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Collective Excitations and Magnetic Ordering in Materials with Singlet Crystal-Field Ground State

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The low-lying magnetic excited states ("Frenkel spin excitons") in rare-earth compounds with a singlet crystal-field ground state are studied. We consider the effect of exchange interaction between the ionic moments as it increases from zero towards the critical value necessary for magnetic ordering at zero temperature. For simplicity, we consider the two-level system where the first-excited crystal-field state is also a singlet. By employing a pseudospin formalism, we avoid many of the fundamental difficulties encountered in previous treatments which introduce fermion operators for each of the crystal-field states. Applying techniques similar to those used in treating standard spin problems such as the Heinsenberg ferromagnet, we obtain an improved collective-excitation spectrum with a gap which decreases as the exchange increases. The critical value of exchange for magnetic ordering found is substantially greater than that obtained from molecular-field theory, and also is somewhat greater than that found with the constant-coupling approximation.

1. INTRODUCTION

In rare-earth compounds, the crystal electric field can be comparable to or even dominant over the exchange field between rare-earth ions. Thus, the crystal field is expected to play a very important role in the nature of the macroscopic magnetic properties and of the collective excitations for such materials. Indeed, for rare-earth compounds with a singlet crystal-field ground state for the rare-earth ion, the exchange interaction must exceed a certain critical value relative to the crystal field to have magnetic ordering even at zero temperature.[1–4] The magnetic moment which occurs in such a case is essentially an induced moment corresponding to the Van Vleck susceptibility, where the exchange field takes the place of an applied external magnetic field. (This is then a sort of "bootstrap" process where, at zero temperature, the induced moment in the ground state gives an exchange field which self-consistently determines the induced moment.) Trammell[1,2] first pointed out the existence of a critical value for the exchange necessary, even at zero temperature, for such a bootstrap process to give magnetic ordering. Bleaney[3] has also discussed this effect using the molecular-field approximation. Recently, Cooper[4] calculated this critical value by use of the constant-coupling approximation. The critical value of exchange necessary for magnetic ordering was significantly increased over that necessary in the molecular-field approximation. As Cooper pointed out, it is the short-range correlation that gives rise to the change in critical value. It should be possible[4] to examine experimentally the critical ratio of the exchange to the crystal field necessary for magnetic ordering by using mixed rare-earth crystals.[4a]

The energy of the collective excitations for such singlet ground-state systems is of interest both in itself and also because the theory of the excitation behavior provides a criterion for the critical value of the exchange necessary for magnetic ordering. If one investigates the nature of the collective excitations in the paramagnetic regime at zero temperature (exchange less than the critical value) for ferromagnetic exchange, this criterion for ferromagnetic ordering is that the zero wave-vector mode becomes unstable. If one investigates[4] the low-lying excited states using the Bogoliubov-type[5] approximation developed by Van Vleck,[6] Trammell,[2] and Grover,[7] the critical ratio of exchange to crystal-field interactions necessary for magnetic ordering is exactly the same as that in the molecular-field approximation. Therefore, an improved calculation of the collective-excitation spectrum is desirable that will include correlation effects on the determination of the critical condition.

The energy behavior of the elementary excitations is also of interest since understanding it provides the basis for calculating the various thermodynamic properties. Perhaps even more important, one can hope to observe directly the excitation spectrum by neutron inelastic scattering. Then comparison with theory for the excitation energies should allow direct determination of the exchange interaction, as for example has recently been done in terbium[8,9] and erbium[10] metals.

We have therefore studied the collective excitations for the crystal-field singlet ground-state problem using a technique that takes better account of short-range correlation than the Bogoliubov-type approximation. In particular, we have calculated the energies of collec-

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tive excitations for the two-level system where the first excited state is also a singlet. This has been done using a pseudospin formalism where the expectation value of S_{iz}, the pseudospin for the ith ion, corresponds to the occupation of the molecular-field states for that ion. (The expectation value of S_{iz} for the true ground state would be $-\frac{1}{2}$ if the molecular-field approximation were exact.) This method allows us to take into account the fluctuations of the ground state as well as the interactions of the excitation waves. Restricting our study to the two-level system simplifies the algebra greatly; however, it should be possible to generalize the formalism to any type of crystal-field level configuration. In practice, our calculation would apply, for example, to Pr^{3+} in an hexagonal environment.

In this paper, we then obtain the improved dispersion relation which takes into account the correlation effect of excitation waves for the two-singlet-level problem. The critical value of the ratio of exchange to crystal-field splitting necessary for ferromagnetic ordering is obtained using the criterion of the instability of the $\mathbf{k}=0$ excitation energy (i.e., the $\mathbf{k}=0$ excitation energy becomes imaginary for exchange greater than the critical value). This critical value is larger than that found in the molecular-field approximation. For nearest-neighbor exchange, the increment for a simple cubic lattice is 18%, and for body-centered cubic 14%, over the corresponding molecular-field results. For purpose of comparison we have also calculated these values in the constant-coupling approximation. The increments then are smaller: 12% for simple cubic, 9% for body-centered cubic.

In Sec. 2 we review the molecular-field theory for the singlet ground-state system and the elementary excitation theory using the Bogoliubov-type approximation. The treatment of the collective-excitation theory, and the resulting criterion for magnetic ordering using the pseudospin formalism, is presented in Secs. 3 and 4. The pseudospin Hamiltonian is solved using the equation-of-motion technique with two different approximations. First, in Sec. 3, a random-phase approximation (RPA) is adopted to linearize the equations of motion. The results of the RPA reflect the fact that the molecular-field ground state is not the true ground state of the system. However, correlation effects of excitations on different sites are not included in the RPA. Therefore, in Sec. 4, an improved approximation is used which should be more accurate in taking care of correlation effects at low temperatures where the population is mainly in the molecular-field ground state.

2. MOLECULAR-FIELD THEORY AND ELEMENTARY EXCITATIONS IN BOGOLIUBOV-TYPE APPROXIMATION

To review the earlier theories, we consider the Hamiltonian

$$\mathcal{H}=\sum_i V_{ci}-\sum_{\langle i,j\rangle}\mathcal{J}_{ij}\mathbf{J}_i\cdot\mathbf{J}_j. \tag{2.1}$$

Here V_{ci} is the single-ion crystal-field potential which gives a singlet ground state and a singlet excited state, separated by an energy gap Δ. In (2.1), $\mathbf{J}_i$ is the total angular momentum of the rare-earth ion at the ith site, and $\mathcal{J}_{ij}$ represents the effective exchange integral. The sum in the exchange term is over all interacting pairs of ions.

We can express the total Hamiltonian as follows:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+N\mathcal{J}(0)\langle J\rangle^2, \tag{2.2}$$

where

$$\mathcal{H}_0=\sum_i V_{ci}-2\mathcal{J}(0)\langle J\rangle\sum_i J_{iz}, \tag{2.3a}$$

$$\mathcal{H}_1=-\sum_{\langle i,j\rangle}\mathcal{J}_{ij}\mathbf{j}_i\cdot\mathbf{j}_j, \tag{2.3b}$$

with the definitions

$$\mathbf{j}_i\equiv\mathbf{J}_i-\langle J\rangle\hat{\mathbf{e}}_z \tag{2.4a}$$

and

$$\mathcal{J}(\mathbf{k})\equiv\sum_j\mathcal{J}_{ij}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}. \tag{2.4b}$$

$\mathcal{H}_0$ is the molecular-field Hamiltonian. In (2.4a), $\hat{\mathbf{e}}_z$ denotes a unit vector in the z direction. The quantity $\langle J\rangle$ is the statistical average of the angular momentum per ion, J_z, and must be determined self-consistently. At zero temperature and in the molecular-field approximation, $\langle J\rangle$ is the expectation value of J_z over the molecular-field ground state.

In the molecular-field approximation, $\mathcal{H}_1$ is discarded and $\mathcal{H}_0$ is diagonalized to give the molecular-field eigenstates $|0\rangle$ and $|1\rangle$.

$$|0\rangle=\cos\theta\,|0_c\rangle+\sin\theta\,|1_c\rangle, \tag{2.5a}$$

$$|1\rangle=-\sin\theta\,|0_c\rangle+\cos\theta\,|1_c\rangle. \tag{2.5b}$$

Here $|0_c\rangle$ and $|1_c\rangle$ are the crystal-field ground and excited state, respectively, which can be obtained by solving the crystal-field Hamiltonian V_c. In our general discussion we do not need the explicit form of the two states which may differ from material to material. We only assume that they are magnetic singlets.

The rotation angle which diagonalizes $\mathcal{H}_0$ is given by

$$\tan 2\theta=4\mathcal{J}(0)\alpha\langle J\rangle/\Delta, \tag{2.6}$$

where

$$\alpha\equiv\langle 1_c\,|\,J_z\,|\,0_c\rangle \tag{2.7}$$

is the off-diagonal element of the angular momentum which leads to the Van Vleck susceptibility in the presence of an external magnetic field. It is to be recalled that Δ is the energy gap between the two crystal-field-only singlets.

Now $\langle J\rangle$ is obtained self-consistently. At $T=0$,

$$\langle J\rangle=\langle 0\,|\,J_z\,|\,0\rangle=\alpha\sin 2\theta \tag{2.8}$$

or

$$\langle J\rangle=4\mathcal{J}(0)\alpha^2\langle J\rangle/\{\Delta^2+[4\mathcal{J}(0)\alpha\langle J\rangle]^2\}^{1/2}. \tag{2.9}$$

The condition for an infinitesimal moment at $T=0$ is therefore

$$4\mathcal{J}(0)\alpha^2/\Delta=1. \tag{2.10}$$

At finite temperatures, the critical condition can be obtained similarly. In that case $\langle J\rangle$ is the thermal average rather than the ground-state expectation value. For details we refer to the paper by Bleaney.[3]

The behavior of the collective excitations for singlet crystal-field ground-state systems was studied first by Van Vleck[6] and by Trammell,[2] and later by Grover,[7] using the Bogoliubov approximation[5] originally applied to the liquid-helium problem. The collective excitations so obtained are analogous to the spin waves obtained for the ordinary Heisenberg ferromagnet; where, however, in the present case the basic excitation transmitted between ions is that from one single-ion crystal-field level to another.

The Bogoliubov-type theory proceeds by assigning fermion operators to each molecular-field energy level at each ion site. Then $d_{i1}^\dagger$ creates and d_{i1} annihilates a particle in the molecular-field excited state $|1\rangle$ at site i. We then rewrite the Hamiltonian in the second quantized form:

$$\mathcal{H}_0=\sum_i\left[\epsilon_0 d_{i0}^\dagger d_{i0}+\epsilon_1 d_{i1}^\dagger d_{i1}\right], \tag{2.11}$$

where ϵ_0 and ϵ_1 are the single-ion molecular-field energy levels,

$$\epsilon_0=-\tfrac{1}{2}\Delta\cos2\theta-2\mathcal{J}(0)\langle J\rangle\alpha\sin2\theta, \tag{2.12a}$$

$$\epsilon_1=-\epsilon_0, \tag{2.12b}$$

with θ given by (2.6); and

$$\mathcal{H}=-\sum_{i,j}\sum_{n,m,n',m'}\mathcal{J}_{ij}\langle n\mid\mathbf{j}_i\mid m\rangle\cdot\langle n'\mid\mathbf{j}_j\mid m'\rangle \times d_{in}^\dagger d_{im}d_{jn'}^\dagger d_{jm'}, \tag{2.13}$$

where n, m, n', m' are summed over the two single-ion states.

It should be noted that the Hamiltonian in this fermion representation is not exact since $\mathcal{H}_0$ of (2.11), besides having eigenstates where, for the ith ion, either the state $|0\rangle$ or the state $|1\rangle$ is occupied, also has unphysical eigenstates where both $|0\rangle$ and $|1\rangle$ are occupied, or both unoccupied, for the ith ion. This source of inaccuracy exists even at $T=0$, since the presence of $\mathcal{H}_1$ means that the ground state of $\mathcal{H}_0$ (the molecular-field ground state) is not the true ground state of the system. The mixing caused by $\mathcal{H}_1$ of the excited states of $\mathcal{H}_0$ to the ground state of $\mathcal{H}_0$ to give the true ground state (fluctuations giving rise to occupation of excited states from the molecular-field point of view) then means that the unphysical eigenstates of the fermion expression for $\mathcal{H}_0$ given in (2.11) contribute to the calculated behavior even at $T=0$. This problem of the unphysical states of $\mathcal{H}_0$ and the resultant inaccuracy is, of course, much worse as temperature increases, and one has thermal population of the excited states of $\mathcal{H}_0$ even neglecting the mixing effects of $\mathcal{H}_1$.

It should also be pointed out that if one does adopt the fermion Hamiltonian of (2.11) and (2.13), strictly speaking the quantity $\langle J\rangle$ should be determined self-consistently. At zero temperature, the expectation value should be taken over the true ground state instead of the molecular-field ground state. Grover,[7] however, took the molecular-field approximation value for $\langle J\rangle$ to simplify the calculation in the ordered phase. In the paramagnetic phase, no such question will arise since $\langle J\rangle=0$ is exact.

With the Hamiltonian given by (2.11) and (2.13) one proceeds further by introducing the operators

$$a_{i1}\equiv d_{i0}^\dagger d_{i1},\qquad a_{i1}^\dagger\equiv d_{i1}^\dagger d_{i0}. \tag{2.14}$$

The commutation relations for these operators are

$$[a_{i1},a_{j1}]=[a_{i1}^\dagger,a_{j1}^\dagger]=0, \tag{2.15a}$$

$$[a_{i1},a_{j1}^\dagger]=\delta_{ij}n_{i0}-\delta_{ij}n_{i1}\approx\delta_{ij}. \tag{2.15b}$$

Here n_{i0} and n_{i1} are the occupation-number operators for the molecular-field ground and excited states, respectively, on the ith ion. The last step of Eq. (2.15b) follows by neglecting n_{i1}, the population of the molecular-field excited state, and replacing n_{i0} by unity, a c number. This approximation is consistent with that introduced in the fermion representation of the Hamiltonian. Therefore, a_{i1} and $a_{i1}^\dagger$ are approximated as boson annihilation and creation operators. The Hamiltonian [Eqs. (2.11) and (2.13)] can then be rewritten in terms of these boson operators; and one retains only the quadratic terms. Diagonalization of the quadratic boson Hamiltonian then proceeds by standard technique.

The energy spectrum obtained in the paramagnetic phase where $\langle J\rangle=0$ is

$$E_k=\Delta(1-A\gamma_k)^{1/2}, \tag{2.16}$$

with

$$A\equiv4\mathcal{J}(0)\alpha^2/\Delta \tag{2.17a}$$

and

$$\gamma_k\equiv\mathcal{J}(\mathbf{k})/\mathcal{J}(0). \tag{2.17b}$$

The excited state characterized by the wave vector $\mathbf{k}$ is analogous to the spin-wave state in the spin-$\frac{1}{2}$ Heisenberg ferromagnet. However, instead of spin deviations, excitations from the crystal-field ground state to the excited state are passing from one site to another. The energy spectrum shows a gap, and in the ferromagnetic case the minimum of the spectrum occurs at $\mathbf{k}=0$, where $\gamma_k=1$. It is seen that the gap decreases as A increases toward 1 and becomes imaginary for $A>1$, indicating that the paramagnetic ground state is not stable for $A=1$. This signals the transition to the ferromagnetic phase. The critical ratio of exchange to crystal-field interaction for the phase transition is identical to that predicted by molecular-field theory.

3. PSEUDOSPIN FORMALISM: RPA

To treat the behavior of the two-level system more accurately, especially in the vicinity of magnetic ordering, we use a pseudospin representation to describe the system. This is based on the fact that the matrix elements of the Hamiltonian for a two-level system can always be written in terms of the Pauli matrices, and thus the Hamiltonian for such a system can always be written in terms of an effective spin Hamiltonian with spin equal to $\frac{1}{2}$. We assign $S_z=-\frac{1}{2}$ to the molecular-field ground state and $S_z=\frac{1}{2}$ to the excited state. It is a simple matter to project the exchange Hamiltonian onto this manifold, and thereby to express the exchange interaction in terms of pseudospin variables. This involves recognizing the form of the four spin-$\frac{1}{2}$ operators which correspond to 2×2 matrices, with unity as one element and zero as the other three elements. These operators, for the ith ion, are S_i^+, S_i^-, $S_i^-S_i^+$, and $S_i^+S_i^-$. For example,

$$S_i^+=\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}.$$

Then, by inspection, the total Hamiltonian of (2.2), (2.3a), and (2.3b) is given in the pseudospin representation as

$$\mathcal{H}=\sum_i w_0 S_{iz}-\sum_{\langle i,j\rangle}\mathcal{J}_{ij}(\alpha_{01}S_i^-+\alpha_{10}S_i^++\alpha_{00}S_i^-S_i^+ +\alpha_{11}S_i^+S_i^-)(\alpha_{01}S_j^-+\alpha_{10}S_j^++\alpha_{00}S_j^-S_j^+ +\alpha_{11}S_j^+S_j^-)+N\mathcal{J}(0)\langle J\rangle^2, \quad (3.1)$$

where

$$w_0=\Delta\cos2\theta+4\mathcal{J}(0)\langle J\rangle\alpha\sin2\theta \quad (3.2)$$

so that $-\frac{1}{2}w_0$ equals the molecular-field ground-state energy per ion, and $+\frac{1}{2}w_0$ equals the molecular-field excited-state energy.

$$\alpha_{10}=\alpha_{01}=\langle 1\,|\,j_z\,|\,0\rangle=\alpha\cos2\theta, \quad (3.3)$$

$$\alpha_{00}=\langle 0\,|\,j_z\,|\,0\rangle=\alpha\sin2\theta-\langle J\rangle, \quad (3.4)$$

$$\alpha_{11}=\langle 1\,|\,j_z\,|\,1\rangle=-\alpha\sin2\theta-\langle J\rangle, \quad (3.5)$$

and

$$\tan2\theta=4\mathcal{J}(0)\alpha\langle J\rangle/\Delta. \quad (3.6)$$

Here α, as defined in (2.7), is the off-diagonal element of angular momentum between the crystal-field-only states. It is to be recalled that $|\,0\rangle$ and $|\,1\rangle$ are the single-ion molecular-field states. The energy gap between these two states is w_0, which equals Δ in the absence of magnetic ordering or applied field.

We point out that we have chosen the z axis of the crystal so that only the z component of angular momentum, J_z, has nonzero matrix elements between the crystal-field-only singlet states. The off-diagonal matrix elements of J_x and J_y vanish. (Of course, all diagonal matrix elements of angular momentum vanish for a singlet state.) Such a choice of axis is always possible for an even-electron two-singlet-level system.[11] For a hexagonal system, such as Pr^{3+} in PrF_3, the z axis is the axis of hexagonal symmetry.

We also emphasize that the transformation to the pseudospin representation, and the consequent treatment below, proceeds in the same way when the exchange is anisotropic. For the two-singlet model being discussed, anisotropic exchange of the form $\mathcal{H}=\sum_{\langle i,j\rangle}\mathcal{J}_{ij}J_{iz}J_{jz}$ introduces no changes. This is because the vanishing of the J_x and J_y matrix elements means that the treatment is exactly the same as for Heisenberg exchange. However, for situations as discussed in Sec. 5, where the excited state is a triplet, anisotropic exchange would introduce new effects. (Of course, there is no real even-electron system where the *only* states of the system are two singlet levels. There would always be higher-lying states whose J_x and J_y matrix elements with the two singlet states would, in general, be nonzero. Thus, in all real systems anisotropy of exchange would affect the magnetic properties to a finite extent.)

In the paramagnetic regime with no applied field $\langle J\rangle=0$, and consequently $\theta=0$ in Eqs. (3.2)-(3.6). The Hamiltonian is consequently simplified:

$$\mathcal{H}=\sum_i\Delta S_{iz}-\sum_{\langle i,j\rangle}\mathcal{J}_{ij}\alpha^2(2S_i^+S_j^-+S_i^+S_j^++S_i^-S_j^-). \quad (3.7)$$

The exchange term can be rewritten so that

$$\mathcal{H}=\sum_i\Delta S_{iz}-4\sum_{\langle i,j\rangle}\mathcal{J}_{ij}\alpha^2 S_{ix}S_{jx}. \quad (3.8)$$

Thus, the Hamiltonian is seen to be quite anisotropic in the pseudospin variables, and S_z is not conserved. (The Hamiltonian is, in form, identical to that for an Ising spin system with a transverse magnetic field.) However, since S_z describes the population of the two molecular-field energy levels (the two crystal-field singlets in the present paramagnetic case), we can anticipate that S_z deviates from $-\frac{1}{2}$ by only a very small amount at low temperature. The nonzero population of the excited molecular-field state at $T=0$ arises from the fact that the molecular-field ground state is not an eigenstate of the total Hamiltonian. This is analogous to a Heisenberg ferromagnet with dipole-dipole interaction, where the zero-temperature moment is not saturated.

To find the low-lying excited states which are described by the collective motions, we study the equations of motion of the spin operators for the gth ion, S_g^+ and S_g^-.

$$i\dot{S}_g^+=[S_g^+,\mathcal{H}]=-\Delta S_g^+-4\alpha^2\sum_f\mathcal{J}_{fg}(S_{gz}S_f^++S_{gz}S_f^-), \quad (3.9)$$

$$i\dot{S}_g^-=[S_g^-,\mathcal{H}]=\Delta S_g^-+4\alpha^2\sum_f\mathcal{J}_{fg}(S_{gz}S_f^++S_{gz}S_f^-). \quad (3.10)$$

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In the RPA we make the replacement

$$S_{gz}S_f^{\pm}\xrightarrow[g\neq f]{}\langle S_z\rangle S_f^{\pm}, \qquad (3.11)$$

where $\langle S_z\rangle$ denotes the average value of the operator S_{gz}. Multiplying both sides by $(1/\sqrt{N})\exp(-i\mathbf{k}\cdot\mathbf{r}_g)$ and summing over g we obtain the equations of motion in k space.

$$i\dot{S}^+(\mathbf{k})=-\Delta S^+(\mathbf{k})-4\alpha^2\mathcal{J}(\mathbf{k})\langle S_z\rangle[S^+(\mathbf{k})+S^-(-\mathbf{k})], \qquad (3.12)$$

$$i\dot{S}^-(-\mathbf{k})=\Delta S^-(-\mathbf{k})+4\alpha^2\mathcal{J}(\mathbf{k})\langle S_z\rangle[S^+(\mathbf{k})+S^-(-\mathbf{k})], \qquad (3.13)$$

where

$$S^+(\mathbf{k})\equiv(1/\sqrt{N})\sum_g S_g^+\exp(-i\mathbf{k}\cdot\mathbf{r}_g) \qquad (3.14)$$

and $\mathcal{J}(\mathbf{k})$ is defined in (2.4b).

The generating operator for the elementary excitations, $\mathcal{S}^+(\mathbf{k})$, is therefore a linear combination of $S^+(\mathbf{k})$ and $S^-(-\mathbf{k})$ such that

$$[\mathcal{H},\mathcal{S}^+(\mathbf{k})]\mid\Phi_0\rangle=E_k\mathcal{S}^+(\mathbf{k})\mid\Phi_0\rangle, \qquad (3.15)$$

where $\mid\Phi_0\rangle$ designates the *true ground state* of the system. Using Eqs. (3.12) and (3.13), it is a simple matter to find $S^+(\mathbf{k})$ such that

$$-i\partial\mathcal{S}^+(\mathbf{k})/\partial t=[\mathcal{H},\mathcal{S}^+(\mathbf{k})]=E_k\mathcal{S}^+(\mathbf{k}). \qquad (3.16)$$

This gives the elementary excitation energy

$$E_k=\Delta[1+8\langle S_z\rangle\alpha^2\mathcal{J}(\mathbf{k})/\Delta]^{1/2}=\Delta(1+2\langle S_z\rangle A\gamma_k)^{1/2}, \qquad (3.17)$$

where

$$A\equiv4\mathcal{J}(0)\alpha^2/\Delta, \qquad (3.18a)$$

$$\gamma_k\equiv\mathcal{J}(\mathbf{k})/\mathcal{J}(0). \qquad (3.18b)$$

The generating operators for the excitation modes are then given by

$$\mathcal{S}^+(\mathbf{k})=\cosh\beta_k S^+(\mathbf{k})-\sinh\beta_k S^-(-\mathbf{k}), \qquad (3.19)$$

with

$$\tanh2\beta_k=-\langle S_z\rangle A\gamma_k/(1+\langle S_z\rangle A\gamma_k). \qquad (3.20)$$

From (3.17) we see that a knowledge of $\langle S_z\rangle$, the average value of the operator S_{gz}, is necessary to determine the excitation-energy spectrum, the behavior of which in turn determines the critical value of A necessary for magnetic ordering. For this purpose $\langle S_z\rangle$ must be determined self-consistently. At $T=0$, $\langle S_z\rangle$ is an expectation value over the true ground state, $\mid\Phi_0\rangle$, which satisfies the condition

$$\mathcal{S}^-(\mathbf{k})\mid\Phi_0\rangle\equiv0 \qquad (3.21)$$

for all $\mathbf{k}$. To evaluate $\langle S_z\rangle$ we make use of the relationship

$$S_{gz}=-\tfrac{1}{2}+S_g^+S_g^-, \qquad (3.22)$$

replace S_g^+ and S_g^- by their Fourier expansions, and take the ground-state expectation value. This gives

$$\langle S_z\rangle=-\tfrac{1}{2}+(1/N)\sum_{k_1,k_2}\exp[+i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_g]\times\langle\Phi_0\mid S^+(\mathbf{k}_1)S^-(\mathbf{k}_2)\mid\Phi_0\rangle. \qquad (3.23)$$

Then we write $S^+(\mathbf{k})$ and $S^-(\mathbf{k})$ in terms of $\mathcal{S}^+(\mathbf{k})$ and $\mathcal{S}^-(-\mathbf{k})$ by use of the inverse transformation to that of (3.19). This replacement together with use of the property (3.21) leads to

$$\langle S_z\rangle=-\tfrac{1}{2}+(1/N)\sum_{k_1,k_2}\exp[-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}_g]\sinh\beta_{k_1}\sinh\beta_{k_2}\times\langle\Phi_0\mid\mathcal{S}^-(\mathbf{k}_1)\mathcal{S}^+(\mathbf{k}_2)\mid\Phi_0\rangle. \qquad (3.24)$$

Also,

$$\langle\Phi_0\mid\mathcal{S}^-(\mathbf{k}_1)\mathcal{S}^+(\mathbf{k}_2)\mid\Phi_0\rangle=[-2\langle\Phi_0\mid S_z(0)\mid\Phi_0\rangle+\langle\Phi_0\mid\mathcal{S}^+(\mathbf{k})\mathcal{S}^-(\mathbf{k})\mid\Phi_0\rangle]\delta_{k_1k_2}=(1-2\delta)\delta_{k_1k_2}, \qquad (3.25)$$

where we have used (3.20) and (3.21) and introduced the definitions

$$\delta\equiv\langle S_z\rangle+\tfrac{1}{2}, \qquad (3.26a)$$

$$S_z(\mathbf{k})\equiv(1/N)\sum_g S_{zg}\exp(-i\mathbf{k}\cdot\mathbf{r}_g). \qquad (3.26b)$$

Then,

$$\langle S_z\rangle=-\tfrac{1}{2}+(1/N)\sum_k\sinh^2\beta_k(-2\langle S_z\rangle) \qquad (3.27)$$

or

$$\langle S_z\rangle=-\tfrac{1}{2}[1+(2/N)\sum_k\sinh^2\beta_k]^{-1}, \qquad (3.28)$$

so that

$$\langle S_z\rangle\approx-\tfrac{1}{2}+(1/N)\sum_k\sinh^2\beta_k \qquad (3.29)$$

and

$$\delta\approx(1/N)\sum_k\sinh^2\beta_k. \qquad (3.30)$$

The smallness of δ follows from expecting the admixture of the molecular-field excited state into the true ground state to be small. One expects δ to take on its maximum value at $A=A_{\text{crit}}$, since then the excitation energy gap vanishes. However, even in that case, we expect δ to be small; and this, indeed, is the result of our calculation.

From (3.20) we see that β_k depends on $\langle S_z\rangle$ so that (3.29) must be solved self-consistently to find $\langle S_z\rangle$ for specified A. In particular, we are interested in finding $\langle S_z\rangle$ when A has the critical value necessary for magnetic ordering at zero temperature. This critical value is obtained from the condition that some E_k given by (3.17) go to zero (and would become imaginary for exchange of greater magnitude). For ferromagnetic exchange the minimum of the dispersion curve given by (3.17) occurs at $k=0$, so that A_{crit} is that value of A

for which E_k vanishes in (3.17) with $k=0$. Since

$$E_k=\Delta[1-(1-2\delta)A\gamma_k]^{1/2}, \qquad (3.31)$$

the relationship between A and δ, when A is equal to the critical value, is

$$A_{\text{crit}}=1/(1-2\delta). \qquad (3.32)$$

Then, for $A=A_{\text{crit}}$ we can rewrite (3.20) and (3.29) as

$$\tanh 2\beta_k=\gamma_k/(2-\gamma_k). \qquad (3.33)$$

Thus, for $A=A_{\text{crit}}, \beta_k$ is just a function of γ_k. For nearest-neighbor exchange, it is a straightforward matter to evaluate the sum in (3.30) to give δ for a given lattice. (The general method used in evaluating sums of this sort is illustrated in Appendix A.) Numerical calculation shows $\delta=0.02$ for the simple cubic lattice and $\delta=0.015$ for the body-centered-cubic lattice with nearest-neighbor exchange interactions. Therefore, in the RPA ground state only 4% of the molecular-field excited states are populated for the simple cubic, and 3% for the body-centered-cubic lattice. The critical ratios A_{crit} are increased by about the same amounts over the molecular-field-theory results. This increment directly reflects the zero-point population in the single-ion molecular-field excited levels. The Bogoliubov-type calculation which ignores this effect, corresponds to taking $\langle S_z\rangle=-\frac{1}{2}$ in the approximation of Eq. (3.11). This is a very strong approximation for finite temperatures and restricts the Bogoliubov-type calculation to very low temperature even if one is willing to accept inaccuracies connected with the zero-point population of the molecular-field excited levels. The RPA represents an improvement over the Bogoliubov-type calculation in this respect, in that at finite temperatures $\langle S_z\rangle$ is taken as the self-consistent thermal average of S_{gz} for the system.

4. PSEUDOSPIN FORMALISM: TWO-SITE CORRELATION APPROXIMATION

The RPA given by (3.11) is not an ideal approximation. This can be seen by considering Callen's discussion[12] of the Green's-function theory of ferromagnetism for the Heisenberg ferromagnet. The correlation effects of excitation waves are neglected in the RPA; and, because of the highly anisotropic form of our Hamiltonian (3.8), these effects could be very important.

Callen[12] suggested an approximate way to replace S_{gz} in the equations of motion which is valid both at low temperature where $\langle S_z\rangle$, the thermal average of S_{gz}, is approximately $-\frac{1}{2}$ and at high temperature, where $\langle S_z\rangle$ approaches zero. Following Callen, one writes S_z in the form

$$S_z=\langle S_z\rangle+[(\tfrac{1}{2}-\langle S_z\rangle)S^+S^--(\tfrac{1}{2}+\langle S_z\rangle)S^-S^+] \qquad (4.1)$$

before doing any approximation. Since

$$S^+S^-+S^-S^+=1 \qquad (4.2)$$

for spin $\frac{1}{2}$ and

$$[S^+,S^-]=2S_z, \qquad (4.3)$$

Eq. (4.1) is exact. The quantity to be treated approximately is in the square brackets and is always small. This term in brackets then introduces effects into the equations of motion which are neglected in the RPA.

Before going on to the actual treatment of the collective excitations, we can see the nature of the new effects (beyond RPA) introduced by using the approximation of (4.1). In the Fourier-transformed equations of motion, corresponding to (3.12) and (3.13), there appear new three-spin terms of the form

$$(1/N)\sum_{k_1k_2}\mathcal{J}(\mathbf{k}-\mathbf{k}_1+\mathbf{k}_2)S^+(\mathbf{k}-\mathbf{k}_1+\mathbf{k}_2)S^+(\mathbf{k}_1)S^-(\mathbf{k}_2). \qquad (4.4)$$

A reasonable linearization procedure is the following:

$$\begin{aligned}(1N)\sum_{k_1k_2}&\mathcal{J}(\mathbf{k}-\mathbf{k}_1+\mathbf{k}_2)S^+(\mathbf{k}-\mathbf{k}_1+\mathbf{k}_2)S^+(\mathbf{k}_1)S^-(\mathbf{k}_2)\\ &\to(1/N)\sum_{k_1}\mathcal{J}(\mathbf{k})\langle S^+(\mathbf{k}_1)S^-(\mathbf{k}_1)\rangle S^+(\mathbf{k})\\ &+(1/N)\sum_{k_1}\mathcal{J}(\mathbf{k}_1)\langle S^+(\mathbf{k}_1)S^-(\mathbf{k}_1)\rangle S^+(\mathbf{k})\\ &+(1/N)\sum_{k_1}\mathcal{J}(\mathbf{k}_1)\langle S^+(\mathbf{k}_1)S^+(-\mathbf{k}_1)\rangle S^-(-\mathbf{k}). \qquad (4.5)\end{aligned}$$

This linearization approximation comes from taking all possible expectation values for two spin operators. At zero temperature, it is easy to see then that only the terms shown on the right side in (4.5) survive if we anticipate that the transformation to the generating operators for excited states is of the form given in (3.19). This follows from the definition of the ground state given in (3.21), which leads to the condition

$$\langle S^+(\mathbf{k})S^-(\mathbf{q})\rangle=0 \qquad (4.6)$$

for $\mathbf{k}\neq\mathbf{q}$. Equation (4.6) is also true at finite temperature, when the canonical thermal average is taken, because of the conservation of the linear momentum. [We note that (4.5) is equivalent to the symmetrical decoupling approximation used by Callen in the Green's-function theory of ferromagnetism.[12]]

We can now see what additional physical effects beyond the RPA are introduced by the terms on the right of (4.5). Considering the special case of nearest-neighbor exchange, this can be seen by noting that

$$(1/N)\sum_{k_1}\mathcal{J}(\mathbf{k}_1)\langle S^+(\mathbf{k}_1)S^-(\mathbf{k}_1)\rangle =[\mathcal{J}(0)/z]\sum_{\delta'}\langle S_0{}^+S_{\delta'}{}^-\rangle, \qquad (4.7a)$$

$$(1/N)\sum_{k_1}\mathcal{J}(\mathbf{k}_1)\langle S^+(\mathbf{k}_1)S^+(-\mathbf{k}_1)\rangle =[\mathcal{J}(0)/z]\sum_{\delta'}\langle S_0{}^+S_{\delta'}{}^+\rangle. \qquad (4.7b)$$

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[12] H. B. Callen, Phys. Rev. **130**, 890 (1963).

[These relationships are easily obtained by explicitly considering the Fourier sums on the left side of (4.7a) and (4.7b).] Here δ' designates the vector from one site to each of its z nearest neighbors. Thus, we see that the terms on the right of (4.5) give the correlation function of the excitations on two exchange coupled sites. Such correlations are neglected in the RPA. We therefore call the approximation described by (4.1) and (4.5) the two-site correlation approximation (TSCA).

To examine the nature of the collective excitations in the TSCA we first replace S_{gz} in the equations of motion (3.9) and (3.10) by the expression (4.1). Then the equations of motion are Fourier-transformed and the approximation corresponding to (4.5) is used for all three spin-operator terms. This procedure gives the linearized equations of motion

$$i\dot{S}^+(\mathbf{k}) = -[\Delta+4\langle S_z\rangle\alpha^2\mathcal{J}(\mathbf{k})-8\langle S_z\rangle\epsilon\alpha^2\mathcal{J}(0)]S^+(\mathbf{k}) -[4\langle S_z\rangle\alpha^2\mathcal{J}(\mathbf{k})-8\langle S_z\rangle\epsilon\alpha^2\mathcal{J}(0)]S^-(-\mathbf{k}), \tag{4.8}$$

$$i\dot{S}^-(\mathbf{k}) = [\Delta+4\langle S_z\rangle\alpha^2\mathcal{J}(\mathbf{k})-8\langle S_z\rangle\epsilon\alpha^2\mathcal{J}(0)]S^-(-\mathbf{k}) +[4\langle S_z\rangle\alpha^2\mathcal{J}(\mathbf{k})-8\langle S_z\rangle\epsilon\alpha^2\mathcal{J}(0)]S^+(\mathbf{k}), \tag{4.9}$$

where

$$\begin{aligned}\epsilon &= (1/N)\sum_k \gamma_k[\langle S^+(\mathbf{k})S^-(\mathbf{k})\rangle+\langle S^+(\mathbf{k})S^+(-\mathbf{k})\rangle] \\ &= (1/N)\sum_k \gamma_k[\langle S^+(\mathbf{k})S^-(\mathbf{k})\rangle+\langle S^-(\mathbf{k})S^-(-\mathbf{k})\rangle],\end{aligned} \tag{4.10}$$

with γ_k as defined in (2.17b).

A transformation of the same form as (3.19) for the RPA gives the generating operators and dispersion law for the elementary excitations.

$$\mathcal{S}^+(\mathbf{k}) = \cosh\beta_k S^+(\mathbf{k}) - \sinh\beta_k S^-(-\mathbf{k}), \tag{4.11}$$

$$E_k = \Delta[1+2\langle S_z\rangle A(\gamma_k-2\epsilon)]^{1/2}, \tag{4.12}$$

with

$$\tanh 2\beta_k = \frac{-\langle S_z\rangle A(\gamma_k-2\epsilon)}{1+\langle S_z\rangle A(\gamma_k-2\epsilon)}. \tag{4.13}$$

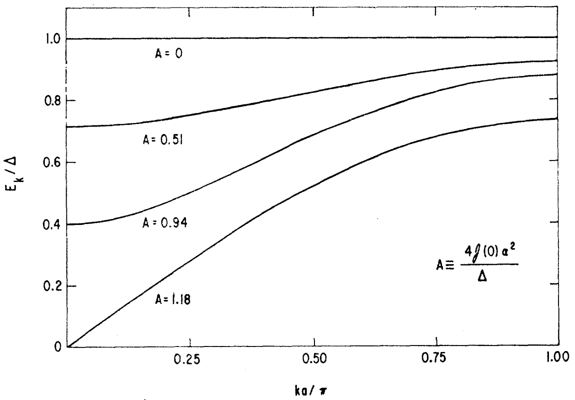

FIG. 1. Dispersion curve at zero temperature of elementary excitations for simple cubic lattice with nearest-neighbor ferromagnetic exchange calculated for several values of A in the TSCA.

TABLE I. Critical value of $A \equiv 4\mathcal{J}(0)\alpha^2/\Delta$.

	Simple cubic	Body-centered cubic	Face-centered cubic
Molecular field	1.00	1.00	1.00
Bogoliubov-type approximation	1.00	1.00	1.00
Constant coupling	1.12	1.09	1.06
Pseudospin formalism:			
RPA ($S^z \to \langle S^z\rangle$ in equations of motion)	1.04	1.03	···
TSCA	1.18	1.14	···

For a given A [as defined in (2.17a)], $\langle S_z\rangle$ and ϵ are to be calculated self-consistently. This procedure is described in Appendix A. The dispersion curve at zero temperature for a simple cubic lattice with nearest-neighbor exchange is shown in Fig. 1 for several values of A. The energy gap at $k=0$ decreases as the exchange increases. The critical value of A at which the gap vanishes, signaling the onset of magnetic ordering, is given as

$$A_{\text{crit}} = 1/(1-2\delta)(1-2\epsilon) \tag{4.14}$$

for ferromagnetic coupling. We see that A_{crit} is modified from the RPA value, Eq. (3.31), by a factor $(1-2\epsilon)^{-1}$. This change is due to correlations of excitations on different sites. By means of the self-consistent calculation described in Appendix A, we obtain $A_{\text{crit}}=1.18$ for a simple cubic lattice and $A_{\text{crit}}=1.14$ for a body-centered-cubic lattice with nearest-neighbor exchange.

Values of A_{crit} in the various approximations are shown in Table I. The constant-coupling calculation, which follows that of Cooper,[4] is presented in Appendix B. The fact that A_{crit} is greatest for the TSCA indicates that more of the short-range order effects are included in that treatment. It is interesting to note that the percentage increase of the constant-coupling value from the molecular-field value for the critical value of $\mathcal{J}(0)/\Delta$ necessary for magnetic ordering is much smaller for the two-singlet-level case than for the case where the excited state is a triplet.[4] (For example, with $z=6$, the critical value of $\mathcal{J}(0)/\Delta$ increases by 12% for the singlet-singlet case, and by 23% for the singlet-triplet case.) Thus, we might expect the percentage increase over the molecular-field value of the critical value of $\mathcal{J}(0)/\Delta$ to be correspondingly greater for the singlet-triplet case than for the singlet-singlet case in the TSCA. The singlet-triplet situation is that occurring in the rare-earth compounds of NaCl structure with group-V and -VI elements.

In Fig. 2, for the two values of A we compare the

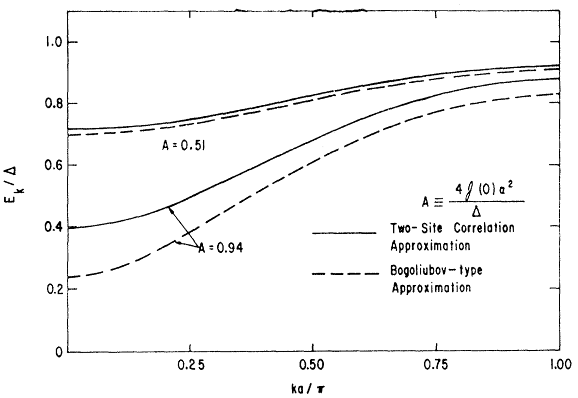

FIG. 2. Comparison of dispersion curve calculated in the TSCA with that calculated in the Bogoliubov-type approximation. Calculations are for simple cubic lattice with nearest-neighbor ferromagnetic exchange at zero temperature.

dispersion law for the TSCA to that using the Bogoliubov-type approximation. (The calculations are for a simple cubic lattice with nearest-neighbor exchange at zero temperature.) The difference between the curves for the two approximations is quite substantial as A approaches the critical value, and is very small for $A<\frac{1}{2}A_{\text{crit}}$. This is expected since the smaller the A value is, the bigger the gap becomes and consequently the closer the molecular-field ground state is to the true ground state. (The corresponding curves for the RPA would lie between those for the TSCA and those for the Bogoliubov-type approximation, but closer to the latter. For $A=0.94$ the RPA curve has $E_k/\Delta=0.28$ for $k=0$ and $E_k/\Delta=0.83$ for $k=\pi/a$. As temperature increases the RPA curve moves toward the TSCA curve, and both then substantially deviate from the curve for the Bogoliubov-type approximation.) Again, as in the case of the critical value of $\mathcal{J}(0)/\Delta$ for magnetic ordering, for the singlet-ground-state–triplet-excited-state situation, we may expect even greater differences between the dispersion law for the TSCA and that using the Bogoliubov-type approximation than for the singlet-singlet case as $\mathcal{J}(0)/\Delta$ approaches the critical value.

In the discussion above, we have taken a ferromagnetic exchange interaction. For antiferromagnetic coupling, the calculation is the same, since we are in the paramagnetic regime. However, the minimum of the dispersion curve occurs at $k=\pi/a$, where $\gamma_k=-1$ instead of at $k=0$. Then

$$A_{\text{crit}}=1/(1-2\delta)(1+2\epsilon). \tag{4.15}$$

The self-consistent calculation shows that δ is the same as that in the ferromagnetic case, and ϵ differs from the ferromagnetic value by only a sign. Therefore $|A_{\text{crit}}|$ is identical to A_{crit} for the ferromagnetic case. This is different from the constant-coupling calculation,[4] where there is a small numerical difference between A_{crit} for the ferromagnet and $|A_{\text{crit}}|$ for the antiferromagnet. This difference may result from the fact that in the present pseudospin calculation the critical point is approached from the paramagnetic region; while in the constant-coupling calculation, the critical point is approached from the antiferromagnetic region. Thus, any zero-point effects associated with the nature of an assumed antiferromagnetic ground state do not appear in the result of the present calculations using the pseudospin formalism.

5. DISCUSSION

In the present work, we have developed a technique for studying the collective excitations in singlet crystal-field ground-state systems. The treatment developed here especially represents an improvement over previous treatments as the exchange approaches the critical value necessary for magnetic ordering with infinitesimal moment at zero temperature. It is worthwhile to consider the various ways in which the present results can be generalized to apply to specific materials of interest.

While the numerical examples for the TSCA cited in Table I and in the figures treated the special case of nearest-neighbor exchange, this was done for illustrative purposes and to give comparison with the results of other approximations. Both the RPA and TSCA in the pseudospin formalism, as presented in Secs. 3 and 4, respectively, are applicable to exchange of any range. In this respect they represent an improvement over the constant-coupling approximation for evaluating A_{crit}. While the constant-coupling treatment can be extended to farther than nearest-neighbor exchange, the treatment becomes quite involved even when the only addition is second nearest-neighbor exchange.

The treatment of collective excitations with the pseudospin formalism can also be extended in a straightforward fashion to the magnetically ordered regime, or to the paramagnetic regime when an applied magnetic field is present. This involves treating the complete Hamiltonian of (3.1) rather than the reduced Hamiltonian of (3.8). Since the transition to magnetic ordering at $T=0$ as exchange increases is second-order, the value of A_{crit} (the ratio of exchange to crystal-field interaction necessary for magnetic ordering) is the same whether calculated, as here, for the paramagnetic regime going into the ordered regime, or vice versa. For the magnetically ordered case, the present techniques can also be used to study the behavior near the ordering temperature. The results for the applied field and magnetically ordered cases will be presented in a future publication.

The pseudospin formalism can also be extended to treat cases where the excited state is not a singlet; for instance, the rare-earth group-V compounds of NaCl structure where the first excited state is a triplet. When the excited state is a triplet, the pseudospin takes the value $\frac{3}{2}$, and the spin Hamiltonian is more complicated than that of (3.1). Besides the angular-momentum matrix element α linking the singlet ground state to the excited triplet state, there is a second, independent, angular-momentum matrix element linking the states of the triplet.[4] Also, the treatment of anisotropic exchange becomes more complicated than in the singlet-singlet case. This is because one no longer can use the fact stated at the beginning of Sec. 3, that in the singlet-singlet case one can always choose a z axis such that the matrix elements of J_x and J_y vanish.

It is, of course, possible that in a real crystal there is in addition to magnetic ordering a lattice distortion as exchange increases. In the present paper, we have calculated the critical value necessary for magnetic ordering of the *ratio* of the exchange to the crystal-field interaction. Therefore, we could allow the crystal-field splitting Δ to change at the same time as the exchange. For a more involved situation than the two-singlet-level problem treated herein, a change of symmetry (say cubic to some lower symmetry) associated with distortion could introduce a further complication.

With actual physical systems, one will sometimes desire to treat excited states beyond the first excited state. For example, the anisotropic magnetization[13–15] for rare-earth compounds of NaCl structure with group-V elements arises from the effect of excited states above the first triplet.[4] In practice, one can probably use a hybrid approximation to treat the states lying above the first excited state. The critical value of exchange for magnetic ordering is basically determined by the mixing of the first excited state into the singlet ground state. Therefore, one can treat the effect of the higher excited states more approximately than that of the first excited state. One could treat the first excited state in the TSCA, but use an RPA or molecular-field approximation to treat the effect of higher-lying states.

Before discussing some compounds with singlet ground states where experiments can be performed showing the effects treated herein, we should point out that even when the crystal-field ground state for a magnetic ion is not a singlet, the crystal field can profoundly effect the magnetic ordering process. For example, the ordering temperatures and ordered moment of Er compounds of NaCl structure with group-V elements are considerably lowered by crystal-field effects.[1,2,16] The present pseudospin formalism could be extended to dealing with the ground-state degenerate manifold, and if necessary to also include the first-excited-state manifold, for such a compound.

The most extensively studied compounds involving magnetic ordering in systems with crystal-field singlet ground state are the rare-earth compounds of NaCl structure with group-V elements.[1,2,16–19] (The behavior of the rare-earth compounds of NaCl structure with group-VI anions is probably basically the same,[20] although not so extensively studied.) The Tb compounds of this type order, even though Tb^{3+} with $J=6$ has a crystal-field-only singlet ground state. Therefore, the value of exchange is presumably greater than that necessary for magnetic ordering. As pointed out by Cooper,[4] it is feasible to substitute Y for Tb in the compounds. Since Y^{3+} is nonmagnetic (unoccupied $4f$ shell), this would enable one to reduce the exchange below the critical value necessary for magnetic ordering. Then one could observe the critical effects described in the present paper. As pointed out in the discussion of the constant-coupling calculation in Sec. 4, we might expect the percentage increase over the molecular-field value of the critical value of $\mathcal{J}(0)$ to be correspondingly greater for the singlet-triplet case than for the singlet-singlet case in the TSCA.

Such mixed Tb–Y compound experiments are not as desirable as the ideal situation where one homogeneously varied the exchange at each rare-earth site; however, the results of neutron inelastic scattering experiments[9] on Tb–10%-Ho alloys hold out hope for a reasonably straightforward situation. In those experiments Møller *et al.* observed a well-defined dispersion curve for the spin waves. Superposed on this, and well localized in $\mathbf{k}$ space, was an anomaly attributed to a localized excitation.

Besides being useful for dealing with magnetic properties near the critical value of exchange, the present pseudospin theory, and its extension to the applied field and magnetically ordered situations, is also useful for dealing with crystal-field singlet-ground-state systems with significant exchange effects, but where the exchange is not in the immediate vicinity of the critical value. For such systems, the RPA treatment of Sec. 3 gives a better generalization to finite temperatures than the Bogoliubov-type approximation for treating the behavior of collective excitations and the related thermodynamic and transport properties. (For exchange appreciably different from the critical value, the calculated excitation spectra for the RPA and TSCA approach each other. It is then easier to use the simpler RPA rather than the TSCA in the calculations.) An example, besides the compounds already mentioned, of a material for which such a treatment could be valuable is UF_4. For UF_4, Leask *et al.*[21] have shown that the most promising explanation for their susceptibility measurements and the specific-heat measurements of Burns *et al.*[22] is that the U^{+4} ions have an f^2 configuration with singlet crystal-field ground state. While UF_4 is paramagnetic, Leask *et al.* present evidence for significant exchange interaction between the U^{+4} ions. The situa-

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tion for UF_4 is more complicated than that treated in this paper, since there is more than one type of uranium site. Nevertheless, the formalism presented herein should serve as a basis for understanding collective-excitation behavior and thermodynamic properties for such compounds. The prospects for a study of the collective excitations in UF_4 is particularly promising since large single crystals can be grown, and the neutron absorption properties are quite reasonable for inelastic scattering experiments.[23]

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APPENDIX A

The quantities $\langle S_z\rangle$ and ϵ in Eqs. (4.12) and (4.14) are calculated self-consistently at zero temperature in this Appendix. Also, we show how the calculation is readily generalized to finite temperature using the Green's-function formalism.

The inverse transformation to (4.11) gives

$$S^+(\mathbf{k})=\cosh\beta_k\mathcal{S}^+(\mathbf{k})+\sinh\beta_k\mathcal{S}^-(-\mathbf{k}),\qquad\text{(A1)}$$

$$S^-(\mathbf{k})=\cosh\beta_k\mathcal{S}^-(\mathbf{k})+\sinh\beta_k\mathcal{S}^+(-\mathbf{k}).\qquad\text{(A2)}$$

At zero temperature, the statistical averages reduce to expectation values over the true ground state, $|\Phi_0\rangle$, which is defined as

$$\mathcal{S}^-(\mathbf{k})\,|\,\Phi_0\rangle=0\qquad\text{(A3)}$$

for all **k**.

It is convenient to write $\langle S_z\rangle$ in terms of δ defined in (3.26):

$$\langle S_z\rangle\equiv-\tfrac{1}{2}+\delta.\qquad\text{(A4)}$$

Therefore,

$$\delta=\langle\Phi_0\,|\,S^+S^-\,|\,\Phi_0\rangle$$
$$=(1/N)\sum_k\langle\Phi_0\,|\,S^+(\mathbf{k})S^-(\mathbf{k})\,|\,\Phi_0\rangle.\qquad\text{(A5)}$$

In terms of the generating operators for elementary excitations we have

$$\delta=(1/N)\sum_k\sinh^2\beta_k\langle\Phi_0\,|\,\mathcal{S}^-(-\mathbf{k})\mathcal{S}^+(-\mathbf{k})\,|\,\Phi_0\rangle\qquad\text{(A6)}$$

or

$$\delta=(1-2\delta)(1/N)\sum_k\sinh^2\beta_k,\qquad\text{(A7)}$$

since

$$\langle\Phi_0\,|\,\mathcal{S}^-(-\mathbf{k})\mathcal{S}^+(-\mathbf{k})\,|\,\Phi_0\rangle$$
$$=-2\langle\Phi_0\,|\,S_z(0)\,|\,\Phi_0\rangle$$
$$+\langle\Phi_0\,|\,\mathcal{S}^+(-\mathbf{k})\mathcal{S}^-(-\mathbf{k})\,|\,\Phi_0\rangle=1-2\delta.\qquad\text{(A8)}$$

Next we evaluate the summation appearing in (A7).

$$(1/N)\sum_k\sinh^2\beta_k=(1/2N)\sum_k(\cosh2\beta_k-1)$$
$$=1/2N\sum_k[(1-\tanh^22\beta_k)^{-1/2}]-\tfrac{1}{2}\qquad\text{(A9)}$$

and using Eq. (4.13)

$$(1/N)\sum_k\sinh^2\beta_k$$
$$=(1/2N)\sum_k\frac{2-(1-2\delta)(\gamma_k-2\epsilon)A}{2[1-(1-2\delta)(\gamma_k-2\epsilon)A]^{1/2}}-\tfrac{1}{2}.\qquad\text{(A10)}$$

Then δ depends on A, the ratio of exchange interaction to crystal-field splitting. For convenience of calculation, we define another variable λ such that

$$A\equiv\lambda/(1-2\delta)(1-2\lambda\epsilon),\qquad\lambda\leq1.\qquad\text{(A11)}$$

(At the critical point $A_{\text{crit}}=1/[(1-2\delta)(1-2\epsilon)]$ and $\lambda=1$.) It should be noted that δ and ϵ are evaluated self-consistently and therefore depend on λ.

By inserting (A10) and (A11) into (A7) we obtain

$$\delta/(1-2\delta)=\tfrac{1}{4}(\Lambda_\lambda a_\lambda)+(b_\lambda/4\Lambda_\lambda)-\tfrac{1}{2},\qquad\text{(A12)}$$

where

$$\Lambda_\lambda=(1-2\lambda\epsilon)^{1/2},\qquad\text{(A13)}$$

$$a_\lambda=(1/N)\sum_k(1-\lambda\gamma_k)^{-1/2},\qquad\text{(A14)}$$

$$b_\lambda=(1/N)\sum_k(1-\lambda\gamma_k)^{1/2}.\qquad\text{(A15)}$$

Equation (A12) provides one relationship between δ and ϵ. Another such relationship can be obtained from the definition of ϵ.

$$\epsilon\equiv(1/N)\sum_k\gamma_k(\langle S^+(\mathbf{k})S^-(\mathbf{k})\rangle+\langle S^+(\mathbf{k})S^+(-k)\rangle).\qquad\text{(A16)}$$

Using (A1) and (A2) with (A3) and (4.13), it is easy to show that

$$(1/N)\sum_k\gamma_k\langle S^+(\mathbf{k})S^-(\mathbf{k})\rangle$$
$$=(1-2\delta)[\tfrac{1}{4}\Lambda_\lambda c_\lambda+(d_\lambda/4\Lambda_k)],\qquad\text{(A17)}$$

$$(1/N)\sum_k\gamma_k\langle S^+(\mathbf{k})S^+(-\mathbf{k})\rangle$$
$$=(1-2\delta)[\tfrac{1}{4}\Lambda_\lambda c_\lambda-(d_\lambda/4\Lambda_\lambda)],\qquad\text{(A18)}$$

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[23] We are grateful to Professor W. P. Wolf for his comments on UF_4.

where

$$c_\lambda=(1/N)\sum_k\left[\gamma_k/(1-\lambda\gamma_k)^{1/2}\right]=(1/\lambda)(a_\lambda-b_\lambda),\quad\text{(A19)}$$

$$d_\lambda=(1/N)\sum_k\gamma_k(1-\lambda\gamma_k)^{1/2}.\quad\text{(A20)}$$

Therefore,

$$2\epsilon=(1-2\delta)\Lambda_\lambda c_\lambda.\quad\text{(A21)}$$

Thus, for specified λ, Eqs. (A12) and (A21) give two equations that can be solved for δ and ϵ. Once δ and ϵ are known, one obtains the corresponding A from (A11). (We remember that $\lambda=1$ for A_{crit}.)

The quantity ϵ enters (A21) both explicitly and through the function Λ_λ. Algebraically, it is convenient to eliminate ϵ from (A21) with the help of (A13).

$$\Lambda_\lambda^2=1-2\lambda\epsilon=1-(1-2\delta)\Lambda_\lambda\lambda c_\lambda.\quad\text{(A22)}$$

It is also convenient to define ζ:

$$\zeta=1-2\delta.\quad\text{(A23)}$$

Then we can rewrite Eqs. (A12) and (A22) as

$$a_\lambda\Lambda_\lambda^2-(2/\zeta)\Lambda_\lambda+b_\lambda=0,\quad\text{(A24)}$$

$$\Lambda_\lambda^2+\zeta(a_\lambda-b_\lambda)\Lambda_\lambda-1=0.\quad\text{(A25)}$$

Assigning a value of $\lambda\leq1$, we then compute a_λ and b_λ, and solve Eqs. (A24) and (A25) for the value of Λ_λ and of ζ. Once Λ_λ and ζ are known, (A23) and (A13) give δ and ϵ for the specified λ.

In the procedure just described, a_λ and b_λ are calculated by resumming the leading 40 terms in the series expansion of Eqs. (A14) and (A15). For example,

$$a_\lambda=(1/N)\sum_k\left\{1+\tfrac{1}{2}(\lambda\gamma_k)+\frac{1\times3}{2\times4}(\lambda\gamma_k)^2+\frac{1\times3\times5}{2\times4\times6}(\lambda\gamma_k)^3+\frac{1\times3\times5\times7}{2\times4\times6\times8}(\lambda\gamma_k)^4+\cdots\right\}\quad\text{(A26)}$$

and[24]

$$1/N\sum_k\gamma_k^{2n}=3^{-2n}2^{-2n}\binom{2n}{n}\sum_{p,q=0}^{n}\binom{n}{q}^2\binom{q}{p}^2\quad\text{(A27)}$$

for the simple cubic lattice.

$$(1/N)\sum_k\gamma_k^{2n}=\left[2^{-2n}\binom{2n}{n}\right]^3\quad\text{(A28)}$$

for the body-centered-cubic lattice. Here, the odd-order terms in (A26) obviously vanish for both lattices.

At the critical point, $\lambda=1$. For a simple cubic lattice and a body-centered-cubic lattice we obtain

Simple cubic	Body-centered cubic
$a_1=1.111$	1.084
$b_1=0.975$	0.981
$2\delta=0.039$	0.028
$2\epsilon=0.122$	0.095
$A_{\text{crit}}=1.18$	1.14

It is interesting to point out that there is an internal self-consistent check of the calculations for a two-level problem. This is to see how well the kinematic constraint

$$(S^+)^2=(S^-)^2=0\quad\text{(A29)}$$

for such a system is obeyed. In general, it is difficult to properly treat kinematic restrictions in approximating the behavior of interacting spin systems. Typically, these restrictions are not obeyed, and some unphysical states are included in the description of the behavior. It is, therefore, interesting to calculate $\langle(S^+)^2\rangle$ or $\langle(S^-)^2\rangle$ at the critical point where such kinematic effects are most important.

$$\langle(S^+)^2\rangle=(1/N)\sum_k\langle S^+(\mathbf{k})S^+(-\mathbf{k})\rangle=\tfrac{1}{4}\Lambda_1a_1-(1/4\Lambda_1)b_1.\quad\text{(A30)}$$

The present calculation (TSCA) gives a number of the order 10^{-3} for $\langle(S^+)^2\rangle$, while the Bogoliubov-type calculation or the RPA would give 10^{-1}. This is evidence that the kinematic restrictions are very well accounted for in the TSCA.

Green's-Function Treatment for Finite Temperature

The finite-temperature calculations are more easily carried out in the Green's-function formalism. Here, we shall only outline the procedures, since the calculation parallels what we have already done.

We define two types of Green's functions:

$$G^-(g,l)=-i\langle[S^-_g(t),S_l^+(0)]\rangle\theta(t)\equiv\langle\langle S_g^-(t);S_l^+(0)\rangle\rangle,\quad\text{(A31)}$$

$$G^+(g,l)=-i\langle[S_g^+(t),S_l^+(0)]\rangle\theta(t)\equiv\langle\langle S_g^+(t);S_l^+(0)\rangle\rangle,\quad\text{(A32)}$$

where the canonical thermal average is indicated by the single angular brackets. The equation of motion of the Green's function is best described in the energy Fourier space:

$$EG_E^-(g,l)=(1/2\pi)\langle[S_g^-,S_l^+]\rangle+\langle\langle[S_g^-(t),\mathcal{H}];S_l^+(0)\rangle\rangle_E,\quad\text{(A33)}$$

$$EG_E^+(g,l)=(1/2\pi)\langle[S_g^+,S_l^+]\rangle+\langle\langle[S_g^+(t),\mathcal{H}];S_l^+(0)\rangle\rangle_E.\quad\text{(A34)}$$

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[24] R. Kubo, Phys. Rev. **87**, 568 (1952). [The final equality in Eq. (4.9) of Kubo's paper is incorrect. However, the present Eq. (A27) follows from the next to final equality in Eq. (4.9) of Kubo.]

The subscripts E indicate the Fourier components of the functions. The commutators $[S_g^{\pm}, \mathcal{H}]$ have been given in Eqs. (3.9) and (3.10). To linearize the equations, we choose Callen's decoupling[12]:

$$\langle\langle S_{gz}S_f^-;\, S_l^+\rangle\rangle \xrightarrow[g\neq f]{} \langle S_z\rangle[G_E^-(f,l)-2\langle S_g^+S_f^-\rangle G_E^-(g,l) -2\langle S_g^-S_f^-\rangle G_E^+(g,l)]. \quad \text{(A35)}$$

Similarly,

$$\langle\langle S_{gz}S_f^+;\, S_l^+\rangle\rangle \xrightarrow[g\neq f]{} \langle S_z\rangle[G_E^+(f,l)-2\langle S_g^-S_f^+\rangle G_E^+(g,l) -2\langle S_g^+S_f^+\rangle G_E^-(g,l)]. \quad \text{(A36)}$$

After performing a spatial Fourier transformation, the coupled equations are solved.

$$G_E^-(k)=-\frac{\langle S_z\rangle}{2\pi E_k}\left(\frac{E_k+\Delta+\xi}{E-E_k}+\frac{E_k-\Delta-\xi}{E+E_k}\right), \quad \text{(A37)}$$

$$G_E^+(k)=\frac{\langle S_z\rangle\xi}{2\pi E_k}[(E-E_k)^{-1}-(E+E_k)^{-1}], \quad \text{(A38)}$$

where

$$\xi=4\mathcal{J}(0)\alpha^2\langle S_z\rangle(\gamma_k-2\epsilon) \quad \text{(A39)}$$

and

$$E_k=\Delta[1+2\langle S_z\rangle A(\gamma_k-2\epsilon)]^{1/2}. \quad \text{(A40)}$$

The equal-time correlation functions are obtained from the Green's functions[25]

$$\langle S_k^+S_k^-\rangle=\lim_{\nu\to 0} i\int_{-\infty}^{\infty}\frac{G_{E+i\nu}^- - G_{E-i\nu}^-}{\exp(E/k_BT)-1}dE, \quad \text{(A41)}$$

$$\langle S_k^+S_k^-\rangle = -\frac{\langle S_z\rangle}{E_k}\left(\frac{E_k+\Delta+\xi}{\exp(E_k/k_BT)-1}+\frac{E_k-\Delta-\xi}{\exp(-E_k/k_BT)-1}\right). \quad \text{(A42)}$$

Similarly,

$$\langle S_k^+S_{-k}^+\rangle=-\frac{\langle S_z\rangle\xi}{E_k}\left[-\frac{1}{\exp(E_k/k_BT)-1}+\frac{1}{\exp(-E_k/k_BT)-1}\right]. \quad \text{(A43)}$$

As $T\to 0$, Eqs. (A42) and (A43) reduce to the previous results given in the first part of this Appendix. At finite temperatures δ and ϵ can be determined numerically, and the critical value A_{crit} is temperature-dependent through the quantities δ and ϵ.

APPENDIX B

In this Appendix we summarize the calculation of A_{crit} for the two-singlet-level problem in the constant-coupling approximation. This calculation follows that of Cooper,[4] but the details are somewhat different, since Cooper treated the singlet-triplet problem.

We first consider a single-ion Hamiltonian where the exchange effects of each of the z neighbors are incorporated in an effective field H'.

$$\mathcal{H}_1=V_c-g\mu_B zH'J_z. \quad \text{(B1)}$$

Here g is the Lande factor, and μ_B is the Bohr magneton. We can find a magnetization per ion for this Hamiltonian, and this magnetization $\bar{M}_1$ will be a function of zH'. Next we consider a two-ion Hamiltonian for ions a and b, where the exchange effects of all other neighbors are given by the same effective field H'.

$$\mathcal{H}_2=V_{ca}+V_{cb}-g\mu_B(z-1)H'(J_{za}+J_{zb})-2\mathcal{J}\mathbf{J}_a\cdot\mathbf{J}_b. \quad \text{(B2)}$$

Again, we can find a magnetization per ion, $\bar{M}_2$, which for the two-ion Hamiltonian is a function of $(z-1)H'$. Then the condition

$$\bar{M}_1(zH')=\bar{M}_2((z-1)H') \quad \text{(B3)}$$

self-consistently determines the effective field H' and hence the magnetization.

To find the critical value of A, where A is defined in the nearest-neighbor exchange case as

$$A\equiv 4z\mathcal{J}\alpha^2/\Delta, \quad \text{(B4)}$$

we consider the condition (B3) at zero temperature when the ordered moment, and consequently the effective field H', is infinitesimal. Then by regarding the effective field term in (B1) as a perturbation, we find

$$\bar{M}_1=2g^2\mu_B^2H'z\alpha^2/\Delta, \quad \text{(B5)}$$

where α is the off-diagonal matrix element of J_z between the crystal-field-only states $|0_c\rangle$ and $|1_c\rangle$, and Δ is the energy splitting between those states.

To find $\bar{M}_2$, we similarly regard the effective-field term in $\mathcal{H}_2$ as a perturbation. Then we have

$$\mathcal{H}_2=\mathcal{H}_{20}+\mathcal{H}_2', \quad \text{(B6)}$$

with

$$\mathcal{H}_{20}=V_{ca}+V_{cb}-2\mathcal{J}\mathbf{J}_a\cdot\mathbf{J}_b, \quad \text{(B7)}$$

$$\mathcal{H}_2'=-g\mu_B(z-1)H'(J_{za}+J_{zb}). \quad \text{(B8)}$$

The ground state of the two-ion Hamiltonian $\mathcal{H}_{20}$ is

$$|g_0\rangle=\cos\theta_1|0_c,0_c\rangle+\sin\theta_1|1_c,1_c\rangle, \quad \text{(B9)}$$

with energy

$$E_{g0}=\Delta-(\Delta^2+4\mathcal{J}^2\alpha^4)^{1/2}, \quad \text{(B10)}$$

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[25] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

where

$$\tan\theta_1 = -E_{g0}/2\mathcal{J}\alpha^2. \tag{B11}$$

$\mathcal{H}_2'$ mixes $|g_0\rangle$ with only one of the three excited two-ion states of $\mathcal{H}_{20}$, viz.,

$$|e_0\rangle = (1/\sqrt{2})(|0_c, 1_c\rangle + |1_c, 0_c\rangle), \tag{B12}$$

which has energy

$$E_{e0} = \Delta[1-2(\mathcal{J}/\Delta)\alpha^2]. \tag{B13}$$

Treating the mixing of $|e_0\rangle$ into $|g_0\rangle$ by perturbation theory gives

$$\bar{M}_2 = \frac{2g^2\mu_B^2H'(z-1)\alpha^2}{E_{e0}-E_{g0}}(1+\sin2\theta_1). \tag{B14}$$

Then using (B4) and (B14) in (B3) gives the critical condition for magnetic ordering to occur with infinitesimal moment at zero temperature.

$$\frac{z}{z-1} = \frac{1+\sin2\theta_1}{[1+(A/2z)^2]^{1/2}-A/2z}, \tag{B15}$$

with

$$\tan\theta_1 = -2z\{1-[1+(A/2z)^2]^{1/2}\}/A. \tag{B16}$$

We have the result that for given z in the constant-coupling approximation (B15) and (B16) are a set of transcendental equations determining the critical value of A and the value of θ_1 when A has this critical value. The values of A_{crit} shown in Table I were obtained by numerical solution of this set of equations.

It is interesting to note that the percentage increase in the critical value of $\mathcal{J}(0)/\Delta$ necessary for magnetic ordering on going from the molecular-field approximation to the constant-coupling approximation is much smaller for the two-singlet-level problem than in the case where the excited state is a triplet.[4] (For example, with $z=6$, the critical value increases by 12% for the singlet-singlet and by 23% for the singlet-triplet case.) This occurs because the excited state of $\mathcal{H}_{20}$ mixed into the ground state by $\mathcal{H}_2'$ has a much stronger mixing with the ground state in the singlet-triplet case.

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Atomic Displacement Relationship to Curie Temperature and Spontaneous Polarization in Displacive Ferroelectrics

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The phase transition from nonpolar to polar in displacive ferroelectric crystals is accompanied by the displacement Δz of certain atoms from their higher-temperature symmetry positions. A study of all displacive ferroelectrics in which atomic positions have been determined has shown that a fundamental relationship exists between Δz and the Curie temperature T_C. This relation has the form $T_C = (\mathcal{K}/2k)(\Delta z)^2$, where $\mathcal{K}$ has the dimensions of a force constant, k is Boltzmann's constant, and T_C is in absolute units. A least-squares fit, based on Δz and T_C for ten different ferroelectrics, gives $\mathcal{K}/2k = (2.00\pm0.09)\times10^4$ °K Å^{-2}. In addition, the spontaneous polarization P_s is found to be related to Δz by the equation $P_s = (258\pm9)\Delta z\,\mu$C cm^{-2}. $\mathcal{K}$ is discussed in terms of the interatomic force constant along the polar axis.

The phase transition from nonpolar to polar in displacive ferroelectric crystals is accompanied by the displacement of certain atoms from their higher-temperature symmetry positions. Until recently, very few reliable determinations of the detailed atomic arrangement in displacive ferroelectrics have been available,[1] making comparisons with ferroelectric theories inconclusive. In this article, we report for the first time a simple experimental relationship between atomic displacement and the macroscopic ferroelectric properties of Curie temperature and spontaneous polarization, valid over a wide range of materials. From simple physical considerations, it is shown that this experimental relationship may be interpreted as an equivalence between the lattice vibrational energy and the displacive energy of the ferroelectric state.

We define Δz as the displacement developed by the "homopolar" metal atom, as listed in Table I, along the polar direction at $T \ll T_C$. The values of atomic displacement Δz, Curie temperature T_C, and spontaneous polarization P_s for a group of twelve compounds are given in Table I, together with their estimated standard deviations. We derive Δz for one material as an illustrative example. In the case of $LiNbO_3$ above T_C, the oxygen atoms most probably[2] are arranged in planes with $z=\frac{1}{12}(2n+1)$, where n is integral. The homopolar Nb atom is at $z=0$, the position with point symmetry $\bar{3}$. At $T \ll T_C$, the oxygen framework may be

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[1] F. Jona and G. Shirane, *Ferroelectric Crystals* (The McMillan Company, New York, 1962).

[2] S. C. Abrahams, H. J. Levinstein, and J. M. Reddy, J. Phys. Chem. Solids **27**, 1019 (1966).