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Magnetocaloric (Fe–B)-based amorphous alloys

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ABSTRACT

We report on the systematic variation of the Curie temperature in Fe–B-based amorphous alloys, which are potential candidates for magnetocaloric cooling applications. Fe–B-based amorphous alloys doped with nonmagnetic atoms (Nb, Y) were prepared by rapid quenching from the liquid state using the melt-spinning technique. By varying the atomic fraction of nonmagnetic dopants, the Curie temperature T_C decreases systematically and approaches room temperature. At the same time, the maximum of the magnetic entropy change decreases upon doping. For the alloys with T_C closest to room temperature, the magnetic entropy change is of comparable magnitude ($\Delta S_{mag} \sim 1.3$ J/kg K) despite a large difference in Fe content.

1. Introduction

A material with second-order ferromagnetic to paramagnetic transition changes temperature when exposed to alternating magnetic fields at temperatures close to the Curie temperature. This phenomenon is called the magnetocaloric effect [1–3] and it might be the working principle of an alternative "magnetic" cooling technology for consumer use in the near future. Since the discovery of materials with large ("giant") magnetocaloric responses [2], research in this area has taken up pace [3].

The magnetocaloric effect is usually quantified by the isothermal magnetic entropy change (ΔS_{mag}), which is derived from the Maxwell relations to be [3]:

$$\Delta S_m = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH \quad (1)$$

The largest values of the magnetic entropy change are currently attained using materials which undergo a magnetostructural transition [4–7]. However, large hysteresis losses and mechanical instability upon magnetic field reversal limit their application potential in a cooling device. This is why magnetocaloric materials with second order magnetic transition are studied as alternative materials. Materials with second-order magnetic transition show no structural transition at the Curie temperature that could enhance the change of magnetization [8,9]. Hence, particularly the amorphous magnetocaloric materials exhibit smaller changes of the magnetic entropy for a given change of field ΔH than first order materials. At the same time, however, they offer a broader operating range compared to first order materials. Fe-based amorphous alloys [10–15] are prototypical second-order type materials, which are also particularly cheap since they mainly consist of Fe, a clear advantage compared with rare-earth-based alloys [16–22]. Fe-based amorphous alloys have excellent soft-magnetic properties and hence do not generate hysteresis losses upon magnetic field reversal [8]. Moreover, they exhibit good corrosion resistance and their production can easily be adapted to the requirements of large scale production. Ideally, for an application as a refrigerator, the Curie temperature is close to room temperature. In Fe-based amorphous alloys, the Curie temperature T_C is known to be easily adjustable [11,13,23–25] without drastic effects on the magnetocaloric performance, i.e. the magnetic entropy change.

However, considering the many possibilities to vary the composition in amorphous Fe-based alloys, a systematic understanding of the Curie temperature dependence upon dopant variation and its consequences for the tuning of the magnetocaloric effect is still lacking for amorphous Fe-based alloys. In this paper, we show that the Curie temperature is systematically adjustable in ternary Fe–B-based alloys, when Fe is replaced with a nonmagnetic atom.

2. Material and methods

Amorphous ribbons of $Fe_{88}B_{12-x}Nb_x$ ($x=8$, 9, 10), $Fe_{86-x}B_{14}Nb_x$ ($x=2$, 4, 6, 8) and $Fe_{83}B_{17-x}Y_x$ ($x=5$, 10, 22) were prepared by rapid quenching of the melt on a copper wheel [8]. The rotation

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speed of the wheel was $v=41$ m s^{-1}. The prepared ribbons have a width of approximately $w=4$ mm and a thickness in the range of $d=50-70$ μm. The amorphous nature of the metals was confirmed by X-ray diffraction using Cobalt K_α radiation. Magnetic measurements were performed using a SQUID magnetometer (MPMS, Quantum Design®). For measurements of the magnetization as a function of magnetic field, the magnetometer was equipped with a furnace to reach temperatures up to $T=600$ K. At these high temperatures, a capillary made of borosilicate glass with an inner diameter of $d_i=1$ mm was used as a sample holder. The magnetic moment of the sample was determined for fields up to $\mu_0 H=2$ T, at temperatures around the Curie point of each material. For these measurements, the temperature was varied in increments of $\Delta T=10$ K. From the magnetization curves, the change in magnetic entropy was calculated using a numeric approximation [3] of the Maxwell relation [2]:

$$|\Delta S_{mag}| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i \quad (2)$$

3. Results

The results for the magnetic entropy change are shown in Figs. 1–3 for the three alloy systems studied in this paper. The magnetic entropy change ΔS_{mag} for each alloy shows the typical dependence on temperature, with a local maximum corresponding to the largest change of entropy and accordingly the largest change of magnetization (cf. Eq. (1)). For all compositions, the magnitude of the magnetic entropy change decreases only moderately upon dopant introduction, reaching values which are typically around $\Delta S_{mag}=1.5$ J/kg K. Overall, the Curie temperature, which approximately corresponds to the maximum position of ΔS_{mag}, decreases upon substituting Fe atoms with nonmagnetic dopants, i.e. Nb or Y. The Curie temperature can be shifted over large temperature intervals by changing the dopant fraction, e.g. in $Fe_{86-x}B_{14}Nb_x$ from $T_C=523$ K (Nb=2 at%) to $T_C=374$ K(Nb=8 at%). The Curie temperatures closest to room temperature are $T_C=295$ K for Y=22 at% in the series $Fe_{83}B_{17-x}Y_x$ (see Fig. 3) and $T_C=306$ K for Nb=9 at% in the series $Fe_{88}B_{12-x}Nb_x$ (see Fig. 1).

In the following, we present a summary of our data regarding the Curie temperature of the Fe-based amorphous alloys (black points in Fig. 4). The magnetic ordering temperature T_C is plotted as a function of the Fe content for all studied alloys in Fig. 4. Literature data [26–28] has been added to support our findings (grey points). From Fig. 4, it can be seen that the Curie temperature of the studied Fe–B-based amorphous alloys is linearly proportional to their Fe atomic fraction. For the Nb-doped alloys, T_C increases by approximately 22.6 K for every 1 at% rise of the Fe content. This is the same rate of change as it has been found for another Nb doping series in the literature [28]. Similarly, for the Y-doped alloys, T_C increases by approximately 14.9 K for every 1 at% change of the Fe fraction. For Nd-doped alloys, T_C values studied by Hassanain et al. [27] have been added to the graph. For Nd doping, T_C increases by approximately 10.8 K for every 1 at% change in Fe content.

For comparison, we have plotted the Curie temperature of binary, undoped $Fe_{100-x}B_x$ ($12 \le x \le 28$) amorphous alloys, the data of which can be found in the literature [26]. The Curie temperature decreases with increasing Fe content for high B contents. Starting from this curve for the binary alloys, all of our measured data and the data from the literature for other Fe-based amorphous alloys with different compositions can be understood in the following simple framework, which can be regarded as an instruction for tuning T_C in magnetocaloric amorphous Fe–B-based alloys.

For estimating the Curie temperature of Fe–B-based amorphous alloys, the B content of the undoped alloy plays a crucial role, since it determines the starting point (T_C vs. Fe content) for each doping series. From this point, introducing nonmagnetic atoms (Nb, Nd or Y) for Fe leads to decrease of the Curie temperature. The rate of the T_C decrease seems to depend on the element used for doping. By

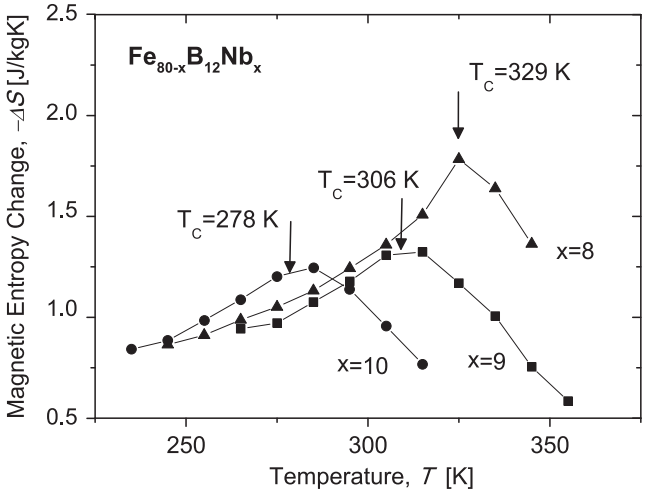

Fig. 1. Magnetic entropy change for $Fe_{88}B_{12-x}Nb_x$ ($x=8, 9, 10$) vs. temperature for a field change of $\Delta H=2$ T.

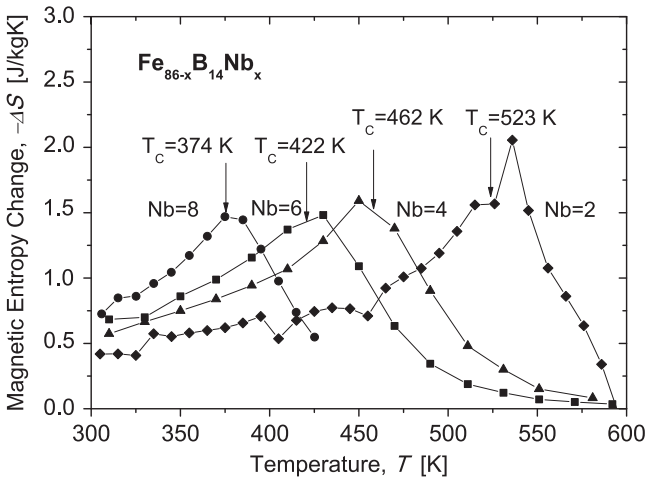

Fig. 2. Magnetic entropy change for $Fe_{86-x}B_{14}Nb_x$ ($x=2, 4, 6, 8$) vs. temperature for a field change of $\Delta H=2$ T.

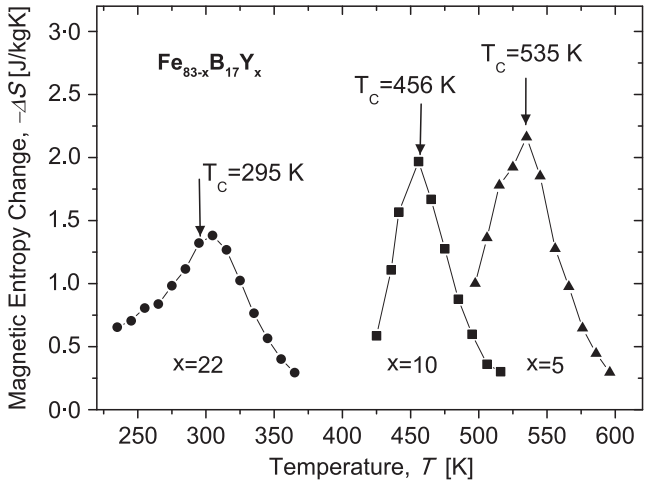

Fig. 3. Magnetic entropy change for $Fe_{83}B_{17-x}Y_x$ ($x=5, 10, 22$) vs. temperature for a field change of $\Delta H=2$ T.