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Magnetic properties and magnetocaloric effect of melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys

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The $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys obtained by rapid quenching from the melt have been studied by X-ray diffraction and magnetization measurements in order to reveal how the substitutions in the 3*d*-metal subsystem at the constant Gd content affect the magnetic and magnetocaloric properties of alloys. The glass forming ability is observed to decrease with increasing Fe content in $Gd_{75}(Co_{1-x}Fe_x)_{25}$. The magnetic state of all the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys is characterized as ferrimagnetic one. Assuming the magnetic moment of Gd to be constant (7 μ_B), it is found that the magnetic moment per transition metal atom varies from 1.6 μ_B in $Gd_{75}Co_{25}$ (x = 0) to 1.1 μ_B in the $Gd_{75}Fe_{25}$ (x = 1) melt-spun alloy. The replacement of Co by Fe atoms allows tuning the magnetocaloric properties and working temperature intervals of alloys.

1. Introduction

Although the history of the study of magnetism in amorphous alloys containing rare earth (R) metals has been going on for several decades, interest in their research has not weakened to this day. Amorphous R-based alloys have been used as a magnetic thin film with magnetic bubble domains for magneto-optical (thermomagnetic) recording [1,2]. Some of these alloys were observed to exhibit increased coercivity at low temperature [3,4]; amorphous Gd-Co alloys demonstrate invar effects [5] and outstanding magneto-thermal properties [6–8]. The study of the magnetocaloric effect (MCE) in R-containing intermetallic compounds and amorphous alloys substantially expanded after the discovery of the giant MCE around room temperature in the $Gd_5(Si_2Ge_2)$ compound exhibiting the magnetostructural transition of the first-order type [9]. Compounds and alloys with high gadolinium content are considered most preferred for use in magnetic cooling devices [10]. Highest rare-earth content within the binary Gd-Co family exhibits the intermetallic compound Gd_3Co. It crystallizes in a low symmetry orthorhombic structure of the Fe_3C type (space group *Pnma*) [11–13]. The Gd_3Co is an antiferromagnet (AF) with T_N = 131 K [14] having a complicated non-collinear magnetic structure which arises from the indirect exchange interaction of RKKY-type (Ruderman-Kittel-Kasuya-Yosida) between the highly localized Gd 4*f*-electrons. There is no evidence in the literature that the Co atoms carry an ordered magnetic moment in crystalline R_3Co. However, a reduced magnetic moment per Gd ion observed in the amorphous $Gd_{75}Co_{25}$ alloy at low temperature was considered as an indication of the appearance of a magnetic moment on Co atoms [15]. This assumption is supported by the fact that the amorphous Gd-rich Gd-Co alloys exhibit enhanced values of the magnetic ordering temperatures (from 145 K up to 190 K [6,15–24]).

According to the Gd-Fe phase diagram the crystalline compounds with the Gd contents higher than 33.3 at.% don't exist. However, a partial substitution of Fe (up to 10 at.%) for Co in the crystalline compound Gd_3Co is observed to reduce the critical field of the metamagnetic transition toward zero [25]. As it turned out, the Gd-Fe alloys enriched by Gd above 33.3 at.% may be obtained by rapid solidification because of the presence of eutectic composition at about of 70 at.% and a low melting point. It should be noted that there is substantial scatter in the Curie temperatures of Gd-rich Gd-Fe amorphous alloys obtained by different authors. Yano et al. [26–28] found the concentration dependence of T_C for melt-spun $Fe_{100-x}Gd_x$ alloys with maximum $T_C(x)$ value at x = 40; for the $Gd_{70}Fe_{30}$ the T_C value was obtained to be 395 K unlike T_c = 297 K reported by Foldeaki et al. [29] for the alloy with the same composition. In both these cases, T_C exceeds the magnetic ordering temperatures obtained in [30,31].

Assuming that the Gd magnetic moment is equal to 7 μ_B in all the melt-spun $Fe_{100-x}Gd_x$ alloys the magnetic moment of Fe ion was estimated from the magnetization data to be about 2 μ_B in the concentration range 18 ≤ x ≤ 70 [27,28,31]. However, for vapor deposited films, the Fe magnetic moment was observed to decrease linearly with increasing Gd concentration [31]. For instance, the Fe magnetic moment is estimated as 1.4 μ_B for x = 60 [28].

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Bearing in mind the presence of contradictory data in the literature in respect to the magnetic characteristic of Gd-based amorphous alloys we, in the present work, obtained the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys and studied their properties in order to reveal how the Fe for Co substitution keeping the Gd content invariable affects the magnetic characteristics and magnetocaloric effect.

2. Experimental

The $Gd_{75}(Co_{1-x}Fe_x)_{25}$ samples with x = 0, ¼, ½, ¾, and 1 were prepared in two stages. At first, the crystalline samples were obtained by arc-melting in a helium atmosphere. To obtain the uniform composition of samples, the ingots were turned over after each melting in the arc furnace and melted repeatedly. Then, the liquid quenched samples were prepared by a melt-spinning technique in argon atmosphere onto a rotating copper wheel with a surface velocity of 50 m/s. The x-ray diffraction (XRD) patterns have been measured at room temperature using a diffractometer with monochromatic Cr Kα radiation. The magnetic measurements were performed by means of a SQUID magnetometer (Quantum Design MPMS-7XL, USA) in magnetic fields up to 70 kOe and in the temperature range from 2 K to 350 K. To obtain the data on magnetic part of the isothermal entropy change (ΔS_m) we used an indirect method based on the thermodynamic Maxwell relations [32]: $\Delta S_m = S_m(T, H_f) - S_m(T, 0) = \int_0^{H_f} \left(\frac{\partial M}{\partial T}\right)_H dH$, where H_f is the maximum magnetic field. The magnetization was measured with a sufficiently high precision (< 1%). As for calculating the entropy changes, the error in determining ΔS_m can be estimated at about 5%. Apart from the value of ΔS_m the refrigerant capacity values were determined by numerically integrating of the $\Delta S_m(T)$ curve [33]: $q = -\int_{T_1}^{T_2} \Delta S_m(T) dT$, where T_1 and T_2 are temperatures at half maximum of the $-\Delta S_m$ peak as the integration limits.

3. Results and discussion

The XRD patterns for the $Gd_{75}(Co_{1-x}Fe_x)_{25}$ samples obtained by melt-spinning technique are presented in Fig. 1. Two broadened peaks are observed for all investigated samples in the vicinity of $2\Theta \approx 50°$ and 90° indicating that the samples are mostly amorphous. However, the Bragg peaks from the crystalline Gd_3Co-type phase are found to persist after rapid solidification. As can be seen from Fig. 1, the Bragg peaks from crystalline phases became more visible in the pattern for $Gd_{75}Fe_{25}$.

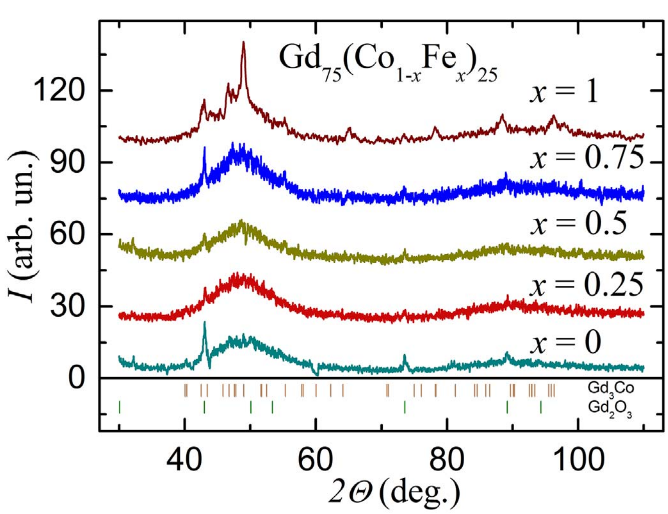

Fig. 1. X-ray diffraction patterns of the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys. Vertical bars indicate the main Bragg peaks positions for the crystalline Gd_3Co (upper row) and Gd_2O_3 (lower row) phases.

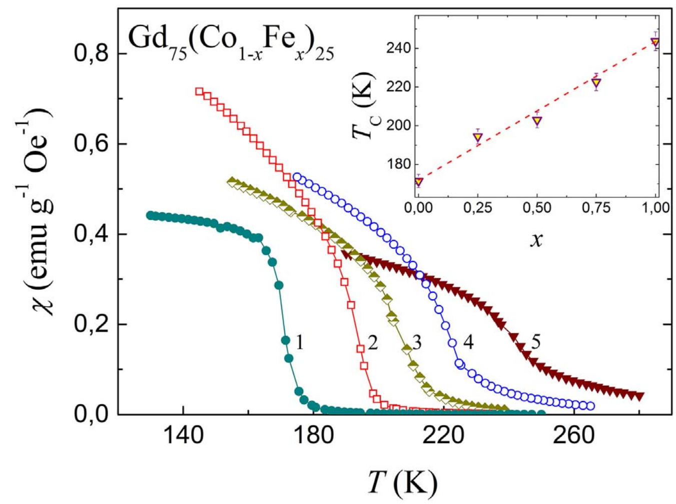

Fig. 2. Temperature dependences of the magnetic susceptibility for the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys, where 1–5 correspond to x = 0, 0.25, 0.5, 0.75 and 1, respectively. Inset shows the variation of the magnetic ordering temperature T_C with the Fe for Co substitution. The line on the inset is drawn as a guide to the eyes.

Moreover, some amount of the crystalline phase of Gd_2O_3 was found in melt-spun samples. Vertical bars in the bottom in Fig. 1 indicate the main Bragg peaks positions corresponding to the orthorhombic Gd_3Co (*Pnma* space group) and cubic Gd_2O_3 ($Ia\bar{3}$ space group) phases. Due to the formation of the gadolinium oxide, it can be assumed that the composition of the main amorphous phase is slightly different from the nominal composition toward Gd reduction. Furthermore, it turned out that it is difficult to obtain the $Gd_{75}Fe_{25}$ alloy in the fully amorphous state by melt-spinning presumably due to insufficiently rapid cooling of the liquid. A similar conclusion was made by authors of Ref. [19], in which the alloys $R_{65}Fe_{35}$ (R = Nd, Gd, Er) alloys could not been obtained in an amorphous state by splat-cooling. Bearing in mind that the amorphization of alloys is mainly controlled by the cooling rate and the composition our results indicate that the glass forming ability decreases with increasing Fe content in $Gd_{75}(Co_{1-x}Fe_x)_{25}$.

The Curie temperatures of the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys were determined from the temperature dependences of the magnetic susceptibility at H = 100 Oe (shown in Fig. 2). As one can see, the Curie temperature T_C of the melt-spun samples varies linearly from 172 K for $Gd_{75}Co_{25}$ up to 244 K for $Gd_{75}Fe_{25}$ (see inset in Fig. 2), and an increase in the Fe content makes the magnetic phase transition more extended on the temperature scale. The fact that the amorphous Gd-Co alloys with high Gd concentrations have lower Curie temperatures compared with Gd-Fe alloys was reported earlier by Buschow and Van der Kraan [34]. It is worth to mention that the amorphous $Gd_{75}Co_{25}$ only exhibits a substantially increased magnetic ordering temperature (T_C = 172 K) compared to its crystalline counterpart Gd_3Co (T_N = 131 K) while other $R_{75}Co_{25}$ alloys have almost the same magnetic critical temperatures as their crystalline analogs [15,35].

As was shown earlier [14], the crystalline antiferromagnetic compound Gd_3Co under application of the magnetic field shows a sharp growth of the magnetization at a critical field $H_{cr} \sim 7.5$ kOe associated with the field-induced AF-F phase transition while the amorphous Gd_3Co exhibit soft-magnetic properties and assumingly has a ferrimagnetic structure. The $M(H)$ dependences of some liquid quenched $Gd_{75}(Co_{1-x}Fe_x)_{25}$ samples are shown in Fig. 3, where the magnetization is calculated per formula unit. To determine the saturation magnetization we used the expression [36]: $\sigma = \sigma_s(1 - A/H - B/H^2)$, where A and B are coefficients associated with the presence of the structural disorder and with a local magnetic anisotropy. The calculated σ_s values at T = 2 K for a series of melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys are listed in Table 1. At the replacement of Co by Fe, the saturation magnetization