Specific heat in some gadolinium compounds. II. Theoretical model

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A detailed thermodynamical analysis of commensurate and incommensurate magnetic phases in localized magnetic systems within a mean-field theory is presented. Interesting results are obtained concerning the specific heat of amplitude-modulated magnetic structures: In particular, the specific-heat discontinuity at the ordering temperature T_N is reduced by a factor of $\frac{2}{3}$ relative to that expected in ferromagnetic or helimagnetic structures. In addition, the exact shape of the specific-heat curves strongly depends on the relative magnitude of the successive exchange couplings $J(n\mathbf{Q})$. Under certain conditions, the maximum of specific heat at T_N is shifted to a temperature lower than T_N. Recent experimental data on $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$, and $GdCu_5$ compounds support very well these peculiarities.

I. INTRODUCTION

In the preceding paper,[1] a detailed experimental study of the magnetic contribution to the specific heat in several Gd intermetallic compounds led to the conclusion that the exact shape of this thermodynamical property over the whole ordered state closely reflects the type of magnetic ordering involved. In particular a fundamental distinction has to be made between equal-moment (EM) and amplitude-modulated (AM) systems. The first category includes ferromagnetic, simple antiferromagnetic but also helical and cycloidal magnetic structures, although these latter two are usually incommensurate with the lattice periodicity. In the second category, the magnetic moment amplitude varies periodically from one site to another, evolving from a sine-wave shape immediately below the ordering temperature T_N to an antiphase-type one (with equal moments) at low temperature.

In many systems, both types of EM and AM arrangements are successively observed according to the temperature: indeed the AM arrangement is often stabilized immediately below T_N, due to a particular shape of the Fourier transform $J(\mathbf{q})$ of the exchange interactions. However, at lower temperature due to entropy effects associated with the modulation of the magnetic moment amplitude, the spin system may[2,3] (i) suddenly jump through a first-order transition to an EM structure often having a different propagation vector or (ii) keep the same propagation vector and evolve toward a full antiphase structure at 0 K, through the progressive squaring up of the modulation; this is accompanied by the growth of high-order harmonics of the propagation vector. Only this latter case will be considered in the present paper, and the assumption will be made that the conditions required to stabilize this AM state with regard to other incommensurate states with equal moments, e.g., helical, are satisfied by an appropriate additional term in the free energy. For example, a weak crystal-field anisotropy or an anisotropy in the exchange coupling can lead to the existence of a preferential direction for the magnetic moments, preventing the system from ordering within a helical magnetic structure.[4]

It has been shown[1] that the well-known λ anomaly observed on the temperature dependence of the specific heat in ferromagnets and more generally in EM compounds is strongly reduced in magnitude and possibly smoothed off in AM systems. It is the purpose of the present work to extensively develop the theoretical model which is able to account for these properties, within the frame of the mean-field approximation. The main features of this model have been published recently[2,3] and will be widely developed and extended below. Section II is devoted to the description of the formalism used in our model. The behavior of specific heat near the ordering temperature is investigated in Sec. III. The next section shows the theoretical specific-heat curves calculated for various situations. A discussion is made in the last section.

II. FORMALISM

The present model is based on the Heisenberg Hamiltonian describing the isotropic bilinear exchange interactions between total angular momenta $\mathbf{J}$ of rare earth at the sites i and j:

$$\mathcal{H}=-\tfrac{1}{2}\sum_i \sum_{j\,(\neq i)} J(ij)\mathbf{J}(i)\cdot\mathbf{J}(j)\ . \tag{1}$$

Here we will focus on the case of gadolinium, i.e., $J=\frac{7}{2}$ and no crystal-field effects. Moreover, magnetic fluctuations above the ordering temperature T_N as well as collective excitations below T_N will not be considered. Within the mean-field approximation, the interaction produced on the ith site by all the others is replaced by the following effective exchange field:

$$\mathbf{H}_{ex}(i)=(g_J\mu_B)^{-2}\sum_{j\,(\neq i)} J(ij)\langle\mathbf{M}(j)\rangle\ , \tag{2}$$

where $\langle\mathbf{M}\rangle=g_J\mu_B\langle\mathbf{J}\rangle$ is the magnetic moment of the rare earth calculated by thermal average on the $2J+1$ quantum levels of the $4f$ ion.

The main purpose of the present work is to consider the case of an amplitude-modulated magnetic structure in which the magnitude of the magnetic moments may be expanded in a Fourier series as

$$\langle \mathbf{M}(j) \rangle = \sum_{n\,(\neq 0)} \mathbf{M}_{n\mathbf{Q}} e^{in\mathbf{Q}\cdot\mathbf{R}_j} , \tag{3}$$

where $\mathbf{Q}$ is the propagation vector of the incommensurate structure and $\mathbf{M}_{-n\mathbf{Q}} = \mathbf{M}^*_{n\mathbf{Q}}$ so that $\mathbf{M}(j)$ is real. In the absence of external magnetic field, and due to the symmetry, only the odd values of n have to be considered. For the sake of simplicity, we will restrict ourselves to the case of a collinear structure where all the moments and accordingly the Fourier components $\mathbf{M}_{n\mathbf{Q}}$ are aligned along the same direction, e.g., the z direction. It can be noticed that the relative magnitude of the $\mathbf{M}_{n\mathbf{Q}}$'s is closely connected with the degree of squaring of the modulated structure, this latter evolving from a quasisinusoidal structure just below T_N towards a full antiphase one at 0 K (see below).

Inserting (3) in (2) provides a new expression for the exchange field:

$$\mathbf{H}_{\text{ex}}(i) = (g_J \mu_B)^{-2} \sum_{n\,(\neq 0)} J(n\mathbf{Q}) \mathbf{M}_{n\mathbf{Q}} e^{in\mathbf{Q}\cdot\mathbf{R}_i} , \tag{4}$$

where $J(\mathbf{q})$ is the Fourier transform of the exchange interactions $J(ij)$. Equation (4) shows that the exchange field is also periodic with the same periodicity as the magnetic moment, its harmonics $\mathbf{H}_{n\mathbf{Q}}$ being related to the corresponding ones $\mathbf{M}_{n\mathbf{Q}}$ through the relations

$$\mathbf{H}_{n\mathbf{Q}} = (g_J \mu_B)^{-2} J(n\mathbf{Q}) \mathbf{M}_{n\mathbf{Q}} . \tag{5}$$

This equation shows that the periodic shape of the exchange field does not necessarily follow that of the magnetic moment, so that various behaviors should be expected according to the relative values of the couplings $J(n\mathbf{Q})$. For example, the exchange field remains sinusoidal at any temperature if only the first coefficient $J(\mathbf{Q})$ is taken into consideration, whatever the values of the $\mathbf{M}_{n\mathbf{Q}}$'s. The $J(n\mathbf{Q})$'s appear therefore as a kind of "filter" which can strengthen, weaken, or neutralize the effect of the different magnetic harmonics on the exchange field (see Fig. 1).

The effective Hamiltonian may now be written as

$$\mathcal{H} = -\sum_i \mathbf{M}(i) \cdot \mathbf{H}_{\text{ex}}(i) + \tfrac{1}{2} \sum_i \langle \mathbf{M}(i) \rangle \cdot \mathbf{H}_{\text{ex}}(i) , \tag{6}$$

where the second term is a corrective energy term due to the mean-field treatment, because in the first summation

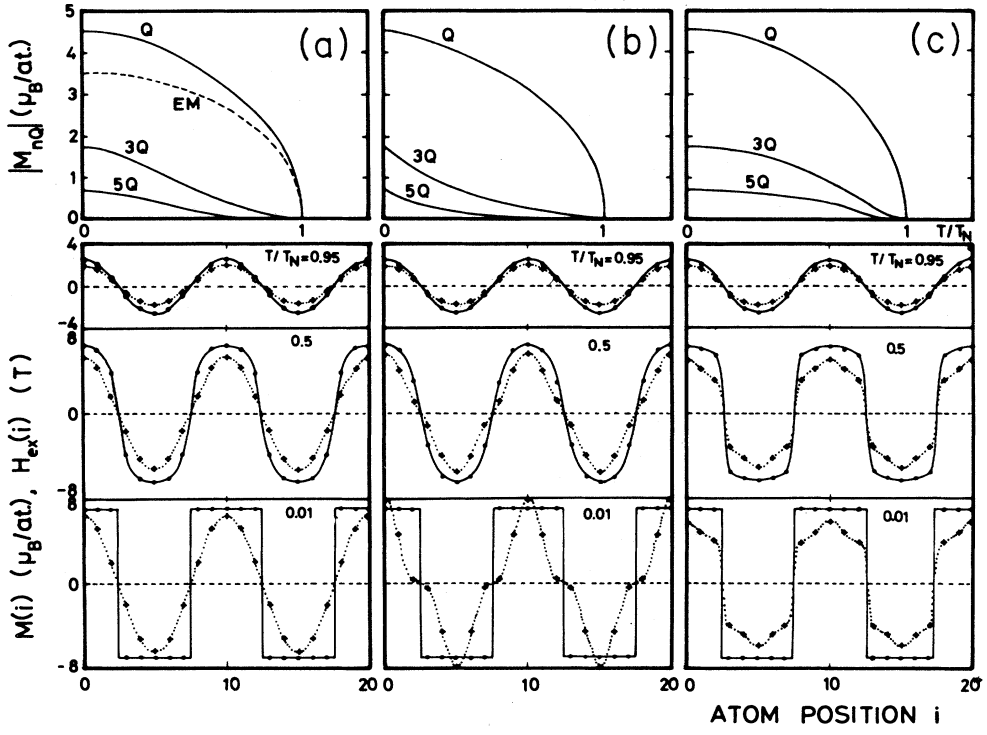

FIG. 1. Upper part: calculated variation of the Fourier harmonics $|M_{n\mathbf{Q}}|$ of the magnetic moments ($n=1,3,5$) vs the reduced temperature T/T_N for various exchange coefficients: (a) $J(Q)=10$; (b) $J(Q)=10$, $J(3Q)=-8$; (c) $J(Q)=10$, $J(3Q)=5.67$, $J(5Q)=8$; the dashed line represents the variation of $\frac{1}{2}M_0$, M_0 being the magnetic moment in the ferromagnetic or EM case. Lower part: corresponding spatial variation of the magnetic moments (circles, continuous lines) and associated exchange fields (crosses, dotted lines) as a function of the atom position along the propagation vector, at different reduced temperatures T/T_N. Note that the exchange field shape does not follow that of the magnetic moment because of the different relative amplitudes of the $J(nQ)$'s.

over i, each pair is counted twice. For a long-period commensurate structure, this Hamiltonian reduces to an N-site Hamiltonian, N being the number of magnetic ions over one or several periods, i.e., i runs from 1 to N. Obviously an AM structure strictly incommensurate with the lattice cannot be exactly described by this model, however, it can always be approximated by a long-period commensurate structure with a nearly identical propagation vector. As N becomes large, there should not be fundamental differences between the results obtained with both types of structure.

The N-site Hamiltonian, Eq. (6), has to be diagonalized in a self-consistent manner for the N ions, i.e., the Fourier coefficients $\mathbf{M}_{n\mathbf{Q}}$ calculated after diagonalization must be reinjected into the Hamiltonian through Eq. (4) until the self-consistency is achieved. This procedure has to be carried out at each temperature below T_N. That leads to a different temperature dependence for the different $\mathbf{M}_{n\mathbf{Q}}$'s, giving rise to a thermal evolution of the shape of the moment modulation (see Fig. 1). Just below the ordering temperature T_N, the leading term is the first harmonic $\mathbf{M}_{\mathbf{Q}}$ (see below), and the modulation is mainly sinusoidal. As the temperature is lowered, the other harmonics $N=3,5,\ldots$ must appear and ultimately, at 0 K, the full antiphase-type structure is reached, i.e., all the moments have equal magnitude M_0; the successive harmonics are then related to each other by

$$M_Q=M_{-Q}=\frac{2}{\pi}M_0;\quad M_{3Q}=M_{-3Q}=-\tfrac{1}{3}M_Q\ ;$$
$$M_{5Q}=M_{-5Q}=\tfrac{1}{5}M_Q;\ldots . \tag{7}$$

The way the whole squaring process takes place between T_N and 0 K is associated with the relative variation of the various $\mathbf{M}_{n\mathbf{Q}}$'s and depends on the relative magnitude of $J(\mathbf{Q}),J(3\mathbf{Q}),J(5\mathbf{Q}),\ldots$ through Eq. (5) and the self-consistency (see Fig. 1).

In the last stage, the internal energy can be calculated for each ion at any temperature as

$$U_i=-\tfrac{1}{2}\langle\mathbf{M}(i)\rangle\mathbf{H}_{\rm ex}(i)\ . \tag{8}$$

Averaging these values over one period provides the mean internal energy U per magnetic ion, the expression of which is written, using Eqs. (3) and (4), as

$$U=\frac{1}{N}\sum_{i=1}^{N}U_i=-\tfrac{1}{2}(g_J\mu_B)^{-2}\sum_{n\ (\neq 0)}J(n\mathbf{Q})|M_{n\mathbf{Q}}|^2\ . \tag{9}$$

It is worth noting that this general expression is no more valid for a simple commensurate propagation vector, i.e., $\mathbf{Q}=0$ or $\frac{1}{2}\mathbf{K}$ where $\mathbf{K}$ is a reciprocal lattice vector, because a complete Fourier expansion of the moments is no longer needed. In that case, the approximate expression for one magnetic ion is

$$U_0=-\tfrac{1}{2}(g_J\mu_B)^{-2}J(\mathbf{Q})|M_0|^2\ , \tag{10}$$

the magnetic moment being $\pm\mathbf{M}_0$. Note also that for the incommensurate antiphase structure, at 0 K, the relations (7) lead to the following expression for the internal energy:

$$U(\text{antiphase})=-\frac{4}{\pi^2}(g_J\mu_B)^{-2}|\mathbf{M}_0|^2 \times[J(\mathbf{Q})+\tfrac{1}{9}J(3\mathbf{Q})+\tfrac{1}{25}J(5\mathbf{Q})+\cdots]\ . \tag{11}$$

The propagation vector being usually defined as that where $J(\mathbf{Q})$ is maximum, it follows that all the $J(n\mathbf{Q})$'s $(n\neq 1)$ are smaller than $J(\mathbf{Q})$, then a lower limit for $U(\text{antiphase})$ is

$$U(\text{antiphase})\geq-\frac{4}{\pi^2}(g_J\mu_B)^{-2}J(\mathbf{Q})|\mathbf{M}_0|^2 \times(1+\tfrac{1}{9}+\tfrac{1}{25}+\cdots)=U_0\ , \tag{12}$$

the equality occurring in the only case where $J(n\mathbf{Q})=J(\mathbf{Q})$ for all n, i.e., the simple commensurate structure quoted above ($\mathbf{Q}=0$ or $\frac{1}{2}\mathbf{K}$).

Finally, the specific heat C is easily obtained by performing the thermal derivative of U at any temperature. From the above considerations, various behaviors may be expected for the temperature dependence of C, according to the relative magnitude of the $J(n\mathbf{Q})$'s and through the different thermal variations of the $M_{n\mathbf{Q}}$'s. As well, the C versus T variation in incommensurate AM systems will be shown to strongly differ from that of simple commensurate structures. That will be the purpose of the next sections.

III. BEHAVIOR OF $C(T)$ NEAR THE CRITICAL TEMPERATURE

The critical behavior of the specific heat $C(T)$ in the vicinity of the ordering temperature T_N can be analytically obtained by using an expansion of the magnetic moment at each site as a function of the corresponding exchange field:

$$\langle M(i)\rangle=g_J\mu_B J\mathcal{B}_J(g_J\mu_B H_{\rm ex}(i)/k_BT) =\frac{C^{(1)}}{T}H_{\rm ex}(i)+\frac{C^{(3)}}{T^3}[H_{\rm ex}(i)]^3 +\frac{C^{(5)}}{T^5}[H_{\rm ex}(i)]^5+\cdots\ , \tag{13}$$

where $\mathcal{B}_J(x)$ is the Brillouin function giving the magnetic response of the system to an external or an effective magnetic field. Note that the vectors are no longer used in this equation, because here we restrict our analysis to a collinear AM structure. The $C^{(n)}$'s are the Curie constants of nth order:

$$C^{(1)}=(g_J\mu_B)^2J(J+1)/(3k_B)\ ,$$
$$C^{(3)}=-(g_J\mu_B)^4J(J+1)(2J^2+2J+1)/(90k_B^3)\ , \tag{14}$$
$$C^{(5)}=(g_J\mu_B)^6[(2J+1)^6-1]/(30\,240k_B^5)\ .$$

Replacing $\langle M(i)\rangle$ and $H_{\rm ex}(i)$ by their Fourier expansion [Eqs. (3) and (4)] in Eq. (13) and identifying the corresponding Fourier harmonics provides a nonlinear system of coupled equations in $M_Q,M_{3Q},\ldots$. This system can be solved by expanding the $M_{n\mathbf{Q}}$'s in ascending (odd)

powers of the reduced variable $t=(1-T/T_N)^{1/2}$ and by identifying the corresponding terms in $t,t^3,\ldots$. At the first order, the ordering temperature T_N is derived:

$$T_N=(g_J\mu_B)^{-2}C^{(1)}J(\mathbf{Q})=J(J+1)J(\mathbf{Q})/(3k_B)\ . \tag{15}$$

The next two orders in perturbation provide the temperature dependence of the first two harmonics of the magnetic moment Fourier expansion:

$$M_Q=\left[-\frac{1}{3}\frac{(C^{(1)})^3}{C^{(3)}}\right]^{1/2}t(1-A_QT^2+\cdots)\ , \tag{16}$$

$$M_{3Q}=-\frac{1}{3}\left[-\frac{1}{3}\frac{(C^{(1)})^3}{C^{(3)}}\right]^{1/2}\frac{t^3}{1-J(3Q)/J(Q)}+\cdots\ , \tag{17}$$

with

$$A_Q=\frac{1-\frac{7}{6}J(3Q)/J(Q)}{1-J(3Q)/J(Q)}-\frac{5}{9}\frac{C^{(1)}C^{(5)}}{(C^{(3)})^2}\ . \tag{18}$$

More generally it could be shown that M_{nQ} varies as t^n in the vicinity of T_N.[4] For completeness, the corresponding relations for the initial temperature dependence of the magnetic moment M_0 in the simple commensurate case are

$$M_0=\left[-\frac{(C^{(1)})^3}{C^{(3)}}\right]^{1/2}t(1-A_0t^2+\cdots) \tag{19}$$

with

$$A_0=1-\frac{1}{2}\frac{C^{(1)}C^{(5)}}{(C^{(3)})^2}\ , \tag{20}$$

the ordering temperature T_N (or T_c for $Q=0$) being given by the same expression as Eq. (15).

Inserting Eq. (16) in Eq. (9) provides the first two terms in the t expansion of U, the thermal derivative of which gives the following expression for $C(T)$ near T_N:

$$C(T)=\Delta C_{\mathrm{AM}}+C'_{\mathrm{AM}}\frac{T-T_N}{T_N}+\cdots\ . \tag{21}$$

The first term

$$\Delta C_{\mathrm{AM}}=-\frac{1}{3}\frac{(C^{(1)})^2}{C^{(3)}}=\frac{10}{3}\frac{J(J+1)}{2J^2+2J+1}k_B \tag{22}$$

is the amplitude of the specific-heat discontinuity at T_N, the value of C vanishing above T_N in the mean-field approximation.[5–7] The second (linear) term in Eq. (21) provides the slope of the C versus T variation immediately below T_N:

$$C'_{\mathrm{AM}}=-\frac{4}{3}\frac{(C^{(1)})^2}{C^{(3)}}A_Q=\frac{40}{3}\frac{J(J+1)}{2J^2+2J+1}A_Qk_B\ . \tag{23}$$

Equations (22) and (23) have to be compared with the corresponding expressions for simple commensurate structures or more generally EM systems:

$$C_{\mathrm{EM}}(T)=\Delta C_{\mathrm{EM}}+C'_{\mathrm{EM}}\frac{T-T_N}{T_N}+\cdots \tag{24}$$

with

$$\Delta C_{\mathrm{EM}}=-\frac{1}{2}\frac{(C^{(1)})^2}{C^{(3)}}=\frac{5J(J+1)}{2J^2+2J+1}k_B \tag{25}$$

and

$$C'_{\mathrm{EM}}=-2\frac{(C^{(1)})^2}{C^{(3)}}A_0=\frac{20J(J+1)}{2J^2+2J+1}A_0k_B\ . \tag{26}$$

The first consequence of these relations [Eqs. (22) and (25)] is that *the jump of specific heat at T_N for AM systems is $\frac{2}{3}$ of that expected in EM systems.* This is an important result of the present study because it should allow one to distinguish, in principle, between helical and amplitude-modulated magnetic structures. Indeed, these latter are both incommensurate and there often subsists an ambiguity between both cases from experimental data. For example, they may produce the same neutron diffraction pattern. In such cases, the specific heat may appear as a useful macroscopic probe in the determination of the actual magnetic structure. The strong reduction of the specific-heat discontinuity at T_N for AM systems can be qualitatively explained by considering that only a part of the magnetic ions have been ordered at T_N, the others remaining in a state close to the paramagnetic one so that they contribute only a little to the variation of the internal energy.

The second important consequence of the above analytical treatment is the *dependence of the slope of C at T_N on the ratio $r=J(3Q)/J(Q)$ for AM systems* [see Eqs. (18) and (23)]. It follows that there exists a critical value r_c (≈ 0.567 for $J=\frac{7}{2}$) for which the slope C'_{AM} vanishes at T_N (see Fig. 2). Moreover, for r values ranging from r_c to 1, the slope of C at T_N is *negative,* leading to the original feature that a maximum of specific heat must occur at a temperature below T_N (see below). This is a quite exotic behavior since the mean-field theory always predicts a maximum of specific heat at the critical temperature.[5–7] From these results, various behaviors are expected for the temperature dependence of C in AM systems; these will

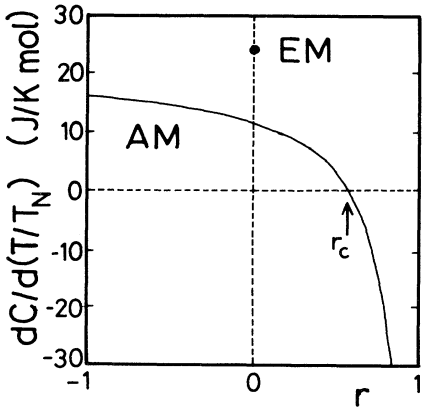

FIG. 2. Calculated dependence of the slope of specific heat immediately below T_N on the ratio $r=J(3Q)/J(Q)$ for AM systems; for comparison, the slope for EM structures is also reported: r_c is the critical ratio for which the slope vanishes at T_N.

be shown in the next section for several particular situations.

IV. THERMAL DEPENDENCE OF THE SPECIFIC HEAT

In this section, several theoretical variations of the specific heat calculated with the present formalism are presented for some particular values of $J(n\mathbf{Q})$. First, the effect of the incommensurability is emphasized in Fig. 3, where the calculated specific heat for an AM structure with only one exchange coefficient $J(\mathbf{Q})$ is shown together with the ferromagnetic result for comparison. Here N has been taken as 10, i.e., the propagation vector is $|\mathbf{Q}|=0.1$ in reduced units, in order to be able to describe one full period. The associated modulated structure then is long-period commensurate, but we expect the same behavior for any other $|\mathbf{Q}|$ value strictly incommensurate. The Fourier expansion has been limited up to the fifth term as well, i.e., at most three exchange coefficients $J(\mathbf{Q}),J(3\mathbf{Q}),J(5\mathbf{Q})$ are considered. Moreover, for the sake of comparison, all the calculated curves are drawn versus the reduced temperature T/T_N.

For the ferromagnetic case, identical to any EM case (simple antiferromagnetic or helical), the well-known λ anomaly at T_N is calculated with the present formalism by taking $Q=0$. The jump of C at T_N is in agreement with the exact value $\Delta C_{\mathrm{EM}}=20.15$ J/K mol. In addition, a hump arises around $T/T_N\approx 0.25$: it corresponds to a Schottky-like anomaly in the ordered state involving quantum levels the energy position of which depends on the temperature through the thermal variation of the exchange field. Although its origin has never been well explained in the literature,[5,6,8,9] it arises naturally within the mean-field theory for a $(2J+1)$-fold degenerate multiplet.

For the most simple AM case, namely, one single exchange coefficient $J(\mathbf{Q})$, a λ-like anomaly is also calculated (see Fig. 3), but with a discontinuity at T_N strongly reduced with regard to the EM case, as predicted by the above analytical treatment (see Sec. III). Consequently, the low-temperature hump is noticeably strengthened in order to compensate the loss of entropy just below T_N. In all the cases, the full entropy $S=R\ln(2J+1)$ is reached at T_N, as expected.

The dependence of specific heat on the ratio $r=J(3\mathbf{Q})/J(\mathbf{Q})$ for AM systems is shown in Fig. 4. The change of the slope $dC/d(T/T_N)$ just below T_N is particularly well emphasized as r increases from -0.8 to 0.8. As a consequence, the low-temperature part adjusts itself in order to recover the full entropy at T_N. It is worth noting that these changes of C at low temperature may be weak compared to those in the vicinity of T_N because their weight is noticeably strengthened by the factor $1/T$ in the expression of the entropy. The next exchange coefficient $J(5\mathbf{Q})$ influences the calculated variation in the whole temperature range, reinforcing or weakening in particular the low-temperature hump. When the slope $dC/d(T/T_N)$ is negative at T_N, it becomes apparent that a maximum of C occurs at a temperature lower than T_N, as expected from our analytical treatment (Sec. III).

In Fig. 5, some particular C versus T variations are shown. First, two curves corresponding to the critical ratio $r_c=0.567$ are presented: they start horizontally just below T_N, as predicted in Sec. III for this peculiar ratio r_c. In the absence of other exchange coefficients, a negative curvature is calculated for C in the whole temperature range except at very low temperature. In the presence of a positive $J(5\mathbf{Q})$ coefficient, the $C(T)$ curve exhibits a quite exotic shape with a maximum at $T/T_N=0.8$. The case where the $J(n\mathbf{Q})$'s approach the value of $J(\mathbf{Q})$ is also shown in Fig. 5: the initial slope $dC/d(T/T_N)$ below T_N becomes nearly vertical, the maximum value of C increases, and the whole curve progressively approaches the variation calculated for the ferromagnetic case. As already quoted above about Eq. (12), this evolution is consistent with the fact that, for any simple commensurate structure (ferromagnetic or simple antiferromagnetic), the relations $J(n\mathbf{Q})=J(\mathbf{Q})$ are satisfied for all n values.

V. DISCUSSION

In this work, a theoretical model for describing the specific-heat variation in incommensurate amplitude-modulated systems has been extensively studied within

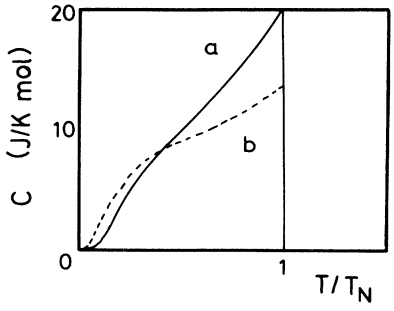

FIG. 3. Calculated magnetic part of the specific heat vs reduced temperature T/T_N for (curve a) ferromagnetic and (curve b) amplitude-modulated structures. The exchange coefficients are (curve a) $J(0)=10$; (curve b) $J(Q)=10$ (arbitrary units, see text).

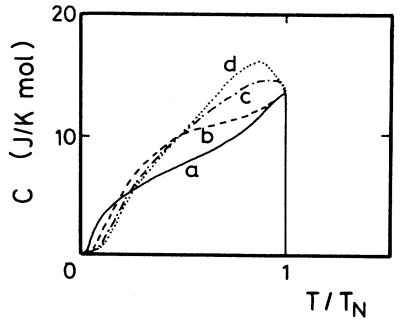

FIG. 4. Calculated specific heat for various exchange coefficients: (curve a) $J(Q)=10$, $J(3Q)=-8$, $J(5Q)=8$; (curve b) $J(Q)=10$, $J(5Q)=8$; (curve c) $J(Q)=10$, $J(3Q)=8$; (curve d) $J(Q)=10$, $J(3Q)=J(5Q)=8$.

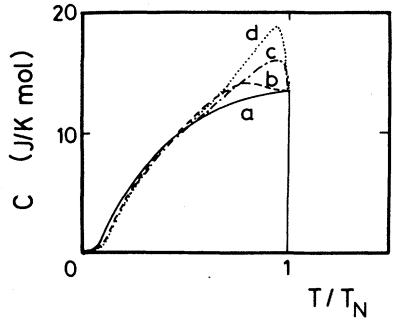

FIG. 5. Calculated specific heat for various exchange coefficients: (curve a) $J(Q)=10$, $J(3Q)=5.67$; (curve b) $J(Q)=10$, $J(3Q)=5.67$, $J(5Q)=8$; (curve c) $J(Q)=10$, $J(3Q)=9.5$; curve (d) $J(Q)=10$, $J(3Q)=J(5Q)=9.5$; for curves a and b, the slope $dC/d(T/T_N)$ vanishes at T_N.

the mean-field approximation. Two main results have been proved. (i) First, the amplitude of the specific-heat discontinuity at the ordering temperature has been shown to be strongly reduced (by $\frac{1}{3}$) with regard to that expected in ferromagnetic and more generally EM systems. (ii) Secondly, the exact shape of the specific-heat variation within the ordered phase depends on the relative magnitude of the exchange coefficients $J(n\mathbf{Q})$ under consideration and may exhibit a maximum at a temperature lower than T_N.

These quite original results can throw a new light on the experimental curves shown in the preceding paper[1] as well as on other data found in the literature. Among the four Gd compounds presented in Ref. 1, $GdCu_2Si_2$ is the only one exhibiting a specific-heat shape very close to that expected for an EM system (see Fig. 6), and this is consistent with its simple antiferromagnetic structure.[10] The differences between observed and calculated variations can be accounted for by the effects of inhomogeneities in the sample and the presence of noticeable

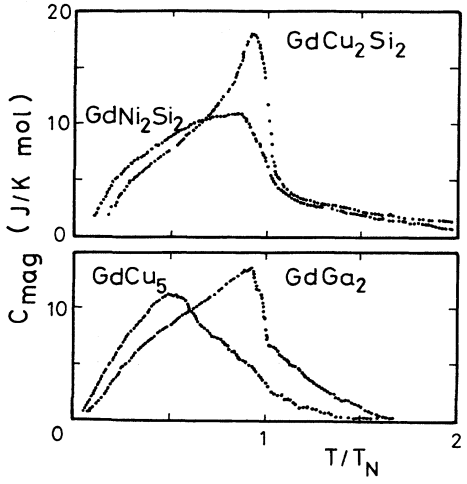

FIG. 6. Magnetic part of the specific heat for the compounds indicated (T_N is the ordering temperature).

magnetic fluctuations persisting above T_N. The experimental specific heat of $GdNi_2Si_2$, in particular the wide range where the curvature is negative, can be well described in our model by considering one single exchange coefficient $J(\mathbf{Q})$ (see Fig. 3, curve b). Again the remaining differences with the calculated curves may be ascribed, at least in part, to the magnetic fluctuations. These conclusions are coherent with the AM magnetic structure determined by neutron diffraction.[10]

For the $GdGa_2$ compound, among the two structures proposed in Ref. 11, namely a collinear AM structure and a cycloidal structure, the first one appears more consistent with the experimental specific-heat variation. Indeed this latter is very far from the λ anomaly expected for a cycloidal structure. For the hexagonal $GdCu_5$ compound, the experimental incommensurate propagation vector $\mathbf{Q}=(\frac{1}{3},\frac{1}{3},0.223)$ found by neutron diffraction[11] led us to consider only a helimagnetic structure. However, the same neutron diffraction pattern is obtained in the hypothesis of a collinear AM structure, the moments lying along one particular direction of the basal plane. This last solution is more likely if the experimental shape of the specific heat is taken into account, especially the presence of the maximum of $C(T)$ far below T_N cannot be explained in the case of a helimagnetic structure.

Concerning other Gd compounds investigated in the literature, it turns out that some of them behave as expected in EM systems, like, e.g., Gd metal[12] or GdRh,[13] both ferromagnets, as well as antiferromagnetic $GdCu_6$.[14] The case of $GdAl_2$ is quite puzzling: this compound is considered as being a ferromagnet, but its magnetic contribution to the specific heat has been found extremely broad, culminating at only 9 J/K mol for $T=153$ K.[15] Its general shape is very far from the λ anomaly expected for a ferromagnet, and the assumption of a ferromagnetic structure may be questioned in the light of the present work: for instance, an AM structure with a relatively small propagation vector could produce magnetization processes very close to those of a ferromagnet, and a specific-heat variation similar to that observed experimentally. The question remains open.

The case of the orthorhombic $Gd_xY_{1-x}Cu_2$ compounds is worth being considered. They have been reported as antiferromagnets.[16] However, their specific-heat variation, although exhibiting a well-defined λ anomaly at T_N, culminates at only ~ 15 J/K mol Gd (for $x=1,0.8,0.6$), i.e., 25% less than the expected value for a simplified antiferromagnet. From our model, it is then likely that the actual structure of this system is AM type. This hypothesis is strongly supported by the existence of such modulated magnetic structures in all the neighboring compounds RCu_2 (R =Tb, Dy, Ho, Er, Tm).[17]

A last comment can be made concerning the magnetic fluctuations which are systematically observed above T_N in all the compounds quoted above and are neglected in our model. The existence of such fluctuations has been theoretically predicted,[9,18,19] their variation following a T^{-2} law as observed in $GdCu_2Si_2$ (Ref. 1) and GdRh (Ref. 13) compounds. In gadolinium compounds, an ensuing decrease of the specific heat below T_N may then be

expected in order to compensate the gain of entropy above T_N. This loss of specific heat can obviously contribute to a reduction of the jump at T_N, but it can be noticed that both commensurate and modulated systems should be affected in the same way by this effect. As well, the fraction of entropy measured above T_N, i.e., $\sim 15\%$,[1] remains weak compared to the 33% reduction of the specific-heat jump calculated in our model for modulated systems.

In conclusion, the specific heat of magnetic systems may provide useful information about the type of magnetic structure involved, in particular the EM and AM structures may be distinguished from each other, in principle. The model developed here for Gd compounds with no crystal-field effects can be extended without difficulty to other rare-earth compounds with crystal-field effects, where additional features are expected to arise according to the nature of the ground state.

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