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Impact of structural disorder on the magnetic ordering and magnetocaloric response of amorphous Gd-based microwires

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We have studied the impact of structural disorder on the magnetic ordering and magnetocaloric response of amorphous $Gd_{68}Ni_{32}$ and $Gd_{53}Al_{24}Co_{20}Zr_3$ microwires. We find that the presence of structural disorder significantly broadens the paramagnetic to ferromagnetic (PM-FM) transition and the temperature-dependent magnetic entropy change, while the nature of the second-order magnetic transition and long-range ferromagnetic order are not essentially affected by this effect. The large magnetic moment of Gd and the presence of the long-range ferromagnetic order are believed to result in a large magnetic entropy change, which together with the broadening of the PM-FM transition due to structural disorder contribute to a large refrigerant capacity. The excellent magnetocaloric properties of the amorphous microwires make them very promising candidates for active magnetic refrigeration. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4864143]

Magnetic refrigeration based on the magnetocaloric effect (MCE) is considered to be a viable alternative to conventional gas compression refrigeration technologies.[1] Generally magnetic materials exhibiting large MCE (e.g., the large isothermal magnetic entropy change or the large adiabatic temperature change) over a wide temperature range are promising magnetic refrigerants. In addition, it is desirable for a magnetic refrigerant to have minimal magnetic hysteresis and eddy current losses. In this context, exploring the MCE in soft ferromagnetic amorphous materials is of practical importance,[1–4] since these materials exhibit negligible magnetic hysteresis and possess reduced eddy current losses as compared to their crystalline counterparts. In particular, those developed recently in the form of microwires are very interesting, as they show large MCE and large refrigerant capacity (RC).[5,6] Relative to their bulk counterparts, these microwires possess enhanced surface areas desirable for heat transfer, and a magnetic bed made of these microwires is highly preferable for engineering actual magnetic regenerators.[6–8] Apart from their technological relevance, the magnetic structures in amorphous materials are often complicated, mainly due to the presence of structural disorder.[2] While the MCEs have been reported in various amorphous magnetic systems,[1–8] the impact of structural disorder on the magnetocaloric response, such as the broadening of the magnetic ordering transition[2] and the enhancement of the RC,[6] remains to be investigated. Such knowledge is essential to gain better control over the material performance.

To shed some light on this important issue, we have performed a systematic study of the impact of structural disorder on the magnetic ordering and magnetocaloric response of amorphous $Gd_{68}Ni_{32}$ (sample A) and $Gd_{53}Al_{24}Co_{20}Zr_3$ (sample B) microwires.

The microwires were fabricated using a home-built-melt-extraction technique.[6] The X-ray diffraction patterns confirmed the amorphous nature of the fabricated microwires. The average diameter of the wires was determined from scanning electron microscopy to be $\sim 50\,\mu$m. A quantum design physical property measurement system equipped with a vibrating sample magnetometer probe was used to investigate the magnetic and magnetocaloric properties of the fabricated microwires.

The temperature dependence of magnetic susceptibility $[\chi(T)]$ reveals a paramagnetic to ferromagnetic (PM-FM) transition at $T_C \sim 122$ K and ~ 97 K for sample A and sample B, respectively (Fig. 1(a)). We studied the magnetic field dependence of magnetization [M(H)] at different temperatures (T) in the magnetic field range of 0–30 kOe. As an example, the isothermal $M(H)$ curves of sample A are shown in the inset of Fig. 1(a). From the isothermal M(H) curves, ΔS_M was calculated using the Maxwell's relation[1] $\Delta S_M = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH$, where M is the magnetization, H is the magnetic field, and T is the temperature. Figure 1(b) shows the temperature dependence of ΔS_M for sample A for different magnetic fields, and the inset of Fig. 1(b) shows the $\Delta S_M(T)$ curves for both sample A and sample B for $\mu_0 \Delta H = 30$ kOe. Both samples exhibit large ΔS_M around their T_C. In fact, for $\mu_0 \Delta H = 30$ kOe, the maximum value of ΔS_M near T_C (ΔS_M^{max}) is ~ 4.5 J/kg K for sample A, while it is

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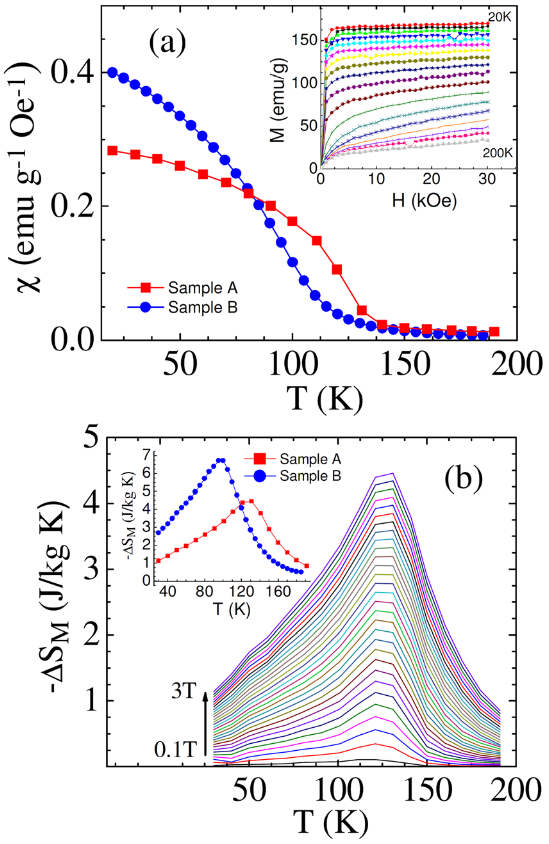

FIG. 1. (a) Temperature dependence of magnetic susceptibility at a field of 500 Oe for sample A and sample B. Inset shows the isothermal $M(H)$ curves of sample A; (b) temperature dependence of $-\Delta S_M$ at different fields for sample A. Inset shows the temperature dependence of $-\Delta S_M$ for $\mu_0\Delta H = 30$ kOe for samples A and B.

~7 J/kg K for sample B (inset, Fig. 1(b)). These values of ΔS_M^{max} are considerably larger than those reported for other microwires.[5,7] For $\mu_0\Delta H = 30$ kOe, the ΔS_M^{max} for $Gd_{68}Ni_{32}$ is almost 1.5 times larger than that obtained for a bulk amorphous $Gd_{70}Ni_{30}$ alloy.[2] Besides ΔS_M, RC—an important figure of merit of a magnetic refrigerant material—was calculated as[1] $RC = -\int_{T_1}^{T_2} \Delta S_M(T)dT$, where T_1 and T_2 are the temperatures corresponding the full width at half maximum of a $\Delta S_M(T)$ curve. For $\mu_0\Delta H = 30$ kOe, the RC values of sample A and sample B are determined to be ~322 J/kg and ~415 J/kg, respectively. The large values of RC make the present microwires very promising candidates for active magnetic refrigeration.[8]

Now, we attempt to elucidate the effect of structural disorder on the nature of magnetic phase transition of the microwires. Conventionally, the type of magnetic phase transition is determined from Arrott plots using Banerjee's criterion.[9] However, if a first-order phase transition (FOPT) is too weak to have a significant impact on the free energy derivative at the transition, this method can be insufficient to discriminate FOPT from the second-order phase transition (SOPT).[10] On the other hand, for ferromagnetic systems undergoing SOPT, a universal curve can be constructed to describe $-\Delta S_M(T)$ at different H. All $-\Delta S_M(T)$ curves obtained for different H can be collapsed into a universal master curve, when ΔS_M is normalized to ΔS_M^{max} and the temperature axis is rescaled as[11]

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C) & T \le T_C \\ (T - T_C)/(T_{r2} - T_C) & T \ge T_C, \end{cases} \tag{1}$$

where T_{r1} and T_{r2} are two reference temperatures below and above T_C satisfying the relation, $\Delta S_M(T_{r1}) = \Delta S_M(T_{r2}) = f \times \Delta S_M^{max}$, with $f = 0.5$ for this study. It has been pointed out that the existence of a universal behavior of $-\Delta S_M(T)$ is a conclusive proof of the SOPT nature.[10] For the FOPT, however, such a universal curve cannot be constructed. As shown in Figs. 2(a) and 2(b), a universal behavior does hold for both the microwire samples, confirming the SOPT type of the materials. This result clearly indicates that the presence of structural disorder in the amorphous microwires broadened the PM-FM transition and the $-\Delta S_M(T)$ curve, while preserving the nature of the SOPT transition.

It is widely accepted that the magnetism of Gd-based crystalline alloys is dominated by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, which is long-range ferromagnetic in nature and often described by the mean-field theory.[2] However, amorphous $Gd_{65}Mn_{35-x}Ge_x$ ($x = 0$, 5, and 10) alloys were reported to show short-range ferromagnetism, where the mean-field theory failed.[12] It is therefore essential to understand how the structural disorder impacts the magnetic ordering in our amorphous microwires. In an earlier study, using the mean-field methodology, Oesterreicher and Parker have shown that ΔS_M follows a power law dependence of magnetic field: $\Delta S_M \sim H^n$ with n

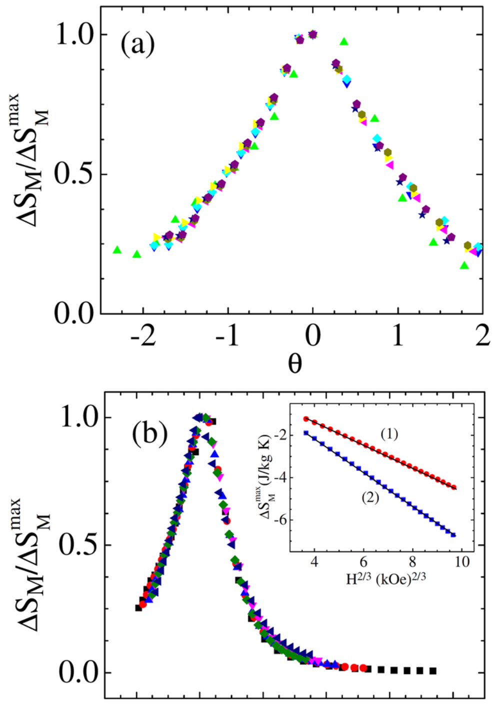

FIG. 2. Universal $\Delta S_M/\Delta S_M^{max}$ vs. θ curve for (a) sample A and (b) sample B. Inset shows the $-\Delta S_M^{max}$ vs. $H^{2/3}$ curves for (1) sample A and (2) sample B.

$\approx 2/3$ at a transition temperature.[13] A more general framework has been formulated later by Franco *et al.* to find out the local exponent n for any ferromagnetic materials obeying the mean-field theory.[11] According to this approach, n can be associated with δ and β as $n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right)$. According to the mean-field theory, the values of β, γ, and δ should be 0.5, 1, and 3, respectively, yielding $n = 2/3$.[13] We have examined the magnetic field dependence of ΔS_M near T_C for both samples and obtained a linear relationship between $-\Delta S_M^{max}$ vs. $H^{2/3}$ with an intercept at the $-\Delta S_{Max}$ axis (see inset of Fig. 2(b)). This result suggests that our present samples follow the mean-field theory, with long-range ferromagnetic interactions.

Using the mean-field approach, the magnetic entropy $S(\sigma)$ of a ferromagnetic system can also be expressed as[14]

$$-\Delta S(\sigma) = \frac{3}{2}\frac{J}{J+1}NK_B(\sigma^2 - \sigma^2_{spont}), \tag{2}$$

where N is a number of spins, J is a spin value, k_B is the Boltzmann constant, σ is the reduced magnetization, σ_{spont} is the reduced spontaneous magnetization. From Eq. (2), it is obvious that ΔS vs. σ^2 plots below T_C must have a horizontal drift from the origin, which corresponds to σ_{spont}. Similarly, if a $-\Delta S_M$ vs. M^2 plot for a ferromagnetic system shows a linear dependence with a constant slope and a horizontal drift from the origin below T_C, it can be assumed that Eq. (2) and so the mean-field theory is valid for that system. Furthermore, it is possible to determine its spontaneous magnetization (M_{sp}) from the horizontal drift of $-\Delta S_M$ vs. M^2 curves from the origin.

For samples A and B, the $-\Delta S_M$ vs. M^2 curves at different temperatures are linear with nearly constant slope in the entire temperature range below T_C (the non-linearity of the curve is only observed at very low fields when magnetic domains start to be formed), as shown in the insets of Figs. 3(a) and 3(b) for selected temperatures. We calculated M_{sp} at different temperatures from the horizontal shifts of the curves, the results of which are in excellent agreement with those obtained from the conventional method using Arrott plots (see Figs. 3(a) and 3(b)). It appears that in the paramagnetic region ($T > T_C$), the $-\Delta S_M$ vs. M^2 curves pass through the origin as M_{sp} do not exist. This further proves that the present microwires obey the mean-field theory and that the long-range ferromagnetic interactions occur in these systems.

In summary, we have demonstrated that the presence of structural disorder significantly broadens the magnetic transition and the temperature-dependent magnetic entropy change in amorphous $Gd_{68}Ni_{32}$ and $Gd_{53}Al_{24}Co_{20}Zr_3$ microwires. The large magnetic moment of Gd and presence of the long-range ferromagnetism are believed to retain the large magnetic entropy change, which, together its large temperature distribution caused by the structural disorder, contributes to the large refrigerant capacity in the amorphous microwires.

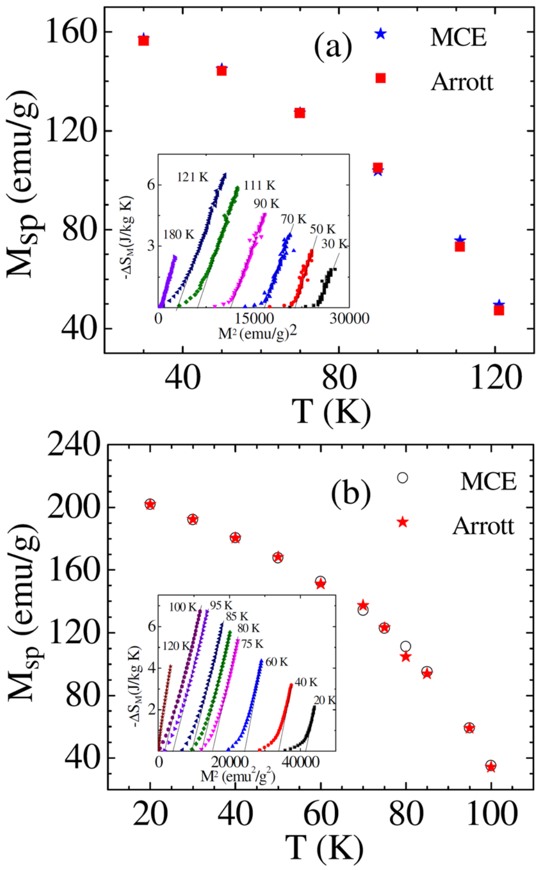

FIG. 3. Comparison between the spontaneous magnetization (M_{sp}) at different temperatures calculated from the magnetocaloric data and Arrott plots for (a) sample A and (b) sample B. Insets show the $-\Delta S_M$ vs. M^2 plots for selected temperatures.

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