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Possibility of Multipolar Ordering in the Exchange-Interaction Model of Ferromagnetism

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It is shown that for the spin- S exchange-interaction model of ferromagnetism the 2S-"independent" multipolar (4S-polar) phase transitions are in fact exactly degenerate with the usual dipolar transition.

The Heisenberg Hamiltonian linear in $\vec{S}_f \cdot \vec{S}_g$ which forms the point of departure for most modern theories of magnetism is in fact only the lowest-order significant term in a perturbation expansion¹ which when carried further leads to terms non-linear in $\vec{S}_f \cdot \vec{S}_g$. Because of the presence of these (small?) nonlinear terms in $\vec{S}_f \cdot \vec{S}_g$ for systems of spin $S > \frac{1}{2}$, there exists the possibility of phase transitions associated with the various multipole moments of the system^{3, 4} in addition to the one usually associated with its dipole moment. There is as yet no rigorous statistical mechanical calculation which goes very far in taking such terms into account.⁵ Recently, however, the Schrödinger exchange operator⁶ which is an essentially non-linear operator in $\vec{S}_f \cdot \vec{S}_g$ (for $S > \frac{1}{2}$) has been used to form an exchange-interaction model of ferromagnetism.^{7, 8} The coefficients of the terms in $(\vec{S}_f \cdot \vec{S}_g)^n$ ($1 \leq n \leq 2S$) are chosen such that this operator permutes the spin coordinates of atoms labeled f and g . For the case $S=1$, the coefficients of the terms linear and quadratic in $\vec{S}_f \cdot \vec{S}_g$ have equal magnitude. A large number of terms in the high-temperature expansion of various thermodynamic quantities have been obtained by the use of group-theoretic techniques.⁹ While these combinations of nonlinear terms may not be realized in nature, considerable insight into the effect of nonlinear terms in the Hamiltonian on critical prop-

erties has been obtained.¹⁰ For this model, the critical index γ which characterizes the divergence of the (dipolar) susceptibility is quite different from that of any other model (for $S > \frac{1}{2}$). Furthermore, it appears that experimental¹¹ values of γ are bracketed from below by those of the exchange model¹⁰ and from above by those predicted for the Heisenberg model.¹² The purpose of the present paper is to show that for this model all of the 2S-independent multipolar (4S-polar) transitions are in fact *exactly* degenerate with the dipolar transition. This means that considerable care must be exercised in the interpretation of proposed experimental attempts to observe such transitions. For the case $S=1$, a null result in attempts to resolve dipolar and quadrupolar ordering effects could equally well be used as evidence for the fact that the ratio of biquadratic to bilinear terms in the Hamiltonian is very small, or quite close to unity.

The Hamiltonian for the exchange-interaction model of ferromagnetism is

$$\vec{\mathcal{H}} = -J\vec{\mathcal{O}} - mH\vec{Q} = \vec{\mathcal{H}}_0 - mH\vec{Q}, \quad (1)$$

where

$$\vec{\mathcal{O}} = \sum_{\langle f, g \rangle} \vec{P}_{fg}, \quad \vec{Q} = \sum_{f=1}^N \vec{S}_{zf}, \quad (2)$$

and J is the magnitude of a nearest-neighbor exchange interaction, \vec{P}_{fg} is the Schrödinger exchange

operator, $^6 H$ is an external magnetic field, N is the number of spins in the system, and $m = g\mu_B$, with g the gyromagnetic ratio and μ_B the Bohr magneton. The low-field susceptibility is given by

$$\chi = \lim_{H \rightarrow 0} \beta^{-1} \frac{\partial^2}{\partial H^2} \ln \text{tr} e^{-\beta \mathcal{H}} = m^2 \beta \Delta(\vec{Q}), \quad (3)$$

where

$$\beta = (k_B T)^{-1}, \quad \text{and} \quad \Delta(\vec{Q}) = \langle \vec{Q}^2 \rangle_\beta - \langle \vec{Q} \rangle_\beta^2 \quad (4)$$

is the zero-field thermal fluctuation of \vec{Q} with

$$\langle \vec{Q} \rangle_\beta = \text{tr} \vec{Q} e^{-\beta \mathcal{H}_0} / \text{tr} e^{-\beta \mathcal{H}_0}. \quad (5)$$

k_B is the Boltzmann constant and T is the thermodynamic temperature. As $T \rightarrow T_c^*$, the susceptibility $\chi \rightarrow \infty$, and hence $\Delta(\vec{Q}) \rightarrow \infty$.

As previously mentioned, for systems with spin $S > \frac{1}{2}$, there are other kinds of order parameters besides \vec{Q} with which phase transitions might be associated. In order to study the possibility of such transitions, we consider first the following modified Hamiltonian:

$$\vec{\mathcal{H}}_n = \vec{\mathcal{H}}_0 - \xi \vec{Q}_n, \quad (6)$$

where

$$\vec{Q}_n = \sum_{f=1}^N \vec{S}_{zf}^n, \quad n = 1, 2, \dots, 2S \quad (7)$$

and ξ is some (fictitious) external field. We define a generalized susceptibility χ_n by

$$\chi_n = \lim_{\xi \rightarrow 0} \beta^{-1} \frac{\partial^2}{\partial \xi^2} \ln \text{tr} e^{-\beta \vec{\mathcal{H}}_n}. \quad (8)$$

By definition $\chi_1 \sim \chi$. Since $\vec{\mathcal{O}}$ and \vec{Q}_n commute, as did $\vec{\mathcal{O}}$ and \vec{Q} , we have

$$\chi_n = \beta \Delta(\vec{Q}_n). \quad (9)$$

We are then able to prove that

$$\chi_n / \chi_1 = D_n(S), \quad (10)$$

where $D_n(S)$ is a quantity which is independent of both *lattice* and *temperature*. This means then that for a given lattice, all of the $\chi_n \rightarrow \infty$ at the same temperature T_c in exactly the same way.

Since the (dipolar) susceptibility, Eq. (3), can also be written in the form

$$\chi = \frac{1}{3} m^2 \beta \sum_{f,g} \langle \vec{S}_f \cdot \vec{S}_g \rangle_\beta, \quad (11)$$

it is really necessary to investigate quantities of the form $\sum_{f,g} \langle (\vec{S}_f \cdot \vec{S}_g)^n \rangle_\beta$ for $1 \leq n \leq 2S$. However, for both computational and theoretical reasons, we have restricted our attention to the single quantity $\sum_{f,g} \langle \vec{P}_{fg} \rangle_\beta$. We are then able to prove that

$$\sum_{f,g}' \langle \vec{P}_{fg} - (1/Y) \vec{1} \rangle_\beta = (4/Y) \sum_{f,g}' \langle \vec{S}_f \cdot \vec{S}_g \rangle_\beta. \quad (12)$$

Here $Y = 2S + 1$, and $\vec{1}$ is the identity operator. The primes in the double sums over f and g mean that terms for which $f = g$ are to be excluded. Since $\langle \vec{S}_f^2 \rangle_\beta = S(S+1) = X$, it immediately follows from this result and Eq. (11) that the left-hand side of Eq. (12) diverges at the same T_c as χ in exactly the same way.

Since both χ_n and $\sum_{f,g}' \langle \vec{P}_{fg} - (1/Y) \vec{1} \rangle_\beta$ are extensive quantities, it follows from the cluster-expansion method¹³ that we need only prove Eqs. (10) and (12) for all finite clusters. Let us define a quantity $W_n(S)$ by¹⁴

$$W_n(S) = Y^{-1} \sum_{m=-S}^S m^n. \quad (13)$$

We now prove the following two theorems.

Theorem I. Let f and g be any two sites in a finite cluster of N sites. Then

$$\langle \vec{S}_{zf}^n \vec{S}_{zg}^n \rangle_\beta - \langle \vec{S}_{zf}^n \rangle_\beta \langle \vec{S}_{zg}^n \rangle_\beta = (W_{2n} - W_n^2) X^{-1} \langle \vec{S}_f \cdot \vec{S}_g \rangle_\beta. \quad (14)$$

Proof. It is shown in the Appendix that for any element \vec{P} of the symmetric group G of degree N

$$\text{tr} \vec{S}_{zf}^n \vec{P} = W_n \text{tr} \vec{P}, \quad f \leq N. \quad (15)$$

It is then straightforward to show that

$$\langle \vec{S}_{zf}^n \rangle_\beta = W_n. \quad (16)$$

Hence

$$\begin{aligned} \langle \vec{S}_{zf}^n \vec{S}_{zg}^n \rangle_\beta - \langle \vec{S}_{zf}^n \rangle_\beta \langle \vec{S}_{zg}^n \rangle_\beta \\ = \sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} (\vec{S}_{zf}^n \vec{S}_{zg}^n \vec{\mathcal{O}}^r - W_n^2 \vec{\mathcal{O}}^r) / \sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} \vec{\mathcal{O}}^r, \end{aligned} \quad (17)$$

with $K = \beta J$. It is also shown in the Appendix that for $f, g \leq N$ and $\vec{P} \in G$,

$$\begin{aligned} \text{tr} \vec{S}_{zf}^n \vec{S}_{zg}^n \vec{P} &= W_{2n} \text{tr} \vec{P} \quad \text{if } f=g \text{ or } f, g \text{ belong to the} \\ &\quad \text{same cycle in } \vec{P} \\ &= W_n^2 \text{tr} \vec{P} \quad \text{if } f, g \text{ belong to different} \\ &\quad \text{independent cycles in } \vec{P}. \end{aligned} \quad (18)$$

If the finite cluster of N sites contains l_c nearest-neighbor pairs, there are nl_c terms in $\vec{\mathcal{O}}^r$. Each term is the multiplication of r group elements \vec{P}_{fg} and hence is also an element in G . Denote the sum of terms with f, g in the same cycle by $\vec{\mathcal{O}}_r^{(1)}$ and the sum of terms with f, g in different independent cycles by $\vec{\mathcal{O}}_r^{(2)}$:

$$\vec{\mathcal{O}}^r = \vec{\mathcal{O}}_r^{(1)} + \vec{\mathcal{O}}_r^{(2)}. \quad (19)$$

It then follows from Eq. (18) that for any r in Eq. (17)

$$\text{tr} \vec{S}_{zf}^n \vec{S}_{zg}^n \vec{\mathcal{O}}^r - W_n^2 \text{tr} \vec{\mathcal{O}}^r = (W_{2n} - W_n^2) \text{tr} \vec{\mathcal{O}}_r^{(1)}. \quad (20)$$

Hence

$$\begin{aligned} & \langle \vec{S}_{xf} \vec{S}_{zg} \rangle_\beta - \langle \vec{S}_{xf} \rangle_\beta \langle \vec{S}_{zg} \rangle_\beta \\ &= (W_{2n} - W_n^2) \sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} \vec{\Phi}_r^{(1)} \left/ \sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} \vec{\Phi}_r \right. . \quad (21) \end{aligned}$$

For $n=1$, $\langle \vec{S}_{xf} \rangle_\beta = W_1 = 0$, $W_2 = \frac{1}{3}X$, and

$$\begin{aligned} & \langle \vec{S}_f \cdot \vec{S}_g \rangle_\beta = 3 \langle \vec{S}_{xf} \vec{S}_{zg} \rangle_\beta \\ &= X \left(\sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} \vec{\Phi}_r^{(1)} \right) \left/ \sum_{r=0}^{\infty} \frac{K^r}{r!} \text{tr} \vec{\Phi}_r \right., \quad (22) \end{aligned}$$

Comparison of Eqs. (21) and (22) immediately yields the statement of Theorem I, Eq. (14).

Theorem II. Let f and g be two different sites in a finite cluster of N sites. Then

$$\langle \vec{P}_{fg} - (1/Y) \vec{1} \rangle_\beta = (4/Y) \langle \vec{S}_f \cdot \vec{S}_g \rangle_\beta . \quad (23)$$

Proof. From a consideration of Eqs. (5) and (22), we need only prove for each r that

$$\text{tr} [\vec{P}_{fg} - (1/Y) \vec{1}] \vec{\Phi}_r = (12/Y) \text{tr} \vec{S}_{xf} \vec{S}_{zg} \vec{\Phi}_r . \quad (24)$$

It is shown in the Appendix that for any pair of sites f, g and for $\vec{P} \in G$,

$$\begin{aligned} & \text{tr} \vec{P}_{fg} \vec{P} = Y \text{tr} \vec{P} \quad \text{if } f, g \text{ belong to the} \\ & \quad \text{same cycle in } \vec{P} \\ &= Y^{-1} \text{tr} \vec{P} \quad \text{if } f, g \text{ belong to different} \\ & \quad \text{independent cycles in } \vec{P}. \quad (25) \end{aligned}$$

Hence from Eqs. (19) and (25)

$$\begin{aligned} & \text{tr} [\vec{P}_{fg} - (1/Y) \vec{1}] \vec{\Phi}_r = (Y - 1/Y) \text{tr} \vec{\Phi}_r^{(1)} \\ &= (4X/Y) \text{tr} \vec{\Phi}_r^{(1)} . \quad (26) \end{aligned}$$

Now let $n=1$ in Eq. (20):

$$\text{tr} \vec{S}_{xf} \vec{S}_{zg} \vec{\Phi}_r = \frac{1}{3} X \text{tr} \vec{\Phi}_r^{(1)} . \quad (27)$$

Equation (24), and thence (23), follows directly from Eqs. (26) and (27), so that Theorem II is proved.

Performing the appropriate sums over lattice sites, Eqs. (10) and (12) follow directly from Theorems I and II, respectively. Note that Theorems I and II also hold for f, g belonging to different (disconnected) clusters, and they contain considerably more information in them than that which we have utilized. For example, since for $T > T_c$, $\langle \vec{S}_0 \cdot \vec{S}_\infty \rangle_\beta = 3M^2/m^2 = 0$, it follows from Theorem II that $\langle \vec{P}_{0\infty} - Y^{-1} \vec{1} \rangle = 0$. Here the subscripts indicate the limit of infinite separation and M is the spontaneous magnetization per spin. It also follows from these theorems that for $S=1$, $\langle \vec{S}_{xf} \vec{S}_{xg} \vec{S}_{yf} \vec{S}_{yg} \rangle_\beta = 0$, $f \neq g$.

Hence we conclude that for the exchange-interaction model the 2S-“independent” multipolar (4S-polar) phase transitions are in fact exactly degenerate with the dipolar transition. This means that the unusual values of γ (for $S > \frac{1}{2}$) predicted on the basis of an analysis of the high-temperature

susceptibility series are completely characteristic of this model.¹⁰

APPENDIX: PROOF OF EQS. (15), (18), AND (25)

Each element of the symmetric group can be written as a product of commuting cycles. Any group element, say \vec{P} , can be written in the form

$$\vec{P} = (abc \dots de)(ijk \dots m) \dots (xy \dots z) , \quad (A1)$$

where

$$(abc \dots de) = (ae)(ad) \dots (ac)(ab) = \vec{P}_{ae} \vec{P}_{ad} \dots \vec{P}_{ac} \vec{P}_{ab} . \quad (A2)$$

The indices in each cycle refer to different lattice sites.

We first prove the following three results:

$$\begin{aligned} \text{tr}(ijk \dots m) &= \sum_{s_{zi}} \sum_{s_{zj}} \sum_{s_{zk}} \dots \sum_{s_{zm}} (\delta_{s_{zi}, s_{zj}} \delta_{s_{zj}, s_{zk}} \\ &\quad \dots \delta_{s_{zi}, s_{zm}}) = \sum_{s_{zi}} (1) = Y . \quad (A3) \end{aligned}$$

All sums in this equation, and the next two, range from $-S$ to $+S$. Similarly,

$$\begin{aligned} \text{tr} \vec{S}_{zi}^n (ijk \dots m) &= \sum_{s_{zi}} \sum_{s_{zj}} \sum_{s_{zk}} \dots \sum_{s_{zm}} (S_{zi}^n \delta_{s_{zi}, s_{zj}} \delta_{s_{zj}, s_{zk}} \\ &\quad \dots \delta_{s_{zi}, s_{zm}}) = \sum_{s_{zi}} (S_{zi}^n) = Y W_n \quad (A4) \end{aligned}$$

and

$$\begin{aligned} & \text{tr} \vec{S}_{zi}^n \vec{S}_{zj}^n (ik \dots jl \dots m) \\ &= \sum_{s_{zi}} \sum_{s_{zk}} \dots \sum_{s_{zj}} \sum_{s_{zl}} \dots (S_{zi}^n S_{zj}^n \delta_{s_{zi}, s_{zk}} \dots \delta_{s_{zi}, s_{zj}} \\ &\quad \dots \delta_{s_{zi}, s_{zl}} \dots \delta_{s_{zi}, s_{zm}}) \\ &= \sum_{s_{zi}} (S_{zi}^{2n}) = Y W_{2n} . \quad (A5) \end{aligned}$$

Now, in Eq. (A1), since there are no common indices in each cycle, \vec{P} may be considered as the direct product of each cycle:

$$\vec{P} = (abc \dots de) \times (ijk \dots m) \times \dots \times (xy \dots z) . \quad (A6)$$

Since the order of the individual cycles, as well as the first index in each cycle, is arbitrary in Eqs. (A1) and (A6), Eqs. (15) and (18) of the text follow immediately from Eqs. (A3)–(A5), since $\text{tr} \vec{A} \times \vec{B} = (\text{tr} \vec{A})(\text{tr} \vec{B})$.

It is straightforward to show that

$$(fg)(fa \dots bgc \dots d) = (fa \dots b)(gc \dots d) \quad (A7)$$

and

$$(fg)(fa \dots b)(gc \dots d) = (fa \dots bgc \dots d) . \quad (A8)$$

Equations (A7) and (A8) imply that for any group element \vec{P} , $(fg)\vec{P}$ has one more cycle than \vec{P} if f, g belong to the same cycle in \vec{P} and one less cycle

than \bar{P} if f, g belong to different independent cycles in \bar{P} . Since by Eq. (A3) the trace of each cycle is

just Y , use of Eq. (A6) and the trace property of the direct product then directly gives Eq. (25).

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Optical and Ferroelectric Properties of Barium Sodium Niobate

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Optical absorption, refractive index, dielectric constant, nonlinear optical coefficients, and linear electro-optic coefficients are reported for single-domain crystals of $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ between room temperature and the Curie temperature. Orthorhombic ($mm2$) barium sodium niobate, a filled tungsten-bronze structure, is stable to intense laser radiation, and its phase-matchable nonlinear coefficients are 3 times those of LiNbO_3 and LiIO_3 . For the 1.064- μm laser fundamental, the observed phase-match temperatures and the angular half-widths of the phase-matched second-harmonic intensity due to the coefficients d_{31} and d_{32} are found to be in good agreement with the values calculated from refractive-index data. The dielectric constant and electro-optic half-wave voltage data indicate that $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ is a useful electro-optic modulator material. The temperature variation of the spontaneous polarization P_S is deduced from the birefringence, electro-optic, nonlinear optical, and pyroelectric data. It is concluded that the ferroelectric transition in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ is of the first order.

I. INTRODUCTION

A large number of single crystals of a series of ferroelectric mixed alkali-metal alkaline-earth niobates¹⁻³ have been grown that have very advantageous nonlinear and electro-optic properties. These compounds have structures that are related to tetragonal tungsten bronze with a general formula $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$. The term "tungsten bronze" derives from the potassium tungsten oxide compositions that have this structure, which have been discussed by Magnelli and Blomberg,⁴ Wadsley,⁵ Francombe⁶ and by Jamieson, Abrahams, and Bernstein.⁷ The unit cell contains 10-NbO₆ octahedra

which can accommodate up to four cations in 10-coordinated tricapped trigonal prismatic (A2) sites, two cations in somewhat smaller 12-coordinated cubo-octahedral (A1) sites, and four cations in relatively small 3-coordinated planar trigonal (C) sites. The number of A and C sites occupied is determined by the cations available in accordance with the requirements of electroneutrality. When all of the A1 and A2 sites are occupied by cations the structure is termed as "filled" whereas a "completely filled" structure implies that the C sites are occupied as well.

A very attractive property of these filled and completely filled tungsten-bronze-type niobates is