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# Tunable magneto-caloric effect in $\text{Gd}_{1-x}\text{Tb}_x$ heterostructures thin film

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The magnetic and magneto-caloric properties of  $(\text{Gd}_{1-x}\text{Tb}_x)$  alloy thin films and  $[\text{Gd}/\text{Tb}]$  multilayers have been investigated. All the samples had a total thickness of 100 nm and were deposited by DC sputtering. By changing the composition of the system, the ordering temperature ( $T_c$ ) and the magnetic entropy changes of the compounds could be tuned. The results show that the  $T_c$  of the alloy thin films is close to 270 K for  $x = 0.2$ . Moreover, creating  $[\text{Gd}/\text{Tb}]$  multilayers with the same thickness and concentration of the studied  $\text{Gd}_{80}\text{Tb}_{20}$  alloy film enables to strongly increase the relative cooling power, and reach values twice as big as from the corresponding alloys. These results suggest that nanostructuring of  $[\text{Gd}/\text{Tb}]$  multilayers may be a promising route to tailor the magnetocaloric response of materials.



The possibility of using magnetic refrigeration has become more reliable during the last twenty years, which will enable it to replace conventional refrigeration systems<sup>1,2</sup>. Such a change is desirable due to the advantages of using the magnetocaloric effect (MCE) for magnetic refrigeration application<sup>3-5</sup>, thus leading to high refrigeration efficiency, small volume requirement, low cost, environmental friendliness, no noise pollution and better performance<sup>6-8</sup>. An excellent magnetic refrigerant should have large magnetic entropy change ( $\Delta S_M$ ) induced by low magnetic field change. According to the Curie-Weiss law for ferromagnetism, large magnetic entropy change  $\Delta S_M(T, H)$  is expected at the Curie temperature ( $T_c$ ) and for materials with larger values of effective magnetic moment. When a magnetic field is applied adiabatically to a magnetic material, the unpaired spins are aligned parallel to the field. The magnetic entropy of the material is lowered and the sample warms recovering the lost magnetic entropy through the increase of its lattice entropy. On the other hand, when the field is removed from the magnetic sample, the spin tends to randomize, increasing the magnetic entropy and lowering the lattice entropy and the temperature of the material<sup>9-11</sup>.

MCE has mainly been investigated for bulk crystal and polycrystal materials<sup>8,12,13</sup>. However, a few studies have concentrated on thin films to investigate the role of size on the MCE. For instance, recent studies have shown that nanostructured Gd has a different magnetocaloric behavior when compared with the bulk counterparts<sup>14,15</sup>. The origin of this change appears to be a combination of interface defects and lower size effects. Moreover, an experimental investigation by Miller *et al.* based on magnetocaloric behavior of nanostructured Gd was done to carry diapers and Gd heterostructures<sup>16</sup>. The results showed that the maximum entropy is increased in Gd/W multilayer relative to the bulk state<sup>16,17</sup>. In this paper, we concentrate on Gd-Tb based alloys and multilayers in order to investigate how MCE can be tuned using

nanoscale material.

The studied samples were grown at room temperature (RT) on (100)-silicon substrates using sputtering deposition with a base-pressure lower than  $10^{-7}$  Torr. The Gd and Tb layers were deposited at RT. A 3 nm-Ta buffer layer was used, as well as a 3 nm-Ta capping layer to avoid oxidation of the rare-earth elements. The total magnetic thickness of the samples is kept constant and equal to 100 nm to ease the comparison of the magnetocaloric values. Two sets of samples were deposited : a series of  $(\text{Gd}_{1-x}\text{Tb}_x)$  samples with  $x$  (the atomic ratio) varying from 0 to 100; and a series of multilayers with a given  $(\text{Gd}_{80}\text{Tb}_{20})$  equivalent composition and an increasing segregation of the Gd and Tb elements in regular alternating layers.

Magnetic measurements were performed using a Quantum Design SQUID Vibrating Sample Magnetometer. The magnetization isotherms were measured in the range of 0-2 T with the field oriented out-of-plane compare to the sample, for different temperatures in steps of 5 or 10 K. In this configuration, the change of entropy due to an applied field from 0 to  $H_0$  can be evaluated using the following equation<sup>16</sup>:

$$\Delta S_M(T, H_0) = \mu_0 \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H \quad (1)$$

where  $\mu_0$  is the permeability of free space. Figure 1 illustrates the type of measurements that have been performed on a typical  $\text{Gd}_{80}\text{Tb}_{20}$  alloy sample. We observe that the maximum variation of magnetization is occurring at the Curie temperature where the material is subject to a second-order transition between its ferromagnetic and paramagnetic state. The corresponding curve of the entropy variation can then be obtained as shown in figure 2. The modification of  $T_c$  can directly be tracked following the drift of the maximum variation

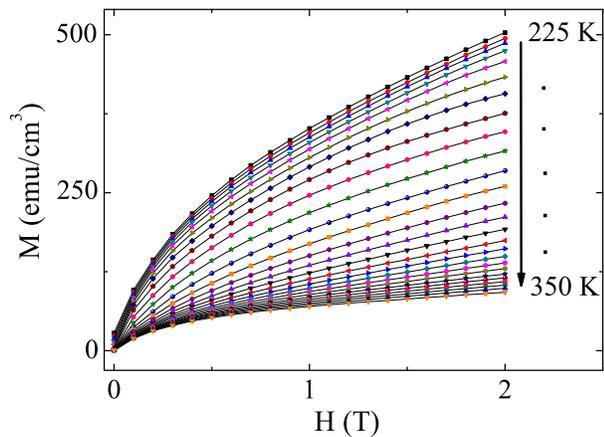


FIG. 1. Magnetic isotherms of a  $\text{Gd}_{80}\text{Tb}_{20}$  alloy compound measured at several temperatures around  $T_c$  in a magnetic field applied out-of-plane.

of entropy as the Tb concentration increases. The decrease in the transition temperature with increasing the Tb concentration is due to the fact that the Curie temperature of Tb ( $T_c = 222$  K)<sup>18,19</sup> is lower than that of Gd ( $T_c = 294$  K)<sup>12</sup>. Hence, alloying Gd and Tb decreases the exchange interactions, which causes the reduction of  $T_c$ . However, it was shown that a  $\text{Gd}_{50}\text{Tb}_{50}$  alloy in bulk sample has decreased  $T_c$  from 294 K to 264 K, without affecting the magnetocaloric properties of the material<sup>20</sup>. Figure 2 shows that by alloying Gd and Tb, we can cover a range of refrigeration between 260 K and 300 K (-13 °C and 25 °C). In addition, the active magnetic regenerative refrigeration (AMRR) requires a strong magnetocaloric material power over a wide temperature range. In the case of systems that use the Ericsson cycle as a refrigeration cycle, the change in the total entropy of the refrigerant must be as constant as possible over the relevant temperature range, which is not the case for the  $\text{Gd}_x\text{Tb}_{1-x}$  bulk alloys<sup>20</sup>.

Even if the position of the peak is easily controlled by the ratio between the two elements, the amplitude of the peak and the relative cooling power (RCP) coefficient associated to the area under the curve evolve differently and are strongly varying depending on the composition. Indeed, the amplitude of the peak increases with the Tb content, and is attributed to the increase of the magnetic moment of the  $\text{Gd}_{1-x}\text{Tb}_x$  film upon alloying with the Tb element<sup>21</sup>. Moreover, for  $x = 20, 40$  and 60%, the RCP is lower than for pure Gd, while for  $x = 80\%$  the properties are enhanced compared to pure Gd.

To study the effect of interface and low dimension on the MCE, we compare the magnetocaloric behavior of Gd-Tb compounds with the same thickness and net concentration but with a different atomic ordering, namely Gd-Tb alloys and multilayers. We started with the con-

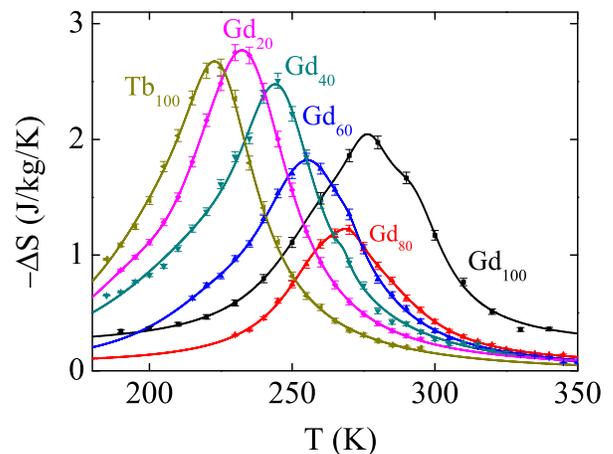


FIG. 2. Temperature dependence of magnetic entropy change in  $\text{Gd}_{1-x}\text{Tb}_x$  alloys compounds in a field of 2 T. Lines are just guides to the eyes.

centration giving an entropy peak close to RT:  $\text{Gd}_{80}\text{Tb}_{20}$  (100 nm). Then, we grew multilayers with the same atomic composition, but containing a segregation between the Gd and Tb atoms. Figure 3 show that the peak of entropy variation is evolving between a single peak when the [Gd/Tb] multilayer is very similar to an alloy (100 and 50 layers) (Fig. 3(a)-3(c)), to a double peak when the two elements are more spatially separated (10 and 2 layers) (Fig. 3(d)-3(e)). Indeed, the position of the two peaks matches with those of the pure Tb and Gd elements and their associated  $T_c$ , as depicted in Fig. 3(f). Moreover, the studied [Gd/Tb] multilayers show a much broader entropy peak than for the corresponding alloy, reaching a value of approximately 50 K. Furthermore, a higher number of layers (100 and 50 layers) strengthens the exchange interaction between the two rare-earth elements. This exchange ends up in an interaction between neighbors very similar to the one of an alloy. However, one can see from figure 4 that the RCP for multilayers is much higher than for the corresponding alloy. In our case, we define the RCP as followed :

$$RCP = \int_{T_1}^{T_2} \Delta S(T) dT \quad (2)$$

where  $T_1$  and  $T_2$  are the temperatures corresponding to the limits of the FWHM of the entropy variation peak.

Whatever the number of layers, the RCP is almost twice as big as the one from the corresponding  $\text{Gd}_{80}\text{Tb}_{20}$  alloy for an equal thickness of the film. Furthermore, the temperature at which the maximum entropy is obtained is not changing much, and is very close to the one of a pure Gd film. This finding is probably due to the unbalance between the two elements (80 % of Gd in this example). Therefore, the ordering of the atoms seems to play a key effect in the MCE, which is in agreement with

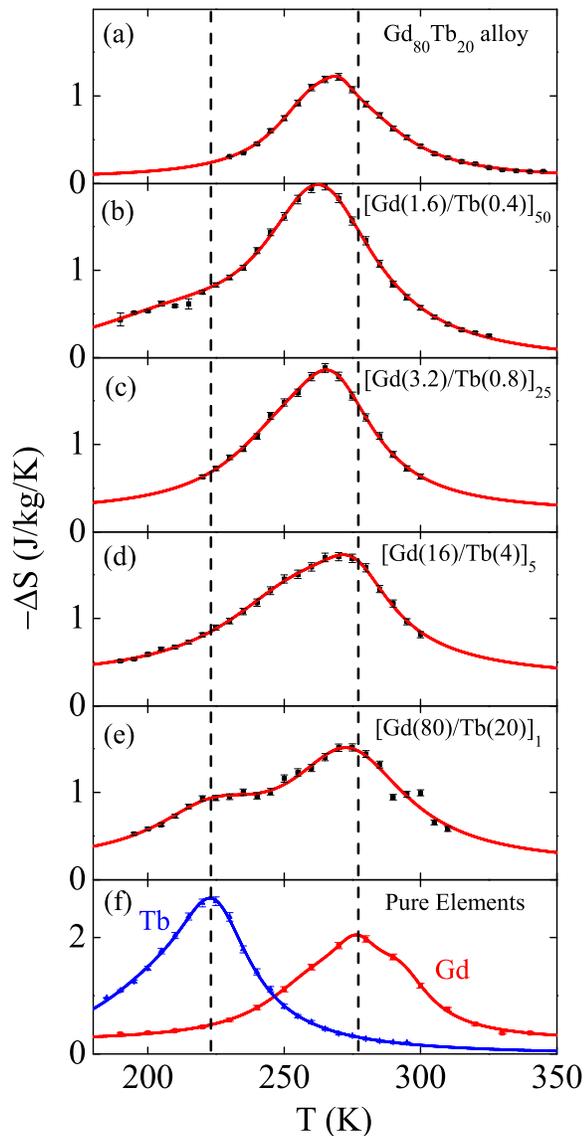


FIG. 3. Temperature dependence of magnetic entropy change for various Gd-Tb compounds with the same net concentration in a field of 2 T. (a)  $\text{Gd}_{80}\text{Tb}_{20}$  (100 nm) alloy. (b)  $[\text{Gd}(1.6\text{nm})/\text{Tb}(0.4\text{nm})]_{50}$  multilayers. (c)  $[\text{Gd}(3.2)/\text{Tb}(0.8)]_{25}$  multilayers. (d)  $[\text{Gd}(16)/\text{Tb}(4)]_5$  multilayers. (e)  $\text{Gd}(80\text{nm})/\text{Tb}(20\text{nm})$  multilayer. (f) pure Gd and Tb elements to compare with the studied Gd-Tb compounds. The lines indicated the maximum entropy change for pure elements. Lines are just guides to the eyes.

previous studies<sup>20,22-24</sup>. This finding had also been seen in the case of annealed samples where the properties are enhanced, thanks to a better crystallinity<sup>25</sup>. These results suggest that a multilayer stacking could greatly improve the magnetocaloric properties in the Gd-Tb system without requiring the introduction of additional elements. From the comparison with Gd data as well as from the technological point of view, our results underline that our material can be considered as a

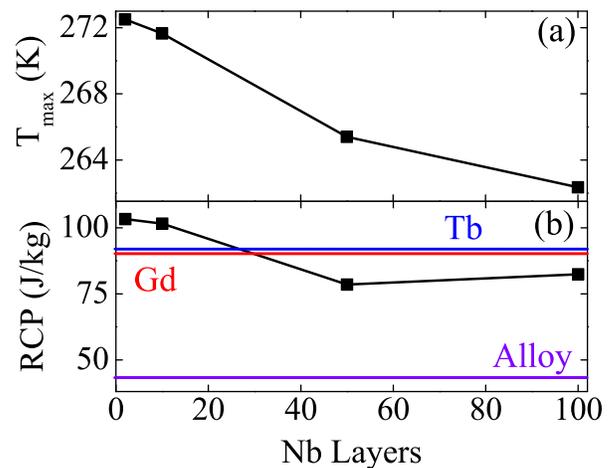


FIG. 4. (a) Temperature at which the maximum variation of entropy is observed as a function of the number of layers for the studied  $[\text{Gd}/\text{Tb}]$  multilayers with the same net concentration. (b) The respective RCP values obtained as a function of the number of layers for the studied  $[\text{Gd}/\text{Tb}]$  multilayers. The purple line represents the value of an alloy sample with an equivalent composition, while the red and blue lines indicate the values for a sample of pure Tb or Gd.

relevant potential candidate material to be used in cooling system based on the magnetic refrigeration.

In conclusion, we demonstrated the possibility to independently tune the position and amplitude of the peak of entropy variation in Gd-Tb systems. The ordering temperature and magnetic entropy changes of  $\text{Gd}_{1-x}\text{Tb}_x$  alloy thin films could be tuned by changing the alloy's composition. Moreover, we demonstrate that creating  $[\text{Gd}/\text{Tb}]$  multilayers with the same thickness and concentration of the studied  $\text{Gd}_{1-x}\text{Tb}_x$  alloy films enables to strongly increase the relative cooling power, and reach values twice as big as from the corresponding alloys. Thanks to this approach, the variation of entropy can be controlled continuously from the individual properties of its constituting elements. This study opens up new possibilities in the control and optimization of the magnetocaloric effect in magnetic thin films.

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