" sites. However, the approximation is apparently a good one for all of the simple ferrites, excepting those of magnesium and copper.

In magnesium and copper ferrites, the magnetic properties have been observed to depend on the previous heat treatment. Néel² has suggested that in these cases the energy required to interchange the divalent and trivalent ions among the A and B sites is relatively small, so that the ionic distributions vary appreciably with temperature. Pauthenet³ has measured the saturation magnetization of quenched magnesium and copper ferrites; the measured moments reflect the "frozen-in" distribution which was the equilibrium distribution for the quenching temperature. His results are in excellent agreement with a theoretical formula

obtained by Néel² for the equilibrium distribution as a function of temperature.

Little detailed work has been done on the ionic distribution in mixed ferrites; Sage and Guillaud⁴ have noted, however, that the Verwey rules do not seem to hold as generally as they do for the single ferrites. In this paper, we discuss some of the features of the ionic distribution problem for mixed ferrites.

EQUILIBRIUM DISTRIBUTIONS

Let the basic ferrite have the formula $MO \cdot N_2O_3$, where M and N are divalent and trivalent ions, respectively. (Strictly speaking, the material is not a ferrite unless $N=Fe$, but we use the term loosely here to include any material with the spinel structure.) We shall consider two special cases of mixed ferrites which have been the subject of considerable experimental study.

Case A—Two Kinds of Divalent Ions

We wish to determine the distributions of ions on the A and B sites for a ferrite with the formula $M_{(1-d)}P_dO \cdot N_2O_3$. Here P is a divalent ion and d varies from 0 to 1. The distribution can be described by two parameters, x and y . Suppose that for ν molecules of the material we have

$x\nu$	M^{++} ions on A sites,
$y\nu$	P^{++} ions on A sites,
$(1-x-y)\nu$	N^{3+} ions on A sites,
$(1-d-x)\nu$	M^{++} ions on B sites,
$(d-y)\nu$	P^{++} ions on B sites,
$(1+x+y)\nu$	N^{3+} ions on B sites.

The number of ways in which such a distribution can be achieved are

$$w = \frac{[(1-d)\nu]!(d\nu)!(2\nu)!}{(x\nu)!(y\nu)![(1-x-y)\nu]![(1-d-x)\nu]!(d-y)\nu![(1+x+y)\nu]!} \quad (1)$$

¹ Verwey, Haayman, and Romeijn, *J. Chem. Phys.* **15**, 181 (1947).

² L. Néel, *Compt. rend.* **230**, 375 (1950).

³ R. Pauthenet, thesis, Grenoble, 1951.

⁴ M. Sage and C. Guillaud, *Comptes rend.* **230**, 1751 (1950).

The entropy per molecule corresponding to such a situation can be expressed with the aid of Stirling's approximation as

$$s = (k/\nu) \ln w = k[(1-d) \ln(1-d) + d \ln d + 2 \ln 2 - x \ln x - y \ln y - (1-x-y) \ln(1-x-y) - (1-d-x) \ln(1-d-x) - (d-y) \ln(d-y) - (1+x+y) \ln(1+x+y)]. \quad (2)$$

In order that x and y represent equilibrium distributions, they must have values which minimize the free energy,

$$f = u - Ts, \quad (3)$$

where u is the internal energy per molecule. By requiring that the first derivatives of f with respect to x and y vanish, we find

$$x(1+x+y) = (1-x-y)(1-d-x) \exp(-u_x/kT), \quad (4a)$$

$$y(1+x+y) = (1-x-y)(d-y) \exp(-u_y/kT), \quad (4b)$$

where $u_x = \partial u / \partial x$ and $u_y = \partial u / \partial y$. The exact form of u_x and u_y is not known in general; for the important case P=Zn and N=Fe, u_x is believed to be positive and u_y to be negative. As a first approximation we shall assume that u_x and u_y are constant. This is equivalent to assuming that the net work required to interchange various ions between the A and B sites is independent of x and y (though not the same for different types of interchanges). A dependence of u_x and u_y on x and y might lead to ordered arrangements at finite temperatures. Such an ordering has been observed by Braun⁵ for lithium-iron spinel. Also, the well-known low-temperature transition in magnetite^{1,6,7} is believed to be a result of the ordering of the divalent and trivalent atoms on the B sites. These effects, however, seem to be exceptions rather than the rule, so that the assumption of u_x and u_y as being constant is probably justified as a first approximation.

From Eqs. (4) we can obtain two simultaneous nonlinear equations in the distribution parameters x and y . They are

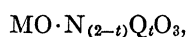
$$[1-A_x]x^2 + [1-A_x]xy + (1+(2-d)A_x)x + (1-d)A_xy - (1-d)A_x = 0, \quad (5a)$$

$$[1-(A_x/A_y)]xy - dx + (1-d)(A_x/A_y)y = 0, \quad (5b)$$

with $A_x = \exp(-u_x/kT)$.

Case B—Two Kinds of Trivalent Ions

Consider a spinel with the composition



where Q is a trivalent ion and t varies from 0 to 2. Let

⁵ P. B. Braun, *Nature* **170**, 1123 (1952).

⁶ L. R. Bickford, *Revs. Modern Phys.* **25**, 75 (1953).

⁷ S. Abrahams and B. Calhoun, *Acta. Cryst.* **6**, 105 (1953).

there be

$x\nu$	M^{++} ions on A sites,
$z\nu$	Q^{3+} ions on A sites,
$(1-x-z)\nu$	N^{3+} ions on A sites,
$(1-x)\nu$	M^{++} ions on B sites,
$(t-z)\nu$	Q^3 ions on B sites,
$(1-t+x+z)\nu$	N^{3+} ions on B sites.

By the same procedure as in Case A, we find that the equilibrium distribution is given by

$$x(1-t+x+z) = (1-x)(1-x-z) \exp(-u_x/kT), \quad (6a)$$

$$z(1-t+x+z) = (t-z)(1-x-z) \exp(-u_y/kT), \quad (6b)$$

or by

$$[1-A_x]x^2 + [1-A_x]xz + [1-t+2A_x]x + A_xz - A_x = 0, \quad (7a)$$

$$[1-(A_x/A_y)]xy + t(A_x/A_y) - z = 0. \quad (7b)$$

Numerical solutions of Eqs. (5) for various values of A_x and A_y and of Eqs. (7) for various values of A_x and A_y have been computed by Miss Elise Fisher of the Applied Mathematics Division of the U. S. Naval Ordnance Laboratory. Tables of these solutions may be obtained upon request from Miss Fisher.

A SUGGESTED METHOD OF DETERMINING CATION DISTRIBUTIONS

The cation distributions in both single and mixed ferrites may be determined experimentally (in principle, at least) by either x-ray or neutron diffraction.⁸⁻¹⁰ However, the x-ray and neutron diffraction methods become tedious and inaccurate if different types of ions have nearly equal scattering cross sections; this is especially true for mixed ferrites. We wish to suggest an alternate method of determining the ionic distributions of mixed ferrites (with three kinds of metallic ions) which should be reasonably accurate whenever the different kinds of ions have sufficiently different magnetic moments and g factors.

The Néel theory gives for the average net magnetic moment per molecule of a ferrite the relation

$$\mu = \mu_b - \mu_a, \quad (8)$$

where μ_b is the average net moment on two B sites and μ_a the average net moment on an A site. Tsuya¹¹ and Wangness¹² have recently derived an expression for the effective g value of a ferrite:

$$g = \mu / (S_b - S_a), \quad (9)$$

where S_b and S_a are the net average spins per molecule on B and A sites. Here μ is given in Bohr magnetons and

⁸ F. Bertaut, *Compt. rend.* **230**, 213 (1950).

⁹ G. E. Bacon and F. F. Roberts, *Acta. Cryst.* **6**, 57 (1953).

¹⁰ Corliss, Hastings, and Brockman, *Phys. Rev.* **90**, 1013 (1953).

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

¹² R. K. Wangness, *Phys. Rev.* **91**, 1085 (1953).

the S 's in units of \hbar . If we evaluate Eqs. (8) and (9) for absolute zero then μ_b , μ_a , S_b , and S_a all depend on the distribution parameters x and y , or x and z , in a simple linear fashion. Thus if experimental measurements on μ and g can be accurately extrapolated to 0°K , we have two simultaneous linear equations which can easily be solved for the distribution parameters.¹³

For example, in Case B, as mentioned, the equations would be

$$2(\mu_N - \mu_M)x + 2(\mu_M - \mu_Q)z = \mu - \mu_M + t(\mu_N - \mu_Q), \quad (10a)$$

$$2(S_N - S_M)x + 2(S_N - S_Q)z = \mu/g - S_M + t(S_N - S_Q). \quad (10b)$$

For a comparison with experiment, we shall consider the series $\text{NiO} \cdot \text{Fe}_{(2-t)}\text{Al}_t\text{O}_3$. Measurements of both μ and g have been made on this complete series at the U. S. Naval Ordnance Laboratory.

Before beginning the comparison, we note that there is an additional complication in that the Ni^{++} ion does not have the same magnetic properties on the A sites as on the B sites. Van Vleck¹⁴ has pointed out that the effect of crystalline electric fields in compounds of the transition elements is, first, to break up the spin-orbit coupling and, second, to at least partially lift the remaining orbital degeneracy. The extent to which the orbital degeneracy is raised depends on the ion and on the symmetry of the crystalline field but for Ni^{++} with $L=3$, the sevenfold degenerate orbital level is usually split into two adjacent triplets and a singlet. When the Ni^{++} ion has an octahedral coordination of surrounding negative ions, i.e., is on the B site, the singlet level lies lowest and is widely separated from the triplet levels. Penney and Schlapp¹⁵ have shown that in this case the magnetic moment and g factor have essentially the spin-only values with a relatively small correction which depends on the ratio of the spin orbit coupling parameter to the singlet-triplet separation. This case has been studied experimentally many different times with the results that $g_{\text{Ni}(\text{oct})} \cong 2.2-2.3$. (For Ni^{++} , $S=1$ and μ and g are numerically equal if μ is given in Bohr magnetons.)

For Ni^{++} with tetrahedral coordination, the multiplet is inverted with one of the triplet levels lying lowest; the problem here is complicated because the intratriplet separations are ordinarily not large compared to kT . In a cursory survey of the literature we were unable to find any detailed studies of this case; however Abragam and Pryce¹⁶ and Bleaney and Ingram¹⁷ have both made theoretical and experimental studies of a case which

should be similar—that of Co^{++} in a distorted octahedral coordination. Here they find that the g values are highly anisotropic and vary from about 3 to about 6. For our purposes, we shall assume that for polycrystalline samples of the Ni ferrite aluminates, such as have been studied experimentally, the relation

$$\mu_{\text{Ni}(\text{tet})} = g_{\text{Ni}(\text{tet})} S_{\text{Ni}} \quad (11)$$

holds. Here $\mu_{\text{Ni}(\text{tet})}$ is an average magnetic moment as determined from magnetization measurements and $g_{\text{Ni}(\text{tet})}$ is an average g value determined from magnetic resonance measurements. We shall expect that $g_{\text{Ni}(\text{tet})}$ may be relatively large, of the order of 3 or greater.

In order to obtain a value of $g_{\text{Ni}(\text{tet})}$ which is appropriate for the nickel ferrite-aluminate series, we have made use of the results of x-ray diffraction and susceptibility measurements which were carried out on $\text{Ni} \cdot \text{Al}_2\text{O}_4$ ($t=2$) at the U. S. Naval Ordnance Laboratory. Pickart and Greenwald¹⁹ have found from x-ray measurements that $x=0.15 \pm 0.03$ and $z=0.85 \pm 0.03$ for $\text{Ni} \cdot \text{Al}_2\text{O}_4$.† Grannis¹⁹ has measured the magnetic susceptibility from room temperature to 1500°C . The effective magnetic moment per molecule can be determined from the slope of the $1/\chi - T$ curve; then, using the measured values of x and z and assuming a specific value for $g_{\text{Ni}(\text{oct})}$, say 2.3, one can calculate $g_{\text{Ni}(\text{tet})}$. Actually, the $1/\chi - T$ curve for $\text{Ni} \cdot \text{Al}_2\text{O}_4$ is not a straight line, probably due to ferrimagnetic interactions and to variation of x and z with temperature. Thus we cannot get a precise value of the effective magnetic moment, but taking all the sources of error into account, it is still clear from the data that $g_{\text{Ni}(\text{tet})}$ is about 4.0. This value will be used in our calculations for all t ; it should be noted that the values of x and z calculated for the nickel ferrite-aluminates are not very sensitive to the exact value of $g_{\text{Ni}(\text{tet})}$ chosen, since a relatively small amount of nickel goes to the A sites in these compounds. Detailed accounts of the x-ray and susceptibility measurements will be published separately.

The Fe^{3+} ions are in S states; consequently, we expect them to show little deviation from spin-only behavior and to have essentially the same μ and g values in the A sites as in the B sites. We assume $\mu_{\text{Fe}}=5.0$ and $g_{\text{Fe}}=2.0$. The Al^{3+} ions of course have no magnetic moment.

With a slight generalization to take care of the two g values for Ni^{++} , we find that the form of Eqs. (10) appropriate to the nickel ferrite-aluminate series is

$$3.7x + 10z = \mu + 5t - 2.30, \quad (12a)$$

$$3x + 5z = \mu/g + 5t/2 - 1.00. \quad (12b)$$

¹³ A method essentially the same as this has been proposed independently by E. W. Gorter, *Nature* **173**, 123 (1954). We are indebted to Dr. Gorter for communicating his results to us prior to publication.

¹⁴ J. H. Van Vleck, *Phys. Rev.* **41**, 208 (1932).

¹⁵ W. G. Penney and R. Schlapp, *Phys. Rev.* **42**, 666 (1932).

¹⁶ A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **206**, 173 (1951).

¹⁷ B. Bleaney and D. J. E. Ingram, *Nature* **164**, 116 (1949); *Proc. Roy. Soc. (London)* **208**, 143 (1951).

¹⁸ S. J. Pickart and Selma Greenwald (private communication).

† *Note added in proof.*—F. C. Romeijn, Philips Research Repts. **8**, 321 (1953) gives $x=0.24$ for NiAl_2O_4 . We have considered only the value obtained by Greenwald and Pickart since their measurements were made on the samples whose properties are listed in Table I.

¹⁹ F. H. Grannis and T. R. McGuire (private communication).

TABLE I. Ionic distribution parameters for $\text{NiO} \cdot \text{Fe}_{(2-t)}\text{Al}_t\text{O}_3$.

t	μ	g	μ/g	x	z
0.00	2.12	2.35	0.90	-0.01	-0.02
0.25	1.14	2.7	0.42	0.00	0.01
0.50	0.58	5.3	0.11	-0.03	0.09
0.63	0.15	-3.8	-0.04	0.03	0.09
0.75	-0.22	1.6	-0.14	0.10	0.08
0.85	-0.39	1.6	-0.24	0.09	0.12
1.00	-0.58	1.5	-0.39	0.04	0.20
1.25	-0.44	1.5	-0.29	0.07	0.33
1.50	-0.11	1.55	-0.07	0.12	0.47
1.75	-0.07	1.6	-0.04	0.13	0.59

Table I shows the experimental μ and g values (extrapolated to 0°K) and the values of x and z calculated therefrom with the aid of Eqs. (12). The data were taken on samples which had been cooled from 1400°C at the rate of 1°C/min. The g values were measured at a frequency of 9240 Mc/sec. It should be noted that the experimental measurements do not give the sign of either μ or g ; these must be deduced indirectly. It is believed that the above choices are correct for reasons which will be discussed in the experimental papers on the nickel ferrite-aluminate series.²⁰

In Fig. 1, x and z are plotted as functions of t ; the indicated errors were estimated very crudely and are probably too small if anything. The solid line shows theoretical values of x and z calculated from Eqs. (7) for $A_x=0.02$, $A_z=0.08$. A detailed agreement between the experimental and theoretical values would be expected only if u_x and u_z were independent of t as well as x and z . However, it is of interest to note that for both cases (x vs t and z vs t) the experimental and theoretical curves show the same shapes.

There is some question as to whether the data for $t=1.50$ and 1.75 should be used for calculating x and z since it seems likely that in this region $\mu(0)$ may not be the difference in magnetization of a saturated B lattice and a saturated A lattice. For example, the triangular arrangements studied by Yafet and Kittel²¹ may occur. However, for the particular case of nickel ferrite-aluminates, μ and μ/g for large t are both small compared to the other terms on the right-hand side of Eqs. (12); thus a relatively large percentage error in μ will not change x and z very much. It is seen that x and z for $t=1.50$ and 1.75 agree well with the trend of the values for smaller t .

In regard to agreement with experiment, the values of x and z calculated from Eqs. (12) are certainly of the

right order of magnitude for all values of t . In addition, there is good agreement with the results of Pickart and Greenwald¹⁸ for the two cases where they have made measurements ($t=1.0$ and 1.75). We believe that the over-all results indicate that the suggested method may be used to give reasonably accurate values of the distribution parameters in mixed ferrites.

It should be mentioned in conclusion that resonance measurements on the nickel ferrite-aluminate series were made at 20 800 Mc/sec as well as 9240 Mc/sec and that the g values did show a slight frequency dependence. This discrepancy was not enough to cause any significant error in the calculation of x and z . However, preliminary measurements on the series $\text{NiO} \cdot \text{Fe}_{(2-t)}\text{Ga}_t\text{O}_3$ indicate that there is a large fre-

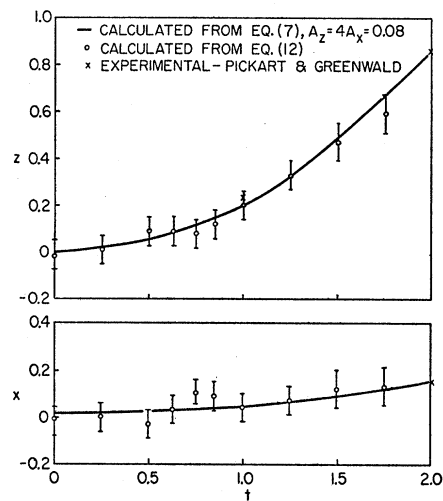


Fig. 1. The circled points are values of x and z calculated from Eqs. (12) with the data from Table I. The solid lines are theoretical curves calculated from Eqs. (7) for $A_x=0.02$, $A_z=0.08$. The \times points are the experimental values observed by Pickart and Greenwald.

quency dependence of g values here; the values taken at 20 800 Mc/sec seem to give better agreement with experiment than do the 9240-Mc/sec values. A detailed report of this apparent frequency dependence and its interpretation will be made in a future publication of the U. S. Naval Ordnance Laboratory Solid State Division.

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²⁰ L. R. Maxwell and S. J. Pickart, Phys. Rev. **92**, 1120 (1953); T. R. McGuire, Phys. Rev. **93**, 682 (1954).

²¹ Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).