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Magnetic coupling between Gd and Pr ions and magnetocaloric effect in $Gd_{0.5}Pr_{0.5}Al_2$ compound

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ABSTRACT

In this work, we report the theoretical and experimental investigations on the magnetic and magnetocaloric properties for $Gd_{0.5}Pr_{0.5}Al_2$ compound in different magnetic fields. The magnetization features indicate that $Gd_{0.5}Pr_{0.5}Al_2$ is ferrimagnetic at low temperatures. We also present data from X-ray magnetic circular dichroism (XMCD) experiments for this compound, with which we have confirmed that the magnetic moments of the Pr ions are antiparallel to the magnetic moments of the Gd ions. The magnetocaloric parameters, ΔT_S and ΔS_T, were obtained from calorimetric data and both curves present normal and inverse magnetocaloric effect. A theoretical model for ferrimagnetic coupling, including the crystalline electrical field anisotropy, was used to describe the ΔT_S and ΔS_T experimental results.

1. Introduction

RAl_2 (R = rare-earth) compounds with cubic Laves phase have been extensively studied [1–4] and the ground state is found to be ferromagnetic for most of them. $GdAl_2$ is ferromagnetic with a Curie temperature laying between 153 and 182 K and its effective magnetic moment is around 7.93 μ_B [5]. The Curie temperature of the $PrAl_2$ compound is around 34 K and its effective magnetic moment is 3.5 μ_B [6]. These distinct characteristics can induce interesting ground states for a system where the two rare-earth compounds, Gd and Pr, occupy the R site in the RAl_2 cubic lattice. In fact, Williams et al. [7] have studied five systems $R_{1-x}R'_xAl_2$, where R and R′ = rare-earth elements, including the series $Gd_{1-x}Pr_xAl_2$. Their experimental work has indicated that the systems in which both lanthanides are light (the ions occurring before Eu) or alternatively both are heavy (the ions from Gd to Lu) couple ferromagnetically, whereas for light–heavy combinations the coupling is ferrimagnetic. Such compounds are interesting in terms of the magnetocaloric effect (MCE), because they can present field-induced transitions or even high crystal field anisotropy. For this reason, it is our goal to investigate the role of rare-earth microscopic interactions into the magnetic properties of the compounds and consequently its magnetocaloric behavior.

In this paper, we discuss our results on X-ray magnetic circular dichroism (XMCD), magnetization and magnetocaloric effect (MCE) for the $Gd_{0.5}Pr_{0.5}Al_2$ compound. Using the XMCD technique, we intend to investigate the antiparallel coupling between Pr and Gd atoms, as it has been proposed in the literature to be antiparallel [7]. The MCE data for the compounds $GdAl_2$ and $PrAl_2$ have been reported elsewhere [8,9] and in the present work we report on the MCE for $Gd_{0.5}Pr_{0.5}Al_2$. Our experimental results will be compared to calculations obtained using a theoretical model that takes in account the coupling between the two magnetic sublattices.

2. Experimental procedure

Polycrystalline samples of $Gd_{0.5}Pr_{0.5}Al_2$, $GdAl_2$ and $PrAl_2$ compounds were prepared by arc-melting the elements in high-purity argon atmosphere on a water-cooled copper hearth. The purity of the starting materials was 99.99 wt% for aluminum and

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99.9 wt% for the rare-earth metals. We have repeated the melting process four times to obtain homogeneous samples, which were subsequently annealed under argon atmosphere in a quartz ampoule at 1270 K for 5 h. The X-ray diffraction analyses for all samples show a single-phase formation with the C15 cubic Laves phase structure.

The XMCD measurements were performed on the dispersive XAS beam line at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). A right circularly polarized X-ray beam was selected by a 0.1 mm-wide slit, positioned at half intensity above the orbit plane (maximum intensity), ensuring a circular polarization rate from approximately 0.7. Data were recorded in transmission mode, fixing the polarization and reversing the 0.9 T permanent magnetic field, applied along the beam propagation direction.

The magnetic measurements were performed in a commercial SQUID magnetometer (Quantum Design) and the calorimetric experiments were performed in the commercial equipment (PPMS; Quantum Design).

3. Theoretical description

To calculate the magnetic and magnetocaloric properties of the $Gd_{0.5}Pr_{0.5}Al_2$ compound, we consider a two-magnetic-sublattice Hamiltonian:

$$H = H(\mathrm{Gd}) + H(Pr), \tag{1}$$

where:

$$H(\mathrm{Gd}) = -g^{\mathrm{Gd}}\mu_B[\vec{B} + \vec{B}_m^{\mathrm{Gd}}]\vec{J}^{\mathrm{Gd}}, \tag{2}$$

$$H(Pr) = -g^{Pr}\mu_B[\vec{B} + \vec{B}_m^{Pr}]\vec{J}^{Pr} + H_{CF}, \tag{3}$$

Relations (2) and (3) are the single-ion Hamiltonian of Gd and Pr coupled sublattices, g the Landé factor, μ_B the Bohr magneton, $\vec{B}$ the applied magnetic field, $\vec{B}_m^{\mathrm{Gd}}$ and $\vec{B}_m^{Pr}$ the molecular field acting on Gd and Pr ions, respectively, and $\vec{J}$ the total angular momentum operator. Besides the molecular and applied magnetic fields, the 4f electrons of the Pr ions experience the influence of a crystalline electrical field (CEF), which for cubic symmetry (in the Lea–Leask–Wolf notation) is given by [10]:

$$H_{CF} = W\left[\frac{x}{F_4}(O_4^0 + 5O_4^4) + \frac{1-|x|}{F_6}(O_6^0 - 21O_6^4)\right] \tag{4}$$

In relation (4), O_n^m are the Stevens equivalent operators [11] and W and x the parameters that determine, respectively, the strength and the ordination of the splitting of the $(2J+1)$-fold degenerate Hund ground state, F_4 and F_6 are dimensionless constants [10].

The molecular fields $\vec{B}_m^{\mathrm{Gd}}$ and $\vec{B}_m^{Pr}$ (which couple the Gd and Pr sublattices) can be written as follows:

$$\vec{B}_m^{\mathrm{Gd}} = \lambda_{\mathrm{Gd}}\vec{M}_{\mathrm{Gd}} + \lambda_{\mathrm{Gd-Pr}}\vec{M}_{\mathrm{Pr}} \tag{5}$$

and

$$\vec{B}_m^{Pr} = \lambda_{\mathrm{Pr}}\vec{M}_{\mathrm{Pr}} + \lambda_{\mathrm{Gd-Pr}}\vec{M}_{\mathrm{Gd}} \tag{6}$$

where λ_{Gd}, $\lambda_{\mathrm{Gd-Pr}}$ and λ_{Pr} are, respectively, the molecular field parameters for Gd ions, Gd–Pr ions and Pr ions interactions, and $\vec{M}_{\mathrm{Gd}}$ and $\vec{M}_{Pr}$ are the magnetization of each ion sublattice.

From the eigenvalues ε_k^δ and eigenvectors $|\varepsilon_k^\delta\rangle$ ($\delta = \mathrm{Gd}$, Pr) of Hamiltonians (2) and (3), the sublattice magnetizations are obtained from the usual relation:

$$\vec{M}^\delta = \langle\vec{\mu}^\delta\rangle = g_\delta\mu_B\langle\vec{J}^\delta\rangle = g_\delta\mu_B\frac{\sum_{\varepsilon_i^\delta}\langle\varepsilon_i^\delta|\vec{J}^\delta|\varepsilon_i^\delta\rangle e^{-\beta\varepsilon_i^\delta}}{\sum_{\varepsilon_i^\delta}e^{-\beta\varepsilon_i^\delta}}, \tag{7}$$

where $\beta = 1/k_BT$ and k_B is the Boltzmann constant.

The projection of the magnetization of Gd and Pr ions along the applied magnetic field direction is given by

$$M_B^\delta(T,B) = M_x^\delta\cos\alpha + M_y^\delta\cos\beta + M_z^\delta\cos\gamma, \tag{8}$$

where M_k^δ ($k = x, y, z$) are the Cartesian components of the magnetization and α, β and γ the angles formed by the applied magnetic field with the Cartesian axes. Then, the total magnetization for $Gd_{0.5}Pr_{0.5}Al_2$ is:

$$M_B(T,B) = 0.5M_B^{\mathrm{Gd}}(T,B) + 0.5M_B^{Pr}(T,B), \tag{9}$$

The magnetic entropy can be calculated from the general relation

$$S_{mag}^\delta(T,B) = \frac{1}{T}\frac{\sum_{\varepsilon_i^\delta}\varepsilon_i^\delta e^{-\beta\varepsilon_i^\delta}}{\sum_{\varepsilon_i^\delta}e^{-\beta\varepsilon_i^\delta}} + k_B\ln\left(\sum_{\varepsilon_i^\delta}e^{-\beta\varepsilon_i^\delta}\right), \tag{10}$$

The lattice contribution to the entropy is obtained using the Debye formula

$$S_{lat}^\delta(T) = -3R\ln(1-e^{-\theta_D^\delta/T}) + 12R\left(\frac{\theta_D^\delta}{T}\right)^3\int_0^{\theta_D^\delta/T}\frac{x^3dx}{e^x-1}, \tag{11}$$

where R is the gas constant and θ_D the Debye temperature.

The electronic contribution to the total entropy is calculated by means of usual expression:

$$S_{el}(T) = \bar{\gamma}^\delta T, \tag{12}$$

where the Sommerfeld coefficient $\bar{\gamma}$ was taken as 9.87 mJ mol^{-1} K^{-2}, which is an average of the values of $\bar{\gamma}$ for the compounds $LaAl_2$ and $LuAl_2$ [12].

The entropy of each magnetic sublattice is considered as the summation of the three main contributions described above:

$$S^\delta(T,B) = S_{mag}^\delta(T,B) + S_{lat}^\delta(T) + S_{el}^\delta(T), \tag{13}$$

and for the compound $Gd_{0.5}Pr_{0.5}Al_2$ we have:

$$S_{tot}(T,B) = 0.5S^{\mathrm{Gd}}(T,B) + 0.5S^{Pr}(T,B), \tag{14}$$

To calculate the magnetocaloric effect, we adopted the values: $\lambda_{\mathrm{Gd}} = 1.70\,\mathrm{meV}/\mu_B$, $\lambda_{\mathrm{Gd-Pr}} = -0.49\,\mathrm{meV}/\mu_B$ and $\lambda_{\mathrm{Pr}} = 0.21\,\mathrm{meV}/\mu_B$, obtained by comparing the calculated critical temperature with the experimental one. The CEF parameters, $x = 0.739$ and $W = -0.329$ meV, were taken from Ref. [13] for $PrAl_2$. The applied field was chosen to be in the [1 0 0] direction (the easy direction of magnetization of $PrAl_2$ [13]).

The magnetocaloric thermodynamic quantities, ΔS_T and ΔT_S, are calculated by means of the usual relations:

$$\Delta S_T(T,B) = S_{tot}(T,B=0) - S_{tot}(T,B\neq 0), \tag{15}$$

$$\Delta T_S(T,B) = T(T,B\neq 0) - T(T,B=0), \tag{16}$$

4. Results and discussion

The magnetic transition temperature of $Gd_{0.5}Pr_{0.5}Al_2$ compound is around 108 K, obtained from derivatives of the magnetization curves shown in Fig. 1 and it has an effective magnetic moment of 5.4 μ_B. After reducing temperature of the system in zero magnetic field (ZFC process), the thermomagnetic curves were measured on heating (FW) and cooling process (FC) with an applied magnetic