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Spin-One Heisenberg Ferromagnet in the Presence of Biquadratic Exchange

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The statistical-mechanical properties of a spin-one Heisenberg ferromagnet with isotropic nearest-neighbor biquadratic interactions are discussed. First, conditions for having an exact ferromagnetic ground state are found and the dispersion relation for magnons is derived. Then the relevant thermodynamical properties are obtained in a generalized molecular-field approximation (MFA). It is shown that if three stable phases, paramagnetic, "quadrupolar," and ferromagnetic, come into play in the discussion, ferromagnetic ordering is always preferred to "quadrupolar" ordering, preventing the latter from appearing as a separate phase transition. The critical ratio of bilinear to biquadratic exchange for the onset of a first-order ferromagnetic transition is obtained.

I. INTRODUCTION

The superexchange mechanism is known[1,2] to give rise to isotropic biquadratic interactions of the form $-j(\vec{S}_i\cdot\vec{S}_j)^2$, in addition to the usual Heisenberg bilinear ones $-J(\vec{S}_i\cdot\vec{S}_j)$. These additional interactions have been of current theoretical interest,[3-7] since Harris and Owen,[8] Rodbell *et al.*,[9] and others[10-14] pointed out that they could have significant effects on the magnetic properties of antiferromagnets, like MnO, α-MnS, EuSe, and ferrimagnets and, in particular, cause the magnetic transition to become first order. More recently, Blume and Hsieh[15] noted that since two order parameters at least are to be considered for such systems [that is $\langle S_z\rangle = m$ and $\langle S_z^2\rangle - \frac{1}{3}S(S+1) = y$], ordering in the "quadrupolar" parameter y might occur as a separate phase transition.

In this paper, we study the statistical mechanics of a Heisenberg ferromagnet with isotropic biquadratic nearest-neighbor interactions between ions with spin one on a translationally invariant lattice. The ferromagnetic case has been chosen since in this case we can be sure that we know the exact ground state, provided certain conditions are fulfilled which we derive in Sec. II. In this section, the instability condition for magnons is also obtained. Section III solves for the relevant thermodynamical quantities in a generalized molecular-field approximation (MFA) and discusses the temperature and the order of the associated phase transitions. It is shown that if indeed three stable phases, paramagnetic (P), "quadrupolar" (Q), and ferromagnetic (F), are found, ferromagnetic ordering (that is the transition from P to F) is always preferred to "quadrupolar" ordering (the transition from P to Q), whatever the ratio j/J of biquadratic to bilinear exchange might be, provided this ratio is such that the ground state is ferromagnetic. The critical ratio for the onset of a first-order ferromagnetic transition is also derived.

II. GROUND STATE AND MAGNONS

A. Ground State

We consider a system of ions with spin quantum number s, described by the Hamiltonian

$$H = -2J\sum_{\langle i,j\rangle}\vec{S}_i\cdot\vec{S}_j - 2j\sum_{\langle i,j\rangle}(\vec{S}_i\cdot\vec{S}_j)^2 = \sum_{\langle i,j\rangle} H_{ij}\,. \tag{2.1}$$

The summation runs over nearest-neighbor pairs. The ground state of this Hamiltonian is unknown in general. Let us make no *a priori* assumption on the signs of J and j and see if we can find a situation in which we are sure the ground state is ferromagnetic. If $\vec{S}$ is the total spin of any pair of nearest neighbors i and j, since

$$\vec{S}_i\cdot\vec{S}_j = \tfrac{1}{2}S(S+1) - s(s+1)\,,$$

the expectation value u of $\vec{S}_i\cdot\vec{S}_j$ may vary in the range from $-s(s+1)$ (for $S=0$) to s^2 (for $S=2s$). It is easily shown that the ferromagnetic state for a couple minimizes the expectation value $-Ju-ju^2$ of H_{ij} and thus the expectation value of the total Hamiltonian H, when the following inequalities are both satisfied:

$$J>0\ , \qquad -J/2s^2<j<J/s\ . \tag{2.2}$$

When these conditions are fulfilled we are sure the ground state is ferromagnetic, the ground-state energy being $E_0=-Js^2-js^4$. We emphasize, however, that these are not necessary, but sufficient conditions for ferromagnetism.

Let us make a comment on this result which is not exactly what one might expect from a classical point of view. One might be tempted to conclude that provided J and j are positive, the ground state is ferromagnetic no matter how large j is, since the biquadratic energy is degenerate for $\theta=0$ and $\theta=\pi$ (θ is the "angle" between two spins). The quantum result is different because $S=0$ gives a lower expectation value than $S=2s$ for $(\vec{S}_i\cdot\vec{S}_j)^2$.

Since we intend to solve the Hamiltonian (2.1) in a MFA, we need to verify that at least under the same conditions (2.2), the ground state obtained in the MFA is the exact ground state, i.e., is ferromagnetic, with the same energy E_0. This is indeed the case: Using the method outlined in Sec. III A, we may write the internal energy of the spin system in the MFA as

$$U/Nz=-\tfrac{1}{2}(2J-j)m^2-j\left\{\tfrac{1}{2}[s(s+1)-x]^2+x^2\right\}\ , \tag{2.3}$$

where

$$\begin{aligned} m&=\langle S_{zi}\rangle=\langle S_z\rangle\ ,\\ x&=\langle S_{zi}^2\rangle=\langle S_z^2\rangle=y+\tfrac{1}{3}s(s+1)\ . \end{aligned} \tag{2.4}$$

Here N is the number of spins and z the number of nearest neighbors of a spin. It can be shown that if conditions (2.2) are satisfied, the lowest value of U in the region $0\leqslant m\leqslant s$, $0\leqslant x\leqslant s^2$, $m^2\leqslant x$ of the (m, x) plane is E_0 and is obtained for $m^2=x$ and $x=s^2$.

B. Magnons

We only give the result, which has already been derived for antiferromagnets.[2] Here the magnon spectrum of the Hamiltonian (2.1) is the same as in the absence of a biquadratic term, with a simple renormalization of the exchange constant which is to be replaced by $J^*=J+2js(s-1)$. We again verify that if (2.2) is satisfied, the effective J^* is positive. The instability condition for magnons $J<-2js^2+2js$, seems to suggest that conditions (2.2) are too drastic. This might come from the fact that in Sec. II A, we have erroneously treated u as a continuous variable in our discussion. We should also point out the peculiar behavior of spin-one ions, whose magnon spectrum is unchanged by the biquadratic term. The reason for this is that for a pair of such ions the state with one-spin deviation on one ion in the pair is an eigenstate of the biquadratic energy which is degenerate with the ferromagnetic ground state. Thus, no additional excitation energy associated with the biquadratic term is required to excite a magnon.

III. THERMODYNAMICAL BEHAVIOR

We now specialize in the case of spin-one systems with a ferromagnetic ground state. As there is an additional requirement ($j>0$) for the "quadrupolar" phase to appear in the discussion, we will assume

$$j>0 \quad \text{and} \quad J>j\quad . \tag{3.1}$$

A. Free Energy

We calculate the free energy of the system described by the Hamiltonian (2.1) in a generalized MFA, based on the Peierls variational theorem.[16] We choose a trial density matrix ρ_t to satisfy the following conditions: (a) It is factorized. H_i is a one-spin Hamiltonian which we do not need to define explicitly:

$$\rho_t=\exp(-\beta\textstyle\sum_i H_i)/\mathrm{Tr}\exp(-\beta\sum_i H_i)\ , \tag{3.2}$$

where $\beta=1/k_BT$. (b) It is translationally invariant. (c) It is invariant under rotations around the z axis, which has been singled out as the direction of preferential spin alignment. Condition (c) is an assumption on the symmetry of the ordered phases to appear in the problem.

Minimization of the variational free energy

$$F=U-TS=\mathrm{Tr}[\rho_tH]-S(\rho_t)\ , \tag{3.3}$$

with respect to appropriate variational parameters will lead to the "best" form for ρ_t. In (3.3) the expression $S(\rho_t)$ indicates that the entropy is to be calculated with the aid of the trial density matrix.

Conditions (a)-(c) are sufficient to obtain the expression (2.3) for the internal energy U. Indeed the form of the density matrix allows the decoupling of any average value of a product of spin operators associated with two different sites into a product of average values relative to one site. Furthermore, the latter are site independent due to translational invariance. Finally, rotational invariance around the z axis makes it possible to express all mean values in terms of two of them, namely m and x, as defined in (2.4). The internal energy in the case of spin-one systems is obtained by setting $s=1$ in (2.3):

$$U=-Nz[Jm^2+\tfrac{1}{2}j(4-4x+3x^2-m^2)]\ . \tag{3.4}$$

The entropy may be written[17]

$$S = -Nk_B \sum_{m_s} p_{m_s} \ln p_{m_s} , \tag{3.5}$$

where m_s is the quantum number associated with the operator S_{zi}, p_{m_s} is the related probability, and $\sum_{m_s}$ runs over the values $-s, \ -s+1 \ldots s-1, \ s$. The general relations

$$m = \sum_{m_s} m_s p_{m_s} , \tag{3.6a}$$

$$x = \sum_{m_s} m_s^2 p_{m_s} , \tag{3.6b}$$

$$\sum_{m_s} p_{m_s} = 1 \tag{3.6c}$$

may now be used to get for spin-one systems[18] explicit values of the probabilities p_1, p_0, and p_{-1} in terms of m and x. These lead to the following expression of the entropy:

$$S = -Nk_B \left[\tfrac{1}{2}(x+m)\ln \tfrac{1}{2}(x+m) + \tfrac{1}{2}(x-m)\ln\tfrac{1}{2}(x-m) + (1-x)\ln(1-x) \right] . \tag{3.7}$$

Combining (3.4) and (3.7), we get the expression for the free energy per ion

$$F = -\tfrac{1}{2}(2J-j)m^2 - \tfrac{1}{2}j\,(4-4x+3x^2) + T\left[\tfrac{1}{2}(x+m)\ln\tfrac{1}{2}(x+m) + \tfrac{1}{2}(x-m)\ln\tfrac{1}{2}(x-m) + (1-x)\ln(1-x)\right] . \tag{3.8}$$

Here and in the following, we write J and j for Jz and jz and T for $k_B T$. Minimization of F with respect to m and x leads to

$$\frac{\partial F}{\partial m} = -(2J-j)\,m + \frac{T}{2}\ln\frac{x+m}{x-m} = 0 , \tag{3.9a}$$

$$\frac{\partial F}{\partial x} = -j(3x-2) + \frac{T}{2}\ln\frac{(x+m)(x-m)}{4(1-x)^2} = 0 . \tag{3.9b}$$

Each couple of solutions (m, x) is to be associated with a different phase, the spin system choosing at any temperature to be in the phase characterized by the lowest free energy. Before looking for these solutions we might get a better insight into the physics of the problem by considering it from the point of view of Landau's theory of phase transitions.

B. Landau's Theory

Let us first assume that all transitions are of second order. The free energy [Eq. (3.8)] is analytic in the order parameters and may be expanded as

$$F = -\tfrac{4}{3}j - T\ln 3 + \tfrac{3}{4}(T-T_0)m^2 + \tfrac{9}{4}(T-T_2)y^2 + \tfrac{9}{8}T\left[y^3 - m^2y\,(1-\tfrac{3}{2}y) + \tfrac{1}{4}m^4(1-\tfrac{9}{2}y) + \tfrac{9}{40}m^6\right] , \tag{3.10}$$

with

$$T_0 = \tfrac{2}{3}(2J-j) , \tag{3.11}$$

$$T_2 = \tfrac{2}{3}j . \tag{3.12}$$

At high temperatures the spin system is in a paramagnetic phase ($m_P = 0$, $y_P = 0$). T_0 and T_2 are two transition temperatures associated, respectively, with ferromagnetic and "quadrupolar" ordering. According to Landau's theory, there will first occur the type of ordering associated with the higher temperature provided, as assumed, that both transitions are of second order. Now we note that the condition for a ferromagnetic ground state can be written $T_0 > T_2$. This, however, cannot lead us to a conclusion since, as we show in Secs. III C and III D, both transitions[19] are of first order in the region $T_2 < T_0 2T_2$, so that neither T_0 nor T_2 is the real transition temperature. It is thus necessary to examine separately the two phase changes by starting from the exact expression of the free energy and to find by another procedure the transition temperatures in order to be able to determine the thermal evolution of the spin system.

C. "Quadrupolar" Ordering

This ordering is associated with the transition from the paramagnetic isotropic phase to a "quadrupolar" phase of symmetry $D_{\infty h}$ with zero magnetization. The paramagnetic solution obviously satisfies the couple of equations (3.9). In the "quadrupolar" solution $[m_Q = 0, \ x_Q(T)]$ the function $x_Q(T)$ has to be determined as a solution of Eq. (3.9b), where we have set $m = 0$, that is, of

$$(j/T)(3x-2) = \ln[x/2(1-x)] . \tag{3.13}$$

We keep in mind that we have to verify whether all these solutions lead to extrema which are stable minima for the free energy. A graphical interpretation of Eq. (3.13) leads to the functions $x(T)$ which are plotted in Fig. 1 together with $x_P = \frac{2}{3}$. Figure 2 represents the relative positions of the associated free-energy-vs-T curves. Figure 3 illustrates the changes of the free-energy-vs-x curve as the temperature varies. Figures 1–3 may be read in parallel: At high temperatures the only stable minimum corresponds to the paramagnetic solution [Fig. 3(a)]. At $T_1 = 0.73j$ (as determined graphically), a new stable minimum appears in the free-energy curve [Figs. 3(b) and 3(c)] and its abscissa is the "quadrupolar" solution x_Q. This solution becomes more stable than the paramagnetic one [Figs. 3(d)–3(f)] at temperatures below $T_Q = j/2\ln 2$, which is the first-order transition temperature associated with "quadrupolar" ordering. At T_Q the order parameter x varies discontinuously from $x_P = \frac{2}{3}$ to $x_Q(T_Q) = \frac{1}{3}$ (Fig. 1).

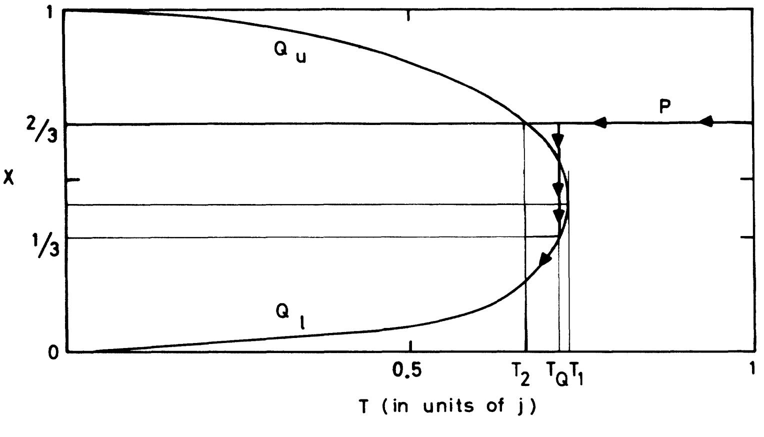

FIG. 1. Extrema $x(T)$ of the free energy $F(T, x, m=0)$ as calculated from Eq. (3.13). A part from the paramagnetic extremum, one observes for $T < T_1$ a double-branched "quadrupolar" solution, the lower branch of which always has a lower free energy than the upper branch (see Fig. 2).

We now have to determine under what condition $m=0$ is a stable minimum for F: The condition is that the coefficient of m^2 in the expansion of F in powers of m is positive, that is,

$$-\tfrac{1}{2}(2J-j)+T/2x>0 . \qquad (3.14)$$

This is always the case at high temperatures. The requirement for the "quadrupolar" phase to be a stable minimum down to the "quadrupolar" transition is

$$J<\tfrac{1}{2}j(1+3/4\ln 2) , \qquad (3.15)$$

which is not incompatible with the condition for a ferromagnetic ground state.

In concluding this section we have shown that the "quadrupolar" phase becomes more stable than the paramagnetic phase at a temperature T_Q, if condition (3.15) is satisfied. We know that a nonzero magnetization has to appear at some temperature, since the ground state is ferromagnetic. We thus are left with the problem of finding out the position of the ferromagnetic ordering temperature relative to T_Q.

D. Ferromagnetic Ordering

The ferromagnetic phase is associated with a solution $m_F(T)$, $x_F(T)$ of Eqs. (3.9) with $m_F \neq 0$ and $x_F \neq \frac{2}{3}$. Equations (3.9) can be written

$$m/x=\tanh\left(\tfrac{3}{2}(T_0/T)m\right) , \qquad (3.16a)$$

$$m=\left\{x^2-4(1-x)^2\exp[9(T_2/T)(x-\tfrac{2}{3})]\right\}^{1/2} , \qquad (3.16b)$$

where T_0 and T_2 are defined in (3.11) and (3.12). For $m=0$ Eq. (3.16a) is satisfied and Eq. (3.16b) represents the x-vs-T curves plotted in Fig. 1. Since the expression in the curly brackets in (3.16b) must be positive for m_F to exist, we may delimit the regions in the (x, T) plane where the ferromagnetic solution $x_F(T)$ cannot be present. These regions are shadowed in Fig. 4. Combining (3.16a) and (3.16b), we find the equation which has to be satisfied by $x_F(T)$:

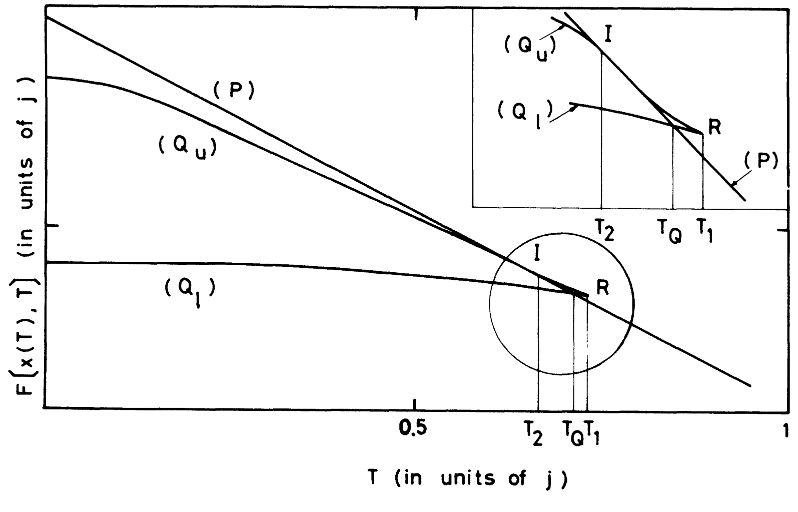

FIG. 2. Calculated free-energy-vs-T curves for the three extrema P, Q_u, Q_l (see Figs. 1 and 3).

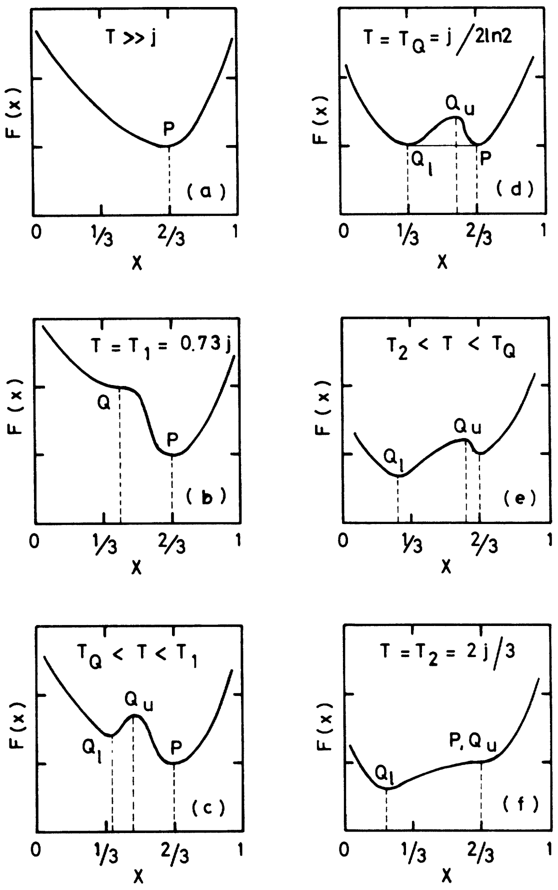

FIG. 3. Schematic free-energy-vs-x curves [from Eq. (3.8) with $m=0$] as a function of temperature for $T > T_2$. For details see text.

$$[x^2-4(1-x)^2 e^{(9T_2/T)(x-2/3)}]^{1/2} = x\tanh\left(\tfrac{3}{2}\,\frac{T_0}{T}\,[x^2-4(1-x)^2 e^{(9T_2/T)(x-2/3)}]^{1/2}\right). \tag{3.17}$$

The solution of this equation should be determined numerically. However, as we are more interested in the general features than in the details of the thermal evolution of the system, we will rather proceed as follows.

(a) We first wish to know at what temperature, in the (x, T) plane, the ferromagnetic solution $x_F(T)$ intersects the paramagnetic line $x_P=\frac{2}{3}$, and what its behavior is in the vicinity of this point. This will tell us the order of the transition from paramagnetism to ferromagnetism. The answer is obtained by developing Eq. (3.17). It is found that the intersection takes place for $T=T_0$, and that near this point

$$x-\tfrac{2}{3} \sim \tfrac{2}{3}(T_0-T)/(T_0-2T_2)\ . \tag{3.18}$$

There is also an additional requirement

$$(x-\tfrac{2}{3})(T_0-T_2) \geqslant 0 \tag{3.19}$$

in order to ensure the definiteness of the square root. Since $T_0 > T_2$, (3.19) may be written

$$x-\tfrac{2}{3} \geqslant 0\ ,$$

which enables us to find out immediately the order of the ferromagnetic transition: If $T_0 > 2T_2$, $T_0 - T$ has to be positive and the transition is second order. In this case T_0 is the effective transition temperature. For $T_0 < 2T_2$ the transition is first order. This last condition may be written

$$j > \tfrac{2}{3}J\ . \tag{3.20}$$

The variety of behavior of the ferromagnetic solution in the vicinity of the paramagnetic line is illustrated in Fig. 4.

It is interesting to note that condition (3.20) may also be derived by using Landau's theory. If we come back to the expression of the free energy as developed in powers of m^2 and y, minimization with respect to y gives the result that y behaves as m^2, which allows us to develop F in powers of m^2 alone. More precisely, we find

$$y \sim \alpha m^2 + \beta m^4\ , \tag{3.21}$$

with

$$\alpha = T/4(T-T_2)\ , \tag{3.22a}$$

$$\beta = -3\alpha(\alpha^2+\alpha-\tfrac{3}{8})\ , \tag{3.22b}$$

so that to the order m^6,

$$F \sim -\tfrac{4}{3}j - T\ln 3 + \tfrac{3}{4}(T-T_0)m^2 + \tfrac{9}{32}\,T(1-2\alpha)m^4 + \tfrac{9}{8}T(\alpha^3+\tfrac{3}{2}\alpha^2-\tfrac{9}{8}\alpha+\tfrac{9}{40})m^6\ . \tag{3.23}$$

The condition for a ferromagnetic first-order transi-

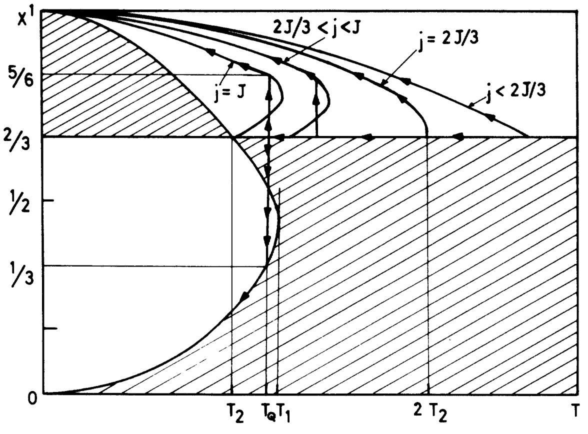

FIG. 4. Ferromagnetic and quadrupolar solutions $x(T)$ for various ratios j/J (schematic). The ferromagnetic transition becomes first order for $J < 3j/2$ (in this figure j is fixed). For $J=j$, the ferromagnetic and "quadrupolar" transition temperatures are equal, as shown.

tion is thus $\alpha > \frac{1}{2}$, which is nothing but condition (3.20). We cannot go much further with the developed expression of F and have to come back to the preceding approach to determine the first-order transition temperature T_F.

(b) In principle, T_F may be found as a solution of the equation

$$F_{\min} - F_P = 0 \,, \qquad (3.24)$$

where $F_P = F(m=0,\ x=\frac{2}{3},\ T)$ is the free energy of the paramagnetic phase and $F_{\min}$ is the value of the free energy when x and m have been replaced by their values as a function of temperature from the minimization equations (3.16). As the latter equations contain all solutions, all transition temperatures are solutions of (3.24), as we will verify. In fact, $F_{\min}$ cannot be expressed explicitly as a function of temperature and we have to solve the coupled equations

$$T \ln 3(1-x) + \tfrac{3}{4} T_0 [x^2 - 4(1-x)^2 e^{(9T_2/T)(x-2/3)}] + \tfrac{9}{4} T_2 (x^2 - \tfrac{4}{9}) = 0 \,, \qquad (3.25)$$

and (3.17) to get T_F and $x_F(T_F)$, the corresponding value of $m_F(T_F)$ being obtained from (3.16b). Equation (3.25) is one possible form for (3.24), where m but not x has been eliminated with the aid of (3.16). It is easily shown that (3.17), (3.25), and (3.16) are satisfied for $T = T_Q = j/2\ln 2$ and the two solutions already known $\{(m_P = 0,\ x_P = \frac{2}{3})$ and $[m_Q(T_Q) = 0,\ x_Q(T_Q) = \frac{1}{3}]\}$, which are the coordinates associated with the paramagnetic and "quadrupolar" phases at the transition temperature T_Q. We will now look for the third solution $[m_F(T_F),\ x_F(T_F)]$ and T_F associated with ferromagnetic ordering and we will only consider the limiting case $J = j$ or $T_0 = T_2$: This is the most favorable case for the "observation" of the "quadrupolar" phase, since it is associated to the lowest transition temperature T_F. It is easily found that the third solution of (3.17) and (3.25) is

$$T_F = T_Q = \frac{j}{2\ln 2} \,, \quad x_F = \frac{5}{6} \,, \qquad (3.26)$$

the associated value of m being $m_F = 0.5$, so that at the transition temperature T_F, m, and x undergo a discontinuous change from zero and $\frac{2}{3}$ to 0.5 and $\frac{5}{6}$ (Fig. 4).

Hence, in the most favorable case, the first-order transition temperatures associated to ferromagnetic and "quadrupolar" ordering, respectively, are equal. We may infer that in all more general cases $T_0 > T_2$, T_F will be higher than T_Q (which is independent of J), so that ferromagnetic ordering will always occur first, preventing the "quadrupolar" phase from appearing.

IV. CONCLUSION

We have studied in a MFA the thermal evolution of a spin-one Heisenberg ferromagnet in the presence of biquadratic exchange. A "quadrupolar" ordering which comes into the discussion proves never to occur, as long as we consider cases ($J > j > 0$) where the exact ground state of the spin system is ferromagnetic. The system always undergoes one phase transition, from the paramagnetic phase to the ferromagnetic phase, which becomes first order when j is larger than $\frac{2}{3}J$. We wish to emphasize that we have especially limited our study to situations where the exact ground state has been found, because the MFA predictions for the ground state are known not to be *a priori* reliable: Thus, for instance, MFA might predict the existence of zero- and low-temperature phases without any vectorial ordering,[20] the occurrence of which appears nevertheless not to be proved.

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[18] For other values of the spin quantum number one cannot obtain the entropy as an explicit function of m and x. Analogous problems for any value of the spin can nevertheless be easily solved by expressing the entropy as a function of two Lagrange multipliers related to m and x. See, for instance, A. Castets, thèse de 3^c cycle (Paris, 1972) (unpublished); and A. Castets and M. Nauciel-Bloch, Solid State Commun. (to be published).

[19] "Quadrupolar" ordering always occurs as a first-order transition as a consequence of Landau's theory of symmetry changes associated with phase transitions. Indeed, the "quadrupolar" ordering corresponds to an order parameter belonging to the D_2 irreducible representation of the group 0(3) of all rotations around a fixed point, and the symmetrical cube of D_2 contains the identical representation [cf. N. Boccara, Ann. Phys. (N.Y.) (to be published).] There is no such requirement for the ferromagnetic ordering, which can be (and is) found to be either first or second order.

[20] H. H. Chen and P. M. Levy, Phys. Rev. Letters 27, 1383 (1971). In this letter a nonmagnetically ordered phase is predicted at zero temperature for isotropic and Ising-like spin-one systems with large biquadratic exchange.

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Far-Infrared Stark and Zeeman Splitting of Pr^{3+}, Nd^{3+}, Er^{3+}, Ho^{3+}, and Dy^{3+} in Some Lanthanide Fluorides

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The Zeeman effect has been studied in several rare-earth ions imbedded in lanthanide fluorides. A special cryostat has been constructed with two liquid-helium tanks. One, at 4 K, contains a superconducting coil giving magnetic fields as high as 60 kOe. The other, at 1.3 K, contains a Ge:Ga bolometer to detect far-infrared radiation. Large splittings, as high as 30 cm^{-1}, have been observed with Nd^{3+}, Er^{3+}, and Dy^{3+} where the ground state is a Kramers doublet. For Pr^{3+} and Ho^{3+}, which do not give Kramers doublets, the effect of a magnetic field is not so significant. The effect is negligible for Pr^{3+}. For Ho^{3+}, a 3-cm^{-1} shift and a line broadening are observed. On the other hand, whereas the spectra of $LaF_3:Nd^{3+}$ and NdF_3 are very similar, for PrF_3 a pair of ions seems to be present and gives twice as many electronic lines compared to $LaF_3:Pr^{3+}$. Localized modes are observed close to 73 cm^{-1} for both Er^{3+} and Dy^{3+}, while an absorption band is observed at 64 cm^{-1} for Dy^{3+} which seems to be slightly sensitive to the magnetic field and has still to be explained. An average spectroscopic g value for the ground-state and first-excited-state Kramers doublet has been calculated for Nd^{3+}, ER^{3+}, and Dy^{3+}. For the ground-state Kramers doublet, these values are well within the limits of the reported g tensor based upon ESR. For the first-excited-state Kramers doublet the determinations are, respectively, $g_2 = 1.7$, 3.6, and 11.5 and they constitute new data.

I. INTRODUCTION

The electric field in a crystal at a rare-earth-ion site may split the ground state to produce a series of sublevels extending from zero to a few hundred wave numbers in energy. Transitions between these sublevels may be infrared active, and a number of them have been observed at temperatures low enough to get rid of the absorption occurring from two-phonon difference modes.[1] Lanthanum fluoride is a good host for rare-earth ions because it can be grown in large-size crystals which are not hygroscopic.

A few studies in the far infrared have been published and a lot of low-frequency lines have been described.[2–5] Nevertheless, all the absorption lines are not due to electronic transitions, as we thought in our first paper.[2] The spectra are certainly complicated by low-frequency infrared-active phonon modes. Fortunately, in the case of lanthanum fluoride the phonon spectrum is simple enough to make it possible to identify the pure lattice absorption unambiguously by looking at the whole series of lanthanide fluorides.

Only relatively small frequency shifts are expected from compound to compound because the increase in the rare-earth-ion mass is small from lanthanum to erbium: La = 139, Ce = 140, Pr = 141, Nd = 144, Dy = 163, Ho = 163, and Er = 168.

The increase in mass seems largely compensated by an increase of force constants due to the increase in ionic size.

The remaining absorption lines are not necessarily all due to electronic excitations. In the case