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

A. Magnus G. Carvalho [a,*], F. Garcia [b], V.S.R. de Sousa [c], P.J. von Ranke [c], D.L. Rocco [d], G.D. Loula [e], E.J. de Carvalho [b], A.A. Coelho [e], L.M. da Silva [f], F.C.G. Gandra [e]

[a] Divisão de Metrologia de Materiais (DIMAT), Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO), Duque de Caxias, Rio de Janeiro, 25250-020, Brazil
[b] Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, São Paulo, Brazil
[c] Instituto de Física, Universidade do Estado do Rio de Janeiro-UERJ, Rua São Francisco Xavier, 524, 20550-013, Rio de Janeiro, Brazil
[d] Departamento de Física, Universidade Federal de Ouro Preto, 35400-000, Ouro Preto, MG, Brazil
[e] Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Unicamp, 13083-970, Campinas, São Paulo, Brazil
[f] Centro de Ciências Sociais, Saúde e Tecnologia (CCSST), Universidade Federal do Maranhão, Imperatriz-MA, Brazil

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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

* Corresponding author.
E-mail address: amcarvalho@inmetro.gov.br (A.M.G. Carvalho).

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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

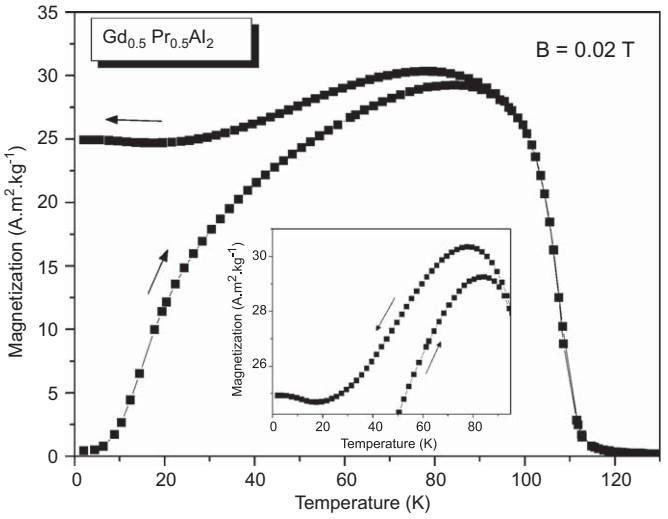

Fig. 1. Magnetization as a function of temperature, in a magnetic field of 0.02 T. The heating and cooling curves were measured after a zero-field-cooling process.

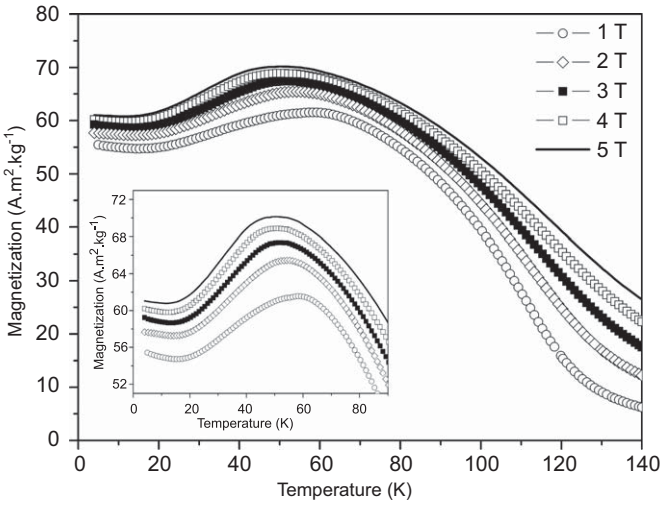

Fig. 2. Magnetization as a function of temperature, in different magnetic fields, for the $Gd_{0.5}Pr_{0.5}Al_2$ compound.

field. We observe that in the heating process the magnetization is lower when compared to the cooling cycle, but both curves show a maximum just below the transition temperature. These features (minima and maxima) are consistent with a ferrimagnetic coupling [14,15].

In Fig. 2, we show the field-cooled magnetization as a function of the temperature measured at different magnetic fields. In the inset of this figure one can see a minimum followed by a maximum as the temperature increases. We believe that the minimum observed can be due to the Pr magnetic sublattice (antiparallel to the Gd sublattice), which could be composed by non-collinear magnetic moments that tend to align while temperature is increased until achieving the temperature of the minimum. However, this hypothesis must be checked by some technique, such as, X-ray magnetic diffraction on a single crystal of the $Gd_{0.5}Pr_{0.5}Al_2$ compound. The maximum in the thermomagnetic curves can be originated by different behaviors between Pr and Gd magnetic sublattices as a function of the temperature.

We present in Figs. 3 and 4 the results on X-ray magnetic circular dichroism for the $Gd_{0.5}Pr_{0.5}Al_2$ compound. Fig. 3 shows

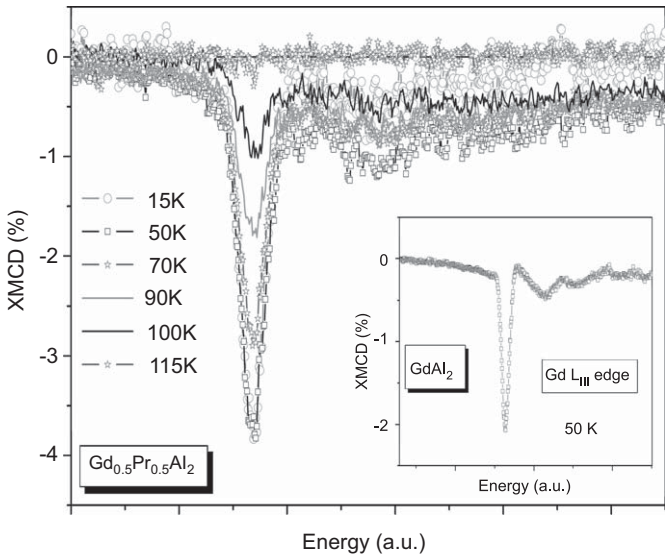

Fig. 3. X-ray magnetic circular dichroism obtained in several temperatures at Gd L_{III} edge for the $Gd_{0.5}Pr_{0.5}Al_2$ compound. The inset shows XMCD signal for the $GdAl_2$ compound at the same edge.

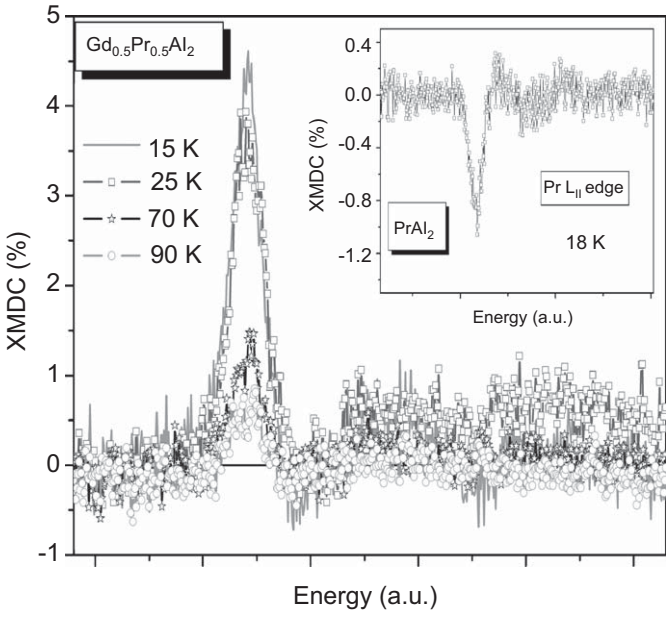

Fig. 4. X-ray magnetic circular dichroism obtained in several temperatures at Pr L_{II} edge for the $Gd_{0.5}Pr_{0.5}Al_2$ compound. The inset shows XMCD signal for the $PrAl_2$ compound at the same edge.

the XMCD profiles at several temperatures obtained from the absorption data at Gd L_{III} edge. We notice that the XMCD signal is consistently reduced with increasing temperature and fades out above 108 K, the transition temperature. The inset in Fig. 3 shows the XMCD signal for $GdAl_2$, used as a reference compound. Since both $Gd_{0.5}Pr_{0.5}Al_2$ and $GdAl_2$ present negative signals, we can conclude that the Gd moments are oriented parallel to the external magnetic field in both materials.

On the other hand, X-ray absorption measurements at Pr L_{II} edge at different temperatures resulted in the XMCD profiles for $Gd_{0.5}Pr_{0.5}Al_2$ shown in Fig. 4. By comparing with the Gd results, we see that the Pr L_{II} signal is inverted. To know if magnetic moments of the Pr ions are parallel or antiparallel to the applied

magnetic field, it is necessary to compare with a ferromagnetic Pr-based compound. The inset in Fig. 4 shows XMCD signal of the ferromagnetic $PrAl_2$ compound. We note that this signal is negative and contrary to the one observed in the $Gd_{0.5}Pr_{0.5}Al_2$ compound. Since the magnetic moments of the Pr ions in the $PrAl_2$ compound are parallel to the applied magnetic field, we conclude that in $Gd_{0.5}Pr_{0.5}Al_2$ these moments are antiparallel to the magnetic field. This definitely shows that the magnetic moments of the Pr ions are antiparallel to the magnetic moments of the Gd ions in the $Gd_{0.5}Pr_{0.5}Al_2$ compound. By increasing the temperature, the XMCD signal decreases, following the same behavior observed in the measurements at Gd L_{III} edge.

Fig. 5 shows the isothermal variation of the entropy (ΔS_T) and the adiabatic variation of the temperature (ΔT_S) for $Gd_{0.5}Pr_{0.5}Al_2$ compound obtained from specific heat data collected at 0 T and 2 T. ΔS_T and ΔT_S are the thermodynamic quantities defined in relations (15) and (16) that characterize the magnetocaloric effect. For the magnetic field variation from 0 to 2 T, the maximum values of ΔS_T and ΔT_S are 4.1 J kg^{-1} K^{-1} and 1.7 K, respectively. We notice that there is an inverse magnetocaloric effect (both $-\Delta S_T$ and ΔT_S present negative values) at low temperatures. This is certainly due to the ferrimagnetic coupling between Pr and Gd ions. Using different sets of parameters in the theoretical model described above, we obtain ΔS_T and ΔT_S curves that also present the inverse magnetocaloric effect. The *set* 1 includes $g_{eff}^{Gd} = 2$ and the other parameters described in the *theory* section; the *set* 2 considers

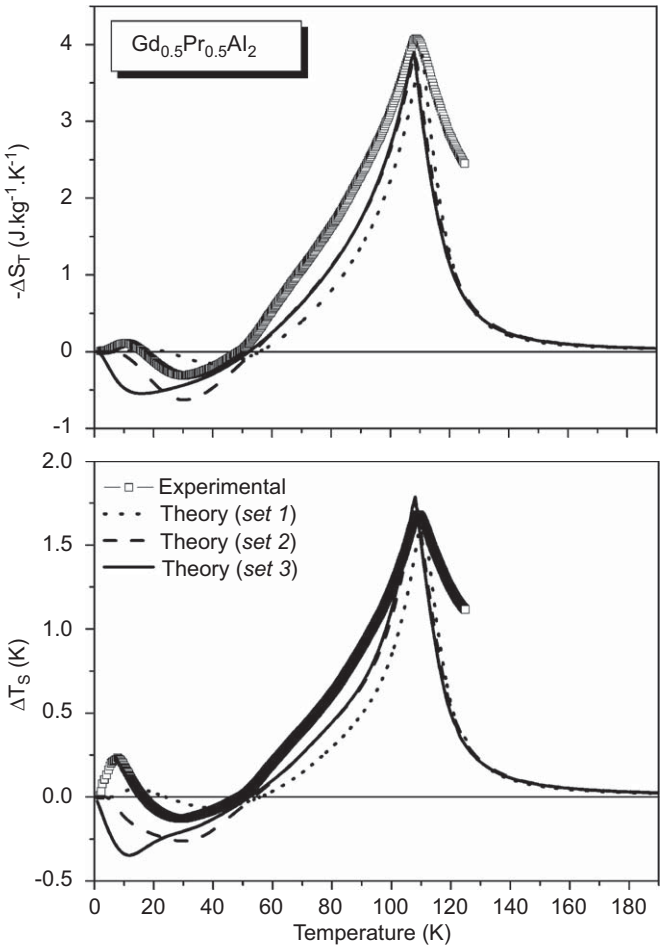

Fig. 5. Experimental (symbols) and theoretical (solid, dashed and dotted lines) results for (a) isothermal variation of the entropy (ΔS_T) as a function of the temperature and (b) adiabatic variation of the temperature (ΔT_S) as a function of the temperature for $Gd_{0.5}Pr_{0.5}Al_2$ compound. Both were obtained for a magnetic field variation of 2 T. *Set* 1 ($g_{eff}^{Gd} = 2$); *set* 2 ($g_{eff}^{Gd} = 2.16$); *set* 3 ($g_{eff}^{Gd} = 2$, $W = -0.879$).

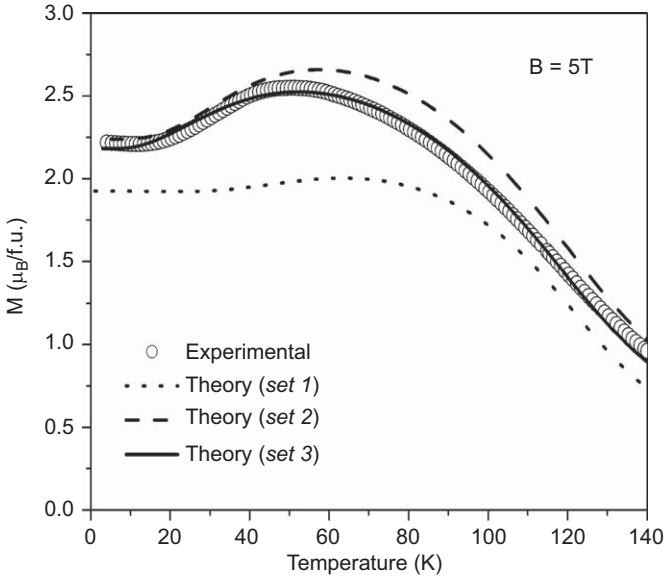

Fig. 6. Experimental (symbol) and theoretical (solid, dashed and dotted lines) magnetization isofields for $Gd_{0.5}Pr_{0.5}Al_2$ compound measured at 5 T. *Set* 1 ($g_{eff}^{Gd} = 2$); *set* 2 ($g_{eff}^{Gd} = 2.16$); *set* 3 ($g_{eff}^{Gd} = 2$, $W = -0.879$).

$g_{eff}^{Gd} = 2.16$; the *set* 3 considers $g_{eff}^{Gd} = 2$ and $W = -0.879$ meV. In spite of the differences among the theoretical curves, it is hard to guess which is the best physical scheme for only analyzing ΔS_T and ΔT_S results.

Supposing collinear magnetic moments, the theoretical model (*set* 1, $\mu_{teo}^{Gd} = 7.0$) yields a magnetization of 1.93 μ_B at 5 T and near 0 K (dotted line in the Fig. 6), while experimental magnetization at $T = 2$ K and at the same magnetic field is around 2.21 μ_B (symbols). The theoretical model (*set* 1) considers $\mu_{teo}^{Gd} = 7.0\,\mu_B$ for Gd magnetic moment, while experimental results for pure Gd show that $\mu_{exp}^{Gd} \cong 7.55\,\mu_B$ [16]. The difference of almost 0.3 μ_B between theoretical and experimental magnetization at 5 T and low temperatures could be an indicative of the influence of the 5d electron in the total magnetic moment of $Gd_{0.5}Pr_{0.5}Al_2$ compound. Thus, we have performed calculations considering $g_{eff}^{Gd} = 2.16$ and $\mu_{teo}^{Gd} = 7.55\,\mu_B$ (*set* 2) and, at low temperatures, the theoretical magnetization isofield is closer to the experimental data, when compared to results from *set* 1 (Fig. 6).

Besides that, we may suppose that the divergence between experimental and theoretical (*set* 1) magnetization at 5 T and low temperatures could be also an indicative of the non-collinear magnetic moments in the Pr sublattice. Supposing that the non-collinear behavior could be a manifestation of a modified crystalline field acting on the Pr magnetic sublattice, we used other set of parameters (*set* 3), which considers $g_{eff}^{Gd} = 2$ and $W = -0.879$ meV. The theoretical magnetization reproduces well the experimental data and it is an indication that the CEF influence could be responsible for the large magnetization at low temperatures, as well as the larger Gd magnetic moments (5d electrons contribution).

5. Conclusions

In this work, we studied the thermomagnetic properties of the pseudo-binary compound $Gd_{0.5}Pr_{0.5}Al_2$. The base compounds, $GdAl_2$ (T_C between 153 and 182 K) and $PrAl_2$ ($T_C = 34$ K) are ferromagnetic, while $Gd_{0.5}Pr_{0.5}Al_2$ present a transition at 108 K, in an intermediary position. Magnetization data indicates that the compound does not show a ferromagnetic behavior, in agreement with the literature. In fact, using the XMCD technique, we have

confirmed that the magnetic moments of the Pr ions are oriented antiparallel to the magnetic moments of the Gd ions. Besides that, the magnetization suggests that the minima that occur in the thermomagnetic curves are due to non-collinear magnetic moments in the Pr sublattice. Both experimental and theoretical ΔS_T and ΔT_S results present inverse MCE at low temperatures, which is expected for a ferrimagnetic material. The comparison between calculations and experimental magnetization isofield curves suggests that the CEF acting on Pr ions and the 5d electrons from Gd ions could be contributing to the magnetization of $Gd_{0.5}Pr_{0.5}Al_2$ compound.

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