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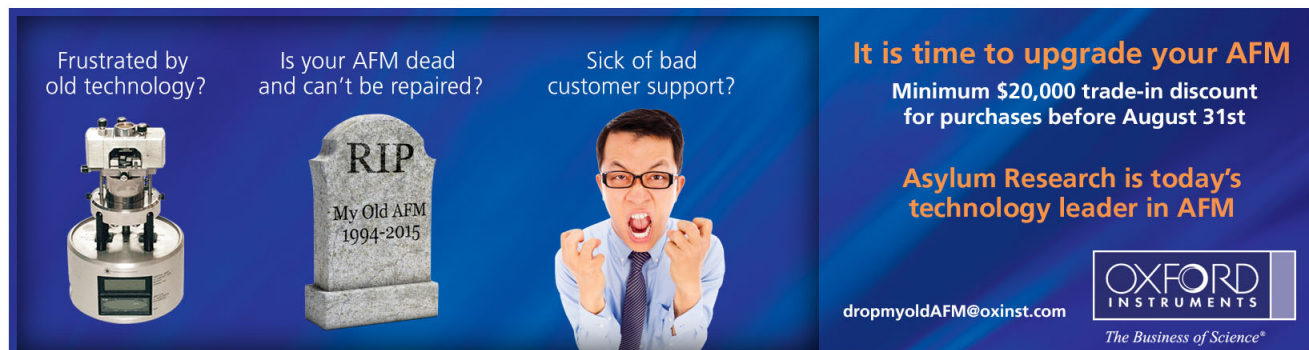
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Experimental and theoretical analyses of PrAl₂ and NdAl₂ composite for use as an active magnetic regenerator

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We report the theoretical and experimental investigations on the magnetocaloric effect in the PrAl₂ and NdAl₂ compounds and a composite of these compounds for use as an active magnetic regenerator. The theoretical calculations were performed considering the crystalline electrical field anisotropy and the magnetocaloric potentials were calculated in the three main crystallographic directions. The experimental data, obtained for the polycrystalline samples, are in good agreement with the theoretical results. Also, an optimum molar fraction of the PrAl₂ and NdAl₂ composite was determined theoretically and experimentally and discussed in the framework of the optimum regeneration Ericsson cycle. © 2005 American Institute of Physics. [DOI: 10.1063/1.1876575]

INTRODUCTION

Since Brown¹ described a practical near-room-temperature magnetic refrigerator using magnetocaloric effect (MCE), and the discovery of the giant MCE in Gd₅(Si₂Ge₂) (Ref. 2) and recently in MnFeP_{0.45}As_{0.55} (Ref. 3) and MnAs_{1-x}Sb_x,^{4,5} the interest in this research area has been considerably enhanced. Magnetic refrigeration is based on the MCE, the ability of magnetic materials to heat up when they are magnetized, and cool down when removed from the magnetic field in an adiabatic process. The two thermodynamic quantities that characterize the MCE are ΔS_{mag} (the isothermal magnetic entropy change) and ΔT_{ad} (the adiabatic temperature change), which are observed upon changes in the external magnetic field. Improving in magnetic refrigeration requires investigations on the microscopic mechanisms that are responsible for an increase in these two thermodynamic quantities, and this subject is of our current research interest.^{6,7}

In order to better understand the microscopic mechanisms of the MCE in simple compounds we chose to study compounds of the family RAl₂. To describe them and calculate the MCE along the crystallographic directions, we used a model that includes the exchange and crystalline electric-field (CEF) interactions, and applied it to the compounds with R=Pr or Nd. This work describes the theoretical results and compares them with available experimental data.

Also, an optimum molar fraction of PrAl₂ and NdAl₂ was determined for the assembling of a composite to be used as an active magnetic resonator (AMR) at low temperatures. The MCE for the composite was calculated and measured, and the results are discussed in the framework of an optimum regeneration Ericsson cycle.

THEORETICAL MODEL

The PrAl₂ and NdAl₂ compounds crystallize in the cubic MgCu₂-type structure, and their magnetism is described using a magnetic Hamiltonian that includes the CEF and the Zeeman-exchange interaction terms.

$$\hat{H} = W \left[\frac{X}{F_4} (O_4^0 + 5O_4^4) + \frac{(1-|X|)}{F_6} (O_6^0 - 21O_6^4) \right] - g\mu_B (B_m^x J^x + B_m^y J^y + B_m^z J^z), \quad (1)$$

where

$$B_m^x = B \cos(\alpha) + \lambda M^x, \quad (2)$$

$$B_m^y = B \cos(\beta) + \lambda M^y, \quad (3)$$

$$B_m^z = B \cos(\gamma) + \lambda M^z, \quad (4)$$

$$M^\eta = \left[\sum_n \exp\left(-\frac{e_n}{k_B T}\right) \right]^{-1} \sum_n \langle e_n | M^\eta | e_n \rangle \exp\left(-\frac{e_n}{k_B T}\right). \quad (5)$$

The $\cos(\alpha)$, $\cos(\beta)$, and $\cos(\gamma)$ are the direction cosines of the external magnetic field with respect to the crystallographic axis. The component of the magnetization in the direction of the applied magnetic field, M^η , is obtained using Eqs. (2)–(4), together with relation (5) using self-consistent calculations. The magnetic, lattice, and electronic entropies are given by^{8,9}

$$S_{\text{mag}}(B, T) = R \left\{ \ln \left[\sum_n \exp\left(-\frac{e_n}{k_B T}\right) \right] + \frac{\langle E \rangle}{k_B T} \right\}, \quad (6)$$

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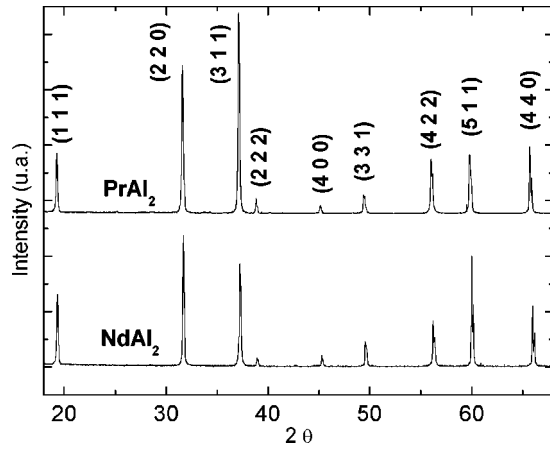


FIG. 1. X-ray powder-diffraction patterns for PrAl_2 and NdAl_2 compounds (the numbers in parentheses are the planes Miller indices).

$$S_{\text{latt}} = -3R \ln \left[1 - \exp\left(-\frac{T_D}{T}\right) \right] + 12R \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^3 dx}{\exp(x) - 1}, \quad (7)$$

$$S_{\text{el}} = \bar{\gamma}T, \quad (8)$$

where T_D is the effective Debye temperature and $\bar{\gamma}$ is the electronic heat-capacity coefficient.

EXPERIMENTAL PROCEDURE

Polycrystalline samples were prepared by arc-melting the appropriate mixtures of the elements in high-purity argon atmosphere on a water-cooled copper hearth. We repeated the melting process three times in order to obtain high homogeneity samples. The purity of the starting materials was 99.99% for aluminum and 99.9% for the rare-earth metals. The samples were characterized using metallographic examination, x-ray powder-diffraction measurements with $\text{Cu } K\alpha$ radiation, and magnetic measurements using a commercial Quantum Design superconducting quantum interference device (SQUID) 7-T dc magnetometer in the temperature ranges of interest. The NdAl_2 and PrAl_2 composite was obtained simply by manually grinding the materials into a fine powder and mixing the calculated amounts of the compounds.

We obtained $\Delta S_{\text{mag}}(T)$ versus temperature curves from the magnetization versus temperature experimental data (using the Maxwell relation) for these compounds.

RESULTS AND DISCUSSIONS

The x-ray powder-diffraction measurements for both compounds (Fig. 1) show the presence only of the desired C-15 pure phase, and this is confirmed by metallographic analyses.

Figure 2 shows the magnetization as a function of temperature for the compounds PrAl_2 and NdAl_2 . We note that the magnetic transition temperatures are 32.5 and 77 K, respectively, in close agreement with literature data, where the

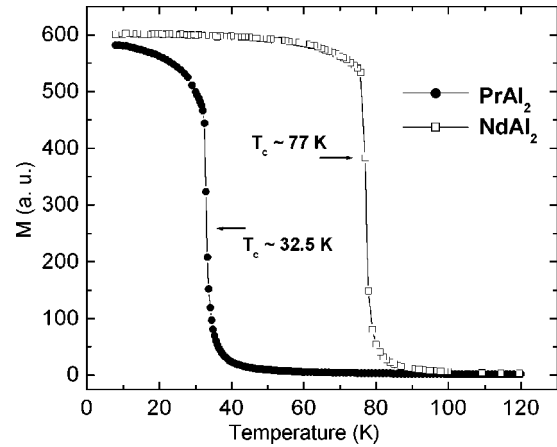


FIG. 2. Magnetization of PrAl_2 and NdAl_2 compounds as a function of temperature, with an applied magnetic field $H=100$ Oe.

transition temperatures are reported to lie in the range from 31 up to 38.5 K for PrAl_2 (Refs. 10–13) and in the range from 65 up to 80 K for NdAl_2 .^{14,15}

The model parameters used for PrAl_2 and NdAl_2 were $W=-0.329$ meV, $X=0.739$, $\lambda=256.3T^2/\text{meV}$, and $W=0.16$ meV, $X=-0.37$, $\lambda=418.1T^2/\text{meV}$, respectively, taken from Ref. 16. The effective Debye temperature was taken from the nonmagnetic and isostructural systems LaAl_2 and LuAl_2 using an interpolation procedure.¹⁰ The electronic heat-capacity coefficient, $\bar{\gamma}=5.4$ $\text{mJ mol}^{-1} \text{K}^{-2}$, was assumed to be equal to that of the nonmagnetic compound LuAl_2 .⁸

Figures 3 and 4 show the temperature dependence of the theoretical and experimental isothermal $\Delta S_{\text{mag}}=S(H=0)-S(H \neq 0)$, in PrAl_2 and NdAl_2 compounds, respectively, for a magnetic-field change from 0 to 5 T. The solid lines represent the theoretical results and the open circles show the experimental data. The ΔS_{mag} maximum values occur at the Curie temperatures since at this temperature an applied field has a maximum reduction effect on the magnetic entropy in normal ferromagnetic systems. For PrAl_2 , our theoretical results are in excellent agreement with the experiment, considering that no parameter adjustment was performed in order to

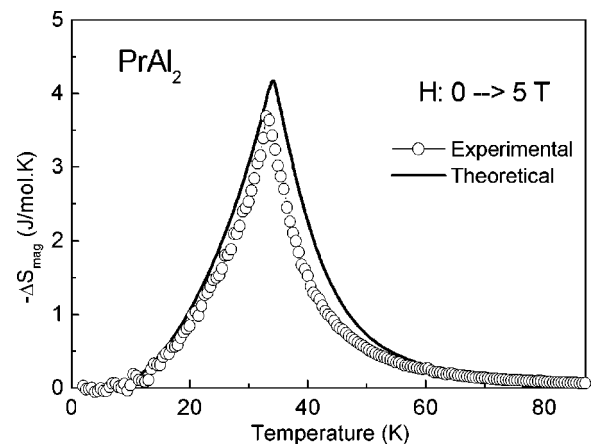


FIG. 3. Temperature dependence of ΔS_{mag} in PrAl_2 for a magnetic-field change from 0 to 5 T calculated for the easy magnetic direction (001) and measured in a polycrystalline sample. The solid line represents the theoretical results using the model parameters given. The open circles show the experimental data.

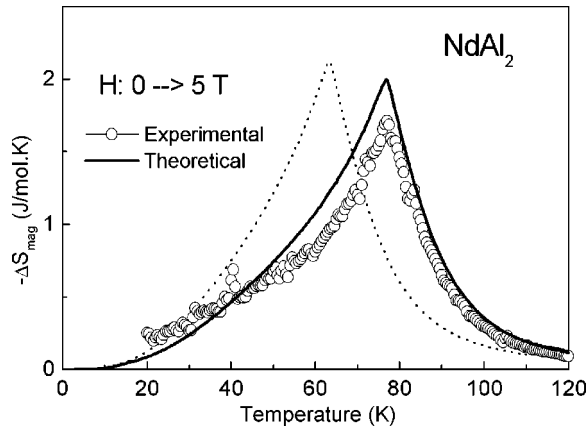


FIG. 4. Temperature dependence of ΔS_{mag} in NdAl_2 for a magnetic field change from 0 to 5 T calculated for the easy magnetic direction $\langle 001 \rangle$ and measured in a polycrystalline sample. The solid line represents the theoretical results using the model parameters given and the dotted line was calculated using the CEF and exchange parameters from Ref. 7. The open circles show the experimental data.

obtain a better fit to the data. On the other hand, for NdAl_2 our theoretical results do not agree with the experimental ones (see the dotted line). The Curie temperature experimentally observed in our sample ($T_C \sim 77$ K) differs from the literature value ($T_C \sim 65$ K), to which the value of the exchange parameter, $\lambda = 418.1 T^2 / \text{meV}$, was ascribed.¹⁶ In order to adjust the experimental Curie temperature for our sample, the exchange parameter $\lambda = 491 T^2 / \text{meV}$ was determined for NdAl_2 .

Figure 5 shows the magnetocaloric effect, ΔS_{mag} and ΔT_{ad} , calculated for the three main crystallographic cubic directions, namely, $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ in PrAl_2 . Figure 6 shows the same data for NdAl_2 . The dotted and solid lines represent the magnetocaloric effect considering the external magnetic field from 0 to 2 T and from 0 to 5 T, respectively. In both PrAl_2 and NdAl_2 compounds the easy and hard magnetic directions are, respectively, $\langle 001 \rangle$ and $\langle 111 \rangle$, which

were determined by considering the magnetization versus magnetic-field curves, data not presented in this work. Also, the free-energy analysis confirms these easy directions for both compounds. We note that, applying the magnetic field in the PrAl_2 easy magnetic direction, much heat can be extracted over the whole temperature range, as expected. Nevertheless, in the NdAl_2 this is not true for the whole temperature range. The small and anomalous peak in the ΔT_{ad} vs T curve appearing at about $T = 12.8$ K increases the magnetocaloric effect in the $\langle 110 \rangle$ crystallographic direction ($\Delta T_{\text{ad}} = 0.7$ K) followed by the lower values for field in the hard direction $\langle 111 \rangle$ ($\Delta T_{\text{ad}} = 0.45$ K) and in the easy direction $\langle 001 \rangle$ ($\Delta T_{\text{ad}} = 0.3$ K). The small peak comes from the crystal electric-field anisotropy considered in our model calculation, since this anomalous peak disappears when we take $W = 0$ (no crystal-field interaction). Note that in PrAl_2 , below the critical temperature ($T \sim 32.5$ K), an anomalous peak also emerges for field applied along the hard direction. This peak could not be associated with a high density of crystal-field states as in the case of $(\text{Dy}_{1-z}\text{Er}_z)\text{Al}_2$, in which a similar anomalous peak was experimentally observed and theoretically understood for concentrations $z = 0.5$ and $z = 0.3$.¹⁷ The anomalous magnetocaloric effect theoretically predicted for PrAl_2 and NdAl_2 in the hard directions requires further experimental investigations using single crystals of these compounds. This study is in progress.

The Ericsson cycle is the appropriate one to be used in magnetic refrigerator when the ferromagnetic material presents Curie temperature above 20 K, since the lattice entropy, which works as a heat load, grows considerably in comparison with the magnetic entropy.^{1,18} The peak observed and calculated in the ΔS_{mag} vs T curves is not desirable for a magnetic refrigerant material to operate a magnetic refrigerator using an Ericsson cycle. An ideal Ericsson cycle employs a constant value for the ΔS_{mag} in the temperature range of refrigeration, which is necessary for the improvement of the regenerative processes.¹⁹ Considering the two compounds in-

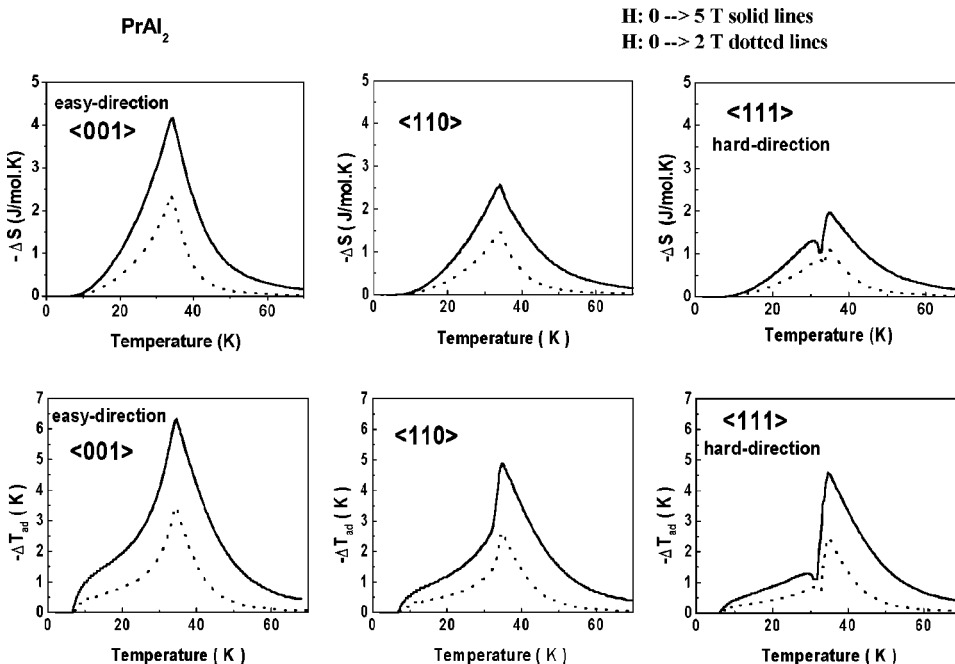


FIG. 5. Temperature dependence of ΔS_{mag} and ΔT_{ad} for a magnetic-field change from 0 to 2 T and 0 to 5 T calculated in the three main crystallographic cubic directions for the PrAl_2 compound.

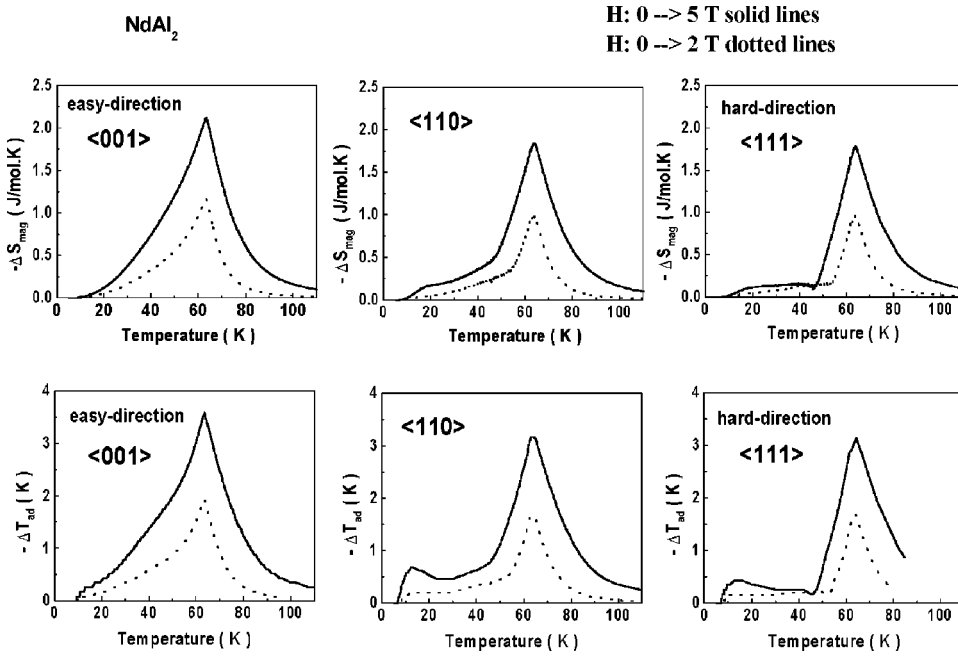


FIG. 6. Temperature dependence of ΔS_{mag} and ΔT_{ad} for a magnetic field change from 0 to 2 T and 0 to 5 T calculated in the three main crystallographic cubic directions for the NdAl₂ compound.

investigated in this work to be used as low-temperature magnetic regenerators, we calculated the optimum molar proportions that a composite material, formed by PrAl₂ and NdAl₂, should present in order to produce ΔS_{mag} as constant as possible between the cold and hot temperatures. Figure 7 shows the calculated $\Delta S_{\text{mag}}^{\text{composite}} = y\Delta S_{\text{mag}}^{\text{PrAl}_2} + (1-y)\Delta S_{\text{mag}}^{\text{NdAl}_2}$ versus temperature. The molar proportion value obtained for the easy direction was $y=0.290$ for an external magnetic-field change from 0 to 5 T and $y=0.282$ when the magnetic field was varied from 0 to 2 T. The used optimum numerical approach can be found in Ref. 20, which considers optimum proportions that a composite material must present between the low and high critical Curie temperatures. For other temperature intervals, different y values can be determined to realize the regenerative balance.²¹ The dotted lines in Fig. 7 represent the calculated ΔS_{mag} vs T for the individual PrAl₂ and NdAl₂ compounds for the above-considered magnetic-field changes. The solid lines give the $\Delta S_{\text{mag}}^{\text{composite}}$ vs T for the same considered magnetic-field changes. It is worth noticing that the y value is weakly dependent on the magnetic-field changes considered (at about 2.8%).

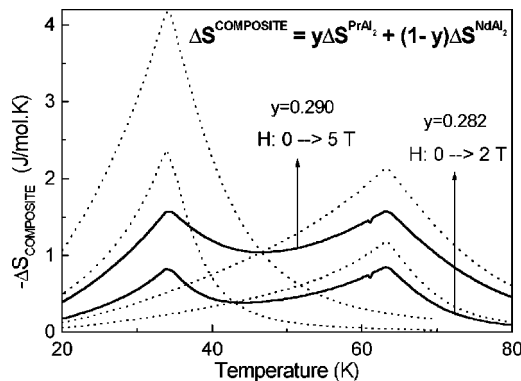


FIG. 7. Temperature dependence of $\Delta S_{\text{mag}}^{\text{composite}} = y\Delta S_{\text{mag}}^{\text{PrAl}_2} + (1-y)\Delta S_{\text{mag}}^{\text{NdAl}_2}$ for a magnetic-field change from 0 to 2 T, using $y=0.282$, and 0 to 5 T (the upper curve), using $y=0.290$. The dotted lines represent $\Delta S_{\text{mag}}^{\text{PrAl}_2}$ and $\Delta S_{\text{mag}}^{\text{NdAl}_2}$ vs temperature for the two considered magnetic-field changes.

From the theoretical curves that fit the experimental data for PrAl₂ and NdAl₂ compounds (Figs. 3 and 4, solid lines), we calculated the best y value ($y=0.292$) for the composite to be prepared. This composite was prepared from the compounds in powder form. These powders were mixed to produce a homogeneous mixture. Then, we performed the magnetic measurements and calculated the isothermal magnetic entropy change (ΔS_{mag}) and recalculated the ΔS_{mag} theoretical curve (Fig. 8), using the same parameters used for fitting the PrAl₂ and NdAl₂ compounds curves. We see that there is a good agreement between the model and experiment, as observed for the individual MCE's. The difference between the experimental and theoretical results can be ascribed to the fact that calculations were done for single crystals in the easy direction, whereas the measurements were performed on a polycrystalline composite.

CONCLUSIONS

In this paper, theoretical and experimental investigations were performed in the PrAl₂ and NdAl₂ magnetocaloric po-

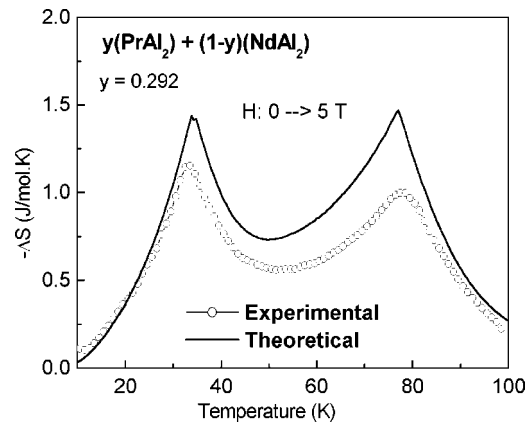


FIG. 8. Theoretical and experimental magnetocaloric effect (ΔS_{mag}) for the $y(\text{PrAl}_2) + (1-y)(\text{NdAl}_2)$ composite, with $y=0.292$.

tentials. The strong dependence of the magnetocaloric potentials on the choice of applied magnetic-field direction was first predicted using a Hamiltonian that takes into account the CEF anisotropy. The comparison between our theoretical and experimental results for the temperature dependence of ΔS_{mag} in PrAl_2 and NdAl_2 for a magnetic-field change from 0 to 5 T showed good agreement. Also, we determined theoretically the optimum molar fraction of these two compounds in order to form a composite to be considered as an optimal refrigerant material working in an Ericsson cycle in the temperature interval defined by their transition temperatures. The criterion to obtain the optimal molar ratios is from Ref. 20. The molar fraction is weakly dependent on the two magnetic-field changes (0–2 T and 0–5 T) considered in this work. Experiment with a powdered composite built in accordance with the theoretical calculated proportion showed a good agreement with the calculations.

Presently, we are growing single crystals in order to perform magnetic measurements along the crystallographic directions to verify the theoretical predictions of this model.

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