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Investigation on the magnetocaloric effect in $DyNi_2$, $DyAl_2$ and $Tb_{1-n}Gd_nAl_2$ ($n = 0$, 0.4, 0.6) compounds

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ABSTRACT

The magnetocaloric effect (MCE) in the $DyNi_2$, $DyAl_2$ and $Tb_{1-n}Gd_nAl_2$ ($n = 0$, 0.4, 0.6) was theoretically investigated in this work. The $DyNi_2$ and $DyAl_2$ compounds are described considering a model Hamiltonian which includes the crystalline electrical field anisotropy. The anisotropic MCE was calculated changing the magnetic field direction from $\langle 111 \rangle$ to $\langle 001 \rangle$ in $DyNi_2$ and from $\langle 100 \rangle$ to $\langle 011 \rangle$ in $DyAl_2$. The influence of the second- and first-order spin-reorientation phase transitions on the MCE that occurs in these systems is discussed. For the calculations of the MCE thermodynamic quantities in the $Tb_{1-n}Gd_nAl_2$ systems we take into account a two sites magnetic model, and good agreement with the available experimental data was obtained.

1. Introduction

Many magnetic materials studied in the past have been experimentally and theoretically investigated recently in what concern their magnetocaloric effect (MCE)—the ability of normal ferromagnetic materials to heat up when a magnetic field is applied and cool down when it is removed. The recent interest in the MCE appears after the discovery of the first giant magnetocaloric effect in the $Gd_5(Si_2Ge_2)$ compound near room temperature [1]. The magnetocaloric materials present great technological interest in the refrigeration, since magnetic refrigeration may provide one of the most efficient and ecological methods of cooling around room temperatures. Besides the technological interest much effort has been concentrated on the understanding of the MCE from the basic physical point of view.

The usual magnetocaloric effect of magnetic materials is described, upon magnetic field intensity variation, by two thermodynamic quantities: (1) the adiabatic temperature change (ΔT_{ad}) and (2) the isothermal entropy change (ΔS_{iso}). However, for anisotropic magnetic materials where the magnetization dependence on the magnetic field direction is relevant it is convenient to define these magnetocaloric quantities for a relative rotation of the applied magnetic field (of constant intensity) from one direction to another non-equivalent crystallographic direction [2].

In this work, we report on the anisotropic magnetocaloric effect in the $DyAl_2$, $DyNi_2$ and $Tb_{1-n}Gd_nAl_2$ compounds. The model Hamiltonian for these magnetic systems takes into account the Zeeman, the crystalline electrical field (CEF, which is responsible in this model for the magnetic anisotropy) and the exchange interactions. The exchange interaction was treated in the mean field approximation. As an interesting result our model predicts that the spin-reorientation process can occur continuously or discontinuously. The last case leads to pronounced peaks in the magnetocaloric curves what is associated to the discontinuity in the temperature dependence of the magnetization.

For the $DyNi_2$ compound the anisotropic MCE was calculated considering a variation in the magnetic field direction from $\langle 111 \rangle$ to $\langle 001 \rangle$. The spin-reorientation process in this compound occurs continually and its influence on the MCE is discussed and compared with the case where the spin reorientation presents discontinuity, as is the case of the $DyAl_2$ [3]. The $Tb_{1-n}Gd_nAl_2$ compounds present two different magnetic sites and were theoretically investigated extending the model used in the treatment of $DyNi_2$ and $DyAl_2$ in order to account for a two coupled magnetic sublattices model, which allows a detailed study of the influence of the Gd concentration (n) on the MCE. The obtained curves for ΔS_{iso} and ΔT_{ad} show a good with the available experimental data [4,5].

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2. Theory

2.1. DyNi$_2$ and DyAl$_2$

The Hamiltonian used to describe the magnetic properties of DyNi$_2$ and DyAl$_2$ includes the CEF, Zeeman and exchange interactions:

$$\mathscr{H} = W\left[\frac{x}{F_4}(O_4^0+5O_4^4)+\frac{1-|x|}{F_6}(O_6^0-21O_6^4)\right] - g\mu_B\sum_k(\mu_0 H\cos\alpha_k+\lambda M_k)J^k. \tag{1}$$

In the above relation the first term is the CEF Hamiltonian, written in the LLW notation [6], where W gives the CEF energy scale, x gives the relative contribution of terms of fourth and sixth degrees in the $O_n{}^m$ Stevens equivalent operators [7], F_4 and F_6 are dimensionless factors. The second term in relation (1) is the magnetic Hamiltonian in the mean-field approximation, where g is the Landé factor, μ_B the Bohr magneton, μ_0 the vacuum magnetic permeability, H the applied magnetic field which forms an angle α_k with the k ($k = x$, y, z) crystallographic axes, λ the exchange parameter, M_k the k-th component of the magnetization vector and J^k the k-th component of the total angular momentum operator.

The component of the magnetization vector along the magnetic-field direction is given by

$$M_{\mathrm{H}} = M_x\cos\alpha_x + M_y\cos\alpha_y + M_z\cos\alpha_z, \tag{2}$$

and M_x, M_y and M_z are calculated by the usual thermodynamic relation.

$$M_k = g\mu_B\frac{\sum_i\langle\varepsilon_i|J^k|\varepsilon_i\rangle e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}, \tag{3}$$

where ε_i ($|\varepsilon_i\rangle$) are the eigenvalues (eigenvectors) of Hamiltonian (1).

The total entropy used in the calculations of the magnetocaloric effect is assumed as a summation of the three main contributions: magnetic, electronic and lattice entropies, i.e.,

$$S(T,H) = S_{\mathrm{mag}}(T,H) + S_{\mathrm{el}}(T) + S_{\mathrm{lat}}(T) \tag{4}$$

The anisotropic magnetocaloric potentials, ΔS_{an} and ΔT_{an}, are defined as a function of the temperature, the intensity of the magnetic field (which is kept fixed) and the direction of the applied magnetic field as follows:

$$\Delta S_{\mathrm{an}}(T,H) = S(T,H,\alpha_x^e,\alpha_y^e,\alpha_z^e) - S(T,H,\alpha_x,\alpha_y,\alpha_z), \tag{5}$$

$$\Delta T_{\mathrm{an}}(T,H) = T(S,H,\alpha_x^e,\alpha_y^e,\alpha_z^e) - T(S,H,\alpha_x,\alpha_y,\alpha_z). \tag{6}$$

In the above relations the superscript "e" stands for the easy magnetization direction.

2.2. Tb$_{1-n}$Gd$_n$Al$_2$

For the Tb$_{1-n}$Gd$_n$Al$_2$ compounds we extend the Hamiltonian (1) for two coupled magnetic sublattices. This is performed assuming that Hamiltonian (1) represents both sublattices, a and b which are coupled by the exchange fields

$$\mathscr{H} = W^\delta\left[\frac{x_\delta}{F_4}(O_4^0+5O_4^4)_\delta+\frac{1-|x_\delta|}{F_6}(O_6^0-21O_6^4)_\delta\right] - g^\delta\mu_B(\mu_0 H\cos\alpha_k^\delta+Z_{\delta\delta}\lambda^{\delta\delta}M_k^\delta+Z_{\delta\rho}\lambda^{\delta\rho}M_k^\rho)J_\delta^k \tag{7}$$

In the relation (7), the symbols δ and ρ stand for the sublattices a or b, respectively. Note that it was explicitly considered the dependency of the mean field with the number of nearest neighbors $Z_{\delta\delta}$ (nearest neighbors of type δ in the vicinity of an ion of type δ) and $Z_{\delta\rho}$ (nearest neighbors of type ρ in the vicinity of an ion of type δ). The extra term $\lambda^{\delta\rho}M_k{}^\rho$ should be read as the mean field generated by the sublattice ρ on the ion of the other sublattice $\delta\,(\delta\neq\rho)$.

The total projection of the magnetization along the magnetic field direction is calculated by the relation $M_{\mathrm{H}}(T,H) = (1-n)M^{\mathrm{Tb}}+nM^{\mathrm{Gd}}$. The entropy for the entire compound is $S(T,H) = (1-n)S^{\mathrm{Tb}}+nS^{\mathrm{Gd}}$. The magnetization and entropy of each sublattice is given by relations (2) and (4), respectively. We have considered the concentration values $n = 0$, 0.4, 0.6. The magnetocaloric quantities were calculated as usual.

3. Results and discussion

The compound DyNi$_2$ was studied using the following parameters: $x = -0.10$, $W = -0.019$ meV and $\lambda = 15.5\,\mathrm{T}^2/\mathrm{meV}$ [8]. In DyNi$_2$ the easy magnetization direction is along the $\langle 111\rangle$ crystallographic direction.

Fig. 1 shows the usual and the anisotropic isothermal entropy change curves for DyNi$_2$. The usual ΔS_{iso} curve was calculated in the easy magnetization direction by changing the intensity of the magnetic field from 0 to 2 T. The anisotropic ΔS_{an} curve was calculated varying the direction of a magnetic field of 2 T from the easy magnetization direction to $\langle 001\rangle$ direction. One should note that the peak values occur at the critical temperature (T_{C}) for the former and at the spin-reorientation temperature (T_{SR}) for the latter, see the arrows in Fig. 1. The transition at T_{SR} is continuous and the MCE peak value in this case is lower than the one at T_{C}. This could be attributed to the fact that a spin-reorientation transition is of order–order type, i.e., it occurs in the ferromagnetic phase. On the other hand, the transition at the critical temperature is of order–disorder (ferro–paramagnetic) type, so that a more amount of entropy change is expected to be extracted from the sample in this case. The open triangles represent experimental results obtained from Ref. [8].

Fig. 2 shows the calculated isothermal entropy changes for DyAl$_2$. These curves were calculated using the following set of parameters: $x = 0.3$, $W = -0.0111$ meV and $\lambda = 41.6\,\mathrm{T}^2/\mathrm{meV}$. The easy magnetization direction in DyAl$_2$ is $\langle 100\rangle$ [9]. It is worth

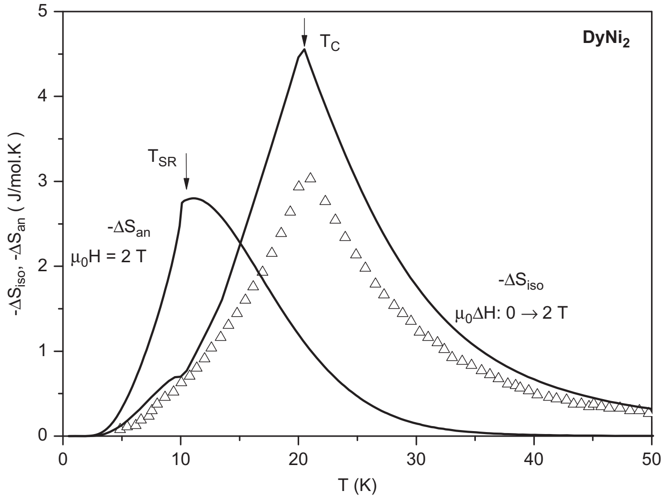

Fig. 1. Isothermal entropy change curves vs. temperature. The anisotropic ΔS_{an} curve was obtained changing the direction of the magnetic field of 2 T from $\langle 111\rangle$ to $\langle 001\rangle$, and the usual one varying the intensity of the magnetic field from 0 to 2 T, in the easy magnetic direction. The open triangles represent experimental results [8].