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Direct magnetocaloric measurements of Fe-B-Cr-X (X = La, Ce) amorphous ribbons

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A procedure has been developed to directly measure the adiabatic temperature change of amorphous melt-spun Fe-based ribbons displaying attractive room temperature magnetocaloric properties. Polycrystalline Gd ribbons are used as a reference material to compensate for the contribution of the sample holder to the experimental values. $Fe_{78}B_{12}Cr_8Ce_2$ and $Fe_{75}B_{12}Cr_8Ce_5$ melt-spun ribbons exhibited a peak adiabatic temperature change $(\Delta T_{ad}^{pk}) \sim 58\%$ larger than $Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$ amorphous ribbons. The ΔT_{ad}^{pk} in $Fe_{78}B_{12}Cr_8Ce_2$, $Fe_{75}B_{12}Cr_8Ce_5$, and $Fe_{79}B_{12}Cr_8La_1$ ribbons displayed ~ 18-33% enhanced ΔT_{ad}^{pk} compared to a $GdAl_2$ alloy. © *2011 American Institute of Physics*. [doi:10.1063/1.3613666]

I. INTRODUCTION

The magnetocaloric effect (MCE) has been attracting great interest due to its application in energy efficient magnetic refrigeration (MR) technology.[1,2] The magnetocaloric parameters of a magnetocaloric material (MCM), which are crucial to its practical application in MR, are the adiabatic temperature change (ΔT_{ad}) and the isothermal magnetic entropy change (ΔS_M) associated with a magnetic phase transition. The ΔT_{ad} is directly related to the temperature span achievable by a MCM; hence, ΔT_{ad} is an important factor in the performance evaluation of MCM.

Many MCM in the form of ribbons or thin films have been reported.[3–6] Soft magnetic MCM ribbons offer low magnetic hysteresis, high electrical resistivity, enhanced corrosion resistance, good mechanical properties, and tunable T_C by composition variation.[5,7,8] However, little attention has been paid to ΔT_{ad} investigations in MCM ribbons, due to the intrinsic difficulties for its measurement. Direct MCE measurements of MCM are usually performed using a ΔT_{ad} measurement device, such as the magnetocaloric measuring setup (MMS) (Advanced Magnetic Technologies and Consulting, Ltd. (AMT&C), Russia). However, this kind of device is optimized for characterizing ΔT_{ad} of bulk materials, for which the thermal mass of the sample holder is negligible with respect to that of the sample. Challenges in measuring direct MCE in materials with small mass and thickness (e.g., ribbons) are due to the small thermal mass of the ribbons. While polycrystalline materials in ribbon shape can be replaced by bulk samples for performing such measurements, that is not the case for amorphous alloys, since the high cooling rate required for obtaining amorphous microstructures prevents the fabrication of most of these alloys in bulk form.

Hence, in order to characterize the ΔT_{ad} of our amorphous ribbons, a procedure to extend the MMS to characterize ΔT_{ad} of samples of small size and mass has been developed. The method involves using Gd ribbons to calibrate the response of the measuring device, allowing us to find a correction factor due to the shape and thermal mass of the sample. Using this relationship, analysis of the Fe-based amorphous samples was carried out.

II. EXPERIMENTAL

Gd (Alfa Aesar, 99.99% purity) ribbons of 3 mm width and 20-28 μm thickness were prepared by melt spinning (Edmund Bühler GmbH., Melt Spinner SC). The ΔT_{ad} of the samples was measured by a magnetocaloric measuring setup ("MagEq MMS 902," manufactured by AMT&C Corporation, Moscow, Russia). The measurement details were similar to those reported earlier.[9–11] The magnetic field (H) was produced by a permanent magnet Halbach magnetic field source with variable H in its working bore ($H_{max} = \pm$ 1.775 T). ΔT measurements were obtained by a differential thermocouple with its measuring junction secured between two pieces of sample under investigation and a reference junction positioned on the nonmagnetic metallic sample holder. ΔT and H values were recorded simultaneously over the whole cycle of ΔH. Bulk Gd samples ($8 \times 4 \times 0.75$ mm, 397 mg) were used to calibrate the MMS and as a reference for the amorphous ribbon samples. Ten (22.72 mg), twenty (43.74 mg), or forty (88.02 mg) pieces of Gd ribbon, with 8 mm length, were stacked on top of one another with the aid of vacuum grease. The ΔT_{ad} for the optimized number of ribbons was measured at magnetizing speeds ranging from 1 to 3 Ts^{-1}. $Fe_{80-x}B_{12}Cr_8Re_x$ (RE = La or Ce, x = 1–5 at.%) melt-spun ribbons were then measured for their direct MCE and their preparation method, and other characterization results have been reported elsewhere.[12] The measurements were performed for temperatures ranging from 180–350 K in $\leq 10^{-3}$ Torr vacuum, with the magnetic field applied along

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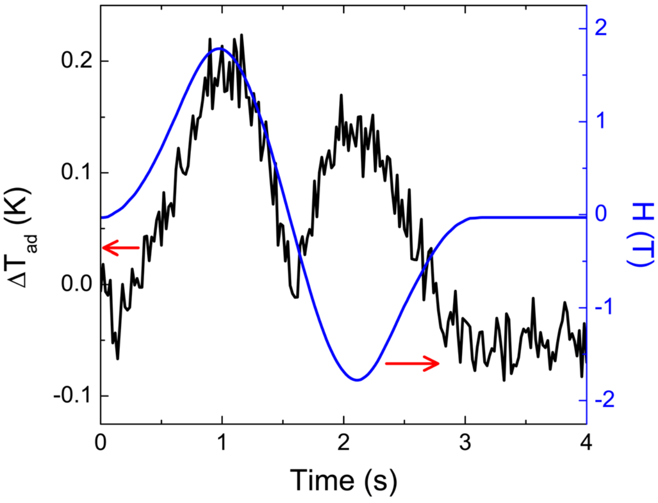

FIG. 1. (Color online) Time dependence of the magnetic field (H) and the difference between the temperature of the sample and the temperature of the sample holder (ΔT_{ad}) for 40 ribbon pieces of $Fe_{78}B_{12}Cr_8Ce_2$ alloy at 332 K.

the ribbons axis, and recorded over a full cycle of the magnetic field change (0 → H_{max} → $-H_{max}$ → 0). Figure 1 shows the time dependence of the magnetic field and the difference between the temperature of the sample and the temperature of the sample holder (ΔT_{ad}) for a $Fe_{78}B_{12}Cr_8Ce_2$ alloy at a temperature of 332 K.

III. RESULTS AND DISCUSSION

The ΔT_{ad} (T) curve for the Gd bulk sample for a maximum H value of 1.775 T is presented in Fig. 2. Its peak adiabatic temperature change (ΔT_{ad}^{pk}) was observed at 297 K; near the Curie temperature (T_C) of Gd, the $\Delta T_{ad}^{pk}/\Delta H_{max}$ is ~2.34 KT^{-1}, in good agreement with the literature.[9] Hence, this value was used for comparison with Gd ribbons.

The ΔT_{ad} (T) curves for Gd ribbon stacks ranging from 10 to 40 ribbon pieces are presented in Fig. 3. It was observed that less noise was obtained for a larger number of Gd ribbons, being the improvement especially noticeable when increasing from 10 to 20 pieces. When 40 ribbon pieces were used, the ΔT_{ad}^{pk} value was not significantly altered from that of 20 ribbon pieces. The experimentally obtained ΔT_{ad}^{pk} value for 40 ribbons was 0.77 K. However, this value is affected by the thermal mass of the sample holder (which, in this case, is not negligible with respect to the thermal mass of the sample), thermal contact between the ribbons, presence of vacuum grease (which, although in a minimal amount, is necessary to stack the pieces), etc. These factors, which are mainly associated with the geometry of the samples, will produce a lower value reported by the instrument compared to the value determined for the bulk sample.

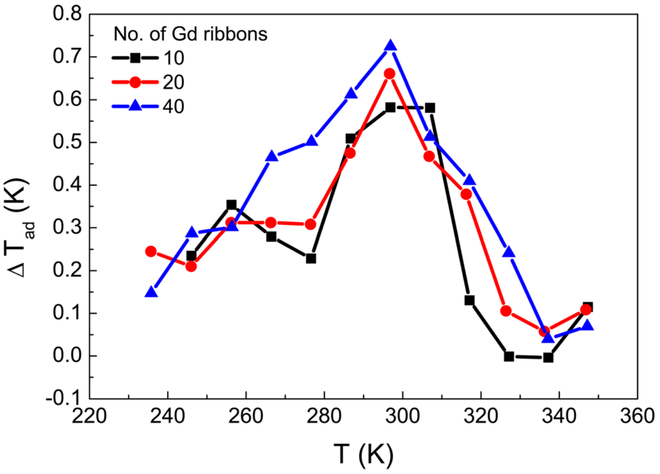

FIG. 3. (Color online) Temperature dependence of ΔT_{ad} (H = 1.775 T) for different number of pieces of Gd ribbons.

The ΔT_{ad} (T) curves of Gd ribbon stack containing 40 ribbons subjected to different magnetic field sweeping rates are shown in Fig. 4. For magnetic field sweep rate (dH/dt) of 3 Ts^{-1}, the ΔT_{ad} (T) curve was less noisy with a larger ΔT_{ad}^{pk} value of 0.99 K. The larger field ramp rate allows for a better approximation to adiabatic conditions and minimizes, to some extent, losses associated with the small thermal mass of the sample.

If the value provided by the MMS setup for the set of ribbons has to be corrected for the effect of their small thermal mass, it can be assumed that

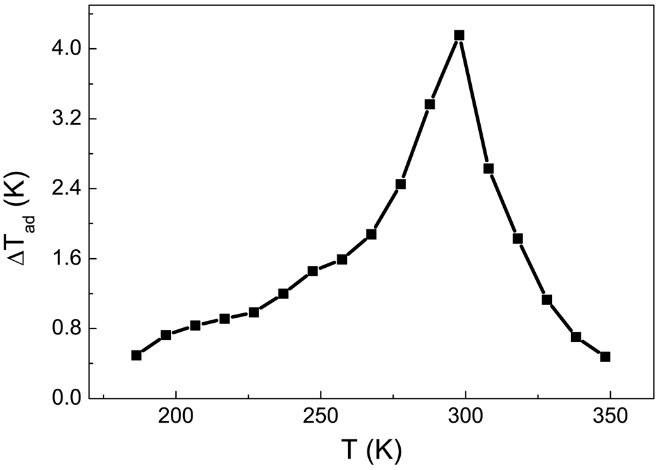

FIG. 2. Temperature dependence of adiabatic temperature change measured in Gd bulk sample (dH/dt = 1 Ts^{-1}, ΔH = ± 1.775 T).

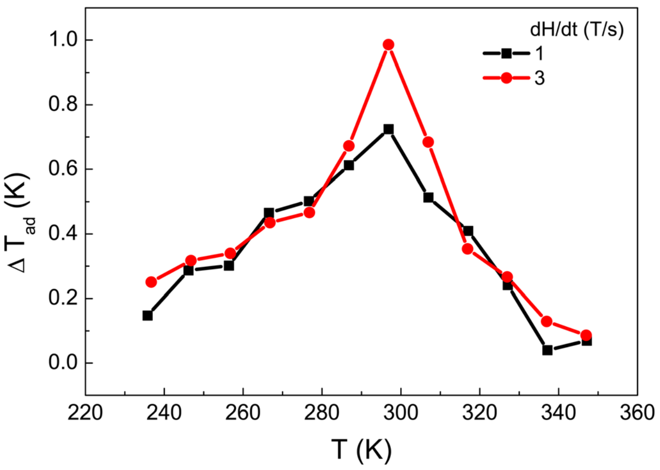

FIG. 4. (Color online) Temperature dependence of ΔT_{ad} for 40 Gd ribbons at various dH/dt.

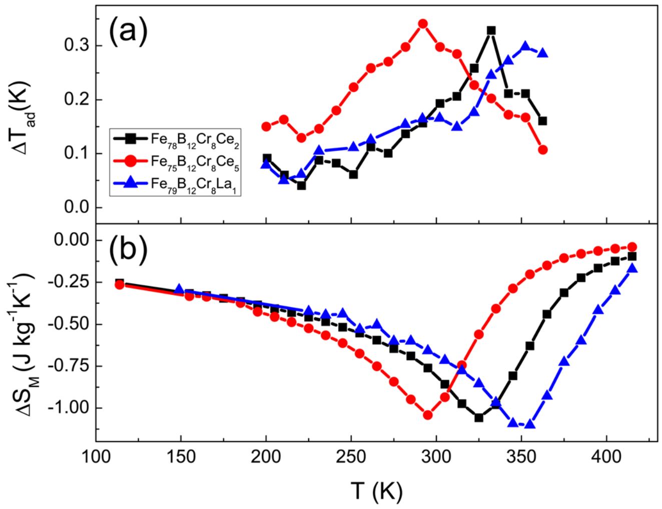

FIG. 5. (Color online) Temperature dependence of (a) ΔT_{ad} for dH/dt = 3 Ts^{-1} and (b) ΔS_M for the Fe-based ribbons.

$$\Delta T^{pk}_{ad}(corrected) = k\Delta T^{pk}_{ad}(ribbons), \tag{1}$$

where k is a proportionality constant, which depends on the thermal contact between the ribbon pieces and the sample holder, the number of pieces used, the field ramp rate, etc. For experiments performed under the same experimental conditions, the value of k should be independent of compositions. As mentioned before, after stacking a certain number of ribbons, the experimental value for ΔT^{pk}_{ad} is not altered, which demonstrates the weak dependence of k on the mass of the samples and simplifies the obtention of the corrected values of ΔT^{pk}_{ad}. For 40 pieces of Gd ribbon and a field ramp rate of 3 Ts^{-1}, $k \sim 4.2$ was determined from Eq. (1). This correction factor was used for the subsequent analysis of the rare-earth containing amorphous alloys measured under similar experimental conditions.

It is worth mentioning, however, that the adiabatic temperature change of materials with a second order phase transition have a typical caret-like shape and that it scales with field in a certain way.[13] Therefore, if a low mass sample is measured and it does not follow a caret-like behavior, the correction procedure described in this paper should not be used. Moreover, the temperature at which the peak entropy change and the peak adiabatic temperature change take place should be similar (within the experimental error).

The ΔT_{ad} (T) curves of $Fe_{80-x}B_{12}Cr_8RE_x$ (RE = Ce or La, x = 1–5 at.%) were plotted in Fig. 5. $Fe_{78}B_{12}Cr_8Ce_2$ melt-spun ribbons exhibited a $\Delta T^{pk}_{ad(ribbons)}$ of 0.33 K, occurring at 332 K, which agrees with the temperature of the peak magnetic entropy change (T_{pk}). When the ΔT^{pk}_{ad} of the ribbons was multiplied by the k factor determined earlier, $\Delta T^{pk}_{ad(corrected)}$ of 1.4 K was obtained (see Table I). For $Fe_{75}B_{12}Cr_8Ce_5$ melt-spun ribbons, ΔT^{pk}_{ad} of 0.34 K at 292 K was obtained in excellent agreement with its T_{pk}, its $\Delta T^{pk}_{ad(corrected)}$ value was also 1.4 K (Table I). The ΔT^{pk}_{ad} of $Fe_{79}B_{12}Cr_8La_1$ ribbons was observed to be 0.30 K at 352 K, which is also in agreement with its T_{pk}, the $\Delta T^{pk}_{ad(corrected)}$ value was estimated to be 1.3 K (Table I).

The adiabatic temperature change of a sample can be expressed as

$$\Delta T_{ad} = -\mu_0 \int_0^H \frac{T}{c_p}\left(\frac{\partial M}{\partial T}\right)_H dH. \tag{2}$$

If we approximate c_p as field independent, Eq. (2) can be rewritten as

$$\Delta T_{ad} \approx \frac{T\Delta S}{c_p}. \tag{3}$$

The specific heat capacity of La (188.41 J kg^{-1} K^{-1}) is larger than that of Ce (175.85 J kg^{-1} K^{-1}); this could explain why the La containing alloy has a lower ΔT^{pk}_{ad}.

The field dependence of ΔT^{pk}_{ad} as well as the corrections from experimental ribbon values to bulk-like form are presented in Table I. The direct MCE values of some other magnetocaloric materials are also listed. When the field dependence of $Fe_{78}B_{12}Cr_8Ce_2$ and $Fe_{75}B_{12}Cr_8Ce_5$ ribbons were calculated, they showed a ~ 58% larger ΔT^{pk}_{ad} than the corresponding values for $Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$ amorphous ribbon.[14] For $Fe_{79}B_{12}Cr_8La_1$ melt-spun ribbons, ΔT^{pk}_{ad} was ~ 42% larger than that of $Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$ ribbon.[14] The ΔT^{pk}_{ad} of our samples was ~ 33% higher than that of $GdAl_2$, ~ 20% smaller than

TABLE I. Peak temperature and peak adiabatic temperature change measured by MMS and calculated field dependences, including corrections from ribbons to bulk material form. For comparison, results for $Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$ alloy of Ref. 14, $REAl_2$ alloys, and $TbCo_2$ and RE_2Fe_{17} alloys from Ref. 9 are also presented.

Nominal composition	Crystallinity C - crystalline A - amorphous	Material form	$T_{pk(\Delta Tad)}$ ($T_{pk(\Delta S^{pk}_M)}$) (K)	ΔT^{pk}_{ad} (experimental, ribbon form) (K)	ΔT^{pk}_{ad} (corrected) (K)	ΔT^{pk}_{ad} /ΔH_{max} (corrected) (KT^{-1})	Ref.
Gd	C	Bulk	297	0.99 (1.775T)	4.2 (1.775T)	2.4	This work
$Fe_{78}B_{12}Cr_8Ce_2$	A	Ribbons	332 (325)	0.33 (1.775T)	1.4 (1.775T)	0.78	This work, (12)
$Fe_{75}B_{12}Cr_8Ce_5$	A	Ribbons	292 (295)	0.34 (1.775T)	1.4 (1.775T)	0.80	This work, (12)
$Fe_{79}B_{12}Cr_8La_1$	A	Ribbons	352 (348)	0.30 (1.775T)	1.3 (1.775T)	0.71	This work, (12)
$Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$	A	Ribbons	302	0.24 (2T)			14
$GdAl_2$	C	Bulk	168			0.6	9
$TbAl_2$	C	Bulk	107			1	9
$TbCo_2$	C	Bulk	232			1	9
Y_2Fe_{17}	C	Bulk	328			0.9	9
Nd_2Fe_{17}	C	Bulk	325			0.9	9

$TbAl_2$ and $TbCo_2$, and ~ 11% smaller than Y_2Fe_{17} and Nd_2Fe_{17} alloys.[9]

IV. CONCLUSIONS

The adiabatic temperature change of iron based amorphous alloy ribbons was directly measured. In order to extract the information which is characteristic of the material, the experimental results of bulk and ribbon shaped Gd samples have been used as calibrating samples. A correction factor was calculated for the experimental conditions used. The ΔT_{ad}^{pk} of $Fe_{78}B_{12}Cr_8Ce_2$ and $Fe_{75}B_{12}Cr_8Ce_5$ ribbons was ~ 58% larger than that of $Co_{82.9}Si_{5.9}Fe_{4.5}Cr_4B_{2.7}$ amorphous ribbon. The ΔT_{ad}^{pk} in $Fe_{78}B_{12}Cr_8Ce_2$, $Fe_{75}B_{12}Cr_8Ce_5$, and $Fe_{79}B_{12}Cr_8La_1$ ribbons displayed ~ 18–33% enhancement when compared to $GdAl_2$ bulk alloy.

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