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Influence of magnetic fluctuations in the magnetocaloric effect on rare-earth intermetallic compounds

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A theoretical model including both crystal-field and exchange interactions that considers the effect of magnetic fluctuations is developed to evaluate the temperature dependence of the isothermal magnetic entropy changes in ferromagnetic rare-earth-based intermetallic compounds. The Green's functions are derived from their equation of motion. The magnetic moment correlation functions are determined beyond the random phase approximation by incorporating a measure of magnetic spontaneous fluctuations in a way that ensures self-consistency with regard to the fluctuation-dissipation theorem. In particular, the exact magnitude of the entropy change without magnetic moment fluctuations depends on the ratio of both the crystal-field first- and the crystal-field third-order magnetic susceptibilities at the Curie temperature, T_C. These theoretical predictions are compared with experimental data on cubic RM_2 (R = rare earth and M = Al and Ni) compounds, where the principal crystal-field and exchange parameters are well known.

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I. INTRODUCTION

Tailored materials have long been one of the most important issues in solid state physics. They often provide insights into the underlying mechanisms governing the properties of materials and their potential applications. Nowadays, researchers are fascinated with and involved in the design of a prototype of magnetic refrigerator that exploits the magnetocaloric effect (MCE), because this technology is thought to be less harmful to the environment than that based on the conventional gas compression-expansion method.[1–7]

The MCE is a magnetothermodynamical phenomenon characterized by the entropy change (ΔS_{iso}) in an isothermal (iso) process and by the temperature change in an adiabatic process as a result of a magnetic field variation. This phenomenon has been extensively and intensively studied over the last four decades. In 1997, $Gd_5Si_2Ge_2$ was found to undergo a magnetic first-order transition accompanied by an unusually very large entropy change ($-\Delta S_{\text{iso}} \approx 18.8$ J/K mol under a magnetic field variation from 0 to 50 kOe at 273 K).[8] These findings stimulated a great deal of activity that still remains cutting-edge research into what have been called giant magnetocaloric materials.[9–11] Since then, the MCE has been investigated in rare earth (R)–transition metal (M) compounds[12–16] and metallic glasses,[17,18] among others. In particular, in conventional RM ferromagnets undergoing a second-order phase transition such as cubic RM_2 (M = Al and Ni) compounds, the temperature dependence of $-\Delta S_{\text{iso}}$ exhibits a peak around the Curie ordering temperature T_C. The magnitude of this peak depends on the applied magnetic field H, and the direction of H has an important effect on the energetic level ordering of the Zeeman states in rare earth compounds, which can easily be calculated on the basis of an interaction Hamiltonian. This dependence is studied in the present work. The MCE in R-based compounds has been numerically described by including the relevant crystalline electric field (CEF) and exchange interactions involved in coupling localized magnetic moments.[19]

Motivated by these considerations, the aim of this paper is to gain a better understanding of the MCE through comparison of the experimental and calculated temperature dependence of isothermal magnetic entropy changes at temperatures for which thermal energies are comparable with those related to CEF splitting and exchange energies. We have thus focused our interest on cubic systems where the determination of the CEF parameters is much easier than in uniaxial compounds, such as tetragonal or hexagonal ones, or systems with lower local symmetry.[20,21] The effects of magnetic fluctuations are considered using the Green's function calculation. The method goes beyond the random phase approximation (RPA) by taking into account spontaneous fluctuations through the fluctuation-dissipation theorem.

Our article is arranged as follows. Section II contains essential information and definitions for analyzing the role of magnetic fluctuations in the MCE. Details of the critical mean-field behavior of $-\Delta S_{\text{iso}}$ are given in the Appendix. The theory developed is applied to RM_2 (R = rare earth and M = Al and Ni) compounds in Sec. III, which also includes the self-consistent correlation effects that are determined numerically and the comparisons with the experimental data. We likewise discuss the success and shortcomings of the present theory and the molecular-field theory in its application to RM_2. Section IV concludes the article.

II. THEORY

We use a general formulation developed for a periodic-field model, which is based on an N-site Hamiltonian $\mathcal{H}$, N being the number of magnetic ions over one period of the magnetic structure.[22,23] To investigate the effects of fluctuations, our starting point is the simplest model used to describe the occurrence of most of the observed properties in rare earth magnetism. The Hamiltonian is thus written as the sum of the CEF, Zeeman, and isotropic Heisenberg terms. Regrouping these terms into a single-ion part $\mathcal{H}_1$ and an interion exchange part $\mathcal{H}_2$, we obtain

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{Z}} + \mathcal{H}_{\text{ex}} \equiv \mathcal{H}_1 + \mathcal{H}_2, \qquad (1)$$

with the one-ion term $\mathcal{H}_1$ defined as

$$\mathcal{H}_1=\sum_{j=1}^{N}\mathcal{H}_{\rm CEF}(j)-\sum_{j=1}^{N}\mathbf{H}\cdot\mathbf{M}(j)-\sum_{i,j\neq i}^{N}J(ij)J_z(i)\langle J_z(j)\rangle, \tag{2}$$

where $\mathcal{H}_{\rm CEF}$ represents the single-ion CEF Hamiltonian appropriate for cubic symmetry; that is,[24]

$$\begin{aligned}\mathcal{H}_{\rm CEF}&=B_4\big(O_4^0+5O_4^4\big)+B_6\big(O_6^0-21O_6^4\big)\\&=W\left(\frac{x}{F_4}\big(O_4^0+5O_4^4\big)+\frac{1-|x|}{F_6}\big(O_6^0-21O_6^4\big)\right),\end{aligned} \tag{3}$$

where O_l^m and B_l are the Stevens operators and crystal-field parameters, respectively. Furthermore, according to (3), B_l can also be written in terms of the parameters x and W used by Lea *et al.*[24] The parameter x is limited to the range $-1\leqslant x\leqslant 1$, while W scales the energy splittting (F_4 and F_6 are factors that are common to all matrix elements and specific to each rare earth ion).[25] The second term in (2) represents the Zeeman coupling of the $4f$ magnetic moments with the applied magnetic field **H**, while the third term is the mean-field approximation of an isotropic bilinear Heisenberg-type interaction.

Thus, the Hamiltonian $\mathcal{H}_1$ defines the standard-basis operators and hence $\mathcal{H}_1$ can be written as

$$\mathcal{H}_1=\sum_{j=1}^{N}\sum_{n=0}^{2J}E_n|n_j\rangle\langle n_j|. \tag{4}$$

The eigenfunctions at site i and the energy levels are denoted $|n\rangle_i$ and E_n, respectively. On the other hand, the two-ion term $\mathcal{H}_2$ is given by

$$\begin{aligned}\mathcal{H}_2=&-\frac{1}{2}\sum_{i,j\neq i}^{N}J(ij)J_z(i)(J_z(j)-2\langle J_z(j)\rangle)\\&-\frac{1}{4}\sum_{i,j\neq i}^{N}J(ij)(J_+(i)J_-(j)+J_-(i)J_+(j)).\end{aligned} \tag{5}$$

We introduce the Green's functions for the total angular momentum components,

$$G^{\alpha\beta}(ij,t)=-i\theta(t)\langle[J_\alpha(i,t),J_\beta(j,0)]\rangle, \tag{6}$$

to find the magnetic fluctuations at finite temperature taking into account all energy levels.

The Fourier transform of $G^{\alpha\beta}(ij,t)$ is

$$G^{\alpha\beta}(\vec{q},\omega)=\frac{1}{N}\sum_{i,j\neq i}e^{(-i\vec{q}\vec{R}_{ij})}\int_{-\infty}^{+\infty}dte^{i\omega t}G^{\alpha\beta}(ij,t). \tag{7}$$

The equations of motion of the Green's functions are derived using appropriate commutator relations. These equations of motion for G are set and high-order Green's functions are reduced using RPA decoupling developed according to the formalism described by Jensen *et al.*[26] Solving the equation of motion for these functions within the RPA theory leads to a system of linear coupled equations,

$$\begin{aligned}G^{\alpha\beta}(\vec{q},\omega)=&\,g^{\alpha\beta}(\omega)-J(\vec{q})g^{\alpha z}(\omega)G^{z\beta}(\vec{q},\omega)\\&-\tfrac{1}{2}J(\vec{q})(g^{\alpha+}(\omega)G^{-\beta}(\vec{q},\omega)+g^{\alpha-}(\omega)G^{+\beta}(\vec{q},\omega)),\end{aligned} \tag{8}$$

where the single-ion CEF susceptibilities are given by

$$g^{\alpha\beta}(\omega)=\sum_{m,n}\frac{\langle m|\,J_\alpha\,|n\rangle\langle n|\,J_\beta\,|m\rangle}{\omega-\omega_n+\omega_m}(f_m-f_n), \tag{9}$$

where f_m and f_n are the thermal population factors for CEF states $|m\rangle$ and $|n\rangle$, respectively, and $J(\vec{q})=\sum_{i,j\neq i}J(ij)e^{(-i\vec{q}\vec{R}_{ij})}$ is the Fourier transform of the intersite exchange coupling constant $J(ij)$. As previously mentioned, a decoupling of the different excitation modes is needed to solve linear system (8) by using symmetry rules for the matrix elements that appear in $g^{\alpha\beta}(\omega)$. These symmetry considerations allow us to define longitudinal and transverse excitations that can be well separated, yielding to $g^{zz}(\omega)$, $g^{+-}(\omega)$, and $g^{-+}(\omega)$, respectively. Taking these considerations into account, linear system (8) is reduced to

$$G^{zz}(\vec{q},\omega)=g^{zz}(\omega)-J(\vec{q})g^{zz}(\omega)G^{zz}(\vec{q},\omega), \tag{10}$$

and

$$G^{\pm\mp}(\vec{q},\omega)=g^{\pm\mp}(\omega)-\tfrac{1}{2}J(\vec{q})g^{\pm\mp}(\omega)G^{\pm\mp}(\vec{q},\omega). \tag{11}$$

Hence the expression of $G^{zz}(\vec{q},\omega)$ and $G^{\pm\mp}(\vec{q},\omega)$ can be easily obtained. On the other hand, the matrix of equal-time correlation functions,

$$\begin{aligned}C_{\vec{q}}=&\frac{1}{N}\sum_{i,j\neq i}^{N}\exp(-i\vec{q}\vec{R}_{ij})\\&\times\begin{pmatrix}\langle J_+(i)J_+(j)\rangle & \langle J_+(i)J_-(j)\rangle & \langle J_+(i)J_z(j)\rangle\\ \langle J_-(i)J_+(j)\rangle & \langle J_-(i)J_-(j)\rangle & \langle J_-(i)J_z(j)\rangle\\ \langle J_z(i)J_+(j)\rangle & \langle J_z(i)J_-(j)\rangle & \langle J_z(i)J_z(j)\rangle\end{pmatrix},\end{aligned} \tag{12}$$

should, according to the well-known fluctuation-dissipation theorem, be related to $G^{\alpha\beta}(\vec{q},\omega)$:[26]

$$C_{\vec{q}}=-\frac{1}{\pi}\int_{-\infty}^{+\infty}d\omega\frac{1}{1-e^{-\beta\omega}}{\rm Im}G^{\alpha\beta}(\vec{q},\omega), \tag{13}$$

where Im represents the imaginary part of $G^{\alpha\beta}(\vec{q},\omega)$. Thus, the internal energy per ion in this combined RPA/molecular-field model is found to be

$$U=U_1+U_2=\sum_{n=0}^{2J}E_nf_n-\frac{1}{2N}\sum_{\vec{q}}J(\vec{q})\big(C_{\vec{q}}^{33}+C_{\vec{q}}^{12}\big). \tag{14}$$

Finally, the specific heat C is easily obtained by performing the temperature derivative of U at any temperature, and the magnetic entropy can be calculated by integrating C/T. In the following section we present the calculated dependencies for the RM_2 comparing the results obtained using the mean-field approximation and the RPA/molecular-field model from Eq. (14). For evaluating the latter equation we have considered the information on $J(\vec{q})$ along the three principal symmetry directions, ⟨100⟩, ⟨110⟩, and ⟨111⟩, as determined by Purwins *et al.*[27] We can anticipate that the strongest effect of the fluctuations is found to be around T_C.

III. RESULTS AND DISCUSSION

In this paper, a theoretical model for describing the isothermal magnetic entropy change $-\Delta S_{\text{iso}}$ in intermetallic compounds has been studied within the RPA/mean-field formalism. The main result is that the exact shape of $-\Delta S_{\text{iso}}$ is determined by the relative magnitude of the exchange and CEF parameters and the incorporation of fluctuations has a major effect near T_C. This quite original result can shed light on the experimental curves shown here, as well as on other data found in the literature. We start by presenting the special case of $ErAl_2$. The temperature dependence of the experimental and numerically calculated [using Eq. (14) and within the mean-field approximation] isothermal magnetic entropy change on the magnetic field from 0 to 50 kOe for $ErAl_2$ is shown in Fig. 1. $-\Delta S_{\text{iso}}$ has a maximum near T_C (∼15 K), with an experimental value close to 8.2 J/K mol. The calculated value around T_C obtained from the mean-field approximation when the magnetic field is applied along the [111] easy-axis magnetization is almost 10 J/K mol. This difference can be explained by taking into account the fact that the theoretical entropy change is markedly dependent on the direction of the applied magnetic field (see inset in Fig. 1). This means that it is necessary to perform an azimuthal average to obtain the theoretical temperature dependence of the isothermal magnetic entropy change in a polycrystalline sample of this material, assuming that all orientations of the easy-axis [111] magnetization with respect to the applied magnetic field are possible. The value thus obtained is found to be 8.7 J/K mol when the calculations are done using the mean-field approximation; when considering the effect of fluctuations from Eq. (14), the magnitude is 8.3 J/K mol, which is much closer to the experimental value reported above. Apart from that, the theoretical variation satisfactorily describes the observed experimental dependence within the paramagnetic phase of this compound, indicating that the crystal-field scheme accounts well for the temperature dependence of the magnetic entropy change. The calculated variation in the ordered region is quite similar to the experimental one, with small deviations below 10 K. In contrast, other RM_2 ($M = Ni$ or Al) do not present large azimuthal magnetic dependencies of $-\Delta S_{\text{iso}}$ like that already shown for $ErAl_2$. In particular, $-\Delta S_{\text{iso}}$ values for $ErNi_2$, $DyNi_2$, and $DyAl_2$ have a maximum near their respective T_C values, with experimental values around 5.8, 6.0, and 4.0 J/K mol, respectively. These values are near the 5.5, 5.7, and 4.0 J/K mol predicted by the RPA/molecular-field formalism for these materials and are not far from those calculated using the mean-field estimations (see Table I; further details on the analytical determination of the magnitude of $-\Delta S_{\text{iso}}$ at T_C are given in the Appendix). As a result, the incorporation of magnetic fluctuations provides a better model for the magnitude of $-\Delta S_{\text{iso}}$ near T_C. In addition, the temperature dependence of $-\Delta S_{\text{iso}}$ shows trends in the paramagnetic phase for $ErNi_2$, $DyNi_2$, and $DyAl_2$ (see Fig. 2) similar to that found previously for $ErAl_2$. As in the preceding case, these results clearly indicate the reliability of the parametrization employed, where only two CEF parameters were used, together with the wave-vector-dependent Fourier transform of the intersite exchange coupling constant. Taking into account the success of the model, due mainly to the high-cubic symmetry environment of the rare earth ions in the paramagnetic phase of RM_2, the CEF scheme is well established. This simple model probably works despite the highly complex physics involved in these materials, as

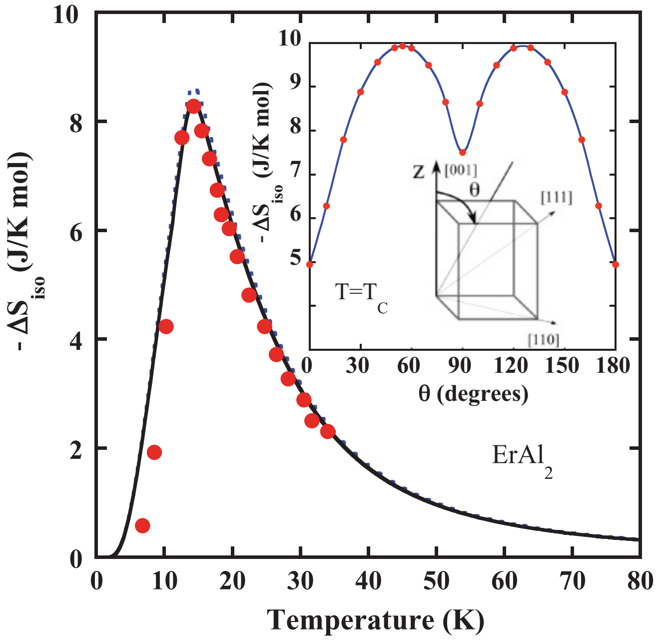

FIG. 1. (Color online) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_{\text{iso}}$ in $ErAl_2$ on the magnetic field variation from 0 to 50 kOe. Solid lines are calculations obtained from the RPA/molecular-field model, Eq. (14), while symbols correspond to experimental data taken from Oliveira *et al.*[19] The dashed line corresponds to the mean-field calculation. Inset: Theoretical magnetic field azimuthal dependence of the isothermal entropy change calculated at T_C.

TABLE I. Calculated isothermal magnetic entropy change $\Delta S_{\text{iso}}^{\text{cal}}$ in several RM_2 compounds at the ordering temperature (T_C) according to expression (A3) on the magnetic field variation from 0 to 50 kOe; experimental or estimated values $\Delta S_{\text{iso}}^{\text{est}}$ are taken from Oliveira *et al.*[19] $PrNi_2$ is a paramagnet, while $TmNi_2$ shows a ferromagnetic transition temperature of 1.1 K and a crystal-field singlet ground state.[30] All data are given in J/K mol.

	RAl_2		RNi_2	
R	$-\Delta S_{\text{iso}}^{\text{cal}}(T_C)$	$-\Delta S_{\text{iso}}^{\text{est}}(T_C)$	$-\Delta S_{\text{iso}}^{\text{cal}}(T_C)$	$-\Delta S_{\text{iso}}^{\text{est}}(T_C)$
Pr	3.7	4.2(1)	–	–
Nd	1.6	2.1(2)	4.7	3.9(2)
Gd	1.6	2.0(2)	3.6	3.5(1)
Tb	3.4	3.7(1)	7.7	7.0(1)
Dy	4.2	4.0(1)	5.9	6.0(1)
Ho	6.3	6.4(2)	8.4	8.7(2)
Er	8.3	8.3(1)	5.7	5.8(2)
Tm	6.0	7.0(2)	–	–

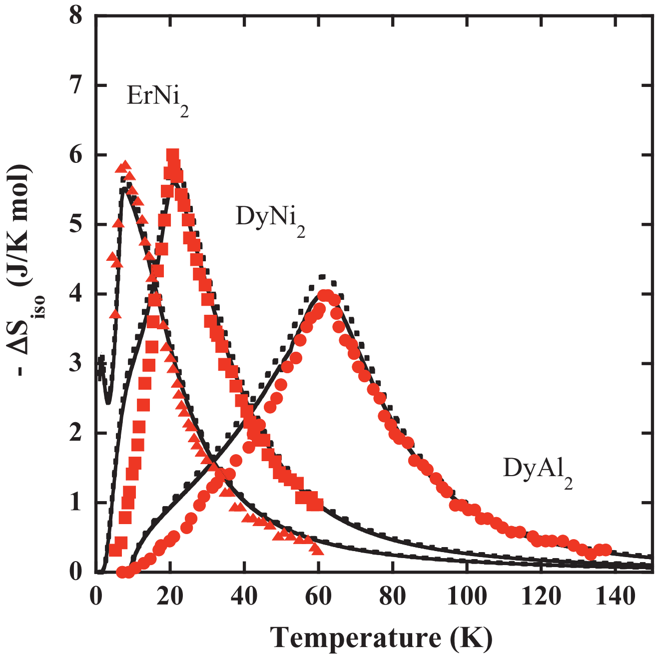

FIG. 2. (Color online) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_{\rm iso}$ for ErNi$_2$, DyNi$_2$, and DyAl$_2$ on the magnetic field variation from 0 to 50 kOe. Solid lines are calculations obtained from the RPA/molecular-field model, Eq. (14), while symbols correspond to experimental data taken from Oliveira *et al.*[19] (see the text for more details). Dashed lines correspond to the mean-field calculation.

we see below. In fact, in Fig. 2 some deviations between theory and experimental dependencies can be observed at low temperatures for ErNi$_2$, DyNi$_2$, and DyAl$_2$. In all of these materials the theoretical variations predict some features that are not experimentally reproduced: a Schottky-like anomaly (related to the fact that four quantum levels are found to be separated at an interval of 10 K) for ErNi$_2$ and slight bumps for DyNi$_2$ and DyAl$_2$ that are not observed experimentally (see Fig. 2). Considering that our calculations include the main interactions in play, these features could suggest that other higher-order interactions such as the one-ion or two-ion magnetoelastic coupling or quadrupolar pair coupling that are expected to be of minor importance could also be of relevance for understanding this low-temperature behavior of $-\Delta S_{\rm iso}$ in these materials. It is thus clear from the discrepancies observed at low temperatures between theory and experiments that a much more complete formalism is needed to remove the remaining deviations. Further research will hence be of interest to elucidate this issue.

IV. CONCLUSIONS

In summary, we have shown that an RPA/mean-field approach is able to describe quite satisfactorily the experimental magnetic entropy changes in the immediacy of the ordering temperature of rare earth intermetallic compounds undergoing a second-order para-ferromagnetic phase transition. This was made possible due to a good knowledge of the crystal-field and exchange interaction parameters in well-known RM$_2$ (M = Al or Ni) cubic systems. In addition, the analysis allows us to extract information on the influence of spin fluctuations near T_C when the calculations are compared with those obtained from the mean-field approximation. These results could be applied to low-symmetric systems to understand the large MCEs observed.

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APPENDIX: CRITICAL MEAN-FIELD BEHAVIOR

Within the mean-field approximation the critical behavior of $\Delta S_{\rm iso}$ in the near vicinity of T_C can be analytically obtained using an expansion of the magnetic moment at each site $\langle M(i)\rangle = M$ for a collinear ferromagnet at powers of the corresponding exchange field up to third order in the presence of CEF effects,

$$M = \chi_0 H_{\rm ex} + \chi_0^{(3)}(H_{\rm ex})^3, \tag{A1}$$

where χ_0 and $\chi_0^{(3)}$ are the first- and third-order CEF single-ion magnetic susceptibilities.[28] The same procedure as in Ref. 22 can be used to derive the magnetic field dependence of the magnetization on the reduced variable $t = (1 - T/T_C)^{1/2}$ in the vicinity of the Curie temperature T_C. The isothermal magnetic entropy change can be calculated by integration of the Maxwell relation:

$$\Delta S_{\rm iso}(T_C) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{A2}$$

Using the latter expression together with the field dependence of the magnetization developed at powers of t up to H^4 as indicated above, we can write

$$\Delta S_{\rm iso}(T_C) = \frac{1}{2}\frac{d\chi_0(T_C)}{dT}\left(\left(-\frac{\chi_0(T_C)}{\chi_0^{(3)}(T_C)}H\right)^{1/3} + H\right)^2 + \frac{1}{4}\frac{d\chi_0^{(3)}(T_C)}{dT}\left(\left(-\frac{\chi_0(T_C)}{\chi_0^3(T_C)}H\right)^{1/3} + H\right)^4, \tag{A3}$$

where $\frac{d\chi_0(T_C)}{dT}$ and $\frac{d\chi_0^{(3)}(T_C)}{dT}$ are the values of the temperature derivatives of the first- and third-order magnetic susceptibilities at T_C. Equation (A3) satisfies two important restrictions. First, for small magnetic fields it complies with the requirement that $\Delta S_{\rm iso}$ tends to 0 when $H \to 0$; and, second, for $H \to \infty$, Eq. (A3) does not diverge because the derivatives of the high-order magnetic susceptibilities are 0 above a certain order.[29]

The first consequence of Eq. (A3) is that the change in isothermal magnetic entropy at T_C for FM systems is governed by the relation $-\frac{\chi_0(T_C)}{\chi_0^{(3)}(T_C)}$. This is an important result of the present study because it should allow us to understand how the magnitude of the isothermal magnetic entropy increases in a second-order magnetic phase transition ($\chi_0^{(3)} < 0$) as the third-order magnetic susceptibility decreases. In addition, $\chi_0^{(3)}$, passing through 0, becomes positive and the second-order magnetic phase transition changes to a first-order transition (the associated isothermal magnetic entropy for a first-order magnetic phase transition is expected to be larger than that for a second-order phase one). On the other hand, expression (A3) is reduced, for low applied magnetic fields, to the well-known expression for the case of gadolinium-based compounds[5] when using the appropriate expressions for $\frac{d\chi_0(T_C)}{dT}$ and $\frac{d\chi_0^{(3)}(T_C)}{dT}$,[29]

$$\Delta S_{\text{iso}}(T_C) = -\frac{3}{2}qR\left(\frac{J(J+1)}{(J^2+(J+1))^2}\right)^{2/3}\left(\frac{10}{9}\frac{g_J\mu_B H}{k_B T_C}\right)^{2/3} + o(H^{4/3}), \quad \text{(A4)}$$

where q is the number of magnetic ions per mole.

The second important consequence of the above analytical treatment is the magnetic field dependence of ΔS_{iso} at T_C. In magnetic systems with small magnetocrystalline anisotropy such as gadolinium compounds or the La(Fe,Si)$_{13}$ family, an $H^{2/3}$ law was normally used to describe the magnetic field dependence of $\Delta S_{\max}$ near the Curie point, T_C. However, very recently Lyubina *et al.*,[31] based on Landau's theory for the second-order magnetic phase transition, also within the mean-field approximation, showed that

$$-\Delta S_{\max} = A(H+H_0)^{2/3} - AH_0^{2/3} + BH^{4/3}, \quad \text{(A5)}$$

where A and B are intrinsic material constants, while H_0 is an extrinsic parameter determined from the purity and homogeneity of the sample. Our present findings agree well with these previous results, since in Eq. (A3), ΔS_{iso} is a combination of different powers of H, for example, $H^{2/3}$, $H^{4/3}$, and H^2, depending on the magnitude of the derivatives of the high-order magnetic susceptibilities. Results of ΔS_{iso} at the Curie temperature for cubic RM$_2$ (M = Al and Ni) obtained using Eq. (A3) are listed in Table I, considering the crystal-field and exchange parameters taken from Oliveira *et al.*[19] and Purwins *et al.*[27] As expected, the calculated isothermal magnetic entropy changes are in quite good agreement with those found experimentally in both RM$_2$ series (M = Al and Ni) (see Table I).

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