Thermal Variation of the Pitch of Helical Spin Configurations

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When the method of Luttinger and Tisza for finding the classical ground state of a system of spins with Heisenberg interactions is applicable, it yields a configuration with the same periodicity as the ordered state existing just below the transition temperature. When the method of Luttinger and Tisza fails to yield the classical ground state then there can occur, with decreasing temperature, either additional transitions or a gradual change in the periodicity of the stable configuration. An example of the latter is the thermal change in pitch of a helical configuration. Such a situation can be described in the internal field approximation when the consistency equations admit as solutions helical states with a continuous range of pitches. The free energy of the stable state with a temperature-dependent pitch can then be obtained as the envelope of the free-energy curves belonging to the family of helical solutions. A one-dimensional diatomic chain whose ground state can be found by a generalization of the method of Luttinger and Tisza illustrates this possibility. It is also pointed out that anisotropic exchange interaction between nearest neighbors can give rise to helically ordered configurations.

I. INTRODUCTION

THE internal field approximation as originally applied by Néel[1] to materials in which there occurred antiferromagnetic exchange integrals involved the *a priori* decomposition of the system into sublattices, the magnetization of each sublattice being assumed to be uniform. With the use of a more flexible sublattice decomposition[2] it was found possible to have states in which the sublattice magnetizations are not collinear. Recent studies[3–7] of the classical ground states of such systems have shown that it is possible to have a helical arrangement of the spins, the pitch of the helix being, in general, incommensurate with the lattice spacing so that it is an ordered state not describable in terms of uniformly magnetized sublattices. The systems studied all involved Heisenberg interactions between ions more distant than nearest neighbors. Villain[4] has applied to such systems a more general form of the internal field approximation and has shown that in Bravais lattices the stable state at absolute zero remains stable at all temperatures up to the temperature of the transition to the disordered state. In other words, there can occur no other transition and no change in pitch of the helix.

Bertaut[6] has considered the classical ground state of lattices having more than one ion per primitive cell under the assumption that associated with each ion in the cell is a helix, all of the helices having the same pitch. Kaplan,[5] treating the spinel, has examined states deviating only slightly from the Néel configuration.

In the works cited, except for that of Villain on the Bravais lattice, attention was restricted either to the ground state or to the first ordered state to appear with decreasing temperature. In general, however, when a stable helical configuration occurs, its pitch will be a function of temperature. The variation with temperature of the pitch of the helical order is describable within the framework of the classical internal field approximation. The occurrence of such a phenomenon will be illustrated here for a one-dimensional diatomic lattice containing nearest and next nearest neighbor interactions.

In Sec. II the transition from the disordered state is considered on the basis of a general formulation of the internal field approximation. In Sec. III the method of Luttinger and Tisza[8] for finding the ground state of a spin configuration is generalized to the case of a lattice containing nonequivalent ions. In Sec. IV the first ordered state and the ground states of the linear diatomic chain are discussed in detail. It is found that for a wide range of parameters a gradual change in the pitch of the helical order can occur with changing temperature. For a specific choice of parameters the free energy is calculated and the actual occurrence of this phenomenon demonstrated.

II. TRANSITION FROM THE DISORDERED STATE

A general formulation of the internal field approximation is given in the Appendix. For the sake of completeness, and the better to contrast this problem with that of finding the ground state, we present here the derivation of the conditions determining the periodicity of the first ordered state that occurs when the temperature decreases. We shall, in the following, restrict attention to isotropic exchange interaction reserving to the end of the section some comments on anisotropic exchange.

We consider a lattice containing f ions per primitive cell, the exchange interaction between ion i in the primitive cell at R and ion j in the cell at R' being

$$J_{ij}^{RR'}\mathbf{S}_i^R\cdot\mathbf{S}_j^{R'}. \tag{1}$$

The f ions in the cell may have different spins,

$$|\mathbf{S}_i^R|=S_i,$$

[1] L. Néel, Ann. Phys. **3**, 137 (1948).
[2] Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).
[3] A. Yoshimori, J. Phys. Soc. (Japan) **14**, 807 (1959).
[4] J. Villain, J. Phys. Chem. Solids **11**, 303 (1959).
[5] T. A. Kaplan, Phys. Rev. **116**, 888 (1959); **119**, 1460 (1960).
[6] F. Bertaut, Compt. rend. **250**, 85 (1960).
[7] B. R. Cooper, Phys. Rev. **118**, 135 (1960).
[8] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

but in a classical treatment these spin magnitudes may be absorbed into the interaction constants, the J's, by the replacement of $J_{ij}^{\mathbf{RR}'}$ by $J_{ij}^{\mathbf{RR}'}S_iS_j$. With this understanding, the expression (1) still holds with $\mathbf{S}_i^{\mathbf{R}}$ having unit magnitude for all i, $\mathbf{R}$. The translational symmetry of the problem is expressed by

$$J_{ij}^{\mathbf{RR}'}=J_{ij}^{\mathbf{R}-\mathbf{R}'',\mathbf{R}'-\mathbf{R}''}, \tag{2}$$

where $\mathbf{R}''$ is any lattice vector. We shall, in addition, assume periodic boundary conditions for a crystal containing N cells.

Equations (A.7) and (A.8) give us

$$\boldsymbol{\sigma}_i^{\mathbf{R}}=\int d\omega_i^{\mathbf{R}}\cdot\mathbf{S}_i^{\mathbf{R}}\exp\{-\beta\mathbf{S}_i^{\mathbf{R}}\cdot\sum_{j,\mathbf{R}'}J_{ij}^{\mathbf{RR}'}\boldsymbol{\sigma}_j^{\mathbf{R}'}\}\Big/\int d\omega_i^{\mathbf{R}}\times\exp\{-\beta\mathbf{S}_i^{\mathbf{R}}\cdot\sum_{j,\mathbf{R}'}J_{ij}^{\mathbf{RR}'}\sigma_j^{\mathbf{R}'}\},\quad(\text{all } i,\mathbf{R}). \tag{3}$$

As noted in the Appendix, (3) can be expressed in terms of the Langevin function. A quantum mechanical formulation of the internal field approximation leads to the same general equations with the Brillouin function replacing the Langevin function. This would complicate the calculation of the magnetization and the free energy without changing the situation qualitatively. At all temperatures, (3) possesses the solution

$$\boldsymbol{\sigma}_i^{\mathbf{R}}=0\quad(\text{all } i,\mathbf{R}) \tag{4}$$

representing the disordered state. At high temperatures this will be the only solution whereas at sufficiently low temperatures (3) may possess many solutions, each of which approaches (4) as the temperature increases. (The temperature at which a given solution vanishes will be denoted by T_b and will be referred to as the branching temperature for that solution, in the language of reference 12, since that is the temperature at which the free energy of the solution branches off from the free energy of the disordered state.) In the neighborhood of the branching temperature the exponentials in (3) can be expanded in powers of the $\boldsymbol{\sigma}_j^{\mathbf{R}}$. In the limit of vanishingly small $\boldsymbol{\sigma}_j^{\mathbf{R}}$, one may retain only the first nonvanishing term and so obtain

$$\sum_{j,\mathbf{R}'}J_{ij}^{\mathbf{RR}'}\sigma_{j,\mu}^{\mathbf{R}'}=\lambda\sigma_{i,\mu}^{\mathbf{R}}\quad(\text{all } i,\mathbf{R};\ \mu=1,2,3), \tag{5}$$

where

$$\lambda=-3/\beta=-3kT_b. \tag{6}$$

The index μ denotes the components of $\boldsymbol{\sigma}_i^{\mathbf{R}}$. Equation (5) is satisfied by the x, y, and z components of the $\boldsymbol{\sigma}_i^{\mathbf{R}}$ separately, this being a consequence of the assumed isotropy of the interaction.

Equation (5) is an eigenvalue problem in a space of Nf dimensions, the eigenvalues yielding the possible branching temperatures, the eigenvectors yielding the limiting ratios of the components of the $\boldsymbol{\sigma}_i^{\mathbf{R}}$ for a given solution as T approaches the branching temperature, T_b, for that solution. The translational symmetry of the matrix of $J_{ij}^{\mathbf{RR}'}$, Eq. (2), implies that Eq. (5) has a complete set of solutions of the form

$$\sigma_{i,\mu}^{\mathbf{R}}=\sigma_{i,\mu}^{0}e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{7}$$

the possible propagation vectors $\mathbf{k}$ being chosen in accord with the periodic boundary conditions. Substitution of Eq. (7) into Eq. (5) yields, with the use of Eq. (2),

$$\sum_j(\sum_{\mathbf{R}'}J_{ij}^{0\mathbf{R}'}e^{i\mathbf{k}\cdot\mathbf{R}'})\sigma_{j,\mu}^{0}=\lambda(\mathbf{k})\sigma_{i,\mu}^{0}, \tag{8}$$

which is again an eigenvalue problem for the f-rowed matrix having as its i,j element

$$\xi_{ij}(\mathbf{k})=\sum_{\mathbf{R}'}J_{ij}^{0\mathbf{R}'}e^{i\mathbf{k}\cdot\mathbf{R}'}. \tag{9}$$

For each $\mathbf{k}$ there will be, in general, f eigenvalues so that there are, altogether, three bands of eigenvalues to which there correspond, at least for negative $\lambda(\mathbf{k})$, three bands of branching temperatures.

The lowest lying eigenvalue gives the temperature of the transition from the disordered state to an ordered state. If the $\mathbf{k}$ yielding this minimum eigenvalue has components 0 or π, then the lattice associated with each ion in the primitive cell is ferromagnetically or antiferromagnetically ordered in the state existing just below the transition temperature. If one or more of the components of $\mathbf{k}$ is different from 0 or π, then the spins of each sublattice are helically ordered and would be given, for example, by

$$\begin{aligned}\sigma_{i,1}^{\mathbf{R}}&=\sigma_{i,1}^{0}\cos(\mathbf{k}\cdot\mathbf{R}+\varphi_i),\\ \sigma_{i,2}^{\mathbf{R}}&=\sigma_{i,2}^{0}\sin(\mathbf{k}\cdot\mathbf{R}+\varphi_i),\\ \sigma_{i,3}^{\mathbf{R}}&=0,\end{aligned} \tag{10}$$

which is a combination of real solutions of Eq. (5) belonging to $\lambda(\mathbf{k})$.

In the case of a Bravais lattice, Eq. (8) yields a single band of branching temperatures given by

$$-3kT_b=\lambda(\mathbf{k})=2\sum_{\mathbf{R}'}J^{0\mathbf{R}'}\cos(\mathbf{k}\cdot\mathbf{R}'), \tag{11}$$

which is Villain's result, aside from a constant factor arising from his use of the Brillouin function in place of the Langevin function.

The point to be noted here is that all real solutions of Eq. (5) are acceptable, the $\boldsymbol{\sigma}_i^{\mathbf{R}}$ being subject to no further conditions. Only the ratios of the $\boldsymbol{\sigma}_i^{\mathbf{R}}$ have significance. The situation will be quite different when we consider the ground state.

We note here, though the point will not be pursued, that when the exchange interaction is anisotropic and is given by Eq. (A.5), then in place of Eq. (5) one gets for the condition determining the branching temperatures

$$\sum_{j,\mathbf{R}'}\mathbf{J}_{ij}^{\mathbf{RR}'}\cdot\boldsymbol{\sigma}_j^{\mathbf{R}'}=\lambda\boldsymbol{\sigma}_i^{\mathbf{R}}. \tag{12}$$

One still has translational symmetry so that there

exists a complete set of solutions of the form

$$\boldsymbol{\sigma}_i^{\mathbf{R}}=\sigma_i^0 e^{i\mathbf{k}\cdot\mathbf{R}}. \tag{13}$$

Substitution of (13) into Eq. (12) yields

$$\sum_j(\sum_{\mathbf{R}'}\mathbf{J}_{ij}^{0\mathbf{R}'}e^{i\mathbf{k}\cdot\mathbf{R}'})\cdot\boldsymbol{\sigma}_j^0=\lambda(\mathbf{k})\boldsymbol{\sigma}_i^0. \tag{14}$$

Whereas in a Bravais lattice with isotropic exchange helical ordering cannot arise unless interactions are included between neighbors more widely separated than nearest neighbors, Eq. (14) can yield a helically ordered state in a Bravais lattice. Consider, for example, a one-dimensional lattice with the interaction between nearest neighbors given by

$$J\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\mathbf{S}_i\cdot\mathbf{D}\times\mathbf{S}_{i+1}, \tag{15}$$

the second term being of the form discussed by Moriya.[9] One can easily show that the ordered state of this system is helical, the angle between successive spins being $\tan^{-1}(D/J)$.

III. THE GROUND STATE

To determine the ground-state configuration we want to minimize the energy of the system,

$$W=\tfrac{1}{2}\sum_{ij}\sum_{\mathbf{RR}'}J_{ij}^{\mathbf{RR}'}\mathbf{S}_i^{\mathbf{R}}\cdot\mathbf{S}_j^{\mathbf{R}'}, \tag{16}$$

subject to the constraints

$$|\mathbf{S}_i^{\mathbf{R}}|^2=1 \quad (\text{all } i,\mathbf{R}). \tag{17}$$

The one general method for solving the problem, due to Luttinger and Tisza,[8] consists of the replacement of the conditions of Eq. (17) by a weaker constraint that is necessary but not sufficient, namely

$$\sum_i\sum_{\mathbf{R}}|\mathbf{S}_i^{\mathbf{R}}|^2=fN. \tag{18}$$

The minimum of W with this weaker condition is a lower bound on the energy of the ground state. If a configuration satisfying Eq. (17) can be found for which W attains this lower bound, then the problem is solved. This procedure leads to the eigenvalue problem

$$\sum_j\sum_{\mathbf{R}'}J_{ij}^{\mathbf{RR}'}\mathbf{S}_j^{\mathbf{R}'}=\lambda\mathbf{S}_i^{\mathbf{R}}, \tag{19}$$

where λ is two times the energy per ion. This is the same problem as Eq. (5). Here, as in Sec. II, we seek the lowest lying eigenvalue but the eigenvector belonging to this eigenvalue yields the ground state configuration only if it satisfies Eq. (17). If it does not, then the method fails. Thus when the method of Luttinger and Tisza is successful, the spin configurations of the ground state and the first ordered state are the same. When the method of Luttinger and Tisza fails then the ground state may differ in its symmetry or periodicity from the first ordered state and additional transitions may occur below the highest branching temperature, or there may be a gradual change in the spin configuration. In particular, there may occur a change in the period of a helical configuration. The latter possibility will be illustrated in Sec. IV.

The method of Luttinger and Tisza is successful when applied to Bravais lattices since for every eigenvalue there are real normal mode solutions of the form given by Eq. (10). The method will fail, in general, for systems containing nonequivalent ions. For such systems one can apply the following generalization of the method of Luttinger and Tisza.[10] For the weak constraints one uses, in place of Eq. (18), the stronger, though still not sufficient condition

$$\textstyle\sum_{\mathbf{R}}|\mathbf{S}_i^{\mathbf{R}}|^2=N \quad (i=1,\cdots,f). \tag{20}$$

The procedure is best described with the use of a normal mode representation. Let

$$\mathbf{S}_i^{\mathbf{R}}=\textstyle\sum_{\mathbf{k}}\mathbf{A}_i(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{21}$$

the sum extending over the first Brillouin zone, where in order that $\mathbf{S}_i^{\mathbf{R}}$ be real we require

$$\mathbf{A}_i^*(\mathbf{k})=\mathbf{A}_i(-\mathbf{k}). \tag{22}$$

The normal modes obey the orthogonality relations

$$\textstyle\sum_{\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{R}}e^{-i\mathbf{k}'\cdot\mathbf{R}}=N\delta_{\mathbf{k}\mathbf{k}'}. \tag{23}$$

With the use of Eq. (2) one obtains for the energy, expressed in terms of the normal mode amplitudes,

$$W=\frac{N}{2}\sum_{\mathbf{k}}\sum_{ij}\xi_{ij}(\mathbf{k})\mathbf{A}_i^*(\mathbf{k})\cdot\mathbf{A}_j(\mathbf{k}), \tag{24}$$

where $\xi_{ij}(\mathbf{k})$ is given by Eq. (9). The $\xi_{ij}(\mathbf{k})$ obey the relations

$$\xi_{ji}(\mathbf{k})=\xi_{ij}^*(\mathbf{k})=\xi_{ij}(-\mathbf{k}). \tag{25}$$

Equations (17) and (20) become, respectively,

$$\sum_{\mathbf{k}\mathbf{k}'}\mathbf{A}_i(\mathbf{k})\cdot\mathbf{A}_i^*(\mathbf{k}')\,e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}=1 \quad (\text{all } \mathbf{R};\ i=1,\cdots,f), \tag{26}$$

$$\textstyle\sum_{\mathbf{k}}\mathbf{A}_i(\mathbf{k})\cdot\mathbf{A}_i^*(\mathbf{k})=1. \tag{27}$$

Minimization of W, as given by Eq. (24), subject to the weak constraints, Eq. (27), yields

$$\textstyle\sum_j\xi_{ij}(\mathbf{k})A_{j,\mu}(\mathbf{k})=\lambda_i A_{i,\mu}(\mathbf{k}), \tag{28}$$

where the λ_i are, except for a factor N, the Lagrange multipliers for Eq. (27), and they are independent of k. W is given by

$$W=\tfrac{1}{2}N\textstyle\sum_i\lambda_i. \tag{29}$$

In order that a nontrivial solution of Eq. (28) exist for some $\mathbf{k}$ we require the vanishing of the f-rowed determinant

$$\det|\xi(\mathbf{k})-\Lambda|=0, \tag{30}$$

[9] T. Moriya, Phys. Rev. **120**, 91 (1960).

[10] This generalization is suggested in a footnote in reference 3.

where Λ is a diagonal matrix whose diagonal elements are the λ_i. Equation (30) gives a relation between the λ_i. The λ_i will be further restricted by the requirement that the corresponding $\mathbf{A}_i(\mathbf{k})$, the solutions of Eq. (28), must satisfy Eq. (27). That the sum of the λ_i is real follows from Eq. (29), since W is a real quantity. To prove that each of the λ_i is real, multiply Eq. (28) by $A_{i,\mu}(\mathbf{k})$ and sum on μ and $\mathbf{k}$. This yields

$$\sum_j \sum_{\mathbf{k}} \xi_{ij}(\mathbf{k})\mathbf{A}_i^*(\mathbf{k})\cdot\mathbf{A}_j(\mathbf{k})=\lambda_i \sum_{\mathbf{k}} \mathbf{A}_i^*(\mathbf{k})\cdot\mathbf{A}_i(\mathbf{k})=\lambda_i,$$

the second result having been obtained with the use of Eq. (27). Since complex conjugation of $\xi_{ij}(\mathbf{k})$ and $\mathbf{A}_i(\mathbf{k})$ is equivalent, according to Eqs. (22) and (25), to the replacement of $\mathbf{k}$ by $-\mathbf{k}$, and since λ_i is expressed here as a sum over all $\mathbf{k}$, we have

$$\lambda_i^*=\lambda_i.$$

Clearly λ_i is the average energy of interaction of an ion of type i with its neighbors.

One can think of Eq. (30) as determining a family of surfaces, parametrized by $\mathbf{k}$, in an f-dimensional space with coordinates $\lambda_1, \cdots, \lambda_f$. On each such surface there will be at least one point at which the corresponding solution for the $\mathbf{A}_i(\mathbf{k})$ will satisfy Eq. (27) and therefore Eq. (26) since if the $\mathbf{A}_i(\mathbf{k})$ are nonvanishing for only one value of $\mathbf{k}$, (26) and (27) are equivalent. These are the one-mode solutions considered by Bertaut.[6] In addition to these solutions of (30) and (27), however, there will in general exist solutions corresponding to points of intersection of the surfaces. Such solutions can yield lower lying values of W than are obtained from the one-mode solutions and if the solution yielding the lowest values of W satisfies (26), then the method is successful and the ground state can be determined. Furthermore, this ground state will not have the same symmetry as the first ordered state.

A formally similar generalization of the method of Luttinger and Tisza was given by Lyons and Kaplan.[11] They introduce, *a priori*, a set of parameters, α_i^2, and replace the strong constraints by the single weak constraint

$$\sum_i \alpha_i^2 \sum_{\mathbf{R}} |\mathbf{S}_i^{\mathbf{R}}|^2=N\sum_i \alpha_i^2.$$

Their procedure leads to a set of homogeneous equations, Eq. (14) in their paper, that is the same as Eq. (28) in this paper with λ_i replaced by $\lambda\alpha_i^2$. Thus, in effect, they examine the solutions of (28) along a single direction in $\lambda_1, \cdots \lambda_f$ space with direction cosines proportional to α_i^2 and seek the $\mathbf{k}$ that minimizes λ. Their method has the advantage that if this solution permits the satisfaction of the strong constraints, then it is guaranteed to be the ground state. It has the limitation, however, of permitting the examination of only one direction at a time in $\lambda_1, \cdots \lambda_f$ space.

[11] D. H. Lyons and T. A. Kaplan, Phys. Rev. **120**, 1580 (1960).

IV. ONE-DIMENSIONAL EXAMPLE

A. Discussion

As was pointed out in the preceding section, in a lattice of nonequivalent spins the internal field approximation yields the possibility of a helical spin configuration whose pitch is a function of temperature. The simplest situation giving rise to a variation in pitch occurs when the consistency equations, Eq. (3), have normal mode solutions at all temperatures below the highest branching temperature. If the family of free energy curves, corresponding to the solutions characterized by different values of $\mathbf{k}$, successively intersect each other, as shown in Fig. 1, then the free energy of the system will be the envelope of the family and $\mathbf{k}$ will be a function of temperature. The remainder of this section will be devoted to illustrating this possibility with a simple one-dimensional example.

We shall consider a system made up of two dissimilar ions alternating in a linear chain, as shown in Fig. 2. Each ion interacts with its nearest and next-nearest neighbors, the exchange energy of the system being

$$W=J_1\sum_l \mathbf{S}_a{}^l\cdot(\mathbf{S}_b{}^l+\mathbf{S}_b{}^{l-1})+J_b\sum_l \mathbf{S}_b{}^l\cdot\mathbf{S}_b{}^{l-1} +J_a\sum_l \mathbf{S}_a{}^l\cdot\mathbf{S}_a{}^{l-1}, \quad (31)$$

where the upper index, l, denotes the cell and the subscripts a and b denote the type of ion. The matrix

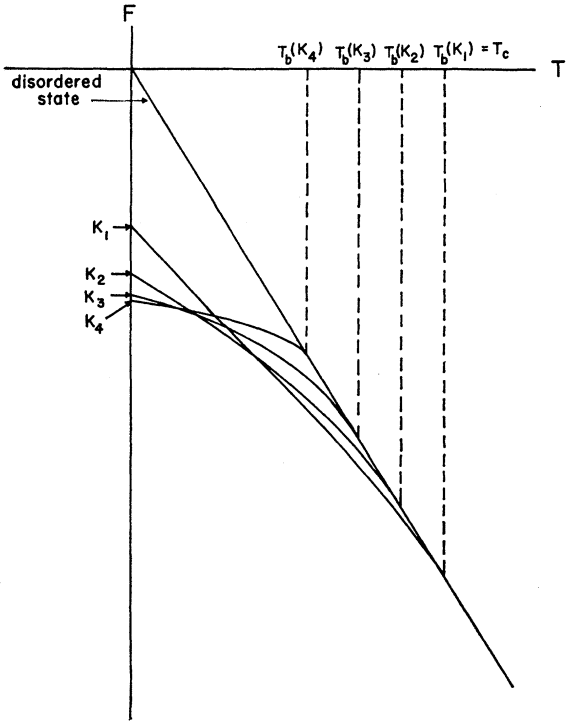

FIG. 1. Free energies of the normal mode solutions of the consistency equations. As illustrated this family of curves possesses an envelope giving the free energy of the system.

$\xi(k)$, given by Eq. (9), is then

$$\xi(k)=\begin{bmatrix} 2J_a\cos k & J_1(1+e^{-ik}) \\ J_1(1+e^{ik}) & 2J_b\cos k \end{bmatrix}, \tag{32}$$

where k is in units of inverse lattice spacing.

B. The First Ordered State

The first ordered state according to Eq. (8) is given by the lowest lying eigenvalue of $\xi(k)$. The eigenvalues are

$$\lambda(k)=(J_a+J_b)\cos k \pm[(J_b-J_a)^2\cos^2 k+2J_1^2(1+\cos k)]^{\frac{1}{2}}. \tag{33}$$

Since we are concerned only with the lowest lying eigenvalue we need consider only the negative root of (33). The relations between the J_i describing the regions in which the various modes yield the highest branching temperature [or the lowest $\lambda(k)$], are most simply expressed in terms of the parameters

$$P=(J_b+J_a)/|J_1|, \quad Q=(J_b-J_a)/|J_1|>0. \tag{34}$$

The choice of Q as a positive quantity involves nothing more than the labeling of the sublattices. One finds the possible minima of $\lambda(k)$ are as follows:

$P>1/Q-Q$, $Q>1/P-P$ *(II and III in Fig. 4)*

$$k=\pi, \quad \lambda=-3kT_b=-2J_b.$$

Sublattice b is antiferromagnetic, sublattice a is paramagnetic.

$Q<1/P-P$, $P<(1+Q^2)/(4+Q^2)^{\frac{1}{2}}$ *(IV, V, VI in Fig. 4)*

$$k=0, \quad \lambda=-3kT_b=(J_b+J_a)-[(J_b-J_a)^2+4J_1^2]^{\frac{1}{2}}.$$

Both sublattices are ferromagnetically ordered and are parallel or antiparallel to each other as J_i is less than or greater than zero. The ratio of the magnitudes of the spins on the two sublattices is, from Eq. (8),

$$\sigma_b^0/\sigma_a^0=1/2J_1\{(J_b-J_a)-[(J_b-J_a)^2+4J_1^2]^{\frac{1}{2}}\}.$$

$(1+Q^2)/(4+Q^2)<P<1/Q-Q$ *(I in Fig. 4)*

$$\cos k=\frac{1}{Q^2}\left\{P\left[\frac{1-2Q^2}{P^2-Q^2}\right]^{\frac{1}{2}}-1\right\},$$

$$\lambda=-3kT_b=\frac{|J_1|}{Q^2}\{[(P^2-Q^2)(1-2Q^2)]^{\frac{1}{2}}-P\}.$$

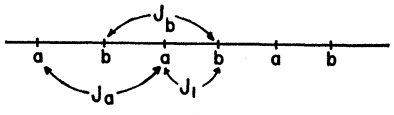

FIG. 2. The example treated in Sec. IV: a linear chain of two dissimilar ions.

Both sublattices are helically ordered, a single k characterizing both helices. A real solution of Eq. (8) for which all of the spins on each sublattice have the same magnitude are

$$\sigma_{a,}{}^l{}_x=\sigma_a\cos kl, \quad \sigma_{a,}{}^l{}_y=\sigma_a\sin kl, \quad \sigma_{a,}{}^l{}_z=0,$$
$$\sigma_{b,}{}^l{}_x=\sigma_b\cos k(l+\tfrac{1}{2}), \quad \sigma_{b,}{}^l{}_y=\sigma_b\sin k(l+\tfrac{1}{2}), \quad \sigma_{b,}{}^l{}_z=0,$$

where

$$\frac{\sigma_b}{\sigma_a}=\frac{\lambda(k)-2J_a\cos k}{2J_1\cos\tfrac{1}{2}k}.$$

C. The Ground State

With $\xi(k)$ given by Eq. (32), the Eqs. (28) for the determination of the ground state are

$$\begin{aligned}(2J_a\cos k-\lambda_a)\mathbf{A}_a(k)+J_1(1+e^{-ik})\mathbf{A}_b(k)=0,\\ J_1(1+e^{ik})\mathbf{A}_a(k)+(2J_b\cos k-\lambda_b)\mathbf{A}_b(k)=0.\end{aligned} \tag{35}$$

There is such a set of equations for each k. Let us first find the solutions for which the ground state contains a single mode, k. In this case the weak constraints, Eq. (27) become identical with the strong constraints, Eq. (26), namely,

$$\mathbf{A}_i(k)\cdot\mathbf{A}_i{}^*(k)=1 \quad (i=a,b). \tag{36}$$

From (35) it then follows that

$$2J_a\cos k-\lambda_a=2J_b\cos k-\lambda_b. \tag{37}$$

The secular equation is

$$(2J_a\cos k-\lambda_a)(2J_b\cos k-\lambda_b)-2J_1^2(1+\cos k)=0, \tag{38}$$

which, with (37), yields

$$\begin{aligned}\lambda_i&=2J_i\cos k-2|J_1|\cos\tfrac{1}{2}k,\\ W/N&=\tfrac{1}{2}(\lambda_a+\lambda_b)=(J_a+J_b)\cos k-2|J_1|\cos\tfrac{1}{2}k.\end{aligned} \tag{39}$$

The possible minima of W/N and the corresponding spin configurations are as follows:

$P<\frac{1}{2}$

$$k=0; \quad W/N=J_a+J_b-2|J_1|.$$

The ordering is ferromagnetic or ferrimagnetic, respectively, as J_1 is less than or greater than zero.

$P>\frac{1}{2}$

$$\cos\tfrac{1}{2}k=\frac{1}{2P}=\frac{|J_1|}{2(J_a+J_b)};$$

$$W/N=-\frac{|J_1{}^2|}{2(J_a+J_b)}-(J_a+J_b).$$

This yields a helically ordered state. Note that even for a range of parameters yielding both a helical ground state and a helical first ordered state, the two helices have different pitches.

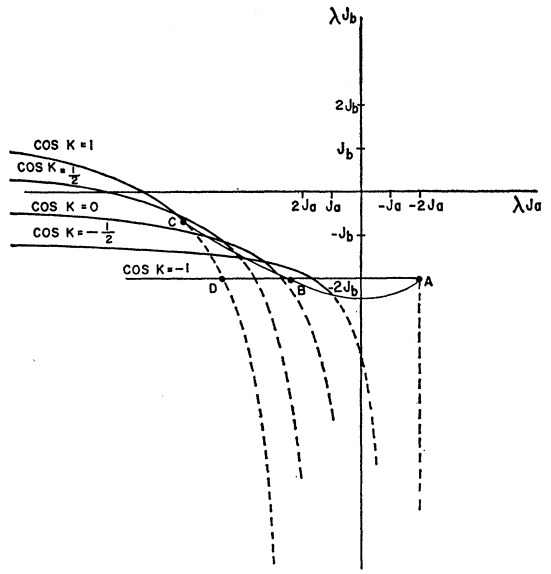

FIG. 3. Curves on which the secular determinant of Eq. (35) vanishes. Curve ABC is the locus of points yielding one-mode solutions. Only intersections within region BCD can yield two-mode solutions.

Thus far we have considered those solutions corresponding to the occurrence of a single mode. The secular Eq. (38), if plotted in a λ_a, λ_b space, yields a family of hyperbolas parametrized by $\cos k$. There are intersections between these hyperbolas and so there remains the possibility that the solution with the lowest value of W/N is a linear combination of two modes. (Except for the case where one of the second-neighbor interactions vanishes, one cannot have more than two hyperbolas intersecting.) Not every intersection, however, allows the weak constraints to be satisfied. Suppose the lower sheets of the hyperbolas associated with k_1 and k_2 intersect. (We need consider only the lower sheets since every point on the lower sheet, and in particular that point yielding a one-mode solution, has a lower value of $\lambda_a+\lambda_b$ than any point on the upper sheet.) We then have

$$[\xi_{aa}(k)-\lambda_a][\xi_{bb}(k)-\lambda_b]=|\xi_{ab}(k)|^2, \quad (k=k_1,k_2). \tag{40}$$

Then the solutions of Eq. (28) are

$$\mathbf{A}_b(k)=-\frac{\xi_{aa}(k)-\lambda_a}{\xi_{ab}(k)}\mathbf{A}_a(k), \quad (k=k_1,k_2) \tag{41}$$

and therefore

$$|\mathbf{A}_b(k)|^2=\left|\frac{\xi_{aa}(k)-\lambda_a}{\xi_{ab}(k)}\right|^2|\mathbf{A}_a(k)|^2$$

$$=\frac{\xi_{aa}(k)-\lambda_a}{\xi_{bb}(k)-\lambda_b}|\mathbf{A}_a(k)|^2, \quad (k=k_1,k_2). \tag{42}$$

The weak constraints then require that either

$$\frac{\xi_{aa}(k_1)-\lambda_a}{\xi_{bb}(k_1)-\lambda_b}>1>\frac{\xi_{aa}(k_2)-\lambda_a}{\xi_{bb}(k_2)-\lambda_b} \tag{43}$$

or

$$\frac{\xi_{aa}(k_1)-\lambda_a}{\xi_{bb}(k_1)-\lambda_b}<1<\frac{\xi_{aa}(k_2)-\lambda_a}{\xi_{bb}(k_2)-\lambda_b}. \tag{44}$$

Thus the region of intersections that allow the weak constraints to be satisfied is bounded in part by the curve

$$\frac{\xi_{aa}(k)-\lambda_a}{\xi_{bb}(k)-\lambda_b}=1, \tag{45}$$

which is just the locus of points that yield one-mode solutions. The situation is illustrated in Fig. 3 which has been drawn for the case $2J_b>|J_1|$, $J_a<0$. The curves for the various values of k have been drawn with solid lines where $\xi_{aa}(k)-\lambda_a>\xi_{bb}(k)-\lambda_b$, and with dashed lines where $\xi_{aa}(k)-\lambda_a<\xi_{bb}(k)-\lambda_b$. The only relevant intersections are those between a dashed line and a solid line, the intersections in the region BCD in the figure. Curve ABC is the locus of one-mode solutions. Point D has the coordinates

$$\lambda_a=2J_a-\frac{J_1^2}{2J_b}, \quad \lambda_b=-2J_b,$$

while the coordinates of point C are

$$\lambda_a=2J_a-2|J_1|, \quad \lambda_b=2J_b-2|J_1|.$$

Thus in this case, $2J_b>J_1$ and $J_a<0$, the lowest value of W/N is given by the linear combination of the $k=\pi$ mode and the $k=0$ mode. This is, in fact, the only case in which the two-mode solution lies below the

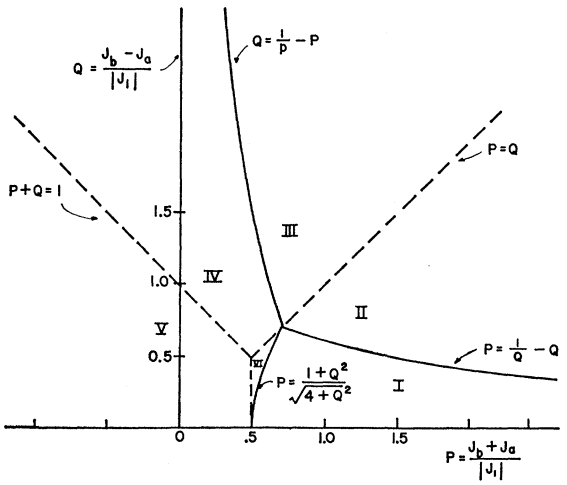

FIG. 4. Regions in parameter space in which different spin configurations occur as first ordered states and ground states, as described in Table I. The solid lines separate the domains for the first ordered state; the dashed lines separate the domains for the ground state.

lowest one-mode solution. A similar analysis shows that for all other ranges of the parameters the ground state is a single mode. In both cases the strong constraints can be satisfied. We give below the possible ground state energies and the corresponding solutions for the $\mathbf{S}_i$ (except for the degeneracy associated with the uniform rotation of all the spins).

$P\geq Q$, $P\geq\frac{1}{2}$ (I, II, VI in Fig. 4)

$$\cos\tfrac{1}{2}k=\frac{|J_1|}{2(J_a+J_b)},$$

$$\lambda_a=-J_b\frac{|J_1|^2}{(J_a+J_b)^2}-2J_a,$$

$$\lambda_b=-J_a\frac{|J_1|^2}{(J_a+J_b)^2}-2J_b,$$

$$W/N=-\frac{1}{2}\frac{|J_1|^2}{J_a+J_b}-(J_a+J_b),$$

$$\mathbf{S}_a{}^l=(\cos kl,\ \sin kl,0),$$

$$\mathbf{S}_b{}^l=\frac{J_1}{|J_1|}(-\cos k(l+\tfrac{1}{2}),\ -\sin k(l+\tfrac{1}{2}),0).$$

The system is helically ordered, the two sublattice helices have the same pitch, the relative phases of the helices being dependent on the sign of J_1.

$P\leq 1-Q$, $P\leq\frac{1}{2}$ (V in Fig. 4)

$$k=0,\quad \lambda_a=-2|J_1|+2J_a,\quad \lambda_b=-2|J_1|+2J_b,$$

$$W/N=-2|J_1|+J_a+J_b,$$

$$\mathbf{S}_a{}^l=(1,0,0),$$

$$\mathbf{S}_b{}^l=\frac{J_1}{|J_1|}(-1,0,0).$$

The spin orientations are collinear. The ordering is ferromagnetic if $J_1<0$, and ferrimagnetic if $J_1>0$.

$P\leq Q$, $P\geq 1-Q$ (III and IV in Fig. 4)

In this case the ground state is a linear combination of the $k=0$ and $k=\pi$ modes,

$$\lambda_a=-\frac{J_1{}^2}{J_b}+2J_a,\quad \lambda_b=-2J_b,$$

$$W/N=-\frac{1}{2}\frac{J_1{}^2}{J_b}-J_b+J_a,$$

$$\mathbf{S}_a{}^l=(1,0,0),$$

$$\mathbf{S}_b{}^l=\left(-\frac{J_1}{2J_b},\ (-1)^l[1-J_1{}^2/4J_b{}^2]^{\frac{1}{2}},\ 0\right).$$

This is the triangular arrangement of Yafet and Kittel.

TABLE I. Types of ordered states occurring in the numbered regions of Fig. 4.

Region	First ordered state	Ground state
I	Helix	Helix
II	Antiferromagnetic b lattice, disordered a lattice.	Helix
III	Antiferromagnetic b lattice, disordered a lattice.	Triangular configuration
IV	Collinear configuration	Triangular configuration
V	Collinear configuration	Collinear configuration
VI	Collinear configuration	Helix

Lyons and Kaplan[11] treat a linear chain with a less general set of interactions than is used here. The parameter μ as defined in Eq. (1.8) of their paper is equal to $1/2P$ in our notation. It may be seen that for the range of parameters they consider, their criterion for the stability of helical and antiferromagnetic configurations is the same as that given here.

The results of this section are summarized in Fig. 4. Table I gives a comparison of the first ordered states and the ground states for the various areas in the figure.

One point that should be noticed is that in region I where both the first ordered state and the ground state are helical the helices do not have the same pitch. A further point of interest is that in region VI the first ordered state has a net magnetic moment whereas the ground state does not. In region III, on the other hand, the ground state has a net moment while the first ordered state does not.

D. Free Energies of the One-Mode Solutions

An examination of Fig. 4 and Table I indicates that it is conceivable that a variation of pitch occurs in several regions, namely in regions I, II, and VI. In order to show that a variation of pitch does in fact occur, it is necessary to calculate the free energies of the various ordered states. We shall first show that the normal modes discussed in the preceding sections provide solutions of Eq. (3) at all temperatures. This being so, the free energies of the various modes can be calculated and the occurrence of a variation of pitch demonstrated. The point for which the numerical calculations were carried out is in region II for which the first ordered state is the $k=\pi$ mode and the ground state is helical. Only the free energies of the one-mode solutions were calculated since it appeared unlikely that any of the two-mode solutions, e.g., the triangular solution (a combination of $k=0$ and $k=\pi$) or a conical solution (a combination of $k=0$ or $k=\pi$ with a $k\neq 0$ or π), would intervene as a stable state between the first ordered and the ground states.

Let us assume a solution of Eq. (3) of the form

$$\boldsymbol{\sigma}_i{}^l=\sigma_i\times(\cos(kl+\varphi_i),\ \sin(kl+\varphi_i),\ 0),\quad (i=a,b). \quad (46)$$

We are free to choose

$$\varphi_a=0, \tag{47}$$

this being nothing more than a determination of the phase of the helix. The effective field acting on the spin of type a in cell l,

$$\mathbf{H}_a{}^l=-\sum_j\sum_{l'} J_{aj}{}^{ll'}\boldsymbol{\sigma}_j{}^{l'}, \tag{48}$$

has the components

$$\begin{aligned} H_{a,}{}^l{}_x&=-2J_a\sigma_a\cos k\cos kl \\ &\quad -2J_1\sigma_b\cos\tfrac{1}{2}k\cos(kl-\tfrac{1}{2}k+\varphi_b), \\ H_{a,}{}^l{}_y&=-2J_a\sigma_a\cos k\sin kl \\ &\quad -2J_1\sigma_b\cos\tfrac{1}{2}k\sin(kl-\tfrac{1}{2}k+\varphi_b), \\ H_{a,}{}^l{}_z&=0. \end{aligned} \tag{49}$$

Equation (3) requires that this field be parallel to $\boldsymbol{\sigma}_a{}^l$ which can be true for all l only of

$$\varphi_b=k/2. \tag{50}$$

This is consistent with the form found for the ground-state helix in Sec. IV. Thus

$$\mathbf{H}_a{}^l=-(2J_a\sigma_a\cos k+2J_1\sigma_b\cos\tfrac{1}{2}k)\frac{\boldsymbol{\sigma}_a{}^l}{\sigma_a}. \tag{51}$$

Similarly one finds

$$\mathbf{H}_b{}^l=-(2J_1\sigma_a\cos\tfrac{1}{2}k+2J_b\sigma_b\cos k)\frac{\boldsymbol{\sigma}_b{}^l}{\sigma_b}. \tag{52}$$

The consistency equations, (3), then reduce to the two coupled equations

$$\begin{aligned} \sigma_a&=L(\beta[-2J_a\sigma_a\cos k-2J_1\sigma_b\cos\tfrac{1}{2}k]), \\ \sigma_b&=L(\beta[-2J_1\sigma_a\cos\tfrac{1}{2}k-2J_b\sigma_b\cos k]). \end{aligned} \tag{53}$$

The free energy per cell for this solution of the consistency equations is

$$\frac{F}{N}=\frac{1}{\beta}\sum_{i=a,b}\left\{\tfrac{1}{2}\sigma_iL^{-1}(\sigma_i)-\ln\left(\frac{\sinh L^{-1}(\sigma_i)}{L^{-1}(\sigma_i)}\right)\right\} -\frac{1}{\beta}2\ln 4\pi. \tag{54}$$

To facilitate the numerical solution of Eqs. (53) we set Boltzmann's constant equal to one and define

$$\begin{aligned} u&=L^{-1}(\sigma_a)=-\frac{2}{T}(J_a\sigma_a\cos k+J_1\sigma_b\cos\tfrac{1}{2}k), \\ v&=L^{-1}(\sigma_b)=-\frac{2}{T}(J_1\sigma_a\cos\tfrac{1}{2}k+J_b\sigma_b\cos k). \end{aligned} \tag{55}$$

Then

$$\sigma_a=L(u)=\frac{T}{2}\frac{-J_bu\cos k+J_1v\cos\tfrac{1}{2}k}{J_aJ_b\cos^2k-J_1{}^2\cos^2(\tfrac{1}{2}k)}. \tag{56}$$

We can write the first of Eqs. (55) in the form

$$u=-(2/T)J_a\cos kL(u)-(2/T)J_1\cos\tfrac{1}{2}kL(v). \tag{57}$$

TABLE II. Branching temperatures and calculated values of $(1/T)(F/N)+2T\ln 4\pi$ of three modes of the linear chain.

cos$k$	T_b	$T=0.2$	0.4	0.6	1.0
−1	1.333		−2.061	−0.835	−0.103
−0.96	1.289	−7.285	−2.108	−0.795	−0.082
−0.92	1.245	−7.313	−2.077	−0.752	−0.063

By solving (56) for v in terms of u and substituting the result into (57), one obtains

$$u=-\frac{2}{T}J_a\cos kL(u)-\frac{2}{T}J_1\cos\tfrac{1}{2}k\times L\left(\frac{J_b\cos k}{J_1\cos\tfrac{1}{2}k}u-\frac{2}{T}\left[J_1\cos\tfrac{1}{2}k-\frac{J_aJ_b}{|J_1|}\frac{\cos^2k}{\cos\tfrac{1}{2}k}\right]L(u)\right). \tag{58}$$

For specific values of J_1, J_a, J_b, T, and k, Eq. (48) can be solved straightforwardly, though tediously, by Newton's method.

The free energy was calculated for three modes at several temperatures for the following point in region II:

$$J_1=1,\quad J_a=0.5,\quad J_b=2.0,\quad P=2.5,\quad Q=1.5. \tag{59}$$

The first ordered state for this point is the mode $k=\pi$ having a branching temperature of 1.333. The ground state is the $k=\cos^{-1}(-0.92)$ mode having a branching temperature of 1.245. The third mode selected for the calculation has a branching temperature that is approximately midway between these two, namely $T_b=1.289$. This is the mode $k=\cos^{-1}(-0.96)$. Table II gives the results of the calculation. It can be seen that at $T=0.6$ the free energy of the first ordered state still lies below that of the other two modes, at $T=0.4$ the mode with $\cos k=-0.96$ lies lowest and at $T=0.2$ the ground-state mode has the lowest free energy of the three. Thus the free energy curves for these modes successively cross each other as illustrated in Fig. 1. We shall next show that the variation of pitch continues down to $T=0$, and is initiated at finite temperature interval below T_c.

E. Near $T=0$

For the point specified by (59) and for k values near that of the ground state the solutions of the consistency equations, (55), have σ_b approaching minus one as T approaches zero and σ_a approaching plus one. To examine the free energies of these modes near zero temperature we put

$$\sigma_a=1-\epsilon_a,\quad \sigma_b=1-\epsilon_b, \tag{60}$$

and use the approximations

$$\begin{aligned} L^{-1}(\sigma_a)&=1/\epsilon_a,\quad L^{-1}(\sigma_b)=-1/\epsilon_b, \\ F/N+2T\ln 4\pi&=T\sum_{i=a,b}\left\{-\frac{1}{2\epsilon_i}-\ln\epsilon_i+\ln 2-\tfrac{1}{2}\right\}, \end{aligned} \tag{61}$$

The solution of Eq. (55) is then

$$\epsilon_a=\frac{T}{-2J_a\cos k+2J_1\cos\frac{1}{2}k}+\frac{4J_aJ_b\cos^2k-8J_aJ_1\cos k\cos\frac{1}{2}k+4J_1^2\cos^2(\frac{1}{2}k)}{(-2J_a\cos k+2J_1\cos\frac{1}{2}k)^3(-2J_b\cos k+2J_1\cos\frac{1}{2}k)}T^2+\cdots \tag{62}$$

with a similar expression for ϵ_b except that J_b replaces J_a. This yields, to terms of order T^2,

$$\begin{aligned}F/N+2T\ln 4\pi&=(J_a+J_b)\cos k-2J_1\cos\tfrac{1}{2}k+T\ln(2J_1\cos\tfrac{1}{2}k-J_a\cos k)\\&\quad+T\ln(2J_1\cos\tfrac{1}{2}k-J_b\cos k)-2T\ln T+2T\ln 2.\end{aligned} \tag{63}$$

The first term in (63) is W/N which, for the point (59) has a minimum at $\cos k=-0.92$. By setting the derivative of (63) with respect to k equal to zero, one obtains the envelope of the free-energy curves, which is found to exist and, to lowest order in T, is given by

$$\cos k=-0.92-0.49T. \tag{64}$$

Thus the variation of pitch persists down to absolute zero.

F. Near T_c

To examine the initiation of the variation of pitch we consider temperatures near T_c and use the approximations

$$\begin{aligned}L^{-1}(\sigma_i)&=3\sigma_i+(9/5)\sigma_i^3+\cdots,\\\frac{F}{NT}+2\ln 4\pi&=-\frac{9}{20}\sum_{i=a,b}\sigma_i^4+\cdots.\end{aligned} \tag{65}$$

The first ordered state for the system with the parameters (59) is the $k=\pi$ mode. In order to examine the modes near this one we put

$$k=\pi-\kappa. \tag{66}$$

Then the consistency equations become

$$\begin{aligned}&(1-\tfrac{1}{2}\kappa^2)\sigma_a-\left(\kappa-\frac{1}{24}\kappa^3\right)\sigma_b=3T(\sigma_a+\tfrac{3}{5}\sigma_a^3)\\&-\left(\kappa-\frac{1}{24}\kappa^3\right)\sigma_a+(4-2\kappa^2)\sigma_b=3T(\sigma_b+\tfrac{3}{5}\sigma_b^3).\end{aligned} \tag{67}$$

The branching temperature for the $\pi-\kappa$ mode is an even function of κ, σ_b is also an even function of κ, while σ_a is an odd function of κ. Through terms of order κ^2 the branching temperature is

$$T_b(\pi-\kappa)=(4/3)-(5/9)\kappa^2. \tag{68}$$

Elimination of T in Eqs. (67) yields

$$\sigma_a=-\tfrac{1}{3}\kappa(\sigma_b+\tfrac{4}{5}\sigma_b^3) \tag{69}$$

which, when substituted back into one of Eqs. (67) gives us, to first order in $T_b(\pi-\kappa)-T$,

$$\begin{aligned}\sigma_b^2&=\frac{5}{4}[T_b(\pi-\kappa)-T]\left(1+\frac{19}{36}\kappa^2\right),\\\sigma_a^2&=\frac{5}{36}\kappa^2[T_b(\pi-\kappa)-T],\end{aligned} \tag{70}$$

and from Eq. (65) we then get for the free energy

$$\frac{F}{NT}+2\ln 4\pi=-\frac{45}{64}\left(1+\frac{19}{18}\kappa^2\right)[T_b(\pi-\kappa)-T]^2, \tag{71}$$

through terms in κ^2 and $[T_b(\pi-\kappa)-T]^2$. By setting the derivative of (71) with respect to κ equal to zero one obtains

$$\kappa^2=(16-57T)/95,$$

which cannot be satisfied unless $T<16/57$. Hence there must be a finite temperature interval below T_c in which the first ordered state remains stable. No good estimate of the temperature at which the variation of pitch begins can be deduced from the result above since the approximations used are valid only very close to the branching temperature.

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APPENDIX

The Internal-Field Approximation

The general formulation of the internal-field approximation that follows is essentially the same as that used by James and Keenan[12] in their treatment of rotational melting in methane. The equations we shall arrive at are equivalent to Villain's Eq. (1).

We consider a lattice of classical spins. The orientation of spin i will be denoted by ω_i, representing the polar and azimuthal angles of the spin direction, and the energy of interaction between spins i and j will be denoted by $E_{ij}(\omega_i,\omega_j)$. Suppose the orientational distribution function for spin i is $p_i(\omega_i)$ where p_i is normalized over all solid angle,

$$\int p_i(\omega_i)d\omega_i=1. \tag{A.1}$$

Then the internal energy and entropy of the system

[12] H. M. James and T. A. Keenan, J. Chem. Phys. **31**, 12 (1959).

are given by

$$U=\tfrac{1}{2}\sum_{ij}\int d\omega_i\int d\omega_j\, p_i(\omega_i)p_j(\omega_j)E_{ij}(\omega_i,\omega_j), \quad \text{(A.2)}$$

$$S=-k\sum_i\int d\omega_i\, p_i(\omega_i)\,\ln p_i(\omega_i). \quad \text{(A.3)}$$

Minimization of the free energy with respect to all the p_i subject to the normalization condition, Eq. (A.1), yields

$$p_i(\omega_i)=\exp\{-\beta\sum_j\int d\omega_j\, p_j(\omega_j)E_{ij}(\omega_i,\omega_j)\}\Big/$$

$$\int d\omega_i\exp\{-\beta\sum_j\int d\omega_j\, p_j(\omega_j)E_{ij}(\omega_i,\omega_j)\}, \quad \text{(A.4)}$$

where $\beta=1/kT$. Suppose the interaction energy is given by

$$E_{ij}(\omega_i,\omega,)=\mathbf{S}_i\cdot\mathbf{J}\cdot\mathbf{S}_j, \quad \text{(A.5)}$$

where, if the exchange is anisotropic, $\mathbf{J}_{ij}$ is a three-rowed square matrix. If the exchange interaction is isotropic $\mathbf{J}_{ij}$, is a constant matrix, that is, it has the form of a constant, J_{ij}, times the unit matrix. Equation (A.4) is most simply expressed in terms of the mean spins

$$\boldsymbol{\sigma}_i=\int d\omega_i\,\mathbf{S}_i p_i(\omega_i). \quad \text{(A.6)}$$

Use of the right-hand side of Eq. (A.4) for $p_i(\omega_i)$ in Eq. (A.6) then yields

$$\boldsymbol{\sigma}_i=\int d\omega_i\,\mathbf{S}_i\exp\{\beta\mathbf{S}_i\cdot\mathbf{H}_i\}\Big/\int d\omega_i\exp\{\beta\mathbf{S}_i\cdot\mathbf{H}_i\}, \quad \text{(A.7)}$$

where

$$\mathbf{H}_i=-\textstyle\sum_j\mathbf{J}_{ij}\cdot\boldsymbol{\sigma}_j. \quad \text{(A.8)}$$

From Eq. (A.7) it follows that $\boldsymbol{\sigma}_i$ is parallel to $\mathbf{H}_i$. Thus the magnitude of $\boldsymbol{\sigma}_i$ is given by

$$\sigma_i=S_iL(\beta S_iH_i) \quad \text{(A.9)}$$

where L is the Langevin function and S_i is the magnitude of spin i.

A convenient expression for the free energy of a solution of Eqs. (A.7) and (A.8) is obtained by substitution of (A.7)–(A.9) and the corresponding expression for p_i into Eqs. (A.2) and (A.3). One then obtains

$$F=\frac{1}{\beta}\sum_i\left\{\left[\frac{1}{2}\frac{\sigma_i}{S_i}L^{-1}\left(\frac{\sigma_i}{S_i}\right)-\sum_i\ln\left(\frac{\sinh L^{-1}(\sigma_i/S_i)}{L^{-1}(\sigma_i/S_i)}\right)\right]-\ln 4\pi\right\}. \quad \text{(A.10)}$$

Since the quantity in the square brackets is negative for σ_i different from zero, the ordered states, at temperatures where they exist, always have free energies lying below that of the disordered state.