Magnetic and magnetocaloric properties on the U 1 − y R y Ga 2 (R = Er and Dy) compound

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Magnetic and magnetocaloric properties on the $U_{1-y}R_yGa_2$ (R=Er and Dy) compound

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The magnetic, calorimetric, and magnetocaloric properties of the pseudobinary $U_{1-y}R_yGa_2$ (R=Er and Dy) series were studied to determine its potential as a candidate for use in cryogenic magnetic refrigeration. The partial substitution of Dy and Er for U provides a wide range of the ordering temperature and increases the saturation magnetic moment. The results for $U_{1-y}Dy_yGa_2$ with $0.6 < y < 0.9$ show evidences of a spin-glass-like (SG) behavior, possibly as a consequence of competing anisotropy and exchange interactions within a frustrated hexagonal spin lattice. The isothermal magnetic entropy change (ΔS_{mag}) observed for UGa_2 shows a well defined peak centered on T_C, which is gradually broadened and shifted to lower temperatures as the Er and Dy content increases. For low concentrations ($0.2 \leqslant y \leqslant 0.4$) a tablelike profile is observed in the ΔS_{mag} curve. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2830689]

The magnetocaloric effect (MCE), the property of some magnetic solids to heat up or cool down when they are submitted to a varying magnetic field in an adiabatic process, has been extensively study in recent years.[1,2] The main focus has been to find good magnetocaloric materials to work as an active magnetic regenerator for near-room-temperature refrigeration[3] or as cryocooler regenerator materials to operate at cryogenic temperatures.[4] The ideal magnetic material to be used as a magnetic refrigerant should exhibit a constant isothermal entropy variation (ΔS_{mag}) and the adiabatic temperature variation (ΔT_{ad}) in the temperature operation range of the refrigerator. Usually, ΔS_{mag} and ΔT_{ad} shows a maximum value in the vicinity of the magnetic ordering temperature and becomes weaker further away. In order to overcome this limitation, it has been suggested the utilization of composite or multilayer systems[5,6] where magnetic materials with varying ordering temperatures are layered according to their transition temperatures. For this purpose, in many cases, it is necessary to adjust the material magnetic ordering temperature by using the chemical substitution process.[7,8]

Our goal in this study is to investigate promising new materials for use in a regenerator. So, materials containing high magnetic moments ions which present magnetic ordering within the desired temperature range must be searched. The system $LnGa_2$ (Ln=lanthanides) orders antiferromagnetically below 15 K (and also presents a metamagnetic phase transition[9–11]) but the isostructural UGa_2 is ferromagnetic (FM) with Curie temperature (T_C) around 122 K (Ref. 12) (here the uranium ion forms a local moment). In this way, this compound can be used as the high temperature end of a new series of pseudobinary compound. Although presenting a small magnetic moment ($\mu_{eff}=3.4\mu_B$), UGa_2 is capable to increase the ordering temperature of the pseudo binary alloys with rare earth. Therefore, the MCE study in the $(U_{1-y}R_y)Ga_2$ (R=Er and Dy) series can provide interesting results in terms of the wide range of temperatures available (15–110 K) in terms of new materials for use in a cryocooler regenerator.

Polycrystalline samples were prepared by melting the high-purity elements in an arc furnace under argon atmosphere and were subsequently annealed at 700 °C for one week. According to the x-ray diffraction the $(U_{1-y}R_y)Ga_2$ alloys are all single phase samples. These data were collected on a Philips x-ray powder diffractometer using Cu $K\alpha$ radiation. The analysis by Rietveld refinement showed the hexagonal AlB_2-type phase in all alloys. The unit cell volume monotonically decreases with Er content (1.1% total) whereas it increases with Dy content (0.76%) [see Figs. 1(a) and 1(b)].

Magnetic measurements were performed in a superconducting quantum interference device (SQUID) magnetometer. The heat capacity, using the thermal relaxation method, and the ac susceptibility (χ_{ac}) measurements were carried out in a physical property measurement system (PPMS) equipment. The magnetocaloric effect (ΔS_{mag} and ΔT_{ad}) was calculated from the heat capacity data.

The dc susceptibility for all $(U_{1-y}R_y)Ga_2$ alloys was found to follow the Curie-Weiss behavior at $T > 150$ K with the paramagnetic Curie temperature (θ_p) reducing strongly with the addition of Er and Dy. The measured effective magnetic moment (μ_{eff}) agrees well with the theoretical value, calculated for noninteracting U^{3+}, Er^{3+}, and Dy^{3+} ions (with $J=7/2$ for U and $J=15/2$ for Er and Dy), proportional to the alloy composition [see Fig. 1(c)].

The magnetization data for UGa_2 show a narrow FM transition which becomes broader and shifts to lower temperature, as the Er and Dy contents increase. The $U_{0.7}Er_{0.3}Ga_2$ sample shows two broad peaks at 40 and 6 K which can be observed in the zero-field-cooling (ZFC) magnetization curve. A single slightly well defined peak is ob-

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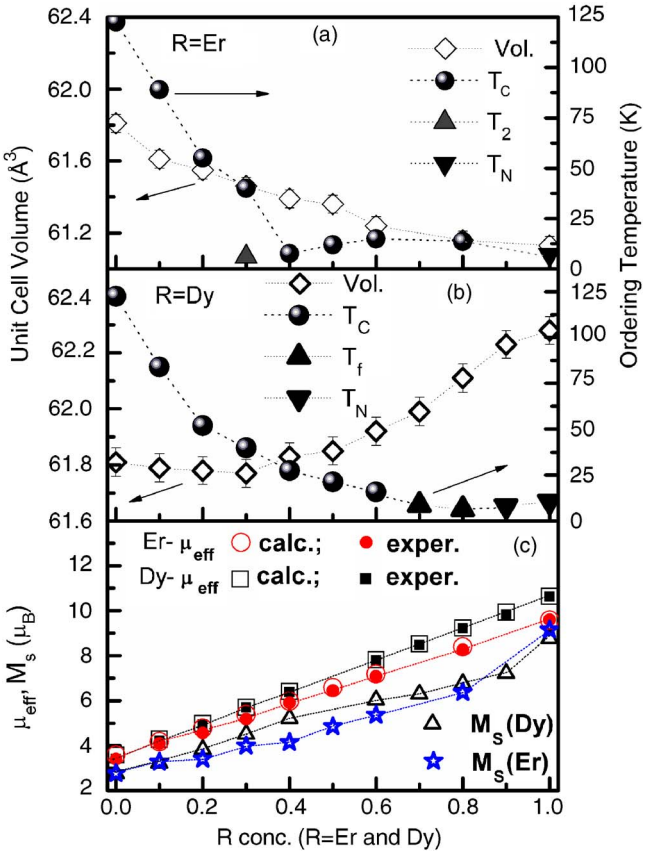

FIG. 1. (Color online) Unit cell volume, ordering temperatures, saturation magnetization and effective moment as a function of the R content. T_C is the Curie temperature, T_N is the Néel temperature, T_f is the freezing temperature, and T_2 is the temperature of a second transition found for $U_{0.7}Er_{0.3}Ga_2$.

served for temperatures lower than 15 K at high Er concentrations ($y \geq 0.5$). The ordering temperature as a function of Er and Dy content is shown in Figs. 1(a) and 1(b).

For the $(U_{1-y}Dy_y)Ga_2$ alloys with $y=0.7$ and 0.8, the ZFC dc magnetization curves at $H=50$ Oe shows a sharp peak with the maximum (T_{max}) centered at 8.8 and 6.6 K, respectively. For $T<T_{max}$, these curves indicate a spin-glass-like (SG) behavior, i.e., the dc susceptibility is irreversible below T_{max} (usually defined as freezing temperature T_f). The χ_{ac} measurements as a function of the temperature show a dependence of T_{max} with the frequency with $\Delta T_{max}/[T_{max}\Delta(\log \nu)] \approx 0.03$ which is similar to those reported for SG systems.[13] The dc magnetization data for $ErGa_2$ and $DyGa_2$ compounds indicate the presence of antiferromagnetic (AFM) ordering at $T_N=7$ and 10.5 K, respectively. However, the increase of the magnetic field in these systems induces a ferromagnetic state, in agreement with previously reported results.[10,11]

The saturation magnetization (M_S) was determined using the extrapolation of $M(H^{-1})$, measured at 2 K, to $1/H=0$. The values of M_S proportionally increase with the increase of the Er and Dy concentration. The $M(H)$ curves of $U_{1-x}Dy_xGa_2$ alloys with $x \geq 0.6$ shows no saturation up to 70 kOe. Therefore, for these samples we decided to show in Fig. 1(c) the magnetization values obtained at 70 kOe.

The magnetic heat capacity (C_{mag}) as a function of the temperature for $(U_{1-y}Er_y)Ga_2$ is shown in Fig. 2. C_{mag} was

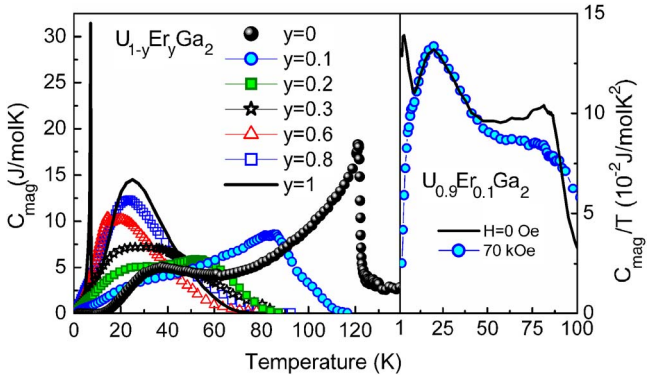

FIG. 2. (Color online) C_{mag} vs temperature for $(U_{1-y}Er_y)Ga_2$ alloys (left). C_{mag}/T for $y=0.1$ at H=0 Oe and 70 kOe (right).

determined by the subtraction of the nonmagnetic reference compound ($LaGa_2$) data from the total heat capacity. A λ-type peak in the zero field C_{mag} is observed at $T=122$ and 7 K for UGa_2 and $ErGa_2$, respectively. The extra anomaly around 35 and 25 K is related to the crystal field Schottky peak. As the R content increases, the λ-type peak at 122 K becomes broader and shifts to lower temperatures overlapping with the Schottky peak. By applying magnetic field, the intensity of the peaks related to the magnetic transition is reduced and show the typical FM transition behavior. The C_{mag} data at 0 and 70 kOe has shown the presence of two broad magnetic ordering in the range of $0.1 \leqslant y \leqslant 0.4$ concentrations. Figure 2 (right side) shows as an example, these two peaks for $U_{0.9}Er_{0.1}Ga_2$ around 80 K and below 7 K.

The ΔS_{mag} peak follows the behavior observed in magnetic and calorimetric measurements (see Fig. 3). For $0.2 \leqslant y \leqslant 0.4$ the ΔS_M peak shows a tablelike shape usually observed in composite materials. The ΔS_M peak broadening is associated with the temperature difference between the upper and lower magnetic transitions. The ΔS_M peak intensity in-

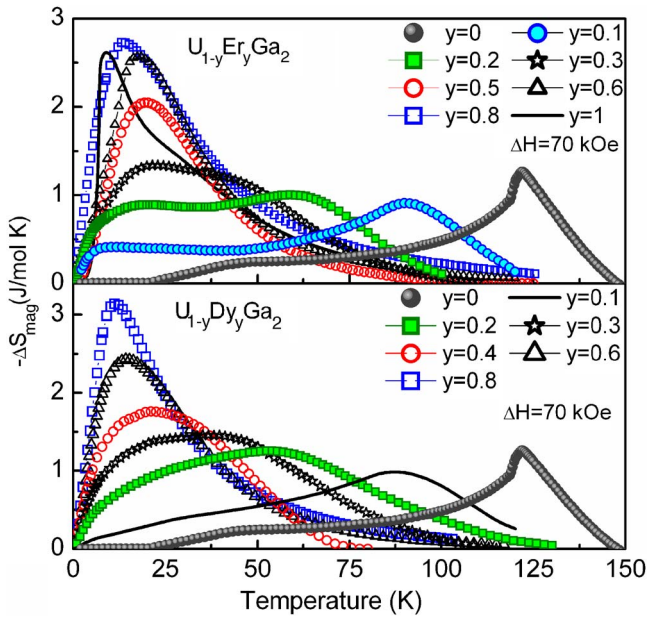

FIG. 3. (Color online) ΔS_{mag} for the $(U_{1-y}Er_y)Ga_2$ (top) and $(U_{1-y}Dy_y)Ga_2$ (bottom) alloys for $\Delta H=70$ kOe.

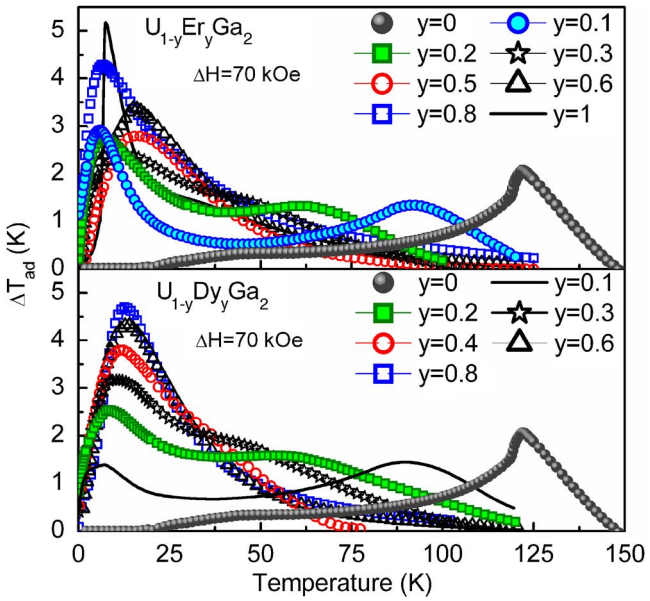

FIG. 4. (Color online) ΔT_{ad} for the $(U_{1-y}Er_y)Ga_2$ (top) and $(U_{1-y}Dy_y)Ga_2$ (bottom) alloys for $\Delta H=70$ kOe.

creases for lower U content due to the higher available magnetic entropy for Er and Dy.

ΔT_{ad} for $(U_{1-y}R_y)Ga_2$ alloys under a magnetic field change of 70 kOe is depicted in Fig. 4. Two relatively well separated peaks appear in ΔT_{ad} curves for the U-rich alloys instead of the broader peak observed for ΔS_{mag} curves. The high temperature peak weakens while the low temperature one is stronger for high contents of Er and Dy. The largest ΔT_{ad} values is approximately 5 K ($ErGa_2$) and 4.7 K ($U_{0.2}Dy_{0.8}Ga_2$), for a field change of 70 kOe.

Our preliminary MCE results for $DyGa_2$ indicated positive ΔS_{mag} and ΔT_{ad} values for temperatures below 7 K. Further heat capacity and magnetization measurements will be presented in a forthcoming paper.

The $U_{1-y}R_yGa_2$ (R=Er and Dy) compounds were studied by dc and ac magnetization and heat capacity. An expressive reduction of the Curie temperature was observed as the Er and Dy contents are increased. The saturation magnetic moment increases with the substitution due to the higher magnetic moment of Er and Dy compared to U. The Er substituted compounds can be considered as composed by two magnetic sublattices, since the easy axis are orthogonal ([001] for $ErGa_2$ (Ref. 10) and [100] for UGa_2 (Ref. 12)). In this case, the Er magnetization affects little the U sublattice magnetization, resulting in an average of the two magnetic contributions for a given concentration, as suggested by Markin *et al.*[14] In this sense, the Er substitution is equivalent to the dilution with a nonmagnetic ion for the U magnetic sublattice. On the other hand, the easy axis for $DyGa_2$ is also in the [100] axis.[11] Therefore, Dy has a significant influence on the total magnetization and it is expected a competition between the two exchange parameters (J_U and J_{Dy}) by varying the Dy content. In fact, for $y=0.7$ and 0.8, this competition promotes the observed spin-glass-like behavior. Below $y=0.7$, the U–U interaction is dominant, and above $y=0.8$ an AFM order is achieved.

The isothermal entropy change and the adiabatic temperature change present a similar trend for both rare-earth ions: starting from the R side, a contribution due to the Schottky anomaly is added to the magnetic ordering contribution. The broad ΔS_{mag} peaks observed for the U-rich alloys ($0.1 \leqslant y \leqslant 0.4$) can be resultant of two broad magnetic transitions occurring in the alloy with comparable magnetic heat capacities. In particular, for the concentration $y=0.2$ for Er, ΔS_{mag} has a tablelike shape close to 1 J/mol K between 10 and 75 K. The ΔT_{ad} values associated with the lower temperature transition is slightly higher in comparison to the high temperature transition ones, possibly due to the smaller heat lost to the lattice in low temperatures. ΔT_{ad} maximum reaches about 5 K for high R concentrations ($y \geqslant 0.8$). Although reasonable values for ΔS_{mag} and ΔT_{ad} in a wide temperature range have been achieved with these compounds, measurements with single crystals are necessary to a better understanding of the exchange competitions occurring in these systems.

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