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A study of pressure and chemical substitution effects on the magnetocaloric properties of the ferromagnetic compound UGa_2

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Abstract

We report on pressure effects on the magnetic and magnetocaloric properties of the compound UGa_2 . Using a mean field approximation, we were able to calculate the isothermal entropy change and the adiabatic temperature change. Neither the applied pressure nor the chemical substitution experiments within the ranges studied revealed a remarkable improvement on the magnetocaloric effect (MCE) except for the Al substitutions. Nevertheless, we found that mechanical pressure and chemical pressure are equivalent in terms of the Curie temperature shift when Al, Ge and Si are substituted for Ga, but a different behavior is found when Ni, Fe and Co are used. Our results also show that a composite to operate between 80 and 120 K can be obtained using different concentrations of $\text{U}(\text{Ga}, \text{Ni})_2$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently [1–3], magnetic materials have been studied with the aim of investigating the real possibilities of applications in magnetic refrigerators. The potential use of a given material may be indicated by the magnitude of the magnetocaloric effect (MCE). For this purpose the two main parameters to be analyzed in a given material are the isothermal entropy variation (ΔS_{mag}) and the adiabatic temperature variation (ΔT_{ad}) caused by a magnetic field change at temperatures close to the Curie temperature (T_C). In particular, compounds with 3d or 4f ions such as MnAs [4, 5], $\text{MnAs}_{1-x}\text{Sb}_x$ [6, 7], $\text{MnFeP}_x\text{As}_{1-x}$ [8, 9] and $\text{Gd}_5(\text{Ge}_x\text{Si}_{1-x})_4$ [10, 11] have been extensively studied since they present a giant effect near room temperature. However, besides the technological interest around room temperature, the investigation of magnetocaloric systems for the application in cryogenic temperatures is also important, as well as the determination of their fundamental

physical properties. In this way, a variety of magnetic materials have been studied such as the low temperature ferromagnetic systems RNi_5 and RM_2 , with $R = \text{rare-earth}$ and $M = \text{Al, Ni and Co}$ [12–15]. Among them, PrNi_5 and DyAl_2 present an anomalous MCE due to the anisotropy of the crystalline electric field (CEF) [16–18]. Furthermore, the study of the MCE in other f ions, such as 5f uranium, is also interesting since it can reveal other promising materials. As far as we know, the study of the MCE in ferromagnetic (FM) U-compounds remains almost unexplored. The literature reports the MCE only for a few non-ferromagnetic U-compounds such as UNiGa [19], UAs [20], UNi_2Si_2 [21], $\text{UNi}_{0.5}\text{Sb}_2$ [22] and URu_2Si_2 [23]. The compounds UNiGa and UAs present complex magnetic phase diagrams. UNi_2Si_2 and $\text{UNi}_{0.5}\text{Sb}_2$ are AF while URu_2Si_2 is a superconducting heavy-fermion with an unusual field dependent transition at 17 K. On the other hand, UGa_2 is an FM compound with a rather high Curie temperature ($T_C = 125 \text{ K}$) compared with other uranium

compounds [24–27]; this characteristic qualifies UGa_2 as a good candidate for this study. In this paper we present a detailed investigation of the MCE in UGa_2 which has been motivated by a significant result previously observed [28]. The two thermodynamic quantities ΔS_{mag} and ΔT_{ad} were determined through heat capacity experiments performed at 0 and 7 T and theoretically calculated using the mean field approximation. We have also investigated the hydrostatic and chemical pressure influence on the magnetocaloric properties of the UGa_2 compound. The chemical pressure was promoted by using small quantities of a substituent at the Ga site and the results for the series $\text{U}(\text{Ga}_{1-x}\text{M}_x)_2$ with $\text{M} = \text{Al}, \text{Ge}, \text{Si}, \text{Ni}, \text{Fe}$ and Co are reported. Also, this substitution process permits the preparation of a composite material with an extended useful temperature region.

2. Theory

The UGa_2 compounds crystallize in the hexagonal AlB_2 -type structure and the magnetism is due to the U ions [26]. In this material, the hybridization of the 5f-states is rather small in comparison with other UM_2 compounds leading to a high magnetic moment. In general, the choice between a local moment or itinerant behavior to describe the U magnetism is not a trivial matter. In fact, there are several papers [26, 27, 29–34] discussing the character of the U moment in UGa_2 but, among them, the studies for bulk material [26, 27, 29–33] indicate that the local moment description is more suitable to describe the 5f electrons. This is further supported by the similarity of the physical properties between UGa_2 and UPd_3 (which present a local moment [35]): low electronic specific heat ($\sim 5 \text{ mJ mol}^{-1} \text{ K}^{-1}$) and high magnetic moment ($\sim 3 \mu_{\text{B}}$). Despite all this evidence, this subject might still be considered as an open question, but in this study we use the local moment description to explain the experimental results for bulk UGa_2 . Within the local moment description, it is difficult to distinguish between the 3^+ and 4^+ valences for the U ion, since the two electronic configurations imply comparable values of the effective magnetic moment, $3.58 \mu_{\text{B}}/\text{U}$ and $3.62 \mu_{\text{B}}/\text{U}$, respectively. Previous attempts to determine the U-valence in this compound were inconclusive [31, 33] so here, both configurations ($5f^2$ and $5f^3$) are used in the calculations for comparison with the experimental data. In our calculations we adopted the mean field approximation where the Hamiltonian is given by [12, 15, 36] the sum of the hexagonal crystal field (CF) and Zeeman contributions, with the effective magnetic field given by $\vec{H} = \vec{H}_0 + \lambda \vec{M}$, where H_0 is the external magnetic field and λ is the molecular field constant.

The magnetization M at an arbitrary direction k can be obtained from the magnetic state equation

$$M = g\mu_{\text{B}}\langle J^k \rangle = g\mu_{\text{B}} \frac{\sum \langle \varepsilon_i | J^k | \varepsilon_i \rangle \exp(-\varepsilon_i/KT)}{\sum \exp(-\varepsilon_i/KT)}, \quad (1)$$

where J^k is the component of the total angular moment in the direction k , ε_i and $|\varepsilon_i\rangle$ are the eigenvalues and eigenvectors, respectively, of the Hamiltonian obtained by a self-consistent process, g is the Landé g -factor and μ_{B} is the Bohr magneton.

The magnetic entropy can be determined from the Helmholtz free energy,

$$S_{\text{mag}} = R \left[\ln \left(\sum \exp(-\varepsilon_i/KT) \right) + \left\langle \frac{E}{KT} \right\rangle \right], \quad (2)$$

$\langle E \rangle$ being the mean energy and R the universal gas constant. The total entropy at any temperature and magnetic field is given by the sum of magnetic, lattice and electronic entropies ($S_T = S_{\text{mag}} + S_{\text{latt}} + S_{\text{el}}$). The lattice entropy can be calculated by the Debye approximation and the electronic contribution is given by $S_{\text{el}} = \gamma T$.

The theoretical and experimental ΔS_{mag} and ΔT_{ad} curves versus temperature were determined at $H_1 = 0 \text{ T}$ and $H_2 = 7 \text{ T}$ magnetic fields by:

$$\Delta S_{\text{mag}}(T)_{\Delta H} = S_T(T)_{H_2} - S_T(T)_{H_1} \quad (3)$$

and

$$\Delta T_{\text{ad}}(T)_{\Delta H} = [T(S)_{H_2} - T(S)_{H_1}]_S. \quad (4)$$

The adiabatic temperature variation in equation (4), for a given pair of curves $S_T(T)_{H_1}$ and $S_T(T)_{H_2}$, is determined by the adiabatic process condition, $S_T(T)_{H_1} = S_T(T)_{H_2}$.

3. Experimental details

Polycrystalline samples of $\text{U}(\text{Ga}_{1-x}\text{M}_x)_2$ with $\text{M} = \text{Al}, \text{Ge}, \text{Si}, \text{Ni}, \text{Fe}$ and Co for concentrations (x) varying from 0 to 0.1 were prepared by melting the high-purity elements in an arc-furnace under argon atmosphere with a subsequent annealing for one week at 700°C . X-ray powder diffraction was used for the structural characterization and the diffraction data were collected at room temperature on an X'Pert PRO MRD Philips diffractometer, using $\text{Cu K}\alpha$ radiation and a diffracted beam graphite monochromator in a Bragg–Brentano geometry. The Rietveld refinement analysis of the obtained patterns confirms the $P6/mmm$ hexagonal single phase for UGa_2 and for all the diluted samples. Specifically for $\text{UGa}_{1.9}\text{Ni}_{0.1}$ and $\text{UGa}_{1.8}\text{Al}_{0.2}$ we observed extra peaks which correspond to less than 5% and less than 3% of UGa_3 , respectively.

Magnetic measurements were performed on a superconducting quantum interference device (SQUID) magnetometer for fields up to 7 T. The heat capacity was measured by the thermal relaxation method in a physical property measurement system (PPMS) from 1.8 to 200 K without and with an applied magnetic field of 7 T. The experimental ΔS_{mag} and ΔT_{ad} curves for the pure compound and for the diluted samples were obtained from the heat capacity data. For the composite and for pure UGa_2 under pressure ΔS_{mag} was obtained from the isothermal magnetization curves using $\Delta S_{\text{mag}} = \int \frac{\partial M}{\partial T} dH$. For the pressure experiments we used a Cu–Be clamp cell, which is able to work up to 10 kbar in the SQUID magnetometer, and the pressure scale in our measurements was determined using the shift of the Curie temperature of UGa_2 under hydrostatic pressure [37]. In this case, ΔS_{mag} has been obtained at 3.4 and 8.6 kbar (values at 120 K) for temperatures varying from 40 to 160 K and with field changes of 7 T.

Table 1. CF parameters found in the literature for $5f^2$ and $5f^3$ U configurations.

U-valence state	B_2^0 (K)	B_4^0 (10^{-2} K)	B_6^0 (10^{-3} K)	B_6^6 (10^{-2} K)	Reference
$U^{4+}—J = 4$	11.98	−45.77	−6.95	5.18	[27]
$U^{3+}—J = 9/2$	8.38	3.62	−0.5	−5.2	[31]

4. Results

In order to theoretically calculate the temperature dependence of the magnetic entropy change, ΔS_{mag} , and the adiabatic temperature change, ΔT_{ad} , for UGa_2 , we used the hexagonal CF parameters B_n^m taken from [27] and [31] (see table 1) and the best value for the molecular field constant found to reproduce T_C . For both U valences, the calculation show that the CF effects induce a strong magneto-crystalline anisotropy with (100) as the magnetic easy axis, and this was also observed in magnetization and neutron diffraction measurements [24, 26]. Because of this strong anisotropy, powdered material may become oriented with the easy axis along the magnetic field. In this case we compare the experimental results to the calculation at the [100] direction. The calculated electronic and lattice entropies for UGa_2 and for the diluted samples were estimated from the isostructural nonmagnetic compound $LaGa_2$, $\gamma = 5 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $\theta_D = 330 \text{ K}$.

In figure 1 we display ΔS_{mag} and ΔT_{ad} versus temperature for the UGa_2 compound, obtained for a magnetic field change from 0 to 7 T and calculated using $\lambda = 35.5 \text{ T}/\mu_B$ and $\lambda = 39.5 \text{ T}/\mu_B$ for the $5f^2$ and $5f^3$ cases, respectively. The maximum values for ΔS_{mag} and ΔT_{ad} occur at the Curie temperature, as expected, since at this temperature an applied magnetic field has a maximum reduction effect on the magnetic entropy for normal ferromagnetic systems. For temperatures lower than 60 K the shoulder in the experimental ΔS_{mag} data is well reproduced by the calculated curve for the $5f^3$ case only. The difference between the two configurations is mainly based on the 5f CF-level scheme. The $5f^3$ CF-level scheme is composed of a ground-state doublet followed by four excited doublets at $\Delta_1 = 102 \text{ K}$, $\Delta_2 = 185 \text{ K}$, $\Delta_3 = 557 \text{ K}$ and $\Delta_4 = 710 \text{ K}$. On the other hand, the CF-level scheme for the $5f^2$ configuration is composed of a singlet ground-state, three excited doublets at $\Delta_1 = 99 \text{ K}$, $\Delta_2 = 413 \text{ K}$ and $\Delta_3 = 633 \text{ K}$ and also two singlets at $\Delta_4 = 1237 \text{ K}$ and $\Delta_5 = 1498 \text{ K}$. In the presence of the exchange interaction the degeneracy of the doublet levels is removed and this leads to the appearance of separated singlet states. When the $5f^3$ CF parameters are used, two of these excited singlet states are thermally accessible up to 140 K whereas, when the $5f^2$ CF parameters are used, the first and second excited singlet states are thermally separated by 196 and 308 K of the singlet ground-state, respectively. Therefore, the shoulder that appears below 60 K in the ΔS_{mag} and ΔT_{ad} curves can be attributed to the crystal field contribution in agreement with the theoretical data calculated assuming a trivalent U ion.

The experimental and theoretical MCE results obtained for the ferromagnetic UGa_2 with a magnetic field change of 7 T are larger than the MCE observed for other U-compounds

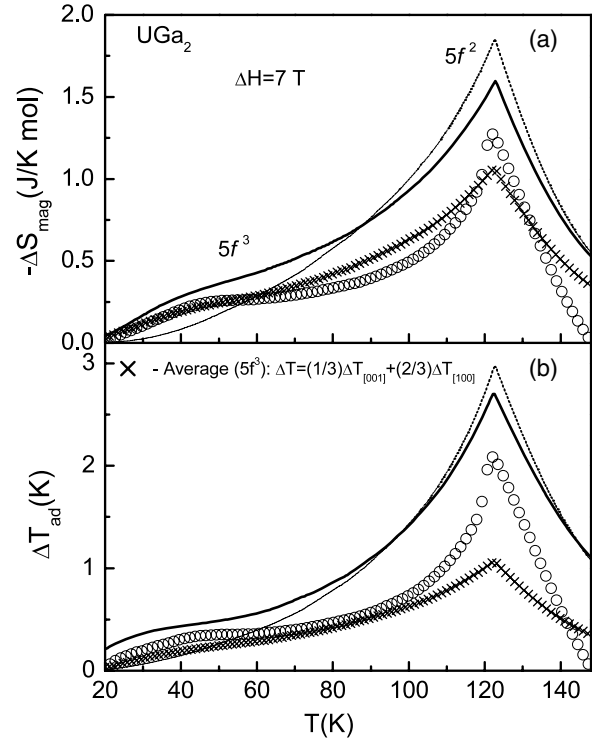


Figure 1. Temperature dependence of the ΔS_{mag} (a) and ΔT_{ad} (b) for UGa_2 for a magnetic field change from 0 up to 7 T. The open circles are the experimental data. The solid and the dotted lines represent the calculated curves for $5f^3$ and $5f^2$ configurations, respectively. The crosses represent the calculated average for the polycrystals ($5f^3$ configuration).

as $UNi_{0.5}Sb_{0.5}$ [22] and URu_2Si_2 @ $\Delta H > 10 \text{ T}$ [23] and are comparable to the MCE found in UAs [20] and UNi_2Si_2 [21] compounds for magnetic field changes higher than 7.5 and 10 T, respectively.

Recent results reported for MnAs [5, 6, 38] and $Gd_5Ge_2Si_2$ [10, 39] show that hydrostatic pressure or chemical substitution can be important parameters for the MCE. They can improve the magnitude of the effect as well as shift T_C such that the temperature where the maximum MCE is observed can be appropriately chosen. So, the good magnetocaloric properties observed for UGa_2 justify a detailed study of the influence of hydrostatic or chemical pressure. We expect the pressure effect to strengthen the RKKY exchange interaction consequently increasing T_C . Pressure can also modify the small U–U hybridization which will have an influence on the U magnetic moment and consequently on the MCE.

Figure 2 shows the ΔS_{mag} data for UGa_2 with $P = 0$ and under 3.4 and 8.6 kbar. As the pressure increases, T_C shifts to higher temperatures following the behavior described in the literature [37]. The MCE shows a small tendency

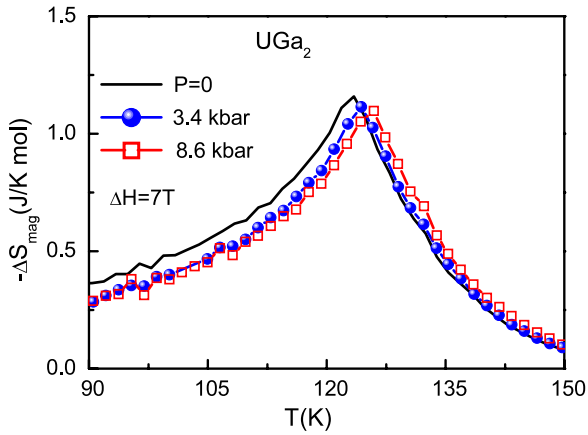


Figure 2. Temperature dependence of ΔS_{mag} for UGa_2 under hydrostatic pressure ($P = 3.4$ and 8.6 kbar). The magnetic field changed from 0 up to 7 T.

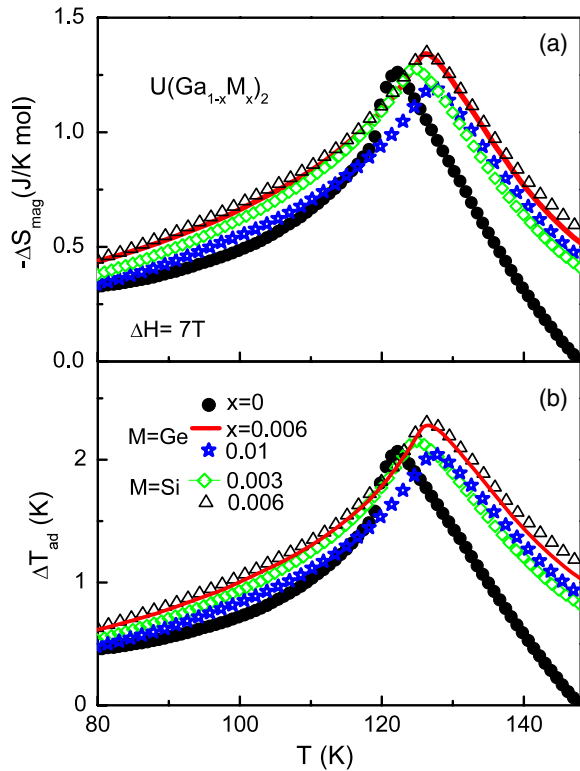


Figure 3. Temperature dependence of ΔS_{mag} (a) and ΔT_{ad} (b) for $\text{U}(\text{Ga}_{1-x}\text{Ge}_x)_2$ and $\text{U}(\text{Ga}_{1-x}\text{Si}_x)_2$ series for a magnetic field change from 0 up to 7 T.

of reduction but this is within the experimental error. A similar behavior is observed with chemical pressure when Ga is replaced by Ge and Si (see figure 3). In this case, we obtained a larger shift in T_C , $\Delta T_C = 3.6$ and 4.9 K for $\text{UGa}_{1.988}\text{Si}_{0.012}$ and $\text{UGa}_{1.98}\text{Ge}_{0.02}$, respectively. From the UGa_2 volume variation as a function of pressure reported by Sanjay Kumar *et al* [40], and also from the unit cell volume contraction obtained for $\text{UGa}_{1.988}\text{Si}_{0.012}$ ($\Delta V/V \sim 0.2\%$) and $\text{UGa}_{1.98}\text{Ge}_{0.02}$ ($\Delta V/V \sim 0.15\%$), we were able to estimate the corresponding pressure values of 1.5 and 2.1 kbar for

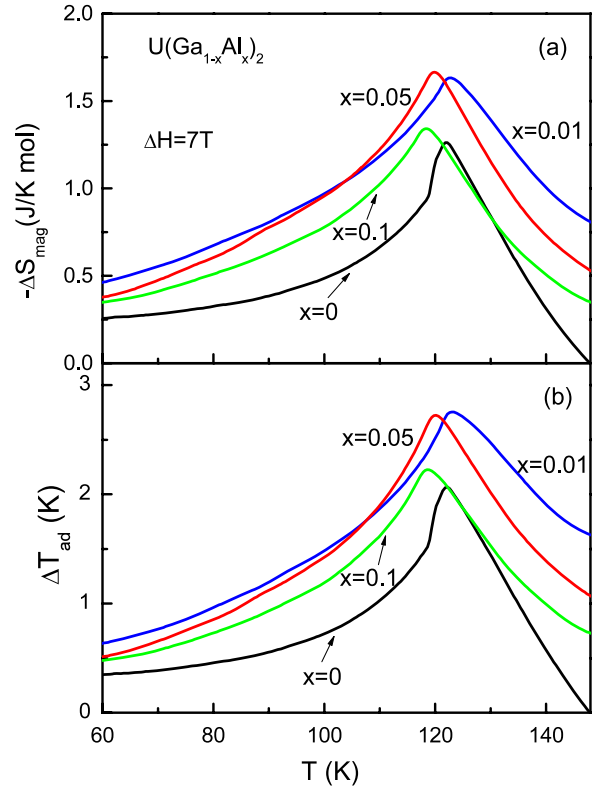


Figure 4. Temperature dependence of ΔS_{mag} (a) and ΔT_{ad} (b) for $\text{U}(\text{Ga}_{1-x}\text{Al}_x)_2$ series for a magnetic field change from 0 up to 7 T.

our samples. These equivalent pressure values are smaller in comparison with the mechanical pressure used in pure UGa_2 but the obtained shift in T_C is larger. This result indicates that the electronic character of the Ga substitute is also important in this process.

Considering now the Al substitution for Ga up to 10%, the opposite behavior was found: although with magnitude similar to the previous case we observed a unit cell volume expansion and a considerably reduced T_C ($\Delta T_C = 4.1$ K) following the tendency expected for negative pressures (i.e. expansion of the crystal lattice). Figure 4 shows the ΔS_{mag} and ΔT_{ad} curves obtained for the $\text{U}(\text{Ga}_{1-x}\text{Al}_x)_2$ series with $0 \leq x \leq 0.1$. For this series, we obtained an increase of the MCE compared to UGa_2 . The ΔS_{mag} maximum value was obtained for $\text{UGa}_{1.9}\text{Al}_{0.1}$ which is 33% larger than the respective value obtained for the UGa_2 . Also, it is important to note that the saturation magnetization (μ_S) shows a small increase ($\sim 0.2 \mu_B/\text{U}$) for $x \leq 0.05$ whereas, for UGa_2 under 8.6 kbar and for the Ge and Si doped samples, the magnetic moment decreases by $\sim 0.1 \mu_B/\text{U}$ [25, 37]. For these last cases, the noticeable increase of T_C and the small decrease of μ_S indicate that the positive pressure (volume reduction) and the Si and Ge electronic character contribute to an enhancement of the RKKY exchange coupling but also favor some hybridization of the U 5f electrons. On the other hand, a small expansion of the crystalline lattice as well as the Al electronic character can be related to the enhancement of the saturation moment and the MCE observed in the Al doped samples.

When Fe, Co and Ni substitute for Ga it is also expected that there will be a positive pressure effect in the UGa_2 lattice,

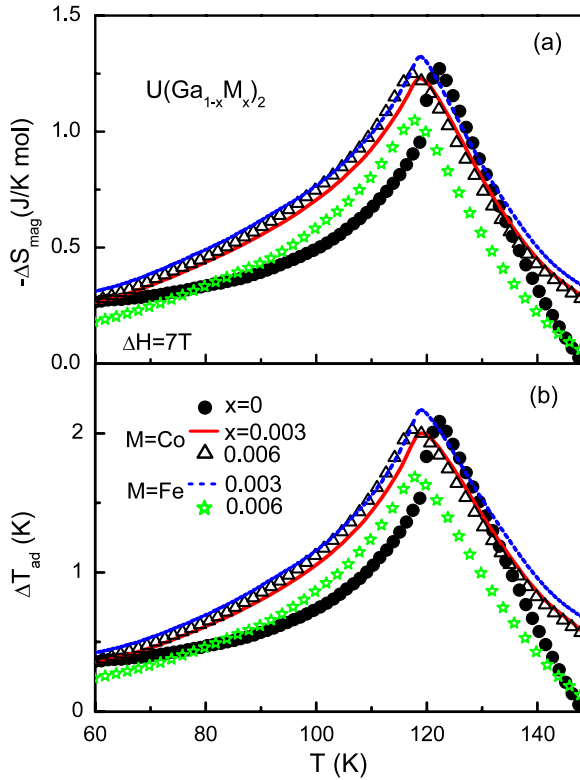


Figure 5. Temperature dependence of ΔS_{mag} (a) and ΔT_{ad} (b) for $\text{U}(\text{Ga}_{1-x}\text{Fe}_x)_2$ and $\text{U}(\text{Ga}_{1-x}\text{Co}_x)_2$ series for a magnetic field change from 0 up to 7 T.

since these ions are smaller than Ga. In particular for Ni we were able to introduce a higher concentration level (around 5%) and a significant pressure effect should be expected. In fact, our results show a volume reduction of $\Delta V/V \sim 0.6\%$ for the $\text{UGa}_{1.9}\text{Ni}_{0.1}$ sample. However, for the Fe and Co series we are restricted to smaller pressure effects because we did not succeed in obtaining single-phase samples for $x > 0.6\%$. Nevertheless, using the $\Delta V/V$ ratio obtained for our samples and the volume variation as a function of pressure reported for UGa_2 [40] mentioned earlier, we estimated the equivalent pressures $P = 6.2, 1.6$ and 1.5 kbar for the samples doped with Ni, Fe and Co, respectively. For this series, T_C values present the opposite trend to that shown by the undoped UGa_2 compound under pressure. These results indicate that the effect of applying external pressure is not equivalent to chemical pressure when the Ga substitute is a 3d-metal. In any case, the MCE is essentially unaffected for the Ni, Fe and Co series, as seen in figures 5 and 6.

In order to calculate the MCE for the $\text{U}(\text{Ga}_{1-x}\text{Ni}_x)_2$ series, we will initially assume that the CF parameters are not significantly altered by the chemical substitution and we therefore used the values listed in table 1 for the $5f^3$ configuration. Also, the initial guess for the molecular field constant was given by $\lambda = C/T_C$, where C is the Curie constant and after a tuning of this value we were able to reproduce the experimental magnetization and heat capacity data. The results show that λ is reduced from $39.5 \text{ T}/\mu_B$ for $x = 0$ to $29.3 \text{ T}/\mu_B$ for $x = 0.05$, indicating that

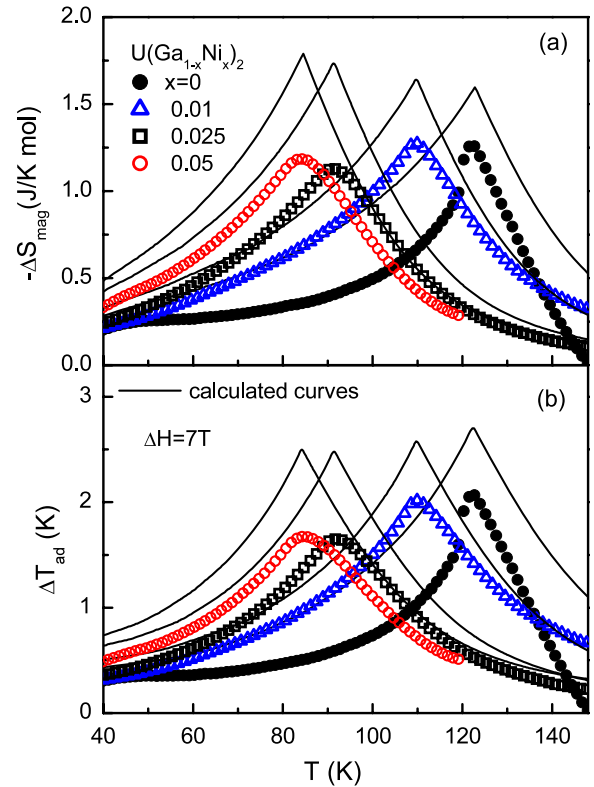


Figure 6. Temperature dependence of ΔS_{mag} (a) and ΔT_{ad} (b) for $\text{U}(\text{Ga}_{1-x}\text{Ni}_x)_2$ series for a magnetic field change from 0 up to 7 T. The solid lines represent the theoretical results and the points stand for the experimental data.

the Ni replacement weakens the exchange interaction between the U atoms. But this is unexpected because the significant volume contraction of this series should promote exactly the opposite trend. A possible explanation for this behavior is a strong influence of the electronic character of the d-metal which surpasses the pressure effect.

The obtained ΔS_{mag} and ΔT_{ad} curves showing the usual bell shape are plotted in figure 6, together with the calculated curves. An interesting feature is that the maximum values of both properties show a rather small relative variation within a 50 K temperature span. The shape of these curves imposes a hard limitation to the use of a single material for applications in a magnetic refrigerator operating in a thermodynamic cycle. In order to overcome this limitation, one can use a composite material formed by the combination of several materials with suitable ordering temperatures [41]. In this way, a composite formed by the pseudobinary $\text{U}(\text{Ga}_{1-x}\text{Ni}_x)_2$ materials should provide a roughly constant MCE in a wide temperature range. We used numerical simulations to determine the mass ratio of each component of the composite sample using $x = 0.0, 0.01, 0.025$ and 0.05 Ni concentrations. The simulation of the isothermal magnetic entropy change of this composite is given by the weighted sum of the individual ΔS_{mag} , as described in [42]. A comparison between the experimental and simulated ΔS_{mag} curves for this composite material is shown in figure 7. Besides the good agreement, this figure shows that the value of $1 \text{ J K}^{-1} \text{ mol}^{-1}$ of the isothermal magnetic entropy change was

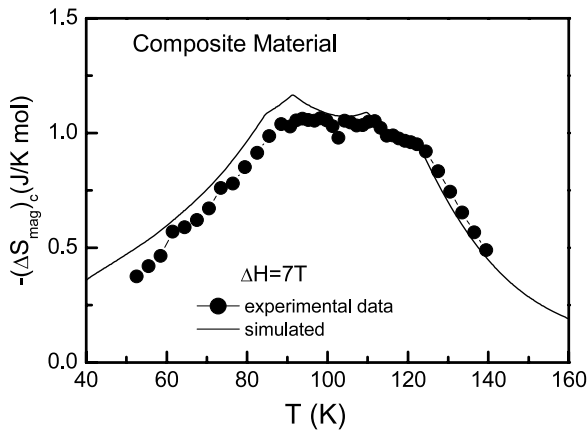


Figure 7. Temperature dependence of the isothermal magnetic entropy change in the composite material $A_{0.35}B_{0.25}C_{0.25}D_{0.15}$, where $A = \text{UGa}_2$, $B = \text{U}(\text{Ga}_{0.99}\text{Ni}_{0.01})_2$, $C = \text{U}(\text{Ga}_{0.975}\text{Ni}_{0.025})_2$ and $D = \text{U}(\text{Ga}_{0.95}\text{Ni}_{0.05})_2$ for a magnetic field variation from 0 up to 7 T. The points are the experimental data and the solid line is the simulated data.

kept basically constant for, at least, a 30 K temperature interval (90 to 123 K).

5. Conclusions

Simple theoretical models like the point charge model for the crystal field and the mean field approximation are capable of reproducing the experimental data for the magnetic entropy variation and the adiabatic temperature variation for bulk UGa_2 and the associated series of compounds $\text{UGa}_{1-x}\text{Ni}_x$. Although ΔS_{mag} and ΔT_{ad} are obtained by indirect measurements, the shape of the theoretical curves for the $5f^3$ configuration is remarkably similar to the experimental result, particularly on the low temperature side (below 60 K). The theoretical values of ΔS_{mag} and ΔT_{ad} obtained with the magnetic field at the [100] axis are a little bigger than the experimental ones obtained with polycrystalline samples.

By applying external pressure in UGa_2 we were able to increase the ordering temperature but not to improve the MCE. A similar behavior is also observed in the case of chemical pressure induced by Ge and Si substitutions. However, when Ni, Fe or Co are substituted for Ga, the ordering temperature is strongly reduced possibly due the influence of the electronic character of the dopant d-metal which surpasses the pressure effect. In spite of this, the MCE remained unaltered. Conversely, when Al substitutes Ga, a small increase of the volume (negative pressure) was obtained together with a considerable increase of the MCE ($\sim 30\%$ in ΔS_{mag} and ΔT_{ad} maximum values). This enlargement of the MCE can be associated with a higher U moment due to the increase of the U–U distance. Also, the electronic character of Al is quite important, i.e. the hybridization of the 5f-states with the Al p-states could be less effective than with Ga p-states. The results indicate that the electronic character of the dopant metal, even for low concentrations, significantly contributes to the U–U exchange interactions in the UGa_2 compound.

Our experimental results and calculation show that a composite material with an almost constant adiabatic entropy change can be prepared by using samples of the $\text{U}(\text{Ga}_{1-x}\text{Ni}_x)_2$ ($0 < x < 0.05$) pseudobinary compounds to work as a refrigerant material in a temperature range from 89 to 123 K.

Acknowledgments

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