

ticular equilibrium position. The effective local anisotropy thus contains in addition to hidden canting contributions also contributions from anisotropic exchange and higher-order terms of the single-ion anisotropy. This can result in a complicated temperature dependence and considerable caution is required in applying a physical interpretation to the data.

### V. CONCLUSION

A complete derivation of the resonances and susceptibilities has been presented, for the various possible magnetic ground states in orthoferrites. The results show a dependence not only on overt canting but also on the hidden canting mechanism. When the anisotropy energy is small compared to the antisymmetric exchange, it is possible to describe the low-frequency behavior on the basis of a formal 2-sublattice model, employing an effective anisotropy energy which includes hidden contributions of an exchange character. At low

frequencies hidden canting cannot be observed directly, but its indirect effect may be noticed in the temperature dependence of measured parameters.

The chief observable effects associated with hidden canting is the susceptibility of the exchange resonances. In a purely antiferromagnetic configuration these modes would be optically inactive. Hidden canting introduces a coupling between exchange modes and antiferromagnetic modes, which result in optical activity of the former.

In general, one may conclude, that out of the large number of coefficients which play a role in the interactions among the four magnetic sublattices, only relatively few are susceptible to macroscopic observation.

### ACKNOWLEDGMENT

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## Low-Temperature Behavior of a Face-Centered Cubic Antiferromagnet

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A detailed description of the ground state of a face-centered cubic antiferromagnetic system with Ising interactions is followed by an investigation of the low-temperature thermodynamic properties by means of a power series expansion of the partition function about  $T=0^\circ\text{K}$ . This expansion has been found to be possible even though the ground state is degenerate because of the existence of a substantial amount of "partial long-range order." Expressions for the zero-field magnetic susceptibility and the specific heat are derived.

### INTRODUCTION

THE low-temperature thermodynamic properties of magnetic spin systems with Ising interactions have been investigated by means of series expansions (for a review, see Ref. 1). The general principle is that at low temperatures the partition function can be expanded in terms of successive deviations ('excited states') from an ordered ground state. This has not hitherto been possible in the case of a face-centered cubic system, because it does not have an ordered ground state when nearest-neighbor interactions only are present. In a previous communication,<sup>2</sup> the present author determined the degeneracy of the ground state of such a system and gave a complete classification of the ground-state configurations. As a result it is found that, although the ground state is degenerate, there exists a

substantial amount of "partial long-range order" which makes it possible for the partition function to be expanded in the usual manner to a limited number of terms. In the following section the ground state of the face-centered cubic system is discussed further; subsequently some of the excited states are evaluated and expressions for the zero-field magnetic susceptibility and specific heat derived.

### II. THE GROUND STATE

We first give a summary of the results reported in Ref. 2 concerning the ground state of a face-centered cubic antiferromagnetic system of  $N$  spin moments each having two possible states ( $\pm$ ). First, the energy of the ground state is  $-2NJ$ , where  $+J$  is the interaction energy between neighboring parallel spins ( $++$ ,  $--$ ) and  $-J$  the interaction energy between neighboring antiparallel spins ( $+-$ ). Second, the configurational state of any one triangular layer of the lattice determines uniquely the configurational state of the whole

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<sup>1</sup> C. Domb, *Phil. Mag.* **9**, Suppl. **34**, 149 (1960).

<sup>2</sup> A. Danielian, *Phys. Rev. Letters* **6**, 670 (1961).

lattice. Third, the number of configurational possibilities within the triangular layer itself is severely restricted, not only because each spin has to be at the center of one of two types of cluster,  $\alpha$  or  $\beta$  [see Figs. 1(a) and 1(b)] but in addition, the existence of a single  $\alpha$  cluster determines that the whole row along a certain axis also consists of  $\alpha$  clusters. As a consequence, each triangular layer consists of rows of  $\alpha$  or  $\beta$  clusters; hence, the degeneracy of the lattice is of the order  $2^R$ ,  $R=N^{1/3}$ . Fourth, both the magnetic susceptibility and the entropy per spin vanish at  $T=0^\circ\text{K}$ .

The interesting feature of this case is that, although the system does not order, both the magnetic susceptibility and the entropy per spin vanish at  $T=0^\circ\text{K}$ . This is not so in the other case where an exact analysis of a degenerate ground state is available, namely that of the triangular lattice<sup>3</sup>; here at  $T=0^\circ\text{K}$ , the entropy per spin is finite and the susceptibility infinite.<sup>4</sup> The marked difference between the thermodynamic properties of the two lattices at  $T=0^\circ\text{K}$  must be due to the existence of a substantial amount of "partial long-range order" in the ground state of the face-centered cubic lattice, as described by the second and third points of the preceding paragraph. The difference in the ground states of the two lattices is seen by noting that if the number of sites on the triangular layer is  $n$ , then the degeneracy of the triangular lattice is of the order  $2^{0.47n}$  (Ref. 3) but that of a triangular layer in the face-centered cubic lattice is  $2^n$  (Ref. 2). It is therefore clear that there is more order in the ground state of the face-centered cubic lattice than in that of the triangular.

The precise extent of the order existing in the ground state of the face-centered cubic lattice is shown as follows: the  $\alpha$  cluster [Fig. 1(a)] has two mutually perpendicular axes  $XOX'$  and  $YOY'$ , along which all clusters in the lattice must be  $\alpha$  clusters (see Ref. 2). As

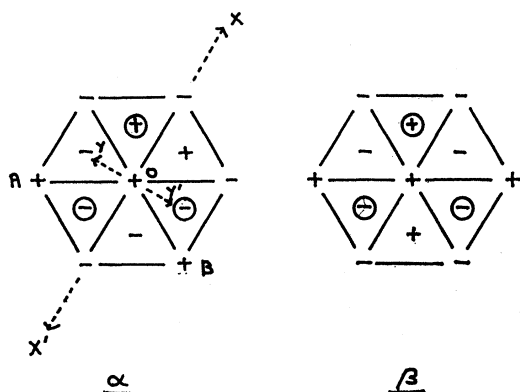


FIG. 1. The  $\alpha$  and  $\beta$  clusters of the ground state of the face-centered cubic lattice. Three successive triangular layers are shown: the triangles form the middle layer; the circles denote sites on the layer below and the remaining three sites are on the layer above.

<sup>3</sup> G. H. Wannier, Phys. Rev. 79, 357 (1950).

<sup>4</sup> M. F. Sykes and I. J. Zucker, Phys. Rev. 124, 410 (1961).

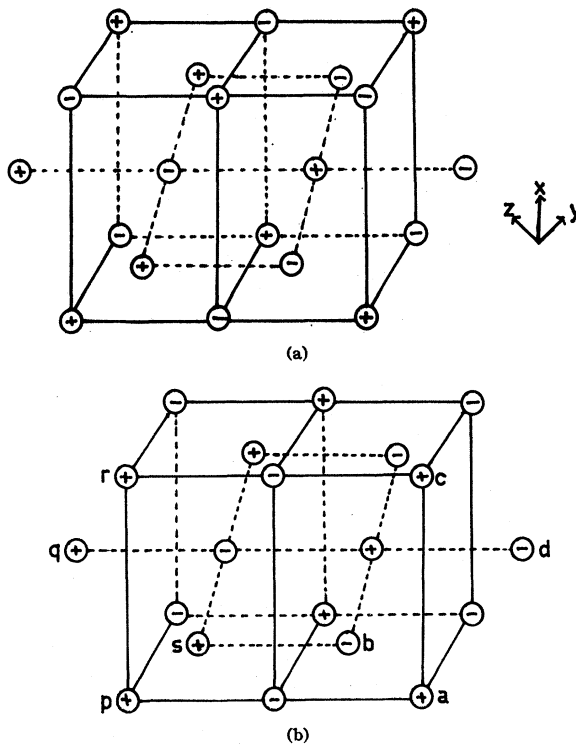


FIG. 2. Two sections from the antiferromagnetic ground state of a face-centered cubic lattice, each consisting of three consecutive antiferromagnetically ordered quadrilateral layers. In case (a) the layers form  $\alpha$  clusters of which two adjacent ones are shown. In (b)  $\beta$  clusters are formed where the spins in the  $x$ - $y$  plane (e.g.,  $a, b, c, d$ ) are also antiferromagnetically ordered while those in  $x$ - $z$  plane (e.g.,  $p, q, r, s$ ) are ferromagnetically ordered.

these two axes define a quadrilateral layer of the lattice, it follows that we have a layer of  $\alpha$  clusters comprising the spins of the  $i$ th,  $(i-1)$ th, and  $(i+1)$ th quadrilateral layers i.e., a total of the order  $3N^{\frac{2}{3}}$  spins. Furthermore, since 3 adjacent spins of the same sign and making an angle of  $120^\circ$  determine an  $\alpha$  cluster [e.g., in Fig. 1(a), spins  $A, O, B$ ], it follows that in the ground state, three spins determine the configuration of approximately  $3N^{\frac{2}{3}}$  spins in the lattice. We now denote by  $X$  the set of quadrilateral layers in the lattice parallel to the quadrilateral layer determined as above, and the other two sets of quadrilateral layers by  $Y$  and  $Z$  (the three being mutually perpendicular). Looking at the lattice as a whole, we find that each layer of the set  $X$  is antiferromagnetically ordered—the spins on each square of a layer being in the state  $(\pm\mp)$ . Any three consecutive layers of this set will consist entirely either of  $\alpha$  clusters or of  $\beta$  clusters; thus, the spins of the  $i$ th,  $(i-1)$ th, and  $(i+1)$ th layers are correlated. In the case of  $\alpha$  clusters the spins of the  $(i-1)$ th layer are antiparallel to those of the  $(i+1)$ th layer whereas in the case of  $\beta$  clusters they are parallel. The arrangements on the  $Y$  and  $Z$  sets of quadrilateral layers are not uniform throughout the lattice, but depend on whether any particular square of spins belonging to either of these sets is part of an  $\alpha$  or  $\beta$

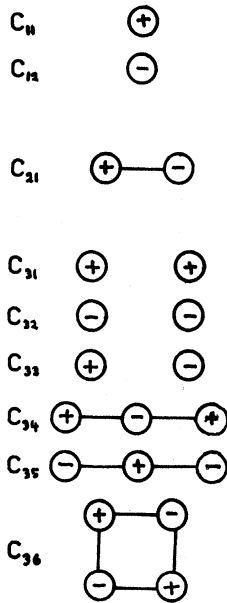


FIG. 3. Configurations utilized in Table I.

cluster. In the case of  $\alpha$  clusters each square of spins belonging to a  $Y$  or  $Z$  set is in the  $(\pm\pm)$  or its equivalent  $(\mp\mp)$  state; in the case of  $\beta$  clusters there is another set, in addition to  $X$ , which is also antiferromagnetically ordered and the third is ferromagnetically ordered—the spins being all parallel.

In Fig. 2(a), a section of three antiferromagnetically ordered quadrilateral layers (of the set  $X$ ) are shown in the case where they form  $\alpha$  clusters (a spin with its 12 nearest neighbors forms a cluster—two  $\alpha$  clusters are shown). In Fig. 2(b), the case is of  $\beta$  clusters: the second antiferromagnetically ordered set of quadrilateral layers is in the  $x$ - $y$  plane (e.g., spins  $a, b, c, d$ ) and the ferromagnetically ordered in the  $x$ - $z$  plane (e.g., spins  $p, q, r, s$ ).

To summarize: the antiferromagnetic ground state of the face-centered cubic lattice may be constructed by using antiferromagnetically ordered quadrilateral layers and placing them one above the other such that any three consecutive layers will conform to one of the two configurational schemes shown in Fig. 2. Each time the  $(i+1)$ th layer is added, there is the option of having the spins parallel or antiparallel to those of the  $(i-1)$ th layer (which are vertically beneath)—it is precisely this which gives rise to the degeneracy of  $2^R$  where  $R$  is the number of layers, of the order  $N^{1/3}$ . It is now easy to see that the presence of a small amount of interaction energy between next-nearest-neighbor (n.n.n.) pairs will remove the degeneracy. For example, a ferromagnetic interaction between n.n.n. pairs (they are along the diagonals of the squares i.e., along the  $x, y, z$  axes) would favor the parallel alignment of the spins of the  $(i-1)$ th and  $(i+1)$  layers i.e.,  $\beta$  clusters [Fig. 2(b)] throughout the lattice; this would result in what is generally known as “ordering of the first kind.” On the other hand a small antiferromagnetic n.n.n. interaction (compared

with  $J$ ) would favor  $\alpha$  clusters [Fig. 2(a)] throughout the lattice: the n.n.n. pairs of spins along the  $x$  axis will align antiparallel because this does not affect the energy due to nearest-neighbor pairs; however, the n.n.n. pairs along the two other axes will still remain parallel otherwise the energy due to nearest neighbors will rise. This is “ordering of the third kind.” The various ordered spin configurations and the energies involved in terms of nearest and n.n.n. interactions have been discussed by Carter and Stevens<sup>5</sup> and described extensively for several lattice structures by Gersch and Koehler.<sup>6</sup>

### III. THE PARTITION FUNCTION

As is usual, a low-temperature expansion of the partition function is obtained by first determining the energy changes  $(\Delta E)_n$ , involved in overturning  $n=1, 2, 3, \dots$  spins from the ground state. In Appendix A we show that

$$(\Delta E)_n = 8nJ + 4J\delta_n + 2mHd_n, \quad (1)$$

where  $\delta_n$  = (number of “even” bonds) — (number of “odd” bonds);  $d_n$  = (number of + spins) — (number of - spins);  $m$  = the magnetic moment per spin;  $H$  = the external magnetic field along the + direction.

By “bonds” we mean those which connect pairs of nearest-neighbor spins; these are “even” or “odd” de-

TABLE I. The energies  $E_{ki}$  of the “excited states” ( $k=1, 2, 3$ ) above the antiferromagnetic ground state ( $k=0$ ) of a face-centered cubic lattice of  $N$  spins.  $g_{ki} \times 2^R$  ( $R=N^{1/3}$ ) is the total number of those ground-state configurations which when overturned each contributes an energy  $E_{ki}$ .

$E_0 = -2NJ$	$E_{ki}$	Configuration <sup>a</sup>	$g_{ki}$
$k=1$	$E_{11} = -2NJ + 8J + 2mH$	$C_{11}$	$N/2$
	$E_{12} = -2NJ + 8J - 2mH$	$C_{12}$	$N/2$
	$E_{21} = -2NJ + 12J$	$C_{21}$	$4N$
$k=2$	$E_{31} = -2NJ + 16J + 4mH$	$C_{31}$	$\frac{N}{4} \binom{N}{2} - 5$
	$E_{32} = -2NJ + 16J - 4mH$	$C_{32}$	$\frac{N}{4} \binom{N}{2} - 5$
$k=3$	$E_{33} = -2NJ + 16J$	$C_{33}$	$\frac{N}{2} \binom{N}{2} - 8$
	$E_{34} = -2NJ + 16J + 2mH$	$C_{34}$	$ION$
	$E_{35} = -2NJ + 16J - 2mH$	$C_{35}$	$ION$
	$E_{36} = -2NJ + 16J$	$C_{36}$	$pN^b$

<sup>a</sup> See Fig. 3.

<sup>b</sup> Depends on the degenerate state.

<sup>5</sup> W. S. Carter and K. W. H. Stevens, Proc. Phys. Soc. (London) **B69**, 1006 (1956).

<sup>6</sup> H. A. Gersch and W. C. Koehler, Phys. Chem. Solids **5**, 180 (1958).

pending on whether the spins are parallel or antiparallel. If all the spins of the cluster are "separated" then  $\delta_n = 0$ .

The "excited states" can now be evaluated by applying (1) to all possible configurations of  $n=1, 2, 3 \dots$  spins, noting that the configurational possibilities are determined not only by the lattice but also by the general configurational scheme of the ground state described in Ref. 2. The important feature of the configurations with  $n=1, 2, 3$  spins is that they are common to all the degenerate states. It is essentially this feature which makes possible the derivation of a series expansion from the ground state, and it is due to the substantial amount of order discussed above.

At this stage we consider the possibility of  $(\Delta E)_{r>n}$  being less than or equal to  $(\Delta E)_n$  (apart from the case of  $r=N-n$  and  $r=n$  which is discussed in Ref. 1). This is easily possible but we have found that  $(\Delta E)_n'$  i.e., the minimum value of  $(\Delta E)_n$  for a given  $n$ , increases monotonically with  $n$  in zero field up to the limited value of  $n$  investigated. We assume that

$$(\Delta E)_{r'} \geq (\Delta E)_n'; \quad p > r > n; \quad (2)$$

where  $p$  is an upper bound imposed to exclude the case mentioned and because (1) is not valid for all  $n$  due to surface effects. In Appendix B, we discuss (2) further and show precisely what its validity depends on.

Applying Eqs. (1) and (2) we find that the first four excited states are:

$$(1) 8J, \quad (2) 12J, \quad (3) 16J, \quad (4) 20J.$$

Table I (Fig. 3) shows the various energy levels  $E_{kl}$  of the lattice beginning with the ground-state energy  $E_0 = -2NJ$ . The subscript "k" denotes the various excited states, e.g.,  $k=3$  refers to an energy jump of 16 J above the ground state. The second subscript "l" denotes those configurations which, when overturned, give rise to the energy jump denoted by "k". If  $E_{kl} = E_0 + \alpha_k J$  (where  $\alpha_k$  is a number), it follows from (2) that all the configurations which can contribute to it are limited to those of clusters of up to  $n$  spins, where  $n$  is determined by  $(\Delta E)_n' = \alpha_k J$ . The last column shows the number  $g_{kl}$  of each configuration on a lattice of  $N$  spins.

We can now write down the partition function for an  $N$ -spin system:

$$Z_N = A 2^R \sum_{k,l} g_{kl} \exp(-E_{kl}/kT),$$

i.e.,

$$Z_N = A 2^R z^{-N} \left[ 1 + \frac{1}{2} N (\mu + \mu^{-1}) z^4 + 4 N z^6 + \dots + \left\{ \frac{1}{4} N (\frac{1}{2} N - 5) (\mu^2 + \mu^{-2}) + \frac{1}{2} N (\frac{1}{2} N - 8) + 10 N (\mu + \mu^{-1}) + p N \right\} z^8 + \dots \right]. \quad (3)$$

$Z$ , the partition function per spin defined by,

$$Z = \lim_{N \rightarrow \infty} (Z_N)^{1/N}, \quad (\text{Ref. 1}) \quad (4)$$

is

$$Z = A z^{-1} \left[ 1 + (\mu + \mu^{-1}) \frac{z^4}{2} + 4 z^6 + \left\{ p - \frac{15}{4} + 10(\mu + \mu^{-1}) - \frac{9}{8} (\mu^2 + \mu^{-2}) \right\} z^8 + \dots \right], \quad (5)$$

where  $z = \exp(-2J/kT)$ ,  $\mu = \exp(-2mH/kT)$ , and  $F$ , the total free energy of the system is given by

$$F = -NkT \ln(Z). \quad (6)$$

#### IV. RESULTS AND DISCUSSION

Using (5) and (6), other thermodynamic functions may be derived from well-known relations; thus, the zero-field magnetic susceptibility and the specific heat  $C_v$  are given by

$$\chi = - \left( \frac{\partial^2 F}{\partial H^2} \right)_{H=0} \quad C_v = \frac{\partial}{\partial T} \left( kT^2 \frac{\partial \ln Z}{\partial T} \right) \quad (7)$$

or in terms of the variables  $z, \mu$ ;

$$\chi = \frac{4Nm^2}{kT} \left( \frac{\partial^2 \ln Z}{\partial \mu^2} \right)_{\mu=1}; \quad (8)$$

$$C_v = R (\ln z)^2 z \frac{\partial}{\partial z} \left( z \frac{\partial \ln Z}{\partial z} \right).$$

Hence we obtain,

$$\chi = \frac{4Nm^2}{kT} z^4 (1 + 10z^4 - 4z^6 \dots), \quad (9)$$

$$C_v/R = \frac{16z^4}{(kT/2J)^2} (1 + 9z^2 \dots). \quad (10)$$

In Fig. 4 we show  $\chi_0 = (2\chi J)/Nm^2$  plotted against  $t = kT/2J$ . Curve A is obtained from (9), and B is a Padé approximant<sup>7</sup> of the high-temperature series of Domb and Sykes<sup>8</sup> consisting of eight terms. The two intersect at  $t \approx 1.2$ , where the last term of (9) contributes 1% and where the values for  $\chi_0$  given by the various Padé approximants are practically identical. Higher terms in A and B may cause this intersection to be smoother, however we tentatively interpret this point as the maximum of the susceptibility or the Néel point  $t_N$ . The ferromagnetic critical point (Curie temperature) has been estimated<sup>8</sup> at  $t_c = 4.9$ , hence  $t_N \approx t_c/4$ .

As we have already seen, the behavior of the magnetic susceptibility and the entropy per spin as  $T \rightarrow 0^\circ\text{K}$  of this nonordering system is an unexpected feature of this case. The question of interest which next arises is

<sup>7</sup> G. A. Baker, Phys. Rev. **124**, 768 (1961).

<sup>8</sup> C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).

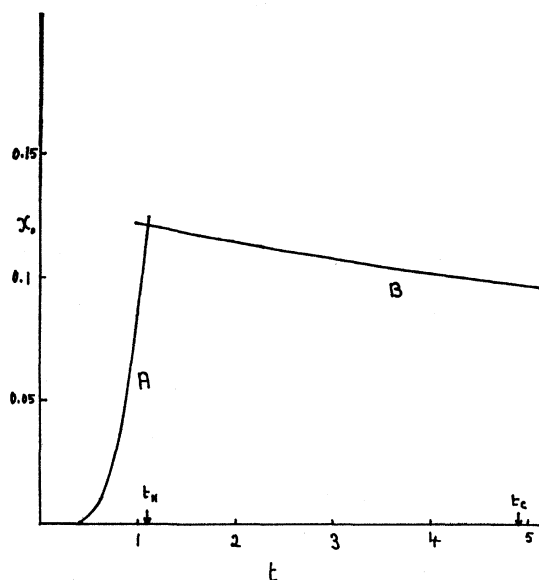


FIG. 4. The reduced zero-field antiferromagnetic susceptibility  $\chi_0$  plotted against the reduced temperature  $t$ .  $t_c$  is the ferromagnetic Curie temperature and  $t_N$ , the Néel temperature at which  $\chi_0$  is a maximum.

whether a transition point exists. The fact that  $\chi \rightarrow 0$  as  $T \rightarrow 0^\circ\text{K}$  shows that  $\chi$  has a maximum, and this could be regarded as the Néel point. This could of course be a simple maximum, on the other hand, other features—apart from Fig. 4—seem to indicate that it may not be so simple: the existence of a substantial amount of order and the existence of power series expansions of the thermodynamic functions about  $T=0^\circ\text{K}$ . From the point of view of order and correlation of spins, one could define a parameter  $S_i$  for the degree of ordering in that section of the lattice comprising the  $i$ th,  $(i-1)$ th, and  $(i+1)$ th quadrilateral layers (see Sec. II, third paragraph); hence, the amount of long-range order in the lattice will be determined by a set of parameters  $S_i$ . In the case of a lattice which orders, the amount of long-range order is determined by a parameter  $S$  and the temperature at which  $S$  is precisely zero is defined as the transition point, the transition being of the second order.<sup>9</sup> In our case, long-range order exists in two dimensions only; however, there must be a temperature at which  $S_i=0$ , all  $i$ ; thus a necessary condition for a transition of the second order, namely, a point at which long-range order vanishes, is satisfied. In the absence of an exact theory, it is not possible to say definitely that this temperature will be a singularity; however, curve A of Fig. 4 seems to indicate an infinite tangent in the susceptibility: if this is in fact the case and not due to the limited number of terms, an infinity in the specific heat follows,<sup>10</sup> in which case a singularity in the free energy is indicated. Alternatively an answer to the ques-

tion we have posed may be sought in the radius of convergence of the series (9) and (10). The results at  $T=0^\circ\text{K}$  seem to preclude the existence of a singularity there, and we ask whether there is a singularity on the real axis. Unfortunately we do not have an adequate number of terms in the series to attempt an investigation of this point; the terms given are limited to the configurations common to all the degenerate states. In principle higher terms may be obtained—by weighting the contributions due to the larger configurations with the proportions of the total number of the degenerate states in which they occur—however, the labor involved would soon be found to be prohibitive.

Finally, we mention results of cluster approximation calculations. Using the quasichemical approximation, Li<sup>11</sup> predicted antiferromagnetic ordering with a transition point of the first order at  $t=1.461$ ; later Danielian<sup>12</sup> showed that according to the constant coupling approximation an antiferromagnetically ordered state was not possible, hence, no transition point was predicted. The latter result is in agreement with the fact that the ground state is degenerate but the analysis fails to reveal the existence of partial long-range order. On the other hand, Li's qualitative argument that the lattice sustains antiferromagnetism because each quadrilateral layer does so is now seen to be partially valid, insofar as each one of the quadrilateral layers belonging to one of the three sets is antiferromagnetically ordered—but even here there is no unique arrangement of the layers relative to one another. It is not easy to determine whether the transition point estimated is somehow related to the existence of partial long-range order, in particular the discontinuous change implied in a transition of the first order. We note the closeness of the estimated values of  $t_N$  to those of the critical point of the square net: the quasichemical estimates of 1.461<sup>11</sup> and 1.442,<sup>1</sup> respectively; our estimate of 1.2 and the exact value for the square net, 1.134.<sup>1</sup> This is not surprising as the ordering has been shown to be over quadrilateral planes. In conclusion it seems to us that a transition point may exist, corresponding to the vanishing of the long-range order along the quadrilateral planes, and with a value not differing greatly from that of a square net. It is hoped that further work will elucidate this point.

#### ACKNOWLEDGMENTS

I should like to thank Dr. M. E. Fisher and Dr. M. F. Sykes for reading this paper and making valuable comments. To John Stephenson, I am indebted for the results of his Padé approximation investigations of the high-temperature susceptibility series.

#### APPENDIX A

Each spin of our system has 12 bonds, and in the ground state 8 of these are "odd" and 4 "even." Consider

<sup>9</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1959), Chap. XIV.

<sup>10</sup> M. E. Fisher, *Phil. Mag.* **7**, 1731 (1962).

<sup>11</sup> Y.-Y. Li, *Phys. Rev.* **80**, 457 (1950); **84**, 721 (1951).

<sup>12</sup> A. Danielian, *Physica* **29**, 67 (1963).

now a cluster of  $n$  spins. Each spin " $i$ " in this cluster will in general have  $p_i$  bonds with other spins of the cluster, such bonds will be described as "internal" bonds; it will also have  $(12-p_i)$  bonds with spins not appearing in the cluster, these bonds will be called 'external' bonds.

Let the  $i$ th spin be connected with:

- $a_i$ , "even internal" bonds;
- $4-a_i$ , "even external" bonds;
- $b_i$ , "odd internal" bonds,  $(a_i+b_i=p_i)$ ;
- $8-b_i$ , "odd external" bonds.

The energy associated with each "even" bond is  $+J$ , and with an "odd" bond  $-J$ . We now consider the energy contribution of the bonds to  $(\Delta E)_n$ , the energy change involved in overturning  $n$  spins in the ground state. When all the spins are overturned, the contribution of the "internal" bonds is zero, because "even" bonds remain "even" and "odd" bonds remain "odd." Therefore it follows that only "external" bonds contribute to  $(\Delta E)_n$ .

The original energy contribution of "external" bonds is

$$\sum_i (4-a_i)J - (8-b_i)J. \quad (\text{A1})$$

After overturning all the spins of the cluster, all "external" bonds change: the "even" bonds becoming "odd" and the "odd" becoming "even." Therefore the final energy contribution of the "external" bonds is:

$$\sum_i -(4-a_i)J + (8-b_i)J. \quad (\text{A2})$$

The contribution to  $(\Delta E)_n$  is therefore

$$\begin{aligned} \sum_{i=1}^n -2J(4-a_i) + 2J(8-b_i) \\ = 8nJ + \sum_{i=1}^n 2J(a_i-b_i) = 8nJ + 4J\delta_n, \end{aligned} \quad (\text{A3})$$

where  $\delta_n = (\text{total number of "even internal" bonds}) - (\text{total number of "odd internal" bonds})$  in the  $n$ -spin cluster.

The magnetic contribution is simply  $2mHd_n$ , where  $d_n$  is the difference between the number of (+) and (-) spins,

$$\therefore (\Delta E)_n = 8nJ + 4J\delta_n + 2mHd_n. \quad (\text{A4})$$

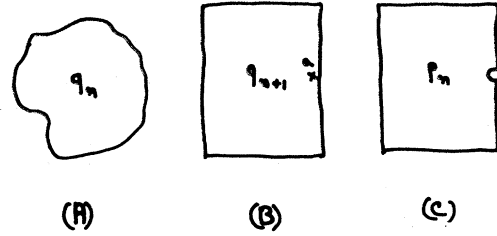


FIG. 5. Clusters of spins from the ground state of the antiferromagnetic face-centered cubic lattice. (A) and (B) consist of  $n$  and  $(n+1)$  spins, respectively: minimum energy is involved in overturning either of them. Cluster (C) is (B) with one spin ( $a$ ) removed.

#### APPENDIX B

Let  $p_n = (\Delta E)_n$ ,  $q_n = (\Delta E)_{n+1}'$ ,  $q_{n+1} = (\Delta E)_{n+1}$ ; where  $q_n$  is the minimum value of  $(\Delta E)_n$ , the energy change involved in overturning a cluster of  $n$  spins in the ground state and similarly  $q_{n+1}$ , the minimum energy involved in overturning a cluster of  $n+1$  spins.

Let (A), (B), (C) (of Fig. 5) represent the clusters of spins corresponding to  $q_n$ ,  $q_{n+1}$ ,  $p_n$ , respectively. (C) is identical to (B) in every respect except that one of the spins ( $a$ ) is removed.

By definition,  $p_n \geq q_n$ , i.e., if the  $n$  spins of (A) are rearranged as in (C), the energy  $(\Delta E)_n$  will remain the same or increase. One can go from (B) to (C) in  $(n+1)$  different ways, corresponding to the  $(n+1)$  different spins one could remove from (B). If it can be shown that (B) must contain at least one spin, which when removed causes  $(\Delta E)$  to decrease (or remain the same), then it would follow that  $q_{n+1} \geq p_n$ , since  $q_{n+1}$  is a minimum. Therefore we would have

$$q_{n+1} \geq p_n \geq q_n.$$

Now from (1),

$$\begin{aligned} q_{n+1} - p_n &= (\Delta E)_{n+1}' - (\Delta E)_n \\ &= 4J(2 + \delta_a), \quad (\text{in zero field}); \end{aligned} \quad (\text{B1})$$

where ( $a$ ) denotes the spin which is removed on going from (B) to (C). It is therefore sufficient to show that (B) must have at least one spin for which  $\delta_a \geq -2$  i.e., (number of odd bonds) - (number of even bonds)  $\leq 2$ . Or alternatively, to show that it is impossible for every spin in (B) to have an excess of 3 or more odd bonds. We have not been able to prove rigorously that this is the case but examining a large number of possibilities indicates that it is highly unlikely that a finite cluster exists in which every spin has an excess of 3 or more odd bonds due to the existence of vertices.