PHYSICAL REVIEW B VOLUME 43, NUMBER 16 1 JUNE 1991

Specific heat in some gadolinium compounds. I. Experimental

M. Bouvier, P. Lethuillier, and D. Schmitt
Laboratoire de Magnétisme Louis Néel, Centre National de la Recherche Scientifique,
166X, 38042 Grenoble CEDEX, France

(Received 30 October 1990)

Specific-heat measurements have been performed on the gadolinium compounds $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$, and $GdCu_5$ in order to investigate the phase transitions between paramagnetic and commensurate or incommensurate antiferromagnetic states. Various shapes of specific-heat curves are observed at and below the ordering temperature T_N. In particular, the specific-heat discontinuity at T_N is strongly reduced in the incommensurate systems. This behavior is related to the exact type of magnetic arrangement involved.

I. INTRODUCTION

Specific-heat measurements consitute a very useful tool for investigating the magnetic properties of rare-earth intermetallic compounds. In these systems with total angular momentum J, the $2J+1$ associated quantum levels are split by the surrounding crystalline electric field (CEF) and/or by a possible exchange magnetic field arising from the magnetic interactions between the $4f$ ions. That leads to a rapid change in the internal energy as the temperature increases from 0 K and the excited CEF levels become populated, whence a large contribution to the specific heat. CEF Schottky anomalies can then be observed in paramagnetic phase while strong anomalies are expected at the critical temperature where the $4f$ magnetic moments order. Furthermore, other contributions to the specific heat may arise from the magnetic excitations present in ordered materials, from critical phenomena in the vicinity of the ordering temperature, or from spin fluctuations above it.

In any case the magnetic entropy should attain its full value $R\ln(2J+1)$ for 1 mol of $4f$ ions at high temperature ($R=8.315$ J/K mol is the molar gas constant). With all the rare earths except Gd, the entropy does not reach this maximum value at the temperatures usually investigated because the total CEF splitting is generally several hundred kelvins. A quantitative interpretation of the temperature variation of the specific heat and of the entropy therefore requires the knowledge of the actual level scheme, i.e., of the CEF parameters. In this respect, Gd compounds are quite suitable for study. Indeed, due to their S state with zero orbital momentum, their ground multiplet $J=\frac{7}{2}$ remains fully degenerate in the CEF. In the absence of external magnetic field, only an exchange magnetic field can raise this $(2J+1)$-fold degeneracy. The temperature dependence of the magnetic specific heat is therefore closely connected with the way the energy levels evolve within the ordered state. In addition, the full entropy $R\ln8$ is attained in principle just above the ordering temperature or as soon as the critical phenomena vanish.

Numerous theoretical models have been developed in order to describe the behavior of the specific heat below the ordering temperature, such as the Weiss, the Heisenberg, the Ising and the mean-field models, working in two- or in three-dimensional space, and theoretical models taking into account statistical theories, critical phenomena, spin fluctuations, etc.[1-3] In all these models, a ferromagnetic or simple antiferromagnetic arrangement of the magnetic moments is always assumed. No analysis of the specific heat is available in the literature concerning more complex magnetic structures, such as incommensurate and more precisely amplitude modulated systems.

The aim of this paper is to present an extensive experimental investigation of the specific heat in four gadolinium compounds which exhibit a large variety of magnetic structures, in particular modulated ones, namely, $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$, and $GdCu_5$. Preliminary results[4,5] have shown that the thermodynamical properties of such systems are strongly affected by the modulated character of the magnetic structure at and below the ordering temperature and by the associated squaring-up process towards the antiphase state occurring at low temperature. In a subsequent paper,[6] a full quantitative analysis of the present experimental data will be developed within the mean-field approximation. Section II is devoted to the experimental details of the specific-heat measurements. In the next four sections, the experimental results are presented for the four compounds investigated as well as for the nonmagnetic isomorphous compounds used for the electronic and lattice corrections. In the last section a discussion about all the experimental results is made.

II. EXPERIMENTAL PROCEDURE

Specific-heat measurements were carried out by using the ac calorimetry technique,[7] at temperatures ranging from 1.7 to 40 K. Passing a sinusoidal heating current of pulsation ω and power P through a resistance heater in thermal contact with the sample gives rise to two effects after the thermal equilibrium is reached. First the mean temperature T of the sample is larger than the bath temperature T_B, the difference depending on both the heating power and the sample-to-bath thermal conductance K_B:

$$T - T_B = \frac{P}{K_B} .$$

Changing the power P allows one to scan very easily a certain range of temperature for the sample, T_B remaining constant, and this can be made by increasing as well as by decreasing the temperature, which constitutes one of the advantages of the ac method. Second, the actual temperature of the sample is oscillating at the pulsation 2ω with an amplitude δT which depends on the total specific heat C of the sample plus the addenda contribution:

$$\delta T = \frac{P}{2\omega C}(1 + A_{\mathrm{corr}}) .$$

The corrective term A_{corr} varies with the pulsation ω and receives a contribution from both the sample-to-bath relaxation time τ_B and the internal response time τ_i of the sample and addenda to heat input. This term can be neglected if $\omega\tau_B$ is kept much greater than unity and $\omega\tau_i$ much less than unity. Experimentally, a scan in frequency ω allows one to easily verify if the system is in these proper thermal conditions, the product $\omega\delta T$ remaining constant in such a case. In our equipment and due to the mass of the samples used (between 0.1 and 0.5 g), ac oscillations with a frequency as low as 0.02 Hz were used to satisfy these conditions, these latter becoming more critical above roughly 40 K. Typical δT values range between 1 and 40 mK, according to the temperature under consideration. When the thermal equilibrium is reached, the system is in a steady state, so that several measurements can be successively performed and averaged, giving a better determination of C.

The sample holder consists of a sapphire slab (9 mm diameter, 2 mm thickness), with an evaporated Ni-Cr heater on one face. The thermometer is a bismuth-ruthenium resistance[8] directly fixed on the sample. Its value, ranging from about 70 kΩ at 1.6 K to 20 kΩ at 40 K, was calibrated against a reference Fe-Rh resistance. In order to limit the extra heating power brought by the thermometer, this latter was supplied with a constant-voltage current. A sampling of the temperature oscillations with five measured points by period over four periods was sufficient to numerically extract the value of δT. The addenda contribution to the specific heat was measured separately and systematically subtracted from the rough data in order to obtain the specific heat of the sample. The entire experimental process, including the specific-heat measurement and the various corrections, was monitored by computer. As a test of the equipment and of the procedure of extracting the specific-heat values, a sample of pure nickel was measured. The obtained values match the experimental one given in the literature[9] within an accuracy better than 2%.

Magnetic contribution to the specific heat

To isolate the magnetic contribution C_{mag} from the total specific heat actually measured, C_S, the following expression is commonly used:

$$C_S = C_{\mathrm{lat}} + C_{\mathrm{mag}} = C_{\mathrm{el}} + C_{\mathrm{ph}} + C_{\mathrm{mag}} .$$

C_{lat} represents the lattice contribution to the specific heat, including the conduction electron part C_{el} and the phonon part C_{ph}. The electronic part C_{el} is given, in the temperature range investigated, as

$$C_{\mathrm{el}} = \gamma T .$$

The phonon part is written, in the simple Debye model, as

$$C_{\mathrm{ph}} = N f_D(\Theta_D/T) = 9NR\,(T/\Theta_D)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx ,$$

where $f_D(\Theta_D/T)$ is the single Debye function, N is the number of atoms per formula unit, R the molar gas constant, and Θ_D the Debye temperature. In the following, the values will be always given for 1 mol of formula unit.

The main difficulty is to properly evaluate the lattice contribution of magnetic compounds, since it cannot be obtained directly. One way is to measure the specific heat at temperatures much higher than the ordering temperature, where the magnetic contribution vanishes, then to extrapolate the values at low temperatures according to the Debye model. This was successfully applied, for example, in the GdRh compound.[10]

In our experiment the high-temperature limit is too low to apply the above procedure. The lattice contributions have therefore been obtained from the measurement of specific heat of isomorphous nonmagnetic compounds, Gd being substituted by La or Y. However, a renormalization of the data has to be performed in order to take into account the different molar masses of Gd, La, and Y. For that purpose, a many-Debye function model has been used, as an extension of the two-Debye model given in Ref. 11. This latter model is well supported, for example, by the specific heat measured in LaB_6 where the strong difference of mass of La and B leads to partial Debye temperatures so different that they are clearly visible as two separate humps.[12]

In this model, the specific heat of a ternary compound $R_m X_n Y_p$ can be represented by the relationship

$$C(R_m X_n Y_p) = m f_D(\Theta_R/T) + n f_D(\Theta_X/T) + p f_D(\Theta_Y/T), \tag{1}$$

where Θ_R, Θ_X, and Θ_Y refer to partial Debye temperatures associated with the R, X, and Y atoms in the given compound, respectively. Making the further simplifying assumption that all the atoms in the crystal have the same mean-square displacement,[11] it follows that

$$M_R(\Theta_R)^2 = M_X(\Theta_X)^2 = M_Y(\Theta_Y)^2 ,$$

M_R, M_X, and M_Y being the molar mass of R, X, and Y atoms, respectively. At low temperature, an effective Debye temperature $\Theta_D(R_m X_n Y_p)$ can be defined by considering a single Debye function:

$$C_{LT}(R_m X_n Y_p) = (m+n+p) f_D(\Theta_D(R_m X_n Y_p)/T) \ . \quad (2)$$

Identifying the coefficients of the T^3 terms in the low-temperature expansion of Eqs. (1) and (2) leads to the following relation between all the Debye temperatures:

$$\frac{m+n+p}{[\Theta_D(R_m X_n Y_p)]^3} = \frac{m}{(\Theta_R)^3} + \frac{n}{(\Theta_X)^3} + \frac{p}{(\Theta_Y)^3} \ .$$

By assuming that the partial Debye temperatures of X and Y atoms are not modified when R is replaced by another atom R', the following relation can be deduced between the corresponding effective Debye temperatures of both compounds:

$$\frac{\Theta_D(R_m X_n Y_p)}{\Theta_D(R'_m X_n Y_p)} = \left[\frac{m(M_{R'})^{3/2} + n(M_X)^{3/2} + p(M_Y)^{3/2}}{m(M_R)^{3/2} + n(M_X)^{3/2} + p(M_Y)^{3/2}} \right]^{1/3} \ .$$

This renormalization ratio can now be used to evaluate the lattice contribution of the magnetic compound $R_m X_n Y_p$ by multiplying the temperature values by this scaling factor in the C versus T curve obtained for the nonmagnetic compound $R'_m X_n Y_p$. This procedure should be valid at least a low temperature, i.e., below roughly $\Theta_D/10$, where the T^3 expansion of the Debye function is a good approximation. Moreover, it is not necessary to consider the electronic contribution C_{el} in this procedure because its influence is negligible.

III. $GdCu_2Si_2$ COMPOUND

The $GdCu_2Si_2$ compound crystallizes in the tetragonal $ThCr_2Si_2$-type structure. As other isomorphous compounds in the rare-earth series,[13] it orders at low temperature within a simple commensurate antiferromagnetic structure.[14] The propagation vector is $\mathbf{Q} = (\frac{1}{2}, 0, \frac{1}{2})$ and the magnetic moment reaches $(7.2 \pm 0.4)\mu_B$ and is aligned along the [010] direction at 2 K.

The total specific heat of $GdCu_2Si_2$ is shown in Fig. 1. A well-defined λ-type anomaly can be observed, leading to an ordering temperature $T_N = 11.9$ K. This value has been determined as the inflection point of the λ anomaly (on the right-hand side) on the magnetic contribution to the specific heat (Fig. 2, see below). A broad hump is also visible around 3 K, i.e., $T/T_N \approx 0.25$; this behavior is associated with the way the $(2J+1)$-fold degeneracy of the multiplet under consideration evolves within the ordered range,[5] which will be developed in Ref. 6.

The specific heat of the isomorphous nonmagnetic compound $LaCu_2Si_2$ is also reported in Fig. 1. It satisfactorily follows a single Debye function in the range 0–40 K, with an effective Debye temperature of $\Theta_D = 310$ K. Applying the above procedure to the determination of the lattice contribution for $GdCu_2Si_2$ leads to a renormalization ratio of $\rho_{ren} = \Theta_D(GdCu_2Si_2)/\Theta_D(LaCu_2Si_2) = 0.965$. When subtracting the corresponding lattice contribution from the rough data of $GdCu_2Si_2$, the magnetic specific heat becomes slightly negative above 30 K, indicating that the lattice contribution was overestimated (see Fig. 2). As the effect of the renormalization by the ratio ρ_{ren} is weak on the lattice contribution, especially below 20 K, we therefore have kept the rough results of $LaCu_2Si_2$ as the lattice contribution of $GdCu_2Si_2$.

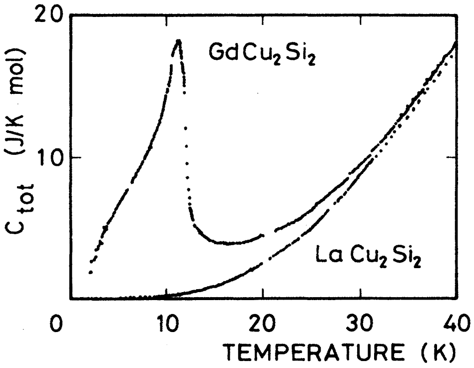

FIG. 1. Total specific heat in $GdCu_2Si_2$ and $LaCu_2Si_2$.

The corresponding magnetic specific heat of $GdCu_2Si_2$ is shown in Fig. 2. The maximum value of C_{mag} at the λ anomaly reaches 18 J/K mol. Moreover, a noticeable magnetic contribution persists up to at least 30 K, revealing the existence of magnetic fluctuations far above T_N. By integrating C_{mag}/T starting from the lowest temperature measured, the magnetic entropy could be calculated (see Fig. 2). It reaches $S_m = 15.4$ J/K mol at 40 K. Taking into account the missing contribution from below the lowest temperatures investigated, evaluated to roughly

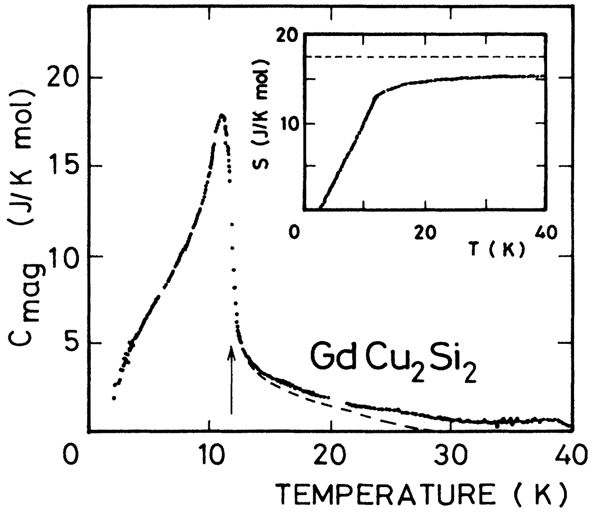

FIG. 2. Magnetic contribution to the specific heat in $GdCu_2Si_2$; points: after lattice correction with rough $LaCu_2Si_2$ data; hatched line: after correction with renormalized $LaCu_2Si_2$ data (see text); the arrow indicates the ordering temperature $T_N = 11.9$ K. Inset: variation of the magnetic entropy; the hatched line indicates the R ln(8) limit.

1.5 J/K mol, the total entropy at 40 K is very close to the theoretical value for 1 mol of Gd^{3+} ions, i.e., $R\ln(8)=17.3$ J/K mol. Note that the magnetic entropy reaches about 83% of its full value at T_N.

IV. $GdNi_2Si_2$ COMPOUND

The $GdNi_2Si_2$ compound crystallizes in the same structure as $GdCu_2Si_2$. As the other compounds in the RNi_2Si_2 series,[15] it orders at low temperature within an incommensurate magnetic structure.[14] The propagation vector is $\mathbf{Q}=(0.207,0,0.903)$ and the magnetic moment is aligned or very close to the [010] direction. That excludes a helimagnetic configuration where the moments lie in a plane. As a consequence, the magnetic structure is a collinear amplitude modulated one and it evolves progressively towards an antiphase-type structure as the temperature is lowered.[5]

The total specific heat of $GdNi_2Si_2$ presents at its ordering temperature an anomaly much less pronounced than in $GdCu_2Si_2$ (Fig. 3). It exhibits a negative curvature in the whole ordered range and no sharp peak occurs at T_N. Nevertheless, and consistently with other magnetic measurements,[14] the ordering temperature is evaluated to be $T_N=14.5$ K.

The specific heat of the two isomorphous nonmagnetic compounds $LaNi_2Si_2$ and YNi_2Si_2 is also shown in Fig. 3. As expected because of the different molar masses, the lattice contribution of YNi_2Si_2 follows a single Debye function with an effective Debye temperature $\Theta_D=370$ K noticeably larger than for $LaNi_2Si_2$ ($\Theta_D=310$ K). However, the lattice contribution of $LaNi_2Si_2$ does not appear as a very good starting point for Θ_D renormalization since it becomes itself larger than the specific heat of $GdNi_2Si_2$ above 30 K. On the contrary, the specific heat of YNi_2Si_2, although the renormalization ratio $\rho_{\text{ren}}=\Theta_D(GdNi_2Si_2)/\Theta_D(YNi_2Si_2)=0.863$ is noticeably different from unity, constitutes a better starting point for the lattice correction (see Fig. 3).

The corresponding magnetic specific heat of $GdNi_2Si_2$ is shown in Fig. 4. It attains a maximum value of only 10.9 J/K mol at $T=12.3$ K, not far below T_N. As in $GdCu_2Si_2$, large magnetic fluctuations persist up to roughly 30 K. The magnetic entropy reaches 16 J/K mol at 40 K. Estimating the missing contribution below 1.6 K as about 0.8 J/K mol leads to a total entropy $S_m=16.8$ J/K mol at 40 K, a value very close to the theoretical one, as in $GdCu_2Si_2$. Note that the magnetic entropy reaches about 86% of its full value at T_N.

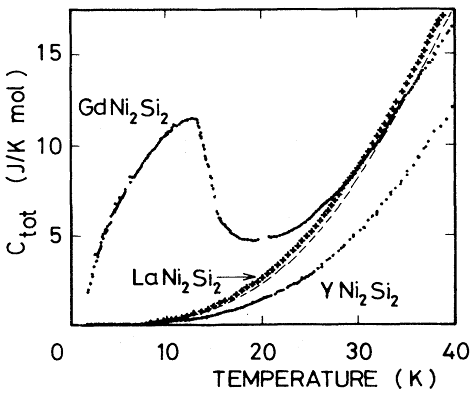

FIG. 3. Total specific heat in $GdNi_2Si_2$, $LaNi_2Si_2$, and YNi_2Si_2; hatched line: renormalized YNi_2Si_2 data, taken as the lattice contribution for $GdNi_2Si_2$ (see text).

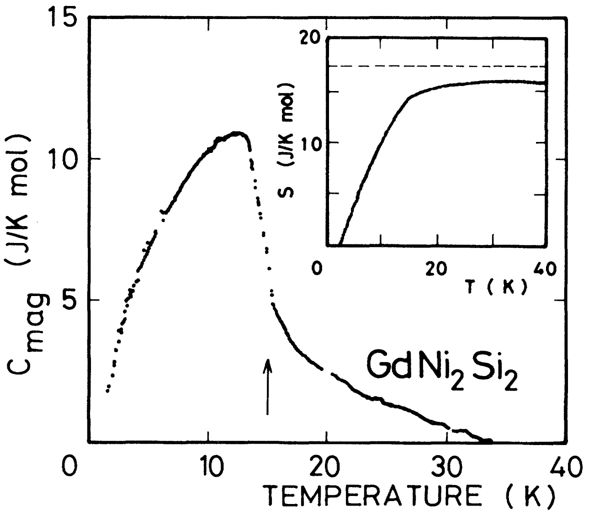

FIG. 4. Magnetic contribution to the specific heat in $GdNi_2Si_2$; the arrow indicates the ordering temperature $T_N=14.5$ K. Inset: variation of the magnetic entropy; the hatched line indicates the $R\ln(8)$ limit.

V. $GdGa_2$ COMPOUND

The $GdGa_2$ compound crystallizes in the hexagonal AlB_2-type structure. It orders below $T_N=23.7$ K within an incommensurate magnetic structure.[16] The propagation vector is $\mathbf{Q}=(0.39,0.39,0)$. From a neutron diffraction experiment, there subsists an ambiguity in the determination of the magnetic structure: it is either amplitude modulated, or cycloidal.[16] In this latter case, all the moments are equal.

The total specific heat of $GdGa_2$ is shown in Fig. 5, together with that of the isostructural nonmagnetic compounds YGa_2 and $LaGa_2$. For these two latter compounds, the variation follows a single Debye function with effective Debye temperatures $\Theta_D=220$ and 215 K, respectively. Note that both values are much closer to each other than expected in the Debye model [$\rho_{\text{ren}}=\Theta_D(LaGa_2)/\Theta_D(YGa_2)=0.894$]. Again, as in Sec. IV, the lattice contribution of $LaGa_2$ is not a very good starting point for the Θ_D renormalization, because it leads here to an underestimation of the lattice contribution in $GdGa_2$. On the contrary, the specific heat of YGa_2 constitutes a more satisfactory starting point for the lattice correction [$\rho_{\text{ren}}=\Theta_D(GdGa_2)/\Theta_D(YGa_2)=0.861$] (see Fig. 5).

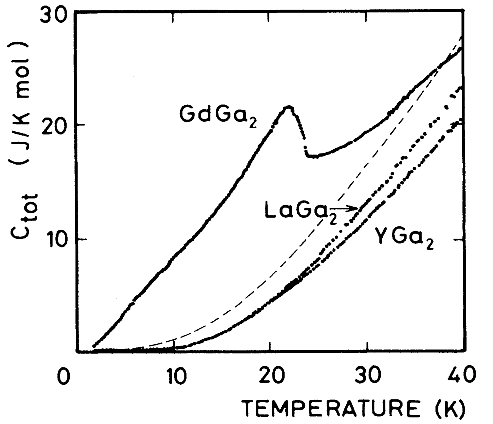

FIG. 5. Total specific heat in GdGa$_2$, LaGa$_2$, and YGa$_2$; hatched line: renormalized YGa$_2$ data, taken as the lattice contribution for GdGa$_2$ (see text).

The deduced magnetic contribution to the specific heat of GdGa$_2$ is shown in Fig. 6. A clear anomaly, although not of λ-type, is present at the ordering temperature. A second transition seems to be evidenced immediately below T_N, at 22.4 K, suggesting the existence of a new magnetic phase different from that observed at lower temperature. However, this could not yet be confirmed by other measurements due to the narrowness of the temperature range. The maximum value of the magnetic specific heat, although larger than in GdNi$_2$Si$_2$, remains noticeably smaller than in GdCu$_2$Si$_2$. Magnetic fluctuations persist here up to roughly 40 K. The magnetic entropy reaches 15.9 J/K mol at 40 K, i.e., $S_m = 16.5$ J/K mol if a reasonable estimation of the missing contribution below 1.7 K is taken into account. Note that the magnetic entropy reaches about 86% of its full value at T_N.

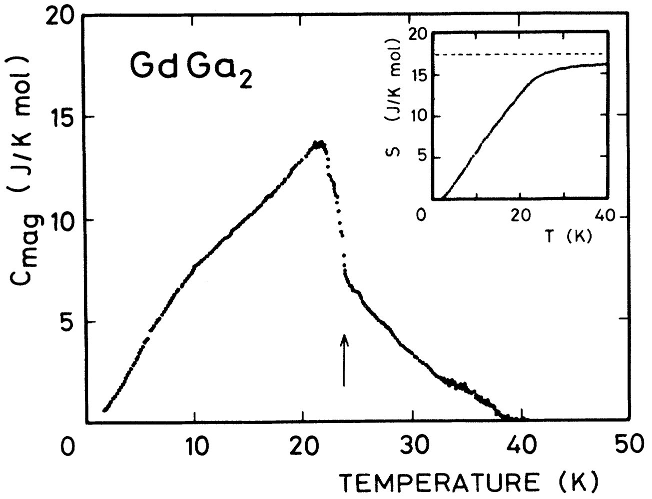

FIG. 6. Magnetic contribution to the specific heat in GdGa$_2$; the arrow indicates the ordering temperature $T_N = 23.7$ K. Inset: variation of the magnetic entropy; the hatched line indicates the R ln(8) limit.

VI. GdCu$_5$ COMPOUND

The GdCu$_5$ compound crystallizes in the hexagonal CaCu$_5$-type structure. Its magnetic structure has been investigated at low temperature by neutron diffraction:[16] it is incommensurate, the propagation vector is $\mathbf{Q} = (\frac{1}{3}, \frac{1}{3}, 0.223)$, and the magnetic moments are confined within the basal plane. A helimagnetic triangular structure has been proposed, leading to moments with equal magnitude. As will be discussed below and in Ref. 6, another structure is also possible which gives the same neutron diffraction pattern, and which has not been considered in Ref. 16, namely, an amplitude-modulated triangular structure. In that case, the moments inside each layer perpendicular to the **c** axis form a triangular lattice; from layer to layer along the **c** direction, the amplitude of the moments is modulated, their direction themselves remaining the same.

The total specific heat of GdCu$_5$ is shown in Fig. 7, together with that of the isomorphous nonmagnetic compound LaCu$_5$. No well-defined anomaly can be observed on the GdCu$_5$ curve, but only a smooth variation. For LaCu$_5$, the temperature variation follows a single Debye function with $\Theta_D = 235$ K. Using the Debye model leads to a weak correction to estimate the lattice contribution for GdCu$_5$ [$\rho_{\text{ren}} = \Theta_D(\text{GdCu}_5)/\Theta_D(\text{LaCu}_5) = 0.975$] (see Fig. 7).

The deduced magnetic contribution to the specific heat of GdCu$_5$ confirms the absence of a well-defined anomaly at the ordering temperature, the determination of which poses a problem (see Fig. 8). A detailed analysis of the magnetization processes led to an ordering temperature of 26 K corresponding to the vanishing of the metamagnetic behavior.[16] However, no anomaly was found at this temperature on the resistivity variation, but a minimum of the resistivity was observed at 30 K. In the same way, the only (weak) anomalies on the specific-heat curve occur at about 20 and 30 K. This latter value $T_N = 30$ K therefore has been taken as the most consistent ordering

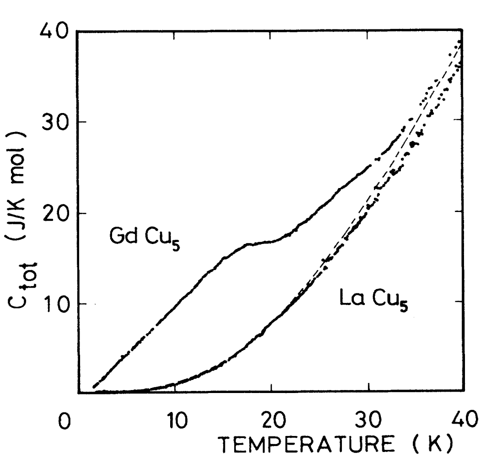

FIG. 7. Total specific heat in GdCu$_5$ and LaCu$_5$; hatched line: renormalized LaCu$_5$ data, taken as the lattice contribution for GdCu$_5$ (see text).

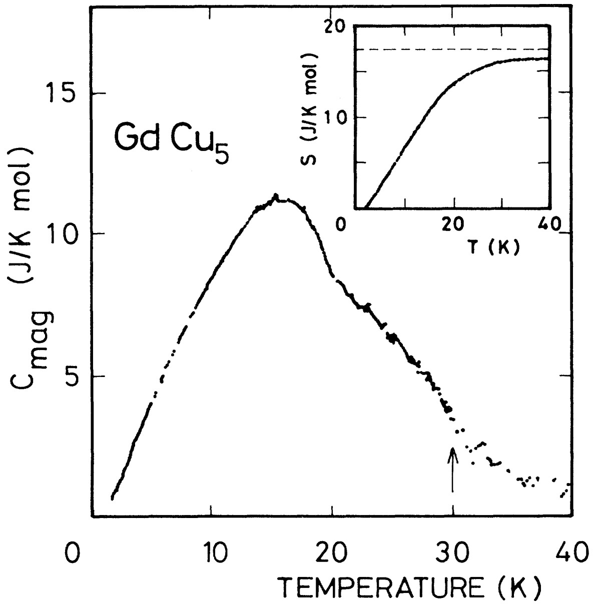

FIG. 8. Magnetic contribution to the specific heat in $GdCu_5$; the arrow indicates the ordering temperature $T_N = 30$ K. Inset: variation of the magnetic entropy; the hatched line indicates the $R\ \ln(8)$ limit.

temperature. Additional experiments should be carried out in order to confirm this conclusion.

As in $GdNi_2Si_2$, the maximum value of the specific heat is much smaller than that measured in $GdCu_2Si_2$. In addition, it occurs at 16 K, i.e., at a temperature far below T_N. This quite unusual behavior will be explained in the frame of an amplitude modulated structure (see Sec. VII) that seems to invalidate the hypothesis of a helimagnetic triangular structure. The magnetic entropy reaches 16.5 J/K mol at 40 K, i.e., 17.2 J/K mol if a reasonable estimation of the missing contribution below 1.7 K is taken into account. The agreement with the expected theoretical value is then excellent. Note that magnetic fluctuations seem to be noticeably weaker here than in the three previous compounds, the magnetic entropy reaching at T_N about 97% of its full value.

VII. DISCUSSION

In this work, the specific heat of four gadolinium compounds, namely, $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$ and $GdCu_5$, has been carefully investigated. An analysis of these data can be made concerning the lattice correction process through the many-Debye function model. For two compounds, i.e., $GdNi_2Si_2$ and $GdGa_2$, two different isostructural nonmagnetic compounds were considered, using Y or La as the nonmagnetic element. That allows us to compare the suitability of both nonmagnetic compounds to be taken as lattice reference. The chosen criterion was based on the high-temperature entropy limit for the magnetic compound after subtraction of its lattice contribution. Note that using Gd as rare earth makes this analysis much easier due to the absence of crystal-field effects. For both systems, the Y compound appears as a better starting point for the Θ_D renormalization process than the La compound. Nevertheless this latter, although less satisfactory (see Sec. III), constitutes a not too bad starting point, as shown by the $GdCu_5$ result, for example. The conclusion is therefore to use preferentially the Y compound as lattice reference. This result is reminiscent of that observed in resistivity measurements in RAg series, for example (R = rare earth), where the La compound was found to behave anomalously compared to Y and Lu ones.[17] This was attributed in part to a stronger electron-phonon coupling in LaAg, in agreement with the appearance of superconductivity in this compound. The same conclusion is valid from elastic constant measurements where the anomalous temperature variation was related to the existence of a lattice instability and/or a coupling between the strain and the zone boundary phonons.[18]

A second comment can be made about the magnetic fluctuations which have been evidenced in the four compounds above the ordering temperature, and which persist up to about $2T_N$. A way to evaluate the importance of these fluctuations is to consider the relative proportion of magnetic entropy above T_N with respect to the full value. It turns out that, in all the compounds except $GdCu_5$, this ratio is remarkably constant, reaching $\Delta S_{\text{fluct}}/R\ \ln(8) = 17\%$, 14%, and 14% in $GdCu_2Si_2$, $GdNi_2Si_2$, and $GdGa_2$, respectively. The behavior of $GdCu_5$, with a proportion of only 3% above T_N, is not yet understood (see below). Moreover, results similar to the present work, i.e., $\Delta S_{\text{fluct}}/R\ \ln(8) \approx 15\%$ above T_N, have been found in GdRh,[10] $Gd_xY_{1-x}Cu_2$,[19] and $GdCu_6$.[20] This behavior seems therefore to be a general tendency in Gd intermetallic compounds.

A tentative analysis of the observed critical behavior can be made using a critical scaling model where $C_{\text{mag}}T^2$ behaves as $(1 - T_c/T)^{-\alpha}$ above the critical temperature T_c.[21] It turns out that $C_{\text{mag}}T^2$ rapidly approaches a constant limit L at high temperature; this is particularly true for $GdCu_2Si_2$. For the three other compounds, this behavior is more approximative, because of the lack of accuracy of the experimental data above T_N due to the lattice correction process. The corresponding magnetic entropy above T_N can be deduced from this limit, as

$$\Delta S_{\text{fluct}} = \frac{L}{2T_N^2} .$$

Taking the experimental limits L leads to $\Delta S_{\text{fluct}}/R\ \ln(8) = 15\%$, 14%, 18%, and 5% in $GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$, and $GdCu_5$, respectively. The good agreement between both determinations of this contribution supports very well the T^{-2} dependence of the specific heat above T_N. This T^{-2} law implies a critical coefficient α close to zero which is the expected value in the mean-field model. Note that such a power law was considered in GdRh.[10]

It is worth noting that, in $GdCu_5$, the temperature for which the proportion of entropy above T_N reaches 15%, namely, $T \approx 20$ K, corresponds to a weak anomaly on the C_{mag} versus T curve (see Fig. 8), and that the "noise" of this experimental curve between 20 K and $T_N = 30$ K is much larger than below 20 K. In the same temperature range (20–30 K), Arrott's plots of the magnetization curves have been found anomalous and the resistivity exhibits a negative slope.[16] One may therefore think that the ordering of this compound between 20 and 30 K is of an unusual type.

The third and most important result of this work concerns the shape of the magnetic contribution to the specific heat. Indeed, in the three incommensurate compounds, the maximum of specific heat is noticeably reduced (up to 40%) with regard to the only compound with a commensurate antiferromagnetic structure, namely, $GdCu_2Si_2$. Moreover, the temperature where this maximum occurs is more or less shifted below the ordering temperature, the extreme case being $GdCu_5$. Among the four compounds, $GdCu_2Si_2$ is the only one exhibiting a shape of specific heat very close to that expected within the mean-field model, with in particular a λ-type anomaly at T_N.[2]

This quite anomalous behavior cannot be ascribed to the existence of magnetic fluctuations quoted above nor to the presence of inhomogeneities in the samples, since all the compounds are affected in a similar way. The explanation we propose is to correlate these exotic specific-heat shapes to the type of magnetic structure of these compounds, and more precisely to the existence or the absence of a modulation of the magnetic moment amplitude. This distinction between equal-moment (EM) and amplitude-modulated (AM) systems leads to the following consequences.

In EM compounds, i.e., those with a ferromagnetic, a simple antiferromagnetic but also a helimagnetic or a cycloidal structure, all the 4*f* ions experience a magnetic exchange field of same magnitude although not always of same direction, at a given temperature below T_c or T_N. Their magnetic states are therefore similar to each other, having in particular the same moment magnitude and the same internal energy. That leads to the shape of specific heat usually expected for a ferromagnet, with a λ anomaly at the ordering temperature.[2]

In AM systems, the quasisinusoidal modulation of the moments just below T_N implies the same type of periodical variation for the exchange field and the various quantum properties such as the internal energy. In particular, the 4*f* ions situated near a node of the sine wave remain in a state close to the paramagnetic one. As a consequence, their contribution to the total internal energy is very weak, and a noticeable reduction of the averaged internal energy and of the specific heat with regard to the EM case can be anticipated at T_N. Moreover, as the temperature is decreased, the AM structure of Gd compounds must evolve toward an antiphase one, unless a first-order transition occurs at some intermediate temperature.[5] The thermal variation of the specific heat can then be expected to be strongly affected by the way this squaring up takes place. That could explain the various shapes observed below T_N in the present work.

It is worth noting that the distinction involved is not between commensurate and incommensurate structures, but between EM and AM systems. In particular, the helimagnetic compounds, although incommensurate, belong to the EM family and then must behave as ferromagnets, as far as the specific heat is concerned. Measuring this latter property therefore appears as a very suitable way to distinguish between helimagnetic and AM compounds, both incommensurate, a distinction which is often not realizable from the other magnetic measurements, e.g., neutron diffraction.

From the above considerations, one may reasonably think that among the four studied compounds, $GdCu_2Si_2$ is the only one exhibiting an EM magnetic structure, while the three others are AM systems. With this respect, it is interesting to look at the behavior of other Gd compounds found in the literature. GdRh (Ref. 10) is a simple ferromagnet the specific heat of which is quite similar to that of $GdCu_2Si_2$. The same holds for ferromagnetic Gd metal[22] as well as for antiferromagnetic $GdCu_6$.[20] $Gd_xY_{1-x}Cu_2$ compounds[19] show at their ordering temperature a well-defined λ-type anomaly, but their amplitude reaches about 15 J/K-mol, i.e., 25% less than the expected value. It is then likely that they order within an AM structure rather than a simple antiferromagnetic one, in agreement with incommensurate magnetic structures evidenced in the RCu$_2$ series.[23] $GdAl_2$ has been always considered as a ferromagnet, however its specific heat is very far from that expected in such a case:[24] the anomaly at T_c is extremely broad and its maximum is about 9 J/K mol, i.e., less than half of the theoretical value. The hypothesis of an AM structure with a very small propagation vector, i.e., a very long period, could explain this behavior without changing drastically the magnetization processes, because such a structure can be destroyed by a weak magnetic field.

Preliminary calculations[4,5] corroborate very well all the considerations of the present work. A more complete quantitative investigation will be developed within the mean-field approximation in the next paper.[6]

ACKNOWLEDGMENTS

We are grateful to Dr. J. Souletie for his interest in this work, in particular about the critical behavior above T_N.

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