

Dipolar and quadrupolar orderings in the Γ_3 - Γ_5 magnetic system

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The dipolar and quadrupolar orderings in the doublet-triplet (Γ_3 - Γ_5) system is studied on the basis of a symmetry-adapted spin-Hamiltonian under molecular-field approximation. One obtains pure quadrupolar ordering or dipolar and quadrupolar orderings either at one particular temperature or at two different temperatures depending on the ratio of the bilinear and biquadratic pair interactions. The separation between the ground Γ_3 and the excited Γ_5 levels plays an important role on the nature of the phase transitions. The cases of TmCd and TmZn are discussed.

I. INTRODUCTION

So far much attention has been paid to the nature of the singlet-triplet transition in various rare-earth (RE) compounds.¹⁻³ Most of these compounds order ferromagnetically with a moment induced on the ground level by the internal field. Recently some interest is being shown on the doublet-triplet systems (Γ_3 - Γ_5) which are also widely found among the RE compounds.⁴⁻⁷ In these systems the ground level of the RE ions is a nonmagnetic doublet Γ_3 with an excited triplet Γ_5 lying close to it. Similar to the singlet-triplet system the moment on the ground levels is an induced one. But, on the contrary, there is a nonvanishing quadrupole moment within the ground doublet Γ_3 which leads to the possibility of dipolar and quadrupolar orderings in this system. Indeed, the cubic intermetallic compounds TmCd (Ref. 4) and TmZn (Ref. 5) which are examples of the Γ_3 - Γ_5 system exhibit interesting properties at low temperatures. TmCd undergoes a first-order structural transition from a cubic to a tetragonal phase at a temperature of 3.16 K without indicating any magnetic ordering down to 40 mK. TmZn, on the other hand, indicates ferromagnetic ordering and possibly crystallographic distortion at a temperature of 10 K.⁵ Thus, TmCd lies at one extreme limit where only the quadrupolar ordering is observed, whereas TmZn shows both dipolar and quadrupolar orderings. Since many more RE compounds might eventually be found which lie in between the cases of TmCd and TmZn, a general study of the type of ordering and the phase diagram of the Γ_3 - Γ_5 system would be worthwhile. In the present paper, we make such a study in the background of the experimental results on TmCd and TmZn. It should be mentioned that Wang⁶ and more recently Egami and Brooks⁷ have studied the Γ_3 - Γ_5 system theoretically without taking into account the quadrupolar coupling. But

the existence of this coupling would cause quadrupolar transitions and excitations in compounds such as TmCd, or modify the magnetic ordering and excitations in other RE compounds. There is now growing interest in the study of the quadrupolar excitations in solids.⁸⁻¹¹ RE compounds with a Γ_3 - Γ_5 system are good examples of where these excitations might be observed. So the present study on the nature of ordering in this system would be useful in understanding the expected excitations in this system.

II. THE SPIN-HAMILTONIAN AND THE MOLECULAR-FIELD SOLUTIONS FOR THE Γ_3 - Γ_5 SYSTEM

Taking into account the dipolar and the quadrupolar interactions, the spin Hamiltonian in cubic symmetry is given by

$$\begin{aligned} \mathcal{H}_{\text{cubic}} = & \sum_i V_i^c - \sum_{i,j} \mathcal{J}_{ij} (J_i^x J_j^x + J_i^y J_j^y + J_i^z J_j^z) \\ & - \sum_{i,j} K_{ij} (Q_i Q_j + \frac{1}{3} P_i P_j) \\ & - \sum_{i,j} L_{ij} (P_i^{xy} P_j^{xy} + P_i^{yz} P_j^{yz} + P_i^{zx} P_j^{zx}), \end{aligned} \quad (1)$$

where

$$V^c = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)$$

$$Q = (J^x)^2 - \frac{1}{3}[J(J+1)],$$

$$P = (J^x)^2 - (J^y)^2,$$

$$P^{xy} = J^x J^y + J^y J^x,$$

In the case of Γ_3 - Γ_5 system we have Γ_3 as the ground and Γ_5 as the first excited level due to the effect of a cubic V_c . The form of the operators J , Q , and P within the Γ_3 - Γ_5 levels can be deduced from the fact that

$$\begin{aligned} [\Gamma_3^2] &= \Gamma_1 + \Gamma_3, \\ [\Gamma_5^2] &= \Gamma_1 + \Gamma_3 + \Gamma_5, \\ \Gamma_3 \Gamma_5 &= \Gamma_4 + \Gamma_5, \end{aligned} \quad (2)$$

and consequently, Q and $P/\sqrt{3}$ which transform as Γ_3 and J^x, J^y, J^z as Γ_4 can be represented by the following matrices:

$$J^z = \begin{bmatrix} 0 & 0 & 0 & 0 & \alpha \\ 0 & S & 0 & 0 & 0 \\ 0 & 0 & -S & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \alpha & 0 & 0 & 0 & 0 \end{bmatrix},$$

$$Q = \begin{bmatrix} 2q_5 & 0 & 0 & 0 & 0 \\ 0 & -q_5 & 0 & 0 & 0 \\ 0 & 0 & -q_5 & 0 & 0 \\ 0 & 0 & 0 & -q_3 & 0 \\ 0 & 0 & 0 & 0 & q_3 \end{bmatrix}, \quad (3)$$

$$P = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & p_5 & 0 & 0 \\ 0 & p_5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & p_3 \\ 0 & 0 & 0 & p_3 & 0 \end{bmatrix}.$$

If the levels Γ_3 and Γ_5 arise from a true spin $J=2$ we have: $S=1$, $\alpha=2$, $q_3=2$, $p_3=2$, and $q_5=1$. In the case of compounds such as TmCd and TmZn, the Γ_3 and Γ_5 levels lie relatively close together and the values of the matrix elements of J , P , and Q can be deduced from a knowledge of the crystal-field wave functions in these compounds.

In the presence of a Zeeman field and a uniaxial strain, the total Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_{\text{cubic}} - h \sum_i J_i^z - D \sum_i Q_i. \quad (4)$$

We now study the ordering in this system on the basis of the molecular-field approximation. In the case of intermetallic compounds the Ruderman-Kittel-Kasuya-Yosida form for the dipolar interaction¹² and the Teitelbaum-Levy form¹³ for the quadrupolar interaction is of long-range nature and consequently the molecular-field approximation is expected to work well for studying the ordering in these systems. The molecular field Hamiltonian is then given by

$$\mathcal{H}_0 = V - HJ_z - \sigma Q. \quad (5)$$

The five energy levels of \mathcal{H}_0 are

$$\begin{aligned} \lambda_1 &= \Delta + q_5\sigma + SH, \\ \lambda_2 &= \Delta + q_5\sigma - SH, \\ \lambda_3 &= q_3\sigma, \\ \lambda_4 &= \frac{1}{2} [\Delta - (q_3 + 2q_5)\sigma + R], \\ \lambda_5 &= \frac{1}{2} [\Delta - (q_3 + 2q_5)\sigma - R], \end{aligned} \quad (6)$$

with $R^2 = \Delta^2 + 4\alpha^2 H^2 + (q_3 - 2q_5)^2 \sigma^2 + 2(q_3 - 2q_5)\Delta\sigma$ where Δ is the cubic crystal field splitting between Γ_3 and Γ_5 . From these eigenvalues we can calculate the partition function Z_0 and the free energy ϕ . The two-order parameters $M = \langle J_i^z \rangle$ and $Q = \langle Q_i \rangle$ are finally obtained as

$$\begin{aligned} Z_0 M &= 2S e^{-\beta(\Delta + q_5\sigma)} \sinh \beta SH \\ &\quad + \frac{4\alpha^2 H}{R} e^{-(\beta/2)(\Delta - q_3\sigma - 2q_5\sigma)} \sinh \frac{1}{2} \beta R, \\ Z_0 Q &= (q_3 + 2q_5) e^{-(\beta/2)(\Delta - q_3\sigma - 2q_5\sigma)} \cosh \frac{1}{2} \beta R \\ &\quad - q_3 e^{-\beta q_3\sigma} - 2q_5 e^{-\beta(\Delta + q_5\sigma)} \cosh \beta SH \\ &\quad + \frac{(q_3 - 2q_5)(q_3 - 2q_5)\sigma + \Delta}{R} \\ &\quad \times e^{-(\beta/2)(\Delta - q_3\sigma - 2q_5\sigma)} \sinh \frac{1}{2} \beta R, \end{aligned} \quad (7)$$

with

$$\begin{aligned} Z_0 &= 2e^{-\beta(\Delta + q_5\sigma)} \cosh \beta SH + e^{-\beta q_3\sigma} \\ &\quad + 2e^{-(\beta/2)(\Delta - q_3\sigma - 2q_5\sigma)} \cosh \frac{1}{2} \beta R, \end{aligned}$$

$$\sigma = D + 2KQ,$$

$$H = h + 2\mathcal{J}M,$$

and the free energy $\phi = -(1/\beta) \ln Z_0 + \mathcal{J}M^2 + KQ^2$. \mathcal{J} and K are the Fourier transform of \mathcal{J}_{ij} and K_{ij} at zero wave vector and $\beta = 1/kT$. We now consider a few particular cases of the general equation given by (7).

Case 1. Pure quadrupolar transition

In this case $h = \mathcal{J} = H = 0$ and this gives

$$\begin{aligned} M &= 0, \\ Z_0 Q &= 2q_5 e^{-\beta\Delta} (e^{2\beta q_5\sigma} - e^{-\beta q_5\sigma}) + 2q_3 \sinh \beta q_3\sigma, \end{aligned} \quad (8)$$

with

$$Z_0 = e^{-\beta\Delta} (e^{2\beta q_5\sigma} + 2e^{-\beta q_5\sigma}) + 2 \cosh \beta q_3\sigma,$$

$$\phi = -\frac{1}{\beta} \ln Z_0 + KQ^2.$$

Performing a Landau development of the free energy ϕ we get

$$\phi = \phi_0 + A(T)Q^2 + B(T)Q^3 + \dots, \quad (9)$$

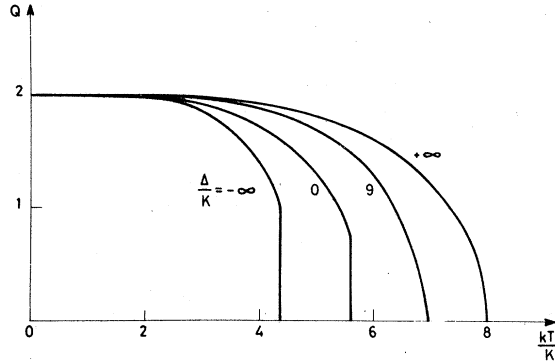


FIG. 1. Quadrupolar transition in a spin-2 Γ_3 - Γ_5 system: thermal variation of the order parameter Q for different values of Δ/K .

where

$$A(T) = K - 4\beta K^2 \frac{q_3^2 + 3q_5^2 e^{-\beta\Delta}}{2 + 3e^{-\beta\Delta}},$$

$$B(T) = -8\beta^2 q_5^3 \frac{e^{-\beta\Delta}}{2 + 3e^{-\beta\Delta}}.$$

The transition in Q is then of the first order except for the two cases, viz., $q_5 = 0$ and $\Delta = \alpha$. In the latter case, where Γ_5 is situated at a high-energy value, we consider only the Γ_3 doublet. The order parameter in the absence of uniaxial distortion is given by

$$Q = q_3 \tanh 2\beta q_3 K Q. \quad (10)$$

The pure quadrupolar transition is then of the second order which occurs at a temperature given by

$$kT_Q = 2q_3^2 K. \quad (11)$$

In fact, the ground state is continuously degenerate since the E_g quadrupolar Hamiltonian is equivalent to a spin- $\frac{1}{2}$ XY model (see Ref. 8). The transition changes to first-order for the two cases: (i) a quadrupolar Γ_5 level is at a finite separation from the ground Γ_3 level and (ii) the anharmonic cou-

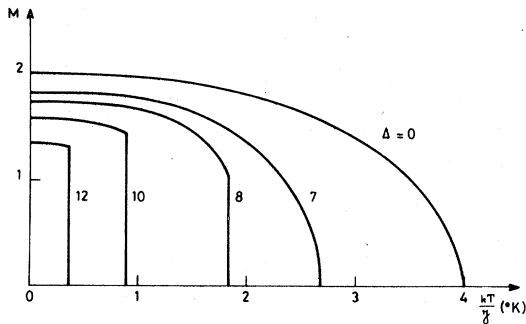


FIG. 2. Dipolar transition in a spin-2 Γ_3 - Γ_5 system: thermal variation of the order parameter M for different values of Δ/\mathcal{J} and $K=0$.

pling between the Γ_3 levels and the doublet modes Q and P is present. In either case the ground state is nondegenerate.

These results are shown in Fig. 1, where we have plotted Q as a function of kT/K . It is shown that for $\Delta/K=9$, the transition is practically of the second order.

Case 2. Pure dipolar interaction, i.e., $D=K=\sigma=0$

In this case, Eq. (7) gives:

$$\begin{aligned} Z_0 M &= 2S e^{-\beta\Delta} \sinh \beta S H + \frac{4\alpha^2 H}{\Delta^2 + 4\alpha^2 H^2} e^{-\beta\Delta/2} \\ &\quad \times \sinh(\beta/2)(\Delta^2 + 4\alpha^2 H^2), \\ Z_0 Q &= (q_3 + 2q_5) e^{-\beta\Delta/2} \cosh(\beta/2)(\Delta^2 + 4\alpha^2 H^2) \\ &\quad - q_3 - 2q_5 \cosh \beta S H + \frac{(q_3 - 2q_5)\Delta}{\Delta^2 + 4\alpha^2 H^2} \\ &\quad \times e^{-\beta\Delta/2} \sinh(\beta/2)(\Delta^2 + 4\alpha^2 H^2), \end{aligned} \quad (12)$$

with

$$Z_0 = 2e^{-\beta\Delta} \cosh \beta S H + 1 + 2e^{-\beta\Delta/2} \cosh(\beta/2)(\Delta^2 + 4\alpha^2 H^2)$$

$$\phi = -\frac{1}{\beta} \ln Z_0 + \mathcal{J} M^2$$

In Fig. 2, we plot the thermal variation of M for various values of Δ following Eq. (12) and using the values of q_3 , q_5 , S and α for the case $J=2$. The transition is of the second order for $\Delta \approx 0$ and becomes first order for $\Delta \approx 7.65$ ($T'_c = 2.15K$). For Δ larger than $\Delta_0 \approx 20$, the magnetic transition disappears. The interesting point to be noted is that the quadrupole moment exists within the $\Gamma_3 - \Gamma_5$ system even if the biquadratic interaction is absent. This arises entirely from the dipolar interaction.

Case 3. Both dipolar and quadrupolar interactions are present

In this case both \mathcal{J} and K are nonzero. Solutions are obtained directly from the Eq. (7) for

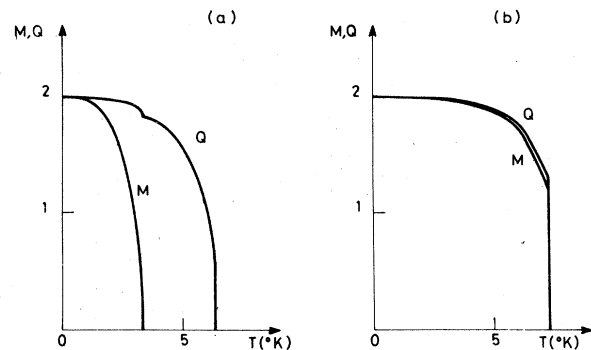


FIG. 3. Dipolar and quadrupolar ordering in a spin-2 Γ_3 - Γ_5 system: $K=1$; $\Delta=5$; (a) $g=0.8$; (b) $g=1.5$.

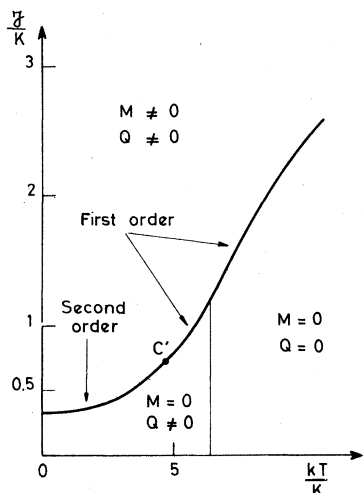


FIG. 4. Dipolar and quadrupolar ordering in a spin-2 Γ_3 - Γ_5 system: $K=1$; $\Delta=5$; \mathcal{J}/K variable. The transition in Q is of first order, the transition in M of first or second order. C' is a tricritical point.

particular values of \mathcal{J} and K . If \mathcal{J} and K are of the same order of magnitude, we get either a first-order transition in M and Q at the same temperature or a quadrupolar transition followed by a second- or first-order dipolar transition. The effect of varying the bilinear exchange \mathcal{J} on the nature of the ordering is shown in Fig. 3 for the case $J=2$ where the thermal variations of M and Q are plotted for $\Delta=5K$, $K=1K$ with $\mathcal{J}=0.8$ and $1.5K$ respectively. The corresponding phase diagram (with $\Delta=5K$, $K=1K$) is shown in Fig. 4. The quadrupolar transition is always of the first order, whereas the dipolar transition might be of the second or the first order depending on the value of \mathcal{J}/K . C' is a tricritical point. The case corresponding to $\Delta=0$ has earlier been treated by Chen and Levy.¹⁴

III. DISCUSSION

We have discussed the general nature of phase transitions to be expected for the Γ_3 - Γ_5 system for different values of \mathcal{J} , K and Δ . We shall now discuss the particular cases of TmCd and TmZn.

A. TmCd

Since no magnetic ordering has been found down to 40 mK we can take this to be a case of pure quadrupolar transition. The ground $J=6$ multiplet of Tm^{3+} ion splits into Γ_1 , Γ_2 , Γ_3 , Γ_4 , and two Γ_5 levels. The excited Γ_5 level is situated at 20 K above the ground Γ_3 level.⁴ The next excited one (Γ_2) is about 80 K above the ground Γ_3 level and can consequently be neglected. These crystal-field levels give $x \approx -1$ on the basis of the Lea,

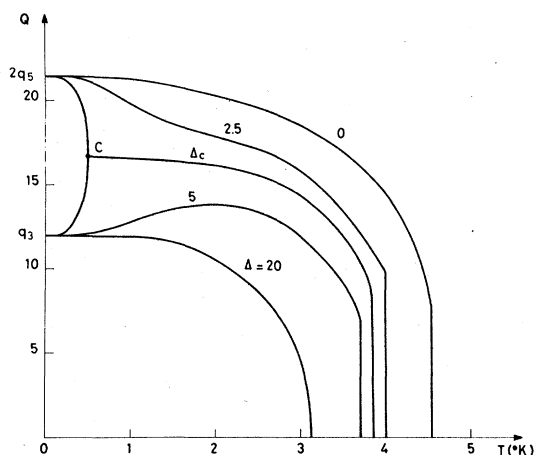


FIG. 5. Quadrupolar transition in TmCd: thermal variation of Q for $K=0.011$ and various values of Δ in $^\circ\text{K}$. $\Delta_c \approx 3.45$, C is a critical point.

Leask, and Wolf diagram¹⁵ and we get: $q_3=12.0$ and $q_5=10.7$. So taking $T_Q=3.16$ K, $q_3=10.7$ we can fix the value of K and this is 0.011 K. The variation of Q as function of T in this case is shown in Fig. 5. In this figure, we have also plotted the thermal variation of Q for other values of Δ but taking always $K=0.011$ K. We find that there is a critical point C corresponding to a critical value of $\Delta_c=3.453K$. For this critical point two symmetrical equally stable solutions of Q exist as we lower the temperature. Existence of such regions in the phase diagram is expected to introduce interesting consequences on the quadrupolar excitations in this system. The phase transition for the case of TmCd is found to be nearly of the first order. The observed first-order transition might be due to the anharmonic Jahn-Teller interactions.

B. TmZn

On the basis of the crystal-field levels given by Morin *et al.*⁵ for TmZn (with $x \approx -0.80$) we get $\alpha = -5.08$, $S = -1.18$, $q_3=12.0$, and $q_5=10.995$. TmZn orders ferromagnetically at $T_c \approx 10$ K. There is indication of a tetragonal distortion occurring at the same temperature. Also, the biquadratic pair interaction has been estimated to be important from the thermal variation of the elastic constants.⁵ Hence we can take TmZn as belonging to the Case 3 of Sec. II.

In Fig. 6 we give the thermal variation of M in this case as calculated from Eq. (7) for two different values of K . The first point to be noted in this case is that the inclusion of a small biquadratic interaction changes the transition to first order. So it would be interesting to measure the specific heat and to make conclusion about the or-

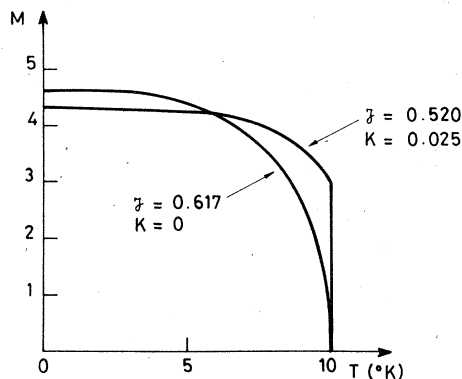


FIG. 6. Dipolar and quadrupolar ordering in TmCd. For $J=0.617$ and $K=0$, the transition is of second order at $T=10$ K. For $J=0.52$ and $K=0.025$, it is of first order at the same temperature.

der of transition in this compound. Secondly we get a spontaneous moment of about $4\mu_B$ at $T=0$. Experimentally, it is rather difficult to extrapolate the value of the magnetization in the limit of zero applied field in this system (Morin and Pierre, private communication). Also if we decrease J from the value 0.617 K to 0.42 K the transitions (dipolar and quadrupolar) occur at the same temperature but the transition temperatures are different below the value of $J=0.42$ K.

There may be other interesting examples of the $\Gamma_3 - \Gamma_5$ system. But it would be interesting to study the system $\text{TmCd}_x\text{Zn}_{1-x}$. We expect to get large range of values of J/K by doping TmCd with Zn and consequently the nature of transitions would also vary drastically. Theoretical analysis

of such a mixed system would also be of current interest. Also, fluctuations in the $\Gamma_3 - \Gamma_5$ system might be important. The possible effects of the coupling between different excitation modes in this system should be studied both theoretically and experimentally.

IV. CONCLUSIONS

We have studied here the nature of the possible phase transitions in the $\Gamma_3 - \Gamma_5$ system under molecular field approximation. It would be interesting to perform systematic measurements of magnetization, specific heat, lattice distortion, elastic constants etc. in RE compounds where the $\Gamma_3 - \Gamma_5$ model is applicable to verify how far the molecular-field approximation is valid. Also Mössbauer experiments on compounds such as TmCd or TmZn would give information about the thermal variation of Q . Specific-heat measurements at very low temperature and also NMR measurements of the hyperfine field and the nuclear-spin lattice relaxation time would give valuable information on the elementary excitations in this system. Neutron experiments on this system for studying the dispersion relations of the excitations would be worthwhile. Polarized neutron experiment to generate $\Delta M=2$ excitations, i.e., quadrupolar waves in this system at low temperature would be of current interest.¹⁶

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