Method for Determining Ground-State Spin Configurations

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The method of Luttinger and Tisza for finding the rigorous minimum of a quadratic form subject to certain strong constraints is generalized. In the extended method, one still minimizes the quadratic form with respect to a single weak constraint, which however now contains adjustable parameters. In determining the ground state for the classical Heisenberg exchange energy, some cases involving crystallographically nonequivalent spins can now be handled. The following applications are made. The ground state for a linear chain with two different types of spins is obtained. We then prove that in the cubic spinel the Néel configuration is the ground state if it is locally stable—that is, it is never metastable. This result was assumed in a recent perturbation theory of spin configurations. Finally, a similar result concerning the Yafet-Kittel triangular configurations in noncubic spinels is discussed. In the course of the analysis it is shown that the ground state is always a spiral for any lattice in which the spins are equivalent.

WE are concerned in this paper with the problem of finding the ground spin-state in complex lattices. More precisely, we wish to determine the set of spin vectors assigned to a set of atomic positions in a crystal which minimizes the classical Heisenberg exchange energy. We use the following notation. Let $\mathbf{R}_n$ be the vectors of the direct lattice and

$$\mathbf{R}_{n\nu}=\mathbf{R}_n+\boldsymbol{\varrho}_\nu, \quad \nu=1, 2, \cdots, p; \quad n=1, 2, \cdots, N, \quad (1)$$

be the positions of the magnetic atoms, so that there are p spins per primitive unit cell, and Np spins in the lattice. If $\mathbf{S}_{n\nu}$ is the spin at position $\mathbf{R}_{n\nu}$, the energy is

$$E=\sum_{n\nu,m\mu} J_{n\nu,m\mu}\mathbf{S}_{n\nu}\cdot\mathbf{S}_{m\mu}, \quad (2)$$

where $J_{n\nu,m\mu}$ is the exchange parameter connecting sites $\mathbf{R}_{n\nu}$ and $\mathbf{R}_{m\mu}$. The problem is to find the set of spins that minimizes E subject to the constraints

$$\mathbf{S}_{n\nu}\cdot\mathbf{S}_{n\nu}=S_\nu^2, \quad (3)$$

which fix the magnitude of each spin vector. Although generally speaking this problem is difficult, Luttinger and Tisza[1] (L-T) noted the following. If we sum the "strong constraints" (3) over all the spins, we obtain

$$\sum_{n\nu}(\mathbf{S}_{n\nu})^2=N\sum_\nu S_\nu^2 \quad (4)$$

as a necessary, but not sufficient condition for the validity of (3). Now consider another problem: that of minimizing E with respect to the "weak constraint" (4). This is a much simpler problem, the solution relating the set of spin vectors to the lowest eigenstate of the matrix of the quadratic form E. If this solution should turn out to satisfy the strong constraints (3), it then follows that this solution is the rigorous answer to the original problem. If however (3) is not satisfied, then no progress has been made towards solving the original problem.

It is sometimes useful to think of the L-T method in geometrical terms. For ease of illustration, consider an Ising problem with two variables, μ_1 and μ_2. The energy is then a function, $\mathcal{E}(\mu_1,\mu_2)$, to be minimized subject to the strong constraints $\mu_i^2=1$, represented by the four dots in Fig. 1. The weak constraint $\mu_1^2+\mu_2^2=2$ corresponds to the circle in Fig. 1. It is clear that if $\mathcal{E}(1,1)$, say, is the minimum value of $\mathcal{E}$ for all (μ_1,μ_2) lying on the circle, then $\mathcal{E}(1,1)\leqslant\mathcal{E}$ evaluated at the other strong constraint points. This is the gist of the Luttinger-Tisza method.

As Luttinger and Tisza showed, the favorable situation where the minimum-energy state for the weak conditions satisfies the strong conditions occurs quite often. In fact, as is well known (and as will be seen explicitly below), the L-T method works whenever $p=1$, i.e., whenever all the spins are equivalent.[2] It has been generally felt that the method fails when $p>1$, i.e., for

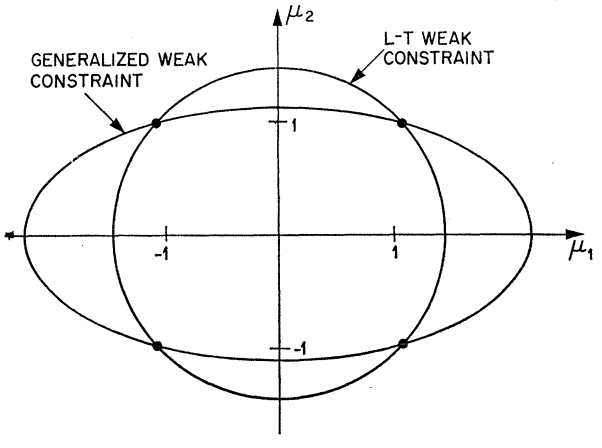

FIG. 1. Constraints for two-particle Ising problem. The strong constraints are satisfied at the dots.

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[1] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946); J. M. Luttinger, Phys. Rev. **81**, 1015 (1951).

[2] This is true for the Heisenberg problem; it is also true for the Ising model defined by $E=\sum J_{ij}S_i^zS_j^z$, where S_i^z is the z component of a vector of fixed length; but it is not true for the Ising model defined by $E=\sum J_{ij}\mu_i\mu_j$ where each μ_i has ±1 as its possible values.

nonequivalent spins. We shall show that this is only partially correct, the L-T method working for some situations when $p>1$; however, it does not work for others.

It is, of course, desirable to find an extension of this method capable of handling a larger class of problems. We shall give such an extension based on the observation that

$$\sum_{n,\nu}\alpha_{n\nu}^2\mathbf{S}_{n\nu}\cdot\mathbf{S}_{n\nu}=\sum_{n,\nu}\alpha_{n\nu}^2S_\nu^2, \tag{5}$$

where $\alpha_{n\nu}$ are any real, nonzero numbers,[3] independent of the spin vectors, is also a necessary but not sufficient condition for (3). That is, the class of all sets of spin vectors $\{\cdots\mathbf{S}_{n\nu}\cdots\}=\mathcal{S}$ that satisfy (5) must include all sets $\mathcal{S}$ that satisfy (3), but includes some $\mathcal{S}$ that do not satisfy (3). Equation (5) represents a $3Np$-dimensional ellipsoid, shown in Fig. 1 for the simple case considered there. Hence, again, if the solution to the problem using the single weak condition (5) happens to satisfy (3), the original problem will have been solved. We shall show that a simple choice of the $\alpha_{n\nu}$ allows us to solve physically interesting problems for which the original L-T method fails.

To take advantage of the translational symmetry, we transform to new variables $\mathbf{Q}_{\mathbf{k}\nu}$ as follows:

$$\mathbf{S}_{n\nu}=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{R}_{n\nu})\mathbf{Q}_{\mathbf{k}\nu}; \tag{6}$$

also write

$$\alpha_{n\nu}^2=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{R}_{n\nu})A_\nu(\mathbf{k}). \tag{7}$$

The $\mathbf{k}$ are the rationalized reduced reciprocal vectors in the first Brillouin zone. Then, since we can write

$$J_{n\nu,m\mu}=J_{\nu\mu}(\mathbf{R}_m-\mathbf{R}_n)=J_{\mu\nu}(\mathbf{R}_n-\mathbf{R}_m), \tag{8}$$

we obtain for the energy (assuming periodic boundary conditions)

$$\mathcal{E}=E/N=\sum_{\mathbf{k}}\sum_{\nu,\mu}L_{\nu\mu}(\mathbf{k})\mathbf{Q}_{\mathbf{k}\nu}^*\cdot\mathbf{Q}_{\mathbf{k}\mu}, \tag{9}$$

and the weak constraint (5) becomes

$$\sum_{\mathbf{k},\mathbf{k}'}\sum_{\nu}A_\nu(\mathbf{k}-\mathbf{k}')\mathbf{Q}_{\mathbf{k}\nu}^*\cdot\mathbf{Q}_{\mathbf{k}'\nu}=\sum_{\nu}A_\nu(0)S_\nu^2. \tag{10}$$

Here

$$L_{\nu\mu}(\mathbf{k})=\sum_{\mathbf{R}_m-\mathbf{R}_n}\exp[i\mathbf{k}\cdot(\mathbf{R}_{m\mu}-\mathbf{R}_{n\nu})]J_{\nu\mu}(\mathbf{R}_m-\mathbf{R}_n)$$
$$=L_{\mu\nu}(\mathbf{k})^*. \tag{11}$$

In the state that minimizes $\mathcal{E}$ subject to the constraint (10), it is easy to show (e.g., by the method of Lagrange multipliers) that the $\mathbf{Q}_{\mathbf{k}\nu}$ must satisfy

$$\sum_\mu L_{\nu\mu}(\mathbf{k})\mathbf{Q}_{\mathbf{k}\mu}=\lambda\sum_{\mathbf{k}'}A_\nu(\mathbf{k}-\mathbf{k}')\mathbf{Q}_{\mathbf{k}'\nu},\quad\text{all }\mathbf{k}, \tag{12}$$

where λ is a constant independent of $\mathbf{k}$. Using (12) and (10), the energy becomes

$$\mathcal{E}=\lambda\sum_\nu A_\nu(0)S_\nu^2. \tag{13}$$

[3] The restrictions on the coefficients in (5) were chosen in order that the minimum of E subject to (5) be bounded.

Hence the minimum $\mathcal{E}$ is obtained for the minimum λ for which solutions of (12) exist.

For the applications to be considered here, it is sufficient to choose the $\alpha_{n\nu}=\alpha_\nu$ independent of n, so that $A_\nu(\mathbf{k}-\mathbf{k}')=\alpha_\nu^2\delta_{\mathbf{k},\mathbf{k}'}$. Then (12) becomes

$$\sum_\mu L_{\nu\mu}(\mathbf{k})\mathbf{Q}_{\mathbf{k}\mu}=\lambda\alpha_\nu^2\mathbf{Q}_{\mathbf{k}\nu}; \tag{14}$$

letting

$$\mathbf{P}_{\mathbf{k}\nu}=\alpha_\nu\mathbf{Q}_{\mathbf{k}\nu}, \tag{15}$$

(14) becomes

$$\sum_\mu\mathfrak{L}_{\nu\mu}(\mathbf{k})\mathbf{P}_{\mathbf{k}\mu}=\lambda\mathbf{P}_{\mathbf{k}\nu}, \tag{16}$$

where

$$\mathfrak{L}_{\nu\mu}(\mathbf{k})=\beta_\nu\beta_\mu L_{\nu\mu}(\mathbf{k}) \tag{17}$$

with

$$\beta_\nu=\alpha_\nu^{-1}.$$

With this specialization, the weak constraint (10) is

$$\sum_{\nu\mathbf{k}}\mathbf{P}_{\mathbf{k}\nu}^*\cdot\mathbf{P}_{\mathbf{k}\nu}=\sum_\nu\alpha_\nu^2S_\nu^2, \tag{18}$$

and the energy in a state satisfying (16) is

$$\mathcal{E}=\lambda\sum\alpha_\nu^2S_\nu^2. \tag{19}$$

The basic equation (16) reduces to that occurring in the L-T method when $\beta_\nu=1$, all ν.

The procedure now is to find the lowest eigenvalue λ of the matrices $\mathfrak{L}_{\nu\mu}(\mathbf{k})$ (one matrix for each $\mathbf{k}$ in the first Brillouin zone). This minimum eigenvalue will, for a given crystal, be a function only of the β_ν:

$$\lambda=\lambda(\beta_1\cdots\beta_p). \tag{20}$$

Let $\mathbf{k}_0$ and $-\mathbf{k}_0$ be values of $\mathbf{k}$ for which this minimum occurs, with corresponding normalized eigenstates $\psi=\{\psi_1\cdots\psi_p\}$ and ψ^*, respectively. Note that these states will also be functions only of the β_ν. According to (16), minimum energy solutions of the weak constraint problem are given by

$$P_{\mathbf{k}\nu}{}^i=\begin{cases}0, & \mathbf{k}\neq\pm\mathbf{k}_0\\ c_i\psi_\nu, & \mathbf{k}=\mathbf{k}_0,\\ c_i^*\psi_\nu^*, & \mathbf{k}=-\mathbf{k}_0\end{cases} \tag{21}$$

where $P_{\mathbf{k}\nu}{}^i$, $i=x, y, z$, are cartesian components of $\mathbf{P}_{\mathbf{k}\nu}$, and the c_i satisfy

$$2\sum_i|c_i|^2=\sum_\nu\alpha_\nu^2S_\nu^2, \tag{22}$$

but are otherwise arbitrary.[4] It follows from (6), (15) and (21) that

$$\mathbf{S}_{n\nu}=\beta_\nu\sum_i\hat{x}_i[c_i\psi_\nu\exp(i\mathbf{k}_0\cdot\mathbf{R}_{n\nu})$$
$$+c_i^*\psi_\nu^*\exp(-i\mathbf{k}_0\cdot\mathbf{R}_{n\nu})], \tag{23}$$

giving, for different choices of the c_i consistent with (22), various minimum energy spin configurations for the weak constraint problem.

[4] This procedure may be looked upon alternatively in terms of the $3p\times3p$ matrix $L_{\nu\mu}{}^{ij}(\mathbf{k})=\delta_{ij}L_{\nu\mu}(\mathbf{k})$, $i, j=x, y, z$. Then the $3p$-dimensional vectors $\Psi_1=(\psi,0,0)$, $\Psi_2=(0,\psi,0)$ and $\Psi_3=(0,0,\psi)$ are degenerate eigenvectors of $L_{\nu\mu}{}^{ij}(\mathbf{k})$ and so any linear combination $\sum c_i\Psi_i$ is also an eigenvector. Equation (23) follows essentially from this consideration.

We must now see if there is any choice of the β_ν (real) and c_i such that (23) satisfies the strong constraints (3). At first sight, it appears that this will always be possible. For, if we choose $c_x=c/2i$, $c_y=c/2$, $c_z=0$, $c=c^*$, and write $\psi_\nu=|\psi_\nu|\exp(i\phi_\nu)$, (23) becomes

$$\mathbf{S}_{n\nu}=c\beta_\nu|\psi_\nu|\{\hat{x}\sin(\mathbf{k}_0\cdot\mathbf{R}_n+\phi_\nu)+\hat{y}\cos(\mathbf{k}_0\cdot\mathbf{R}_n+\phi_\nu)\}. \quad (24)$$

Note that this represents a spiral,[5-7] or rather a set of p spirals, one on each sublattice ν, having the phase ϕ_ν, respectively.[8] Also, to within rotations of the plane to which all of the spins are parallel, Eq. (24) is the only configuration derivable from (23) giving $(\mathbf{S}_{n\nu})^2$ independent of n. Using (24), the strong constraints (3) become p equations in the p unknowns $\beta_1\cdots\beta_p$:

$$C\beta_\nu f_\nu(\beta_1\cdots\beta_p)=S_\nu, \quad \nu=1\cdots p, \quad (25)$$

where $f_\nu(\cdots\beta_\mu\cdots)\equiv|\psi_\nu|$. If these equations have finite real β_ν as their solution, then the original problem will have been solved. However, such solutions do not always exist. For example, some of the f_ν might be identically zero (see Example 3 below), so that if the corresponding $S_\nu\neq0$, there is no solution. On the other hand, for a given lattice with definite exchange parameters $J_{n\nu,m\mu}$, we see that there will always be some set (or generally, sets) of spin-magnitudes S_ν for which the spiral configuration (24) is the ground state.

In the discussion preceding Eq. (24), only the degeneracy with respect to uniform spin rotations and the transformation $\mathbf{k}_0$ to $-\mathbf{k}_0$ was utilized in attempting to satisfy the strong constraints. If there is additional degeneracy of the lowest eigenvalue, there is additional freedom for the construction of a solution to the weak constraint problem that will satisfy the strong constraints. In fact, an essential ingredient in discussing the Yafet-Kittel triangular configurations (Example 3), is to use the β_ν to force some degeneracy.

We conclude this general discussion by considering the simplest case $p=1$ (all spins equivalent). Then it is seen in Eq. (24) that β_1 adds nothing to the L-T method since ψ_1 is arbitrary [$\mathfrak{L}_{\nu\mu}$ is now 1×1, and the eigenvalues are simply $\mathfrak{L}_{11}(\mathbf{k})\equiv\mathfrak{L}(\mathbf{k})$]. Clearly Eq. (24) with $\beta_1|\psi_1|=S_1$ satisfies the strong conditions for any $\mathbf{k}$, so that the original L-T method always works for this case, and the ground state is *always a spiral* defined by the $\mathbf{k}$ that minimizes $\mathfrak{L}(\mathbf{k})$.[9] It is important to realize in this connection that the equivalence of the spins depends entirely on the symmetry properties of the exchange energy (2). In simple terms, in any physical problem, one may determine whether or not the spins are equivalent by the following recipe: first determine the exchange parameters J_{nm} (which may be due to indirect exchange via nonmagnetic atoms); then imagine the lattice with all nonmagnetic atoms removed, assign the number S_ν to the appropriate magnetic site, J_{nm} to the line connecting (magnetic) sites n and m; if the resulting picture is invariant to any translation $n\rightarrow m$, then the spins are equivalent.

Example 1. The Linear Chain with Nonequivalent Spins

We now consider in detail the linear chain $ABAB\cdots$ with nearest and second nearest neighbor interactions as a simple illustration of the foregoing method and one for which a complete solution is obtained. In the course of the discussion we shall see clearly why the original L-T method fails for the linear chain in the case of nonequivalent spins and how the difficulty is overcome.

Letting $\nu=1$, 2 refer, respectively, to the A and B sites, the matrices defined by Eqs. (11) and (17) are

$$\tfrac{1}{2}\mathfrak{L}(k)=\begin{pmatrix}\cos2ka & J\beta\cos ka\\ J\beta\cos ka & \beta^2\cos2ka\end{pmatrix}, \quad (1.1)$$

where we have taken $J_{AA}=J_{BB}=1$, $J_{AB}=J$, $\beta_1=1$, $\beta_2=\beta$ and (a) as the nearest neighbor distance. For definiteness, we assume the interaction parameters are positive. The spin ratio $S\equiv S_B/S_A$ does not appear explicitly in Eq. (1.1) but will influence the choice of β. The original L-T method corresponds to putting $\beta=1$. In this case, the eigenvectors of (1.1) are (1,1) and (1, -1) for all k. Since in general these vectors are not degenerate, the only spin ratio for which this approach would work is $S=1$. (See Eq. 25.)

For arbitrary β and fixed k, let $\lambda(\beta,k)$ be the smaller of the pair of eigenvalues of (1.1), and let

$$\lambda_0(\beta,k_0)=\operatorname*{Min}_k\lambda(\beta,k)\equiv\lambda_0. \quad (1.2)$$

If the eigenvector associated with λ_0 is (ψ_A,ψ_B), then we have from Eq. (1.1),

$$\psi_A\cos2k_0a+\psi_BJ\beta\cos k_0a=\lambda_0\psi_A, \quad (1.3)$$

where we may take ψ_A and ψ_B real. The strong constraints as expressed in Eq. (25) become

$$\beta|\psi_B|/|\psi_A|=S. \quad (1.4)$$

Combining this equation with (1.3) gives

$$\cos2k_0a\pm JS\cos k_0a=\lambda_0. \quad (1.5)$$

[5] A. Yoshimori, J. Phys. Soc. (Japan) **14**, 807 (1959).
[6] T. A. Kaplan, Phys. Rev. **116**, 888 (1959).
[7] J. Villain, J. Phys. Chem. Solids **11**, 303 (1959).
[8] Such configurations have been studied in connection with spinels by E. F. Bertaut, Compt. rend. **250**, 85 (1960).
[9] Villain (reference 7) obtained essentially this result: He showed that the minimum energy spiral [Eq. (24)] is locally stable, i.e., stable with respect to sufficiently small spin deviations, for the general lattice with $p=1$ (Bravais lattice). Our result precludes the possible existence of a lower state which differs from the lowest spiral by large spin deviations. It is to be noted that this result implies that, whenever the spins are equivalent, the only state with nonzero total spin is the ferromagnetic state, which is a $\mathbf{k}=0$ "spiral" (it is impossible to have a ferrimagnetic ground state) and that, except for quite special degenerate cases, the spins are necessarily all parallel to one plane. Any experimental deviations from this must be due to deficiencies in the energy expression (2).

If we can now find a real value of β such that the k_0 and λ_0 defined by (1.2) also satisfy (1.5), we will have shown that the ground state is a spiral of wavelength $2\pi/k_0$, as discussed in the first part of this paper. The determination of such a β is most easily done as follows. The energy of a spiral of wavelength $2\pi/k$ is proportional to

$$\mathcal{E}=(1+S^2)\cos 2ka-2JS\cos ka. \tag{1.6}$$

Hence by differentiating (1.6), k_0 must satisfy

$$\sin k_0a(\cos k_0a-\mu)=0, \tag{1.7}$$

where

$$\mu=JS/2(1+S^2). \tag{1.8}$$

A second differentiation of (1.6) shows easily that minimum energy is obtained at $k_0=0$ for $\mu\geqslant 1$ and at $k_0a=\cos^{-1}\mu$ for $\mu<1$. These values of k_0a may then be seen to satisfy Eqs. (1.5) and (1.2) with the following values of β and λ_0:

Case I. $\mu\geqslant 1$, $k_0a=0$.

$$\beta^2=\frac{JS^2-S}{J-S}. \tag{1.9a}$$

$$\lambda_0=1-JS. \tag{1.9b}$$

Case II. $\mu<1$, $k_0a=\cos^{-1}\mu$

$$\beta^2=\frac{S^2+2\mu^2S^4}{S^2+2\mu^2}, \tag{1.10a}$$

$$\lambda_0=-1-2\mu^2S^2. \tag{1.10b}$$

Note that (1.9a) and (1.10a) are equal when $\mu=1$. This completes the proof that the ground state of the linear chain is rigorously a spiral with wavelength given by the above formulas.

Example 2. The Néel Configuration in Spinels

The chief result to be obtained in this example is a proof that the Néel configuration C_0 is the ground state if it is locally stable (i.e., stable with respect to sufficiently small spin deviations). In other words, C_0 is never a metastable state. This was explicitly assumed in a recent perturbation theory[10] of the ground state in cubic spinels, based on the behavior of the energy as a function of small spin deviations from C_0.

Although a proof of this theorem for nearest neighbor $A-B(J_{AB})$ and $B-B(J_{BB})$ interactions has already been given,[11] using the original L-T method, it is useful to give the derivation in terms of our extended L-T method as a simple illustration. For the spinel there are six spins per primitive cell (two A's and four B's); let $\nu=1, 2$ refer to spins A_1 and A_2, $\nu=3, 4, 5, 6$ refer to the B spins. We restrict ourselves to normal cubic spinels, the generalization to tetragonally distorted spinels including $A-A$ interaction to appear in a future publication.[12] It is sufficient to choose our parameters β_ν as $\beta_1=\beta_2=1$, $\beta_3=\beta_4=\beta_5=\beta_6=\beta$. Then the matrix $\mathfrak{L}\equiv 3J_{AB}\mathfrak{L}'$ defined by Eq. (17) is given by

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

μ	λ_μ	$\mathbf{V}_\mu$
1	$\beta^2\xi-(\beta^4\xi^2+8\beta^2)^{\frac{1}{2}}$	$(1,1,a_1,a_1,a_1,a_1)$
2	$-\beta^2\xi'$	$(0,0,1,-1,0,0)$
3	$-\beta^2\xi'$	$(0,0,0,0,1,-1)$
4	$-\beta^2\xi'$	$(0,0,1,1,-1,-1)$
5	0	$(1,-1,0,0,0,0)$
6	$\beta^2\xi+(\beta^4\xi^2+8\beta^2)^{\frac{1}{2}}$	$(1,1,a_6,a_6,a_6,a_6)$

$$\mathfrak{L}'(\mathbf{k})=\begin{bmatrix} 0 & 0 & \beta\eta_1 & \beta\eta_2 & \beta\eta_3 & \beta\eta_4 \\ 0 & 0 & \beta\eta_1^* & \beta\eta_2^* & \beta\eta_3^* & \beta\eta_4^* \\ \beta\eta_1^* & \beta\eta_1 & 0 & \beta^2\xi'\zeta_{12} & \beta^2\xi'\zeta_{13} & \beta^2\xi'\zeta_{14} \\ \beta\eta_2^* & \beta\eta_2 & \beta^2\xi'\zeta_{12} & 0 & \beta^2\xi'\zeta_{23} & \beta^2\xi'\zeta_{24} \\ \beta\eta_3^* & \beta\eta_3 & \beta^2\xi'\zeta_{13} & \beta^2\xi'\zeta_{23} & 0 & \xi'\zeta_{34} \\ \beta\eta_4^* & \beta\eta_4 & \beta^2\xi'\zeta_{14} & \beta^2\xi'\zeta_{24} & \beta^2\xi'\zeta_{34} & 0 \end{bmatrix}, \tag{2.1}$$

where η_ν and $\zeta_{\nu\mu}$ are functions of $\mathbf{k}$ defined in reference 10, and

$$\xi'=2\xi/3=2J_{BB}/3J_{AB}. \tag{2.2}$$

First consider $\mathbf{k}=0$; then the $\eta_\nu=\zeta_{\nu\mu}=1$, for all ν, μ. The eigenvectors $\mathbf{V}_\alpha$ and eigenvalues λ_μ, $(\mu=1, \cdots 6)$ are given in Table I where $\mathfrak{L}'\mathbf{V}_\mu=\lambda_\mu\mathbf{V}_\mu$, $\mathbf{V}_\mu=(\psi_{\mu 1},\psi_{\mu 2}\cdots\psi_{\mu 6})$ and

$$a_\mu=\lambda_\mu/4\beta, \quad \mu=1, 6. \tag{2.3}$$

Noting that $a_1<0$ (taking $\beta>0$), we see that $\mathbf{V}_1$ represents the Néel configuration. The ratio of the B-spin magnitude to that for the A's is

$$S\equiv S_B/S_A=\beta|a_1|=\tfrac{1}{4}|\lambda_1|. \tag{2.4}$$

The factor of β enters in accordance with Eq. (15) because the components of $\mathbf{V}$ are the values of the P variables. Using the value of λ_1 from Table I, (2.4) can be solved for β giving

$$\frac{\beta^2}{S^2}=\frac{2}{1-\xi S}. \tag{2.5}$$

Note that $\xi S=J_{BB}S_B/J_{AB}S_A=$ the y parameter defined in reference 10. Thus there is a satisfactory solution (β finite, real) only for $y<1$. The nonexistence of a proper solution for $y\geqslant 1$ is of no consequence, however, since

[10] T. A. Kaplan, Phys. Rev. **119**, 1460 (1960). See also the *Fifth Conference on Magnetism and Magnetic Materials, Detroit, Michigan, 1959* [Suppl. J. Appl. Phys. **31**, 364S (1960)].

[11] T. A. Kaplan, Massachusetts Institute of Technology Lincoln Laboratory Group Report 53-30-1, March 17, 1960 (unpublished). The case of nonmagnetic A sites in cubic spinels is also considered in this report. It is shown, using the original L-T method, that the minimum Ising energy is the same as the minimum Heisenberg energy. J. Kanamori (private communication) has obtained the same result. This supports P. W. Anderson's important result [Phys. Rev. **102**, 1008 (1956)], based on an Ising model, concerning the large degeneracy in the ground spin state.

[12] K. Dwight, T. A. Kaplan, D. H. Lyons, and N. Menyuk (to be published).

this occurs outside the region of stability of the Néel configuration,

$$y<\tfrac{2}{3}, \tag{2.6}$$

as determined by the method of small deviations.[10]

An interesting check on Eq. (2.5) may be obtained by noting that the value of y for which the Néel configuration breaks down as deduced from the Yafet-Kittel theory,[13] namely $y=\frac{3}{4}$, should come just from our $\mathbf{k}=0$ modes. From (2.4) we have λ_1 independent of ξ whereas λ_2 monotonically decreases as ξ increases. When $\lambda_1=\lambda_2$, it is easy to see that $\xi S=\frac{3}{4}$.

So, by choosing β as in (2.5), and properly normalizing $\mathbf{V}_1$, we have represented the Néel configuration C_0 as an eigenvector of $\mathfrak{L}'(0)$ (for $\mathbf{k}=0$) that satisfies the strong conditions for any S_A and S_B. Hence, whenever the corresponding eigenvalue, $\lambda_1=-4S$, is the lowest eigenvalue of the matrices $\mathfrak{L}'(\mathbf{k})$, for all $\mathbf{k}$, C_0 is the rigorous ground state. Consider the matrices $\mathbf{K}(\mathbf{k})=\mathfrak{L}'(\mathbf{k})-\lambda_1\mathbf{I}$, where $\mathbf{I}$ is the unit matrix; then C_0 is the ground state whenever $\mathbf{K}(\mathbf{k})$ is positive definite for all $\mathbf{k}$. But the coordinate transformation $\psi_\nu=S^{-\frac{1}{2}}\psi_\nu'$ for $\nu=1$, 2 and $\psi_\nu=S^{\frac{1}{2}}\beta^{-1}\psi_\nu'$ for $\nu=3$, 4, 5, 6, is easily shown to take $\mathbf{K}(\mathbf{k})$ into the matrix $\mathbf{M}(\mathbf{k})$ studied in reference 10 in connection with the small deviations. Hence[14] the signs of the eigenvalues of $\mathbf{K}(\mathbf{k})$ are the same as those of the eigenvalues of $\mathbf{M}(\mathbf{k})$, which were shown[10] to be positive in and only in the range (2.6). This completes the proof that the Néel configuration gives the absolute minimum of E whenever it is locally stable.

To see how the original L-T method works in this case, we put $\beta=1$. Then (2.5) gives S as a function $f(\xi)$ so that $\mathbf{V}_1$ can satisfy the strong conditions only if we happen to be considering a spinel with S_B/S_A related to J_{BB}/J_{AB} by $S=f(\xi)$. However, by writing the energy in terms of unit vectors, it is easy to see that the ground state can depend only on $y=\xi S$. Letting $S_0=f(\xi_0)$, it therefore follows that C_0 is the lowest state for all ξ and S such that $\xi S=\xi_0 S_0$. The details[11] now work out similarly to those given above.

Let us return to the generalized L-T method, with the choice of the β_ν leading to (2.1). When $y=\frac{2}{3}$, there is another eigenvector, $\mathbf{W}$ of $\mathfrak{L}$ which is degenerate with $\mathbf{V}_1$. The state $\mathbf{W}$ arises from the critical value $\mathbf{k}_0$ of $\mathbf{k}$ found in reference 10 ($\mathbf{k}_0$ is in the cubic [110], the wavelength being roughly twice the primitive translation in [110]). When $y\gtrsim\frac{2}{3}$, the lowest eigenvector will be approximately $\mathbf{W}$. $\mathbf{W}$ does not satisfy the strong conditions since in $\mathbf{W}$ there are two different amplitudes $|\mathbf{Q}_\mathbf{k}|$ for the B spins. Thus the method with this choice of the β_ν fails when the Néel configuration becomes unstable in the present case of a cubic normal spinel.

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

[14] This follows from the fact that if we write the coordinate transformation as $\mathbf{V}=\mathbf{T}\mathbf{V}'$, then the quadratic form $(\mathbf{V},\mathbf{K}\mathbf{V})=(\mathbf{V}',\mathbf{T}^+\mathbf{K}\mathbf{T}\mathbf{V}')=(\mathbf{V}',\mathbf{M}\mathbf{V}')$, another quadratic form, with matrix $\mathbf{T}^+\mathbf{K}\mathbf{T}=\mathbf{M}$.

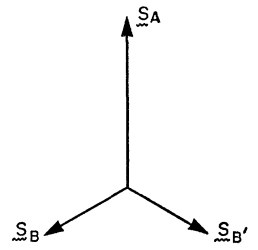

FIG. 2. Schematic diagram of Yafet-Kittel triangular configuration.

Example 3. The Yafet-Kittel Triangular Configurations in Spinels

It has been shown[6,10] that the Yafet-Kittel[11] triangular configurations C_1 do not minimize the exchange energy in cubic spinels, but that[6,12] they are locally stable in a class of tetragonally distorted spinels. It is therefore of interest to prove rigorously that a member of C_1 is the ground state in these distorted cases. In these cases, of course, $\mathfrak{L}(\mathbf{k})$ will be different from (2.1). However, we will not go into the details of the distortion here (they will be given elsewhere[12]), since the crux of the problem lies in the construction of an eigenstate of $\mathfrak{L}(\mathbf{k})$, for some $\mathbf{k}$, that gives the Yafet-Kittel configuration. Hence the essence of the application of our method will be illustrated by working with (2.1).[15] Consider the $\mathbf{k}=0$ states given in Table I. We saw in the previous example that when β was chosen to make $\mathbf{V}_1$ represent the Néel state, C_0, then $\lambda_1\gtrless\lambda_2$ when $y\gtrless\frac{3}{4}$. But Yafet and Kittel showed that the triangular configurations are of lower energy than C_0 when $y>\frac{3}{4}$, showing that the states $\mu=2$, 3, 4 are closely related to C_1. In fact it is clear that these states give C_1 in the case $S_A=0$ (since $\psi_{\alpha 1}=\psi_{\alpha 2}=0$), the B sites being antiferromagnetic. Since, however, we are interested in $S_A\neq 0$, these states cannot satisfy the strong conditions.

But since β is in general a function of the parameters ξ, S [e.g., Eq. (2.5)], there is no reason to preserve (2.5) when $y>\frac{3}{4}$. Now C_1, shown schematically in Fig. 2, is clearly a linear combination of $\mathbf{V}_1$ and, say $\mathbf{V}_4$, with $\mathbf{V}_1$ and $\mathbf{V}_4$ referring, respectively, to the z and x components. This suggests we choose β to make

$$\lambda_1=\lambda_2, \tag{3.1}$$

since then $\mathbf{V}_1$ and $\mathbf{V}_4$ are degenerate, and any linear combination,

$$b\hat{z}\mathbf{V}_1+c\hat{x}\mathbf{V}_4 \tag{3.2}$$

is an eigenvector of $\mathfrak{L}(0)$.[16] Equation (3.1) gives

$$\beta^2/S^2=9/(2\xi^2S^2). \tag{3.3}$$

Equation (2.5) for $y\leqslant\frac{3}{4}$ and Eq. (3.3) for $y>\frac{3}{4}$ define β/S as a continuous function of y. The strong conditions

[15] For distorted spinels, the important $\mathbf{k}=0$ states are as given in Table I, with modified values for a_1 and a_6. The λ_α will be different; in particular the triply degenerate set will be split.

[16] In the sense of reference 4.

may now be satisfied by (3.2) by choosing $b=S_A/\beta$ and

$$c=\frac{S_B}{\beta}\left[1-\left(\frac{3}{4y}\right)^2\right]; \quad (3.4)$$

then

$$S_B{}^x=S_B[1-(\tfrac{3}{4}y)^2]^{\frac{1}{2}}, \quad (y\geq\tfrac{3}{4}), \quad (3.5)$$

in agreement with the Yafet-Kittel result.

If, with the value of β given by (3.3), the eigenvalue (3.1) were the lowest of all the eigenvalues of (2.1), (for all $\mathbf{k}$), then C_1 would have been shown to be the ground state. This is not the case, for any y, giving consistency with the small deviations result.[6,10] For distorted spinels,[12] however, the same procedure yields a proof of the fact that the appropriate Yafet-Kittel configuration is the ground state whenever it is locally stable.[17]

[17] *Note added in proof.* This result, as well as that of Example 2 and the result discussed in reference 9, is easily generalized: In any lattice, local stability of a configuration of *coplanar* spins implies that the configuration is the ground state. However, we have found that metastable configurations of noncoplanar spins exist for some interactions in spinels.

SUMMARY AND DISCUSSION

We have shown that a straightforward generalization of the method of Luttinger and Tisza[1] allows the sloution of the ground spin-state problem in some new and physically interesting cases. The extended method has been applied elsewhere[12] to spinels for which neither the Néel nor the Yafet-Kittel configurations is the ground state. Using the device of "forced degeneracy" discussed in Example 3, it has been shown[12] that the ground state for an interesting class of such spinels is a new type of spiral which is ferrimagnetic.

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Pulsed Field Measurements of Large Zero-Field Splittings: V^{3+} in Al_2O_3

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Use of pulsed magnetic fields for determining large zero-field splittings of paramagnetic ions is considered. Measurements of zero-field splittings of over 50 cm^{-1} are feasible; a numerical example for $S=1$ is discussed in order to indicate the present range and limitations of the method. The method is applied to measurements of the zero-field splitting of V^{3+} in Al_2O_3 at 4.2°K and 1.5°K. Assuming $g_{||}=1.92$, $D=7.85$ cm^{-1} was determined from experiments with 4 mm and 8 mm wavelength radiation and pulsed magnetic fields of the order of 100 kilogauss. The magnitude and sign of D are in good agreement with earlier estimates from optical and microwave measurements.

INTRODUCTION

ENERGY level separations of paramagnetic ions of the order of 10 cm^{-1} cannot in general be readily observed with conventional paramagnetic resonance techniques. The present technology of millimeter wave generation and detection permits only a limited coverage of the frequency range of 10 cm^{-1} and above.[1] If, however, a very large external magnetic field is applied along preferred directions it is possible in many cases to "tune" one or more of the Zeeman levels of higher states so that transitions can be observed at a convenient frequency ν which is much less than the zero-field splitting.[2] Such large magnetic fields can easily be obtained for short times. In this note we indicate some of the possibilities as well as the limitations of pulsed magnetic field techniques as applied to such measurements. In particular we shall discuss the zero-field splitting of V^{3+} in corundum which we have measured using this technique.

PARAMAGNETIC IONS WITH LARGE ZERO-FIELD SPLITTINGS

A large number of paramagnetic ions show Stark splittings between 1 and 50 cm^{-1}. The ions fall into three classes.

(a) Ions with an orbital singlet as the lowest Stark level, and with an odd number of electrons. These ions have long relaxation times in octahedral symmetries but usually show small zero-field splittings. In the few cases where the zero-field splitting is larger than 1 cm^{-1}, the separation among the various Kramers doublets can be inferred from a careful study of the angular dependence of the resonance spectra. This method is, however, not very accurate for $D\gg h\nu$. Zeeman levels of different Kramers doublets can be brought together by the

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† Operated with support from the U. S. Army, Navy, and Air Force.
[1] G. S. Heller (private communication).
[2] S. Foner, J. phys. radium **20**, 336 (1959).