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Structural and Magnetic Study of the MnAs Magnetocaloric Compound

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The temperature induced phase transition in MnAs is analyzed in this work using X ray Rietveld refinement. The results show the presence of the hexagonal phase ($P6_3/mmc$) at room temperature and the first-order structural-magnetic transition to the orthorhombic phase (Pnma) around 318 K was followed in detail. The MnAs magnetic characterization allowed to obtain the transition temperature and a maximum value of 47 J/(kg.K) for the measured magnetocaloric effect for a magnetic field variation of 5 T.

Keywords: *MnAs intermetallic compound, magnetocaloric effect, structural phase transition*

1. Introduction

The MnAs compound presents the hexagonal NiAs-type structure at low temperature and transforms into a paramagnetic phase with an orthorhombic MnP-type structure at Curie temperature $T_c = 318$ K[1-6]. This transformation is a first-order transition accompanied by a structural transformation. According to the literature[7] the maximum magnetocaloric effect is observed near or at the critical Curie temperature.

In this work we present a structural study of the phase transition in the MnAs compound induced by temperature using X ray Rietveld refinement as well as the magnetic characterization including the measurement of the magnetocaloric effect.

2. Experimental

The MnAs sample was prepared following a new procedure developed in our laboratory using a high pressure resistive furnace. The materials used to prepare the sample were Mn with 99.99% purity and electronic grade As with 99.9999% purity. Pieces of these elements were weighted in the appropriate proportions and put in a graphite crucible inside the furnace. The pressure inside the furnace was maintained at 55 bar during the whole melting operation. The temperature of this crucible was slowly raised up to 850 °C, maintained at this value during 15 minutes, and then the temperature was raised to 1374 °C and maintained at this temperature during 8 minutes in order to allow the formation of the MnAs intermetallic compound. After this, the furnace was turned off and the crucible with sample was cooled at the natural variable cooling rate of the furnace.

X ray powder diffraction data for the MnAs compound were collected using a Philips X´Pert PRO MRD system with Cu target (Cu Kα radiation) running at 40 kV and 50 mA with a graphite diffracted beam monochromator, and a scanning step size of 0.02° (2θ). The measurements were performed at room temperature (298 K), at a temperature close to 318 K and also at 328 K by using a Peltier system with resolution of 0.1 K. The temperature of the Peltier element was monitored with a Copper-Constantan thermocouple, calibrated using the ice-water melting point and the water evaporation temperature.

Magnetization measurements were carried out in a conventional SQUID magnetometer (Quantum Design MPMS-XL). Samples with masses of the order of 10 mg were used for the magnetic measurements. The curves of magnetization *vs.* temperature (increasing and decreasing) for a field of 200 Oe (M *vs.* T) were measured in order to obtain the Curie temperatures of the material. We measured also the magnetization *vs.* field (M *vs.* H) curves for magnetic fields in the range 0 up to 5 T. From these data we obtained the magnetocaloric effect for field variations of 2 and 5 T.

3. Results and Discussion

Figure 1 shows the measured X ray powder diffraction patterns together with their Rietveld refinements for several chosen temperatures. The first pattern (Figure 1a) shows that the sample at room temperature is single phase with the NiAs-type structure in the ferromagnetic state, it means, hexagonal symmetry. The second pattern (Figure 1b) shows the diffraction pattern obtained during the phase transition around 318 K, showing the coexistence of both hexagonal and orthorhombic phases, and the third pattern (Figure 1c), obtained at 328 K, shows that the sample has the MnP type orthorhombic structure. The X ray data confirm the characteristics of good homonogeneity and single phase character of the sample that allowed to obtain good refinement fits with Rwp's of the order of 12%. The refinement of the pattern for the hexagonal phase (Figure 1a) provide Rwp = 12.7% and the obtained lattice parameters were: a = 3.730(3) Å and c = 5.700(1) Å, in very good agreement with the literature values (a = 3.70 Å and c = 5.70 Å)[5]. The analysis of the MnAs sample around the transition temperature (T = 318 K) clearly showed the coexistence of both phases which were quantified as 56.1(7)% hexagonal and 43.9(7%) orthorhombic. The refinement result is shown in Figure 1b). The Rietveld refinement for the orthorhombic phase, with Rwp = 11%, is presented in Figure 1c and the lattice parameters obtained for this phase were: a = 5.720(1) Å; b = 3.691(9) Å; and c = 6.375(9) Å. These values are in very good agreement with those presented in the literature[5].

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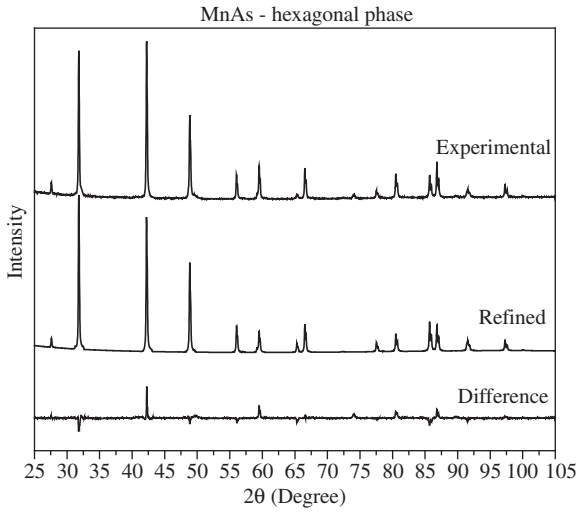
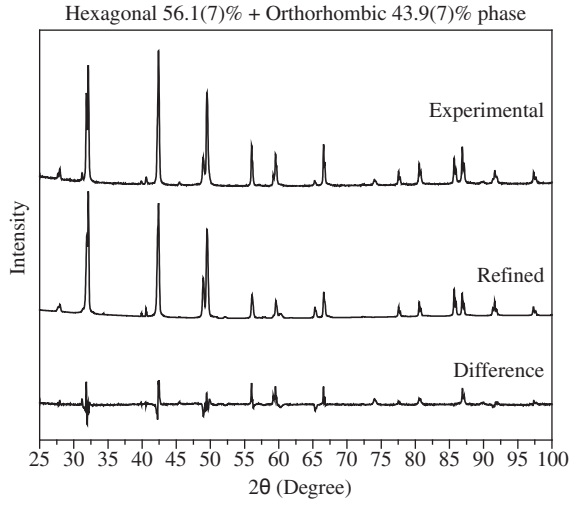
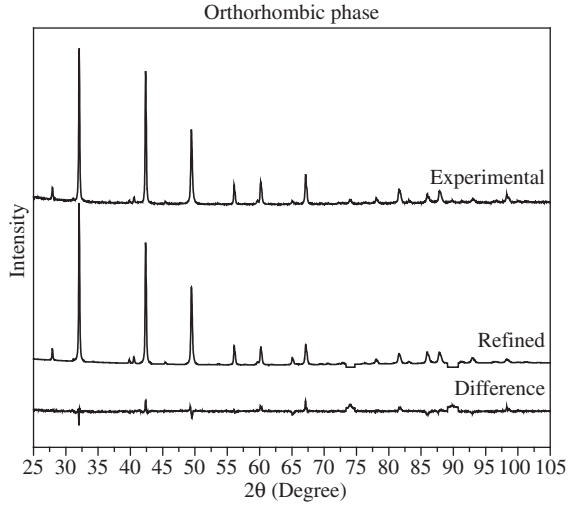


(a)



(b)



(c)

Figure 1. X ray powder diffraction patterns for MnAs obtained at three different temperatures: a) hexagonal phase (room temperature); b) during the phase transition (T = 318 °K) with both structures appearing; and c) orthorhombic phase (T = 328 °K).

The phase transition was followed through the (004) and (022) reflections of the hexagonal phase in the range of $63° < 2\theta < 69°$ measured for several different temperatures around the magnetic transition, Figure 2. In this figure we can observe the transformation of these reflections of the NiAs-type structure (hexagonal) to the (400), (222) and (204) reflections of the MnP structure (orthorhombic). One can also observe the coexistence of both phases between T = 318 K (presence of just a small contribution) and T = 328 K, when the transition has already finished. These results were used in the determination of the lattice parameters for both phases as well as the unit cell volumes, which are shown in Figure 3 as a function of the temperature. Figure 3 shows that the b-parameter essentially does not change during the transition, while the c-parameter, although varying smoothly with temperature, clearly presents the transition around 318 K. The a-parameter exhibits a marked jump at

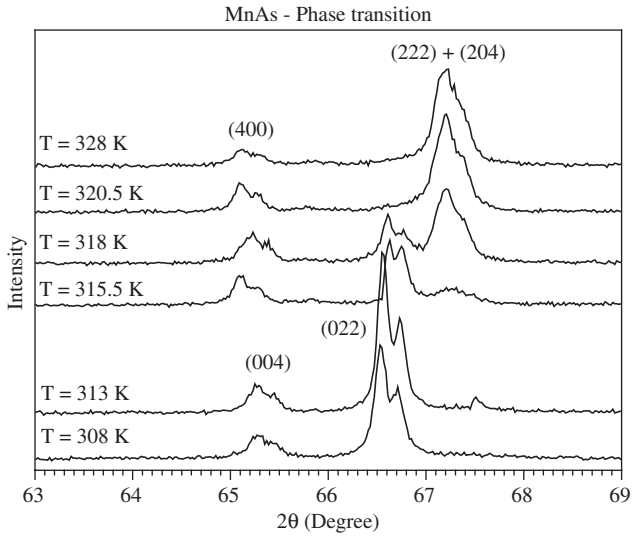


Figure 2. Region of the MnAs X ray pattern for different temperatures in order to show the phase transition in details.

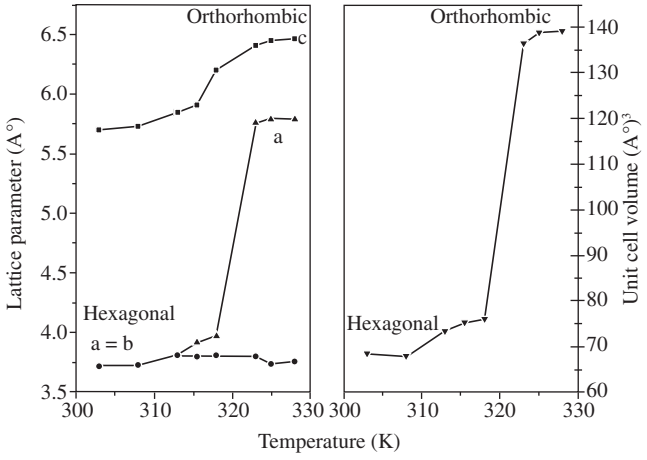


Figure 3. MnAs lattice parameters and unit cell volume as a function of the temperature around the first-order structural transition (318 °K).

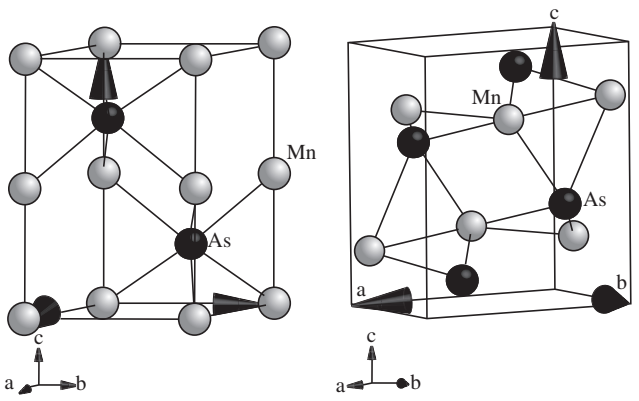


Figure 4. The 3D view of the MnAs crystal in the hexagonal (a) and orthorhombic structures.

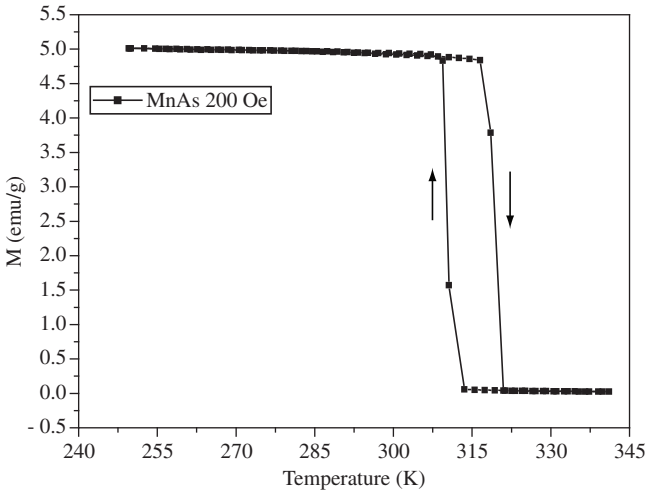


Figura 5. Thermal hysteresis curve for MnAs.

the transition temperature. This jump, together the c-axis variation, determines the MnAs unit cell volume behavior. It is worthwhile to point out the 100% increase in the unit cell volume during the hexagonal-orthorhombic transition that characterizes, the MnAs first-order structural transformation. The atomic distance between the Mn and As atoms also changes from 2.479 Å in the hexagonal phase to 2.581 Å in the orthorhombic phase, when the nearest atoms in the structure are considered. Figure 4 shows the 3D view of the MnAs unit cell for both structures (hexagonal and orthorhombic) obtained with the refined parameters.

The magnetic measurements of the sample give a saturation magnetization at 4 K of 3.2 μ_B/(atMn), with the transition temperature of 318 K for increasing temperature and 311 K with decreasing temperature, as shown in Figure 5. These transition temperatures were obtained as the minimum in the derivatives of the magnetization vs temperature curves. We see from this figure that the magnetic transition is also a first order one, following the structural transition described above. The magnetocaloric effect was measured for this MnAs sample for fields variations of 2 and 5 T, and Figure 6 shows that a maximum value of 47 J/(kg.K) was obtained for – ΔS for a magnetic field variation of 5 T. These results are in excellent agreement with the values in the literature[8-10]. These values of the magnetocaloric effect are in the giant range, and are characteristic of materials presenting first order magnetic transitions, normally coupled to first order structural transitions, as this one from the hexagonal to orthorhombic structures of MnAs.

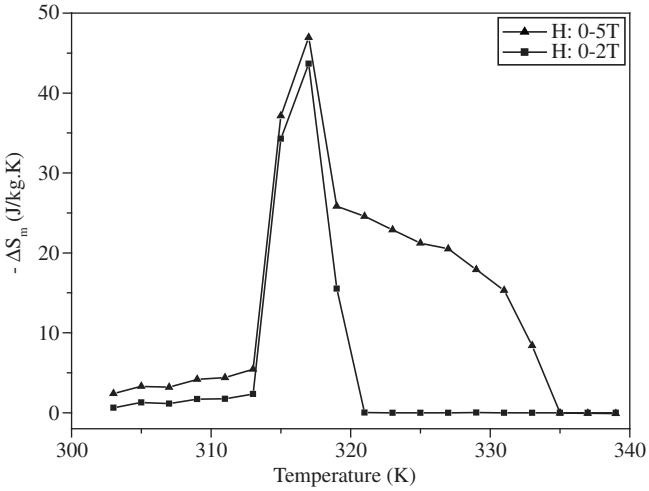


Figura 6. Magnetocaloric effect measurement (ΔS) with magnetic field varying between 0 T - 2T and 0 T - 5T.

4. Conclusions

In this work the first-order temperature induced phase transition (hexagonal – orthorhombic) in MnAs was measured in detail. The unit cell lattice parameters as well as the unit cell volume behavior during the transition were followed. A discontinuous change in the a-parameter and in the unit cell volume was clearly observed. The lattice parameters obtained from the Rietveld refinements are in good agreement with those presented in the literature. Thermomagnetic measurements confirmed the first order nature of the magnetic transition coupled to the structural transition, presenting temperature transitions of 318 K when T increases and 311 K when T decreases. The magnetocaloric effect was measured for field variations of 2 and 5 T, and the results obtained are in excellent agreement with the published values.

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