

Magnetic and quadrupolar phase transitions in cubic rare-earth intermetallic compounds

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A new analytical approach of the problem of magnetic and quadrupolar phase transitions in rare-earth intermetallic compounds is presented, in terms of single-ion susceptibilities and within the Landau theory: The coefficients of the free-energy expansion are simply related to several magnetic, strain, and quadrupolar crystal-field susceptibilities, the expression of which is given for any multilevel system. The analysis of sign and relative magnitude of these susceptibilities leads to the different possible phase diagrams. Several examples are taken among the cubic rare-earth intermetallic compounds.

I. INTRODUCTION

The existence of quadrupolar interactions has been established in several cubic rare-earth intermetallic compounds for the last few years.^{1,2} The most obvious evidence is the possibility of a quadrupolar phase transition, as observed for example in TmCd (Ref. 3) and TmZn (Ref. 4): At a critical temperature T_Q —the quadrupolar ordering temperature—the $4f$ quadrupoles order through a first-order transition, without any magnetic dipolar ordering ($T_Q = 3.16$ K for TmCd). According to the strength of magnetic bilinear interactions, the magnetic $4f$ dipoles (the usual magnetic moments) may possibly order at a lower temperature T_D —the magnetic (dipolar) ordering temperature—as is the case for TmZn ($T_Q = 8.55$ K, $T_D = 8.12$ K).

In the case of bilinear interactions large enough with regard to quadrupolar interactions—the most frequent case—only one magnetic phase transition occurs at T_D and $T_Q = T_D$, since the quadrupoles necessarily follow the dipoles at the magnetic dipolar ordering. Nevertheless, the quadrupolar interactions may act on the nature of the magnetic phase transition: They may change a second-order transition into a first-order one, as observed for example in DySb,⁵ TmCu,⁶ or TbP,⁷ or vice versa, as in PrMg.⁸

Numerous theoretical works have been carried out concerning the existence of dipolar and quadrupolar phase transitions, in particular in systems with an effective spin $S = 1$,⁹ $S = \frac{3}{2}$,¹⁰ or $S = 2$.¹¹ In the presence of bilinear and quadrupolar interactions these systems are characterized by two order parameters, namely $M = g_J \mu_B \langle J_z \rangle$ and $Q = \langle 3J_z^2 - J(J+1) \rangle$, the temperature variations of which are derived within the molecular-field approximation (MFA). According to the Landau

theory, an expansion of the free energy is made as a function of M and Q in the vicinity of the critical temperatures.

In this paper we want to show how a perturbation theory in the nonordered phase may allow one to analytically obtain the first terms in this free-energy expansion relative to a classical Landau theory without fluctuations, in multilevel systems where the precise splitting of the $4f$ ground multiplet by the crystalline electric field (CEF) is fully taken into account. The coefficients of this expansion are found related to several single-ion susceptibilities; within the MFA, effects of symmetry breaking will not be considered here (Sec. II). The analysis of these susceptibilities may allow one to reach conclusions about the existence and the nature of magnetic and/or quadrupolar phase transitions: The case where the quadrupolar interactions transform a second-order magnetic dipolar transition into a first-order one will be particularly emphasized. In order to illustrate the discussion, examples will be given among the cubic rare-earth intermetallic compounds (Sec. III). The conclusion will be given in Sec. IV. The present work constitutes a new analytical approach of the problem of magnetic and quadrupolar phase transitions in rare-earth intermetallic compounds, in terms of single-ion CEF susceptibilities.

II. THEORY

A. The Hamiltonian

The Hamiltonian used for describing the magnetic properties of the $4f$ shell in cubic symmetry has been extensively described in the recent past.¹² It is developed by using the operator-equivalent method, and the MFA for the two-ion bilinear and quadru-

polar interactions. For one $4f$ ion it is written as

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_Z + \mathcal{H}_D + \mathcal{H}_Q + (E_D + E_Q), \quad (1)$$

where

$$\mathcal{H}_{\text{CEF}} = \frac{W_x}{F_4} O_4 + \frac{W(1-|x|)}{F_6} O_6. \quad (2)$$

Equation (2) is the usual cubic CEF Hamiltonian expressed in the fourfold axes system.¹³

$$\mathcal{H}_Z = -g_J \mu_B H J_z \quad (3)$$

represents the Zeeman coupling where the magnetic field H is assumed, in this paper, to be aligned with the z axis.

$$\mathcal{H}_D = -g_J \mu_B H_D J_z \quad (4)$$

is the Heisenberg-type bilinear interaction Hamiltonian written in the MFA as a function of the exchange field H_D acting on a given ion:

$$H_D = nM = ng_J \mu_B \langle J_z \rangle. \quad (5)$$

Note that n will always be taken as positive here; for an antiferromagnet, only one sublattice has to be considered.

$$\mathcal{H}_Q = -H_Q O_2^0 \quad (6)$$

is the quadrupolar Hamiltonian restricted to the tetragonal symmetry where H_Q is the quadrupolar field acting on a given ion,

$$H_Q = G_1 Q = G_1 \langle O_2^0 \rangle = G_1 \langle 3J_z^2 - J(J+1) \rangle. \quad (7)$$

Note that

$$G_1 = \frac{(B_1)^2}{c_{11}^0 - c_{12}^0} + K_1$$

is the total quadrupolar parameter associated with the tetragonal symmetry; it consists of a magneto-elastic contribution plus a two-ion quadrupolar contribution K_1 ; the two corresponding terms appear to

be isomorphous within the MFA after minimization of the free energy relative to the tetragonal strain (see Ref. 14). $E_D = \frac{1}{2} nM^2$ and $E_Q = \frac{1}{2} G_1 Q^2$ are corrective energy terms for, respectively, the dipolar and quadrupolar two-ion interactions originating in the MFA.

B. Perturbation theory

The magnetic properties associated with the above Hamiltonian may be derived from the thermodynamical analysis of the generalized Gibbs free energy $F = -kT \ln Z$, where $Z = \text{Tr} \exp(-\mathcal{H}/kT)$ is the partition function.¹⁵ According to the Landau theory, $F(T, H, M, Q)$ may be expanded in ascending powers of the two order parameters M and Q in the vicinity of the transition temperature. As explained in Ref. 15, $F(T, H, M, Q)$ coincides with the equilibrium Gibbs free energy $G(T, H)$ only when M and Q equal the equilibrium values of, respectively, the magnetization \bar{M} and the quadrupolar moment \bar{Q} . These thermal equilibrium values are obtained by minimizing the generalized free energy F ,

$$\left. \frac{\partial F}{\partial M} \right|_{\bar{M}, \bar{Q}} = \left. \frac{\partial F}{\partial Q} \right|_{\bar{M}, \bar{Q}} = 0.$$

However, it should be noted that M and Q are not fully independent order parameters; indeed, if a solution $\bar{M} = 0, \bar{Q} \neq 0$ is possible, the solution $\bar{M} \neq 0, \bar{Q} = 0$ is obviously meaningless (except a possible accidental cancellation of \bar{Q}). When the magnetic ordering occurs, Q , as all the higher rank of multipolar moments, is driven to be ordered, M remaining the principal order parameter.

The coefficients of the generalized free-energy expansion may be obtained (see the Appendix) by applying a perturbation theory to the zeroth-order Hamiltonian \mathcal{H}_{CEF} , up to the fourth order for H and M , and up to the third order for Q (the Q^3 term will be used only in Sec. III A). The expression of the generalized free energy F is then given by

$$F(T, H, M, Q) = F_{\text{CEF}} - \frac{1}{2} \chi_0 (H + nM)^2 - \frac{1}{4} \chi_0^{(3)} (H + nM)^4 - \frac{1}{2} \chi_s (G_1 Q)^2 - \frac{1}{3} \chi_s^{(2)} (G_1 Q)^3 - \chi_2^{(2)} G_1 Q (H + nM)^2 + \frac{1}{2} nM^2 + \frac{1}{2} G_1 Q^2, \quad (8)$$

where five single-ion susceptibilities are defined: χ_0 is the usual first-order paramagnetic susceptibility; $\chi_0^{(3)}$ is the third-order paramagnetic susceptibility which is related to the initial curvature of the magnetization curves¹⁴; χ_s is the strain susceptibility occurring in the elastic-constant analysis¹⁶; $\chi_s^{(2)}$ is the second-order strain susceptibility; $\chi_2^{(2)}$ is the quadrupolar field susceptibility which is involved in the

parastriction.¹² All these single-ion susceptibilities may be calculated at every temperature starting from the actual cubic CEF level scheme; they depend on the energy spacing and on the matrix elements of J_z and O_2^0 between all the CEF levels (see the Appendix). F_{CEF} is the free energy corresponding to \mathcal{H}_{CEF} alone.

The formalism developed above has been written

assuming the z axis to be parallel to the [001] direction (tetragonal symmetry). However, it could be easily transposed to the trigonal symmetry (z axis parallel to [111]). The bilinear interactions being isotropic, n is unchanged in the new system; however, G_1 has to be replaced by $\frac{1}{12}G_2$, G_2 being the trigonal quadrupolar parameter. The expression of the single-ion CEF susceptibilities remains the same, although their values differ (χ_0 excepted) due to the

$$F(T, H=0, M, Q) = F_{\text{CEF}} + \frac{1}{2}n(1-n\chi_0)M^2 - \frac{1}{4}n^4\chi_0^{(3)}M^4 + \frac{1}{2}G_1(1-G_1\chi_s)Q^2 - \frac{1}{3}G_1^3\chi_s^{(2)}Q^3 - n^2G_1\chi_s^{(2)}QM^2. \quad (9)$$

According to the Landau theory, two critical temperatures t_D and t_Q may be defined from Eq. (9) by canceling the coefficient of the M^2 and Q^2 terms, respectively (t_Q can be defined only if G_1 is positive):

$$1 - n\chi_0(t_D) = 0, \quad (10)$$

$$1 - G_1\chi_s(t_Q) = 0. \quad (11)$$

The actual phase diagram as well as the nature of the different transitions will then be determined by the relative magnitudes of t_D and t_Q , and by the signs and relative magnitudes of the other coefficients of Eq. (9).

A. Quadrupolar phase transition ($t_Q > t_D$)

First we consider the case where G_1 is positive and large enough relative to n for having $t_Q > t_D$. At $T = t_Q$ the free energy F is reduced to

$$F(t_Q, 0, 0, Q) = F_{\text{CEF}} - \frac{1}{3}G_1^3\chi_s^{(2)}Q^3. \quad (12)$$

Because of the odd Q^3 term, the quadrupolar transition is generally a first-order transition with a positive (negative) value of the order parameter Q when the susceptibility $\chi_s^{(2)}$ is positive (negative). The actual quadrupolar transition temperature T_Q is slightly higher than t_Q (see Fig. 1):

$$T_Q = t_Q^+ > t_Q,$$

which is a first-order transition.

Note that the quadrupolar transition may be of second order if $\chi_s^{(2)} \equiv 0$ and if the next term $-\frac{1}{3}G_1^4\chi_s^{(3)}Q^4$ in the Q expansion of the free energy is positive ($\chi_s^{(3)} < 0$). This occurs for instance for an isolated Γ_3 ground state^{11,17} or for any isolated Kramers level as ground state.¹⁸ In these cases the Curie-type contribution, only remaining in the expression of $\chi_s^{(2)}$ (see the Appendix), indeed vanishes. The quadrupolar ordering temperature is then

$$T_Q = t_Q,$$

which is a second-order transition.

new cubic CEF wave functions in the new axis system.¹⁴

III. DIPOLAR AND QUADRUPOLAR PHASE TRANSITIONS

Investigating the possible spontaneous phase transitions associated with the two order parameters M and Q requires one to analyze the behavior of the generalized free energy F in zero field:

1. Application: TmCd

A good example for illustrating the case of a quadrupolar phase transition is TmCd. In this compound a first-order quadrupolar phase transition occurs at $T_Q = 3.16$ K and there is no magnetic dipolar transition below this temperature.^{3,19} Various experiments have been performed in the nonordered phase ($T > T_Q$), giving fully consistent results: elastic constants,²⁰ parastriction,²¹ first- and third-order paramagnetic susceptibility.^{3,14} They have shown that the magnetic bilinear interactions are zero in TmCd ($n=0$), while the tetragonal quadrupolar parameters reach $G_1 = 13$ mK. Starting from these values, and from the cubic crystal-field parameters $W = 0.95$ K, $x = -0.34$, we deduce $t_Q \approx 3$ K. At this temperature $\chi_s^{(2)}$ is positive; therefore, the quadrupolar phase transition is expected to be of first order with a positive value of Q , as observed experimentally.³

B. Dipolar phase transition ($t_D > t_Q$)

1. First case: $G_1 = 0$

We now consider the case where n is large enough for giving $t_D > t_Q$. Let us first analyze the behavior of the system in the absence of quadrupolar interaction ($G_1 = 0$). At $T = t_D$ the free energy F is re-

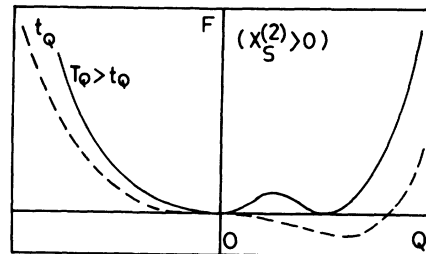


FIG. 1. Variation of the free energy at t_Q (dashed line) and T_Q (solid line) as a function of the order parameter Q , with $\chi_s^{(2)} > 0$.

duced to

$$F(t_D, 0, M, 0) = F_{\text{CEF}} - \frac{1}{4} n^4 \chi_0^{(3)} M^4. \quad (13)$$

Usually $\chi_0^{(3)}$ is negative; this leads to a second-order dipolar phase transition which occurs at (inset of Fig. 2)

$$T_D = t_D,$$

which is a second-order transition. However, in the presence of CEF, the third-order magnetic susceptibility $\chi_0^{(3)}$ may become positive at low temperature, according to the characteristics of the low-lying CEF levels, as for instance with a Γ_3 doublet as ground state^{11,14} (Fig. 3). Therefore, the dipolar phase transition becomes of first order and occurs at a temperature slightly higher than t_D (Fig. 2),

$$T_D = t_D^+ > t_D,$$

which is a first-order transition. To our knowledge, there is no unquestionable experimental example of such a situation in the literature; however, the present susceptibility formalism closely agrees with the calculations of Blume about the Γ_1 - Γ_5 system.²² Note that the limit between these two situations (namely $\chi_0^{(3)} = 0$) corresponds to the tricritical point C in the phase diagram (Fig. 3).

2. Second case: $G_1 \neq 0$

Let us now develop the case where $G_1 \neq 0$. The free energy F is written as

$$\begin{aligned} F(t_D, 0, M, Q) = & F_{\text{CEF}} - \frac{1}{4} n^4 \chi_0^{(3)} M^4 \\ & + \frac{1}{2} G_1 (1 - G_1 \chi_s) Q^2 \\ & - n^2 G_1 \chi_2^{(2)} Q M^2. \end{aligned} \quad (14)$$

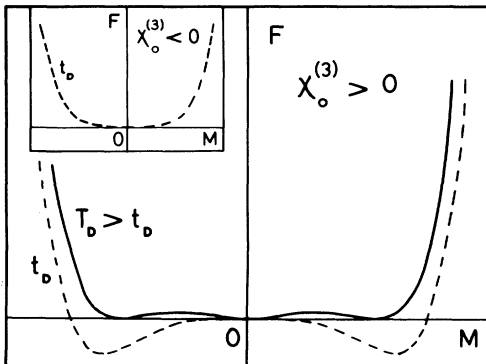


FIG. 2. Variation of the free energy at t_D (dashed line) and T_D (solid line) as a function of the order parameter M , with $\chi_0^{(3)} > 0$ (first-order transition); inset: case $\chi_0^{(3)} < 0$ (second-order transition).

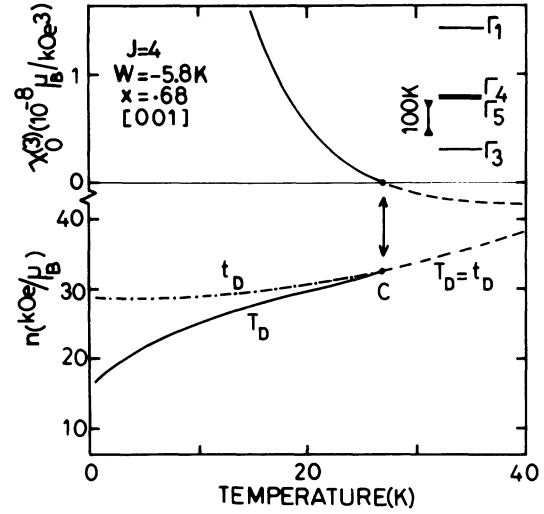


FIG. 3. Upper part: temperature variation of $\chi_0^{(3)}$ calculated for $J=4$ with the CEF parameters $W = -5.8$ K, $x = 0.68$ within the tetragonal symmetry (level scheme indicated on the right). Lower part: deduced magnetic phase diagram $n(T_D)$; the solid (dashed) line represents first- (second-) order transition; the tricritical point C occurs when $\chi_0^{(3)}$ vanishes; the semidotted line corresponds to $n(t_D)$.

However, as said above, Q is no longer an actual independent order parameter and must be related to M as soon as M is different from zero. This can be done by taking the limit of $Q(H)/[M(H)]^2$ when H goes to zero. Starting from Eq. (8) we deduce the following two expressions (see Ref. 14):

$$M = \frac{\chi_0}{1 - n\chi_0} H + \dots, \quad (15)$$

$$Q = \frac{\chi_2^{(2)}}{(1 - n\chi_0)^2 (1 - G_1 \chi_s)} H^2 + \dots, \quad (16)$$

whence we derive the following ratio between Q and M^2 , valid for small values of M and Q :

$$\frac{Q}{M^2} = \frac{\chi_2^{(2)}}{(\chi_0)^2 (1 - G_1 \chi_s)}. \quad (17)$$

Keeping this relation valid also at $T = t_D$ [when $1 - n\chi_0(t_D) = 0$], and inserting it in Eq. (14) gives

$$F(t_D, 0, M, Q) = F_{\text{CEF}} - \frac{1}{4} n^4 \chi_{M,0}^{(3)} M^4, \quad (18)$$

where

$$\chi_{M,0}^{(3)} = \chi_0^{(3)} + 2G_1 \frac{(\chi_2^{(2)})^2}{1 - G_1 \chi_s} \quad (19)$$

is the total third-order magnetic susceptibility including the quadrupolar contribution but without bi-

linear interactions (see Ref. 14).

The above discussion about the nature of the transition (Sec. III B 1) is then still valid, if we consider $\chi_{M,0}^{(3)}$ instead of $\chi_0^{(3)}$. In particular, a value of G_1 large enough may give $\chi_{M,0}^{(3)}$ as positive, even if $\chi_0^{(3)}$ is negative (Fig. 4); in this case the dipolar phase transition then becomes of first-order owing to the quadrupolar interactions, and occurs at a temperature T_D slightly higher than t_D (Fig. 5). This situation was already pointed out in particular systems, such as $S=1$ (Ref. 9) or $S=\frac{3}{2}$ (Ref. 10) systems. However, we emphasize that the present analysis is more general and can be applied to any multilevel system involving all the $(2J+1)$ CEF levels of the rare-earth metal. On the other hand, a large negative value of G_1 may give $\chi_{M,0}^{(3)}$ negative even if $\chi_0^{(3)}$ is positive; the dipolar phase transition then becomes of second order when it should be of first order without quadrupolar interactions. Finally, it should be pointed out that the condition $\chi_{M,0}^{(3)} > 0$ for a first-order magnetic phase transition is only sufficient, but not necessary. Indeed, very particular situations could give $\chi_{M,0}^{(3)} < 0$ and $\chi_{M,0}^{(5)}$ as strongly positive, for instance, leading to a first-order transition; however, this case should be rare.

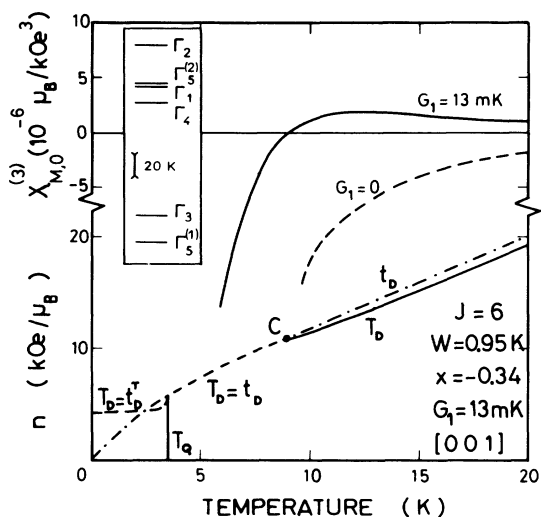


FIG. 4. Upper part: temperature variation of $\chi_{M,0}^{(3)}$ calculated for $J=6$ ($W=0.95$ K, $x=-0.34$, $G_1=13$ mK, tetragonal symmetry); for comparison, the curve with $G_1=0$ is also drawn (level scheme indicated on the left). Lower part: deduced magnetic phase diagram $n(T_D)$; the solid (dashed) line represents first- (second-) order transition; the tricritical point C occurs when $\chi_{M,0}^{(3)}$ vanishes; the semidotted line corresponds to $n(t_D)$; T_Q represents the quadrupolar ordering temperature; t_D^Q corresponds to the temperature t_D but in the quadrupolar phase.

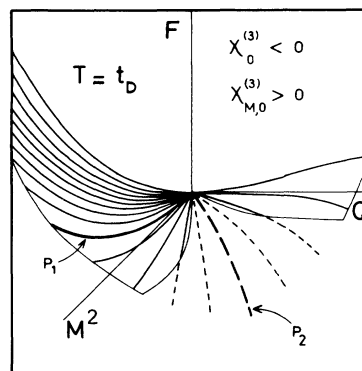


FIG. 5. Variation of the free energy at t_D as a function of the two order parameters M and Q , with $\chi_0^{(3)} < 0$ but $\chi_{M,0}^{(3)} > 0$; solid (dashed) lines correspond to positive (negative) values for F ; the P_1 line corresponds to the inset of Fig. 2 ($Q=0$); the P_2 line satisfies Eq. (17) and is analogous to the dashed line of Fig. 2.

3. Application: *TmCu*, *DySb*, *PrMg₂*

A good example of the effect of the quadrupolar interactions is given by *TmCu*. This compound orders at $T_N=7.7$ K in a modulated antiferromagnetic structure, with all moments parallel to the z axis.²³ The transition is of first-order. Various experiments performed in the paramagnetic state reliably provided the tetragonal quadrupolar parameter $G_1=11$ mK.⁶ Just above T_N and according to the cubic CEF parameters, the CEF third-order paramagnetic susceptibility $\chi_0^{(3)}$ is negative; this should lead to a second-order magnetic dipolar transition. However, the quadrupolar contribution to the total third-order magnetic susceptibility is positive and large enough to change the sign of $\chi_{M,0}^{(3)}$, in the vicinity of T_N , as seen experimentally.¹⁴ Consequently, the magnetic dipolar transition is expected to have a first-order character, as effectively observed.²³

Another analogous example may be taken in the rare-earth pnictides series. *DySb* indeed undergoes a first-order antiferromagnetic transition at $T_N=9.5$ K.²⁴ Numerous experimental and theoretical works have been made in this compound.²⁵ In particular, the use of the value $G_1=+1$ mK deduced from the fit of the elastic constants⁵ leads to a positive value of $\chi_{M,0}^{(3)}$ just above T_N , while the pure CEF contribution $\chi_0^{(3)}$ is negative. This positive value of $\chi_{M,0}^{(3)}$ above T_N explains the first-order character of the transition and should be detected experimentally by third-order paramagnetic susceptibility measurements.

An opposite example is *PrMg₂*. In this compound (which orders ferromagnetically at $T_c=10$ K), a

neutron spectroscopy experiment provided cubic crystal-field parameters giving a nonmagnetic doublet Γ_3 as the ground state.⁸ As said above (Sec. III B 1), this CEF configuration gives rise to a positive value for $\chi_0^{(3)}$ in the vicinity of T_c ; this should produce a magnetic transition with a first-order character, which is not observed experimentally. However, the G_1 value suggested in Ref. 8 for explaining the temperature dependence of the spontaneous magnetic moment, i.e., $G_1 = -13.3$ mK, leads to a negative total third-order magnetic susceptibility $\chi_{M,0}^{(3)}$. This now accounts for the second-order character of the transition.

C. Dipolar phase transition ($t_D < t_Q$)

The last case corresponds to a dipolar phase transition inside the quadrupolar phase ($T < T_Q$, see Sec. III A). Below T_Q the quadrupoles are ordered and the crystal field no longer has the cubic symmetry but the tetragonal symmetry. The various susceptibilities ($\chi_0, \chi_0^{(3)}, \dots$) therefore have new values ($\chi_0^T, \chi_0^{T(3)}, \dots$) according to the new tetragonal CEF level scheme. Note that this level scheme is now temperature dependent, like the ordered quadrupolar moment. We can then define a new critical temperature t_D^T , such that

$$1 - n\chi_0^T(t_D^T) = 0, \quad (20)$$

and a new expansion of the free energy F in zero field at $T = t_D^T$,

$$F^T(t_D^T, 0, M) = F_{\text{CEF}}^T - \frac{1}{4}n^4\chi_0^{T(3)}M^4. \quad (21)$$

Note that the Q terms in the expansion are now included in F_{CEF}^T since the system is quadrupolarly ordered. The discussion of the nature of the dipolar transition is the same as in Sec. III B 1, where $\chi_0^{(3)}$ is replaced by $\chi_0^{T(3)}$. According to the sign of $\chi_0^{T(3)}$ the dipolar phase transition has a first- or second-order character (see Fig. 4).

1. Application: TmZn

A particularly interesting example is given by TmZn, where bilinear and quadrupolar interactions are present together and generate a ferromagnetic ordering ($T_c = 8.12$ K) slightly below the quadrupolar ordering ($T_Q = 8.55$ K).⁴ Numerous studies of the properties in the cubic paramagnetic phase ($T > T_Q$) have been consistently described with a quadrupolar parameter $G_1 = 25$ mK.¹ According to the cubic CEF scheme, the critical temperature t_Q is then calculated to be $t_Q = 5.5$ K, with a positive value of $\chi_s^{(2)}$ in the range 5.5–10 K. This leads to a first-order quadrupolar transition at $T_Q > t_Q$, with a positive value for Q , as observed experimentally.⁴

Below T_Q the cubic ground state $\Gamma_5^{(1)}$ is split into a doublet and a nonmagnetic singlet which becomes the new ground state, and the bilinear interactions are strong enough to induce a magnetic dipolar ordering in the tetragonal phase. Calculations lead to a critical situation for T_c : The nature of the magnetic transition seems to be very sensitive to the values of the various parameters. For instance, T_c is calculated to be of first order for $G_1 = 25$ mK, but would be of second order for $G_1 = 28$ mK, as it experimentally appears.⁴ Consequently, the situation of TmZn with regard to the ferromagnetic transition seems to be not far from a tricritical point.¹¹ In addition, a small shift of some parameters seems to occur below T_Q .²⁶ This makes a more precise and complete description of the ferromagnetic transition difficult.

IV. CONCLUSION

The present work constitutes a new analytical approach to the problem of magnetic (dipolar) and quadrupolar phase transitions in rare-earth intermetallic compounds, in terms of single-ion CEF susceptibilities, related to the Landau free-energy expansion. It is more general than the effective-spin models previously used since the formulation is valid for any multilevel system. In particular, the coefficients in the M and Q development of the free energy are simply related to several single-ion CEF (magnetic, strain, and quadrupolar) susceptibilities. Analyzing the sign and relative magnitudes of these susceptibilities with regard to the two-ion interaction parameters allows one to deduce the possible existence and the nature of magnetic dipolar and/or quadrupolar phase transitions.

In comparison with previous results from effective-spin calculations, one has to note that the inclusion of the $2J + 1$ actual wave functions may sometimes modify the conclusions relative to the phase transitions. For instance, in the Γ_3 - Γ_5 system, the existence of a Γ_5 level at a finite energy above the ground level Γ_3 changes the character of the quadrupolar phase transition from second to first order through the van Vleck quadrupolar matrix elements between Γ_3 and Γ_5 .^{11,17} It is therefore more prudent to take into account all the CEF levels in actual systems rather than only the ground state; this is done easily with the present formulation.

The present approach to phase transitions may be also compared with the cubic model²⁷ which has been applied to HoSb in particular. This cubic model was developed for explaining the magnetic properties of a sixfold degenerate CEF ground state in the presence of an external field and/or quadrupolar pair interactions. HoSb seems to be close to

such a situation in the $J=8$ CEF diagram.¹³ An analysis of this system within the present susceptibility formalism leads to the same conclusions as the cubic model: HoSb is close to being tricritical,²⁸ in the sense that the third-order magnetic susceptibility $\chi_0^{(3)}$ is very close to zero in the transition temperature range, and thus the nature of the antiferromagnetic transition is very sensitive to the presence of quadrupolar interactions.

Another interesting feature of the present analysis is its analytical treatment, which appears to be less difficult than any self-consistent calculation, as well as its applicability to systems with fourfold or threefold easy-magnetization directions. For example, starting from the parameters given in Ref. 2 for some terbium mononictides (TbP, TbAs, TbSb, and TbBi), the present formalism provides the same conclusions relative to the nature of their antiferromagnetic transitions: The calculated values of $\chi_{M,0}^{(3)}$ (M along a $\langle 111 \rangle$ axis) are positive at T_N for TbP and TbAs, and negative for TbSb and TbBi, in agreement with the experimental character of their phase transition, which is, respectively, first and second order. In addition, we find that the transition in TbSb is close to first order; $\chi_{M,0}^{(3)}$ changes its sign at 13 K due to the trigonal quadrupolar coupling, i.e., not far below $T_N=15.5$ K.

It would be very interesting to confirm these analyses by a direct measurement of $\chi_M^{(3)}$ in the paramagnetic range for Tb pnictides as well as for other compounds such as HoSb, DySb, or PrMg₂. It is worth noticing that it is important to know all the

involved parameters well, in particular the crystal-field and the quadrupolar parameters, by means of various and independent experiments, in order to have a reliable ground for the interpretation of the magnetic properties. When these precautions have been taken the analysis within the present formalism and in the molecular-field approximation has always been found to be consistent with experiment.

APPENDIX

In a first stage we define the eigenvalues E_i and the eigenvectors $|ik\rangle$ corresponding to the Hamiltonian \mathcal{H}_{CEF} alone,

$$\mathcal{H}_{\text{CEF}}|ik\rangle = E_i|ik\rangle.$$

In each subspace i the $|ik\rangle$ have to be adapted to the perturbation Hamiltonian. A perturbation theory up to the fourth order for H and to the third-order for Q allows us to obtain the analytical expressions of the perturbed energies E_{ik} :

$$E_{ik} = E_i + \sum_{n=1}^4 E_{ik}^{(n)} + \dots$$

Then the partition function Z ,

$$Z = \sum_{i,k} e^{-\beta E_{ik}},$$

can be calculated (with $\beta=1/k_B T$, k_B being the Boltzmann constant and T the temperature). One then obtains

$$Z = Z_{\text{CEF}} \left\{ 1 + \frac{1}{2} \beta \chi_0 (H + nM)^2 + \frac{1}{2} \beta \chi_s (G_1 Q)^2 + \beta \chi_2^{(2)} G_1 Q (H + nM)^2 + \frac{1}{4} \beta [\chi_0^{(3)} + \frac{1}{2} \beta (\chi_0)^2] (H + nM)^4 + \frac{1}{3} \beta \chi_s^{(2)} (G_1 Q)^3 + \dots \right\},$$

which leads to the expression of the total free energy $F = -k_B T \ln Z$ [Eq. (9)].

The expression of the five CEF susceptibilities χ_0 , χ_s , $\chi_2^{(2)}$, $\chi_0^{(3)}$, and $\chi_s^{(2)}$ are given by the following:

$$\begin{aligned} \chi_0 &= g_J^2 \mu_B^2 \sum_{i,k} f_i \left[-2 \sum_{j \neq i,l} \frac{|J_{ik,jl}|^2}{E_i - E_j} + \frac{1}{k_B T} |J_{ik,ik}|^2 \right], \\ \chi_s &= \sum_{i,k} f_i \left[-2 \sum_{j \neq i,l} \frac{|Q_{ik,jl}|^2}{E_i - E_j} + \frac{1}{k_B T} |Q_{ik,ik}|^2 \right], \\ \chi_2^{(2)} &= g_J^2 \mu_B^2 \sum_{i,k} f_i \left[\sum_{j \neq i,l} \sum_{j' \neq i,l'} \frac{J_{ik,jl} Q_{j'l',ik} J_{j'l',ik} + 2 Q_{ik,jl} J_{j'l',ik} J_{j'l',ik}}{(E_i - E_j)(E_i - E_{j'})} \right. \\ &\quad \left. - \sum_{j \neq i,l} \frac{|J_{ik,jl}|^2 Q_{ik,ik} + 2 Q_{ik,jl} J_{j'l',ik} J_{j'l',ik}}{(E_i - E_j)} \left[\frac{1}{E_i - E_j} + \frac{1}{k_B T} \right] + \frac{1}{2(k_B T)^2} |J_{ik,ik}|^2 Q_{ik,ik} \right], \end{aligned}$$

$$\chi_0^{(3)} = -\frac{1}{2k_B T} (\chi_0)^2 + g_J^4 \mu_B^4$$

$$\times \sum_{i,k} f_i \left[-4 \sum_{\substack{j \neq i, l \\ j' \neq i, l' \\ j'' \neq i, l''}} \frac{J_{ik,jl} J_{jl,j'l'} J_{j'l',j''} J_{j''l'',ik}}{(E_i - E_j)(E_i - E_{j'})(E_i - E_{j''})} \right.$$

$$+ 2 \sum_{\substack{j \neq i, l \\ j' \neq i, l'}} \frac{|J_{ik,jl}|^2 |J_{ik,j'l'}|^2 + 2J_{ik,jl} J_{jl,j'l'} J_{j'l',ik} J_{ik,ik}}{(E_i - E_j)(E_i - E_{j'})} \left[\frac{2}{E_i - E_j} + \frac{1}{k_B T} \right]$$

$$\left. - 2 \sum_{j \neq i, l} \frac{|J_{ik,ik}|^2 |J_{ik,jl}|^2}{(E_i - E_j)} \left[\frac{2}{(E_i - E_j)^2} + \frac{2}{(E_i - E_j)k_B T} + \frac{1}{k_B^2 T^2} \right] + \frac{1}{6k_B^3 T^3} |J_{ik,ik}|^4 \right],$$

$$\chi_s^{(2)} = \sum_{i,k} f_i \left[3 \sum_{j \neq i, l} \sum_{j' \neq i, l'} \frac{Q_{ik,jl} Q_{jl,j'l'} Q_{j'l',ik}}{(E_i - E_j)(E_i - E_{j'})} \right.$$

$$\left. - 3 \sum_{j \neq i, l} \frac{Q_{ik,ik} (Q_{ik,jl})^2}{(E_i - E_j)} \left[\frac{1}{E_i - E_j} + \frac{1}{k_B T} \right] + \frac{1}{2k_B^2 T^2} (Q_{ik,ik})^3 \right],$$

where

$$J_{ik,jl} = \langle ik | J_z | jl \rangle,$$

$$Q_{ik,jl} = \langle ik | O_2^0 | jl \rangle$$

are the matrix elements of J_z and O_2^0 between the cubic CEF levels. For each degenerated CEF level i ,

$$f_i = \frac{1}{Z_{\text{CEF}}} e^{-\beta E_i} = e^{-\beta E_i} / \sum_{i,k} e^{-\beta E_i}$$

is the Boltzmann population factor.

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