

# Effect of Mn substitution on the volume and magnetic properties of $\text{Er}_2\text{Fe}_{17}$

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The effects of Mn substitution on the magnetic properties of  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds have been investigated by different experimental techniques. An unusual composition dependence of the unit cell volume at room temperature occurs due to a strong magnetovolume effect, which has been confirmed by high temperature linear thermal expansion measurements. From magnetization measurements the composition dependence of the spontaneous magnetization of the  $3d$ -sublattice magnetic moment and of the Curie temperature has been determined. Spin reorientation has been detected for compounds with  $3 \leq x \leq 5.5$ , as well as remarkable magnetic history effects. © 2002 American Institute of Physics. [DOI: 10.1063/1.1489718]

## INTRODUCTION

Intermetallic compounds based on rare-earth elements (R) and  $3d$ -transition metals (T) form a large family of materials that is very important from technological and fundamental points of view. It is well known that in these intermetallics, the R-sublattice magnetic moments and the T-sublattice magnetic moments are either ferro- or antiferromagnetically coupled if R is a light or heavy rare-earth element.<sup>1</sup> In general the magnetic behavior of these compounds can be explained by a local moment two-sublattice model. This is also true when magnetic atoms are substituted for by nonmagnetic ones.<sup>2-5</sup> In order to improve the magnetic properties of a compound, deep knowledge of the intrinsic mechanisms of the exchange and crystal electric field interactions is needed. With this in mind a series of experiments that replace either the R or the T atoms by other magnetic atoms<sup>6-9</sup> have been undertaken. In these cases the two-sublattice model is no longer applicable and a multisublattice model has to be introduced to describe the experimental results. Recently, the effects of manganese substitution on R-T intermetallic compounds have attracted significant attention due to possible enhancement of the magnetization, which is expected from the large magnetic moment of Mn atoms.<sup>10-16</sup>

In  $\text{Er}_2\text{Fe}_{17}$ , the rare-earth sublattice and the Fe-sublattice anisotropy constants have opposite signs, and the Fe sublattice contribution to the anisotropy energy prevails over the whole temperature range. The substitution of Fe by Mn modifies the balance between contributions to the anisotropy energy. On the other hand, the presence of Mn will modify

the Curie temperature and the effective magnetic moment of the  $3d$  sublattice. Insight into these effects has been achieved by investigating the spontaneous magnetovolume effect of several compounds with different Mn concentrations.

## EXPERIMENT

$\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  alloys with  $x=0, 1.0, 2.0, 3.0, 3.5, 4.0, 4.5, 5, 5.5$  and  $6.0$  were prepared by arc melting 99.9% purity materials in argon atmosphere. The ingots were annealed in argon atmosphere at 1273 K for 24 h, and subsequently quenched in water. X-ray diffraction (XRD) with Cu  $K\alpha$  radiation was used to check whether the samples were single phase and to determine the lattice parameters. X-ray diffraction of magnetically aligned powder samples allowed us to determine the easy magnetization direction (EMD) at room temperature. Thermal expansion measurements were performed using a "push-rod" linear differential transformer method in the temperature range of 150–550 K. The temperature dependence of the magnetization,  $M(T)$ , was measured in a magnetic field of 500 Oe in a superconducting quantum interference device (SQUID) from 5 to 350 K. The Curie temperatures  $T_C$  were derived from  $M^2$  vs  $T$  plots and by extrapolating  $M^2$  to zero. The magnetization curves at 1.5 K of free powder samples were measured using an extraction sample magnetometer (ESM) in magnetic fields up to 6 T.

## RESULTS AND DISCUSSION

Based on x-ray diffraction analysis and on the temperature dependence of the magnetization at low magnetic field it can be concluded that all the compounds investigated are single phase and crystallize in a hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type

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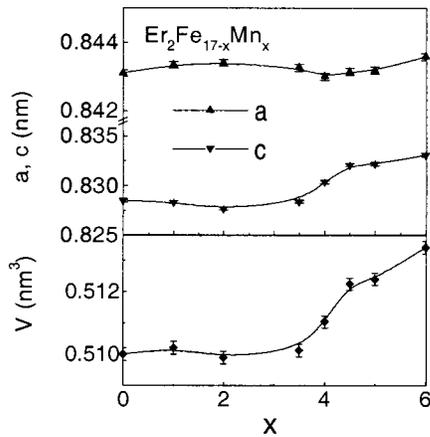


FIG. 1. Composition dependence of lattice parameters  $a$  and  $c$  and unit-cell volume  $V$  at room temperature for  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds.

structure. Lattice parameters  $a$  and  $c$  were obtained from XRD patterns of randomly oriented powder samples and are shown in Fig. 1. It would be expected that the unit-cell volume increases monotonically with an increase in the Mn content, given that Mn atoms are larger than Fe atoms. Nevertheless, our experimental results indicate that the composition dependence of the unit-cell volume at room temperature is not monotonic. Similar behavior was found earlier in  $\text{Pr}_2\text{Fe}_{17-x}\text{Mn}_x$  and  $\text{Tb}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds<sup>14,15</sup> and it was ascribed to the possible existence of magnetovolume effects in those compounds which are magnetically ordered at room temperature. In order to prove this assumption we obtained spontaneous volume magnetostriction,  $\Delta V/V(T)$ , in the  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  series by measuring their linear thermal expansion (LTE),  $\Delta l/l(T)$ , given that  $\Delta V/V(T) = 3 \Delta l/l(T)$ . The measurements were performed up to very high temperatures in order to obtain the nonmagnetic contribution. As an example, in Fig. 2 we show  $\Delta V/V(T)$  and the temperature dependence of the LTE coefficient,  $\alpha(T)$ , of  $\text{Er}_2\text{Fe}_{16}\text{Mn}$  and  $\text{Er}_2\text{Fe}_{15}\text{Mn}_2$ , in which their magnetic ordering temperature,  $T_C$ , is above or close to room temperature.  $\Delta V/V(T)$  tends towards linear behavior at high temperatures and both  $\Delta V/V(T)$  and  $\alpha(T)$  exhibit a clear Invar-like anomaly around the Curie temperature. The magnetic contribution to the thermal expansion which gives rise to Invar behavior can be obtained by comparing the experimental results with the lattice volume contribution,  $(\Delta V/V)_{\text{latt}}$ . This contribution can be calculated through the Grüneisen relation,  $\alpha_{nm}(T) = \kappa \gamma C_v(T)/3$ , with  $\alpha_{nm}$  being the phonon anharmonic LTE coefficient,  $\kappa$  the isothermal compressibility,  $\gamma$  the Grüneisen parameter and  $C_v$  the specific heat. We have calculated  $(\Delta V/V)_{\text{latt}}$ , using a Debye temperature of  $\theta_D = 450$  K.<sup>17</sup>  $(\Delta V/V)_{\text{latt}}$  was fitted to the experimental results in the paramagnetic regime. The thermal dependence of  $(\Delta V/V)_{\text{latt}}$  is shown in Fig. 2 by a dashed line. It can be seen also that even in the paramagnetic phase a considerable value of spontaneous magnetostriction was measured, which indicates the existence of strong short-range magnetic correlations above  $T_C$ .<sup>17</sup> On the other hand, it has been reported that for small amounts of Mn substitution, the Mn atoms preferentially occupy  $6c/4f$  sites of the

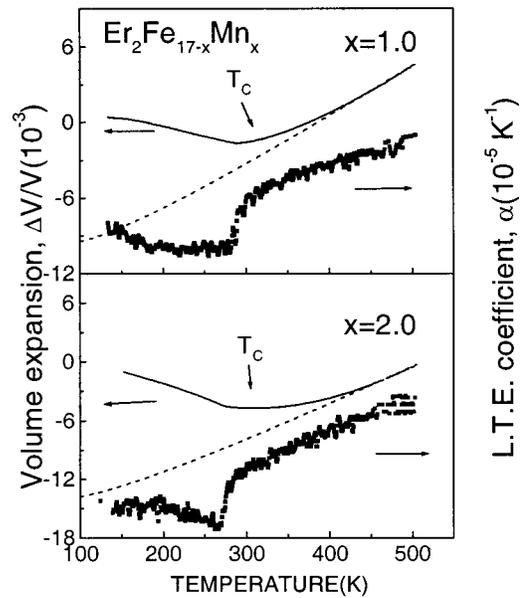


FIG. 2. Volume expansion and thermal dependence of the linear thermal expansion coefficient of  $\text{Er}_2\text{Fe}_{16}\text{Mn}$  and  $\text{Er}_2\text{Fe}_{15}\text{Mn}_2$ . The dashed line represents the calculated nonmagnetic anharmonic phonon contribution.

crystallographic structure, which have the largest Wigner-Seitz cell volume.<sup>18</sup> Therefore, the unusual behavior of the unit-cell volume when  $x \leq 3.5$  mentioned above can be understood by considering the magnetovolume effect in compounds whose Curie temperature  $T_C$  is above or close to room temperature, even though the influence of the  $6c/4f$  site preferential occupation by Mn cannot be completely discarded.

The magnetization curves at 1.5 K of the free powder samples of  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds are shown in Fig. 3. The spontaneous magnetization  $M_s$  was derived from Arrot plots of  $M^2$  vs  $H/M$ . The composition dependence of  $M_s$  at 1.5 K is shown in Fig. 4. It can be seen that with an increase in Mn content the spontaneous magnetization  $M_s$  first decreases almost linearly, going through a minimum at about  $x = 4$ , and then increases with a further increase in Mn content. Based on the slope of the linear part in the composition

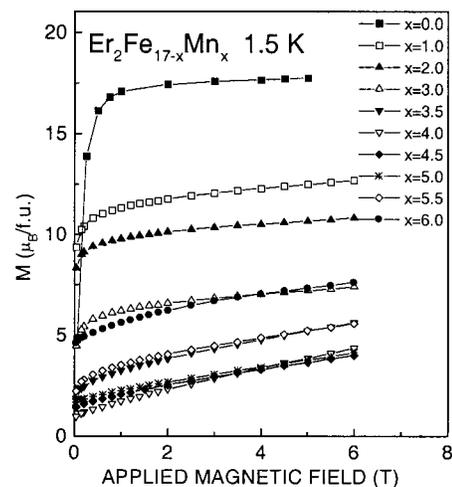


FIG. 3. Magnetization curves at 1.5 K of  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds

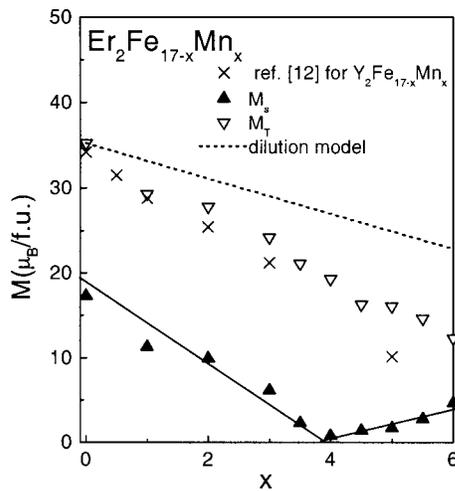


FIG. 4. Composition dependence of the spontaneous magnetization  $M_s$  and of the transition-metal sublattice moment  $M_T$  at 1.5 K for  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds as well as  $M_s$  for  $\text{Y}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds (taken from Ref. 12). The dashed line corresponds to the composition dependence of  $M_s$  according to the dilution model.

dependence of  $M_s$ , it can be derived that for compounds with  $x < 4$  the substitution of Mn atoms for Fe leads to a decrease of around  $4.8\mu_B$  per Mn atom. The appearance of the minimum of the composition dependence of  $M_s$  can be explained in terms of a compensation concentration that originates from the ferrimagnetic coupling between the erbium and the 3d-sublattice magnetization. The transition metal sublattice magnetization  $M_T$  can be obtained from the  $M_s$  measured by subtracting the rare-earth sublattice magnetization. We believe that the rare-earth sublattice magnetization is the same for all the compounds and is obtained from the free ion magnetic moment. The results are shown in Fig. 4. It can be seen that  $M_T$  monotonically decreases with an increase in Mn content. The calculated composition dependence of  $M_s$  based on a simple dilution model, in which the Mn atoms do not have magnetic moment, is also shown for comparison (dashed line). It is obvious that the observed decrease of  $M_T$  with an increase in Mn content is faster than that

expected with a simple dilution model. This suggests that the Mn atoms have magnetic moment which should be aligned antiparallel to the Fe moments. This assumption is supported by neutron diffraction results obtained for the  $\text{Er}_2\text{Fe}_{14-x}\text{Mn}_x\text{B}$  series, in which the presence of manganese induces antiferromagnetic coupling, not only between Mn moments and Fe moments, but also between Fe moments.<sup>11</sup>

From Fig. 3, it can also be seen that for compounds with  $x > 3.0$  the magnetization curves at 1.5 K exhibit a large high field susceptibility. It is particularly high for compounds with  $x = 3.5$  and 4.0 ( $0.434$  and  $0.500T^{-1}\mu_B/\text{f.u.}$ , respectively). A mean-field theory analysis of the ferrimagnetic compounds in terms of the two-magnetic sublattice model<sup>19</sup> indicates that at low magnetic fields the moment configuration is strictly antiparallel, but beyond a critical magnetic field the exact antiparallel configuration is broken up and the two sublattice magnetizations start to bend towards each other. This critical field is given by  $B_{\text{crit}} = |M_T - M_{\text{Er}}|n_{\text{ErT}}$ , where  $n_{\text{ErT}}$

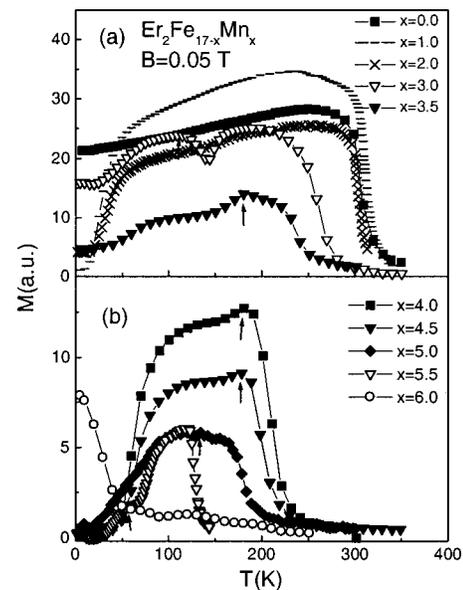


FIG. 5. Temperature dependence of the magnetization in a field of 0.05 T of  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds with  $x = 0.0 - 3.5$  (a) and  $4.0 - 6.0$  (b). The arrows indicate the  $T_{\text{sr}}$ .

stands for the intersublattice molecular-field coefficient and  $M_{\text{Er}}$  for the Er sublattice magnetization. In general, the value of  $B_{\text{crit}}$  in the  $\text{R}_2\text{Fe}_{17}$  compounds with R = heavy rare earth is very high. Nevertheless, in  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds the difference between  $M_T$  and  $M_{\text{Er}}$  becomes smaller as the Mn content increases and therefore  $B_{\text{crit}}$  decreases, making the rotation of the Er- and T-sublattice moments towards each other easily occur at low fields. The existence of this noncollinear magnetic moment structure is responsible for the above-mentioned large high field susceptibility.

The temperature dependences of the magnetization measured in an external magnetic field of 0.05 T are shown in Figs. 5(a) and 5(b). The  $M$  versus  $T$  curve for  $x = 0$  reflects ferrimagnetic behavior. In the case of compounds with  $x = 3.0, 3.5, 4.0, 5.0$  and  $5.5$  an anomaly, marked by arrows in Fig. 5, has been observed, which can be ascribed to spin reorientation: the easy magnetization direction changes from the basal plane at high temperature to the  $c$  axis at low temperature.<sup>12</sup> It is generally accepted that in the R-T compounds the overall anisotropy is determined by the interplay of the R-sublattice and T-sublattice anisotropies. It is known that in  $\text{Er}_2\text{Fe}_{17}$  the Fe-sublattice magnetization tends to lie on the basal plane of the  $\text{Th}_2\text{Ni}_{17}$ -type structure (planar anisotropy) and the Er-sublattice magnetization tends to align parallel to the  $c$  axis (axial anisotropy) over the whole temperature range.<sup>12</sup> The fact that the easy magnetization direction of  $\text{Er}_2\text{Fe}_{17}$  lies on the basal plane means that the Fe-sublattice anisotropy dominates over the whole temperature range below the Curie temperature. The occurrence of spin reorientation in  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds with  $x = 3 - 5.5$  indicates that Mn substitution strongly influences the balance among different contributions to the anisotropy energy. At low temperature the Er-sublattice contribution to the anisotropy energy dominates and the total anisotropy is uniaxial. This is a consequence of the different temperature dependences of Er- and T-sublattice anisotropy energies. For an increase in tem-

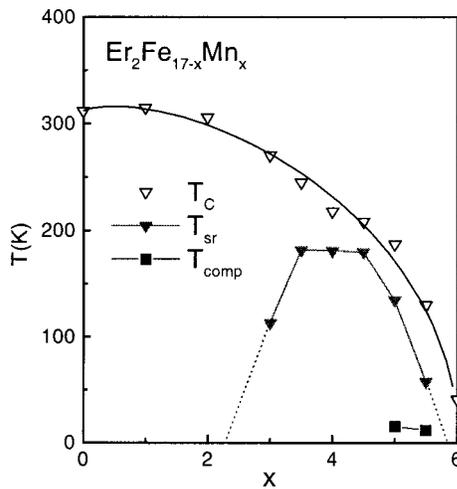


FIG. 6. Composition dependence of the Curie temperature  $T_C$ , spin reorientation temperature  $T_{sr}$  and compensation point temperature  $T_{comp}$  for  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds.

perature the Er-sublattice anisotropy decreases faster than that of the T sublattice. This leads to spin reorientation at a certain temperature,  $T_{sr}$ . The composition dependence of  $T_{sr}$  is shown in Fig. 6.

From Fig. 5 it can also be seen that for compounds with  $x=5$  and  $5.5$  the magnetization has a compensation point at  $T_{comp} \approx 15$  and  $\approx 12$  K, respectively (also see Fig. 6.) The total magnetization is parallel to the rare-earth moments below  $T_{comp}$  and parallel to the T moments above  $T_{comp}$ .

The composition dependence of Curie temperature  $T_C$  is shown in Fig. 6.  $T_C$  first changes very slowly up to  $x=2$  and then decreases rapidly with a further increase in Mn content. This behavior is different from that observed in  $\text{R}_2\text{Fe}_{14}\text{C}$  (Ref. 19) and  $\text{R}_2\text{Fe}_{14}\text{B}$  (Ref. 10) compounds, where Mn substitution for Fe leads to a rapid decrease of  $T_C$  with an increase in Mn content even at  $x=0$ .

In general, we can consider that  $T_C$  is determined by the intensity of the exchange interaction and by  $3d$ -sublattice magnetization  $M_T$ . Among the three types of exchange interaction present in R-T intermetallics (T-T, R-T, and R-R), T-T interaction is the strongest and the R-R interaction is the weakest. The T-T interaction is sensitive to the distance between T-T atoms, and it is represented by the exchange interaction constant,  $J_{TT}$ . According to molecular field approximation, if we only consider the T-T interaction, the relation among  $T_C$ , the T-T interaction and the  $3d$ -sublattice magnetization  $M_T$ , can be written as

$$3k_B T_C = J_{TT} Z_{TT} S_T (S_T + 1). \quad (1)$$

Here,  $S_T$  is the so-called pseudospin, which is related to the  $3d$ -sublattice magnetization:<sup>1</sup>

$$M_T = -g_T \mu_B S_T. \quad (2)$$

In compounds with  $x > 2$  the decrease of  $T_C$  with a further increase in Mn content can be considered a result of the decrease of  $3d$ -sublattice magnetization. In the case of  $x \leq 2$  the observed slow decrease of  $T_C$  with  $x$  could be due to the competition between the variation of the intensity of T-T interaction and the variation of  $M_T$  with the Mn content. This

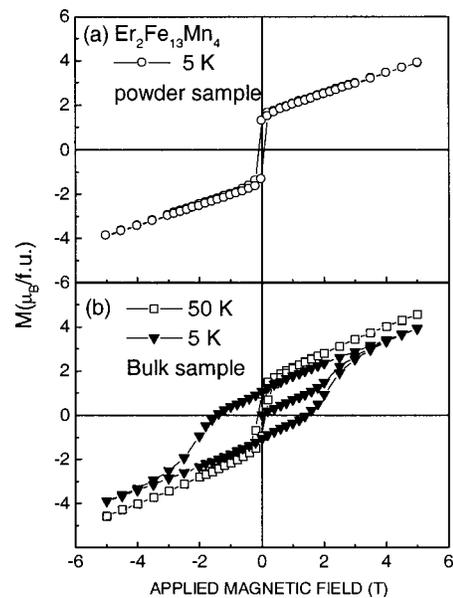


FIG. 7. Hysteresis loop at 5 K of a powder sample (a) and initial magnetization curve at 5 K and hysteresis loop of a bulk sample at 5 and 50 K (b) for an  $\text{Er}_2\text{Fe}_{13}\text{Mn}_4$  compound.

behavior could be related to preferential occupation of the  $6c/4f$  Fe sites by Mn in this doping range, which leads to enhancement of the T-T interaction, as previously reported for the case of  $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds.<sup>18</sup>

The strong decrease of the magnetization at low temperatures observed in the compounds with  $x \geq 1$  (see again Fig. 5) is similar to that observed by Jacobs *et al.*<sup>16</sup> in the  $\text{Ho}_2\text{Fe}_8\text{Mn}_6\text{C}$  compound. In that case it was ascribed to magnetic history effects that resulted from the presence of narrow domain walls. In the case of  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds with  $x=4$  and  $4.5$ , below 50 K the magnetization remains constant. This implies that below this temperature the magnetic domain walls no longer move and that the magnetic domains are randomly oriented. This can be seen by comparing the hysteresis loops at 5 and 100 K. In Fig. 7 the hysteresis loop at 5 K of a free powder sample and the initial magnetization curve at 5 K and hysteresis loops at 5 K and 100 K of a bulk sample of  $\text{Er}_2\text{Fe}_{13}\text{Mn}_4$  are shown. It can be seen that the coercivity of a bulk sample decreases quickly with an increase in temperature from 1.4 T at 5 K to 0.1 T at 50 K.

In Fig. 8 the temperature dependence of the magnetization of  $\text{Er}_2\text{Fe}_{13}\text{Mn}_4$  measured at different magnetic applied fields is displayed. In both the zero-field cooling (ZFC) and the field cooling (FC) processes the measurements were obtained when the temperature was increased. The sample was previously cooled from above the Curie temperature to 1.5 K in zero applied magnetic field (the ZFC curve) and under a certain applied field (FC curve). The ZFC and FC processes exhibit different behavior, which can be considered to be a magnetohistory effect.<sup>16</sup> The critical temperature  $T_{cr}$  at which both curves diverge (marked by an arrow in Fig. 8) decreases as the magnetic field applied increases.

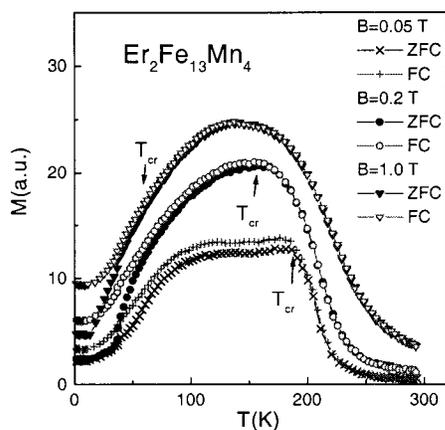


FIG. 8. Temperature dependence of the magnetization at various fields after zero field cooling or field cooling processes for  $\text{Er}_2\text{Fe}_{13}\text{Mn}_4$ .

## CONCLUSIONS

Positive spontaneous volume magnetostriction and a negative thermal expansion coefficient were found below the ordering temperature for  $\text{Er}_2\text{Fe}_{17-x}\text{Mn}_x$  compounds with  $x \leq 3.5$ . This strong magnetovolume effect, together with the Mn initial affinity for the largest Wigner–Seitz cell volume sites, leads to an irregular composition dependence of the unit-cell volume at room temperature. The spontaneous magnetization exhibits a minimum at about  $x=4$  and the 3d-sublattice magnetization decreases monotonically with an increase in Mn content. A spin reorientation transition was detected below room temperature for compounds with  $x \geq 3$ . The large high-field magnetic susceptibility observed at low temperatures suggests a noncollinear arrangement of the R and 3d-sublattice magnetizations in these compounds. The Curie temperature  $T_C$  slightly changes at low Mn doping rates and rapidly decreases with a further increase in Mn content. This variation can be explained in terms of the composition dependence of the 3d-sublattice magnetization and

the strength of the T–T interaction. The compounds with  $x \geq 1.0$  show remarkable magnetic history effects that are ascribed to the presence of narrow domain walls.

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