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# The Annealing Effect on Magnetocaloric Properties of $Fe_{91-x}Y_xZr_9$ Alloys

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**We have carried out the study of magnetocaloric effect for as-quenched and annealed $Fe_{91-x}Y_xZr_9$ alloys. Samples were prepared by arc melting the high-purity elemental constituents under argon gas atmosphere and by single roller melt spinning. These alloys were annealed one hour at 773 K in vacuum chamber. The magnetization behaviours of the samples were measured by vibrating sample magnetometer. The Curie temperature increases with increasing Y concentration (x = 0 to 8). Temperature dependence of the entropy variation $\Delta S_M$ was found to appear in the vicinity of the Curie temperature. The results show that annealed $Fe_{86}Y_5Zr_9$ and $Fe_{83}Y_8Zr_9$ alloys a bigger magnetocaloric effect than that those in as-quenched alloys. The value is 1.23 J/kg K for annealed $Fe_{86}Y_5Zr_9$ alloy and 0.89 J/kg K for as-quenched alloy, respectively. In addition, the values of $\Delta S_M$ for $Fe_{83}Y_8Zr_9$ alloy is 0.72 J/Kg K for as-quenched and 1.09 J/Kg K for annealed alloy, respectively.**

**Keywords :** magnetocaloric effect, entropy change, magnetization behaviour

## 1. Introduction

The thermal effect was discovered in 1881 by Warburg when he applied varying magnetic field to metal iron [1]. Debye and Giauque explained the nature of magnetocaloric effect (MCE) later and suggested achieving an ultra low temperature by adiabatic demagnetization cooling [2, 3]. Room temperature magnetic refrigeration is a new highly efficient and environmentally protective technology [4]. The temperature change of a magnetic materials, associated with an external magnetic field change in an adiabatic process, is defined as the MCE. MCE is intrinsic to magnetic solids and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the total entropy due to a corresponding change in the magnetic field. It can be measured and/or calculated as the adiabatic temperature change $\Delta T_{ad}(T, \Delta H)$, or as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$ [5, 6]. The MCE is a function of both temperature T and the magnetic field change ΔH and is usually recorded as a function of temperature at a constant ΔH.

Recently, a search for new magnetic materials, which exhibit a significant change in the magnetic entropy in response to the change of magnetic field under isothermal conditions, has become an important task in applied physics. Traditionally, diluted paramagnetic slats and rare earth intermetallic compounds that display significant MCE were considered as attractive materials for cryogenic applications [5-8].

In this presentation, we discuss the influence of substitution Fe with Y on the various magnetic properties such as magnetization and magnetocaloric effect of as-quenched and annealed $Fe_{91-x}Y_xZr_9$ (x = 0, 5, 8) alloys. These materials have many interesting properties that are attractive for application as magnetic refrigerants.

## 2. Experimental

$Fe_{91-x}Y_xZr_9$ (x = 0, 5, 8) samples were prepared by arc melting the high-purity elemental constituents under argon gas atmosphere and by single roller melt spinning in the form of long ribbons of 1-2 mm width and 20-40 $\mu$m thickness. These alloys were annealed one hour at 773 K. The amorphous nature of the samples was confirmed through X-ray diffraction studies using Cu-$K\alpha$ radiation. The compositions of the samples were verified through energy dispersive x-ray analysis (EDAX). The magnetization measurements as a function of temperature and field were carried out on a ribbon style sample using a vibrating sample magnetometer (VSM) in the fields up

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to 15 kOe. The magnetic entropy change was calculated by the isothermal magnetization measurements [6-8].

## 3. Results and Discussion

It is known from the Bethe-Slater curve that the sign of the exchange integral between two Fe atoms depends sensitively on their interatomic distance. Therefore, in Fe-rich amorphous alloys leads to a interesting behavior. On the basis of the thermodynamic theory, the magnetic entropy change caused by the variation of the external magnetic field from 0 to $H_{max}$ is given by

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial S}{\partial M}\right)_T dH \qquad (1)$$

From Maxwell's thermodynamic relationship:

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T \qquad (2)$$

Equation (1) can be rewritten as follows:

$$\Delta S_M = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_T dH \qquad (3)$$

Numerical evaluation of the magnetic entropy change was carried out from formula (3) using isothermal magnetization measurements at small discrete field and temperature intervals. $\Delta S_M$ can be computed approximately from Eq. (3) by

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \qquad (4)$$

Thus, the magnetic entropy changes associated with applied field variations can be calculated from Eq. (4). It is known that the favorable soft magnetic properties of Fe-based nanocrystalline alloys come from extremely small magnetic anisotropy and magnetostriction due to small grain size. For this purpose, much work has been done on the Fe-based amorphous alloys by annealing process for very good soft magnetic properties. The nature of the reentrant spin glass transition behavior in Fe-Zr amorphous alloys has been investigated extensively by means of various techniques. The magnetic properties of these materials can easily be tuned either by suitable substitutions [9]. While substitution of Y in place of Fe the magnetic disorder further increases but the system still exhibits reentrant glass behavior [10, 11]. The Y substituted FeZr alloys show some peculiar electrical and magnetic properties. However, it is still debated how and why the magnetic softness increases. It is believed that the enhancement of the soft magnetic properties is due changes in microstructure. We chose a system with higher degree of frustration in order to investigate the reasons for the development of new magnetic caloric materials. The magnetization behavior, which relate thermodynamic quantities near ferromagnetic (FM) – paramagnetic (PM) phase transition, have been performed in order to understand the nature of magnetic phase transition at the near of Curie temperature and type of magnetic ordering. The large magnetocaloric effect can be expected near the order-disorder phase transition of magnetic materials.

Fig. 1(a) and (b) show the temperature dependence of low-field magnetization for the as-quenched and annealed $Fe_{91-x}Y_xZr_9$ (x = 5, 8) samples. The magnetization increases above 710 K for annealed $Fe_{86}Y_5Zr_9$ sample, because of crystallization. The Curie temperature, $T_c$ was found to be 475 K and 615 K, for annealed $Fe_{86}Y_5Zr_9$ and $Fe_{83}Y_8Zr_9$ alloy samples, respectively. With an increase of

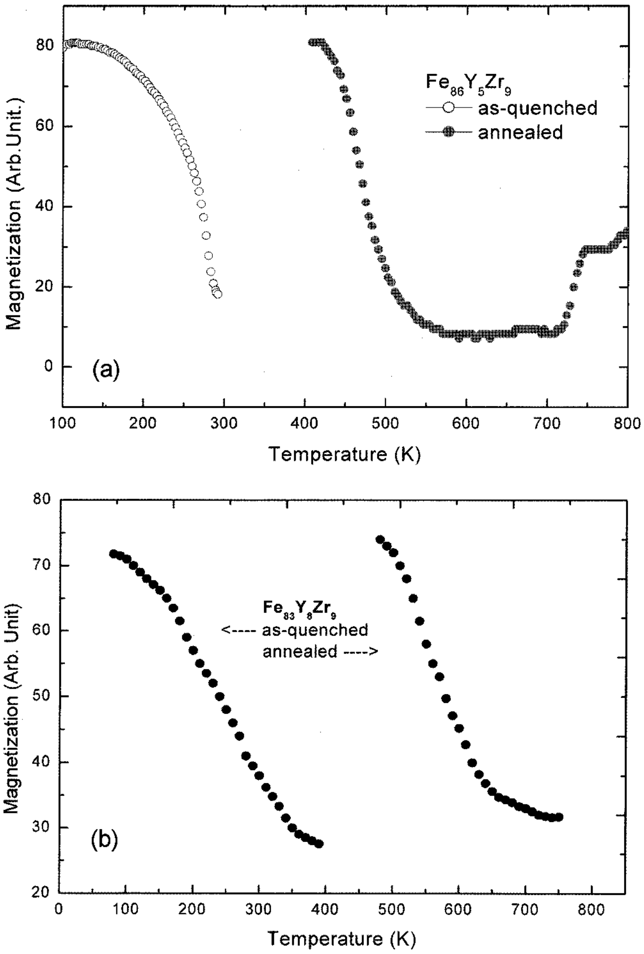

**Fig. 1.** (a) Temperature dependence of the magnetization measured at 100 Oe for the $Fe_{86}Y_5Zr_9$ alloy. The Curie temperature is 284 K and 475 K, respectively. (b) Temperature dependence of the magnetization measured at 100 Oe for the $Fe_{83}Y_8Zr_9$ alloy. The Curie temperature is 303 K and 615 K, respectively.

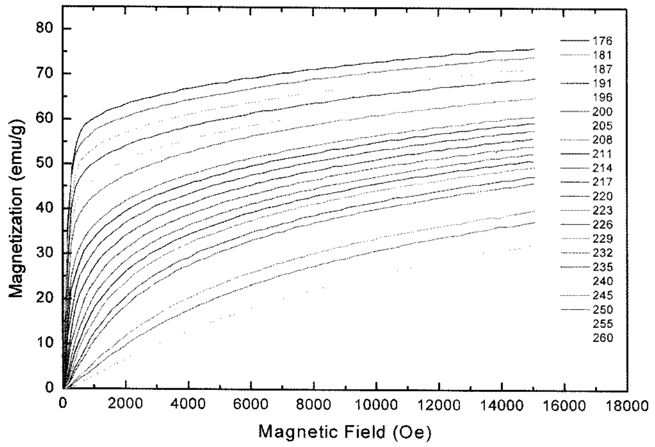

**Fig. 2.** Isothermal magnetization curves in the vicinity of Curie temperature for x = 0 of as-quenched $Fe_{91-x}Y_xZr_9$.

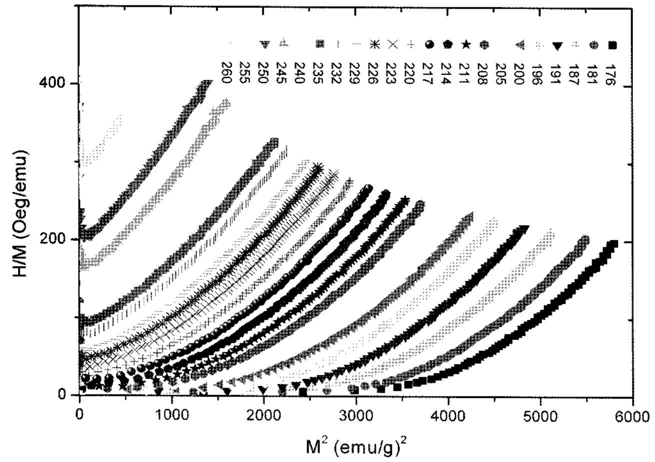

**Fig. 3.** The H/M vs. $M^2$ plots for the isotherms of as-quenched $Fe_{91}Zr_9$ alloy.

the Y concentration, the Curie temperature increases. Isothermal M-H curves for the as-quenched $Fe_{91}Zr_9$ alloy have been measured at various temperatures in Fig. 2. To determine the type of the phase transition for $Fe_{91}Zr_9$, the measured data for the M-H isotherms were transferred in to H/M vs. $M^2$ plots and displayed in Fig. 3. According to the Banerjee criterion, the negative slope in H/M vs. $M^2$ plots means that the ferromagnetic (FM) to paramagnetic (PM) phase transition is first order [12]. For the $Fe_{91}Zr_9$, the negative slopes in the temperature region 232-260 K are clearly seen in the lower $M^2$ region, implying that $Fe_{91}Zr_9$ belongs to the materials displaying a first-order transition. In evaluating the magnetocaloric properties of the $Fe_{91-x}Y_xZr_9$ (x = 0, 5, 8) samples, the magnetic entropy change is calculated by Eq. (4). Fig. 4 show the temperature dependence of magnetic entropy obtained under a field change from 0 to 1.5 T, for x = 0, 5, 8 of as-quenched and annealed $Fe_{91-x}Y_xZr_9$ alloy, respectively. The magnetic entropy change $\Delta S_M$ reaches a maximum value of about 1.22 J/kg K for x = 0 at 233 K, while it is about 0.89 J/kg K, 1.23 J/kg K for as-quenched and annealed on x = 5 alloy, respectively. The Curie temperature is 284 K and 475 K, respectively. On the other hand, the values of $\Delta S_M$ for as-quenched and annealed on x = 8 alloy is 0.72 and 1.09 J/Kg K, respectively. In fact, $\Delta S_M$ is less than that for pure Gd metal ($\Delta S_M \sim 10.2$ J/kg K at $\Delta H = 5T$), however, it is much more uniform, which is desirable for an Ericson-cycle magnetic refrigerator. In comparison with pure Gd metal, these ribbon samples are much cheaper; their Curie temperature can be easily adjusted by tuning the Y concentration and annealing process. In addition, they are much more chemically stable than pure Gd metal. Especially, our results show that annealed $Fe_{86}Y_5Zr_9$ and $Fe_{83}Y_8Zr_9$ alloys have a greater magnetocaloric effect than that those in as-quenched alloys.

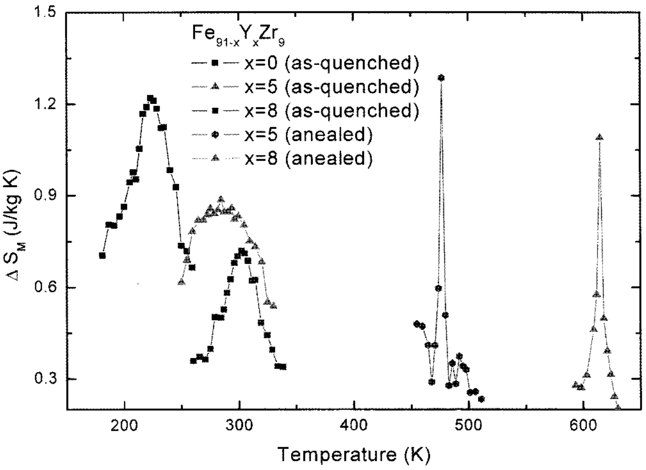

**Fig. 4.** Temperature dependence of magnetic entropy obtained under a field change from 0 to 1.5 T, for x = 0, 5, 8 of as-quenched and annealed $Fe_{91-x}Y_xZr_9$ alloy.

## 4. Conclusion

Our result shows that the substitution Fe with Y seems to favor the increase of magnetic order. From the magnetization data, the magnetic entropy change for isothermal magnetization was calculated by applying the thermodynamic Maxwell equation to a magnetic system. As Y content is increased, Curie temperature is increased and the maximum entropy change ($DS_M$) is seen about Curie temperature in all samples. Our results show that these annealed $Fe_{86}Y_5Zr_9$ and $Fe_{83}Y_8Zr_9$ alloys have a greater magnetocaloric effect than that those in as-quenched alloys, indicating that these alloys can be considered as candidates for magnetic refrigeration applications by proper annealing.

## Acknowledgement

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