Noncollinear amplitude-modulated magnetic order in Gd compounds

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In the present work a model within the mean-field theory is developed in order to analyze the specific heat of magnetically ordered systems. This model allows to draw conclusions about the type of magnetic structure from the specific heat near the magnetic transition. The known description of collinear amplitude-modulated and equal-moment magnetism has been extended to account for noncollinear amplitude-modulated (NCAM) antiferromagnetic order by introducing an anisotropic exchange interaction. Experimental evidence for NCAM order is expected from measurements of the specific-heat anomaly at the ordering temperature and from magnetic scattering experiments. The specific heat of $GdCu_2$ was measured and analyzed within the model and a good agreement is reached. Furthermore, the specific heat of other noncollinear Gd antiferromagnets near the ordering temperature has been calculated and is compared to available experimental data.

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I. INTRODUCTION

In 1991 a mean-field (MF) model has been developed for the magnetic order in compounds with negligible single-ion anisotropy.[1] There the exchange interaction was assumed to be isotropic. Within this description, equal-moment (EM) magnetic structures have been analyzed and the specific heat has been calculated. By taking into account some weak anisotropy of the exchange coupling or crystal field the stabilization of collinear amplitude-modulated (AM) magnetic structures with regard to other possible states with equal moments (e.g., helical or cycloidal) could be shown. It was found that the specific-heat discontinuity at the ordering temperature is reduced for AM compounds relative to that expected in the case of EM magnetism. In addition, a connection between the shape of the specific-heat curves and the exchange constants was predicted. The results of the model were compared to specific-heat measurements on a number of Gd compounds ($GdCu_2Si_2$, $GdNi_2Si_2$, $GdGa_2$, $GdCu_5$).

The purpose of this paper is to develop a theoretical model for noncollinear amplitude-modulated (NCAM) systems. Such intermediate behavior is expected if the anisotropy of the exchange interactions is included *explicitly* into the theory. AM and EM order are derived as special cases in this model. To keep the formalism self-contained the standard MF treatment of the Hamiltonian is rewritten following the notation in Ref. 1 and extending it where necessary. The results of the model are compared to experimental specific-heat data of a number of Gd compounds. For this purpose the specific heat of $GdCu_2$ was measured additionally and analyzed in detail. Other available experimental data are discussed within the framework of the generalized model.

II. FORMALISM

The subsequent analysis is based on an anisotropic bilinear two-ion exchange interaction $\bar{\bar{\mathcal{J}}}(ij)$ between the total angular momenta $\mathbf{J}(i)$ of the rare-earth atoms at different sites i and j. It must be emphasized that in general the magnetic exchange is anisotropic, for instance due to the classical dipole-dipole interaction. In our notation two lines (=) above a symbol denote a tensor and $(\,)^T$ denotes the transposition of a vector (bold-faced symbols denote vectors). Then the Hamiltonian of the magnetic interaction can be written as

$$\mathcal{H}=-\frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{N}\mathbf{J}^T(i)\bar{\bar{\mathcal{J}}}(ij)\mathbf{J}(j). \tag{1}$$

This approach is only valid, when crystal field, multi-ion and higher-order interactions can be neglected. Therefore, Gadolinium and its compounds are good candidates to check the theoretical model (see below). We will use a MF theory and thereby neglect magnetic fluctuations above the ordering temperature T_N. Except for the critical region this is a valid approximation,[2] because Gd^{3+} has a large spin moment and in most cases the exchange is of long range. Introducing thermal averages of the magnetic moment of the rare earth $\langle\mathbf{M}(i)\rangle=g_J\mu_B\langle\mathbf{J}(i)\rangle$ we may define the following effective exchange field

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

Note that in Eq. (2) the multiplication of the interaction tensor $\bar{\bar{\mathcal{J}}}(ij)$ with the moment vector $\langle\mathbf{M}(j)\rangle$ results in a vector that contributes to the exchange field $\mathbf{H}_{\mathrm{ex}}(i)$. In a MF theory the Hamiltonian (1) is approximated by (compare Ref. 1)

$$\mathcal{H}\sim\mathcal{H}_{\mathrm{MF}}=-\sum_i\mathbf{M}^T(i)\mathbf{H}_{\mathrm{ex}}(i)+\frac{1}{2}\sum_i\langle\mathbf{M}^T(i)\rangle\mathbf{H}_{\mathrm{ex}}(i). \tag{3}$$

We now introduce Fourier transforms of the moments $\langle \mathbf{M}(j)\rangle$, the exchange fields $\mathbf{H}_{\mathrm{ex}}(i)$, and of the exchange tensor $\bar{\bar{\mathcal{J}}}(ij)$ by

$$\mathbf{M}_{n\mathbf{Q}}=\frac{1}{N}\sum_i \langle \mathbf{M}(i)\rangle e^{-in\mathbf{Q}\mathbf{R}_i}, \tag{4}$$

$$\mathbf{H}_{n\mathbf{Q}}=\frac{1}{N}\sum_i \mathbf{H}_{\mathrm{ex}}(i) e^{-in\mathbf{Q}\mathbf{R}_i}, \tag{5}$$

$$\bar{\bar{\mathcal{J}}}(n\mathbf{Q})=\sum_j \bar{\bar{\mathcal{J}}}(ij) e^{-in\mathbf{Q}(\mathbf{R}_i-\mathbf{R}_j)}, \tag{6}$$

where $\mathbf{Q}$ is the propagation vector of the magnetic structure under consideration. The magnetic moments can be written as

$$\langle \mathbf{M}(i)\rangle=\sum_{n(\neq 0)} \mathbf{M}_{n\mathbf{Q}} e^{in\mathbf{Q}\mathbf{R}_i}. \tag{7}$$

Note, that n runs from $-\infty$ to $+\infty$ in the sum in Eq. (7) if the propagation $\mathbf{Q}$ is incommensurate. If $\mathbf{Q}$ is commensurate, n numbers all nonequivalent wave vectors $n\mathbf{Q}$. Using the Fourier transforms (4)–(6) Eq. (2) becomes

$$\mathbf{H}_{n\mathbf{Q}}=(g_J\mu_B)^{-2}\bar{\bar{\mathcal{J}}}(n\mathbf{Q})\mathbf{M}_{n\mathbf{Q}}. \tag{8}$$

We may write the internal energy per ion (which is equal to the thermal average of $\mathcal{H}$)[3]

$$U=\frac{\langle \mathcal{H}_{\mathrm{MF}}\rangle}{N}=-\frac{1}{2}(g_J\mu_B)^{-2}\sum_{n(\neq 0)} \mathbf{M}^T_{-n\mathbf{Q}}\bar{\bar{\mathcal{J}}}(n\mathbf{Q})\mathbf{M}_{n\mathbf{Q}}. \tag{9}$$

III. BEHAVIOR OF THE SPECIFIC HEAT NEAR THE NÉEL TEMPERATURE T_N

In the following, the MF approach is taken as a reasonable interpolation near the Néel temperature T_N. This results in a model that can be solved and compared to experimental results (keeping in mind that within the critical region fluctuations will be present). The behavior of the specific heat may be obtained analytically by using an expansion of the magnetic moment on each site i as a function of the corresponding exchange field and the reduced variable $t=(1-T/T_N)^{1/2}$ (a ''$\wedge$'' on top of a vector denotes the corresponding unit vector)

$$\begin{aligned}\langle \mathbf{M}(i)\rangle &= \hat{\mathbf{H}}_{\mathrm{ex}}(i) g_J\mu_B J\mathcal{B}_J(g_J\mu_B H_{\mathrm{ex}}(i)/k_BT)\\ &= \frac{C^{(1)}}{T}\mathbf{H}_{\mathrm{ex}}(i)+\frac{C^{(3)}}{T^3}\mathbf{H}_{\mathrm{ex}}(i)[H_{\mathrm{ex}}(i)]^2+\cdots\\ &= \frac{C^{(1)}}{T_N}\mathbf{H}_{\mathrm{ex}}(i)(1+t^2+t^4+\cdots)+\frac{C^{(3)}}{T_N^3}\mathbf{H}_{\mathrm{ex}}(i)\\ &\quad\times[H_{\mathrm{ex}}(i)]^2(1+3t^2+6t^4+\cdots)+\cdots. \end{aligned}\tag{10}$$

Here $\mathcal{B}_J(x)$ is the Brillouin function and the $C^{(n)}$ are the Curie constants of nth order (for Gadolinium $J=7/2$, $g_J=2$), see Ref. 1:

$$C^{(1)}=(g_J\mu_B)^2J(J+1)/(3k_B), \tag{11}$$

$$C^{(3)}=-(g_J\mu_B)^4J(J+1)(2J^2+2J+1)/(90k_B^3).$$

The expansion (10) is possible, because near the ordering temperature $T\sim T_N$ all magnetic moments are expected to be much smaller than the saturation moment. Therefore also the exchange fields $\mathbf{H}_{\mathrm{ex}}(i)$ will be smaller than $k_BT/g_J\mu_B$ (in a limited temperature range near T_N).

Replacing $\langle \mathbf{M}(i)\rangle$ and $\mathbf{H}_{\mathrm{ex}}(i)$ in Eq. (10) by their Fourier expansion [Eqs. (4) and (5)], substituting $\mathbf{H}_{n\mathbf{Q}}$ by Eq. (8) and identifying the corresponding Fourier components on both sides of the equation provides a nonlinear system of equations in $\mathbf{M}_{\mathbf{Q}},\mathbf{M}_{3\mathbf{Q}},\ldots$. This system can be solved by expanding the $\mathbf{M}_{n\mathbf{Q}}$**'s** in ascending (odd) powers of t and by identifying the corresponding terms in $t,t^3,\ldots$, i.e., the nth harmonic $\mathbf{M}_{n\mathbf{Q}}$ is expanded as

$$\mathbf{M}_{n\mathbf{Q}}=\mathbf{M}_{n1}t+\mathbf{M}_{n3}t^3+\mathbf{M}_{n5}t^5+\cdots. \tag{12}$$

For $n=1$ and first order in t the following eigenvalue problem of $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$ is derived:[4]

$$\bar{\bar{\mathcal{J}}}(\mathbf{Q})\mathbf{M}_{11}=\frac{(g_J\mu_B)^2T_N}{C^{(1)}}\mathbf{M}_{11}. \tag{13}$$

Given the exchange $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$, this eigenvalue problem may be solved for different wave vectors $\mathbf{Q}$. Maximizing the largest eigenvalue $\lambda(\mathbf{Q})$ with respect to $\mathbf{Q}$ gives the ordering wave vector $\mathbf{Q}_0$ of the system, the ordering temperature $T_N=\lambda(\mathbf{Q}_0)C^{(1)}/(g_J\mu_B)^2$ and the eigenvector $\mathbf{M}_{11}$.[5] The components of this eigenvector determine the type of magnetic structure just below the ordering temperature. However, by using the first-order terms in t, only the direction of $\mathbf{M}_{11}$ can be calculated [by solving the eigenvalue problem (13)] but not its length.

The length of $\mathbf{M}_{11}$ is found to be characteristic for the discussed type of magnetic order (AM, NCAM, and EM) and can be calculated by comparing the components of third order in t (see the Appendix), the result is

$$|\mathbf{M}_{11}|^2=\begin{cases}\dfrac{-(C^{(1)})^3}{C^{(3)}[2+|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|^2]} & \mathbf{Q}_0\neq 0,\notin \mathrm{BZB},\\ \dfrac{-(C^{(1)})^3}{C^{(3)}} & \mathbf{Q}_0=0 \quad \text{or} \quad \mathbf{Q}_0\in \mathrm{BZB}.\end{cases} \tag{14}$$

Equation (14) shows, that the length of $\mathbf{M}_{11}$ (i.e., the magnitude of the ordered moment just below T_N) is determined by the Curie constants $C^{(1)},C^{(3)}$ and the product $|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|$, which may vary between 0 (EM order) and 1 (AM order) depending on the (real and imaginary) components of $\hat{\mathbf{M}}_{11}$ as determined by the eigenvalue problem (13). In general the order will be NCAM (see the examples given in Sec. IV and V). In Eq. (14) the ferromagnetic case (i.e., $\mathbf{Q}_0=0$) and the simple antiferromagnetic case (i.e., $\mathbf{Q}_0\in$ BZB, BZB $=$[symmetry points on the Brillouin zone boundary]) have been treated separately, because in these cases the AM and EM (and NCAM) description of the ordering process is equivalent.[6]

In addition to Eq. (14) the third-order terms in t provide an expression for the third harmonic of the magnetic moment (for $\mathbf{Q}_0\neq 0,\ \notin$ BZB, see the Appendix):

$$\mathbf{M}_{3\mathbf{Q}_0}=t^3\left(1-\frac{C^{(1)}}{T_N(g_J\mu_B)^2}\bar{\bar{\mathcal{J}}}(3\mathbf{Q}_0)\right)^{-1}\mathbf{M}_{11}\times\frac{C^{(3)}}{[C^{(1)}]^3}(\mathbf{M}_{11}^T\mathbf{M}_{11}). \tag{15}$$

Equation (15) shows that the size of the third harmonic depends also on the product $|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|$ and becomes zero for EM order. Therefore, any deviation from EM order can be determined by measuring the intensity on the third harmonic in a magnetic scattering experiment. However, such measurements are very difficult, since the magnetic moment near the ordering temperature is usually very small and at lower temperatures the moments tend to saturate thereby destroying NCAM order.

Using Eqs. (9), (13), and (14) the magnetic contribution to the specific heat for temperatures just below T_N can be calculated as

$$C^{\mathrm{mag}}\Big|_{T\to T_N}=\frac{\partial U}{\partial T}\Big|_{T\to T_N}=\begin{cases}-\dfrac{\mathbf{M}_{-11}^T\bar{\bar{\mathcal{J}}}(\mathbf{Q}_0)\mathbf{M}_{11}+\mathbf{M}_{11}^T\bar{\bar{\mathcal{J}}}(-\mathbf{Q}_0)\mathbf{M}_{-11}}{2(g_J\mu_B)^2}\dfrac{\partial t^2}{\partial T}\Big|_{T\to T_N}=\dfrac{|\mathbf{M}_{11}|^2}{C^{(1)}} & \\ \quad=\dfrac{1}{C^{(1)}}\left[\dfrac{\partial|\mathbf{M}_{\mathbf{Q}_0}|}{\partial t}\Big|_{T\to T_N}\right]^2=\dfrac{-(C^{(1)})^2}{C^{(3)}[2+|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|^2]} & \mathbf{Q}_0\neq 0,\notin \mathrm{BZB}\\ -\dfrac{\mathbf{M}_{-11}^T\bar{\bar{\mathcal{J}}}(\mathbf{Q}_0)\mathbf{M}_{11}}{2(g_J\mu_B)^2}\dfrac{\partial t^2}{\partial T}\Big|_{T\to T_N}=\dfrac{|\mathbf{M}_{11}|^2}{2C^{(1)}}=\dfrac{1}{2C^{(1)}}\left[\dfrac{\partial|\mathbf{M}_{\mathbf{Q}_0}|}{\partial t}\Big|_{T\to T_N}\right]^2=-\dfrac{(C^{(1)})^2}{2C^{(3)}} & \mathbf{Q}_0=0\\ -\dfrac{\mathbf{M}_{11}^T\bar{\bar{\mathcal{J}}}(\mathbf{Q}_0)\mathbf{M}_{11}+\mathbf{M}_{11}^T\bar{\bar{\mathcal{J}}}(-\mathbf{Q}_0)\mathbf{M}_{-11}}{4(g_J\mu_B)^2}\dfrac{\partial t^2}{\partial T}\Big|_{T\to T_N}=\dfrac{|\mathbf{M}_{11}|^2}{2C^{(1)}} & \\ \quad=\dfrac{1}{2C^{(1)}}\left[\dfrac{\partial|\mathbf{M}_{\mathbf{Q}_0}|}{\partial t}\Big|_{T\to T_N}\right]^2=-\dfrac{(C^{(1)})^2}{2C^{(3)}}. & \mathbf{Q}_0\in \mathrm{BZB}\end{cases} \tag{16}$$

The specific heat near the ordering temperature shows a discontinuity that corresponds to the size of the derivative of the ordered magnetic moment with respect to t. The jump in the molar heat capacity c^{mag} ($c^{\mathrm{mag}}=N_AC^{\mathrm{mag}}$, $N_A=6.0221\times10^{23}$/mol denotes the Avogadro constant) at T_N may vary between $[-(C^{(1)})^2/3C^{(3)}]N_A=13.43$ J/K mol and $[-(C^{(1)})^2/2C^{(3)}]N_A=20.15$ J/K mol [corresponding to AM and EM magnetic structures, respectively—calculated with $J=7/2$ using Eq. (11)]. Using high-quality specific-heat measurements it is therefore possible to estimate the size of the magnetic contribution at T_N and attempt to obtain information about the type of magnetic structure just below the ordering temperature from the size of the product $|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|^2$. In the following part of this paper some examples will be given.

Note that in Eq. (16) the ferromagnetic ($\mathbf{Q}_0=0$) and simple antiferromagnetic case ($\mathbf{Q}_0\in$ BZB) give specific-heat values as expected for EM order (although the AM and EM descriptions are equivalent for these special values of $\mathbf{Q}_0$). Furthermore, it is worth considering the case where the exchange anisotropy is only due to the classical dipole-dipole interaction: if the basis of the crystallographic structure con-

TABLE I. Magnetic contribution to the molar heat capacity near the magnetic ordering temperature for some Gd compounds. The propagation vector and the moment direction derived from magnetic-scattering experiments is given for comparison. The last column contains the type of magnetic order as suggested by these experiments (see text).

	$c^{\mathrm{mag}}\|_{T\to T_N}$ [J/K mol]	Moment direction	$\mathbf{Q}_0$	Type
Gd	15–25 [Ref. 13]	[001]	(0 0 0)	→EM=NCAM=AM
$GdCu_2Si_2$	15–18 [Ref. 14]	[010]	(1/2 0 1/2) ∈ BZB	→EM=NCAM=AM [Ref. 15]
$GdCu_2$	20	[$x0z$]	(2/3 1 0)	EM
$GdCu_2Ge_2$	18–22 [Ref. 7], [Ref. 16]			EM
$GdBa_2Cu_3O_{7-\delta}$	14–22 [Ref. 17]	[001]	(1/2 1/2 1/2) ∈ BZB	→EM=NCAM=AM [Ref. 18]
GdAg	19–21	[001]	(1/2 1/2 0) ∈ BZB	→EM=NCAM=AM [Ref. 19]
$GdCo_2Si_2$	19–20 [Ref. 7]			EM
GdS	17–20 [Ref. 20]			NCAM
$GdAu_2Si_2$	14–18 [Ref. 7]			NCAM
$GdCo_2Ge_2$	16–17 [Ref. 16]			NCAM
$GdPd_2Ge_2$	14–16 [Ref. 7]			NCAM
$GdNi_2B_2C$	12–16 (at 20 K) [Ref. 21], [Ref. 22] 1 (at 14 K)	[010]	(0.55 0 0) [Ref. 23]	AM[a]
$GdNi_2Ge_2$	12–14 (at 28 K) [Ref. 16] 3 (at 15 K) [Ref. 16]			AM
GdAuGe	10 (at 17 K) [Ref. 24] 3 (at 15 K)			AM
$GdRu_2Ge_2$	7–9 (at 32 K) [Ref. 25] 3 (at 28 K)			AM
$GdAg_2Si_2$	6–7 (at 17 K) [Ref. 7] 6–7 (at 11 K)			AM
GdMg	7–9 (at 105 K) [Ref. 26] 4–6 (at 90 K)			AM
$GdCu_5$	3–4 [Ref. 14]		(1/3 1/3 0.223)	
Gd_2PdSi_3	4–6 [Ref. 27], [Ref. 28]			
$GdGa_2$	13–14 [Ref. 14]		(0.39 0.39 0)	AM
$GdNi_2Si_2$	10–11 [Ref. 14]	[010]	(0.207 0 0.903) [Ref. 15]	AM
$GdFe_2Ge_2$	14–15 [Ref. 16]			AM
$GdPt_2Ge_2$	10–13 [Ref. 7]			AM
$GdNi_2Sn_2$	10–15 [Ref. 7]			AM
$GdPd_2In$	11 [Ref. 29], [Ref. 30]			AM
$GdCu_2In$	9–11 [Ref. 29], [Ref. 30]			AM

[a]Note that below $T_R \sim 0.7T_N$ there is a spin reorientation into a NCAM state.

sists only of one Gd atom, then $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$ is real for any $\mathbf{Q}$ and therefore either AM or (if $\mathbf{Q}_0=0$ or $\mathbf{Q}_0 \in$ BZB) simple collinear EM order is predicted.

It has been pointed out that the analysis of specific heat may lead to important conclusions about the magnetic structure near the ordering temperature. However, in many cases critical fluctuations make it difficult to obtain reliable MF values for $C^{\mathrm{mag}}|_{T\to T_N}$. In addition, the sample quality is an important issue since impurities and microstrains may lead to changes of the specific heat near the magnetic ordering temperature. In Sec. V the specific heat is discussed for some Gd compounds.

For Gd the conclusions from specific-heat data are in some respect as important as results from scattering experiments.[1,7] Candidates for NCAM order are proposed for further study.

IV. THE CASE OF $GdCu_2$

To give an example of how NCAM order might occur, the case of $GdCu_2$ is discussed in more detail. Up to now it seems to be the only Gd compound exhibiting EM order that is noncollinear (compare Table I). Recent neutron-scattering experiments on $GdCu_2$ indicate a noncollinear magnetic structure.[8] The heat capacity has been measured on polycrystals[9] and single crystals.[10] For $c^{\mathrm{mag}}_{\mathrm{GdCu_2}}|_{T\to T_N}$ at the ordering temperature a value of 15 J/K mol has been reported in Refs. 1 and 9 and was taken as evidence for an AM magnetic structure. However, from more recent measurements on a single crystal a larger value of 20 J/K mol can be estimated.[10] Therefore, the heat capacity has been remeasured on a high quality single crystal with the aim to get additional reliable data and compare it to the model. The single crystal was produced by a Bridgeman method, details

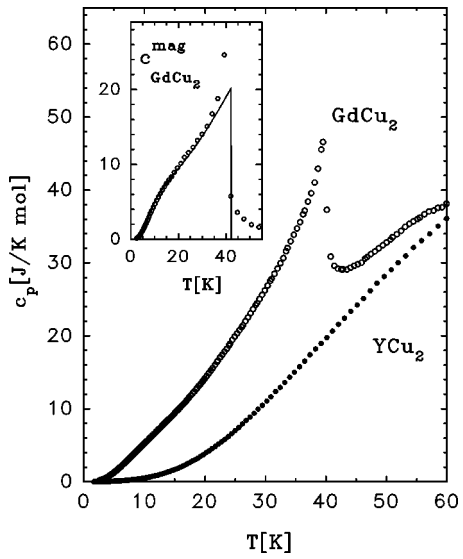

FIG. 1. Molar heat capacity c_P of a $GdCu_2$ single crystal in zero magnetic field in comparison with the isostructural nonmagnetic reference compound YCu_2. The inset shows the magnetic contribution c^{mag} (circles) as derived from these data in comparison with results of a numerical calculation (full line) described in the text.

are given in Refs. 8 and 11. Heat capacity was measured by a conventional quasiadiabatic heat-pulse technique. The molar heat capacity c_P of $GdCu_2$ is shown in Fig. 1 in comparison with the data of YCu_2. One peak has been observed at 42 K corresponding to the Néel temperature in accordance with measurements on polycrystals.[12] Taking into account the part caused by critical fluctuations around T_N we estimate from these data a MF heat capacity jump of 20 J/K mol, approximately, confirming the results of Ref. 10.

It has been shown[8] in a simple model of $GdCu_2$ with a propagation vector $\mathbf{Q}_0=(2/3\,1\,0)$, that the eigenvector corresponding to possible magnetic structures is given by

$$\mathbf{M}_{11}=|\mathbf{M}_{11}|(2+2\sigma\sqrt{1+\sigma^2}+2\sigma^2)^{-1/2}\begin{pmatrix} i \\ 0 \\ \sigma+\sqrt{1+\sigma^2}\end{pmatrix}. \tag{17}$$

Here σ is a parameter that denotes the ratio of some off-diagonal and diagonal components of the exchange tensor

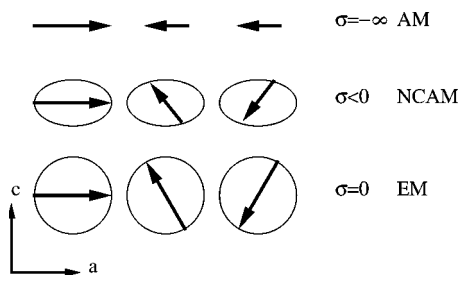

FIG. 2. Types of moment propagation for different values of the parameter σ (see text).

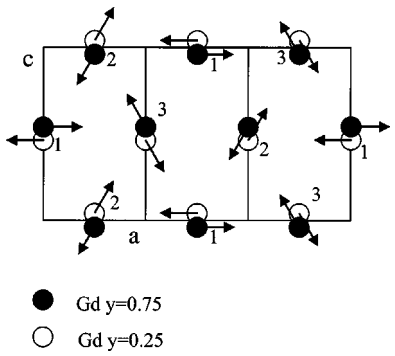

FIG. 3. Magnetic structure of $GdCu_2$. The filled and open circles denote two different neighboring *ac* planes showing the antiferromagnetic propagation in *b* direction. For simplicity the copper atoms are not shown. The magnetic structure can be viewed as a superposition of three simple antiferromagnetic lattices as indicated by the numbers.

(see Ref. 8 for details). For the magnetic structure corresponding to this eigenvector, the magnitude of the magnetic moment varies with its angle according to an ''elliptic'' (i.e., NCAM) propagation (see Fig. 2, the magnetic structure shown in Fig. 3 corresponds to $\sigma=0$). By inserting the eigenvector (17) into Eqs. (14)–(16) it is possible to calculate the magnitude of the linear term in the expansion of the magnetic moment (12)

$$|\mathbf{M}_{11}|^2=\frac{-(C^{(1)})^3}{C^{(3)}[2+\gamma^2]} \quad \text{with} \quad \gamma^2\equiv|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|^2=\frac{\sigma^2}{1+\sigma^2}. \tag{18}$$

Consequently the magnetic contribution to the specific heat at T_N is then calculated from Eq. (16) to be

$$C^{\mathrm{mag}}|_{T\to T_N}=\frac{-(C^{(1)})^2}{C^{(3)}[2+\gamma^2]} \tag{19}$$

For $|\sigma|\ll 1$ the eigenvector $(i\,0\,1)$ corresponds to the cycloidal propagation (shown in Fig. 2, bottom). For this eigenvector the product $\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}$ is zero and the anomaly in the molar heat capacity at T_N is calculated to be

$$c^{\mathrm{mag}}_{\mathrm{GdCu_2}}|_{T\to T_N}=N_A C^{\mathrm{mag}}|_{T\to T_N}$$
$$=\frac{-(C^{(1)})^2}{2C^{(3)}}N_A=20.15 \ \text{J/mol K}. \tag{20}$$

This result is expected for EM structures [compare the discussion of Eq. (16) and Ref. 1] and is in accordance with our experimental data of the heat capacity.

The proposed cycloidal propagation ($\sigma=0$) is in accordance with neutron-scattering experiments performed at $T=4$ K.[8] The corresponding magnetic structure of $GdCu_2$ is

shown in Fig. 3. This type of ordering can be viewed as an *antiferromagnetic* modulation of the moments in *b* direction and a *cycloidal* EM propagation in *a* direction with a pitch angle of 120°. The propagation vector is $\mathbf{Q}_0=(2/3\,1\,0)$. There are two different domains possible, one with a left-handed and another with a right-handed cycloid. The magnetic unit cell consists of three structural unit cells along *a* direction. From the projection into the *ac* plane the cycloidal propagation in *a* direction can be seen.

Assuming that the magnetic structure is the same (EM) at all temperatures the specific heat can be calculated numerically at all temperatures below T_N by solving self-consistently Eqs. (4)–(10). In the inset of Fig. 1 the result of such a calculation is shown by the full line. It compares well to the experimental data except for the critical region, where strong critical fluctuations are present, which are not considered in the MF model.

Moreover, considering temperatures near T_N the neutron technique at present is not sensitive enough to detect a small amplitude modulation $\sigma\neq 0$ of the magnetic moment. Using Eq. (15) it is possible to calculate the magnitude of the third harmonic. The terms linear in *t* are zero

$$|\mathbf{M}_{31}|^2=0 \tag{21}$$

and therefore the third harmonic increases as $\mathbf{M}_{3\mathbf{Q}_0}=\mathbf{M}_{33}t^3$ with $\mathbf{M}_{33}\|\mathbf{M}_{11}$ and

$$|\mathbf{M}_{33}|^2=\left|\left[1-\frac{C^{(1)}}{T_N(g_J\mu_B)^2}\bar{\bar{\mathcal{J}}}(3\mathbf{Q}_0)\right]^{-1}\hat{\mathbf{M}}_{11}\right|^2 \times\frac{\gamma[C^{(1)}]^6}{(2+\gamma^2)^{3/2}\sqrt{-C^{(3)}}}. \tag{22}$$

It might be possible to determine a small deviation from the cycloidal EM propagation near T_N by measuring the intensity on the third harmonic in a synchrotron experiment using the high sensitivity of resonant magnetic x-ray scattering techniques.

At present it is not clear, what is the reason for the observed anisotropy in the exchange interactions of $GdCu_2$. A numerical calculation of the anisotropy of the classical dipole-dipole exchange indicates degenerate eigenvalues in Eq. (13). Probably this degeneracy is lifted by some small additional interaction, which has not been included in the current model and stabilizes the observed magnetic structure. We strongly suggest further theoretical investigations on this subject.

V. DISCUSSION OF OTHER Gd COMPOUNDS

In Table I the heat-capacity data for several Gd compounds are compiled in combination with available data on the magnetic structure. In some cases such as Gd metal strong critical fluctuations near the ordering temperature make it difficult to estimate correctly the MF value of $c^{\mathrm{mag}}|_{T\to T_N}$ and therefore a reliable interval of values is given instead of an accurate value in Table I.

Most compounds exhibiting EM order show strong critical fluctuations (such as Gd, GdS, $GdCu_2Ge_2$, $GdCu_2Si_2$) and order in a simple collinear structure. No Gd compound with a single Gd ion in the crystallographic basis has been reported to show noncollinear EM order. This is in agreement with the predictions of classical dipole-dipole exchange.[31]

Numerical calculations[32] showed that the anisotropy of the classical dipole-dipole exchange fails to describe the moment direction in the case of Gd whereas it describes it correctly in the cases of GdAg, $GdCu_2Si_2$, $GdBa_2Cu_3O_{7-\delta}$, $GdNi_2Si_2$, and $GdNi_2B_2C$.

In the case of $GdAg_2Si_2$ the ordering process is very complex leading to two relatively small discontinuities of 6 and 7 J/K mol at 11 and 17 K, respectively.[7] A similar behavior is found for GdMg, GdAuGe, $GdRu_2Ge_2$, and $GdNi_2Ge_2$. Also in $GdNi_2B_2C$ and $GdPd_2Ge_2$ a second phase transition below the ordering temperature has been reported. Such a behavior has been attributed to higher-order exchange interactions.[26] $GdCu_5$ does not exhibit any anomaly at T_N, but a broad maximum at about $T_N/2$. Also in Gd_2PdSi_3, $GdNi_2Si_2$ and $GdGa_2$ there is no *sharp* transition at the ordering temperature.

Ignoring for the moment these difficulties in the interpretation of specific-heat data, we find strong candidates for NCAM order—$GdAu_2Si_2$, $GdCo_2Ge_2$, and $GdPd_2Ge_2$. We strongly suggest to perform scattering experiments on these compounds in the vicinity of the ordering temperature to find more evidence for the formation of NCAM structures. Considering the experimental difficulties in finding small deviations from an EM structure (as described above for the case of $GdCu_2$) and that only in a few cases scattering experiments have been reported, it is possible, that in many of the mentioned cases NCAM order might be found, perhaps within a small temperature region.

VI. SUMMARY

We have proposed anisotropic exchange as a reason for the formation of NCAM structures in Gd compounds. The specific heat of noncollinear Gd antiferromagnets has been calculated and compared to available experimental data. Some candidates for the formation of NCAM order are suggested and proposed for further study by scattering experiments. The magnetic structure near the ordering temperature is very sensitive to small details of the exchange interaction. A complete set of precise diffraction data for several Gd compounds is necessary to clarify what might be the origin of anisotropy in the exchange interaction of Gd compounds and if classical dipole-dipole exchange can describe it.

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APPENDIX

Here the derivation of Eq. (14) is discussed in detail. Introducing the Fourier transforms [Eqs. (4) and (5)] in Eq. (10) and comparing the components of third order in t results in the following system of equations (for $n=1,3,5,7,...$)

$$\mathbf{M}_{n3}=\frac{C^{(1)}}{T_N(g_J\mu_B)^2}\bar{\bar{\mathcal{J}}}(n\mathbf{Q}_0)(\mathbf{M}_{n1}+\mathbf{M}_{n3})+\frac{C^{(3)}}{T_N^3(g_J\mu_B)^6}\times\sum_{m,r=\pm1}\bar{\bar{\mathcal{J}}}([n-m-r]\mathbf{Q}_0)\mathbf{M}_{(n-m-r)1}\times[M_{m1}^T\bar{\bar{\mathcal{J}}}^T(m\mathbf{Q}_0)\bar{\bar{\mathcal{J}}}(r\mathbf{Q}_0)\mathbf{M}_{r1}]. \tag{A1}$$

Note that the sum in Eq. (A1) contains only one term if $\mathbf{Q}_0=0$ and a prefactor of $\frac{1}{4}$ has to be added to this sum if $\mathbf{Q}_0\in$ BZB. For $n=1$ Eq. (A1) may be rewritten using Eq. (13):

$$\left(\bar{\bar{1}}-\frac{C^{(1)}}{T_N(g_J\mu_B)^2}\bar{\bar{\mathcal{J}}}(\mathbf{Q}_0)\right)\mathbf{M}_{13}=\begin{cases}\mathbf{M}_{11}\left[1+\dfrac{2C^{(3)}}{[C^{(1)}]^3}(\mathbf{M}_{-11}^T\mathbf{M}_{11})\right]+\dfrac{C^{(3)}}{[C^{(1)}]^3}\mathbf{M}_{-11}(\mathbf{M}_{11}^T\mathbf{M}_{11}) & \mathbf{Q}_0\neq0,\notin\text{BZB}\\ \mathbf{M}_{11}\left[1+\dfrac{C^{(3)}}{[C^{(1)}]^3}(\mathbf{M}_{-11}^T\mathbf{M}_{11})\right] & \mathbf{Q}_0=0\\ \mathbf{M}_{11}\left[1+\dfrac{C^{(3)}}{2[C^{(1)}]^3}(\mathbf{M}_{-11}^T\mathbf{M}_{11})\right]+\dfrac{C^{(3)}}{4[C^{(1)}]^3}(\mathbf{M}_{11}+\mathbf{M}_{-11})(\mathbf{M}_{11}^T\mathbf{M}_{11}) & \mathbf{Q}_0\in\text{BZB}.\end{cases} \tag{A2}$$

Comparing the left side of this vector equation to the eigenvalue problem (13) the bracket is equivalent to the projection operator $\bar{\bar{\mathcal{P}}}(\mathbf{Q}_0)$ into the plane normal to the eigenvector $\mathbf{M}_{11}$.

$$\bar{\bar{\mathcal{P}}}(\mathbf{Q}_0)=\left(\bar{\bar{1}}-\frac{\bar{\bar{\mathcal{J}}}(\mathbf{Q}_0)}{\lambda(\mathbf{Q}_0)}\right). \tag{A3}$$

Therefore, the left side vanishes if Eq. (A2) is multiplied by $\mathbf{M}_{11}^\dagger=\mathbf{M}_{-11}^T$ leading to[33]

$$0=\begin{cases}|\mathbf{M}_{11}|^2\left[1+\dfrac{2C^{(3)}}{[C^{(1)}]^3}|\mathbf{M}_{11}|^2\right]+\dfrac{C^{(3)}}{[C^{(1)}]^3}|\mathbf{M}_{11}|^4|\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}|^2 & \mathbf{Q}_0\neq0,\notin\text{BZB}\\ |\mathbf{M}_{11}|^2\left[1+\dfrac{C^{(3)}}{[C^{(1)}]^3}|\mathbf{M}_{11}|^2\right] & \mathbf{Q}_0=0\\ |\mathbf{M}_{11}|^2\left[1+\dfrac{C^{(3)}}{2[C^{(1)}]^3}|\mathbf{M}_{11}|^2\right]+\dfrac{C^{(3)}}{2[C^{(1)}]^3}|\mathbf{M}_{11}|^4 & \mathbf{Q}_0\in\text{BZB}.\end{cases} \tag{A4}$$

The nonzero solution of this equation corresponds to the moment $|\mathbf{M}_{11}|^2$ for $T<T_N$ as given in Eq. (14). Note that in general $\mathbf{M}_{11}^T\mathbf{M}_{11}$ is not equivalent to $|\mathbf{M}_{11}|^2$ ($|\mathbf{M}_{11}|^2=\mathbf{M}_{11}^\dagger\mathbf{M}_{11}$), because $\mathbf{M}_{11}$ is a complex vector.

For $n=3$ in Eq. (A1) we get the following expression for the third harmonic of the magnetic moment (here $\mathbf{Q}_0\neq0,\notin$ BZB)

$$\mathbf{M}_{33}=\frac{C^{(3)}}{[C^{(1)}]^3}\bar{\bar{\mathcal{P}}}^{-1}(3\mathbf{Q}_0)\mathbf{M}_{11}(\mathbf{M}_{11}^T\mathbf{M}_{11}) \tag{A5}$$

from which Eq. (15) can be deduced.

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[1] J. A. Blanco, D. Gignoux, and D. Schmitt, Phys. Rev. B **43**, 13 145 (1991).

[2] I. Affleck, J. Phys.: Condens. Matter **1**, 3047 (1989).

[3] Note: if the reduced wave vector corresponding to $n\mathbf{Q}$ lies on the zone boundary of the first Brillouin zone, it contributes only partly to the sum in Eqs. (7) and (9).

[4] For $|n|>1$ and first order in t the Eq. $\bar{\bar{\mathcal{J}}}(n\mathbf{Q})\mathbf{M}_{n1}=[(g_J\mu_B)^2T_N/C^{(1)}]\mathbf{M}_{n1}$ is derived. For arbitrary $\bar{\bar{\mathcal{J}}}(n\mathbf{Q})$ and T_N calculated by Eq. (13) only the solution $\mathbf{M}_{n1}=0$ is possible. However, if for some special reason such as symmetry the eigenvalue problem of some $\bar{\bar{\mathcal{J}}}(n\mathbf{Q})$ leads to the same eigenvalue as Eq. (13), multiple $\mathbf{Q}$ structures or frustration is the consequence. In this article we will neglect this possibility and assume

$\mathbf{M}_{n1}=0$ for all $|n|>1$ and $\mathbf{Q}\neq\mathbf{Q}_0$.

[5] For $n=-1$ the complex-conjugate problem has to be solved, because from the Fourier transform (6) follows $\bar{\bar{\mathcal{J}}}(\mathbf{Q})=\bar{\bar{\mathcal{J}}}(-\mathbf{Q})^*$ and therefore $\mathbf{M}_{-11}=\mathbf{M}_{11}^*$.

[6] Note: for $\mathbf{Q}_0=0$ the terms containing a sum over $\pm\mathbf{Q}$ in the expansion of Eq. (10) reduce to one term only. For $\mathbf{Q}_0\in$ BZB a factor $\frac{1}{2}$ has to be considered in the Fourier expansions, because the terms containing $\mathbf{Q}_0$ only contribute partly to the sums in Eqs. (7) and (9).

[7] R. Mallik and E. Sampathkumaran, Phys. Rev. B **58**, 9178 (1998).

[8] M. Rotter, A. Lindbaum, E. Gratz, H. Müller, G. Hilscher, H. Sassik, H. E. Fischer, M. T. Fernandes-Diaz, R. Arons, and E. Seidl, J. Magn. Magn. Mater. **214**, 281 (2000).

[9] N. H. Luong, J. J. M. Franse, and T. D. Hien, J. Phys. F: Met. Phys. **15**, 1751 (1985).

[10] A. Koyanagi, Y. Yoshida, Y. Kimura, R. Settai, K. Sugiyama, and Y. Onuki, J. Phys. Soc. Jpn. **67**, 2510 (1998).

[11] M. Rotter, A. Schneidewind, M. Loewenhaupt, M. Doerr, A. Stunault, A. Hiess, A. Lindbaum, E. Gratz, G. Hilscher, and H. Sassik, Physica B **284-288**, 1329 (2000).

[12] M. K. Borombaev, R. Z. Levitin, A. S. Markosyan, V. A. Reimer, A. V. Sinitsyn, and Z. Smetana, Zh. Eksp. Teor. Fiz. **93**, 1517 (1987) [Sov. Phys. JETP **66**, 866 (1987)].

[13] S. Y. Dankov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Phys. Rev. B **57**, 3478 (1998).

[14] M. Bouvier, P. Lethuillier, and D. Schmitt, Phys. Rev. B **43**, 13 137 (1991).

[15] J. M. Barandiaran, D. Gignoux, D. Schmitt, J. C. Gomez-Sal, J. R. Fernandez, P. Chieux, and J. Schweizer, J. Magn. Magn. Mater. **73**, 233 (1988).

[16] N. P. Duong, K. H. J. Buschow, E. Brück, L. T. Tai, and T. D. Hien, in *Trends in Material Science and Technology*, edited by F. Bekker, N. D. Chien, J. J. M. Franse, T. D. Hien, N. T. Hien, and N. P. Thuy (Hanoi National University Publishing House, Hanoi, 1999), pp. 142-145.

[17] B. W. Lee, J. M. Ferreira, Y. Dalichaouch, M. S. Torikachvili, K. N. Yang, and M. B. Maple, Phys. Rev. B **37**, 2368 (1988).

[18] D. McK. Paul, H. A. Mook, A. W. Hewat, B. C. Sales, L. A. Boatner, J. R. Thompson, and M. Mostoller, Phys. Rev. B **37**, 2341 (1988).

[19] T. Chattopadhyay, G. J. McIntyre, and U. Köbler, Solid State Commun. **100**, 117 (1996).

[20] U. Köbler, D. Hupfeld, W. Schnelle, K. Mattenberger, and T. Brückel, J. Magn. Magn. Mater. **205**, 90 (1999).

[21] G. Hilscher and H. Michor, in *Studies of High Temperature Superconductors*, edited by A. V. Narlikar (Nova Science Publishers, New York, 1999), Vol. 28, pp. 241-286.

[22] K. Tomala, J. P. Sanchez, P. Vulliet, P. C. Canfield, Z. Drzazga, and A. Winiarska, Phys. Rev. B **58**, 8534 (1998).

[23] C. Detlefs, A. I. Goldmann, C. Stassis, P. C. Canfield, B. K. Cho, J. P. Hill, and D. Gibbs, Phys. Rev. B **53**, 6355 (1996).

[24] B. J. Gibson, W. Schnelle, R. Pöttgen, K. Bartkowski, and R. K. Kremer, Czech. J. Phys. **46**, 2573 (1996).

[25] A. Garnier, D. Gignoux, D. Schmitt, and T. Shigeoka, Physica B **222**, 80 (1996).

[26] U. Köbler, R. M. Müller, W. Schnelle, and K. Fischer, J. Magn. Magn. Mater. **188**, 333 (1998).

[27] R. Mallik, E. V. Sampathkumaran, M. Strecker, and G. Wortmann, Europhys. Lett. **41**, 315 (1998).

[28] S. R. Saha, H. Sugawara, T. D. Matsuda, H. Sato, R. Mallik, and E. V. Sampathkumaran, Phys. Rev. B **60**, 12 162 (1999).

[29] M. J. Parsons, J. Crangle, K. U. Neumann, and K. R. A. Ziebeck, J. Magn. Magn. Mater. **184**, 184 (1998).

[30] J. W. Taylor, H. Capellmann, K. U. Neumann, and K. R. A. Ziebeck, Eur. Phys. J. B **16**, 233 (2000).

[31] In this case the exchange interaction $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$ is real and symmetric $[\bar{\bar{\mathcal{J}}}(\mathbf{Q})=\bar{\bar{\mathcal{J}}}^T(\mathbf{Q})]$, it has real eigenvalues and it follows that $\hat{\mathbf{M}}_{11}^T\hat{\mathbf{M}}_{11}=1$ (AM). Note that this rule only holds, if the classical dipole-dipole interaction is able to lift the degeneracy of the upmost eigenvalue of $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$.

[32] M. Rotter (unpublished).

[33] Note: in the case of simple antiferromagnetism (i.e., $\mathbf{Q}_0\in$ BZB) the exchange interaction $\bar{\bar{\mathcal{J}}}(\mathbf{Q})$ is real and symmetric $[\bar{\bar{\mathcal{J}}}(\mathbf{Q})=\bar{\bar{\mathcal{J}}}^T(\mathbf{Q})]$, it has real eigenvalues and it follows that the eigenvector $\mathbf{M}_{11}=\mathbf{M}_{-11}$ is also real.