Classical Theory of Spin Configurations in the Cubic Spinel*

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It is shown that the Yafet-Kittel triangular spin-configurations in the cubic spinel do not minimize the classical Heisenberg exchange energy. (Only nearest-neighbor A-B and B-B interactions, J_{AB} and J_{BB}, are included; one spin-magnitude S_A for the A sites, and one, S_B, for the B sites is assumed.) A theory of the classical ground state more general than that of Yafet and Kittel is investigated. This consists of first determining the largest value, y_0, of $y \equiv J_{BB}S_B/J_{AB}S_A$ for which the Néel configuration is stable with respect to arbitrary small spin-deviations. (y_0 is roughly 10% smaller than the value of y found by Yafet and Kittel for the breakdown of the Néel configuration.) A perturbation method for finding the minimum energy configuration when $y-y_0$ is small and positive is then employed. It is concluded, (1) that equilibrium configurations exist which have nonzero angles between spins on the A sites simultaneously with angles between those on the B sites, in contrast with the Yafet-Kittel results; and (2) that there will be long-range-ordered, canted spin configurations in the cubic spinel, contrary to Anderson's suggestion. These conclusions are discussed in connection with experiments on $MnCr_2O_4$ and Mn_3O_4.

I. INTRODUCTION

IN 1948, Néel[1] suggested that in a large class of ferrites there exist low-temperature spin-configurations in which the spins on the tetrahedral (A) sites are antiparallel to those on the octahedral (B) sites. His considerations were based on the molecular field treatment, assuming antiferromagnetic A-A, B-B, and A-B exchange interactions. Later, Yafet, and Kittel[2] showed that for large enough A-A and/or B-B interactions (compared with the A-B terms), certain triangular configurations would have lower exchange energy than the Néel configuration. They also used the molecular field method, but assumed six independent sublattices instead of two, the larger number corresponding to the number of cations per primitive unit cell.

However, there are many known examples where the magnetic unit cell differs from the nuclear cell, so that there is no substantial reason to expect that the Yafet-Kittel (YK) assumption should lead to the minimum energy configuration. In Appendix I we show that, indeed, the YK configurations do not minimize the exchange energy.[3] The method used is again the molecular field theory (at temperature $T=0$), although we use the notation of the classical Heisenberg theory, and we remove the sublattice assumption, which arbitrarily constrains large numbers of spins to be rigidly parallel. We consider only nearest neighbor A-B and B-B interactions (with exchange integrals J_{AB} and J_{BB}, respectively) for normal spinels (with one spin-magnitude S_A on the A sites and one, S_B, on the B's).

Although the basic (YK) concept of noncollinear spins is undoubtedly correct, the above result forces us to reconsider the problem of the ground state.[4] Some insight into this problem can be gained by a perturbation calculation of the minimum energy configuration. Briefly, the idea of the method is as follows. Neglecting A-A interactions, the problem can be described in terms of a parameter $y=J_{BB}S_B/J_{AB}S_A$. The Néel configuration C_0 is rigorously the minimum energy state when $y=0$, and is expected to remain so as y increases up to some critical value y_0; when y exceeds y_0, C_0 becomes unstable. If $y-y_0 \equiv \eta$ is small and positive, the minimum energy configuration is expected to deviate only slightly from C_0. Hence we look for a solution of the extremum condition giving the deviation from C_0 as a power series in η when $\eta>0$, such that the deviation approaches zero as $\eta \to 0$. Two plausible assumptions, needed for the rigor of the method, are stated in Sec. II. The critical value of y is determined in Sec. III and Sec. IV is devoted to the theory for η small and positive.

The principle conclusions drawn from the analysis are the following: The deviations are of order $\eta^{\frac{1}{2}}$, so that the angles between the spins and the axis defined by C_0 increase rapidly with η for small η. Equilibrium configurations exist in which there are simultaneously nonzero angles between A spins and between B spins, as contrasted with the rigorous deduction[2,5] from the YK assumptions. Furthermore, the ground state will exhibit a long-range-ordered array of canted spins in contrast with Anderson's suggestion.[4]

The neutron diffraction cross section is calculated in Sec. V, and the relation between the results and experiments on $MnCr_2O_4$ and Mn_3O_4 is discussed in Secs. V and VI.

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[1] L. Néel, Ann. Phys. **3**, 137 (1948).

[2] Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).

[3] A brief account of this result has been given previously [T. A. Kaplan, Phys. Rev. **116**, 888 (1959)].

[4] P. W. Anderson [Phys. Rev. **102**, 1008 (1956)] did this for the special case of zero A-B interaction, using an Ising model. He showed that there will be no long-range ordering of the B spins for this case in a cubic spinel. Anderson also suggested that long-range-ordered angles would not exist for nonzero A-B interactions, basing his discussion on the Yafet-Kittel picture. This is discussed further below.

[5] F. K. Lotgering, Philips Research Rept. **11**, 190 (1956).

II. GENERAL CONSIDERATIONS

Our problem is to find the set of spin vectors, $\mathbf{S}_i^A$, $\mathbf{S}_j^B$, associated with each point of the tetrahedral and octahedral sublattices, respectively, that minimizes the Heisenberg energy,

$$E=2J_{AB}S_AS_B\{\sum_{\langle i,j\rangle}\boldsymbol{\sigma}_i^A\cdot\boldsymbol{\sigma}_j^B+y\sum_{\langle i,j\rangle}\boldsymbol{\sigma}_i^B\cdot\boldsymbol{\sigma}_j^B\},\quad(1)$$

where

$$\boldsymbol{\sigma}_i^\Gamma=\mathbf{S}_i^\Gamma/S_\Gamma,\quad\Gamma=A,B,\quad(2)$$

$$y=J_{BB}S_B/J_{AB}S_A\geqslant 0,\quad(3)$$

J_{AB} and J_{BB} are positive (for antiferromagnetic interactions), and $\sum_{\langle i,j\rangle}$ indicates a sum over nearest neighbor (n.n.) A-B or B-B pairs. We neglect A-A interaction for simplicity and because it is expected to be small. When $y=0$, it is easy to see that the Néel configuration is the ground state. For any nonzero value of y no such rigor appears possible.[6]

However, the question of local stability can be handled; that is, the energy changes for small deviations from C_0 are calculable for any y. To discuss this point further, consider the deviations from C_0, $\sigma_i^{\Gamma x}$ and $\sigma_i^{\Gamma y}$, where the spin-axis in C_0 is the z axis, and expand the energy

$$E=E_0+E_2+E_4+\cdots,\quad(4)$$

where E_n is of nth order in the deviations. This is obtained by substituting the expansions,

$$\begin{aligned}\sigma_i^{Az}&=[1-(\sigma_i^{Ax})^2-(\sigma_i^{Ay})^2]^{\frac{1}{2}}\\&=1-(1/2)[(\sigma_i^{Ax})^2+(\sigma_i^{Ay})^2]-\cdots,\\\sigma_j^{Bz}&=-[1-(\sigma_j^{Bx})^2-(\sigma_j^{By})^2]^{\frac{1}{2}}\\&=-\{1-(1/2)[(\sigma_j^{Bx})^2+(\sigma_j^{By})^2]-\cdots\},\end{aligned}\quad(5)$$

into Eq. (1). Then C_0 is locally stable if the quadratic form E_2 is positive definite.[7] The determination of the possible signs of E_2 is tractable since the translational symmetry allows one to write E_2 as a sum of 6×6 quadratic forms in the Fourier transforms of the $\sigma_i^{\Gamma u}$, $(u=x,y)$, one form for each point in the Brillouin zone —at worst, a numerical solution could be obtained. It is with this problem of local stability that we shall be concerned—*we shall assume that C_0 is the minimum energy state if it is locally stable.*

As y increases from zero, C_0 will remain locally stable until y reaches a critical value y_0, E_2 becoming indefinite when y exceeds y_0. To determine the minimum energy configuration when $\eta=y-y_0>0$, a perturbation theory is investigated (Sec. IV) which is based on *our other assumption, namely that the $\sigma_i^{\Gamma u}$ can be represented by power series in $\eta(\geqslant 0)$, such that the $\sigma_i^{\Gamma u}\to 0$ continuously as $\eta\to 0$.* The latter assumption clearly requires that C_0 be stable when $\eta=0$; since E_2 can be zero for certain values of the $\sigma_i^{\Gamma u}$ when $\eta=0$, E_4 must certainly be non-negative for these deviations in order that this requirement be satisfied. To conclude this section, we will obtain explicit expressions for E_2 and E_4, and show that E_4 is non-negative when $\eta=0$.

Using (5), (1) can be written in the form

$$\begin{aligned}\mathcal{E}=\frac{E}{6NJ_{AB}S_AS_B}&=\mathcal{E}_0+\mathcal{E}_2(\cdots\sigma_i^{\Gamma x}\cdots;\cdots\sigma_j^{\Gamma y}\cdots)\\&\quad+\mathcal{E}_4(\cdots\sigma_i^{\Gamma x}\cdots;\cdots\sigma_j^{\Gamma y}\cdots)+\cdots,\end{aligned}\quad(6)$$

where $\mathcal{E}_0=-8+4y$ (the value of $\mathcal{E}$ for C_0), $N=$ the No. of primitive unit cells (each containing two A's and four B's),

$$\begin{aligned}3N\mathcal{E}_2(\cdots\sigma_i^{\Gamma x}\cdots;\cdots\sigma_j^{\Gamma y}\cdots)&=\tfrac{1}{2}\sum_{\langle i,j\rangle}^{(AB)}[(\sigma_i^{Ax}+\sigma_j^{Bx})^2+(\sigma_i^{Ay}+\sigma_j^{By})^2]\\&\quad-\frac{y}{2}\sum_{\langle i,j\rangle}^{(BB)}[(\sigma_i^{Bx}-\sigma_j^{Bx})^2+(\sigma_i^{By}-\sigma_j^{By})^2],\end{aligned}\quad(7)$$

$$\begin{aligned}3N\mathcal{E}_4(\cdots\sigma_i^{\Gamma x}\cdots;\cdots\sigma_j^{\Gamma y})&=\tfrac{1}{8}\sum_{\langle i,j\rangle}^{(AB)}[(\sigma_i^{Ax})^2+(\sigma_i^{Ay})^2-(\sigma_j^{Bx})^2-(\sigma_j^{By})^2]^2\\&\quad-\frac{y}{8}\sum_{\langle i,j\rangle}^{(BB)}[(\sigma_i^{Bx})^2+(\sigma_i^{By})^2-(\sigma_j^{Bx})^2-(\sigma_j^{By})^2]^2,\end{aligned}\quad(8)$$

and the letters over the summation signs in (7) and (8) indicate the pertinent n.n. pairs. Comparing (7) and (8), we obtain the functional relation

$$\begin{aligned}\mathcal{E}_4(\cdots\sigma_i^{\Gamma x}\cdots;\cdots\sigma_j^{\Gamma y}\cdots)&=(1/4)\mathcal{E}_2(\cdots w_i^\Gamma\cdots;\cdots 0\cdots),\end{aligned}\quad(9)$$

where

$$w_i^A=(\sigma_i^{Ax})^2+(\sigma_i^{Ay})^2,\quad w_i^B=-(\sigma_i^{Bx})^2-(\sigma_i^{By})^2.\quad(10)$$

Equation (9) yields the theorem: the possible signs of $\mathcal{E}_4$ are identical to those of $\mathcal{E}_2$.[8] Since $\mathcal{E}_2\geqslant 0$ for $y\leqslant y_0$, it follows that $\mathcal{E}_4\geqslant 0$ when $y\leqslant y_0$.

III. THE BREAKDOWN OF THE NÉEL CONFIGURATION

To study the possible signs of E_2, we make the transformation of variables

$$\sigma_{n\gamma}^{\Gamma u}=\sum_{\mathbf{k}}\Gamma_{\gamma,\mathbf{k}}{}^u\exp(i\mathbf{k}\cdot\mathbf{R}_{n\gamma}^\Gamma).\quad(11)$$

Here the $\mathbf{k}$ are rationalized reduced reciprocal vectors in the first Brillouin zone (the direct lattice is face-centered cubic); $u=x,y$; explicit account is taken of the

[6] The only fairly general method for treating this type of problem rigorously, the method of J. M. Luttinger and L. Tisza [Phys. Rev. **70**, 954 (1946)]; J. M. Luttinger [Phys. Rev. **81**, 1015 (1952)], unfortunately seems to fail for the spinel, since there are spins on nonequivalent lattice sites.

[7] Uniform rotation of the spins, with respect to which E is invariant, are excluded in this definition.

[8] It is easy to show that this theorem is valid for the deviations from general collinear configurations on any lattice.

TABLE I. Eigenvalues and eigenvectors for $\mathbf{k}=0$.

ν	$m_\nu(0)$	$\mathbf{U}_\nu(0)$
1	0	$6^{-\frac{1}{2}}(1, 1, -1, -1, -1, -1)$
2	$2(1-4y/3)$	$2^{-\frac{1}{2}}(0, 0, 1, -1, 0, 0)$
3	$2(1-4y/3)$	$2^{-\frac{1}{2}}(0, 0, 0, 0, 1, -1)$
4	$2(1-4y/3)$	$2^{-1}(0, 0, 1, 1, -1, -1)$
5	4	$2^{-\frac{1}{2}}(1, -1, 0, 0, 0, 0)$
6	6	$(12)^{-\frac{1}{2}}(2,2,1,1,1,1)$

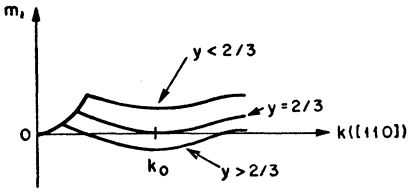

FIG. 1. Qualitative behavior of $m_1(\mathbf{k})$ for $\mathbf{k}$ in [110].

fact that there is more than one site per unit cell: $\gamma=1, 2$ when $\Gamma=A$, $\gamma=1, 2, 3, 4$ when $\Gamma=B$ (n labels the unit cell); $\mathbf{R}_{n\gamma}{}^\Gamma$ is the position vector for site Γ, n, γ. (For a drawing of the six sites per unit cell and a discussion of some of the pertinent lattice properties, see Kaplan.[9]) Since the σ's are real,

$$\Gamma_{\gamma,\mathbf{k}}{}^{u*}=\Gamma_{\gamma,-\mathbf{k}}{}^{u}. \tag{12}$$

Let $\alpha=1, 2$; $\beta=1, 2, 3, 4$, and define the functions

$$\eta_{\alpha\beta}(\mathbf{k})=(1/3)\sum_{m=1}^{3}\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_{\alpha\beta}{}^m),$$
$$\zeta_{\beta\beta'}(\mathbf{k})=\cos\mathbf{k}\cdot\boldsymbol{\sigma}_{\beta\beta'}, \tag{13}$$

where $\boldsymbol{\tau}_{\alpha\beta}{}^m$ connects an A_α with a nearest neighbor B_β[9], and $\boldsymbol{\sigma}_{\beta\beta'}$ connects a B_β with a nearest neighbor $B_{\beta'}$. Although the functions (13) were given by Kouvel,[10] we include them in Appendix II for completeness. Substituting (11) into (7), we obtain[11]

$$\mathcal{E}_2=\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{u}\sum_{\nu,\mu=1}^{6}M_{\nu\mu}(\mathbf{k})\chi_{\nu\mathbf{k}}{}^{u*}\chi_{\mu\mathbf{k}}{}^{u}, \tag{14}$$

where $\chi_\nu=A_\nu$ for $\nu=1, 2$, $\chi_\nu=B_{\nu-2}$ for $\nu=3, 4, 5, 6$,

$$\mathbf{M}(\mathbf{k})=\begin{bmatrix} 4 & 0 & \eta_1 & \eta_2 & \eta_3 & \eta_4 \\ 0 & 4 & \eta_1{}^* & \eta_2{}^* & \eta_3{}^* & \eta_4{}^* \\ \eta_1{}^* & \eta_1 & 2x & y'\zeta_{12} & y'\zeta_{13} & y'\zeta_{14} \\ \eta_2{}^* & \eta_2 & y'\zeta_{12} & 2x & y'\zeta_{23} & y'\zeta_{24} \\ \eta_3{}^* & \eta_3 & y'\zeta_{13} & y'\zeta_{23} & 2x & y'\zeta_{34} \\ \eta_4{}^* & \eta_4 & y'\zeta_{14} & y'\zeta_{24} & y'\zeta_{34} & 2x \end{bmatrix}, \tag{15}$$

$$x=1-y, \quad y'=2y/3, \tag{16}$$

and

$$\eta_\beta\equiv\eta_{1\beta}(\mathbf{k})=\eta_{2\beta}{}^*(\mathbf{k}), \tag{17}$$

since $\boldsymbol{\tau}_{1\beta}{}^m=-\boldsymbol{\tau}_{2\beta}{}^m$.[9] Since $\mathbf{M}(\mathbf{k})$ is hermitean, its eigenvalues, $m_\nu(\mathbf{k})$, are real, and the $U_{\nu\mu}(\mathbf{k})$ in

$$\sum_\mu M_{\nu\mu}(\mathbf{k})U_{\mu\rho}(\mathbf{k})=m_\rho(\mathbf{k})U_{\nu\rho}(\mathbf{k}), \tag{18}$$

may be chosen unitary $[U_{\nu\mu}{}^{-1}(\mathbf{k})=U_{\mu\nu}(\mathbf{k})^*]$. Defining normal coordinates, $q_{\nu\mathbf{k}}{}^u$, by

$$\chi_{\nu\mathbf{k}}{}^u=\sum_\mu U_{\nu\mu}(\mathbf{k})q_{\mu\mathbf{k}}{}^u, \tag{19}$$

(14) becomes

$$\mathcal{E}_2=(1/2)\sum_{\mathbf{k}}\sum_u\sum_\nu m_\nu(\mathbf{k})\,|\,q_{\nu\mathbf{k}}{}^u\,|^2. \tag{20}$$

Thus we have the well-known result that the necessary and sufficient condition for $\mathcal{E}_2\geqslant 0$ for all values of the variables is that all the eigenvalues, $m_\nu(\mathbf{k})$, be $\geqslant 0$.

The problem of determining the $m_\nu(\mathbf{k})$, which are the roots of a sixth order secular equation whose coefficients are given as functions of $\mathbf{k}$, is formidable. However, since it is only the signs and zeros of the $m_\nu(\mathbf{k})$ that concern us, considerable simplification is possible. To begin to get a feeling for the problem consider $\mathbf{k}=0$. The $m_\nu(0)$ and their associated eigenvectors are given in Table I. These $\mathbf{k}=0$ modes permit straightforward physical interpretation. For example, $\mathbf{U}_1(0)$ clearly represents a uniform rotation of the spins. The triply degenerate set ($\nu=2, 3, 4$) or linear combinations thereof, directly represent the Yafet-Kittel configurations with angles on the B sites; in particular, $\mathbf{U}_4(0)$ represents the special Yafet-Kittel configuration invoked by Prince.[12,13] As seen from the corresponding eigenvalue, C_0 is stable with respect to these deformations when $y<\frac{3}{4}$, becoming unstable when $y>\frac{3}{4}$, in agreement with the Yafet-Kittel result.[2]

For the general stability problem we must determine y_0 such that $m_\nu(\mathbf{k})\geqslant 0$ (equality holding only for $\mathbf{k}=0$, $\nu=1$) for $y<y_0$, and some $m_\nu(\mathbf{k})<0$ for $y>y_0$. We first consider symmetry directions for $\mathbf{k}$, [100], [111], and [110], for which the eigenvalue problem can be simplified. It can be shown (see Appendix IV) that the eigenvalues are positive (when $\mathbf{k}\neq 0$) for the first two directions (for $y<\frac{3}{4}$). For the [110], we will find negative eigenvalues for $y>\frac{2}{3}$, with all eigenvalues positive (except at $k=0$) for $y<\frac{2}{3}$. When $y=\frac{2}{3}$ the minimum eigenvalue branch $m_1(k)$ has two zeros, at $k=0$ and $k=k_0$, and looks roughly like the curve in Fig. 1; [the kink probably occurs at the crossing of two branches which connect with $m_1(0)$ and $m_2(0)$ at $k=0$]. When $y>\frac{2}{3}$, $m_1(k_0)<0$. All the eigenvalues and eigenvectors can be easily determined at $\mathbf{k}=\mathbf{k}_0$ when $y=\frac{2}{3}$, and so, by perturbation theory, the minimum eigenvalue function,

[9] T. A. Kaplan, Phys. Rev. **109**, 782 (1958). To accord with the present labeling, interchange the numbers on B sites 2 and 3.

[10] J. S. Kouvel, Technical Report 210, Cruft Laboratory, Harvard, February 1, 1955 (unpublished).

[11] In Appendix III, a relation is obtained between the eigenvalues of $\mathbf{M}$ and the spin wave frequencies which enables a direct check of $\mathbf{M}(\mathbf{k})$ with Kouvel's results.

[12] E. Prince, Acta Cryst. **10**, 554 (1957).

[13] A tetragonal distortion will split the triply degenerate set; e.g., if $c/a<1$ and the J's increase with decreasing ionic separation, $m_4(0)$ will lie lowest (as is physically clear).

$m_1(\mathbf{k})$, can be determined in the neighborhood of $\mathbf{k}_0$.[14] It is found that the linear terms in $m_1(\mathbf{k})$ vanish for $y=\frac{2}{3}$, leaving a positive definite quadratic form in the cartesian components of $\mathbf{k}-\mathbf{k}_0$. A similar calculation for $\mathbf{k}$ near zero yields a similar result. Thus there is strong evidence that when $y=\frac{2}{3}$, $m_1(\mathbf{k})\geqslant 0$, with equality only at $\mathbf{k}=0$, $\mathbf{k}=\mathbf{k}_0$, and of course at the degenerate points, $\mathbf{k}_0'$, in $[1\bar{1}0]$, etc. This was corroborated by a numerical check.[15,16] Hence we conclude that the $m_\nu(\mathbf{k})\geqslant 0$ when $y=\frac{2}{3}$, and some $m_\nu(\mathbf{k})<0$ when $y>\frac{2}{3}$.

Finally, in order to conclude that

$$y_0=\tfrac{2}{3}, \tag{21}$$

it is necessary and sufficient to show that $m_1(\mathbf{k})$ should never decrease as y decreases. Although this is intuitively obvious, a proof is given in Appendix V, where a useful, stronger theorem is proved.

We now investigate in detail the behavior of $\mathbf{M}(\mathbf{k})$ when

$$\mathbf{k}=(k/\sqrt{2})(1,1,0)\equiv\mathbf{k}'. \tag{22}$$

Transforming $\mathbf{M}(\mathbf{k}')$ to the symmetry basis

$$\begin{aligned}
\psi_1&=(1/\sqrt{2})(1,1,0,0,0,0),\\
\psi_2&=(1/\sqrt{2})(0,0,1,1,0,0),\\
\psi_3&=(1/\sqrt{2})(0,0,0,0,1,1),\\
\psi_4&=(1/\sqrt{2})(1,-1,0,0,0,0),\\
\psi_5&=(1/\sqrt{2})(0,0,1,-1,0,0),\\
\psi_6&=(1/\sqrt{2})(0,0,0,0,1,-1),
\end{aligned} \tag{23}$$

and using the definitions of Appendix II, we obtain

$$\mathbf{M}'(\mathbf{k}')=\begin{bmatrix}
4 & 2c & 2z & 0 & 0 & 0\\
2c & 2x+y'\zeta & 2y'c & 0 & 0 & 0\\
2z & 2y'c & 2x+y' & 0 & 0 & 0\\
0 & 0 & 0 & 4 & -2is/3 & 0\\
0 & 0 & 0 & 2is/3 & 2x-y'\zeta & 0\\
0 & 0 & 0 & 0 & 0 & 2(1-4y/3)
\end{bmatrix}, \tag{24}$$

where

$$\begin{aligned}
&c=\cos\rho,\quad s=\sin\rho,\quad \rho=ka/4\sqrt{2},\\
&\zeta=2c^2-1,\quad z=(1/3)(4c^2-1).
\end{aligned} \tag{25}$$

Since the smallest reciprocal lattice vector in $[110]$ is $2a^{-1}(1,1,0)$, the largest k in this direction is $2\pi a^{-1}(1,1,0)$ and therefore $0\leqslant\rho\leqslant\pi/2$, so that $0\leqslant c\leqslant 1$ and

$$-\tfrac{1}{3}\leqslant z\leqslant 1. \tag{26}$$

The eigenvalue corresponding to ψ_6 is just $m_2(0)$ (independent of k). Those arising from the ψ_4–ψ_5 submatrix can easily be shown to be positive.

To discuss the 3×3 submatrix, M_3, it is convenient to define

$$\sigma=(3-4y)/y, \tag{27}$$

so that σ monotonically decreases as y increases and $\sigma=0$ when $y=\frac{3}{4}$. Then the determinant, D, of M_3 can be written

$$D=(16/9)y^2(1-z)g(\sigma,z), \tag{28}$$

where

$$g(\sigma,z)=\textstyle\sum_{n=0}^{2} a_n(z)\sigma^n=\sum_{n=0}^{2} A_n(\sigma)z^n, \tag{29}$$

$$\begin{aligned}
a_0(z)&=-(1+3z)(1-z),\quad a_1(z)=(3z^2+6z+7)/4,\\
a_2(z)&=(7+4z)/8,
\end{aligned} \tag{30}$$

and the $A_n(\sigma)$ follow from these equations. Clearly

$$g(0,z)=a_0(z)\leqslant 0, \tag{31}$$

equality holding only at the end points $z=1$ and $-\frac{1}{3}$, in agreement with Eq. (A.11). Since $a_1(z)$ and $a_2(z)$ are positive, there is a value σ_0, such that for $\sigma>\sigma_0$, $g(\sigma,z)>0$. It follows that $g(\sigma,z)$ will have two real zeros, z_1 and z_2, for $\sigma<\sigma_0$, z_1 and z_2 coalescing (to z_0) when $\sigma=\sigma_0$. Thus σ_0 is determined by

$$A_1(\sigma_0)^2-4A_0(\sigma_0)A_2(\sigma_0)=0. \tag{32}$$

The only solution of (32) consistent with (26) is $\sigma_0=\frac{1}{2}$, which gives the value $\frac{2}{3}$ for y. The zero, z_0, when $\sigma=\sigma_0$ is

$$z_0=-A_1(1/2)/2A_0(1/2)=\tfrac{1}{6}. \tag{33}$$

Thus when $\sigma=\sigma_0$ there is a zero eigenvalue at

$$\mathbf{k}_0=(1.161)(\mathbf{K}_0/4), \tag{34}$$

where $\mathbf{K}_0=2\pi$ times the smallest reciprocal lattice vector in $[110]$. This is nondegenerate since, when $\sigma<\sigma_0$, $g(\sigma,z)<0$ for $z_1<z<z_2$, and trace $(M_3)>0$, so that there is one negative and two positive eigenvalues in this range of z; since $\partial m_\nu(\mathbf{k})/\partial\sigma\geqslant 0$ (Appendix V), the two positive eigenvalues must remain positive as σ increases to σ_0.

It can be directly verified that the eigenstate corresponding to $m_1(\mathbf{k}_0)=0$, written in the basis appropriate to Eq. (15), is

$$\mathbf{U}_1(\mathbf{k}_0)=(2/67)^{\frac{1}{2}}(1,1,-6c_0,-6c_0,\tfrac{3}{2},\tfrac{3}{2}),\quad \text{for } y=\tfrac{2}{3}. \tag{35}$$

To obtain a physical picture of this mode, we use (11)

[14] The details of this calculation will not be given. We only remark that the perturbing matrix, V, is an infinite series in powers of $\mathbf{k}-\mathbf{k}_0$, so that the standard expressions of perturbation theory must be modified slightly.

[15] It is sufficient to compute only the determinant, $D(\mathbf{k})$, of $\mathbf{M}(\mathbf{k})$, when $y=\frac{2}{3}$. This is so because at $\mathbf{k}=0$ and (as shown below) at $\mathbf{k}=\mathbf{k}_0$, the zero eigenvalue is nondegenerate. Since the $m_\nu(\mathbf{k})$ are evidently continuous functions of $\mathbf{k}$, $D(\mathbf{k})\geqslant 0$, equality only at 0 and $\mathbf{k}_0$, implies $m_\nu(\mathbf{k})\geqslant 0$, with the same conditions for equality.

[16] The numerical work was carried out on a cubic mesh with a spacing of a tenth the maximum value of k_x.

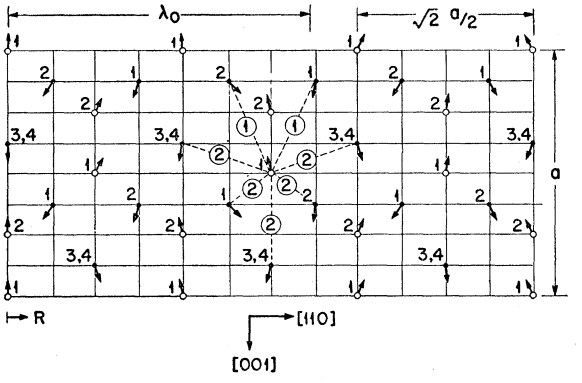

FIG. 2. Configuration $C(\mathbf{k}_0)$: projection on a $(1\bar{1}0)$ plane. A sites are denoted by ○, B sites by ●, the adjacent numbers indicating the type of sites. The dotted lines indicate the connections of an A_1 with its 12 n.n. B's (the encircled number on the line is the number of bonds). The origin of the sine wave is at $R=0$, and its wavelength is λ_0.

and (19), with all $q_{\gamma\mathbf{k}}{}^u=0$ except for $u=x$, $\gamma=1$, and $\mathbf{k}=\pm\mathbf{k}_0$. Choosing the arbitrary phase such that $q(l\mathbf{k}_0)^x=-(i/2)q$, we obtain

$$\sigma_{n\gamma}{}^x=qU_{\gamma 1}(\mathbf{k}_0)\sin\mathbf{k}_0\cdot\mathbf{R}_{n\gamma},\quad \sigma_{n\gamma}{}^y=0, \tag{36}$$

q being an arbitrary amplitude. Using (36) and the wavelength corresponding to (34),

$$\lambda_0/a=(0.861)\sqrt{2}, \tag{37}$$

we obtain, qualitatively, Fig. 2 (in which only the ratios of the angles are significant). Clearly, if λ_0/a were $\sqrt{2}$, the magnetic unit cell could be obtained from the tetragonal nuclear unit cell by simply doubling the (110) edge. However the roughly 14% deviation from this value extends the unit cell—in fact, there is no repetition within the crystal along this direction. Nevertheless, the configuration defined by (36) must be described as having long range order, as is most directly seen by the neutron diffraction pattern (Sec. V) which will exhibit characteristically sharp diffraction peaks corresponding to the wave vector $\mathbf{k}_0$. This configuration seems intuitively reasonable in that there is a tendency for angles to occur between B spins (in deference to the B-B interaction), while the A's tend to remain nearly antiparallel to their nearest B neighbors. Thus we have determined the critical value, $y_0=\frac{2}{3}$, for our stability problem, and have found a spin configuration which gives a lower energy than the Néel configuration when y first exceeds y_0.

IV. PERTURBATION THEORY FOR MINIMUM ENERGY SPIN CONFIGURATIONS

In the previous section we saw that when $y<\frac{2}{3}$, the Néel configuration is stable with respect to an arbitrary set of small spin-deviations. As y increases, a particular set of deviations $C(\mathbf{k}_0)$, essentially sinusoidal in space with a definite wave vector $\mathbf{k}_0$, becomes important; when y reaches $\frac{2}{3}$, the second order terms in the energy no longer increase with the amplitude of this special sine wave, and when y exceeds $\frac{2}{3}$, the second order terms are negative for $C(\mathbf{k}_0)$. This may be pictured alternatively in terms of the configuration space with coordinates $\sigma_i{}^{\Gamma u}$. The energy has a minimum at the origin, 0, in this space when $y<\frac{2}{3}$; when y is (slightly) larger than $\frac{2}{3}$, the energy, $\mathcal{E}$, increases as one moves away from 0 in many "directions," but for certain directions $\mathcal{E}$ decreases near 0. When $y-\frac{2}{3}=\eta$ is small and positive, the direction for the maximum decrease is such that the ratios of the $\sigma_i{}^{\Gamma u}$ are those given by $C(\mathbf{k}_0)$. We will find the fourth order terms to be positive, so that a minimum in $\mathcal{E}$ will occur at some point along this direction, thus determining the amplitude. As $\eta\to 0$, this point will move back to 0, the amplitude $\to 0$. Thus it is almost intuitively obvious that the minimum energy configuration in the neighborhood of C_0 will be $C(\mathbf{k}_0)$ with a definite amplitude.

It is the purpose of this section to derive essentially this result, taking into account the complication introduced by the fact that the set of configurations $C(\mathbf{h})$, where $\mathbf{h}$ is any one of the [110] family with magnitude k_0, are degenerate.

It is convenient to express the energy in terms of the normal coordinates, $q(\gamma\mathbf{k})$, [Eq. (19)], γ now standing for (ν,u). Then the extrema are determined by

$$\partial\mathcal{E}/\partial q(\gamma\mathbf{k})=0. \tag{38}$$

We look for solutions of these equations in the form

$$q(\gamma\mathbf{k})=\eta^\alpha\textstyle\sum_{n=0}^{\infty} q(\gamma\mathbf{k})^{(n)}\eta^n,\quad (\eta\geqslant 0,\ 0<\alpha\leqslant 1). \tag{39}$$

The condition $\alpha>0$ ensures that the q's $\to 0$ as $\eta\to 0$, while the restriction, $\alpha\leqslant 1$, is made for convenience with no loss of generality. Consider the Taylor series expansion of $\mathcal{E}$ in terms of the variables $\chi_{\gamma\mathbf{k}}$ used in (14). Employing (19), we have

$$\mathcal{E}=\mathcal{E}_0+\tfrac{1}{2}\sum_{\mathbf{k},\gamma} m_\gamma(\mathbf{k})\,|\,q(\gamma\mathbf{k})\,|^2 + \frac{1}{4!}\sum_{\cdots\mathbf{k}_i\gamma_i\cdots}\mathfrak{M}(\gamma_1\mathbf{k}_1\cdots\gamma_4\mathbf{k}_4) \times q(\gamma_1\mathbf{k}_1)\cdots q(\gamma_4\mathbf{k}_4)+\cdots, \tag{40}$$

where

$$\mathfrak{M}(\gamma_1\mathbf{k}_1\cdots\gamma_n\mathbf{k}_n)=\sum_{\cdots\gamma_i'\cdots} M(\gamma_1'\mathbf{k}_1\cdots\gamma_n'\mathbf{k}_n) \times U(\gamma_1'\gamma_1;\mathbf{k}_1)\cdots U(\gamma_n'\gamma_n;\mathbf{k}_n), \tag{41}$$

with $U_{\nu\mu}(\mathbf{k})\equiv U(\nu\mu;\mathbf{k})$ and

$$M(\gamma_1\mathbf{k}_1\cdots\gamma_n\mathbf{k}_n)=\partial^n\mathcal{E}/\partial\chi(\gamma_1\mathbf{k}_1)\cdots\chi(\gamma_n\mathbf{k}_n), \tag{42}$$

evaluated at $\chi(\gamma_i\mathbf{k}_i)=0$. Differentiating (40), the equilibrium conditions (38) become

$$m_\gamma(\mathbf{k})q(\gamma\mathbf{k})^*+\frac{1}{3!}\sum_{\cdots\mathbf{k}_i\gamma_i\cdots}\mathfrak{M}(\gamma\mathbf{k},\gamma_2\mathbf{k}_2,\gamma_3\mathbf{k}_3,\gamma_4\mathbf{k}_4) \times q(\gamma_2\mathbf{k}_2)q(\gamma_3\mathbf{k}_3)q(\gamma_4\mathbf{k}_4)+\cdots=0. \tag{43}$$

These always possess the trivial solution $q(\gamma\mathbf{k})=0$ for all γ, $\mathbf{k}$ (the Néel configuration); it is, of course, a nonzero solution for which we look.

We now expand (43) in powers of η. Since $\mathcal{E}$ is linear in y,

$$M_{\gamma\gamma'}(\mathbf{k})=M_{\gamma\gamma'}{}^{(0)}(\mathbf{k})+\eta M_{\gamma\gamma'}{}^{(1)}(\mathbf{k}), \tag{44}$$

so that, with the help of perturbation theory, we may obtain the expansion

$$m_\gamma(\mathbf{k})=\sum_{n=0}^{\infty} m_\gamma{}^{(n)}(\mathbf{k})\eta^n, \tag{45}$$

and from the eigenvectors of (44),

$$\mathfrak{M}(\gamma_1\mathbf{k}_1\cdots\gamma_m\mathbf{k}_m)=\sum_{n=0}^{\infty}\mathfrak{M}(\gamma_1\mathbf{k}_1\cdots\gamma_m\mathbf{k}_m)^{(n)}\eta^n. \tag{46}$$

Using these and (39), the equilibrium equations (43) become

$$\sum_{s=0}^{\infty} W_s{}^{(\gamma\mathbf{k})}\eta^{\alpha+s} + \sum_{s=0}^{\infty}\sum_{r=1}^{\infty} X_{rs}{}^{(\gamma\mathbf{k})}\eta^{[(2r+1)\alpha+s]}=0, \tag{47}$$

where

$$W_s{}^{(\gamma\mathbf{k})}=\sum_{n=0}^{s} m_\gamma{}^{(n)}(\mathbf{k})q(\gamma\mathbf{k})^{(s-n)*}, \tag{48}$$

$$X_{rs}{}^{(\gamma\mathbf{k})}=\frac{1}{\rho!}\sum_{\cdots n_i\cdots}^{(s)}\sum_{\cdots\gamma_i\mathbf{k}_i\cdots}\mathfrak{M}(\gamma\mathbf{k}\gamma_1\mathbf{k}_1\cdots\gamma_\rho\mathbf{k}_\rho)^{(s-\Sigma n_i)} \times q(\gamma_1\mathbf{k}_1)^{(n_1)}\cdots q(\gamma_\rho\mathbf{k}_\rho)^{(n_\rho)}, \tag{49}$$

in which $\rho=2r+1$ and $\sum^{(s)}\cdots n_i\cdots$ means $\sum\cdots n_i\cdots$ with the restriction $0\leqslant\sum_i n_i\leqslant s$.

Since $\alpha>0$, the lowest order term in (47) is $W_0{}^{(\gamma\mathbf{k})}\eta^\alpha$; (every other term is of higher order). Thus for equilibrium $W_0{}^{(\gamma\mathbf{k})}$ must be zero, giving

$$m_\gamma{}^{(0)}(\mathbf{k})q(\gamma\mathbf{k})^{(0)*}=0. \tag{50}$$

We found in the previous section that the eigenvalues for $\eta=0$, $m_\gamma{}^{(0)}(\mathbf{k})$, are positive for all γ and $\mathbf{k}$, except when $\gamma=1$ and $\mathbf{k}$ is either 0 or one of the set of twelve [110]'s with magnitude k_0, in which case the eigenvalues are zero.[17] Calling this set of 13 modes, $\mathcal{S}$, it follows from (50) that

$$\begin{aligned} &q(\gamma\mathbf{k})^{(0)}=0, \quad \gamma,\ \mathbf{k} \text{ not in } \mathcal{S},\\ &q(\gamma\mathbf{k})^{(0)} \text{ arbitrary}, \ \gamma,\ \mathbf{k} \text{ in } \mathcal{S}. \end{aligned} \tag{51}$$

Thus the lowest order terms consist only of the minimum energy normal modes defined at $\eta=0$ (see Sec. III).

To determine the amplitudes, which are arbitrary in Eq. (51), we must consider higher order terms in (47). Using (51), we have

$$W_1{}^{(\gamma\mathbf{k})}=m_\gamma{}^{(0)}(\mathbf{k})q(\gamma\mathbf{k})^{(1)*}+m_\gamma{}^{(1)}(\mathbf{k})q(\gamma\mathbf{k})^{(0)*} =\begin{cases} m_\gamma{}^{(0)}(\mathbf{k})q(\gamma\mathbf{k})^{(1)}, & \gamma,\ \mathbf{k} \text{ not in } \mathcal{S}\\ m_\gamma{}^{(1)}(\mathbf{k})q(\gamma\mathbf{k})^{(0)}, & \gamma,\ \mathbf{k} \text{ in } \mathcal{S}. \end{cases} \tag{52}$$

Also, from the properties of the determinant, Eq. (28), it can be shown that

$$m_1{}^{(1)}(\mathbf{h})<0, \tag{53}$$

where $\mathbf{h}$ is any one of the vectors in the [110] family, with magnitude k_0.

There are two possibilities: (a) Some of the $q(1\mathbf{h})^{(0)}$ are not zero and (b) all the $q(1\mathbf{h})^{(0)}$ are zero. We will now show that there exist solutions of lower energy than C_0 consistent with (a). Then case (b) is not of interest since the energy reduction from $\mathcal{E}_0$, if any, will be of higher order in η than for case (a). Considering, therefore, case (a), the coefficient $W_1{}^{1\mathbf{h}}$ of $\eta^{\alpha+1}$ is not zero, and so this term must cancel the lowest order term in the double sum. The latter is $X_{1,0}{}^{1\mathbf{h}}\eta^{3\alpha}$, so that $\alpha+1=3\alpha$ or

$$\alpha=\tfrac{1}{2}. \tag{54}$$

Setting the coefficient of $\eta^{\frac{1}{2}}$ equal to zero gives

$$W_1{}^{(\gamma\mathbf{k})}+X_{1,0}{}^{(\gamma\mathbf{k})}=0, \tag{55}$$

or

$$m_1{}^{(1)}(\mathbf{k})q(1\mathbf{k})^{(0)*}+X_{1,0}{}^{1\mathbf{k}}=0, \quad (\mathbf{k}=0,\mathbf{h}), \tag{56}$$

and

$$m_\gamma{}^{(0)}(\mathbf{k})q(\gamma\mathbf{k})^{(1)*}+X_{1,0}{}^{\gamma\mathbf{k}}=0, \quad (\gamma\mathbf{k} \text{ not in } \mathcal{S}), \tag{57}$$

where, using (51),

$$X_{1,0}{}^{\gamma\mathbf{k}}=\frac{1}{3!}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}{}'\ \mathfrak{M}(\gamma\mathbf{k},1\mathbf{k}_1,1\mathbf{k}_2 1\mathbf{k}_3)^{(0)} \times q(1\mathbf{k}_1)^{(0)}q(1\mathbf{k}_2)^{(0)}q(1\mathbf{k}_3)^{(0)}. \tag{58}$$

The prime on the summation means the $\mathbf{k}_i$ go over the set $\mathbf{k}=0$ and the $\mathbf{h}$'s. Equation (56) determines the $q(1\mathbf{k})^{(0)}$, and (57) the $q(\gamma\mathbf{k})^{(1)}$ for $\gamma\mathbf{k}$ not in $\mathcal{S}$.

To discuss solutions of (56) we need certain properties of the $M(\gamma_1\mathbf{k}_1\cdots,\gamma_4\mathbf{k}_4)$. Substituting (11) into (8) and using the definitions (41) and (42), one finds that

$$\mathfrak{M}(\gamma_1\mathbf{k}_1,\cdots,\gamma_4\mathbf{k}_4)=0 \quad \text{unless} \quad \sum\mathbf{k}_i=\mathbf{K}, \tag{59}$$

where $\mathbf{K}=2\pi$ times a reciprocal lattice vector and i goes from 1 to 4. When the $\mathbf{k}_i$ are in the set 0, $\mathbf{h}$, the only possible $\mathbf{K}$ in (59) is $\mathbf{K}=0$, since $\mathbf{k}_0$ differs slightly from $\frac{1}{4}\mathbf{K}_0$ [Eq. (34)]. Thus in this case the condition (59) is

$$\sum\mathbf{k}_i=0. \tag{60}$$

The ways in which a set of $\mathbf{k}$'s, drawn from the set, 0, $\mathbf{h}$, can be chosen to satisfy (60) are represented by the diagrams in Fig. 3 (omitting the case $\mathbf{k}_i=0$).

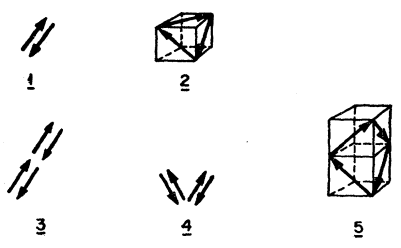

FIG. 3. Sets of four vectors $\mathbf{k}_i$, drawn from the set 0, $\mathbf{h}$, satisfying $\sum\mathbf{k}_i=0$.

[17] $\gamma=1$ means $\gamma\equiv(\nu,u)=(1,u)$; (the possibilities $u=x$ or y are implicit).

The other property needed is that $M(\gamma_1\mathbf{k}_1,\cdots\gamma_4\mathbf{k}_4)=0$ unless there are an even number of differentiations with respect to the x components and likewise for the y components.

From the latter property it follows that we can obtain a solution of (56) in which all the y components, $q(1\mathbf{k})^{y(0)}$, are zero (i.e., all the spins are parallel to the x-z plane). We confine ourselves to this case.

From the first property it follows that it is consistent with (56) to have

$$q(\gamma\mathbf{k})^{(0)}=0, \quad \text{all } (\gamma,\mathbf{k}) \text{ except } (1,\mathbf{k}_0),\ (1,-\mathbf{k}_0). \tag{61}$$

To show this, we first put $\mathbf{k}=\mathbf{k}_0$ in (56), giving

$$m_1^{(1)}(\mathbf{k}_0)q(1\mathbf{k}_0)^{(0)}+(1/3!)\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\mathfrak{M}(1\mathbf{k}_0,1\mathbf{k}_1,1\mathbf{k}_2,1\mathbf{k}_3)^{(0)} \times q(1\mathbf{k}_1)^{(0)}q(1\mathbf{k}_2)^{(0)}q(1\mathbf{k}_3)^{(0)}=0. \tag{62}$$

If $q(1\mathbf{k})^{(0)}=0$ except for $\mathbf{k}=\pm\mathbf{k}_0$, the only contributions to the second term are from diagrams of type 3; i.e., the set $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ must contain one $\mathbf{k}_0$ and two $(-\mathbf{k}_0)$'s. Defining

$$\Lambda\equiv -m_1^{(1)}(\mathbf{h})>0 \tag{63}$$

and dropping the subscripts 1 on $\mathfrak{M}$, (62) becomes

$$\Lambda q(1\mathbf{k}_0)^{(0)*}=(1/2)\mathfrak{M}(\mathbf{k}_0,\mathbf{k}_0,-\mathbf{k}_0,-\mathbf{k}_0)^{(0)} \times q(1\mathbf{k}_0)^{(0)*}|q(1\mathbf{k}_0)^{(0)}|^2, \tag{64}$$

or

$$|q(1\mathbf{k}_0)^{(0)}|^2=2\Lambda/\mathfrak{M}(\mathbf{k}_0,\mathbf{k}_0,-\mathbf{k}_0,-\mathbf{k}_0)^{(0)}. \tag{65}$$

Equation (65) can be satisfied only if $\mathfrak{M}(\mathbf{k}_0,\mathbf{k}_0,-\mathbf{k}_0,-\mathbf{k}_0)^{(0)}>0$, which shows explicitly the importance of having C_0 stable when $\eta=0$. $\mathfrak{M}$ is simply the value (to within a positive numerical factor) of the fourth order terms $\mathcal{E}_4$ when the spins are given by mode $(\gamma\mathbf{k})=(1\mathbf{k}_0)$ and $\eta=0$. The theorem of Sec. II shows this $\mathfrak{M}$ cannot be negative; we had to use direct computation to show that it is not zero.

To complete the proof that (65), with all other q's zero, gives a solution, we must show that (56) is satisfied for the other $\mathbf{k}$'s in our set. Suppose $\mathbf{k}=\mathbf{h}\neq\pm\mathbf{k}_0$. Then the first term in (56) is zero. In the second term, $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ must be $\pm\mathbf{k}_0$; but a glance at Fig. 3 shows that $\mathfrak{M}(\mathbf{h},\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)^{(0)}$, with the $\mathbf{k}_i$ chosen in this way, must be zero. The same argument applies when $\mathbf{k}=0$.

To satisfy the extremum equations to order $\eta^{\frac{3}{2}}$, (57) gives

$$q(\gamma\mathbf{k})^{(1)*}=-\frac{1}{3!m_\gamma^{(0)}(\mathbf{k})}\sum\mathfrak{M}(\gamma\mathbf{k},1\mathbf{k}_1,1\mathbf{k}_2,1\mathbf{k}_3)^{(0)} \times q1\mathbf{k}_1{}^{(0)}q1\mathbf{k}_2{}^{(0)}q1\mathbf{k}_3{}^{(0)}, \quad (\gamma\mathbf{k}\text{ not in }\mathcal{S}), \tag{66}$$

where each $\mathbf{k}_i=\pm\mathbf{k}_0$ in the sum. The $q(\gamma\mathbf{k})^{(1)}$ for $\gamma\mathbf{k}$ in $\mathcal{S}$ will be determined by terms in (47) of order $\eta^{\frac{5}{2}}$, and so on.

It should be pointed out that the solution (61), (66), $\cdots$ is not the only one. If various numbers of the $q(1\mathbf{h})^{(0)}$ are assumed to be nonzero, one obtains different solutions of the extremum conditions, with different energies. Using (56), the energy, to second order in η, can be written

$$\mathcal{E}=\mathcal{E}_0-(\Lambda\eta^2/4)\textstyle\sum_{\mathbf{h}}|q(1\mathbf{h})^{(0)}|^2. \tag{67}$$

Although it appears as though the more modes excited, the lower the energy will be, this is not generally the case, since the amplitudes for the nonzero modes are functions of the number of such modes.[18] We shall not investigate all these possibilities to determine which minimizes (67).

In any case, we have the result that the minimum energy configuration of the form (39) is, in lowest order, a linear combination of the modes $(\gamma\mathbf{k})$ in $\mathcal{S}$, defined at $\eta=0$; the energy, $\mathcal{E}-\mathcal{E}_0$, is negative and of order η^2. As shown explicitly in Sec. V, such a configuration exhibits long-range ordering of the x and y spin-components. Also Eqs. (61) and (65) give an explicit example of an equilibrium configuration (for sufficiently small η) which has angles simultaneously between A spins and between B spins.

V. NEUTRON DIFFRACTION CROSS SECTION

Corliss and Hastings[19] studied the normal, cubic spinel $MnCr_2O_4$ at low temperatures using neutron diffraction techniques. They found a long-range ordered magnetic structure, not of the Néel type, with angles both between the A spins and between the B spins. This was perplexing on the basis of existing theoretical work.[2,4,5] However, as we have seen in the preceding sections, these general aspects of the experimental results are consistent with the classical Heisenberg model.

We will calculate the diffraction cross section in this section although the limitation of the present calculations to small η prohibits a direct comparison with their experiment. Our purpose is to show explicitly that our result (in lowest order) gives rise to extra diffraction peaks characteristic of long-range ordering of the "angles," and that the detailed properties of the spin configuration for large η must be qualitatively different from those of the lowest order result in order to agree with the experiment on $MnCr_2O_4$. The cross section for elastic magnetic scattering of unpolarized neutrons is proportional to[20]

$$Q=|\mathbf{P}|^2-|\hat{e}\cdot\mathbf{P}|^2, \tag{68}$$

where

$$\mathbf{P}=\textstyle\sum_{n\gamma}\exp(i\mathbf{e}\cdot\mathbf{R}_{n\gamma})\mathbf{S}_{n\gamma}\equiv\mathbf{P}(\mathbf{e}), \tag{69}$$

$\mathbf{e}$ is the neutron scattering vector (incident minus scattered neutron wave vectors), $\hat{e}=\mathbf{e}/|\mathbf{e}|$, $\gamma=1,\ 2$

[18] We have investigated the following solutions (all with the y-components zero): any two q's and their conjugates not zero, and an arbitrary number of q's not zero, all real and equal. Of these, (61) is of lowest energy.

[19] L. Corliss and J. Hastings (private communication).

[20] O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).

refers to A sites, $\gamma=3, 4, 5, 6$ to B sites. For simplicity we can assume the spins are all parallel to the x-z plane since this will not affect the location of the diffraction peaks. Using (11) and (19),

$$\sigma_{n\gamma}{}^{x}=\sum_{\mathbf{k},\mu}\exp(i\mathbf{k}\cdot\mathbf{R}_{n\gamma})U_{\gamma\mu}(\mathbf{k})q_{\mu\mathbf{k}},$$

so that with (39), (51), and (54),

$$\sigma_{n\gamma}{}^{x}=\eta^{\frac{1}{2}}\sum_{\mathbf{h}}\exp(i\mathbf{h}\cdot\mathbf{R}_{n})U_{\gamma 1}{}^{(0)}(\mathbf{h})q_{1\mathbf{h}}{}^{(0)}+O(\eta^{\frac{3}{2}}). \quad (70)$$

Using (70) to expand the z component of (69) as $P_z{}^{(0)}(\mathbf{e})+\eta P_z{}^{(1)}(\mathbf{e})+\cdots$, we find

$$Q=(1-e_z{}^2)\{|P_z{}^{(0)}(\mathbf{e})|^2+2\,\mathrm{Re}[P_z{}^{(0)}(\mathbf{e})P_z{}^{(1)}(\mathbf{e})^*]\eta\}+(1-e_x{}^2)|\textstyle\sum_{\mathbf{h}}D(\mathbf{e}+\mathbf{h})q_{1\mathbf{h}}{}^{(0)}F^{(0)}(\mathbf{e},\mathbf{h})|^2\eta. \quad (71)$$

Here e_x and e_z are components of $\hat{e}$, $(1-e_z{}^2)|P_z{}^{(0)}(\mathbf{e})|^2$ is the function Q for the Néel configuration,

$$D(\mathbf{v})=\sum_{n}\exp(i\mathbf{v}\cdot\mathbf{R}_{n}), \quad (72)$$

$\mathbf{R}_n$ are the lattice vectors for one fcc lattice, and

$$F^{(0)}(\mathbf{e},\mathbf{h})=\sum_{\gamma}S_{\gamma}U_{\gamma 1}{}^{(0)}(\mathbf{h})\exp[i(\mathbf{e}+\mathbf{h})\cdot\varrho_{\gamma}] \quad (73)$$

is the structure factor for the x components in mode $(1\mathbf{h})$.

$D(\mathbf{v})$ is the familiar interference function consisting of essentially delta-function peaks at $\mathbf{v}=\mathbf{K}$. Hence *extra* peaks (in addition to those for C_0) occur when

$$\mathbf{e}+\mathbf{h}=\mathbf{K}, \quad (74)$$

(with the restriction that the neutron energy change is zero). Equation (74) is the same condition obtained for spirals.[3,21,22]

The series of peaks (74) was not present in the $MnCr_2O_4$ experiment. In addition, the experimentally observed (200) peak does not appear in (71).[23] Thus we must conclude that the experimental configuration cannot be represented by the first few terms in our perturbation series.

VI. SUMMARY AND DISCUSSION

Having shown that the Yafet-Kittel triangular configurations do not minimize the exchange energy in the cubic spinel, we have investigated a method for determining the classical ground state. This consists of first determining the maximum value, y_0, of y for which the Néel configuration, C_0, is locally stable; and then looking for solutions, C, of the extremum equations as series in powers of $\eta=y-y_0(>0)$, with each spin deviating slightly from its direction in C_0 when η is small. It is assumed that the ground state is given by C_0 for $0\leqslant y\leqslant y_0$, and by the minimum energy solution C for $y>y_0$ (providing the energy of this solution is lower than C_0, of course). These assumptions seem to be plausible *a priori* and they lead to physically reasonable results for the spinel.

We have applied the method in some detail to the cubic spinel. y_0 was determined and certain properties of the solutions C were obtained. Namely, in lowest order the C are linear combinations of the configurations $C(\mathbf{h})$, these being of lower energy than C_0 when $y>y_0$. $\mathbf{h}$ is any of the twelve (110)-vectors with magnitude k_0 corresponding to a wavelength $0.861a\sqrt{2}$. The $C(\mathbf{h})$ exhibit nonzero angles simultaneously between spins on the A sites and between those on the B sites; the x (or y) components of the spins on any one face-centered-cubic sublattice being given by $\psi_{\mathbf{h}}\sin\mathbf{h}\cdot\mathbf{R}_i$, one amplitude $\psi_{\mathbf{h}}$ for each of the six sublattices.[24] Pictorially, this corresponds to spin-deviations from the Néel configuration which vary sinusoidally in a [110] direction, with a wavelength of approximately twice the primitive translation in this direction, as indicated in Fig. 2.

Now a rigorous deduction[2,5] from the Yafet-Kittel assumptions is that in an equilibrium state there can be angles between A spins *or* between B spins, never both. Our results show on theoretical grounds that this is overly restrictive.

The present theory suggests that the ground state, as defined by the classical Heisenberg energy, is a long-range-ordered arrangement of canted spins. On the other hand, Anderson[4] showed that there is an enormous number of ways of placing a given number of +'s and −'s on the octahedral lattice, all with the maximum short-range order and, therefore, with the minimum B-B exchange energy (assuming nearest neighbor B-B interactions only). By identifying the +'s and −'s with the projections on the x-y plane of the canted spins in the Yafet-Kittel picture, he was led to suggest that there would be no long-range ordering of these components. This conclusion is correct in the absence of A-B interactions, but our calculations show that inclusion of the latter will remove this degeneracy.

Our general conclusions are in agreement with the neutron diffraction results of Corliss and Hastings[19] on $MnCr_2O_4$, which indicate that there are long-range-ordered "angles," with angles simultaneously on the A and on the B sites. However, the results of our calculations, which were made only in the lowest order of approximation, do not agree in important detail. This points up the need for carrying the present calculations to higher orders, and, more important, to investigate the correctness of our assumptions.

We should mention the results of Pickart and Nathans[25] on mixed ferrite-chromites (which are cubic), showing no long-range ordering of spin angles. This does

[21] A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959); J. Villain, J. Phys. Chem. Solids (to be published).

[22] It is also the same as for spin-wave scattering; an important difference is that in the latter case the neutron energy does change.

[23] Although the (200) is one of the series $\mathbf{e}=\mathbf{K}$, which applies to C_0, it vanishes in $P_x{}^{(0)}(\mathbf{e})$ because of a zero structure factor; it will appear, however, in the next order term, through $P_z{}^{(1)}(\mathbf{e})$.

[24] It should be emphasized that in these configurations the amplitudes $\psi_{\mathbf{h}}$ are small, the z components never changing sign within one face-centered-cubic sublattice. This constitutes a basic difference between these configurations and "spirals" or "helices" (see references 3 and 21).

[25] S. J. Pickart and R. Nathans, Phys. Rev. **116**, 317 (1959).

not contradict our results, since in these materials there are two different spin magnitudes placed randomly on the octahedral lattice, so that the translational symmetry, which enters in a basic way into our calculations, is destroyed.

Our results appear to have interesting possibilities in connection with recent experiments on hausmannite (Mn_3O_4). The results of Kasper[26] and Jacobs[27] indicate that there are canted spins in this material. The former has shown that there is a doubling of the magnetic unit cell in the [110] direction, and has proposed a particular model to explain his diffraction intensities. However, Dwight and Menyuk[28] have pointed out that there is no energy difference between Kasper's model (which has angles only on the B lattice) and others which do not double the magnetic cell. Our result that the important mode, $C(\mathbf{h})$, approximately doubles the cell in [110] is, therefore, quite suggestive in this connection. We plan to investigate the effect on our calculations of the tetragonal distortion which characterizes Mn_3O_4 and other manganites.

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APPENDIX I. PROOF OF INSTABILITY OF YAFET-KITTEL CONFIGURATIONS IN THE CUBIC SPINEL

We consider a cubic spinel with nearest neighbor A-B and B-B interactions only, so that the energy is given by Eq. (1). Yafet and Kittel showed that, consistent with their sublattice assumption, there were a number of degenerate triangular ground states. To show the instability of these states we clearly need only show the instability of one of them. For our purposes, then, we consider the particular configuration (P) invoked by Prince,[12] in which the A spins all point in the z direction, B_1 and B_2 are parallel to z_1, B_3, and B_4 are parallel to z_3, where z_1 and z_3 make angles θ and $-\theta$ with the negative z direction, as shown in the figure of reference 3. (Also refer to Fig. 1 of reference 7, interchanging B_2 and B_3.)

Since we shall prove instability, we may consider a limited set of configurations, namely

$$\begin{aligned}\boldsymbol{\sigma}_{n\alpha}{}^{A}&=\hat{x}\sigma_{n\alpha}{}^{Ax}+\hat{z}\sigma_{n\alpha}{}^{Az},\\ \boldsymbol{\sigma}_{n\beta}{}^{B}&=\hat{x}\sigma_{n\beta}{}^{Bx}+\hat{z}_\beta\sigma_{n\beta}{}^{Bz_\beta}\\ &=\hat{x}\sigma_{n\beta}{}^{Bx}-(\hat{y}\sin\theta_\beta+\hat{z}\cos\theta_\beta)\sigma_{n\beta}{}^{Bz_\beta},\end{aligned}\tag{A.1}$$

where

$$\theta_1=\theta_2=-\theta_3=-\theta_4=\theta,\qquad z_1=z_2,\quad z_3=z_4,\tag{A.2}$$

and $\hat{x}$ is a unit vector in the x direction, etc. When the x components are zero, (A.1) corresponds to configuration P. For small deviations from P,

$$\begin{aligned}\sigma_{n\alpha}{}^{Az}&\cong 1-(\sigma_{n\alpha}{}^{Ax})^2/2\\ \sigma_{n\beta}{}^{Bz_\beta}&\cong 1-(\sigma_{n\beta}{}^{Bx})^2/2.\end{aligned}\tag{A.3}$$

We will show that for certain deviations in this class, $E<$ the energy of P.

Substituting (A.1) and (A.3) into Eq. (1), keeping only up to quadratic terms in the x components, yields

$$\begin{aligned}E'=E/2J_{AB}S_AS_B=E'(\theta)&+6\mu\textstyle\sum_{n\alpha}(\sigma_{n\alpha}{}^{Ax})^2\\ &+(3\mu-Cy)\textstyle\sum_{m\beta}(\sigma_{m\beta}{}^{Bx})^2+\sum_{\langle n\alpha,m\beta\rangle}\sigma_{n\alpha}{}^{Ax}\sigma_{m\beta}{}^{Bx}\\ &+y\sum_{\langle n\beta,n'\beta'\rangle}\sigma_{n\beta}{}^{Bx}\sigma_{n'\beta'}{}^{Bx},\end{aligned}\tag{A.4}$$

where

$$\begin{aligned}E'(\theta)&=4N(yC-6\mu),\\ \mu&=\cos\theta,\\ C&=1+2\cos 2\theta.\end{aligned}\tag{A.5}$$

(The notation for the summation indices and other symbols is defined in the text.) The angle θ is chosen to minimize $E'(\theta)$, leading to the Yafet-Kittel condition,

$$\mu=3/(4y),\tag{A.6}$$

when $y>\frac{3}{4}$; otherwise, $\mu=1$. We shall consider only the case $y>\frac{3}{4}$. Then

$$3\mu-Cy=y.\tag{A.7}$$

Now consider the deviations

$$\begin{aligned}\sigma_{n\alpha}{}^{Ax}&=N^{-\frac{1}{2}}\psi_1\cos\mathbf{k}\cdot\mathbf{R}_{n\alpha}{}^{A},\\ \sigma_{n\beta}{}^{Bx}&=N^{-\frac{1}{2}}\phi_\beta\cos\mathbf{k}\cdot\mathbf{R}_{n\beta}{}^{B},\end{aligned}\tag{A.8}$$

where $\mathbf{k}$ is a rationalized reduced reciprocal vector in [110] ($\neq\mathbf{K}$), and $\phi_1=\phi_2\equiv\psi_2$, $\phi_3=\phi_4\equiv\psi_3$; (the ψ_i are arbitrary amplitudes). Substituting (A.8) into (A.4), we obtain

$$E'-E'(\theta)=\Delta E'=\textstyle\sum M_{ij}\psi_i\psi_j,\tag{A.9}$$

where

$$\mathbf{M}=\begin{pmatrix}6\mu & 3c & 3z\\ 3c & 2yc^2 & 2yc\\ 3z & 2yc & 2y\end{pmatrix},\tag{A.10}$$

with c and z as defined in Sec. III. For $\Delta E'$ to be positive for any values of the ψ_i, it is necessary that the determinant, D, of $\mathbf{M}$ be positive. But direct calculation gives

$$D=-18yc^2(1-z)^2,\tag{A.11}$$

which is <0 for $k\neq 0$ (y is positive). Hence, there are values of the ψ_i such that $\Delta E'<0$. This completes the proof of the instability.

It is interesting to note that, since $\Delta E=2J_{AB}S_AS_B\Delta E'$, the determinant, D', of the matrix, $\mathbf{M}'$, of ΔE is proportional to $(J_{AB})^3y\propto(J_{AB})^2J_{BB}$. Hence there is an important difference between the limits 1. $y\to\infty$,

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$J_{AB}\to 0$, and 2. $y\to\infty$, $J_{AB}\neq 0$. In the first case, considering the limit $J_{AB}=0$, we see that $D'=0$, so that there is at least one zero eigenvalue of $\mathbf{M}'$. It can be shown that,[29] for general small deviations from the Y-K-Prince configuration in the limit $J_{AB}=0$, there are zero eigenvalues for all $\mathbf{k}$, and no negative eigenvalues. This is consistent with Anderson's result,[4] the zero eigenvalues corresponding to a large degeneracy in the ground state. In the second limit, we see that $D'\to-\infty$ as $J_{BB}\to\infty$, showing that there is at least one negative eigenvalue, and therefore a state of lower energy than the Y-K configuration.

APPENDIX II: FUNCTIONS $\eta_{\alpha\beta}(k)$, $\zeta_{\beta\beta'}(k)$

Writing

$$(\alpha,\beta,\gamma)=(a/8)(\alpha k_x+\beta k_y+\gamma k_z),$$

we have, using the definitions given by Eq. (13),

$$\begin{aligned}
\eta_1&=(1/3)[\exp i(1,1,-3)\\
&\quad+\exp i(1,-3,1)+\exp i(-3,1,1)],\\
\eta_2&=(1/3)[\exp i(-1,-1,-3)\\
&\quad+\exp i(-1,3,1)+\exp i(3,-1,1)],\\
\eta_3&=(1/3)[\exp i(-1,1,3)\\
&\quad+\exp i(-1,-3,-1)+\exp i(3,1,-1)],\\
\eta_4&=(1/3)[\exp i(1,-1,3)\\
&\quad+\exp i(1,3,-1)+\exp i(-3,-1,-1)],
\end{aligned}\tag{A.12}$$

and

$$\begin{aligned}
&\zeta_{12}=\cos(2,2,0),\quad \zeta_{13}=\cos(2,0,2),\quad \zeta_{14}=\cos(0,2,2),\\
&\zeta_{34}=\cos(2,-2,0),\quad \zeta_{23}=\cos(0,2,-2),\quad \zeta_{24}=\cos(2,0,-2).
\end{aligned}\tag{A.13}$$

APPENDIX III: RELATION BETWEEN SPIN-WAVE FREQUENCIES, $\omega_\gamma(k)$, AND THE EIGENVALUES $m_\gamma(k)$

If $E_2=6NJ_{AB}S_AS_B\mathcal{S}_2\equiv cN\mathcal{S}_2$, the linearized spin wave equations of motion are

$$\dot\sigma_j{}^{\Gamma x}=\epsilon_\Gamma\partial E_2/\partial\sigma_j{}^{\Gamma y};\quad \dot\sigma_j{}^{\Gamma y}=-\epsilon_\Gamma\partial E_2/\partial\sigma_j{}^{\Gamma x},$$

where $\epsilon_A=1/S_A$, $\epsilon_B=-1/S_B$. Using the transformation (11) and Eq. (14) these become

$$\begin{aligned}
\dot\chi_{\gamma\mathbf{k}}{}^x&=(\epsilon_\Gamma/N)\partial E_2/\partial\chi_{\gamma\mathbf{k}}{}^{y*}\\
&=c\epsilon_\Gamma\textstyle\sum_{\gamma'}M_{\gamma\gamma'}(\mathbf{k})\chi_{\gamma'\mathbf{k}}{}^y,\\
\dot\chi_{\gamma\mathbf{k}}{}^y&=-(\epsilon_\Gamma/N)\partial E_2/\partial\chi_{\gamma\mathbf{k}}{}^{x*}\\
&=-c\epsilon_\Gamma\textstyle\sum_{\gamma'}M_{\gamma\gamma'}(\mathbf{k})\chi_{\gamma'\mathbf{k}}{}^x.
\end{aligned}\tag{A.14}$$

Writing

$$\chi_{\gamma\mathbf{k}}{}^x+i\chi_{\gamma\mathbf{k}}{}^y=C_{\gamma\mathbf{k}}\exp(-i\omega t),$$

we have

$$\begin{aligned}
(\omega/c)C_{\gamma\mathbf{k}}&=\epsilon_\Gamma\textstyle\sum_\mu M_{\gamma\mu}(\mathbf{k})C_{\mu\mathbf{k}}\\
&\equiv\textstyle\sum_{\nu\mu}\epsilon_\nu\delta_{\gamma\nu}M_{\nu\mu}(\mathbf{k})C_{\mu\mathbf{k}},
\end{aligned}\tag{A.15}$$

where $\epsilon_\gamma=\epsilon_A$, $\gamma=1$, 2, or ϵ_B when $\gamma=3,\cdots,6$. Therefore

$$\begin{aligned}
\textstyle\prod_\gamma[\omega_\gamma(\mathbf{k})/c]&=S_A{}^{-2}S_B{}^{-4}\,\mathrm{Det}[\mathbf{M}(\mathbf{k})]\\
&=S_A{}^{-2}S_B{}^{-4}\textstyle\prod_\gamma m_\gamma(\mathbf{k}).
\end{aligned}\tag{A.16}$$

Equation (A.15) allows us a direct check on our explicit expression for $\mathbf{M}(\mathbf{k})$, Eq. (15). It can be seen that (A.15), keeping in mind the definition given by Eq. (2), agrees with Kouvel's[10] equations (2.5).[30]

The reason we have discussed the stability problem in terms of the $m_\gamma(\mathbf{k})$ instead of the physically more interesting $\omega_\gamma(\mathbf{k})$ is that the latter may be positive or negative whether or not the Néel configuration is stable. (The meaning of the sign of the $\omega_\gamma(\mathbf{k})$ has been discussed previously.)[7] We might add that the symmetry vectors used to factor the secular equation for $\mathbf{k}$ in symmetry directions (Sec. III and Appendix 4) will also factor (A.15).

APPENDIX IV: FACTORIZATION OF THE SECULAR EQUATION FOR k IN [100] AND [111]

Our purpose is to outline the calculations which show that $\mathbf{M}(\mathbf{k})$, for $\mathbf{k}$ in [100] and [111], are positive definite matrices when $y<\frac{3}{4}$ and $\mathbf{k}\neq 0$.

For $\mathbf{k}$ in [100] we transform $\mathbf{M}$ to the basis

$$\begin{aligned}
&(1/\sqrt2)(0,0,1,0,0,-1),\quad (1/\sqrt2)(0,0,0,1,-1,0),\\
&(1/\sqrt2)(1,1,0,0,0,0)\\
&(1/\sqrt2)(0,0,1,1,1,1),\quad (1/\sqrt2)(1,-1,0,0,0,0),\\
&(1/2)(0,0,1,1,1,1).
\end{aligned}$$

$\mathbf{M}$ then consists only of submatrices on the diagonal with dimensionalities 1, 1, 2, 2. The two 1×1's are degenerate with the eigenvalue $2(1-4y/3)$ and the remaining eigenvalues are easily shown to be positive.

For $\mathbf{k}$ in [111], the basis

$$\begin{aligned}
&(1/\sqrt2)(0,0,0,1,-1,0),\quad (1/\sqrt6)(0,0,0,1,1,-2),\\
&(1,0,0,0,0,0),\quad (0,1,0,0,0,0),\quad (0,0,1,0,0,0),\\
&(1/\sqrt3)(0,0,0,1,1,1),
\end{aligned}$$

yields two degenerate eigenvectors (the first two) with eigenvalue $2(1-4y/3)$; the determinant of the remaining 4×4 submatrix can be shown by straightforward calculation to be positive.

APPENDIX V: MONOTONE BEHAVIOR WITH y OF THE $m_\nu(\mathbf{k})$

We shall show that the $m_\nu(\mathbf{k})$ for all ν, $\mathbf{k}$, never increase with increasing y. For any $\mathbf{k}$ we can write our

[29] For arbitrary deviations in this limit one need consider only the (4×4) matrix $\zeta_{\beta\beta'}$ (with $\zeta_{\beta\beta}\equiv1$). This has the interesting property that the cofactor of every element vanishes identically for all $\mathbf{k}$. It follows that there are two zero eigenvalues for each $\mathbf{k}$; the remaining two eigenvalues are easily shown to be positive.

[30] It should be noted that in Eqs. (2.6) [see reference 10], there are misprints involving factors of 2.

matrix as

$$\mathbf{M}(y)=\mathbf{M}_a+y\mathbf{M}_b, \quad (A.17)$$

where $\mathbf{M}_a$ arises from the A-B interactions, $y\mathbf{M}_b$ from the B-B interactions ($\mathbf{M}_a$ and $\mathbf{M}_b$ are independent of y). The eigenvalue equation, in vector notation, is

$$\mathbf{M}(y)\mathbf{U}(y)=m(y)\mathbf{U}(y).$$

Clearly

$$m(y)=(\mathbf{U}(y),\mathbf{M}\mathbf{U}(y))/(\mathbf{U}(y),\mathbf{U}(y)).$$

Letting prime indicate differentiation with respect to y, we have

$$m'(y)=(\mathbf{U}(y),\mathbf{M}_b\mathbf{U}(y))/(\mathbf{U}(y),\mathbf{U}(y)). \quad (A.18)$$

But Eq. (7) shows that the B-B interaction is negative semidefinite; since the right-hand side of (A.18) represents the B-B interaction energy for some set of deviations, it follows that

$$\frac{\partial}{\partial y}m_\nu(\mathbf{k})\leqslant 0, \quad \text{all } \nu, \mathbf{k}. \quad (A.19)$$

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Magnetic Properties of Mn_3O_4 and the Canted Spin Problem*

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The magnetic properties of single crystals of hausmannite (Mn_3O_4) have been investigated between 4.2°K and the ferrimagnetic Curie point at 41.9°K. The c axis was found to be the hard direction of magnetization and the c plane was found to possess considerable anisotropy, with respective anisotropy fields of about 10^5 oe and 10^4 oe. These anisotropy energies decreased slowly with increasing temperature, whereas the coercive force at 15°K was about an order of magnitude less than at 4.2°K. The spontaneous magnetization is 1.85 μ_B/molecule, which agrees with previous polycrystalline values when the observed anisotropies are taken into account. However, several of the observed properties of hausmannite disagree, some quantitatively and others qualitatively, with calculations based on the Yafet-Kittel theory. It is concluded that the concept of canted spins is essentially correct, but that the specific Yafet-Kittel model involves oversimplifications which limit its applicability.

I. INTRODUCTION

CONSIDERABLY more information can be obtained from studies of the magnetic properties of single crystals than from those made with polycrystalline samples. The magnetic anisotropy, which is a sensitive indicator of magnetic symmetry and of changes in that symmetry, can be determined in detail only by measurements on single crystals. Furthermore, an accurate determination of the magnetization of a single crystal can be made independently of the crystalline anisotropy by applying the external field along an easy direction. In polycrystalline samples, however, anisotropy has the effect of reducing the apparent magnetic moment. This effect can be important for materials with large anistropy.

We have investigated the magnetic properties of single-crystal samples of hausmannite (Mn_3O_4),[1] which is known to become ferrimagnetic at about 42°K.[2] Our measurements show that the c axis is a hard magnetization direction and that the c plane also possesses considerable anisotropy, the respective anisotropy fields being approximately 10^5 oe and 10^4 oe. The temperature variations of both these anisotropy energies are small. On the other hand, the coercive force at about 15°K is an order of magnitude less than the 2650 oe observed at 4.2°K. We find the spontaneous magnetization to be 1.85 μ_B/molecule, which is greater than the values 1.4 μ_B/molecule[3] and 1.56 μ_B/molecule[4] previously measured for polycrystalline samples. Both of the latter values are low because of the anisotropy effect, and can be brought into good agreement with our present value by a correction calculated from our anisotropy data. However, our present value is also less than the 3.0 μ_B/molecule predicted by the Néel model of ferrimagnetism.

Many other materials with spinel structure exhibit smaller spontaneous magnetizations than predicted.[5] The Yafet-Kittel theory[6] of spin angles was introduced to account for such reduced moments. Although hausmannite has a cubic spinel structure above 1170°C,

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