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The physical properties of Gd_3Ru: A real candidate for a practical cryogenic refrigerator

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The magnetization, the specific heat, and the magnetocaloric effect (MCE) for Gd_3Ru are presented as function of temperature at different magnetic fields. The results show a maximum entropy change $-\Delta S = 30$ J/kg K @ 5 T, which is the highest value for the R_3M compounds. With a non-hysteretic transition of first order type at $T_C = 54$ K, it presents a temperature change $\Delta T_{max} = 5.7$ K around 59 K with a refrigerating cooling power of 700 J/kg and these results are comparable to values found for giant MCE materials. This compound is stable and able to operate at temperatures between 90 K and 40 K with a minimum $-\Delta S = 5$ J/kg K. These figures were obtained by sweeping the magnetic field without using sample preparation routines. This methodology is appropriate to evaluate the MCE for the cycling process of a cryogenic magnetic refrigerator. © *2015 AIP Publishing LLC*.
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The investigation of magnetocaloric materials has focused in obtaining a compound appropriate to work in magnetic refrigeration either close to the room temperature as well as at cryogenic temperatures. On the high temperature side, the discovery of a giant magnetocaloric effect (MCE) for the $Gd_5Ge_2Si_2$ compound[1] strongly stimulated the study of many other rare earth rich materials of the R_xM_y family (R = rare earth, M = transition metal), among others. The series RM_2 is one of the most investigated because of the simple cubic crystal field calculation involved.[2–6] On the other hand, the series R_3M has attracted attention because it has the highest R/M ratio of the R_xM_y family and possibly a high MCE value.[7] Some of the R_3M compounds with R = Gd, Tb, Er, Y and M = Ni, Co, Rh[8–11] had their physical properties determined. In particular, compounds with R = Gd show the highest ordering temperatures.[10] Gd_3Ni,[9] Gd_3Co,[9] and Gd_3Rh[12] present antiferromagnetic (AF) ordering at intermediate temperatures and a moderate entropy change. The MCE for other R_3M compounds with AF ordering, Dy_3Co[13] and Ho_3Co,[14] and for three other with ferromagnetic (FM) ordering, Er_3Co,[15] Tb_3Co,[16] and Tb_3Rh,[7] was also investigated.

Basically, these are all the MCE results found for the R_3M family in the literature. These studies have shown that for all these compounds, there is only a partial release of the magnetic entropy at the transition temperature and an excess magnetic effective moment, depending on the compound. These characteristics should impact on the MCE since a significant part of the magnetic entropy is not affected by the magnetic field around the transition and also because the excess moment is related to the R-M indirect exchange. However, in order to draw a more complete picture for the Gd_3M series, it is interesting to examine new compounds. In this investigation process we found that up to now, Gd_3Ru is the only compound of this series showing a first order FM transition. This compound meets all the requirements to present a high MCE value and is the main subject of this study. It is known that it crystallizes with the same Fe_3C structure of the R_3M[17] but its physical properties are still to be determined.

The results for the R_3M series mentioned above show a high MCE value only for the FM compounds. Most of these results were obtained indirectly by using magnetization measurements, which might lead to overestimated values for ΔS, especially when a first order magnetic transition is present.[18] Therefore, in this letter, we investigate the physical properties of Gd_3Ru and reexamine the magnetocaloric effect of a few other R_3M compounds by using heat flux measurements while sweeping the magnetic field because it allows a direct comparison of the entropy change for all materials.

The appropriate quantities of high purity elements were used to prepare Er_3Co, Tb_3Rh, Gd_3Co, and Gd_3Ru. The elements were melted in an arc-furnace and the samples were then annealed at 600 °C during four days. The magnetization data were obtained using a Quantum Design (QD) Physical Property Measurement System (PPMS) or a SQUID. The specific heat and the magnetothermal properties were obtained by a heat flux method adapted to the PPMS described elsewhere (QD application note 1805–200 and Ref. 18). Except where noted, all the MCE data are due to a 5 T field change.

The Rietveld analysis of the Cu-K_α X-Ray powder diffractogram of Gd_3Ru, shown in Fig. 1, was obtained using the space group Pnma of the orthorhombic structure of Fe_3C with lattice parameters $\boldsymbol{a} = 7.308$ Å, $\boldsymbol{b} = 9.335$ Å, and $\boldsymbol{c} = 6.327$ Å, and this result is in agreement with the literature data.[17] The X-ray data for Er_3Co and Tb_3Rh were obtained with similar conditions and the results are also in agreement with the literature.[7,19]

The magnetization for Gd_3Ru, shown in Fig. 2, presents a ferromagnetic transition at $T_C = 54$ K which is the lowest ordering temperature among the Gd_3M compounds. The inverse susceptibility is linear above 100 K, corresponding to $\theta_P = 47.7$ K and to an effective moment of $\mu_{eff} = 16.7\ \mu_B$/f.u. (or, per gadolinium ion, $\mu_{eff-Gd} = \frac{\mu_{eff}}{\sqrt{3}} = 9.6\ \mu_B$[11,20]). Considering the effective moment of the Gd^{3+} free ion $7.94\ \mu_B$, we have an expressive excess moment of $1.6\ \mu_B$ which is associated to the Ru ion. For all the R_xM_y series,

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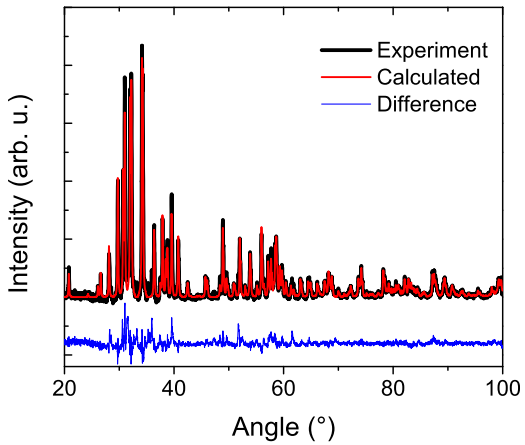

FIG. 1. X-ray diffractogram at 300 K of powdered Gd_3Ru using Cu-K_α radiation. The Rietveld refinement revealed only one phase with the Fe_3C orthorhombic structure.

the R-4f electrons polarize the R-5d electrons which hybridize with the M ion d-electrons, eventually inducing a magnetic moment on M.[9,12,20] Given the similarity between the d-electrons configuration for M = Co ($3d^7$) and Ni ($3d^8$) with Ru ($4d^7$) and Rh ($4d^8$), we expected $\Delta\mu_{\text{eff}}$ to vary in the same way. Surprisingly, $\Delta\mu_{\text{eff}}$ for Gd_3Ru is bigger than for Gd_3Rh ($\Delta\mu_{eff} = 0.55\ \mu_B$), Gd_3Ni ($\Delta\mu_{eff} = 1\ \mu_B$), or Gd_3Co ($\Delta\mu_{eff} \approx 0$) indicating that here the hybridization is more effective. Unfortunately, there is no data for other Gd compound to verify if there is a trend of the excess moment with the d-electrons configuration of the M ion. The upper part of Fig. 2 shows the magnetization as a function of the magnetic field at 2 K. There is no evidence of magnetic hysteresis and a saturation moment of 6.5 μ_B is obtained at 5 T. This reduced saturation moment compared to the calculated free ion value ($\mu_{\text{sat}} = g_J J$) was also observed for the R_3Co series.[15] Since there is no crystal field effect for Gd, this is probably due to the antiparallel alignment between the M ions induced moment and the R ions moment.[21,22] In Fig. 3, we show the Arrott-Belov plots for Gd_3Ru where the appearing of negative slopes starting at 54 K confirms the first order character of the FM to paramagnetic transition. This is also clearly indicated by the sharp peak on the heat

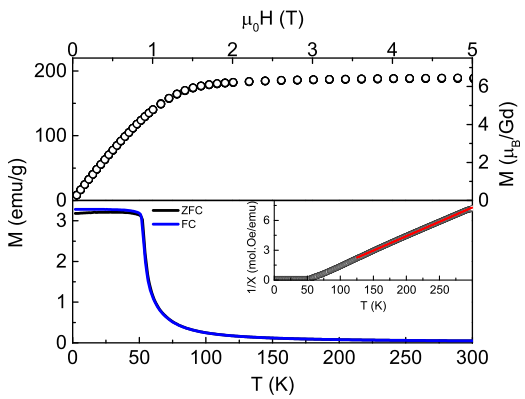

FIG. 2. Magnetization data for Gd_3Ru. The upper graph shows the dependence with the magnetic field sweeping up and down at 2 K. There is no hysteresis. The bottom graph shows the zero-field cooled (ZFC) – field cooled (FC) sequence obtained at 200 Oe and the inset shows the corresponding inverse of the molar susceptibility.

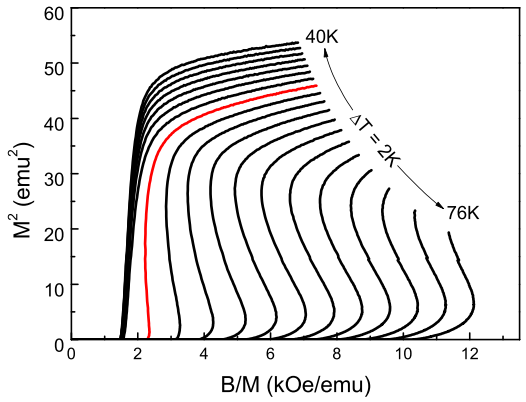

FIG. 3. Arrott-Belov plots for Gd_3Ru from 40 K to 76 K in 2 K steps. The negative slope appears around the 54 K curve (red).

flux sensor voltage which appears due to the latent heat of the phase transformation (see the inset of Fig. 4).

It is also important to look at the Gd_3Ru magnetic entropy through the specific heat and the results obtained using the heat flux technique are shown in Fig. 4. For H = 0, the specific heat shows a very sharp peak at T_C which broadens and significantly shifts to higher temperatures as the field increases. The electronic and lattice contribution to the specific heat ($\gamma T + C_{\text{Debye}}$) can be taken as the corrected specific heat of a non-magnetic reference compound (such as Y_3Ni for Gd_3Ni)[23] or is obtained by simulation using γ and θ_D as parameters, as we did and is shown in Fig. 4. In any case, the determination of the lattice contribution is not straightforward but we know that well above the magnetic transition, the magnetic specific heat goes to zero (considering no crystal field effect). This draws a limit to C at the high temperature side ($T \approx 200$ K for Gd_3Ru). In this case, we used $\gamma = 50$ mJ/mol K and $130\ \text{K} \leq \theta_D \leq 150\ \text{K}$, which are consistent with other R_3M results.[10,24] This analysis reveals that only a fraction of the Gd magnetic entropy of Gd_3Ru ($3R\ln(8) = 52.1$ J/mol K) is released at T_C, around 20 J/mol K for $\theta_D = 130$ K (or 34 J/mol K for $\theta_D = 150$ K). In fact, the Gd_3M (M = Ni, Co, and Rh) compounds present a similar behavior where the magnetic entropy at T_{ord} is about 60% of the full value and it is argued that the remaining part is associated to short range correlations between the Gd ions.[10,22,23]

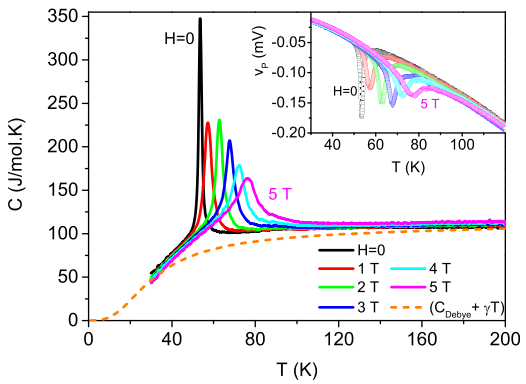

FIG. 4. The specific heat of Gd_3Ru as function of the temperature obtained at different magnetic fields using a heat flux setup. The continuous line correspond to $C_{\text{Debye}} + \gamma T$, where $\gamma = 50$ mJ/mol K and $\theta_D = 130$ K. The inset shows the Peltier voltage due to the heat released by the sample on each field.

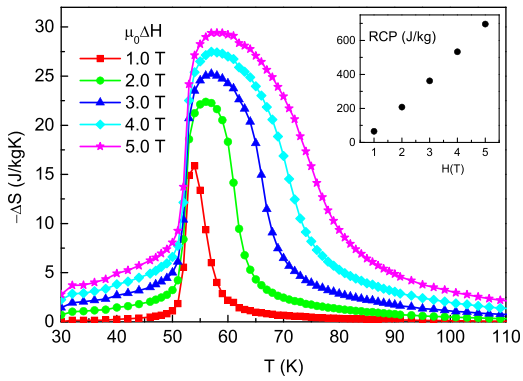

FIG. 5. The field sweep entropy change for Gd_3Ru as function of the temperature. Here, the sample was not prepared to the same initial state. The inset shows the relative cooling power (RCP) defined as $RCP = \Delta S_{max} \times \delta T_{half\text{-}height}$.

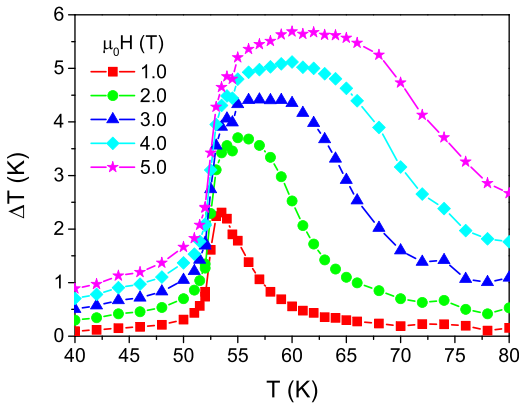

FIG. 7. The experimental ΔT for Gd_3Ru obtained for several field change values measured by a Cernox temperature sensor.

Consequently, there could be a limitation for the MCE and actually ΔS_{max} for Gd_3Ni, Gd_3Rh, and Gd_3Co do not call attention. However, the MCE for Gd_3Ru surprisingly reaches very significant values, as shown in Fig. 5. For a 5 T field change, $-\Delta S$ shows a peak at 59 K, with maximum of 30 J/kg K, while for Gd_3Ni and Gd_3Co it reaches around 5.2 and 11.2 J/kg K, respectively. This scenario situates Gd_3Ru together with other very good MCE materials (the giant MCE materials) but here with no observable hysteresis. The inset of Fig. 5 presents the refrigerating cooling power (RCP) which is quite high. These are the characteristics of a very promising material.

A comparison with other compounds of the R_3M series is found in Fig. 6. The results were obtained in the same manner for all the materials except for Er_3Co which was obtained using the standard PPMS specific heat relaxation technique. Therefore, Gd_3Ru presents the highest entropy change value among the R_3M family.

We have also measured the temperature variation (the direct MCE) for Gd_3Ru and Fig. 7 shows these results for several values of the field change. Here, the experimental $\Delta T_{max} = 5.7$ K is then comparable to the estimate $\Delta T \approx 5$ K for Gd_3Co for $\Delta H = 4$ T (Ref. 8) which was calculated using the approximation $\Delta T_{ad} = -\frac{T}{C_H(T)}\Delta S_H$.

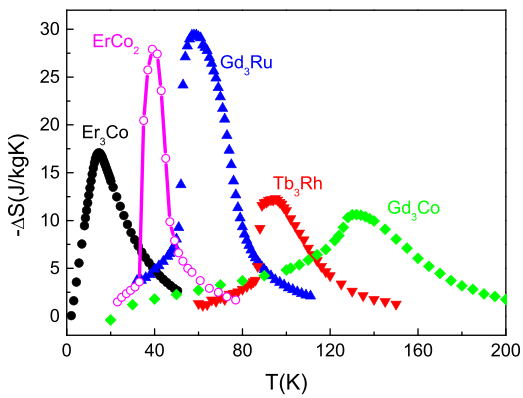

FIG. 6. Entropy change for Er_3Co, $ErCo_2$, Gd_3Ru, Tb_3Rh, and Gd_3Co. Data for $ErCo_2$ were taken from the literature.[25] Except for Er_3Co where the specific heat was used, all the other compounds were measured using the heat flux technique sweeping the field up to 5 T.

The (Gd-5d)–(M-nd) hybridization owing to the M ion polarization and the reduced magnetic entropy released up to T_{ord} are the common characteristics of the R_3M compounds and they are also present in Gd_3Ru. A ΔS threshold line for the R_3M (excluding Ru) situated at −18 J/kg K has only two compounds located close to this limit: Er_3Co and Tb_3Co. Both Er and Tb ions have a bigger moment than Gd and so it is surprising that Gd_3Ru easily overcomes this limit. Also, considering that Co is not magnetic in all the R_3Co compounds while the estimated Ru moment is close to 1.6 μ_B in Gd_3Ru, then we have to consider that the contribution of the 4d-electrons subsystem to the entropy change cannot be neglected. The crystallographic structure of the R_3M can be described by slanted layers of R ions separated by the M ions. According to this model,[26] the competition between the Gd(4f-5d)–(5d-4f)Gd intra layer interaction and the inter layer interaction, mediated by the Gd(4f-5d)–(4d)Ru path, will affect the ordering temperature as well as the type of ordering. Indeed, the Neel temperature sequential decrease for Gd_3M, M = Co, Rh, and Ni, with the corresponding increase of the excess moment (see Table I), indicates that the inter layer interaction is more effective for M = Ni. Table I also shows that lattice parameter **b** for Gd_3Ru is significantly reduced and since the R layer is along the bc plane, a likely dominant Gd-Gd interaction triggered the FM ordering. On the other hand, the increased lattice parameter **a** indicates a weakening of the inter layer interaction mediated by the Ru-4d electrons such that the enhanced $\Delta\mu_{eff}$ observed seems contradictory. Therefore, at this point, we are not able to correlate the excess moment or the ordering temperature

TABLE I. Lattice parameters, magnetic moment associated to the M ion, and ordering temperature for the Gd_3M and Tb_3Rh compounds. The data for M = Ni and Co were taken from Ref. 9 and for Rh from Refs. 12 and 20. The MCE data were obtained for a 5 T field change.

	a (Å)	b (Å)	c (Å)	$\Delta\mu_M$ (μ_B)	T_{ord} (K)	$-\Delta S$ (J/kg K)	$-\Delta S$ (mJ/cm^3 K)
Gd_3Co	7.045	9.516	6.315	≈0	130	11.2	102.8
Gd_3Rh	7.195	9.540	6.328	0.3–0.55	112	8.2	72.3
Gd_3Ni	6.949	9.690	6.350	1.09	100	5.2	42.9
Gd_3Ru	7.308	9.335	6.327	1.62	54	30	262.4
Tb_3Rh	7.149	9.478	6.293	0.3	84	12	107.5

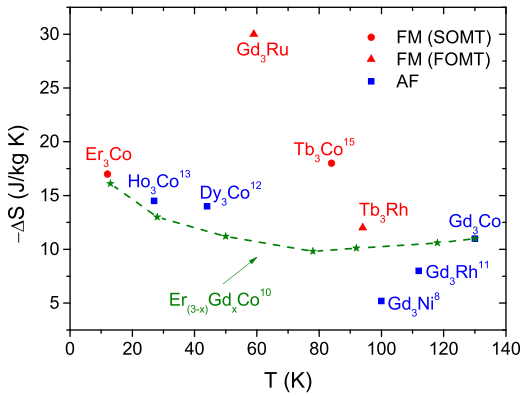

FIG. 8. The magnetic entropy change for several R_3M compounds due to a field change of 5 T. We obtained the entropy change of Er_3Co using conventional specific heat data and of Gd_3Co, Tb_3Rh, and Gd_3Ru with the heat flux technique.

with these structural data. We believe, however, that low temperature X-ray spectroscopy experiments might be important to evaluate the d-electrons contribution and to understand the magnetic behavior of the Gd_3Ru compound.

Fig. 8 shows the maximum entropy change for all the R_3M and clearly Gd_3Ru excel. If we compare these results with those of the hallmark of MCE materials, the compound $Gd_5Ge_2Si_2$, we find that Gd_3Ru is indeed a remarkable material. Most of the experimental results in well prepared samples of $Gd_5Ge_2Si_2$ show $-\Delta S_{max}$ around 15 J/kg K, RCP ≈ 420 J/kg,[27] and $\Delta T \approx 8.5$ K (Ref. 28) compared to 30 J/kg K, RCP = 700 J/kg, and $\Delta T = 5.7$ K for Gd_3Ru. However, due to the very different T_C, a proper comparison is made with other compounds like EuS or $ErCo_2$. EuS is a ferromagnetic semiconductor with $T_C = 18$ K (Ref. 29) and $-\Delta S_{max} = 37$ J/kg K with an estimated RCP = 780 J/kg, results comparable to the Gd_3Ru values. But there are some disadvantages for EuS: it is not a stable material; it is about four times more expensive and has a limited usable temperature range. $ErCo_2$ also presents $-\Delta S_{max} = 30$ J/kg K at 34 K (see Fig. 6) but with a reduced RCP.[1,25] Alternatively, it is interesting to consider the series $Er_{3-x}Gd_xCo$ for a composite material intended to work in a wide range of temperature. However, in this case, a plateau formed between 30 K and 130 K (Ref. 11) presents $-\Delta S$ limited to values around 5 J/kg K, while Gd_3Ru shows a minimum $-\Delta S$ of 5 J/kg K between 40 K and 90 K. All considered we believe that Gd_3Ru is an excellent material for cryogenic refrigeration to work below the liquid nitrogen temperature.

In conclusion, Gd_3Ru is a ferromagnetic material that order at $T_C = 54$ K with a first order transition. It presents an excess effective moment around 1.6 μ_B associated to the Ru ion polarized by the Gd-5d electrons. Opposing to the tendency of a reducing $-\Delta S$ for the other Gd_3M when the transition temperature is lowered and the excess moment is increased, Gd_3Ru exhibits an excellent MCE, comparable to the best known materials. The first order character of the magnetic transition, the absence of hysteresis, and the contribution of the d-electrons subsystem are responsible for the enhanced MCE of Gd_3Ru. It also presents a very high RCP such that this compound presents all the desired characteristics for use in a real regenerative magnetic refrigerator to operate below liquid nitrogen temperature.

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