

It is certain that the long tail of the peak extends far beyond the critical field, so that there is extra flux in the sample after the sample has become normal conducting according to the Silsbee hypothesis. London⁶ found a similar tail for the resistance approach to normal resistance when the transition is made with current alone in zero field. Theoretical description of the paramagnetic flux behavior beyond the peak is not available.

In conclusion one notes the similarity in behavior of the superconducting metals tested, and the agreement with Meissner's theory, at least beyond the threshold.

These facts support the argument that the effect is a property of the intermediate state. The fast response time coupled with the reversible nature of the transition again emphasizes the dependence on current and field, not on method of measurement or history of the specimen.

ACKNOWLEDGMENTS

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Ordering and Antiferromagnetism in Ferrites

P. W. ANDERSON

Bell Telephone Laboratories, Murray Hill, New Jersey

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The octahedral sites in the spinel structure form one of the anomalous lattices in which it is possible to achieve essentially perfect short-range order while maintaining a finite entropy. In such a lattice nearest-neighbor forces alone can never lead to long-range order, while calculations indicate that even the long-range Coulomb forces are only 5% effective in creating long-range order. This is shown to have many possible consequences both for antiferromagnetism in "normal" ferrites and for ordering in "inverse" ferrites.

I. LATTICE OF OCTAHEDRAL SITES

THE ferrites are a class of oxides of iron-group metals, many of them of technical importance as ferromagnets, which crystallize in the spinel structure or structures closely related to it. The ideal ferrite has the formula AB_2O_4 (e.g., $NiFe_2O_4$) and the smaller metal ions A and B occupy certain interstices between the large oxygen ions, which latter are arranged in an approximation to the cubic close-packed structure.

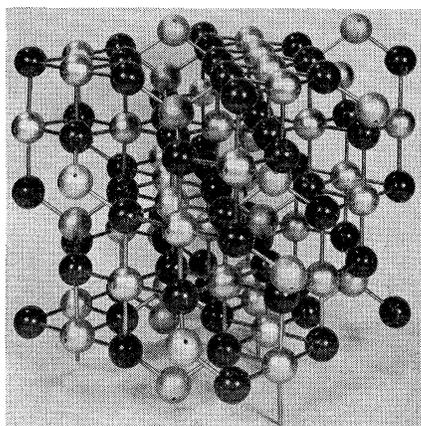


FIG. 1. Photograph of a model of the spinel lattice. The dark balls are oxygen; the tetrahedral sites are connected to their neighboring oxygens by four diagonal bonds, the octahedral by six vertical and horizontal ones.

The structure is shown in Fig. 1.¹ The distortion of the lattice of oxygen ions is such that a cell of 32 oxygens has cubic symmetry again. There are, for each oxygen, one interstice surrounded by an octahedron of oxygen and two surrounded by a tetrahedron; half of the former and only one-eighth of the latter are occupied by metal ions. This means that in the unit cell there are 8 "tetrahedral sites" and 16 "octahedral sites."

In a "normal" spinel, the 8 A ions occupy the 8 tetrahedral sites, the 16 B ions the octahedral ones. In an "inverse" spinel, 8 of the B ions occupy the tetrahedral sites, the other 8 and the 8 A 's occupying the octahedral sites. Ferrites are known which range all the way from purely normal to purely inverse. We are here interested in two problems, both having to do with ordering on the octahedral sites: (a) the problem of atomic ordering in inverse ferrites; (b) in normal ferrites with small or no magnetic moments on the A ions, the problem of antiferromagnetic ordering of spins.

To attack these problems we need to study carefully only the crystal lattice of the magnetic ions, particularly that of the octahedral sites. The occupied tetrahedral sites form a diamond-type lattice, the octahedral sites (see Fig. 2) a somewhat more complex cubic lattice which could be generated from this tetrahedral site lattice by displacing it through half the cube edge and then placing an atom at the center of each bond,

¹ T. F. W. Barth and E. Posnjak, *Z. Krist.* **82**, 325 (1932).

rather than at the original sites. The lattice of octahedral sites is thus identical with the lattice of oxygen atoms in high-temperature cristobalite.

The fact the consequences of which we wish to explore in this paper is the following: on this lattice one can create perfect order, in so far as nearest neighbors are concerned, and nonetheless have a finite entropy; in other words, assuming nearest neighbor interactions only, one can find a number W of configurations of $N(x)$ A atoms and $N(1-x)$ B atoms which all have the lowest possible energy, W being such that $\ln W$ is proportional to N . This statement can be proved explicitly when x is $\frac{1}{2}$ or less than or equal to $\frac{1}{4}$ (correspondingly, also $\geq \frac{3}{4}$) and seems likely to be true for all other values *a fortiori* since $\frac{1}{2}$ and $\frac{1}{4}$ are the values at which the best-looking long-range ordered arrangements occur.

II. THE ZERO-POINT ENTROPY

Of course neither of our two problems corresponds exactly to the situation in which this lattice can be shown rigorously to have a zero-point entropy. This situation is essentially the Ising model with only nearest neighbor forces. In the problem of ordering of metallic ions in the octahedral sites, one can expect the Ising model to be statistically sound, since there are only two states of each site, and the problem is essentially classical; but the interaction is not only between nearest neighbors because a large fraction of it is Coulomb energy.² However, we shall later show that the Coulomb energy of the different structures of perfect short-range order does not differ by very much; in particular, we calculate explicitly the energies of a class of structures containing $2^{N^{\frac{1}{2}}}$ members and find them all within 5% of the lowest. Thus there will be considerable meaning to a calculation of the zero-point entropy in this case.

In the case of antiferromagnetic ordering, the interaction will probably be short-range, because of the rather large distances and long chains of atoms connecting those B -sites which are not nearest neighbors; however, the counting of states and the whole statistical problem will be complicated by the fact that spins are quantum-mechanical vectors and not classical scalars as in the Ising model. Thus we have no hope of making quantitative estimates of zero-point entropy in this case. However, two lines of evidence indicate that nonetheless most lattices which have zero-point entropy in the Ising model will also be at least disordered at absolute zero in the real quantum theory of antiferromagnetism. First, if one thinks of the spins as classical vectors these lattices usually have an even greater zero-point entropy due to the extra freedom of rotation.³

² de Boer, van Santen, and Verwey, *J. Chem. Phys.* **18**, 1032 (1950).

³ Not quite always; the triangular lattice [G. H. Wannier, *Phys. Rev.* **79**, 357 (1950)] is an exception in which one can find an ordered configuration of real vectors.

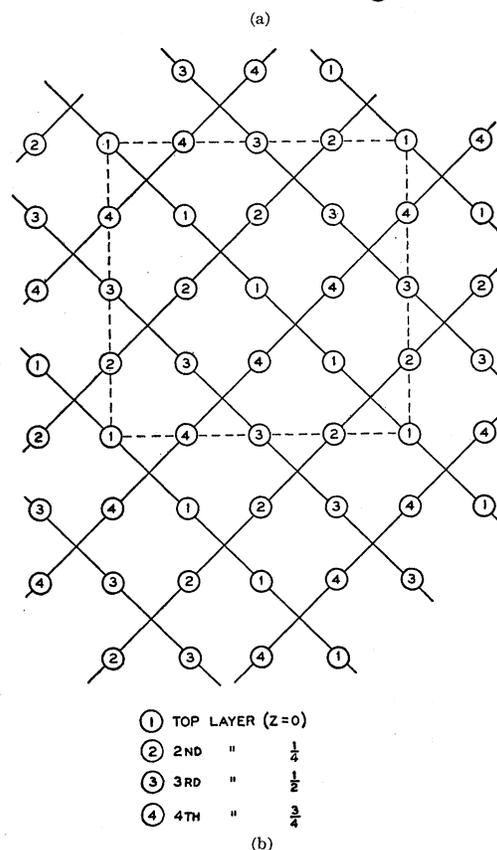
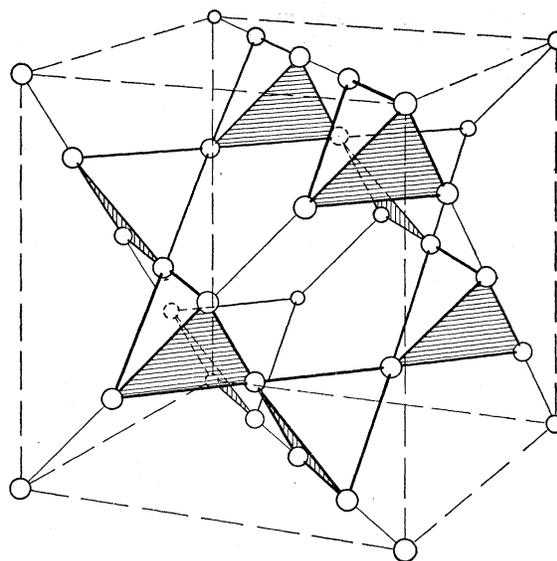


FIG. 2. (a) Perspective view of the lattice of octahedral sites in spinel; (b) Projection of octahedral site lattice on (100) plane.

Second, Stern⁴ has shown that the antiferromagnetic spin wave theory indicates that such systems will not order.

⁴ F. Stern, *Phys. Rev.* **94**, 1412 (1954).

In this section, then, we present some results relating to the Ising model ordering problem, as applied to the lattice of octahedral sites of the spinels.

First we discuss the 50-50 problem: $x = \frac{1}{2}$. Here we find that our problem is very closely related to the old problem of the zero-point entropy of ice. The lattice we are discussing can be seen to be made up of tetrahedra of sites connected at their corners [see Fig. 2(a)]. These tetrahedra are themselves arranged in a diamond lattice. If, instead, they were arranged in a lattice of hexagonal symmetry (as in high-temperature quartz rather than cristobalite) the resulting lattice would be identical with ice. We have, then, a lattice which we might call "cubic ice."

We wish to put on our sites an equal number of + and - signs, in such a way that we get the maximum number of +-pairs. This can easily be seen to be possible only by putting on each tetrahedron two +'s and two -'s; if any tetrahedron has three +'s and one -, or vice versa, the effect is merely to substitute one like pair for one unlike pair, which of course is unfavorable.

In ice, the corresponding criterion of the Pauling theory⁵ is that two of the protons be near the oxygen (which is at the center of the tetrahedron) and two farther away. This seems very similar and is actually an identical criterion, for one can divide the tetrahedra of our lattice into two sets with opposite orientations such that all those in one set touch only those in the other. Then let the +'s on one set mean "proton near the oxygen atom," and vice versa for the other set, and the identity of the two problems is obvious.

Pauling has estimated the entropy in the ice problem, and since this estimate is immediately applicable here and since we shall use a similar method later we repeat his derivation. If we take only one of the two sets of tetrahedra (both contain $N/4$ members, where N is the number of sites of the lattice), we can make $6^{N/4}$ arrangements satisfying the condition that two + and two - be on each, since there are 6 arrangements of each tetrahedron.

Now we approximate the number of these that are acceptable to the second set of tetrahedra by saying that the probability that any one of these tetrahedra is correct is $\frac{3}{8}$ (as it is) and that the probabilities of different ones are uncorrelated (as they are not). Then we have

$$W_{x=\frac{1}{2}} = \left(\frac{3}{8}\right)^{N/4} (6)^{N/4} = \left(\sqrt{\frac{3}{2}}\right)^N, \quad (1)$$

$$S_{x=\frac{1}{2}} = k \ln W = R \ln \left(\sqrt{\frac{3}{2}}\right) = 0.202R. \quad (2)$$

(Note that all entropies quoted in this paper are per mole of octahedral sites, which is $\frac{1}{2}$ mole of ferrite.) Onsager⁶ has proved rigorously that this estimate is actually a lower limit; one might estimate that it is probably no more than 10-20% wrong.

⁵ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1938), p. 303.

⁶ L. Onsager (private communication).

The case of $x = \frac{1}{4}$ is also of special interest since lithium ferrite (LiFe_3O_8) corresponds to this, and is actually one of the few ferrites which do have long-range order. One can here set a rigorous lower limit (see Appendix I) of $S > 0.081R$. Pauling's method gives $S = 0.131R$, and is probably again an underestimate by a small factor. This answer is obtained as follows:

The first set of tetrahedra has $4^{N/4}$ configurations of 1+ and 3-. The probability of any single one of the second tetrahedra then being 1+ and 3- is $4\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)^3 = \left(\frac{3}{4}\right)^3$. In the spirit of Pauling's technique, we reduce the total number of configurations by this factor for each tetrahedron. Then

$$W = \left(\frac{3}{4}\right)^{3N} \times 4^{N/4}, \quad (3)$$

$$S = \frac{1}{4}R \ln(27/16) = 0.131R.$$

For values of x less than $\frac{1}{4}$, the zero-point entropy is obviously finite. We can find (actually in an infinite number of ways) a set of $N/4$ sites, none of which are neighbors of each other. We have xN atoms to assign to these sites, which can be done in

$$\left(\frac{1}{4}N\right)! / \left[\left(\frac{1}{4}N - Nx\right)!(Nx)!\right]$$

ways. The logarithm of this number is proportional to N .

Values in this range, as well as in the range $\frac{1}{4} < x < \frac{1}{2}$, are not of particular interest, although it is almost certain that all possible values of x lead to a zero-point entropy. This is the major conclusion of this section.

III. THEORY AND EXPERIMENT ON ATOMIC ORDERING

If the forces between atoms in ferrites were short-range, we should predict that there would be no cases of long-range ordering on the octahedral sites, but rather that short-range order should set in at a rather high temperature. However, some of the forces are Coulomb ones and no doubt there are other forces of longer than nearest neighbor range.

We have calculated Coulomb ordering energies of various structures with $x = \frac{1}{4}$ and $\frac{1}{2}$ in order to verify our guess, based on the last section, that there should not be a very great Coulomb energy difference between the different structures of perfect short-range order. In Fig. 3 is shown the ordered structure postulated by Verwey, Haayman, and Romeyn⁷ for Fe_3O_4 (again showing only the octahedral sites). The lattice of octahedral sites, when visualized from a 100 direction, can be seen to be made up of lines of atoms laid down in 011 directions. The lines in the same 100 planes are exactly twice as far apart as their own internal spacing, which is $d = a/2\sqrt{2}$, a being the cubic unit cell edge. In successive 100 planes of the cell these lines lie at 90° to each other: 011, 0 $\bar{1}$ 1, 01 $\bar{1}$, etc.; while the lines two planes apart fall in the spaces of the previous set. In

⁷ Verwey, Haayman, and Romeyn, *J. Chem. Phys.* **15**, 181 (1947).

two of the possible sets of 100 planes these lines of the reference 7 ordered structure are alternating *ABAB* etc.; they also have a particular relationship to each other (lines of the same 100 plane "in phase," i.e., *A* closest to *A* and *B* to *B*). It is easily seen, however, that any structure made up from a set of 011 and $\bar{0}\bar{1}\bar{1}$ alternating lines having any relative phase whatever is one of the short-range ordered structures for $x = \frac{1}{2}$. These do not make up all short-range ordered structures, but only a set of $\sim 2^{N^{\frac{1}{2}}}$ of them, since there remains only the freedom to choose one 100 plane of the lattice arbitrarily.⁸ The Coulomb energies of this set of structures can be quite accurately calculated by the original Madelung method.⁹

In the Madelung method, one divides the lattice into neutral lines of atoms and calculates both the self-energy and the potential at external points of these lines. This potential falls off rapidly with distance, making it easy to sum up the interactions of the lines with each other to rather good accuracy. In the present case the method is particularly suitable because the lines in successive planes do not interact, since they cross each other exactly half-way between the two kinds of charges. Thus it is only next-nearest neighboring lines which interact; third nearest again do not and further neighbors can be neglected.

The self-energy of ordering of the lines is, for ordering of charges q_1 and q_2 and on the same basis (per molecule, i.e., pair of octahedral sites) as reference 1,

$$E_{\text{self}} = -[(q_1 - q_2)^2 / 2d] \ln 2 \\ = -0.9802(q_1 - q_2)^2 / a. \quad (4)$$

The potential caused by an alternating line at a distance nd directly opposite one of the positive atoms of the line can be written, to three-figure accuracy,

$$\varphi_{\text{opp}} = (4/d)K_0(n\pi). \quad (5a)$$

Each line has 6 next-neighbor lines with which it can interact, two at $n=2$ in its own 100 plane and four at $n=\sqrt{3}$ in the next-neighbor plane. At most four can be (on the average) opposite in sign; the most favorable case is that in which these are all the $n=\sqrt{3}$ lines, which happens to be the order of reference 7 (Fig. 3). One can show by adding up expressions of the form (5a) that the additional energy is then

$$(E_{\text{inter}})_{\text{min}} = -0.0206(q_1 - q_2)^2 / a, \quad (5b)$$

leading to a total energy

$$E_{\text{tot}} = -1.001(q_1 - q_2)^2 / a \quad (6)$$

in accordance with reference 1. The most unfavorable case is that of all lines "in phase," which has an

⁸ Not in the structure of reference 7, but in all others, one finds hexagons of alternating *A* and *B*, in general a number of order N of them. These may be rotated through 60° without changing short-range order. These two operations (sliding lines and turning hexagons) probably generate all possible structures.

⁹ E. Madelung, *Physik. Z.* **19**, 524 (1918).

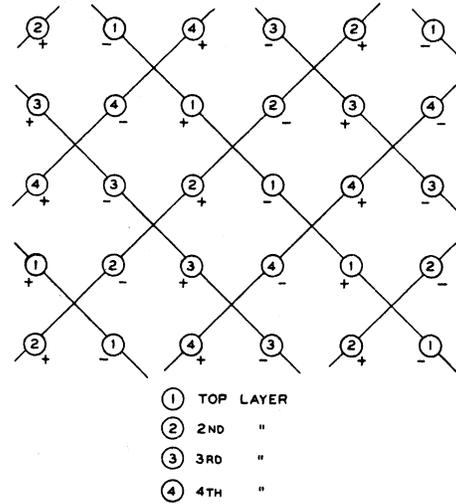


FIG. 3. The Verwey-ordered structure on the octahedral sites (projected on 100 plane).

energy of

$$(E_{\text{inter}})_{\text{max}} = +0.0310(q_1 - q_2)^2 / a, \quad (7)$$

with a total of -0.9492 . All of the $2^{N^{\frac{1}{2}}}$ structures it is possible to make out of alternating lines lie between these limits and thus within 5% of the minimum; one suspects that actually the remainder also lie primarily in this range.

The total ordering energy (6) is of order of magnitude 2–3 eV, i.e., $> 10^4$ K. The extra energy to be gained by long-range order is, however, of order a few percent of this or 500–1000 degrees K. This may be still further reduced by polarization screening effects, so that the transition temperature 100° K for Fe_3O_4 is not surprising.¹⁰ However, it seems certain that Fe_3O_4 will be short-range ordered far above the transition temperature. In fact the observed entropy change in the transition has been found to be little more than $0.3R$ ¹¹ per mole of octahedral sites rather than the $R(\ln 2) = 0.69R$ to be expected in a transition from complete disorder to complete order, in rough agreement with Eq. (2). Long-range ordering on the octahedral sites is observed in no other AB_2O_4 inverse ferrite, although the normal *vs* inverse ordering, with its only slightly larger motivation in Coulomb energy, often occurs. This fact is probably explained by the above considerations: that the energy to be gained by long- as opposed to short-range ordering is very small, while the entropy change is still large. (We appeal here to the qualitative relationship $T_c \propto \Delta u / \Delta s$.) Thus the transition temperatures are too low and the ions are not mobile enough to permit ordering.

There does exist one proven case of atomic ordering

¹⁰ J. H. Van Santen, *Philips Research Repts.* **5**, 282 (1950), has shown that Coulomb and other long-range effects should in any case tend to create short- rather than long-range order and to lower transition temperatures. It is however not clear whether our considerations are logically independent of Van Santen's, so that we do not rely on his effect.

¹¹ J. E. Kunzler (private communication).

on the octahedral sites: the ferrite LiFe_5O_8 , which has been shown¹ to have 1 Li to 3 Fe ordered on these sites and to have a transition at 1200°K. The ordering energy of the observed arrangement has been computed elsewhere¹ to be

$$E_{\text{obs}} = -0.712(q_1 - q_2)^2/a. \quad (9)$$

In Appendix II we calculate the energies, not of this but of a group of structures of multiplicity 2^{N^3} included among the linearly ordered structures. All of these structures have lower Coulomb energies than (9), the lowest being

$$E_{\text{min}} = -0.751(q_1 - q_2)^2/a, \quad (10)$$

some 5% below (9). This indicates that Coulomb energy is not the motivation for the long-range ordering, which suggests that perhaps some kind of valence force is at work here due to the chemical dissimilarity of Li and Fe. Under these circumstances we do not consider it too surprising that the transition temperature is so much higher than that of Fe_3O_4 , since these unknown forces are clearly in control of the situation.

IV. ANTIFERROMAGNETISM ON THE OCTAHEDRAL SITES

Our comments on this subject are necessarily very brief and qualitative, both because (as already mentioned) the theory cannot apply directly to quantum-mechanical vectors and because the observational data are sketchy and unclear.

First we should emphasize that the present notions cannot, unfortunately, help to explain the complex patterns observed by Corliss and Hastings¹² for ZnFe_2O_4 and ZnCr_2O_4 since in these substances what short-range order exists points to a ferromagnetic nearest-neighbor interaction.

For classical vectors with nearest neighbor interaction, instead of the 6 best ways of arranging each tetrahedron there are an infinity: all ways in which $S_{\text{tot}} = 0$. For quantum-mechanical vectors S , there are only $2S+1$, but of course the situation is much more complicated than that. One can only expect that for reasonably large S the classical behavior is not too badly approximated. If so, the least-energy state may be any complicated combination of vectors pointing in various directions, with actual long-range order only enforced by what one expects to be rather small second-neighbor forces.

Antiferromagnetism in the octahedral sites has been invoked in the theory of Yafet and Kittel,¹³ which suggests that with antiferromagnetic coupling on the octahedral sites and a relatively weak coupling of these with the tetrahedral sites, the octahedral sites will remain antiferromagnetically ordered but will turn to some extent into the direction opposite to the tetrahedral sites, thus giving a total magnetization which

however will not be related simply to the atomic moments. We suggest that this phenomenon may occur but that the order on the octahedral sites will be, at least at higher temperatures, short- rather than long-range.

ACKNOWLEDGMENTS

I am indebted to Professor L. Onsager for an interesting and helpful discussion of these problems, and to L. Corliss and J. Hastings for early discussions of their results.

APPENDIX I. RIGOROUS LOWER LIMIT TO THE ZERO-POINT ENTROPY IN THE 3-1 CASE

We here exhibit a group of ordered states of the 3-1 order problem on the octahedral sites which have an entropy $0.0809R$. In order to do this it is useful to look at the lattice from still another viewpoint, along a 111 axis. In the 111 direction there are planes of atoms in a triangular lattice of triangle edge $2d$, interspersed between denser planes (3 times as many atoms) which have the so-called "kagomé" lattice.¹⁴ Figure 4 shows this lattice with the atoms in the two adjoining planes. Note that each small triangle in the kagomé lattice is associated with an atom in one of the two neighboring planes, either above or below the plane; these triangles and the atoms associated with them form tetrahedra which must contain three A and one B atom apiece to satisfy the perfect nearest neighbor ordering.

Our set of states are those in which, in all of these tetrahedra, the B atom is in the triangle belonging to the Kagomé lattice. Figure 5 shows a small portion of the Kagomé lattice having this structure: A_2B . Now we associate with the points at the centers of the large hexagons of the Kagomé lattice plus or minus signs according to the rule that every A atom represents a $+$ bond, every B a $++$ or $--$. That this rule works is clear from Fig. 5. These $+$ and $-$ form a triangle lattice in the perfect antiferromagnetic order; and from any arrangement of such a lattice we can make a perfect arrangement of the A_2B kagomé lattice. But the zero-point entropy of the triangular lattice has been calculated by Wannier^{3,15} to be

$$(S_0)_\Delta = 0.323R, \quad (A1)$$

so that, since there is one triangle site to every four octahedral sites, we get the zero-point entropy of our set of states to be

$$S_{\text{oct}}(A_2B) > \frac{1}{4}S_\Delta = 0.0809R. \quad (A2)$$

This is the result quoted in the text.

¹⁴ G. F. Newell and E. Montroll, *Revs. Modern Phys.* **25**, 373 (1953).

¹⁵ J. Wahl has pointed out that due to a trivial error in the last step the final numerical result for S_0 in Wannier's paper is $0.323R$, not $0.338R$.

¹² L. Corliss and J. Hastings (private communication).

¹³ Y. Yafet and C. Kittel, *Phys. Rev.* **87**, 290 (1952).

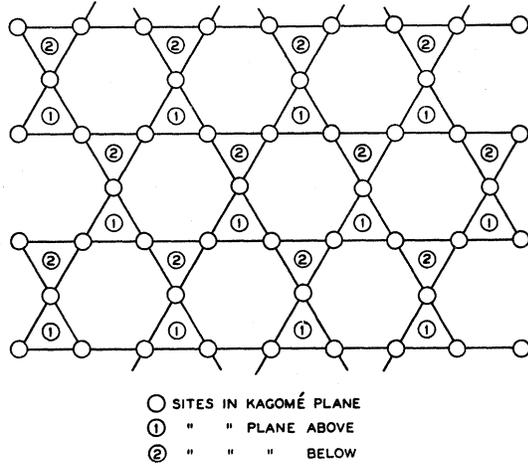


FIG. 4. (111) projection of the lattice of octahedral sites, showing the "kagomé" plane lattice and adjacent sites.

APPENDIX II. COULOMB ENERGIES OF SOME STATES OF THE 3-1 CASE

We calculate here the Coulomb energies of a still different set of states of the A_3B case. This set of states resembles those of the AB case which we investigated in Sec. III very closely. In fact, we again divide the lattice into lines in 011 and $0\bar{1}1$ directions. However, we make only one set of lines alternating, the other set being all A . This gives us a 3-1 ratio and makes the nearest neighbors of all B atoms A . Again we can expect that the best arrangement will put coplanar lines in phase, those out of the plane and only $\sqrt{3}d$ away out of phase. This happens to be the ordered situation one gets by taking the triangular lattice planes of Appendix I to be B and all of the Kagomé planes A . We should mention that the ordered structure observed by Braun¹ for LiFe_5O_8 belongs to neither this group nor to that of Appendix I; we stated in the text that its Coulomb energy is quite poor.

Our technique now is to make A be a charge of -1 , B of $+3$ (we must have a neutral lattice to get convergent answers). We can eliminate the contribution of the all- A lines by a trick. We consider the $ABAB$ lines to be the superposition of $+1 +1 +1 \dots$ and

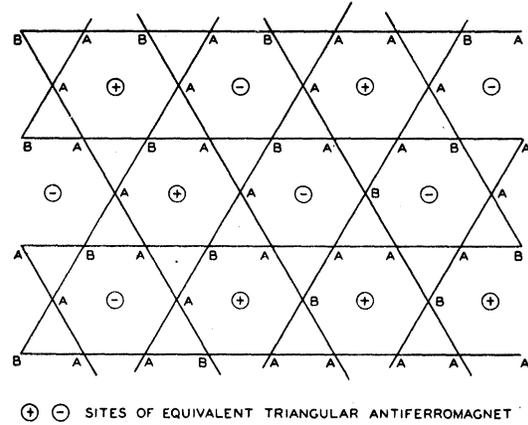


FIG. 5. A portion of the kagomé lattice with A_2B ordering and the equivalent triangular lattice.

$$+2 -2 +2 \dots$$

$$\begin{aligned}
 &3-1 \quad 3-1=1 \quad 1 \quad 1 \quad 1 \\
 &\quad \quad +2-2 \quad 2-2 \\
 &\quad \quad \quad = q_1 + q_2.
 \end{aligned} \tag{A3}$$

The all- A lines have charges $-1 = q_3$. q_1 and q_3 taken together are simply the ordered arrangement of Fe_3O_4 , and have an energy

$$E_{q_1, q_3} = -(1.001/a) \times (2)^2 \tag{A4}$$

per pair of sites. The alternating arrangement q_2 simply does not interact with either q_1 or q_3 because in both cases there are as many $+-$ as $++$ pairs at any distance. Thus Eq. (A4) gives the entire contribution including self-energy of q_1 and q_3 .

The energy of q_2 is simply exactly the same thing we calculated in Sec. III, except that there are only half as many sites and $(\Delta q)^2 = 16$. It depends on the relative phasing of the lines and varies from

$$E_{q_2 \text{min}} = -(1.001/a) \times (16/2), \tag{A5}$$

to

$$E_{q_2 \text{max}} = -(0.949/a) \times (16/2),$$

so that for the whole lattice we add (A4) and (A5) and take into account that the charge difference is 4; we get

$$\begin{aligned}
 E_{\text{min}} &= -(0.751/a)(\Delta q)^2, \\
 E_{\text{max}} &= -(0.725/a)(\Delta q)^2.
 \end{aligned} \tag{A6}$$

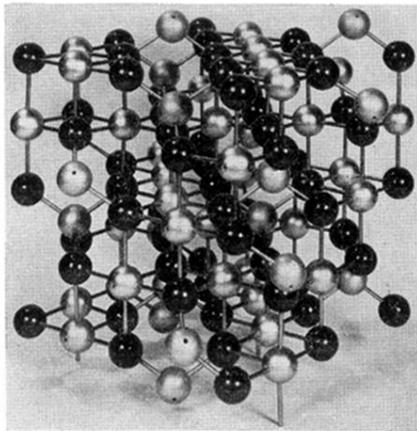


FIG. 1. Photograph of a model of the spinel lattice. The dark balls are oxygen; the tetrahedral sites are connected to their neighboring oxygens by four diagonal bonds, the octahedral by six vertical and horizontal ones.