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The giant anisotropic magnetocaloric effect in DyAl₂

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We report on calculations of the anisotropic magnetocaloric effect in DyAl₂ using a model Hamiltonian including crystalline electrical field effects. The anisotropic effect is produced by the rotation of a constant magnetic field from the easy to a hard magnetic direction in the crystal and is enhanced by the first order nature of the field induced spin reorientation transition. The calculated results indicate that for a field with modulus of 2 T rotating from a hard to the easy direction, the isothermal magnetic entropy (ΔS_{iso}) and adiabatic temperature (ΔT_{ad}) changes present peak values higher than 60% the ones observed in the usual process, in which the field direction is kept constant and the modulus of the field is varied. © 2008 American Institute of Physics.

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I. INTRODUCTION

The interest on the magnetocaloric effect (MCE), as measured by the scientific publications in the past ten years, has grown at an exponential rate mainly due to the technological interest on the MCE application on near room temperature magnetic refrigeration, which does not use hazardous or environmentally damaging chemicals, such as chlorofluorocarbons, and has the potential to lower energy consumption about 20%–30% when compared with the conventional vapor compression technology.¹ The MCE was discovered by Warburg² in 1881 and is marked by two other important recent events. First is Brown's³ report in 1976, proving the feasibility of the near room temperature magnetic refrigerator, and the second is the discovery of the first giant magnetocaloric material by Pecharsky and Gschneidner⁴ in 1997.

In general, the temperature dependence of the MCE quantities ΔT_{ad} and ΔS_{iso} presents peak values around the temperature of the order-disorder magnetic phase transitions that are observed under magnetic field *intensity changes*.¹ However, other mechanisms to obtain the MCE, such as the magnetic field *direction changes* in relation to a crystallographic referential frame, are almost unexplored. Recently, theoretical investigations were performed in rare earth intermetallic compounds, which present magnetic anisotropy due to the crystalline electrical field (CEF) interaction in order to simulate the influence of changing the magnetic field direction on the MCE. In the case of NdAl₂ the existence of a minimum in the magnetic entropy change below the phase transition temperature was observed and ascribed to the jump that occurred in the spin reorientation process.⁵ Heat capacity measurements in HoAl₂ showed two pronounced peaks; one at $T=20$ K associated with the rotation of the easy magnetic

axis from the [110] to the [100] direction and the other at $T=31.5$ K due to the ferromagnetic-paramagnetic phase transition.⁶ The influence of the change of the easy magnetic direction on the MCE of HoAl₂ was studied by Oliveira and *et al.*⁷ They disclosed the existence of a small peak in the ΔS_{iso} curve at the reorientation temperature as compared with a higher peak in ΔS_{iso} at the Curie temperature.⁷ Single crystals of DyAl₂ were used for ΔS_{iso} measurements upon magnetic field intensity changes along the three principal crystallographic directions [100], [110], and [111] by Lima *et al.*,⁸ confirming previous theoretical prediction of the inverse MCE along the [111] direction.⁹ The magnetic field dependence of the spin reorientation temperature in DyAl₂ was fully investigated, reproducing early experimental data,⁸ and was used to construct the magnetic spin reorientation phase diagram¹⁰ for DyAl₂.

In this work we investigate the temperature dependence of the ΔS_{iso} and ΔT_{ad} for DyAl₂, fixing the magnetic field intensity ($B=2$ T) and changing its direction from the [100]-easy magnetic direction to the [110] and to the [011] hard magnetic directions. We called the set of ΔS_{iso} and ΔT_{ad} curves constructed imposing magnetic field *changes of direction* to the material as the anisotropic MCE, and its thermodynamic formulation is also presented in this work. The anisotropic MCE curves were compared with the usual ones, in which the magnetic field intensity changes from 0 up to 2 T occur in the easy direction. As expected from our previous work, the peaks of the anisotropic MCE occur at the spin reorientation temperatures, and we obtained an outstanding result in this work: the anisotropic MCE, in both ΔS_{iso} and ΔT_{ad} curves, is higher than the usual MCE for the same maximum magnetic field intensity.

II. THE ANISOTROPIC MCE

In general, the MCE of a magnetic material is characterized by two thermodynamic quantities, the isothermic en-

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ropy change and the adiabatic temperature change, which are calculated upon magnetic field change intensity. These quantities are given by

$$\Delta S_{\text{iso}}(T, B) = S(T, B = 0) - S(T, B), \quad (1)$$

$$\Delta T_{\text{ad}} = T(T_F, B) - T(T_I, B = 0). \quad (2)$$

Nevertheless, the above formulation does not take into account the influence of the direction of the applied magnetic field on the magnetic system. As it is well known, in anisotropic magnetic materials the magnetization is strongly dependent on the magnetic field direction in relation to the crystallographic referential frame. If the magnetic field change is applied along the easy magnetic direction, a higher MCE is expected than in the case where the magnetic field change occurs along a hard magnetic direction. Therefore, it is expected that for anisotropic magnetic materials, changes in the direction of an applied constant magnetic field result in sizable values of the magnetocaloric potentials $\Delta S_{\text{iso}}(T, B)$ and $\Delta T_{\text{ad}}(B, T)$. So, we propose an alternative formulation of relations (1) and (2) in order to take into account the influence of the applied magnetic field direction on the MCE (the anisotropic MCE formulation),

$$\Delta S_{\text{iso}}[\alpha_e, \beta_e, \gamma_e][\alpha, \beta, \gamma] = S(T, B, \alpha_e, \beta_e, \gamma_e) - S(T, B, \alpha, \beta, \gamma), \quad (3)$$

$$\Delta T_{\text{ad}}[\alpha_e, \beta_e, \gamma_e][\alpha, \beta, \gamma] = T(T_F, B, \alpha_e, \beta_e, \gamma_e) - T(T_I, B, \alpha, \beta, \gamma). \quad (4)$$

In these relations, the set $(\alpha_e, \beta_e, \gamma_e)$ represents the angles formed between the external magnetic field vector applied along the easy magnetic direction and the Cartesian axes x , y , and z , respectively. The set (α, β, γ) represents the angles formed between the applied magnetic field vector applied along a generic direction and the Cartesian axes x , y , and z , respectively. When in bracket form, $[\alpha, \beta, \gamma]$, the usual crystallographic representation of Miller indices is considered, e.g., when the magnetic field is applied along the cubic diagonal direction $[\alpha, \beta, \gamma] = [111]$.

The above formulation for the anisotropic MCE is general and does not depend on the microscopic mechanism that leads to the existence of the anisotropy. Figure 1 shows schematically the entropy versus temperature curves for a magnetic field oriented along the easy magnetic direction and along a noneasy magnetic direction with the same intensity B_0 . The arrows represent the anisotropic MCE quantities defined in relations (3) and (4).

III. THEORETICAL PROCEDURES

The magnetism of the intermetallic compound DyAl_2 comes from the $4f$ unfilled Dy-magnetic state, leading to the existence of local magnetic moments, which are coupled via indirect exchange interaction due to the conduction electrons. Besides the exchange interaction, the coupling of the magnetic ions with the external magnetic field (the Zeeman interaction) and the cubic CEF should be considered to prop-

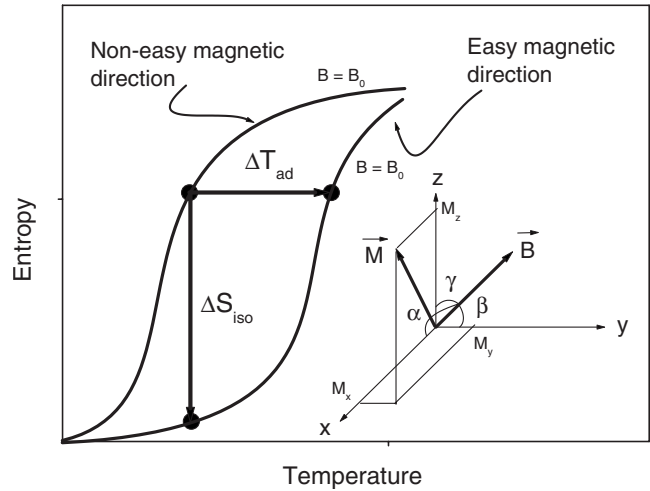


FIG. 1. Temperature dependence of the total entropy for magnetic field applied in the easy magnetic direction and in the noneasy magnetic direction, showing schematically the anisotropic MCE quantities.

erly describe the magnetic anisotropy¹¹ in DyAl_2 . Therefore, our model magnetic Hamiltonian presents the following:

$$\hat{H} = H_{\text{CF}}(W, X) - g\mu_B[(B \cos \alpha + \lambda M_x)J_x + (B \cos \beta + \lambda M_y)J_y + (B \cos \gamma + \lambda M_z)J_z]. \quad (5)$$

The first term describes the crystal field interaction.¹¹ The second term describes the effective Zeeman interaction, which includes the exchange interaction measured by the parameter λ in the molecular field approximation. Here, g is the Landé factor, μ_B is the Bohr magneton, and α , β , and γ are the angles formed between the magnetic field vector \vec{B} with the crystallographic x , y , and z axes, as shown in Fig. 1. The magnetization components $M_k = M_k(B, T, M_x, M_y, M_z)$, where $k = x, y, \text{ and } z$, depend on the magnetic field, temperature, and on the magnetization components itself and are given by the mean thermodynamic value

$$M_k = g\mu_B \frac{\sum \langle \varepsilon_i | J_k | \varepsilon_i \rangle \exp(-\varepsilon_i/k_B T)}{\sum \exp(-\varepsilon_i/k_B T)}, \quad (6)$$

where ε_i and $|\varepsilon_i\rangle$ are the energy eigenvalues and eigenvectors of the Hamiltonian (5). From the self-consistent solution of relation (6), the eigenvalues $\varepsilon_i = \varepsilon_i(T, H, \alpha, \beta, \gamma)$ are obtained and used in the *anisotropic entropy* given by

$$S_{\text{mag}}(T, B, \alpha, \beta, \gamma) = \left(\frac{1}{T}\right) \frac{\sum \varepsilon_i \exp(-\varepsilon_i/k_B T)}{\sum \exp(-\varepsilon_i/k_B T)} + k_B \ln \left[\sum \exp(-\varepsilon_i/k_B T) \right]. \quad (7)$$

In other words, the anisotropic entropy stated in relation (7), which is used in the anisotropic MCE [relations (3) and (4)], must be calculated within the self-consistent procedure. Besides this, we must consider the lattice and electronic contributions to the total entropy. The values of the parameters used in the calculation of these two contributions to the entropy for DyAl_2 were¹² $\Theta_{\text{Debye}} = 380$ K and $\bar{\gamma} = 5.5$ mJ/mol K². The magnetic model parameters¹¹ for DyAl_2 used were $W = -0.0111$ meV, $X = 0.3$, and $\lambda = 41.6$ T²/meV, and the easy magnetic direction is $[100]$.

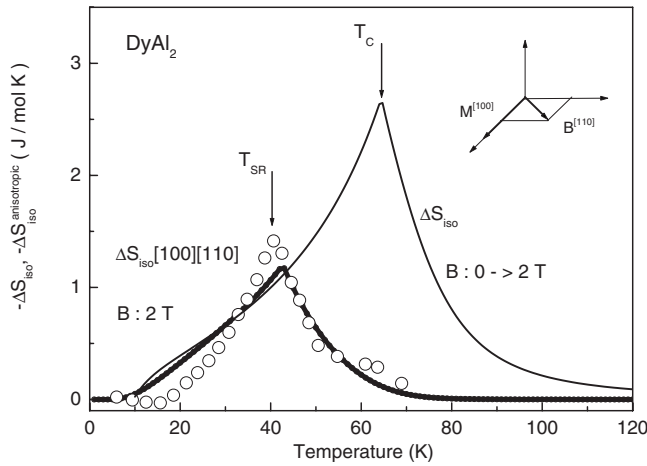


FIG. 2. Temperature dependence of $\Delta S_{\text{iso}}[1,0,0][1,1,0]$ in DyAl_2 for fixed magnetic field intensity $H=2$ T. The solid line represents the theoretical results and the open circles show the experimental data (Ref. 9). The high peak curve shows the theoretical results for the usual ΔS_{iso} calculation for a magnetic field change from 0 to 2 T in the easy magnetic direction.

IV. RESULTS AND DISCUSSIONS

Figure 2 shows the anisotropic magnetic entropy change, $\Delta S_{\text{iso}}[1,0,0][1,1,0]$ versus T , for $B=2$ T. The solid curve represents our theoretical results and the open circles represent the experimental data obtained from the single-crystal sample as reported by Lima *et al.*⁸ It is worth noticing that in the experimental data, the MCE $\Delta S_{\text{iso}}(T, B)$ was measured by the usual process, i.e., the entropy was measured applying a magnetic field change from 0 to 2 T in the easy magnetic direction [100] and in the noneasy magnetic direction [110]. Subtracting these two sets of experimental data, we obtain directly the anisotropic $\Delta S_{\text{iso}}[1,0,0][1,1,0]$ quantity since

$$\Delta S_{\text{iso}}[1,0,0][1,1,0] = [S(T, B=2) - S(T, B=0)]^{[100]} - [S(T, B=2) - S(T, B=0)]^{[110]}. \quad (8)$$

The terms with the zero field in relation (8) cancel, mutually reproducing our definition stated in relation (3). The theoretical results are in excellent agreement with the experimental data. The peak in $\Delta S_{\text{iso}}[1,0,0][1,1,0]$ curve occurs at the spin reorientation temperature $T_{\text{SR}}=41.5$ K. The spin reorientation temperature is strongly dependent on the applied magnetic field intensity and direction and was fully investigated and discussed in a similar magnetic system.⁷ For comparison, Fig. 2 shows the usual theoretical curve for $\Delta S_{\text{iso}}(T, B)$ when the intensity of the magnetic field is changed from 0 to 2 T along the easy magnetic [100] direction showing the peak at Curie temperature, $T_C=64.5$ K. As expected, when the magnetic field change is applied along the easy magnetic direction, more entropic MCE can be obtained. For the sake of clearness of Fig. 2, the experimental data¹² for $\Delta S_{\text{iso}}(T, B)$ upon magnetic field change from 0 to 2 T were included in the Fig. 3, again with the theoretical result.

An outstanding result emerges in DyAl_2 when the anisotropic MCE is calculated applying the magnetic field along the [011] crystallographic direction, which is orthogonal to

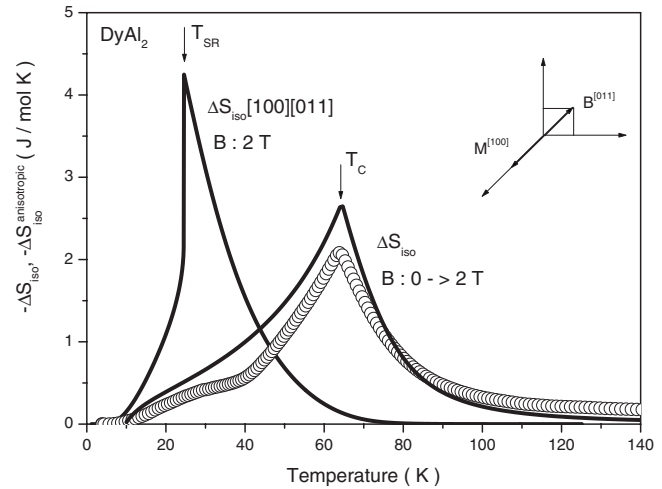


FIG. 3. Temperature dependence of $\Delta S_{\text{iso}}[1,0,0][0,1,1]$ in DyAl_2 for fixed magnetic field intensity $B=2$ T (solid line). The other curves represent the ΔS_{iso} experimental data (circles) and calculation for a magnetic field change from 0 to 2 T in the easy magnetic direction.

the easy magnetic direction as shown by the $\Delta S_{\text{iso}}[1,0,0] \times [0,1,1]$ versus T curve in Fig. 3. The peak value of the anisotropic magnetocaloric potential is about $\Delta S_{\text{iso}}^{\text{peak}}[1,0,0] \times [0,1,1]=4.2$ J/mol K for $B=2$ T at the spin reorientation temperature ($T_{\text{SR}}=24.4$ K) and is higher than the peak associated with the magnetic order-disorder transition that occurs at $T_C=64.5$ K for magnetic field change $\Delta B=2$ T (see the experimental data represented by open circles in Fig. 3). The entropy change peak associated with the spin reorientation phase transition is predicted to overcome (by about 65%) the peak associated with the ferromagnetic-paramagnetic phase transition. In the case of DyAl_2 , the origin of the anisotropic MCE comes from CEF anisotropy, which can produce considerable order-disorder change in the magnetization associated with two main combined effects: the spin reorientation process (which can occur as a first order phase transition process) and a *pure quantum mechanical effect*, which can reduce the angular momentum contribution to the magneti-

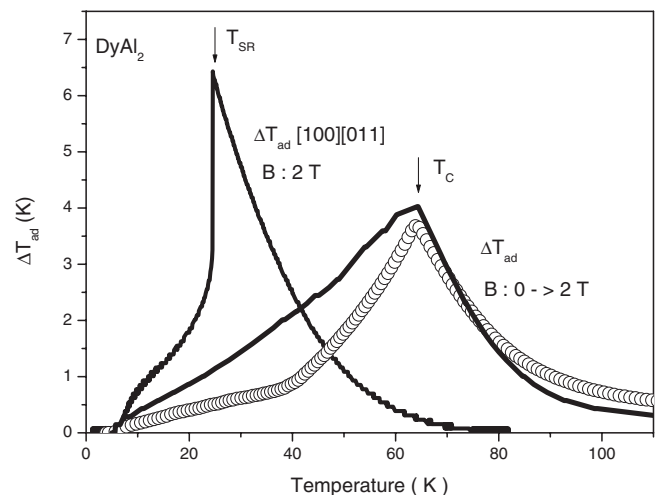


FIG. 4. Temperature dependence of $\Delta T_{\text{ad}}[1,0,0][0,1,1]$ in DyAl_2 for fixed magnetic field intensity $B=2$ T (solid line). The other curves represent the ΔT_{ad} experimental data (circles) and calculation for a magnetic field change from 0 to 2 T in the easy magnetic direction.

zation (the CEF-quenching effect). It should be noted, as discussed above, that the spin reorientation temperature depends on the applied magnetic field direction. For fixed magnetic field intensity of $B=2$ T, we predicted the reduction of the spin reorientation temperature from $T_{SR}=41.5$ K to $T_{SR}=24.4$ K when the magnetic field direction changes from $[110]$ to $[011]$, respectively (see Figs. 2 and 3). Figure 4 shows the anisotropic temperature changes $\Delta T_{ad}[1,0,0] \times [0,1,1]$ versus temperature (solid curve) for $B=2$ T and ΔT_{ad} for magnetic field change along the easy magnetic direction (the open cycles represent the experimental data¹²). The peak in the $\Delta T_{ad}[1,0,0][0,1,1]$ curve occurs as expected at the reorientation temperature $T_{SR}=24.4$ K and is predicted here to be higher (about 67%) than the peak value observed in the usual ΔT_{ad} measurement and calculation.

A. Final comments

The main and outstanding result of the study of the anisotropic MCE is the theoretical possibility, as predicted in this work, of obtaining higher MCE peaks changing the magnetic field direction instead of changes of the field intensity that occurs in the usual MCE measurements and calculations. As far as we are aware, the possibility of achieving higher MCE exploring the magnetic anisotropy, in comparison with the regular order-disorder magnetic phase transition, was never reported before. Nevertheless, experimental data on the anisotropic-MCE potentials ($\Delta T_{ad}[1,0,0][0,1,1]$ and $\Delta S_{iso}[1,0,0][0,1,1]$) for single-crystal $DyAl_2$ are still lack-

ing. If confirmed, our predictions may have a great impact on experimental investigations in order to design new materials with large MCEs.

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