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# Tunable magnetocaloric effect around room temperature by Fe doping in $Mn_{0.98}Cr_{(0.02-x)}Fe_xAs$ compound

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ABSTRACT

In this work, we present an investigation of the magnetic and magnetocaloric properties of $Mn_{0.98}Cr_{(0.02-x)}Fe_xAs$ compounds with x = 0.002, 0.005 and 0.010. Our findings show that as Fe content increases the unit cell volume decreases, which indicates that Fe doping emulates the pressure effect on the crystalline structure. The transition temperature $T_C$ decreases as x increases and it can be set at approximate value of room temperature by changing the doping level. In addition, the magnetic entropy change $\Delta S_M$ was determined using a discontinuous measurement protocol, and realistic values from the magnetocaloric effect presented by MnAs-type compounds under pressure (emulated pressure) could be obtained. The values of $\Delta S_M^{MAX}$ are very large, around $-11$ J kg$^{-1}$ K$^{-1}$ with $\Delta H$ = 15 kOe, which is higher than that observed for most compounds with $T_C$ around room temperature. However, $\Delta S_M$ is confined to a narrow temperature range of 11 K. To overcome this drawback, the composition of a theoretical composite formed by our samples was calculated in order to obtain a table-shaped $\Delta S_M$ curve. The simulated composite showed a high value of full width at half maximum $\delta T_{FWHM}$ of 33 K, which is much higher than that of single sample.



## 1. Introduction

The magnetocaloric effect (MCE) is the basis of magnetic refrigeration, which is considered an environment-friendly technology because it uses no CFC or HCFC gases, besides being noiseless and energetically efficient. The MCE corresponds to the reversible heating and cooling of conventional magnetic materials when they are placed in a magnetic field and removed from it, respectively. The MCE can be expressed either in terms of an adiabatic temperature change $\Delta T_{ad}$ or in terms of an entropy change $\Delta S$ when the magnetic field is applied in isothermal conditions.

MnAs-type compounds have been intensively studied in recent years due to the high values of the MCE, which can lead to their use in magnetic refrigeration working at temperatures near room temperature [1,2] when their hysteresis are eliminated. The intense MCE is associated with magnetic transition, which is coupled to structural transition from hexagonal NiAs-type ($T < T_C \sim 300$ K) to orthorhombic MnP-type ($T_C \sim 300$ K $< T$) structure. In fact, the compound suffers another structural transition from orthorhombic to hexagonal at $T_t = 398$ K [3]. At temperatures above $T_t$, the material is paramagnetic following the Curie–Weiss law, whereas at temperatures between $T_C$ and $T_t$ the material is also considered paramagnetic but it fails in following the Curie–Weiss law [4,5]. In fact, some theoretical studies using density functional [6] and first principles calculations [7] have shown that between $T_C$ and $T_t$ the material exhibits a short-range antiferromagnetic interaction confined to the *ab* plane. This result was recently confirmed by an experimental work[5].

The magnetic and magnetocaloric properties of MnAs and their derivatives are extremely dependent on structural deformation, and therefore, a few kbars of applied hydrostatic pressure can significantly change the magnetic properties. Along with hydrostatic pressure, chemical doping can also generate a structural deformation and emulate the pressure effect. In some cases the two

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approaches are equivalent [5]. Chemical doping can be achieved by replacing Mn or As with other elements. It is important to address that the substitution with Mn is more commonly used to change the magnetic properties compared with the substitution with As, as seen in literature where Mn is replaced by other transition metals [8,9]. In one case, when the Mn was replaced with Fe [1] and Cr [10] a considerable increase in MCE and reduction of thermal hysteresis, respectively, were reported. However, the large MCE values presented by $Mn_{1-x}Fe_xAs$ compounds were overestimated because the MCE depends on the magnetic and thermal history of the system and the hysteresis of the phase transformation is the feature that generates the irreversibility effects. These effects led to overestimation of $\Delta S_M$ values when using isothermal magnetization curves for obtaining the MCE response. Thus, it is well known in the magnetocaloric community that for materials exhibiting first-order magnetic transition it is necessary to adopt some measurement protocol for obtaining the isothermals (M vs H curves) in order to calculate realistic MCE values [11,12], or use isofield curves [13].

In this work, we use chemical doping to emulate the pressure effect and study its effect on the magnetic and magnetocaloric properties of the $Mn_{0.98}Cr_{(0.02-x)}Fe_xAs$ compounds. Our main goal is to obtain realistic values of the MCE exhibited by MnAs and their derivatives under hydrostatic pressure since they were recently overestimated [1,2]. Therefore, a discontinuous measurement protocol [11] was used to avoid miscalculating MCE values, and it was applied to samples with different Fe/Cr doping level, i.e., with different emulated pressures. In addition, the compressibility value of MnAs was used to estimate the equivalent relative hydrostatic pressure, which ranges from 0–0.5 kbar (considering x = 0.002 as 0 kbar), and matched the pressure values used in early works [1,2]. Finally, in order to obtain a table-shaped $\Delta S_M$ curve, the composition of a composite produced with the three samples was determined, and the $\Delta S_M$ curve with a full width at half maximum ($\delta T_{FWHM}$) of 33 K was found.

## 2. Experimental techniques

A previous work [10] has shown that the Cr-doped MnAs compound exhibits a reduced thermal hysteresis, when comparing with pure MnAs compound. On the other hand, the Fe-doped MnAs seem to exhibit the MCE and hysteresis enhanced [1]. Thus, we made a co-doping using the Cr and Fe in order to obtain a compound with optimized properties, namely, a MCE enhanced and hysteresis reduced. Thus, we prepared samples of the $Mn_{0.98}Cr_{(0.02-x)}Fe_xAs$ compound with x = 0.002, 0.005 and 0.010. The samples were prepared following the route presented before [1,14]. The X-ray diffraction at 300 K and Rietveld refinement were used in order to verify if the samples are single phase and to determine the cell parameters. Magnetic properties were studied using a Lakeshore 7407 vibrating sample magnetometer with a maximum applied magnetic field of 1.5 T. The ramping rate at which the M(T) curves were obtained was the same for all samples, around 0.25 K/s. The shape (cubes of ~1 mm of length per side) and mass (around 1.5 mg) of the samples used during the magnetic measurements also were comparable in all cases.

## 3. X-ray diffraction

X-ray diffraction patterns at room temperature were analyzed by the Rietveld method, which shows that the samples are single phase and crystallize in the orthorhombic phase for the samples with x = 0.005 and 0.010. Fig. 1 shows that the sample with x = 0.002 exhibits peaks of two phases (hexagonal and orthorhombic) because of the phase coexistence observed in the hysteresis

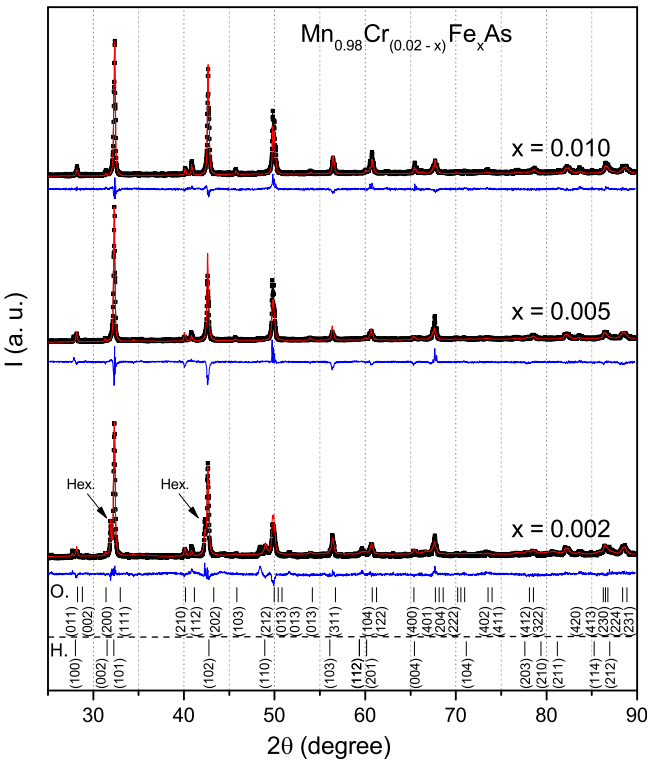


**Fig. 1.** X-ray diffraction patterns with the correspondent Rietveld refinement for all samples at room temperature. In the bottom is shown the Bragg reflections with the corresponding indices of crystallographic plane for the orthorhombic and hexagonal phases. Note that the sample with x = 0.002 shows the peaks of the hexagonal and orthorhombic phases coexisting at that temperature. The main peaks of the hexagonal phase are indicated by arrow.

region [4,15]. Rietveld fitting shows 86(1)% of orthorhombic phase and 14.3(6)% of hexagonal one for the sample with x = 0.002 at 300 K. The refinement parameters are presented in Table 1 (only for the orthorhombic phase), which shows that the lattice parameters decrease as Fe amount increases, as shown in Fig. 2-Top. The resulting effect on the crystalline structure are better visualized in Fig. 2-Bottom, which shows the unit cell volume as a function of the Fe atoms, which decreases with x. This is expected because the average ionic radius of Fe is lower than that of Cr. Previous works on the $Mn_xFe_xAs$ system showed a similar tendency. Note that the Fe doping emulates the positive pressure effect. From the compressibility of MnAs [5], the corresponding hydrostatic pressure could be determined. Considering x = 0.002 as P = 0 kbar, the values for samples with x = 0.005 and 0.010 are 0.3 and 0.5 kbar, respectively, as seen in Fig. 2-Bottom.

**Table 1**
Refined crystallographic data and reliability factors for the $Mn_{0.98}Cr_{(0.02-x)}Fe_xAs$ samples in the orthorhombic phase.

| Parameters | Samples | | |
|---|---|---|---|
| x (Fe amount) | 0.002 | 0.005 | 0.010 |
| *a* (Å) | 5.7062(3) | 5.7026(3) | 5.7015(3) |
| *b* (Å) | 3.6499(3) | 3.6478(2) | 3.6467(2) |
| *c* (Å) | 6.3487(5) | 6.3467(3) | 6.3455(3) |
| Volume (Å$^3$) | 132.22(2) | 132.03(2) | 131.93(2) |
| $R_p$ (%) | 3.8 | 5.7 | 4.8 |
| $R_{wp}$ (%) | 5.1 | 8.8 | 6.6 |
| $R_{exp}$(%) | 3.1 | 3.4 | 3.3 |
| $\chi$ | 1.6 | 2.6 | 2.0 |