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# NEGATIVE MAGNETOCALORIC EFFECT IN $Fe_{1-x}Rh_x$ COMPOUNDS

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## ABSTRACT

On increasing temperature, the $Fe_{1-x}Rh_x$ alloys present a transition from an antiferromagnetic to a ferromagnetic state, which induces a negative magnetocaloric effect (MCE). The magnetocaloric effect, in particular of the $Fe_{0.49}Rh_{0.51}$ alloy, was studied by direct measurements and according to specific heat measurements. Here, we report the recent results obtained on the annealed $Fe_{0.48}Rh_{0.52}$ compound we prepared by arc melting. The isothermal entropy change $\Delta S$ allowing an estimation of the MCE was determined from magnetic measurements. The $\Delta S$ experimentally found is larger than that reported for the annealed $Fe_{0.49}Rh_{0.51}$ sample. However a significant difference occurs between transition temperature of the annealed sample $Fe_{0.48}Rh_{0.52}$ and that reported in literature. This result shows that magnetic and magnetocaloric properties in this kind of materials are very sensitive to the technique of samples preparation. Besides, the magnetocaloric effect close the ferromagnetic – paramagnetic transition in $Fe_{0.48}Rh_{0.52}$ is also discussed.

## INTRODUCTION

The magnetocaloric effect (MCE) is defined as the adiabatic temperature change provoked by the isothermal entropy change upon the application and removal of an external magnetic field. In recent years, much attention has been paid on the studies concerning the magnetic cooling technology. Based on MCE, magnetic refrigeration has economical and ecological advantages over the conventional gas refrigeration such as high efficiency and no use of environmentally harmful gases. This technology appears to be a serious alternative to classical refrigeration. One of the important areas which needs to be advanced before magnetic refrigeration becomes a viable technology is the development of improved solid magnetic refrigerant materials with large MCE. So, experimental characterization of new magnetic materials with respect to their MCE performance still remains an important task for basic and applied physics. A big upsurge in research has occurred in the recent years and many studies have been performed on ferromagnetic materials close to their transition temperature. The discovery of the giant magnetocaloric effect in $Gd_5Ge_2Si_2$ [1] which presents a first order transition from ferromagnetic to paramagnetic states had a great impact in this field. However, interesting magnetocaloric effect has also been reported on transition metals based compounds such as $MnFeP_{1-x}As_x$ [2] and $MnAs_{1-x}Sb_x$ [3]. A common feature of these new classes of magnetocaloric materials is that they undergo a concomitant first order structural and magnetic transition, when cycling around transition temperature. Besides, the equiatomic alloys Fe-Rh undergoes a field-induced antiferromagnetic-ferromagnetic first-order magnetic phase transition, which is accompanied by a large negative magnetocaloric effect [4, 5]. The application of a magnetic field of about 2 T to a quenched sample $Fe_{0.49}Rh_{0.51}$ at 313 K causes a large temperature change of 12.9 K under

adiabatic conditions. So the $Fe_{0.49}Rh_{0.51}$ compounds are interesting working materials for magnetic cooling technology. Many studies on antiferro-ferromagnetic transition have been performed, but there were not enough experimental results on the magnetocaloric properties of theses compounds. So, in this paper we investigate the magnetic and the magnetocaloric effect of sample with $Fe_{0.48}Rh_{0.52}$ composition.

## 1 EXPERIMENTAL

The alloys were prepared by arc melting stoichiometric amounts of the constituent elements (purity ~ 4N) under argon atmosphere and subsequently annealing the ingots to insure homogeneity. Two heat treatments were carried out. First, the fused alloys were annealed in a vacuum at 1100 °C for 48 hours and at 800 °C for 24 h, and then cooled up to room temperature. In the second heat treatment, the compound was annealed at 1100°C for 6 days and at 800 °C for 24 h and also cooled down to room temperature. X-ray diffraction analysis reveals that the samples $Fe_{0.48}Rh_{0.52}$ are single phase with bcc type structure. Magnetization measurements were performed in Louis Néel Laboratory, Grenoble. The magnetocaloric effect represented by isothermal entropy change was calculated using the Maxwell relation from magnetic measurements.

## 2 RESULTS

The temperature dependence of the magnetization of the $Fe_{0.48}Rh_{0.52}$ alloy measured in a magnetic field of 0.1 T at heating is presented in Fig. 1. On heating the sample, a transition from antiferromagnetic to ferromagnetic (AF-F) state takes place at 370 K. Such behaviour was observed in $Fe_{0.49}Rh_{0.51}$ compounds, the AF-F transition occurring at 342 K for the annealed sample and at 313 K for the quenched sample [4, 5]. The transition temperature of the $Fe_{0.48}Rh_{0.52}$ compound is different from that reported in reference [6] which is equal to 333 K. This result shows that the magnetic behaviour of equiatomic Fe-Rh alloys are very sensitive to the preparation technique, heat treatment process and to the Rh concentration. As an example, the critical transition temperature may vary from 143 K up to 408 K when changing the Rh content within 47 – 63 % and from 155 K to 585 K by 3d-, 4d- and 5d-metal impurities [7]. Moreover, as was pointed out by Wayne [8], Polovov et al.[9], Annaorazov [4,5] et al and observed in this present work, the properties of Fe-Rh alloys are extremely sensitive to the slightest details of the thermal treatment. This problem requires further investigation. However, in $Fe_{0.48}Rh_{0.52}$ alloy another transition from ferromagnetic to paramagnetic state occurs at 675 K as shown in Fig. 1.

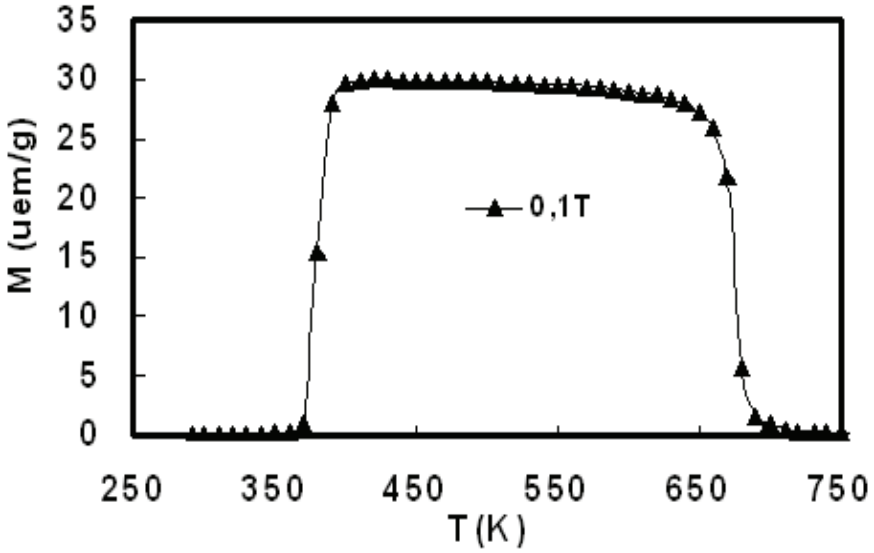


Figure 1: Temperature dependence of magnetization of $Fe_{0.48}Rh_{0.52}$ upon heating under the field of 0.1 T

The magnetocaloric effect has been measured directly in $Fe_{0.49}Rh_{0.51}$ by Annaorazov et al [4, 5]. Under 5 T the maximum adiabatic temperature change occurred near AF-F is -3.8 K for an annealed sample and about -13 K for a quenched sample. Besides, as has been theoretically shown [6], the application of a pulsed field under adiabatic conditions to an $Fe_{0.48}Rh_{0.52}$ alloy causes a temperature change of -20 K at T = 333 K and of -2 K at T = 77 K in a magnetic field *B* = 30 T. Here, we used magnetic measurements to determine of the isothermal change of total entropy based on the Maxwell relation:

$$\Delta S(T,0 \rightarrow H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_{H'} dH' \qquad (1)$$

the accuracy of $\Delta S$ calculated using this technique is about 3 – 10 % [10].

Fig. 2 shows the *M-H* curves for selected temperatures. The traces are determined during heating in the temperature region in which the magnetic transition AF-F occurs. The magnetization increases with the temperature increasing at the corresponding magnetic field range. Especially at the transition temperature, magnetization increases more rapidly. The magnetocaloric effect represented by the entropy change can by obtained from data of Fig. 2 by numerical integration of the relation (1) which becomes:

$$\Delta S = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \qquad (2)$$

where $M_{i+1}$ and $M_i$ are the magnetization values measured in a field *H*, at temperatures $T_{i+1}$ and $T_i$, respectively. The above relation shows that $\Delta S$ is equivalent to the area between two magnetic isotherms divided by the temperature difference between the isotherms.

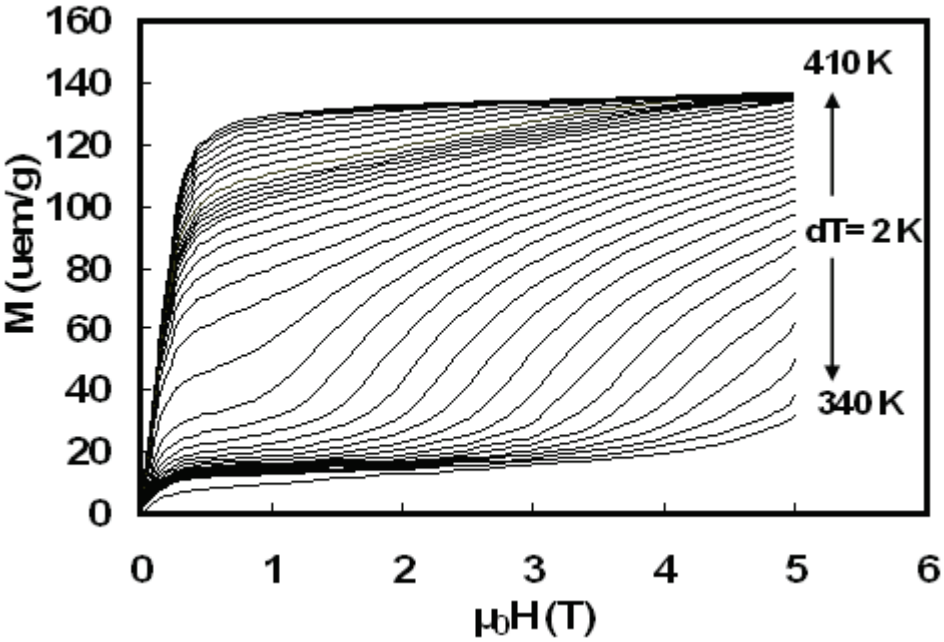


Figure 2: Magnetization isotherms of the $Fe_{0.48}Rh_{0.52}$ alloy between 340 and 410 K

The entropy change $\Delta S$ as a function of temperature for $Fe_{0.48}Rh_{0.52}$ under different magnetic fields is plotted in Fig. 3. The entropy changes are large and reach their maximum near the AF-F transition temperature. For a field change of 2 and 5 T, the entropy change is about 12 and 18 J/kg K respectively close to 370 K. These values are similar to those obtained in $Gd_5Ge_2Si_2$ [1] and $MnFeP_{0.45}As_{0.55}$ [2] compounds where the absolute value of $\Delta S$ under 5 T is 18.5 and 18 J/kg K respectively close to their Curie temperatures. The large magnetocaloric effect observed in $Fe_{0.48}Rh_{0.52}$ is essentially due to first order transition from AF to F states and is associated with a large and sudden change of magnetization. Besides, $\Delta S$ obtained with the annealed sample $Fe_{0.48}Rh_{0.52}$ is about twice higher than that found in the annealed $Fe_{0.49}Rh_{0.51}$ where $\Delta S$ = 6.5 J/kg K at 342 K and under 2 T.

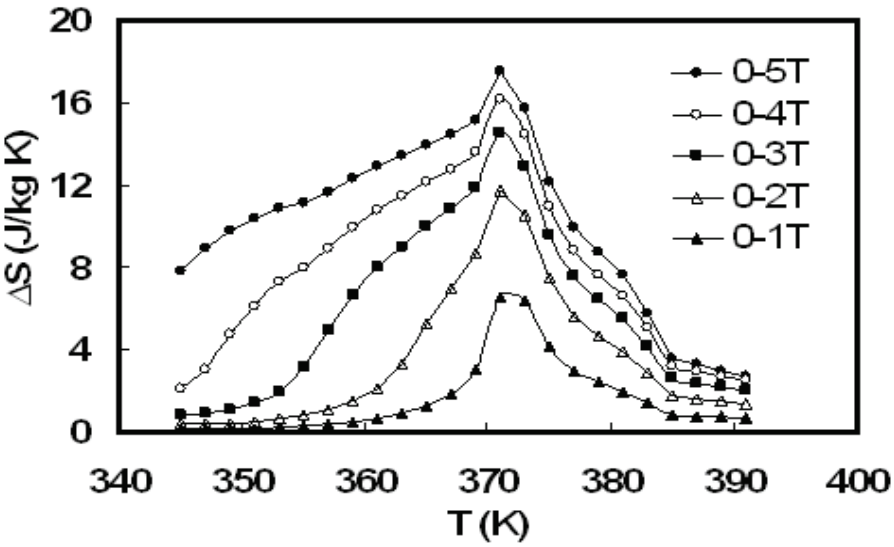


Figure 3: Isothermal entropy change of $Fe_{0.48}Rh_{0.52}$ as a function of temperature under different applied fields close to the AF-F magnetic transition

The $Fe_{0.48}Rh_{0.52}$ compound exhibits a second order transition from ferromagnetic to paramagnetic phase at 675 K, but as shown in Fig. 4 we measured a smaller change of entropy (4.9 J/kg K for 0 – 5 T). To have an idea about the adiabatic temperature change in the annealed $Fe_{0.48}Rh_{0.52}$ alloy, the determination of the MCE was based on the specific heat taken from reference [4] and for magnetic field variations of 2 and 5 T. $\Delta T_{ad}$ is about -9.6 and -14.5 K, respectively.

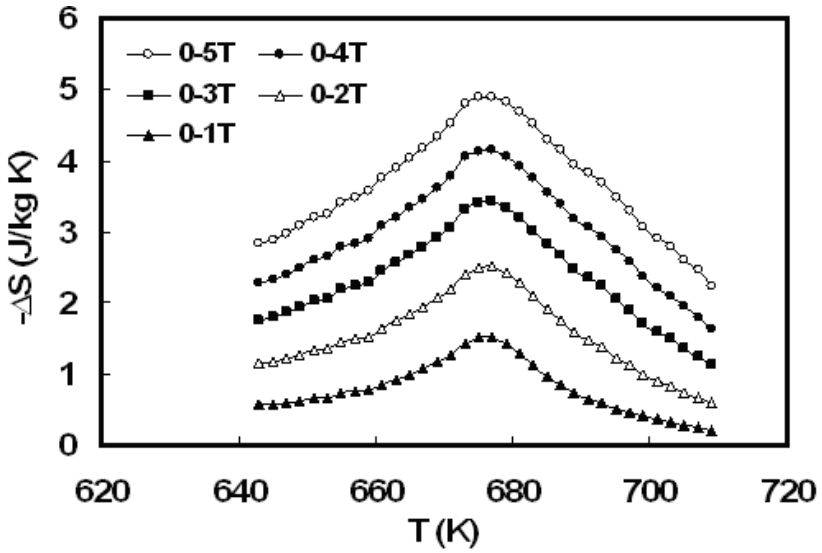


Figure 4: Isothermal entropy change of $Fe_{0.48}Rh_{0.52}$ close to the F-P magnetic transition

## CONLUSION

We have studied the magnetic properties and the MCE of annealed $Fe_{0.48}Rh_{0.52}$ alloy prepared by arc melting. The transition from the antiferromagnetic to ferromagnetic states occurring at T = 370 K is accompanied by a large and sudden change of magnetization, which leads to a large negative magnetocaloric effect (positive $\Delta S$ ). At this transition, the maximum of the isothermal entropy change is about 18 J/kg K for 5 T. Moreover, a transition from ferromagnetic to paramagnetic phase takes place at high temperature ($T_C$ = 675 K), but at this transition we measured a smaller change of entropy (negative $\Delta S$ ). Besides, the magnetic properties of Fe-Rh alloys are markedly sensitive to the composition, technique of preparation and heat treatment process. This question requires further investigation and will be treated in a forthcoming communication.

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