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Influence of sample geometry on determination of magnetocaloric effect for $Gd_{60}Co_{30}Al_{10}$ glassy ribbons using direct and indirect methods

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ABSTRACT

Rare-earth based metallic glasses with high saturation magnetization show a sizeable magnetocaloric effect (MCE) and are subject of extensive research concerning magnetic refrigeration materials. In this work, the magnetic phase transition from paramagnetic to ferromagnetic of $Gd_{60}Co_{30}Al_{10}$ metallic glass has been characterized and three different methods were applied for the determination of its magnetocaloric specific parameters: (a) direct measurement of the adiabatic temperature change by exposing the material to an adiabatically applied magnetic field; (b) determination of the magnetization $M(H,T)$ and calculation of the temperature dependent magnetic field induced entropy change ΔS_m by application of the Maxwell relation and (c) measuring the total heat capacity $C_p(H,T)$ in zero and non-zero magnetic field. $Gd_{60}Co_{30}Al_{10}$ glassy ribbons were prepared by melt spinning, a technique that offers very high cooling rates due to the low dimensionality of the sample. Depending on the particular method of measurement, pieces of these glassy ribbons form samples with different appropriate total volume and dimensions. We show that the combination of the pronounced two-dimensionality of the ribbon pieces (aspect ratio ~ 100) together with the very high magnetic permeability principally can cause strong internal demagnetizing fields that cannot be neglected when evaluating the intrinsic MCE parameters obtained from different methods.

1. Introduction

The magnetocaloric effect is characterized by an adiabatic temperature change ΔT_{ad} of a magnetic material resulting from a magnetic entropy change ΔS_m upon the application and removal of a magnetic field [1–3]. Large MCE was found for crystalline materials with a first-order magneto-structural transition like $Gd_5(Si,Ge)_4$ [4], $La(Fe,Si)_{13}$ [5–8], MnAs [9,10], MnFe(P,As) [11–13] and Ni_2MnGa [14]. However, irreversible magnetic/structural processes related to the first-order transition, respectively, crystallinity of the material, that manifest themselves as magnetic and/or thermal hysteresis reduce the refrigeration efficiency. Materials with second-order magnetic phase transition generally exhibit a comparable lower maximal change of magnetic entropy. On the other hand the soft magnetic representatives of this species neither show magnetic nor thermal hysteresis and therefore they are also promising candidates for magnetic refrigeration. In most cases metallic glasses also show second-order magnetic phase transition with very low hysteresis losses, because the lack of long range atomic order prevents effective magnetic domain wall pinning (on the condition that residual stress/strain has been removed by proper heat treatment for most alloys). The maximum entropy change of Gd- [15–21], Dy- [22], Ho- [23] and Er-based [24] metallic glasses is comparable in size with that of conventional crystalline Gd [25] and, furthermore, the continuous variability of composition within a certain range allows to tune the ordering temperature. Additionally, the absence of atomic long range order causes high electrical resistivity and minimizes eddy current heating caused by fast varying magnetic fields [26].

In this work, the magnetic properties of $Gd_{60}Co_{30}Al_{10}$ glassy ribbons have been determined and the MCE has been evaluated by three different methods: (a) by direct measurement of the adiabatic temperature change $\Delta T_{ad}(T)$ by exposing the material to an adiabatically applied magnetic field; (b) by determination of the magnetization $M(H,T)$ and calculation of the temperature dependent magnetic field induced entropy change $\Delta S_m(T)$ by application of the Maxwell relation. $\Delta T_{ad}(T)$ can be obtained therefrom, once the heat capacity in zero magnetic field $C_p(0,T)$ has been measured; and (c) by measuring the heat capacity $C_p(H,T)$ in zero and non-zero magnetic field and deriving $S_m(H,T)$ from which $\Delta S_m(H,T)$ and $\Delta T_{ad}(T)$ were determined. The maximal magnetic field change was technically limited to 1.9 T for the direct measurement and this maximal field was also used for the

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other methods. Principally, the preparation of metallic glasses requires high cooling rates of the metallic melt. Melt spinning is a commonly used technique offering very high cooling rates by producing ribbons that are several mm broad, but only several tens of micrometers thick. Pieces of these ribbons naturally possess very large aspect ratios in the range of ~ 100. However, the combination of the pronounced two-dimensionality of the sample in the as prepared state together with the very high permeability that is prerequisite for a high MCE can lead to strong internal demagnetizing fields in dependence on sample form and orientation with respect to the applied magnetic field. While the effect of demagnetizing fields on the magnetocaloric properties is of importance for any kind of material with high permeability [27] it naturally emerges for metastable metallic glasses that have to be prepared with pronounced low dimensionality and resulting high aspect ratio of individual sample pieces. Each method for determining the MCE specific values poses different requirements for the total volume and the dimensions of the sample. Therefore, the effect of demagnetizing fields has to be taken into consideration when comparing the results obtained from different methods.

2. Experimental

Pre-alloyed $Gd_{60}Co_{30}Al_{10}$ ingots were prepared by arc-melting of elements with a purity of 99.9 at.% or better (purity against other rare-earth elements, oxygen content was not determined) in a Ti-gettered argon atmosphere. For reaching homogeneity, the sample was remelted several times. From this pre-alloy, a 5 mm wide and approximately 35 μm thick amorphous ribbon was prepared by means of rapid quenching from the melt using a single-roller melt-spinner under argon atmosphere. The amorphous structure was checked by X-ray diffraction (XRD) using a Panalytical X'Pert PRO diffractometer in reflection geometry and Co-K_α radiation. Ac and dc magnetic measurements were done with a MPMS (Quantum Design) and heat capacity was measured with a standard puck for PPMS (Quantum Design) applying the relaxation method. Direct measurements of the adiabatic temperature change T_{ad} were performed in a home-built experimental setup [28]. The magnetic field was produced by permanent magnets in the Halbach-cylinder configuration. Melt-spun ribbons were milled into powder with maximum size 50−100 μm and formed to a square block of $10 \times 5 \times 5$ mm^3 with the thermocouple inside under 20 MPa pressure using a special-designed press-form. Finally, the specimen was fixed on nylon threads to maintain adiabatic conditions. For the same reason all measurements were performed in high vacuum. The external magnetic field was measured by a Hall probe.

3. Results and discussion

Magnetization M was determined as a function of temperature T at various constant magnetic fields $\mu_0 H_0 =$ 0.01, 0.1, 0.5, 1 and 2 T. The temperature of highest slope $(\delta M/\delta T)_{max}$ does not show a shift in temperature in dependence of the applied magnetic field H_0 within the experimental accuracy and is 140(1) K for $\mu_0 H_0 = 10$ mT (Fig. 1). From the slope of the linear dependence of inverse dc susceptibility versus temperature in the paramagnetic region an effective magnetic moment $\mu_{eff} = 7.24(7)\mu_B$ and the Weiss constant $\theta = 149(2)$ K were obtained. The ac-susceptibility χ_{ac} was determined for 10 and 1000 Hz at different constant magnetic fields $\mu_0 H_0 =$ 0, 0.1, 0.5, 1 and 2 T. There is no dependence on frequency and the susceptibility's real part χ'_{ac} has a maximum at the critical temperature T_c in zero magnetic field that is shifted in an applied field according to $(\mu_0 H_0)^{2/3}$ (Fig. 1). After [29] this 2/3 power law can be described within the mean-field Landau's theory for a second-order phase transition independently of a spin model. From the $(\mu_0 H_0)^{2/3}$ fit, T_c is precisely determined to be 140.7(2) K. The fact that θ is pretty close to T_c indicates that no magnetic frustration is present in this system. Altogether, $Gd_{60}Co_{30}Al_{10}$ represents a high spin magnetic system with a sharp second-order transition at medium temperature to a very soft ferromagnetic phase. This is mainly due to the fact that Gd as S state rare-earth element excludes spin-orbit coupling. Therefore, only magnetic shape anisotropy plays a role for the sample investigated in this work. In order to investigate the effect of magnetic shape anisotropy in dependence of the specimen dimensions two different types of samples were prepared for magnetization measurements: On the one hand a $3.0(1) \times 3.0(1) \times 0.033(3)$ mm^3 sheet (total mass: 2.33(1) mg) was cut from the glassy ribbon. On the other hand another piece of a ribbon was thoroughly ground in a mortar and particles with a volume diameter less than 0.01 mm (total mass of 3.75 mg) were selected with a sieve and strewed into a cylindrical gelatine container (diameter: 3 mm) to form a loose accumulation of ribbon pieces that were fixed with glue.

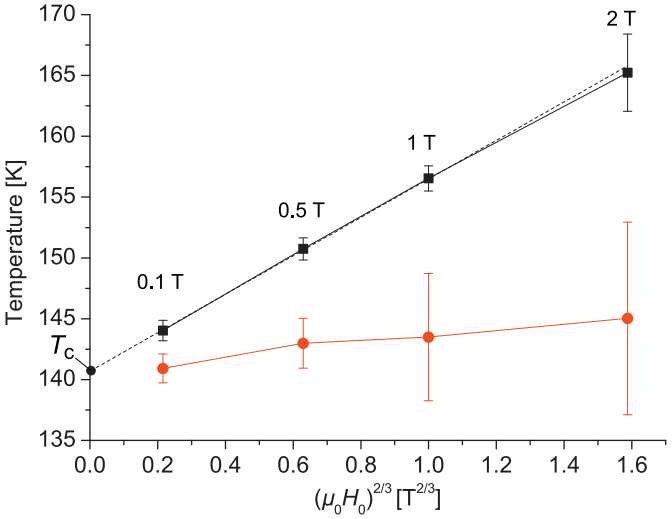

Fig. 1. Temperatures of highest slope $(\delta M/\delta T)_{max}$ (filled circles) and temperatures of the ac-susceptibility's real part maximum $T(\chi_{AC,max})$ (filled squares) vs. $(\mu_0 H_0)^{2/3}$ for different constant magnetic fields $\mu_0 H_0 =$ 0, 0.1, 0.5, 1 and 2 T. The dashed line indicates the 2/3 power law of the latter quantity.

For each type the magnetization M_z was measured as a function of magnetic field H_z ($\mu_0 H_{max} = 1.9$ T) and temperature T (60–200 K, $\Delta T = 10$ K) with two different orientations of the sample, i.e. with H_z parallel and perpendicular to the sheet's, respectively, to the container bottom's surface. Fig. 2 exemplarily shows $M_z(H_z,T)$ for the sheet form sample with the surface parallel (a) and perpendicular (b) to H_z. Most strikingly is the large difference of initial susceptibility (up to 50 Oe) below T_c for parallel ($\chi_{para}^{60\,K} =$ 90090(10)) and perpendicular ($\chi_{perp}^{60\,K} = 3349(10)$) orientation. For the latter the magnetization even at maximum field strength is considerably smaller. Also in the paramagnetic regime there still exists a difference of susceptibility between the two different orientations ($\chi_{para}^{200\,K} =$ 91(1), $\chi_{perp}^{200\,K} =$ 77(1)). In perpendicular orientation much more hypothetical magnetic surface charges are built up on the large area ($3.0(1) \times 3.0(1)$ mm^2) that is perpendicular to the field direction and cause a much stronger demagnetization field than in parallel orientation ($3.0(1) \times 0.033(3)$ mm^2) (see [30,31] for further information). Only for a homogeneous body whose surface is of the second degree, as for example the ellipsoid, the magnetic field as well as