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Citation: Appl. Phys. Lett. **93**, 261910 (2008); doi: 10.1063/1.3058712
View online: http://dx.doi.org/10.1063/1.3058712
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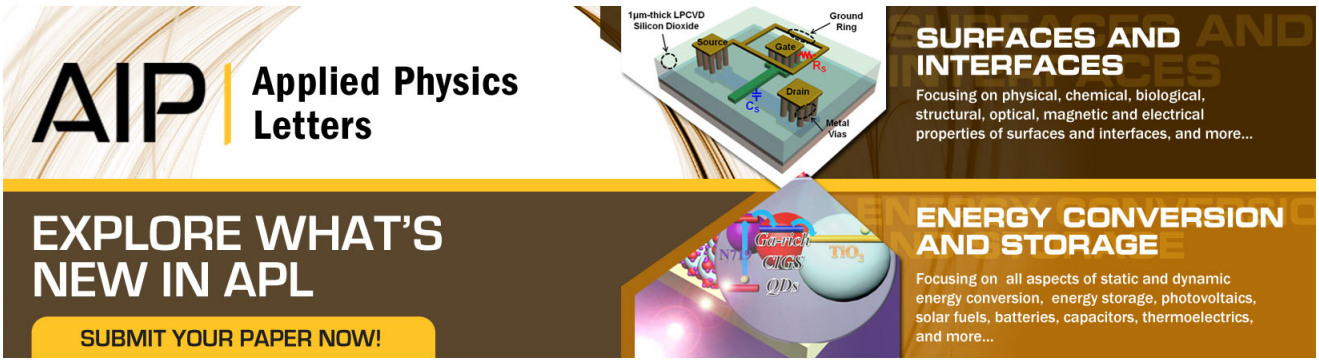

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Irreversibility in cooling and heating processes in the magnetocaloric MnAs and alloys

A. L. Lima Sharma,[1,a] S. Gama,[2] A. A. Coelho,[3] and A. de Campos[4]
[1]*Department of Physics, Tuskegee University, Tuskegee, Alabama 36088, USA*
[2]*Department of Physics, Universidade Federal do Est. de Sao Paulo, Rua Prof. Artur Riedel, 275 Jd. Eldorado, Diadema, São Paulo 00972-270, Brazil*
[3]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), C.P. 6165, Campinas, São Paulo 13083-970, Brazil*
[4]*Department of Physics, Montana State University, Bozeman, Montana 59717-3840, USA*

(Received 6 October 2008; accepted 6 December 2008; published online 31 December 2008)

Irreversibility of adiabatic processes in the magnetocaloric MnAs and alloys is presented here. We used a differential scanning calorimeter to record the heat flux as a function of the temperature and applied field for MnAs (Mn,*X*)As, where *X* stands for Fe or Cu in 0.6% of doping. We extracted the latent heat and entropy in a cycle. In the cooling process, we observed that $S^c_{\mathrm{Mn}} > S^c_{\mathrm{Fe}} > S^c_{\mathrm{Cu}}$, and for the heating process, $S^h_{\mathrm{Fe}} \approx S^h_{\mathrm{Mn}} > S^h_{\mathrm{Cu}}$. The difference in the entropy obtained between processes was found to be as high as 37%. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3058712]

A magnetic refrigeration device is based on the idea that a magnetic solid can be made to cool down by isothermally applying magnetic field (magnetizing), then adiabatically demagnetizing. The process is connected to the so-called "magnetocaloric" effect (MCE): the change in entropy (ΔS) of a material under the isothermal application of a magnetic field and the adiabatic change in temperature (ΔT) under an adiabatically applied field. The discovery of the giant magnetocaloric effect[1] gave a new impulse toward the development of magnetic cooling technology.

The bulk MnAs has attracted attention recently for its magnetocaloric properties,[2,3] although thin films have been well known for their shape memory properties and broad application in heterostructure Ge/MnA[4] and GaAs/MnAs,[5] among others. In the Mn_xAs compounds, Mn clusters are substantially enhanced by single As doping by having their hybridized *sd* electrons bond with *p* electrons of As. This stabilization is also accompanied by the ferromagnetic Mn–Mn coupling.[6]

MnAs exhibits a first-order magnetostructural transition at the Curie temperature and a second order structural transition at higher temperature. There is a relative agreement in the literature about the temperature in which the second transition occurs near 398 K.[6–15] However, for the Curie temperature T_C, many different values from 313 to 320 K have been published. The crystal structure of MnAs is a hexagonal NiAs type in a ferromagnetic state and turns into an orthorhombic MnP-type structure in a paramagnetic state with thermal hysteresis. The MnP-type structure reverts to a NiAs type at 398 K. Using neutron diffraction measurements,[16,17] it was observed for a certain range of temperatures, both the NiAs-type and the MnP-type structures coexist, the hexagonal-orthorhombic transformation starts at 313 K and finishes at 317 K. Applying a magnetic field of 4 T induces a transformation from a MnP-type to a NiAs-type structure at 319 K. It was reported that a magnetic field of 5 T restored fully the hexagonal phase at 321 K.[17]

Bean and co-worker[11,12] described the susceptibility maximum above T_C to the onset of the orthorhombic distortion.[10] However, Goodenough *et al.*[14] pointed out that two crystallographic phases of MnAs could reflect two distinct spin states of manganese with high-spin manganese configuration and low-spin state. The stable structure of the ferromagnetic state is found to be the high-spin structure. The ferromagnetic exchange coupling parameters that increase when the volume is increased have been confirmed.[14] For the experimentally observed distortions some of the in-plane exchange coupling coefficients become antiferromagnetic. This is the reason for the stability of the low-spin state structure for those configurations of the magnetic moments that have an antiferromagnetic component in the hexagonal plane.

In this work, we consider the irreversibility of thermodynamic processes since MnAs and alloys have been considered for magnetic refrigeration technology. We used a differential scanning calorimeter (DSC) in order to record the heat flux as a function of the temperature for MnAs and (Mn,*X*)As for *X*=Fe or Cu for a concentration of 0.6%. From the measured heat flux, we extracted the latent heat and entropy (*S*) associated with cooling and heating processes. In the cooling curve, we observed that $S^c_{\mathrm{Mn}} > S^c_{\mathrm{Fe}} > S^c_{\mathrm{Cu}}$, and for the heating process, $S^h_{\mathrm{Fe}} \approx S^h_{\mathrm{Mn}} > S^h_{\mathrm{Cu}}$. The difference in the entropy obtained from cooling and heating processes was found to be as high as 37%.

Samples were prepared by arc melting under argon atmosphere. The materials were heat treated in a resistive furnace at 1070 °C for 2 h and quenched at room temperature. A second heat treatment was performed at 800 °C for 48 h and water quenched at ambient temperature. Samples were characterized by metallographic analyses, x-ray diffraction, and magnetic measurements. Details can be found elsewhere.[4] All doped samples formed a single phase, as shown by both metallography and x-ray diffraction. The heat flow was measured in both homemade DSC[17] based on similar apparatus[18,19] and commercial DSC. The latent heat and the entropy change are then given by $L = \int_{T_i}^{T_f} (dQ/dT)dT$ and $\Delta S = \int_{T_i}^{T_f} (1/T)(dQ/dT)dT$, where T_f

[a]Author to whom correspondence should be addressed. Electronic addresses: lima.sharma@gmail.com and sharmaa@tuskegee.edu.

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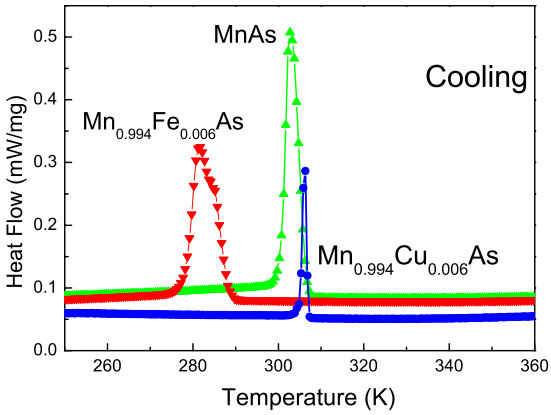

FIG. 1. (Color online) Heat flow as a function of the temperature for MnAs and alloys. The temperature decreases.

and T_i are the initial and final temperatures for the starting and ending transition temperatures. Another method to measure latent heat is fixing a temperature above T_C and sweeping the applied magnetic field H. A high enough H can also induce the first-order transition. This fact gives rise to a direct measurement of the MCE since the isothermal entropy change achieved by the application of a magnetic field can be measured. In this case, the heat flow and the increasing/decreasing field $H(t)$ are recorded, leading to the magnetic field rate $dH=dt$. L and ΔS are thus given by $L=\int_{H_i}^{H_f}(dQ/dH)dH$ and $\Delta S=\int_{H_i}^{H_f}(1/T)(dQ/dH)dH=L/T$, where H_f and H_i are, respectively, the applied magnetic fields above and below the starting and ending transition fields.

We present the heat flux as a function of the temperature for MnAs, (Mn,Fe)As, and (Mn,Cu)As for cooling process in Fig. 1 and for the heating processes in Fig. 2. The heat/cooling rate was 10 K/min. Both the heat flow curve vertical displacements are proportional to the heat capacity of the sample and it is expected to change for different compositions. The transition temperature is taken at the temperature where the heat flux curve changes slope, instead of the temperature where the maximum value occurs. In the cooling process (Fig. 1), the heat flux curves for the pure MnAs and for the Cu-doped samples present a sharp clear peak implicating the first-order phase transition which can be associated with the ferromagnetic to paramagnetic transition plus the structural transition. On the other hand, for the Fe-doped sample, a broad lower peak is observed and it might be an

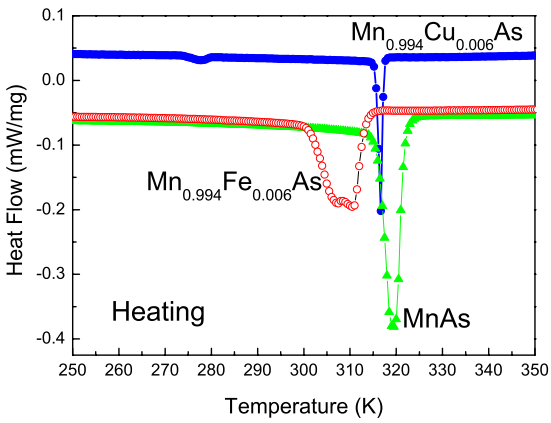

FIG. 2. (Color online) Heat flow as a function of the temperature for MnAs and alloys. The temperature increases.

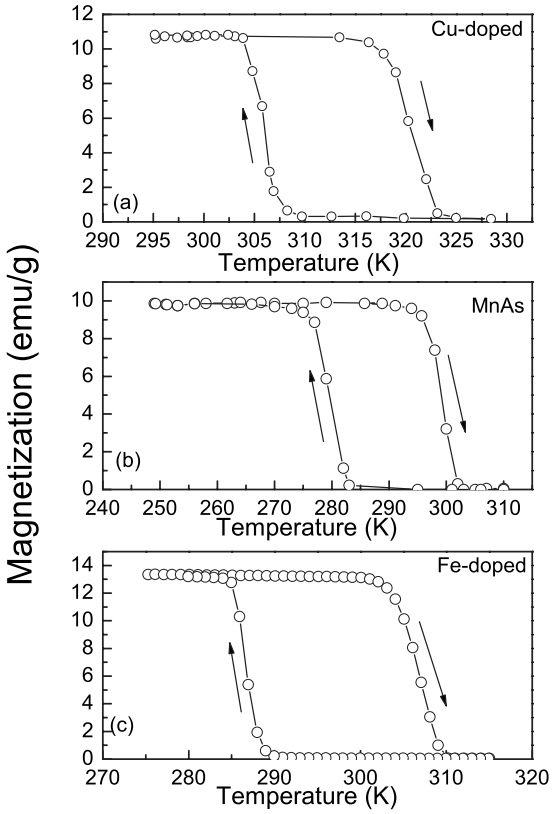

FIG. 3. Magnetization data as a function of the temperature: (a) Cu doped, (b) MnAs, and (c) Fe doped. The applied field was kept constant at 0.02 T.

indication that structural transition is disconnected from the magnetic transition. This displacement in Fe-doped sample can be more clearly observed in the heat flux measured during the heating process.

During the heating process (Fig. 2), the heat flux associated with the pure MnAs is also higher than the doped samples, and comparing with the cooling curve, thermal hysteresis is observed for all samples. The presence of doping shifts the temperature upward for Cu alloys and downward for Fe doping. The large hysteresis observed in the temperature shift for the heat flux is also observed in the magnetization as a function of the temperature data, as expected in the first-order phase transition (see Fig. 3). We should remark that the transition temperature in the magnetization does not change significantly for the Cu doping. In particular, for the Fe-doped sample, one might see more clearly that there are more than one transitions occurring in different temperatures.

The latent heat associated with the transition in MnAs is obtained from the cooling curve of ~9.58 J/g and from the heating curve of ~7.13 J/g. For the Cu-doped sample, the latent heat is ~6.26 J/g for the cooling process and ~5.25 J/g for the heating process. Similarly, for the Fe-doped compound, the latent heat values are ~8.58 and ~7.0 J/g for cooling and heating, respectively. In order to clarify the secondary transition proposed by Goodenough *et al.*,[14] we measure the heat flow as a function of field for a fixed temperature (Fig. 4). The field is applied and removed in a continuous cycle. The rate of change of H may influence the shape of the peak; however, the amount of the entropy involved in the process is not altered. In Table I, we summarize the values obtained for the latent heat and entropy for each sample with the respective intervals of temperature for each transition that happens. In the heating curve, we observed

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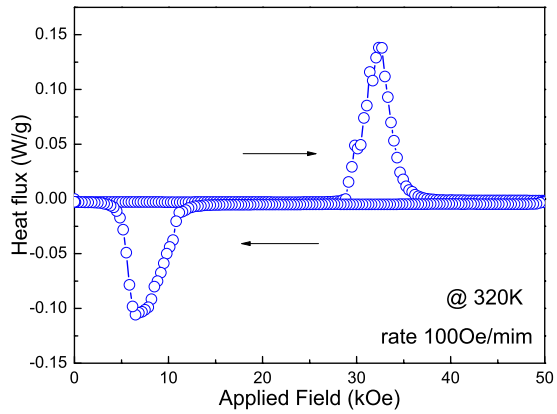

FIG. 4. (Color online) The heat flow in a full cycle of the magnetic field for MnAs for a fixed temperature, field sweep from 0 to 50 kOe.

that $S^c_{Mn} > S^c_{Fe} > S^c_{Cu}$ (where Mn, Fe, and Cu stand for MnAs, (Mn,*X*)As for *X*=Cu or Fe for 0.6% doping, and the index *c* refers to the cooling process). Similarly, for the heating process, $S^h_{Fe} \approx S^h_{Mn} > S^h_{Cu}$. The change in the absolute value of entropy in the cooling and heating processes is 37% for the pure MnAs, 30.7% for the Fe doped, and 25% for the Cu doped. The difference in entropy for a complete cooling and heating cycle gives an estimate of the energy that would be wasted during the process. If the compound is to be used as a magnetic refrigeration material, one must need to take in account energy losses and provide extra energy to the system during thermo-magnetodynamic cycle.

The observed thermomagnetic behavior is consistently explained by a localized double-exchange model of MnAs ferromagnetism. The ferromagnetic state is more favorable for MnAs,[20,21] which has larger equilibrium volumes and thereby reduced *p-d* and *d-d* couplings for the majority spin channels.[18,19] Due to the volume and different bonding effects, MnAs shows a large exchange splitting for the *d* states and exhibits a nearly half-metallic behavior. The effect of the doping with Cu and Fe, decreasing the entropy, can be seen as a similar process to (Ga,Mn)As compounds, where Zener's *p-d* exchange mechanism dominates, the interactions are weaker but long ranged because the extended valence hole states mediate the ferromagnetic interaction.[20,22]

In particular in the case of Fe doping, while the local on-site electron-electron interaction in Fe is strong enough to create local atomic moment fluctuating on a short-length scale, there is also a strong hybridization of the 3*d* states from the neighboring atoms. The possibility that Fe in MnAs can be either in low-spin or high-spin state and how those configurations contribute to increasing and decreasing the entropy of the system should be suggested as a possible explanation for the behavior of the entropy obtained from heat flux measurements.

TABLE I. Summary of the values obtained for the entropy associated with the transition.

	Cooling			
Compound	$T_{initial}$ (K)	T_{final} (K)	Latent heat (J/g)	Entropy (mJ/g K)
MnAs	303	307	9.58	31.3
$Mn_{0.94}Fe_{0.06}As$	275.6	289	8.58	29.3
$Mn_{0.94}Cu_{0.06}As$	298	308.3	6.26	21.0
	Heating			
Compound	$T_{initial}$ (K)	T_{final} (K)	Latent heat (J/g)	Entropy (mJ/g K)
MnAs	313	318	7.13	22.7
$Mn_{0.94}Fe_{0.06}As$	306	315	7.0	22.8
$Mn_{0.94}Cu_{0.06}As$	314	323	5.25	16.7

For the Cu-doped sample, we observed the lowest difference between cooling and heating entropies. It had been suggested previously[4] that the presence of Cu in MnAs would reduce the total volume of the unit cell and cause second order effects associated with magnetoelastic interactions. Under such interpretation, one should have expected a higher ratio between the entropies. Further considerations on the nature of the bounding in (Mn,Cu)As are in progress.

In summary, we confirmed the transition with field observed by neutron scattering experiments,[16,17] and we obtained the entropy associated with the transitions. We used a DSC to obtain the heat flux. Comparing the entropy calculated from the heat flux, we observed that in the cooling process, $S^c_{Mn} > S^c_{Fe} > S^c_{Cu}$, and for the heating process, $S^h_{Fe} \approx S^h_{Mn} > S^h_{Cu}$. On the doped samples, the thermomagnetic behavior is compatible with a scenery where Zener's *p-d* exchange mechanism dominates, i.e., the interaction range is weaker but long ranged because the extended valence hole states mediate the ferromagnetic interaction. The difference in the entropies obtained from cooling and heating processes was found to be as high as 37%. Having an estimate of the energy loss during the heating and cooling is important for magnetic refrigeration applications and the future considerations for new magnetocaloric materials should include an entropy study as well.

A.L.L.S. would like to thank P. A. Sharma, R. Arita, and H. Takagi for fruitful discussions. S.G. and A.C. would like to acknowledge the support of the Brazilian agencies Fapesp, CAPES, and CNPq.

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