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The determination of crystal field parameters in rare earth intermetallic compounds

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Abstract

The behavior of the 4f systems is strongly influenced by the crystal field interaction as is evidenced in most of their magnetic properties. A systematic analysis of these properties can thereby be used to extract general trends for the determination of this fundamental interaction through the crystal field parameters. Although for cubic systems it is sufficient the information provided by the inelastic neutron scattering method, in low symmetry systems a single experiment is not usually enough, leading to several admissible possibilities. In order to determine without ambiguity the crystal field parameters it is then necessary to consider the information drawn from different magnetic properties in a self-consistent way. To illustrate these ideas some selected examples in tetragonal $REAg_2$ and $RENi_2Si_2$ systems will be presented and discussed.

Keywords: Rare earth intermetallics; Crystal field; Magnetic properties

1. Introduction

During the last thirty years, rare earth (RE) alloys have attracted considerable technological as well as theoretical attention by virtue of their magnetic properties and applications, being widely investigated first on binary compounds and more recently on ternary and even on quaternary compounds [1–3]. RE compounds with nonmagnetic metals constitute an almost unlimited field for the study of very different topics of magnetism. In particular, from a fundamental point of view, this interest has been also grown up by the fact that they provide useful examples for the understanding of the localized magnetism, in which quantitative analysis can be performed in order to determine their relevant interactions.

As it is well-known, in this type of metallic materials, the magnetic properties are mainly governed by two basic mechanisms: (i) the bilinear RKKY exchange interactions which have a long range and an oscillatory character and are responsible for the appearance of the magnetic order, and (ii) the crystal field (CF) interaction which is at the origin of the magnetocrystalline anisotropy. Furthermore, in concentrated 4f systems, CF and exchange interactions are usually of comparable strength. For this reason, the CF plays an important role in most of the physical properties and constitutes a fundamental term acting on the RE ions which should not be neglected in any quantitative analysis.

Up to now most of the investigations devoted to the CF interaction were performed for RE intermetallic compounds with high local symmetry. However, for systems in which the RE ion occupies a low local symmetry site, more complicated and quite less conventional magnetic behaviors have been observed during the last years, such as the metamagnetic process with multiple sharp step-like transitions [2], longitudinal sinusoidal magnetic structures [4] and mixed magnetic phases [5]. The determination of the CF scheme then becomes essential in order to account for all these different behaviors.

In cubic systems, inelastic neutron scattering (INS) experiments remain the most powerful tool to investigate the CF splitting [6], however for the case of low symmetry systems a single experiment is not always sufficient in order to determine the CF parameters and a joint analysis of additional experiments is needed. This feature is one of the most relevant consequences to be concluded from this work and it will be stressed throughout this paper.

The theoretical computation of the CF parameters from a microscopic theory is a quite difficult task and we will not deal with it in detail here. For the RE intermetallic compounds there is a considerable amount of results available treating this problem and a semiempirical understanding of the CF parameters has been reached. During

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[1] In memory of Prof. S. Velayos.

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the last decade a reliable quantitative determination of the CF effects in some systems with hexagonal and tetragonal symmetries has been performed. We shall discuss in the following sections some general aspects and the experimental procedure to determine the CF parameters. More complete information can be found in the review articles [7–9].

Although we shall concentrate our effort on the INS spectroscopy technique for RE intermetallic systems, it is important to mention other alternative methods which have been used as optical (for transparent samples), ESR and hyperfine techniques. In addition to these methods, the thermal effects on some magnetic properties play an important role in the determination of the CF splittings (magnetic susceptibility and magnetization in single crystals, specific heat and INS). Nevertheless, the magnetic properties of the RE intermetallic compounds can also be influenced by other interactions as quadrupolar and/or magnetoelastic ones [10]. However, due to the complexity of the problem in the ordered phase it is convenient to first start extracting the information concerning the CF interaction from the analysis of the physical properties in the paramagnetic phase. In this way, the determination of the CF level scheme and the associated quantum states constitutes an initial step quite unavoidable and fundamental in all these studies. For this reason, in order to determine the CF anisotropy an important effort in the synthesis of single crystals must be undertaken using different experimental methods to perform realistic analysis afterwards from numerical calculations. Among the RE compounds with low symmetry fulfilling these conditions we have emphasized the case of the $REAg_2$ and $RENi_2Si_2$ series because they present original and quite complex magnetic phase diagrams.

2. Crystal field theory

2.1. General considerations

As is well known, the CF interaction corresponds to the electrostatic coupling between the 4f shell and its surroundings. Within the CF theory, this interaction acting on the RE ions will be substituted by an effective Hamiltonian which may be expressed as a function of the Stevens operators O_l^m as:

$$H_{\mathrm{CF}} = \sum_{l,m} B_l^m O_l^m \tag{1}$$

where the B_l^m are the so-called CF parameters. This Hamiltonian can be obtained from group theory considering that H_{CF} must be invariant for all the symmetry operators which leave the system itself invariant, and at the same time this mathematical tool allows us to predict the number of CF operators and the expression for their linear combination. In Eq. (1) the O_l^m used are expressed in the symmetrized notation of Hutchings [11]. Obviously, the number of independent CF parameters increases with rapidity as soon as the symmetry is lowered (from 2 in cubic symmetry to already 5 in the tetragonal one) and the problem of their unambiguous determination becomes consequently more and more complicated. General considerations for the case of the lowest symmetries, such as orthorhombic, monoclinic and triclinic systems can be found in Refs. [12,13] where the number of CF parameters to be determined is as high as of 9, 14 and 26, respectively.

In order to illustrate the method for determining the CF parameters, we shall concentrate our attention on the tetragonal symmetry, for the space group *I4/mmm* (D_{4h}), so that there are five independent CF parameters and the Hamiltonian of Eq. (1) can be written then as:

$$\begin{aligned} H_{\mathrm{CF}} &= \alpha_J V_2^0 O_2^0 + \beta_J (V_4^0 O_4^0 + V_4^4 O_4^4) + \gamma_J (V_6^0 O_6^0 + V_6^4 O_6^4) \\ &\equiv \alpha_J A_2^0 \langle r^2 \rangle O_2^0 + \beta_J \langle r^4 \rangle (A_4^0 O_4^0 + A_4^4 O_4^4) + \gamma_J \langle r^6 \rangle (A_6^0 O_6^0 \\ &\quad + A_6^4 O_6^4) \end{aligned} \tag{2}$$

where α_J, β_J and γ_J are the Stevens coefficients and $\langle r^n \rangle$ is the expectation value of the *n*th power of the 4f shell characteristic for each RE. Within this notation, in which individual RE coefficients are taken out, the parameters A_l^m are roughly constant or are expected to vary regularly with the RE for a given series of compounds, allowing to extrapolate the coefficients for a RE compound from those for the nearest RE one.

The best information is obtained at low temperatures, when the thermal energy $k_B T$ is less than the distance to the first excited levels and therefore the RE is in its ground state. In this situation it is possible to determine from INS the position of the excited CF levels which are connected with non-zero matrix elements to the ground state in the differential cross-section for the magnetic neutron scattering. The magnetic response $S(\theta, \omega)$ is a function of the matrix elements of the component of the total angular momentum perpendicular to the scattering vector $\vec{q}$ between the different CF states [6]. For a polycrystalline sample, averaging over all the orientations of the scattering vector leads to the following simplified expression for this matrix element [14]:

$$\sum_{m,n} |\langle m|\vec{J}^{\perp}|n\rangle|^2 = \frac{4}{3} |\langle \Gamma_i|J_x|\Gamma_j\rangle|^2 + \frac{2}{3} |\langle \Gamma_i|J_z|\Gamma_j\rangle|^2 \tag{3}$$

where the $|m$ and $|n\rangle$ are the CF states. Within the paramagnetic phase, there are generally several degenerated CF levels, and in Eq. (3) the summation over m must be performed for all the quantum states belonging to a given representation Γ_i and satisfy the selection rules imposed by the corresponding matrix elements.

2.2. CF effects and INS experiments

The J-ground state multiplet of the RE^{3+} ion splits into different energy levels depending on the symmetry of the

CF. The space of functions used to describe all the magnetic properties of the 4f shell is built from the $2J+1$ functions $|LSJM_J\rangle \equiv |JM_J\rangle$ corresponding to the eigenstates of the operators $\vec{L}^2$, $\vec{S}^2$, $\vec{J}^2$ and J_z. In this way, the study of these properties will then provide information on the CF parameters through the diagonalization of Eq. (1). The procedure to reach this aim must be divided into several steps depending on the properties used for the determination of the CF parameters.

2.2.1. Magnetic susceptibility, $\chi(T)$

As a starting point this information can be very useful. Indeed in the case of the tetragonal systems, χ is isotropic in the basal plane and the anisotropy between this basal plane and the c-axis allows us to estimate the value of the second order CF parameter V_2^0 [15] given by:

$$\theta_p^x - \theta_p^z = \frac{3}{10}\alpha_J V_2^0 (2J-1)(2J+3) \tag{4}$$

where the θ_p^x and θ_p^z are, respectively, the paramagnetic Curie temperatures measured along the x and z directions on a single crystal. Furthermore, at low temperature in most of the cases the reciprocal susceptibility χ^{-1} shows deviations from the linear high temperature Curie–Weiss behavior. These differences are related with the influence of the higher order CF parameters. According to the general expression for the temperature dependent Van Vleck susceptibility, the most striking effect arises when the CF ground state is a nonmagnetic level, because in this case χ is almost temperature independent at low temperatures while it diverges in the normal cases. Through two examples we show hereafter that from the low temperature variation of χ^{-1} alone it is impossible to obtain a unique set of CF parameters. The joint analysis of several complementary experiments is then indispensable.

2.2.2. Specific heat, C_{mag}

The splitting of CF levels gives rise to Schottky anomalies, the positions of which are closely related to the energy separation of the corresponding CF energy levels. Their degeneracies can be obtained from the magnetic entropy by integration of C_{mag}/T. However, the infor-

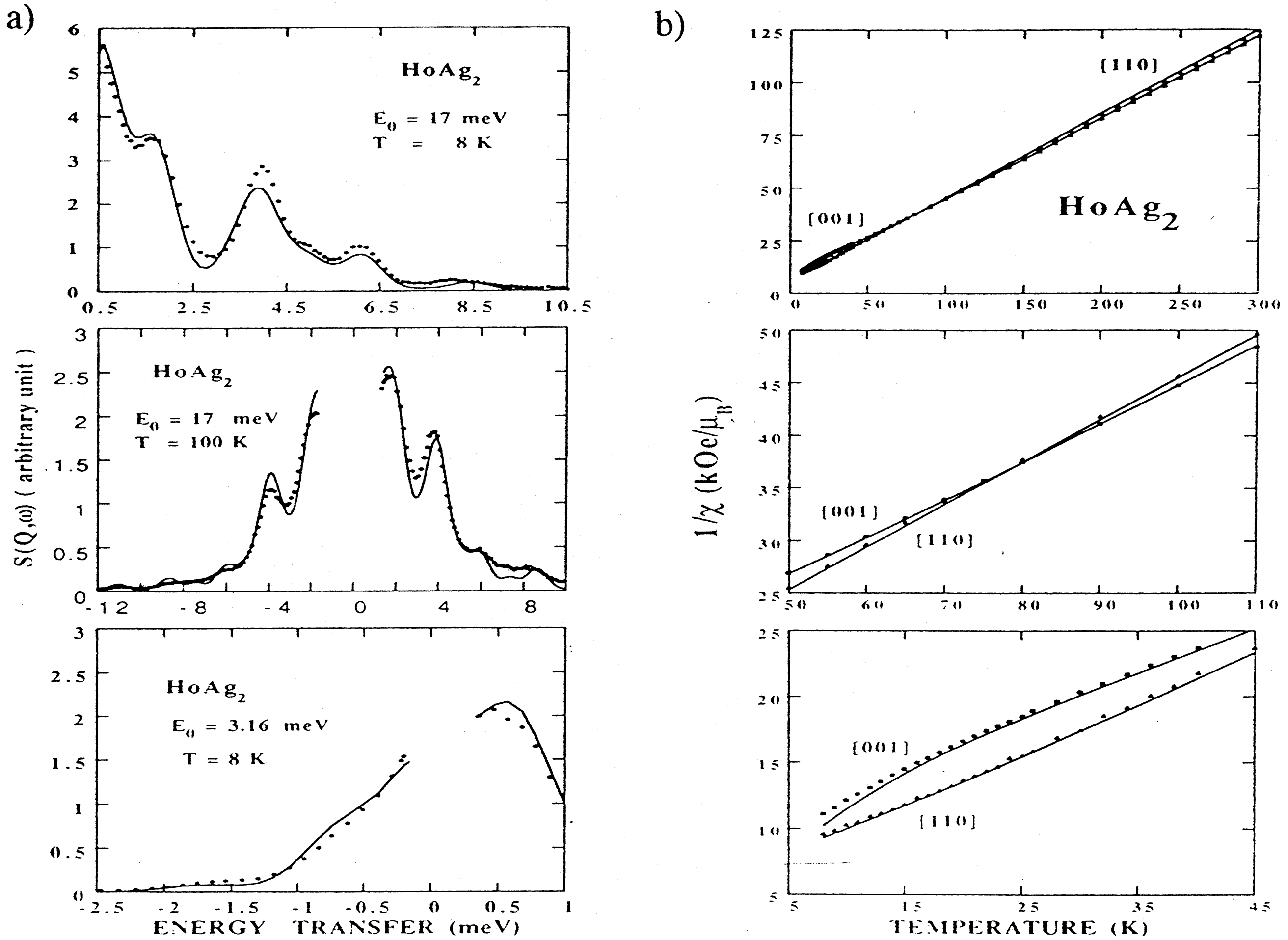

Fig. 1. Experimental and calculated: (a) INS spectra at IN4 with the conditions of temperature and incident energy indicated; and (b) thermal dependence of the reciprocal magnetic susceptibility in HoAg$_2$. The solid lines are calculations obtained from the same set of CF parameters (for more details see text): V_2^0=55 K; V_4^0=3.5 K; V_4^4=400 K; V_6^0=−15 K; V_6^4=−200 K.

mation can be limited at low temperatures by the magnetic order and at high temperatures by the phonon contribution. The first inconveniency can be avoided by substituting part of the RE ions by yttrium or lanthanum in order to depress the magnetic order totally or shift it to lower temperatures.

2.2.3. Magnetization, M(H)

In low symmetry systems, the magnetization like the behavior of the magnetic susceptibility, is generally anisotropic, showing different features which can be directly related to CF effects. Among them, the value of the magnetic moment in the paramagnetic phase under an applied magnetic field can give some idea about the composition of the ground state; the crossing or anticrossing of CF levels which lead to sharp or smooth metamagnetic transitions as a function of the magnetic field, respectively. This behavior has been evidenced in the hexagonal $PrNi_5$ compound [16]. It is important to mention that the analysis of the magnetization curve may reflect also the effects of other mechanisms, already mentioned, such as magnetoelastic and quadrupolar interactions, and therefore the analysis of the magnetization process in a first step has to be considered with some caution.

2.2.4. INS experiments, $S(\theta, \omega)$

Apart from the thermal effects observed in the different magnetic properties, the most direct way to determine the CF parameters in RE intermetallic systems is the INS technique, by the fact of inducing transitions between the CF levels, owing to the interaction of the incoming neutrons with the 4f electrons.

In a cubic environment, only two CF parameters are present and according to the LLW notation (Lea, Leask and Wolf) [17], they can be parameterized into a scale factor W and a parameter x ($-1 \leq x \leq 1$) which represents the relation between the fourth and sixth order terms in the Hamiltonian (Eq. (1)). This LLW parameterization has the advantage that the relative position of the CF levels and the composition of the quantum states within the $|JM_J\rangle$ basis depends only on the parameter x, while the factor W fixes the total amplitude of the scheme. However, in compounds with lower symmetry, e.g., hexagonal or tetragonal, the use of an ansatz like the LLW parameterization is not advantageous for several reasons, mainly because this transformation makes the mathematical expression for the Hamiltonian (Eq. (1)) numerically unstable [13]. To avoid these difficulties, different procedures can be undertaken. In this way, some authors try to get a

Table 1
Sets of CF parameters (in Kelvin) describing the thermal dependence of the reciprocal susceptibility χ^{-1} ($\theta^* = -11.3$ K) and the INS spectra in $HoAg_2$ at 8 K

	V_4^0	V_4^4	V_6^0	V_6^4
Sets of CF parameters from χ^{-1}				
1	−45	−375	40	30
2	10	175	8	−300
3	85	60	−32	90
4	4	−132	−10	300
5	−65	−40	35	5
6	−160	1420	−20	45
7	190	940	−15	175
Sets of CF parameters from INS				
1	7	330	−15	−200
2	−33	850	−36	−88
3	18	−33	10	97
4	−23	83	−9	50
5	−22	−125	−9	−70
6	26	45	40	14

The value of the second order CF parameter V_2^0 was fixed to 27.5 K (see text).

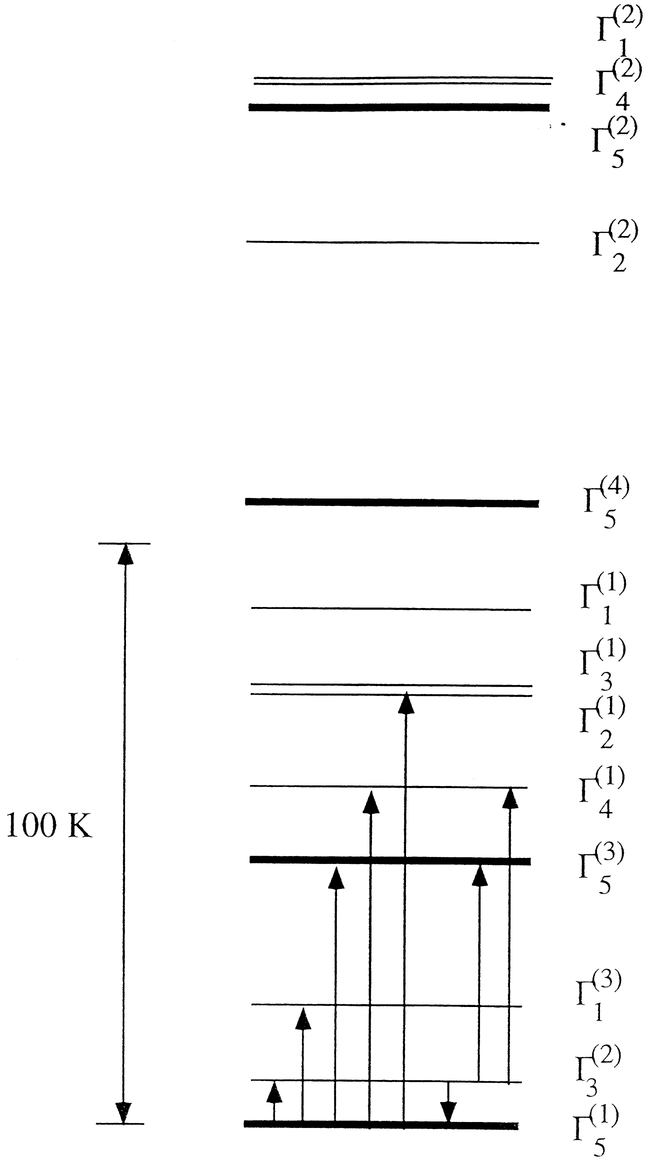

Fig. 2. Overall CF level scheme of $HoAg_2$; arrows indicate the main transitions observed by INS from the groundstate and the first excited levels. Details concerning the notation used can be found in Ref. [17]. Thin lines correspond to singlet states, while the thick ones are those of the doublet states.

new transformation more useful for the Hamiltonian in terms of normalized Stevens' operators, O_l^m. However, thanks to the advent of fast computers, random or systematic searchs of CF parameters can be performed in which several thousands of parameters are easily tested. This last method has been used in all the examples presented in the following. Information concerning the experimental techniques and the instruments used for these studies can be found in Refs. [4,18].

3. Selected experimental examples: $HoAg_2$ and $PrNi_2Si_2$

In order to illustrate the difficulties in determining the five CF parameters in tetragonal symmetry we have selected two well characterized systems: $HoAg_2$ [18] and $PrNi_2Si_2$ [4]. Both compounds crystallize in the *I4/mmm* space group, with the the RE-ions in the (0, 0, 0) position, the former in the $MoSi_2$- and the latter in the $ThCr_2Si_2$-type structures. Moreover both show an incommensurate amplitude modulated structure below their Néel temperature of 5.7 and 20.0 K, respectively. From the eigenstates and eigenvalues obtained by the diagonalization of the Hamiltonian, we have calculated the different magnetic properties. To refine the best set of CF parameters, a nonlinear least-squares procedure, using a narrow range of initial starting parameters V_l^m, has been used. In the first step the second order CF parameter V_2^0 was initially fixed to the value estimated from Eq. (4).

3.1. $HoAg_2$

For Ho^{3+} ions, the tetragonal symmetry CF interaction removes the degeneracies of the $J=8$ groundstate multiplet into 9 singlets and 4 doublets. Searching, in an independent way, the CF parameters from the thermal dependence of the reciprocal magnetic susceptibility and the INS data (see Fig. 1) leads to no common set of parameters (see Table 1). This feature shows that neither χ^{-1} nor INS information are so selective as initially could be believed, in spite of the fact that the anisotropy of the susceptibility decreases and changes sign around 75 K, passing the easy magnetization axis from the [001] direction to that of the basal plane (see Fig. 1). Qualitatively, this result evidences an enhanced role of the higher CF parameters $V_4{}^m$ and $V_6{}^m$ at low temperatures and therefore the search for a best compromise must be performed using successive cross-checks between both types of fits.

The first set of parameters obtained from INS in Table 1 provides us with the best solution. Information coming from the high temperature INS spectra with $E_0=17$ and 3.16 meV was also considered (see Fig. 1). In all the fits the CF parameters rapidly converge to the values (in Kelvin) $V_4^0=6\pm3$; $V_4^4=390\pm20$; $V_6^0=-15.0\pm1.5$; $V_6^4=-195\pm5$, while the value of the second order CF parameter V_2^0 can vary from 39 to 55 K without significantly altering the results [18]. The overall CF level scheme is reported in Fig. 2 together with the main transitions observed in the INS technique. It is clear from a simple inspection of this figure that the determination of the five first excited levels can be easily done from Fig. 1, but those of the highest levels can be very difficult or even impossible from the present analysis.

Similar analyses of Tb-, Dy-, Er- and $TmAg_2$ evidence a coherence behavior across the series. In fact, the weakness of the second order parameter V_2^0 appears to be a general trend in the $REAg_2$ series, being responsable for the

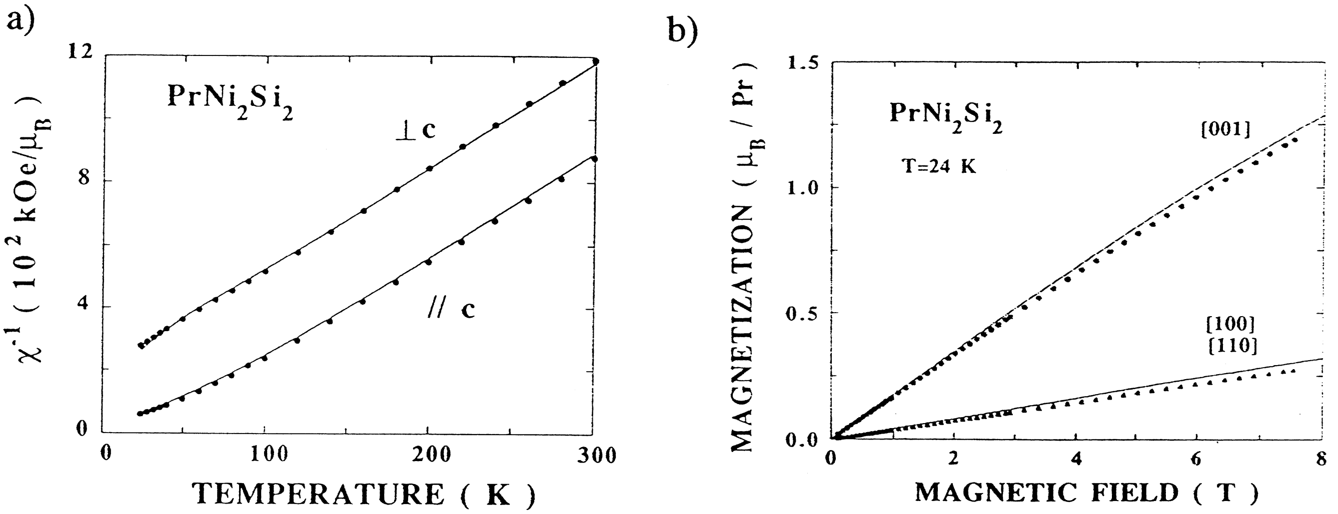

Fig. 3. (a) Thermal dependence of the reciprocal magnetic susceptibility in $PrNi_2Si_2$ along and perpendicular to the *c* easy magnetization direction. The paramagnetic Curie temperatures reaching $\theta_p^z=26$ K and $\theta_p^x=-60$ K parallel and perpendicular to the [001] direction, respectively. From Eq. (3), a first estimation leads to a value of $V_2^0=175\pm5$ K. (b) Field dependence of the magnetization along the main direction of the tetragonal symmetry. In both figures lines are calculated using the CF parameters: $V_2^0=172$ K; $V_4^0=37.6$ K; $V_4^4=318$ K; $V_6^0=64.8$ K; $V_6^4=-90.7$ K.

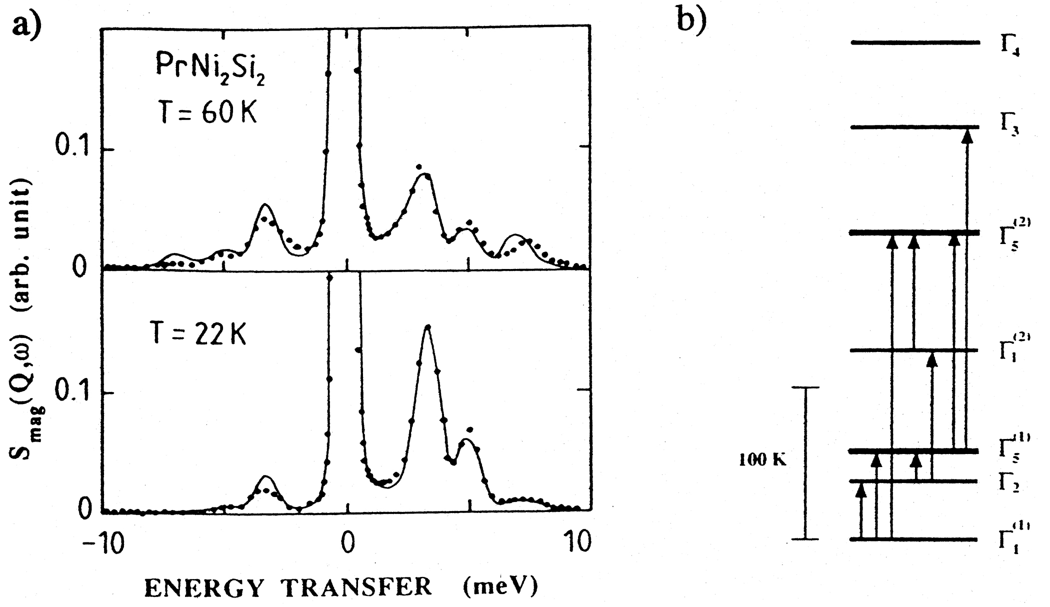

Fig. 4. (a) Experimental and calculated INS spectra at IN4 for $PrNi_2Si_2$. Lines are calculations performed from the same CF parameters used in Fig. 3. (b) Overall CF level scheme. Thin lines correspond to singlet states, while the thick ones are those of the doublet states. Arrows indicate the main transitions observed by INS. The transfer from $\Gamma_5^{(1)}$ to Γ_3 has been observed with incoming neutron energies of 50 meV.

change of the easy magnetization axis observed in the magnetic susceptibility. This value is clearly smaller than that observed in other intermetallic compounds (in hexagonal symmetry ≈ -500 K in $RENi_5$ [19], ≈ -500 K in $RECo_5$ [20] and ≈ -200 K in $REGa_2$ [21], while in tetragonal symmetry ≈ 172 K in $PrNi_2Si_2$ (see below)).

3.2. $PrNi_2Si_2$

In Figs. 3 and 4, using the above least square procedure, a joint analysis of the INS, the magnetic susceptibility and magnetization in $PrNi_2Si_2$ is quite relevant [4]. The CF level scheme ($J=4$, 5 singlets and 2 doublets) leads to a nonmagnetic singlet as the ground state which is well separated from the two first excited levels (see Fig. 4). This particular CF level scheme allows us to explain the persistence of the incommensurate longitudinally amplitude modulated magnetic structure observed below T_N down to 0 K in this compound. With the information obtained in the paramagnetic phase it is possible to study the magnetic properties of the modulated phase at low temperatures [22] as well as the magnetic excitations [23].

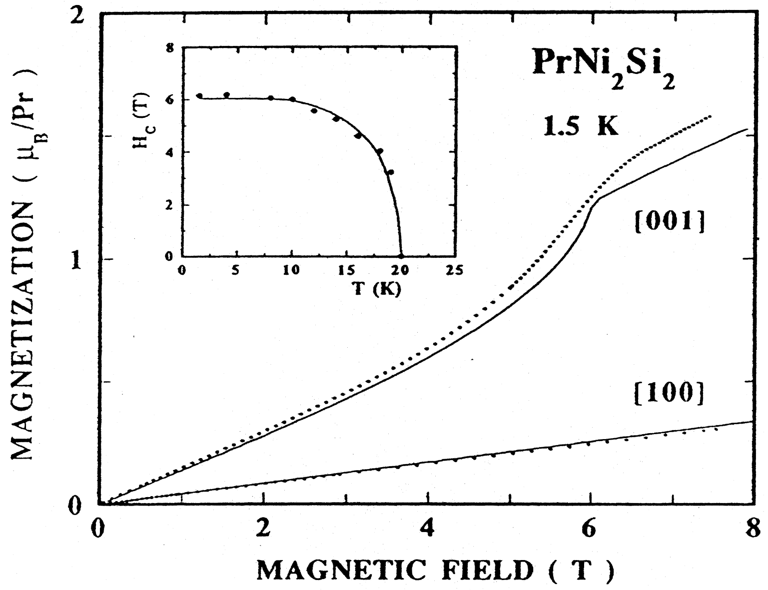

Fig. 5. Magnetization process in $PrNi_2Si_2$ at 1.5 K along and perpendicular to the *c* easy axis; note the cusp when the induced ferromagnetic state is reached along the *c*-axis. Inset shows the magnetic phase diagram. Lines are calculated from the CF parameters of Figs. 3 and 4.

Fig. 5 shows the magnetization along the *c*-axis at 1.5 K which is characterized by a positive curvature up to $H_C = 6$ T where a cusp is observed. This curvature corresponds to the progressive disappearence of the modulation under an applied magnetic field and the cusp is associated with the entrance into the induced ferromagnetic phase. Moreover, within the magnetically ordered phase, the thermal dependence of this critical field H_C is in good agreement with that calculated from a self-consistent periodic field model [22].

On the other hand, in other $RENi_2Si_2$ compounds such as $TbNi_2Si_2$, the determination of the CF parameters is not yet completely well established [24]. However, this system is a good example to show how the information of the specific heat can help us with the analysis of the CF interaction. Indeed, substituting Tb ions by nonmagnetic Y ones in $TbNi_2Si_2$ depresses the magnetic ordering temperature ($T_N = 15.0$ K) to a value below 1.5 K. Fig. 6 shows the magnetic contribution to the specific heat of $Tb_{0.2}Y_{0.8}Ni_2Si_2$. In addition to the wide hump centered around 20 K, related to the CF levels at about 40 K, a second Schottky anomaly is clearly detected around 3 K. The absence of any anomaly in the susceptibility and the magnetization measurements allows us to exclude the hypothesis of any magnetic order in this range of temperature. Therefore, this low temperature Schottky anomaly evidences the existence of two lying CF levels separated from each other by just a few Kelvin (see Fig. 6), being both two singlets, as deduced from the entropy. In fact this CF scheme is responsible for a quite complex phase diagram characterized by the appearance of different commensurate and incommensurate magnetic phases observed by means of neutron diffraction and magnetic measurements on a single crystal [25].

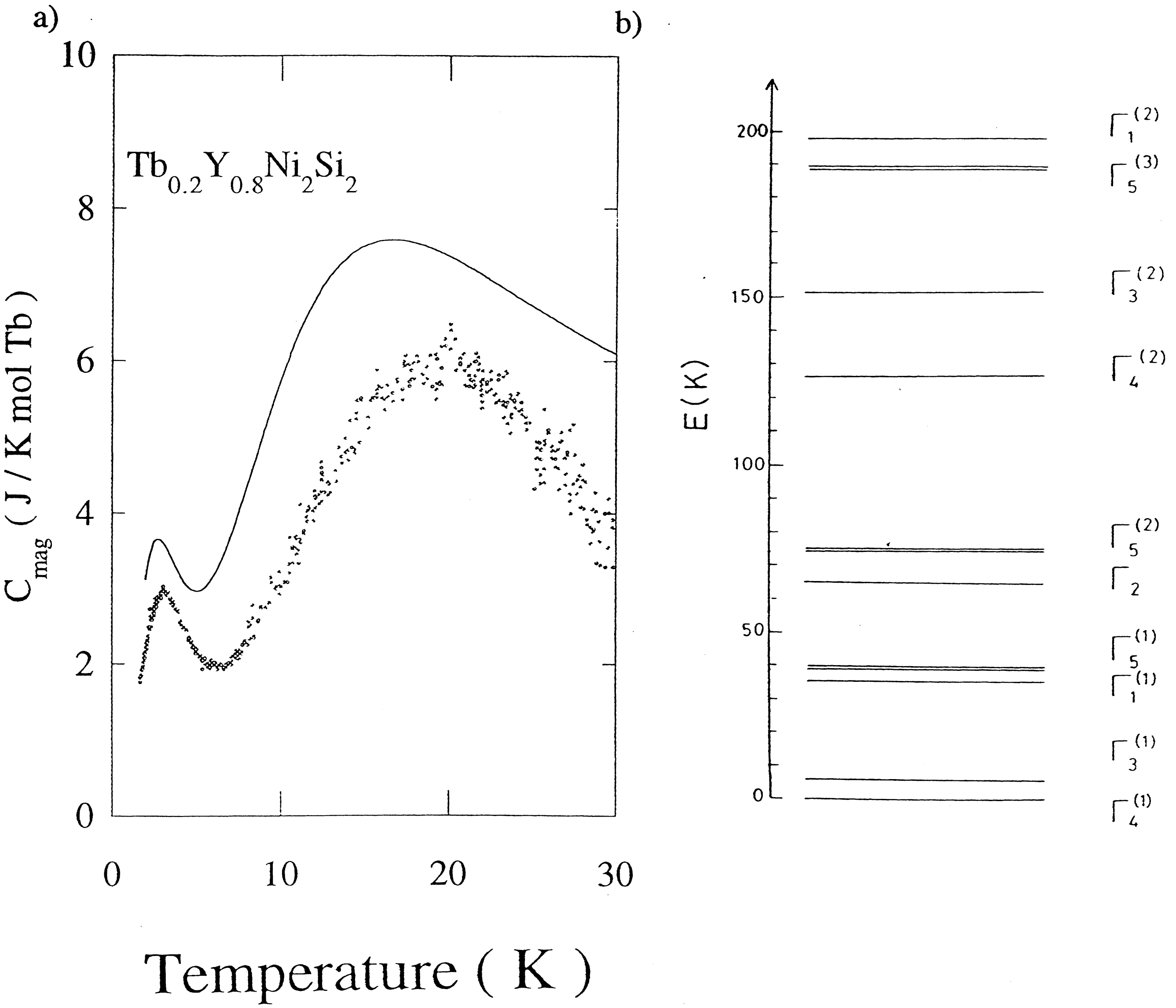

Fig. 6. (a) Magnetic part of the specific heat in $Tb_{0.2}Y_{0.8}Ni_2Si_2$. Note the two Schottky anomalies observed in the temperature range investigated. (b) Overall CF level scheme in $TbNi_2Si_2$ obtained from Ref. [24].

Table 2
CF parameters A_l^m (in units of Ka_0^{-n}) of the trivalent RE ions in the investigated RNi_2Si_2 compounds

Compound	A_2^0	a_4^0	A_4^4	A_6^0	A_6^4
$PrNi_2Si_2$	158.4	13.3	112.7	4.1	−5.8
$TbNi_2Si_2$	128.9	16.5	322.2	10.9	−162.4
$DyNi_2Si_2$	62.3	−17.6	36.7	2.3	35.0

Finally, for all the RNi_2Si_2 compounds studied, the most reliable sets of CF parameters A_l^m are compared in Table 2. It is worth noting that the parameters of Pr and Tb seem to be qualitatively quite consistent with all of them, but those associated with Dy are significantly different [26]. The decrease of the parameter V_2^0 indicates that the anisotropy of the magnetic susceptibility beween the *c*-axis and the basal plane is smaller for the heavy RE ions than that of the lighter ones. For the higher CF parameters V_l^m no simple interpretation has been obtained at the moment. Further investigations in other RE compounds of this series are needed in order to make a general discussion of the variations observed.

Summarizing the above survey shows that in low symmetry RE intermetallic compounds where only the rare earth is magnetic, the determination of the CF parameters is a quite complex task and a reliable set of these parameters can only be given when all available data for the isostructural series of all rare earths (INS, susceptibility and magnetization, specific heat, Mösbauer spectroscopy, . . .) are consistently explained.

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