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Specific heat and metamagnetic process in a modulated compound: $PrNi_2Si_2$

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Low-temperature specific-heat and magnetization measurements have been performed on the tetragonal $PrNi_2Si_2$ compound. This compound orders at $T_N = 20$ K in a sine-wave-modulated magnetic structure which remains stable down to 0 K owing to the existence of a nonmagnetic singlet as the crystal-field ground state. A self-consistent periodic-field model including the crystal-field effects accounts quantitatively very well for the observed properties in the modulated phase.

Over the last two decades, the study of modulated magnetic systems has attracted great interest. Intensive theoretical works have been centered on Ginzburg-Landau formalism[1,2] or anisotropic Ising models,[3] in which the modulation results from competing interactions. Experimentally, an increasing number of compounds have been found to exhibit this type of modulated ordering, at least in a limited temperature range.

In this context, rare-earth intermetallic compounds are particularly interesting to study because they exhibit a great variety of magnetic structures, due to the oscillatory and long-range character of the indirect exchange interactions of Ruderman-Kittel-Kasuya-Yosida–type, mediated from one site to another through the conduction electrons. Thus, in addition to ferromagnetic and simple antiferromagnetic structures, complex magnetic arrangements (helical, conical, cycloidal, triangular, amplitude modulated,...) have been found in many systems.[4–6] These complex structures are characterized in particular by their propagation vector **Q** which is often incommensurate (strictly or not) with the lattice periodicity. An important subdivision of these complex structures has to be considered, namely, the *equal-moment* (EM) structures and the *amplitude-modulated* (AM) ones. The first category includes, for example, the helimagnetic systems.

For all the rare earths except gadolinium, the existence of a nonzero orbital angular momentum leads to an electrostatic coupling between the $4f$ shell and its environment known as the crystalline electric field (CEF).[7] This CEF coupling generally imposes the ordered $4f$ magnetic moments to be confined along or perpendicular to a given crystallographic direction. In these conditions, the exchange interactions and the CEF may be antagonistic with each other. The most typical case occurs when the CEF anisotropy forces the moments to lie along the c axis of an uniaxial system while the exchange coupling $J(\mathbf{q})$ leads to an incommensurate propagation vector **Q**. This competition prevents the system from ordering in an helimagnetic structure, which is, *in principle,* always favored from an energetic point of view. It rather produces an AM magnetic structure, at least just below the ordering temperature T_N. In CEF systems, a helimagnetic structure is compatible only with the existence of an easy magnetization plane, for instance, the basal plane of an hexagonal compound, as found in some rare-earth metals.[4]

A second CEF effect involves the temperature evolution of such AM structures.[8] Indeed, at low temperature, due to entropy effects associated with the modulation of the magnetic-moment amplitude, the spin system may either (i) suddenly jump through a first-order transition to an EM structure having often a different propagation vector (this is the case of $TbNi_2Si_2$ compound)[9,10] or (ii) remain incommensurate. In this latter case, and in the presence of a magnetic CEF ground state, the system must evolve to an antiphase structure at 0 K, through the progressive squaring up of the modulation; this is accompanied by the growing of high-order harmonics of the propagation vector, as observed, for example, in the metal Tm.[11] If the ground state is nonmagnetic, the modulated structure can remain stable down to 0 K.

The body-centered tetragonal ($ThCr_2Si_2$-type) rare-earth compound $PrNi_2Si_2$ appears as a typical example where three characteristics are realized:[9,12,13] (i) nickel is nonmagnetic, there is only one magnetic Pr^{3+} ion in the primitive unit cell (position $4/mmm$) and this Pr sublattice orders at $T_N = 20.0 \pm 0.5$ K in an *incommensurate* antiferromagnetic structure with $\mathbf{Q} = (0,0,0.870)$; (ii) the CEF anisotropy fixes the magnetic moments along the c axis, then the magnetic structure is AM; (iii) there is no other transition below T_N and the ground state has been proved to be a nonmagnetic singlet so that the AM structure actually subsists down to 0 K.

The aim of the present study is to carefully investigate the consequences of the existence of an AM magnetic

structure in $PrNi_2Si_2$ on two particular magnetic properties, namely, the specific heat and the magnetization process. For that purpose, we will use a *periodic-field* (PF) *model* based upon a similar recent study which was, however, restricted to gadolinium compounds.[14] We thus have extended this previous model by including the CEF effects, and we will show that the main result obtained in Ref. 14, namely, the noticeable *reduction of the specific-heat discontinuity at* T_N, is not affected by the presence of CEF. In addition, the way the modulation is destroyed by application of a magnetic field will be analyzed in detail.

The PF model is based on a N-site Hamiltonian $\mathcal{H}$, N being the number of magnetic ions over one period of the AM magnetic structure:

$$\mathcal{H}=\sum_{i=1}^{N}\mathcal{H}_{\mathrm{CEF}}(i)-\sum_{i=1}^{N}[\mathbf{H}_{\mathrm{ex}}(i)+\mathbf{H}_{\mathrm{app}}]\cdot\mathbf{M}(i)+\frac{1}{2}\sum_{i=1}^{N}\langle\mathbf{M}(i)\rangle\cdot\mathbf{H}_{\mathrm{ex}}(i)\,. \tag{1}$$

Here, $\mathcal{H}_{\mathrm{CEF}}$ represents the CEF Hamiltonian appropriate for the tetragonal symmetry, i.e., $\mathcal{H}_{\mathrm{CEF}}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4$, the B_l^m being determined by other experiments in $PrNi_2Si_2$.[13] $\mathbf{H}_{\mathrm{app}}$ is the applied magnetic field while $\mathbf{H}_{\mathrm{ex}}(i)$ is the exchange field acting on the ith site, within the mean-field approximation. The last term is a corrective energy term due to the mean-field treatment. In the present case, only the z direction will be considered because the magnetic moments in $PrNi_2Si_2$ are aligned along this direction in the modulated phase. Moreover, magnetic fluctuations above T_N as well as collective excitations below T_N will not be considered.

As explained previously,[14] the exchange field as well as the magnetic moments can be expanded in Fourier series, both being connected with each other through the successive bilinear exchange couplings $J(n\mathbf{Q})$:

$$M_z(i)=\sum_n M_{n\mathbf{Q}}e^{in\mathbf{Q}\cdot\mathbf{R}_i}\,, \tag{2}$$

$$H_{\mathrm{ex}}(i)=(g_J\mu_B)^{-2}\sum_{j\neq i}J(ij)\langle M_z(j)\rangle=\sum_n H_{n\mathbf{Q}}e^{in\mathbf{Q}\cdot\mathbf{R}_i}\,, \tag{3}$$

with

$$H_{n\mathbf{Q}}=(g_J\mu_B)^{-2}J(n\mathbf{Q})M_{n\mathbf{Q}}\,. \tag{4}$$

In the absence of H_{app}, the Fourier expansion includes only odd harmonics. However, when the external magnetic field differs from zero, the $n=0$ term (ferromagnetic component) and the other even terms have to be considered. Then the $J(0)$ coupling coefficient becomes involved in addition to all the other $J(n\mathbf{Q})$'s. It must be noticed that among all these coefficients, two can be easily determined from the experiment, namely, $J(\mathbf{Q})$ and $J(0)$: They are directly connected with the Néel temperature T_N and the paramagnetic mean-field coefficient λ, respectively. In $PrNi_2Si_2$, T_N and λ lead to $J(\mathbf{Q})=2.26$ K and $J(0)=-0.20$ K. The determination of the other coefficients would require the analysis of magnetic excitations measured by inelastic neutron scattering in order to obtain the Fourier transform $J(\mathbf{q})$ of the exchange interaction throughout the whole Brillouin zone.

The Hamiltonian equation (1) has been diagonalized in a self-consistent manner for the N ions of one magnetic period, the Fourier coefficients $M_{n\mathbf{Q}}$ after a diagonalization being reinjected into the initial Hamiltonian through Eqs. (3) and (4). In $PrNi_2Si_2$, N has been taken as the most simple integer compatible with the experimental value of $\mathbf{Q}$, i.e., $N=16$. Note that the results actually do not depend on N. The internal energy then can be evaluated for each ion at any temperature and the thermal derivative of the values averaged over one period finally provides the mean specific heat per magnetic ion. In the same way, the averaged magnetization can be achieved in the presence of the external magnetic field.

First, the specific heat of $PrNi_2Si_2$ has been calculated without any additional parameters, i.e., taking into account only the five CEF parameters B_l^m (Ref. 13) and one single exchange coefficient $J(\mathbf{Q})$ (see Fig. 1). Above the ordering temperature, a Schottky anomaly is calculated as expected from a simple CEF theory. At T_N in $PrNi_2Si_2$, the PF model predicts a λ-type anomaly with a calculated discontinuity $\Delta C_{\mathrm{AM}}\sim 3.5$ J/K mol very close to the experimental value $\Delta C_{\mathrm{exp}}\sim 3.3$ J/K mol, while the jump expected for an EM system is noticeably larger $\Delta C_{\mathrm{EM}}\sim 5.3$ J/K mol. In addition, the general shape of the temperature variation within the ordered phase is well accounted for. The vertical shift between experimental and calculated curves can be attributed to an imperfect lattice correction, while the shape of the variation just above T_N suggests the presence of magnetic fluctuations.[15]

Therefore, the main conclusion of the previous study in Gd systems,[14] namely, the strong reduction of the specific-heat discontinuity for AM structures, is found again in anisotropic systems. It can be noticed that introducing higher harmonics in our calculation does not modify the results greatly. This is related to the existence of the AM structure down to 0 K in $PrNi_2Si_2$, leading to a Fourier expansion of $M_z(i)$ which remains essentially a sine wave, so that the higher-order terms have only a very weak influence. This is not true in magnetic ground-state systems where the structure evolves toward an antiphase one with all moments equal at low temperature.[14]

The critical behavior of $C(T)$ in the near vicinity of T_N can be analytically obtained by using an expansion of the magnetic moment at each site in powers of the corresponding exchange field in the presence of CEF effects:

$$\langle M(i)\rangle=\chi_0 H_{\mathrm{ex}}(i)+\chi_0^{(3)}[H_{\mathrm{ex}}(i)]^3+\cdots\,. \tag{5}$$

The same procedure as in Ref. 14 can be used again to derive the dependence of the $M_{n\mathbf{Q}}$'s on the reduced variable $t=(1-T/T_N)^{1/2}$ in the vicinity of T_N. The internal energy can then be averaged over one period, the temperature derivative providing the calculated specific heat at T_N^-, i.e., immediately below T_N:

$$C_{\mathrm{AM}}(T_N^-)=C_{\mathrm{CEF}}(T_N)+\Delta C_{\mathrm{AM}}=C_{\mathrm{CEF}}(T_N)-\frac{1}{3}\frac{T_N[d\chi_0(T_N)/dT]^2}{\chi_0^{(3)}(T_N)}\,, \tag{6}$$

where the first term is the usual CEF contribution and the second term corresponds to the expected jump of the

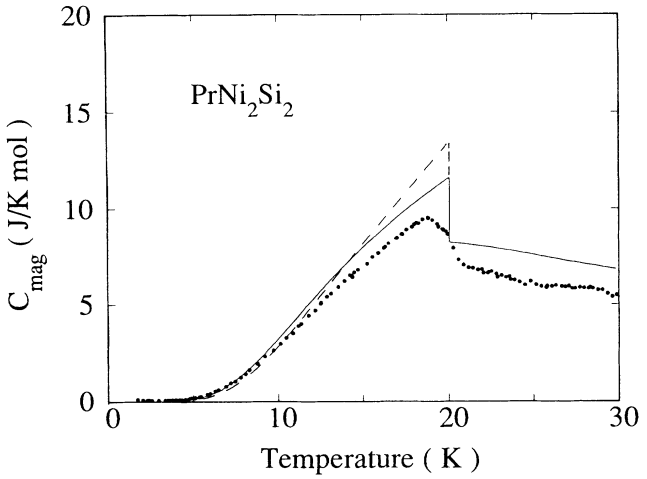

FIG. 1. Magnetic specific heat of $PrNi_2Si_2$; calculated specific heat within the PF model, for the equal-moment (EM, dashed line) and the amplitude-modulated (AM, solid line) case. The crystal-field parameters are $B_2^0 = -3.61$ K, $B_4^0 = -2.77 \times 10^{-2}$ K, $B_4^4 = -0.234$ K, $B_6^0 = 3.95 \times 10^{-3}$ K, and $B_6^4 = -5.53 \times 10^{-3}$ K.

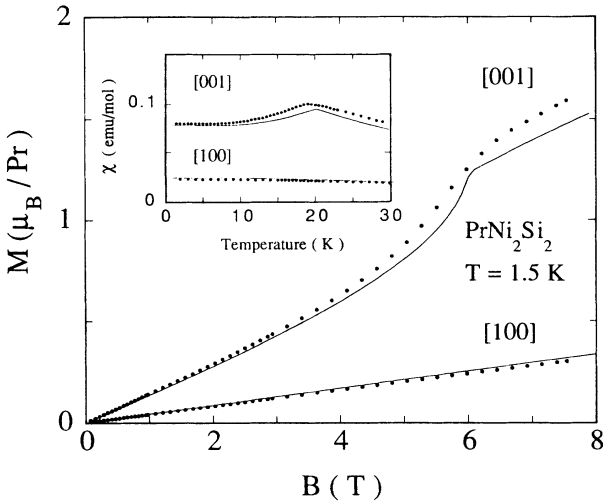

FIG. 2. Magnetization processes in $PrNi_2Si_2$ at 1.5 K along the [001] and [100] axes; the inset shows the temperature variation of the magnetic susceptibility; lines are calculated by the PF model.

specific heat at T_N. The same calculation can be applied to EM systems, providing the following expression:

$$C_{EM}(T_N^-) = C_{CEF}(T_N) + \Delta C_{EM}$$
$$= C_{CEF}(T_N) - \frac{1}{2} \frac{T_N [d\chi_0(T_N)/dT]^2}{\chi_0^{(3)}(T_N)} . \quad (7)$$

The specific-heat discontinuity at T_N, calculated analytically, is then strongly reduced in anisotropic AM systems, reaching only $\frac{2}{3}$ of that expected in EM systems, i.e., the same reduction that was calculated in gadolinium compounds, where there are no CEF effects. The only difference here is the presence of an additional CEF contribution. In $PrNi_2Si_2$, taking into account the known CEF parameters provides $\Delta C_{AM} = 3.56$ J/K mol, in good agreement with the value obtained by the self-consistent PF model.

The PF model has been used in the presence of a magnetic field to calculate the low-temperature magnetization process along and perpendicular to the [001] easy magnetization direction (see Fig. 2). It is worth noting that the agreement is remarkable, without the addition of any other adjustable parameter. In particular, the smooth metamagnetic behavior along [001] is well accounted for and corresponds to the progressive vanishing of the modulation; the induced ferromagnetic state is achieved at about 6 T where a cusp can be observed on both experimental and calculated curves.

Along the [100] direction, the calculated variation is linear and much weaker than along the c axis, as the experiment. During this magnetization process, the modulated structure is twisted, the field inducing a [100] magnetic component which is also modulated with a period 2 times smaller than the modulation along [001]. This is due to the fact that the weak magnetic moments in the modulated structure can align parallel to the field much more easily than the large moments which remain confined close to the c easy axis. Finally, the magnetic susceptibility is calculated to be very close to the experimental variation by our PF model (Fig. 2), the [001] variation exhibiting a clear maximum at T_N while the [100] variation is very smooth.

In summary, we have shown that the periodic-field model is able to describe quite satisfactorily the experi-

TABLE I. Calculated specific-heat discontinuity at the ordering temperature according to the type of magnetic structure (EM, equal moment; AM, amplitude modulated) in several rare-earth compounds; experimental values and type of structure are taken from the given reference.

Compound	ΔC_{calc}(EM) (J/K mol)	ΔC_{calc}(AM) (J/K mol)	ΔC_{exp} (J/K mol)	Magnetic structure	Ref.
$TmNi_5$	11.91	7.94	12.4	EM	16
HoCu	14.80	9.87	14.7	EM	17
ErCu	23.20	15.45	15.5	AM	17
$CeAl_2Ga_2$	9.97	6.65	6.3	AM	18

mental results of specific heat and magnetization in the AM compound $PrNi_2Si_2$. This was made possible owing to a good knowledge of the crystal-field effects in this compound. The PF model predicts a specific-heat discontinuity at T_N clearly smaller in AM than in FM (ferromagnetic or simple antiferromagnetic) systems. This PF model can be applied to any AM magnetic system as soon as all the relevant parameters, in particular the crystal-field ones, have been determined. Some examples taken in the literature support very well all these considerations, as far as the specific heat is concerned (see Table I).

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