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Magnetic properties of singlet ground states in RM_2X_2 compounds

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Abstract

A simple survey of the magnetic properties of new tetragonal RM_2X_2 compounds is given. Particular attention is paid to the interaction of Crystal Field in the case of nonmagnetic singlet ground states. A number of physical effects which result from this situation are discussed. In particular, the nature of this type of ground state is proved to be indispensable for the existence of amplitude magnetic structures at 0 K and for the most amazing of mixed magnetic phases, in which Rare Earth ions with two magnetic states are involved. Evidence of this behaviour through several examples in such compounds as $PrNi_2Si_2$, $TbNi_2Si_2$, $TbRu_2Si_2$ and $TbRu_2Ge_2$ from the joint analysis of different magnetic properties will be presented. © 1998 Elsevier Science S.A.

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During the last decades, the intermetallic compounds containing Rare Earth (RE) have been the subject of intensive studies because of their intriguing and fascinating physical properties, which have both fundamental and practical interest [1–3]. One of the families is the ternary body-centered tetragonal REM_2X_2 (M=Ni or Ru, X=Si or Ge) with a large number of compounds showing new and less conventional magnetic properties [4]. There is a great variety of RE in this series exhibiting metamagnetic process with single or multiple sharp step-like transitions under an applied magnetic field. Moreover, most of the compounds have an incommensurate magnetic structure, at least, below T_N [2]. This behaviour could be related to the competing and highly frustrated exchange interactions together with the presence of a strong uniaxial anisotropy exhibited in this series, as will be stressed in the following.

In order to explain all these interesting properties, an adequate determination of the relevant interactions involved, namely, Crystal Field (CF) and exchange parameters, is required [5]. In particular, the CF splitting and the composition of the related CF levels is quite important in relation to the magnetic properties of the system. In the case of non Kramers ions, the ground state can be a nonmagnetic singlet state leading to the existence of Amplitude Modulated (AM) structures at 0 K or to the appearance of Mixed Magnetic (MM) phases in which zero and high magnetic moments could coexist within the same magnetic periodicity. For the determination of these parameters, a single experiment is not at all sufficient in low symmetry systems due to the complexity of the analysis, which involves a large number of CF parameters that often lead to several sets of different possibilities when only one property is considered [6]. Special attention has been paid in Ref. [5] to the procedure used to unambiguously determine the CF parameters in tetragonal symmetry.

The aim of this contribution is to show, through such examples as $PrNi_2Si_2$, $TbNi_2Si_2$, $TbRu_2Si_2$ and $TbRu_2Ge_2$ compounds, how an appropriate determination of the CF parameters can cast some light on the understanding of the magnetic properties in these materials. The calculations carried out in the ordered range of these systems were performed using the information of CF and exchange coupling constants previously determined in the paramagnetic phase. The Hamiltonian of the problem is then resolved using a self-consistent periodic field model in which the exchange field is expanded in Fourier series [6].

As commented on before, most of the compounds of these series are characterized by the existence of incommensurate or long range commensurate magnetic structures in the ordered phase or, at least, just below T_N. Among them, one of the unique cases found in nature is $PrNi_2Si_2$, which presents a longitudinal AM magnetic structure along the **c** direction which remains stable from T_N down to 0 K. In the inset of Fig. 1, the magnitude of the main and the third harmonics are represented as obtained from a single

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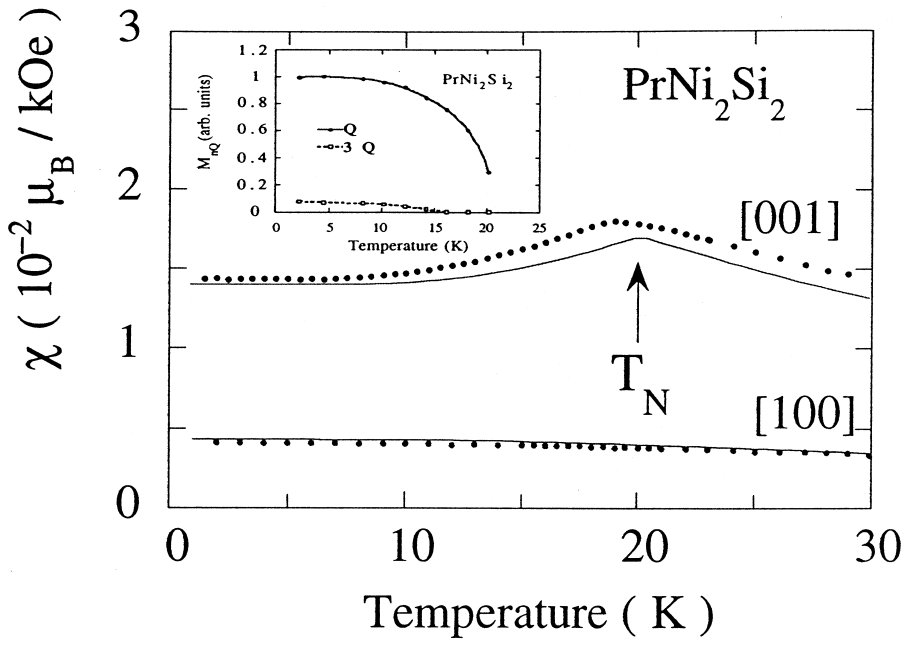

Fig. 1. Magnetic susceptibility along [100] and [001] directions in $PrNi_2Si_2$. Solid lines are the calculated variation obtained from the periodic field model. Inset: thermal dependence of the harmonics M_Q and M_{3Q} of the AM magnetic structure. The lines are guides for the eye in this case.

crystal diffraction experiment performed recently [7]. These data show that the magnetic structure has an essentially sinusoidal AM character in all the ordered range. The reason for this special circumstance is the existence of a nonmagnetic singlet ground state, well isolated in energy from the excited levels [4]. In this situation, exchange interactions are not strong enough to induce a first order transition at lower temperatures which can stabilize a commensurate magnetic structure (as in $TbNi_2Si_2$, see below); or to produce a squaring up of the sinusoidal structure (as in $TbRu_2X_2$, see below). A magnetic property which is particularly influenced by the nature of the ground state is the magnetic susceptibility. The experimental variation along the main directions of the tetragonal symmetry together with the calculated one are also depicted in Fig. 1 and are found to be very close to each other. The variation along the [001] direction exhibits a clear maximum at T_N while the variation corresponding to the [100] one is almost temperature independent, as was also observed.

On the other hand, the behaviour of $TbNi_2Si_2$ is quite similar to that of $PrNi_2Si_2$, because it also presents an AM structure below T_N. However, when the temperature is lowered it undergoes a first order transition in which the propagation vector $Q_1=(0.5+\tau, 0.5-\tau, 0)$, with $\tau=0.074$ corresponding to the AM structure stabilized below T_N, is replaced by a propagation vector $Q_2=(0.5, 0.5, 0)$ associated with a simple antiferromagnetic Equal Moment (EM) structure. Furthermore, as a direct consequence of this thermal behaviour, a succession of commensurate or incommensurate induced-field structures are observed leading to the existence of a complex magnetic phase diagram, when the magnetic field is applied along the moment direction. i.e., the **c** direction [8]. This magnetic behaviour could be understood in a simple way by the fact of the particular CF splitting in $TbNi_2Si_2$. In fact, the two lowest CF levels are nonmagnetic singlet states which under an applied magnetic field and/or temperature behave as a magnetic pseudodoublet [9]. This feature is the reason for the appearance of an EM magnetic structure at temperatures below $T_t=8.5$ K and the different magnetic transitions observed in this compound under a magnetic field. In the same way, in Fig. 2, the magnetic part of the specific heat of $TbNi_2Si_2$ and the calculated variation using the CF and the exchange parameters determined in the paramagnetic phase are represented. For comparison, the calculated curve for an EM structure, like a simple antiferromagnetic, is also depicted. In this case the jump of C_{mag} at T_N is quite large with regard to that of the experimental one, while the corresponding one associated with the AM is quite similar.

The magnetic properties of $RERu_2X_2$ series (X=Si and Ge) appear to be quite similar. In principle the properties of these compounds are not expected to be drastically modified by the substitution of Ge for Si, considering the same external electronic configuration of these latter atoms. These compounds are ferromagnetic at the beginning of the series and long-period commensurate antiferromagnetic at the end of the series. Among them, the most striking behaviour was recently reported in $TbRu_2X_2$ compounds (X=Si and Ge) [10]. In fact, $TbRu_2Ge_2$($TbRu_2Si_2$) orders at $T_N=37$ K (57 K) in an AM structure with a propagation vector $\boldsymbol{Q}=(\tau, 0, 0)$ with $\tau=0.2352$ (0.23). At lower temperatures, it becomes antiphasic with the magnetic moments aligned along the **c** direction owing to the uniaxial anisotropy and reaching the

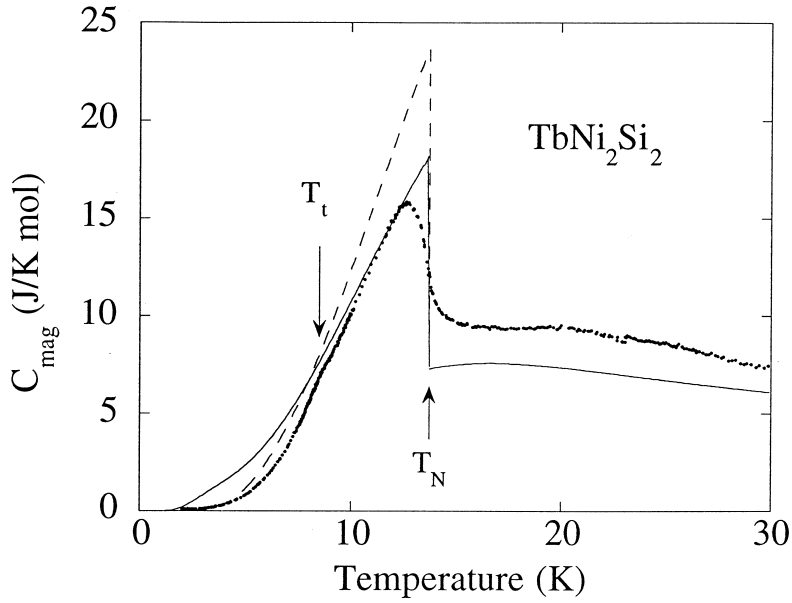

Fig. 2. Calculated and experimental thermal variation of the magnetic part of the specific heat in $TbNi_2Si_2$.The solid line corresponds to the AM magnetic structure, while the dashed one is that associated with the EM structure.

maximum saturated value for Tb free ions, namely, M_s= 9.0 μ_B, [10]. Furthermore, below T_t=4.3 K (5 K) several metamagnetic transitions appear in low magnetic fields as is shown in Fig. 3 for the case of $TbRu_2Ge_2$. In this case, it is possible to explain the observed metamagnetic transitions assuming a $0 \rightarrow M_s$ process or a $-M_s \rightarrow 0$ one, instead of a spin flip $-M_s \rightarrow M_s$ as generally occurs in strong uniaxial systems. In order to account for this surprising behaviour, the first step is to find a set of coherent CF parameters in which two magnetic states are possible [11], one with an almost zero magnetic moment and other with a high magnetic moment when the local exchange field overcomes a determined critical field, H_C. This situation is fulfilled if the ground state is a nonmagnetic level and the first excited states are levels rich in the J_z-component $|\pm J>$. Moreover owing to the composition of these excited states, a level crossing occurs as a function of the effective field acting on each Tb^{3+} ion. This feature is a clear indication of the important role played by the CF splitting in the magnetic properties of this system.

In summary, this simple survey has proved that the magnetic properties of intermetallic RE compounds for non Kramers systems are not only especially sensitive to the composition of the ground state, but also to the energy separation and composition of the first excited levels, modifying drastically the properties of these systems. In Fig. 4 the different situations found in this analysis are presented in schematic form. In this way, if the CF ground state is nonmagnetic and well isolated from the excited levels, at lower temperatures, the energy related to the

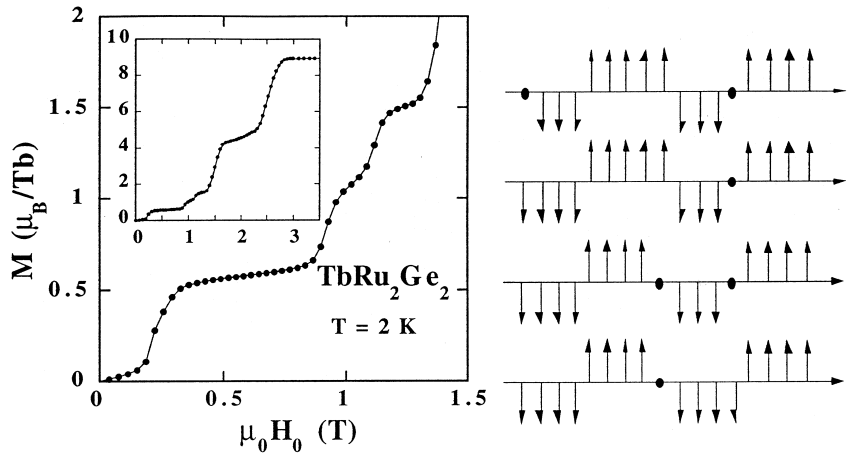

Fig. 3. Metamagnetic process in $TbRu_2Ge_2$. Left part: low field magnetization process in increasing field at 2 K. The inset shows the variation of M vs. H at 2 K up to 3.5 T. Right: magnetic structures at 2 K in zero field and the first three induced phases. Magnetizations of 17 successive Tb planes perpendicular to Q are represented. Black dots correspond to nonmagnetic planes.

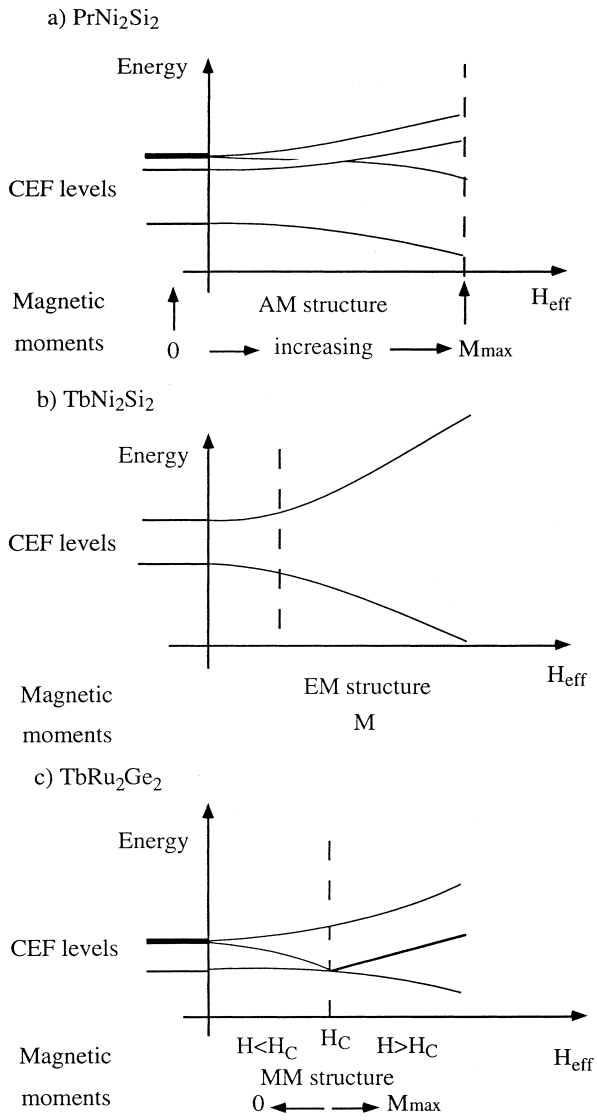

Fig. 4. Schematic field dependence of the CF levels corresponding to the investigated RM_2X_2 compounds (M=Ni or Ru; X=Ge or Si): (a) $PrNi_2Si_2$; (b) $TbNi_2Si_2$; and (c) $TbRu_2Ge_2$. At zero effective field, the thin lines are associated with nonmagnetic singlet states, while the thick ones are those of the doublet states. Note that, depending on the effective magnetic field, different ground states are possible on each site. For more details see text.

exchange interactions will not be strong enough to induce an EM moment on each site along the magnetic periodicity, resulting in an AM structure which can be stable down to 0 K. The magnetic moment varies from 0 to a maximum value, M_{max}, depending on the effective field, H_{eff}, acting on each site (case of $PrNi_2Si_2$, part a) in Fig. 4).

On the contrary, when the strength of the exchange interactions is intense enough, two situations could be found depending on the magnetic character of the first excited level. Firstly, in most of the cases, the magnetic behaviour evolves progressively to an EM structure because the dependence of the energy levels with H_{eff} favours those states with a maximum magnetic moment on all the magnetic sites, even if the first excited level is also a nonmagnetic singlet state (the case of $TbNi_2Si_2$, part (b) in Fig. 4), being the slope of the field dependence of the energy levels (related to the magnetic moment) larger than that of the case (a). Also, for an appropriate composition of the quantum states in the J_z-component of the first excited level, i.e., $|\pm J>$, the ground state under an effective magnetic field has two favourable situations (the case of $TbRu_2Ge_2$, part (c) in Fig. 4) depending on the value of H_{eff}: if this effective field acting on each ion is larger (or smaller) than a critical field, H_C, it leads to a maximum (or zero) magnetic moment. This last situation gives rise to the existence of mixed magnetic phases and explains well (qualitatively and quantitatively) the behaviour observed in $TbRu_2Ge_2$.

Finally, it is worth noting that it has been more recently reported that the $DyRu_2X_2$ compounds (X=Si and Ge) also exhibit a magnetic phase diagram [12] quite similar to that of the Tb compounds. Some authors have also proposed a similar explanation in terms of mixed magnetic phases. This possibility seems to be, in our opinion, quite puzzling due to the Kramers character of the Dy^{3+} ion. Consequently, other mechanisms must be invoked to account for the observed magnetic properties of $DyRu_2X_2$ compounds.

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