

Structural and Magnetic Phase Diagram of $MnSe_{1-x}Te_x$

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Abstract

Neutron diffraction studies as a function of temperature on solid solutions of $MnSe$ and $MnTe$ in the Se rich region are presented. As Te is doped in $MnSe$, the structural phase transition wherein some portion of the sample converts to antiferromagnetic NiAs phase disappears completely and reappears in $MnSe_{0.5}Te_{0.5}$ at room temperature. In this compound the room temperature phase is a mixture of both cubic and hexagonal phases in a ratio of 90:10. The magnetic ordering temperature of the cubic phase decreases with increasing Te content, while that of the hexagonal phase remains constant.

INTRODUCTION

Solid solutions of $MnSe_{1-x}Te_x$ exhibit interesting magnetic and structural phase diagram. The studies reported so far indicate different solid solubility regions of two parent phases, viz NaCl type cubic and NiAs type hexagonal [1-4]. First studies on this system by Pausen and Johnston [1] determined the solubility range over the entire phase diagram in the temperature range 500 to 1100° C. The compositions in the range $0.4 \leq x \leq 0.7$ were biphasic (NaCl + NiAs) with NiAs phase content increasing with Te concentration. For the same system Kamat Dalal et al [2] showed that compounds up to $x = 0.55$ are purely cubic while those with $x > 0.55$ are hexagonal. Chehab et al [3,4] reported two different phase diagrams for compounds annealed at two different temperatures. For alloys annealed at 960° C a biphasic region was observed in the concentration range $0.2 < x < 0.6$ that increased to $0.15 < x < 0.75$ for the alloys annealed at 600° C. It should be noted that method of preparation of all three groups referred above were significantly different.

Another interesting feature of these solid solutions is their magnetic phase diagram. All the samples show more than one magnetic transition [1-5]. In the case of $MnSe$, two antiferromagnetic transitions at 270K and 130K are attributed to ordering of hexagonal phase and parent cubic phase respectively [6]. Here, about 30% of the sample converts from parent cubic to an antiferromagnetically ordered hexagonal phase at 270K. $MnTe$, which is a NiAs type hexagonal antiferromagnet with $T_N = 310K$ shows ferromagnetic like transition below 80K which has been explained to be due to a magnetoelastic coupling that strengthens ferromagnetic interactions in the basal plane over antiferromagnetic interactions along c-axis [5]. The situation about the intermediate compounds however is not very clear. The magnetic transitions are not properly attributed, as well as there is a contradiction about the ordering temperature as a function of Te concentration. It is with an aim of understanding the structural and magnetic transitions occurring in $MnSe_{1-x}Te_x$, neutron diffraction studies were

undertaken and results on Se rich compounds are presented.

EXPERIMENTAL

$MnSe_{1-x}Te_x$ with $x = 0, 0.3$ and 0.5 were prepared by solid-state reaction method as employed by Kamat Dalal et al [2]. In particular the pure metals (purity > 99.99%) were taken in stoichiometric amount, ground thoroughly, sealed in evacuated quartz tube (vacuum $\sim 10^{-6}$ Torr) and sintered at different temperatures as mentioned in reference [2]. The main difference between this and other methods of preparation is that in this method the samples are heated at a very slow rate (0.7°/min) and then annealed for a long time while other methods heat the samples to a very high temperature and then quench it to annealing temperature. The samples were characterized by X-ray diffraction, magnetic susceptibility and resistivity. Neutron diffraction measurements were performed on Profile analysis diffractometer at Dhruva in the temperature range 10K - 300K.

RESULTS AND DISCUSSION

Neutron diffraction patterns for $MnSe_{1-x}Te_x$, where $x = 0, 0.3$ and 0.5 recorded at R.T. (300K) are presented in figure 1. It can be clearly seen that both $MnSe$ and $MnSe_{0.7}Te_{0.3}$ are cubic at R.T. while the 50% doped sample shows extra peaks that with Rietveld refinement could be identified to be due to $\sim 10\%$ of NiAs phase. The lattice parameters of the cubic phase show expected increase with Te doping. The cell constant for $MnSe$ is $a = 5.467 \pm 0.002 \text{ \AA}$ which increases to $5.577 \pm 0.001 \text{ \AA}$ in 30% Te doped sample and to $5.667 \pm 0.001 \text{ \AA}$ in $MnSe_{0.5}Te_{0.5}$. At 270K $MnSe$ undergoes a structural transition wherein a part of the sample converts to NiAs type hexagonal phase, which is antiferromagnetically ordered. The percentage of hexagonal phase increases with decreasing temperature but even at 10K the sample remains biphasic with 70% of cubic and 30% hexagonal phases. The NiAs type phase observed in $MnSe_{0.5}Te_{0.5}$ also orders antiferromagnetically at 270K but its

percentage remains almost constant at 10% down to 10K. No such structural transition is seen in $\text{MnSe}_{0.7}\text{Te}_{0.3}$.

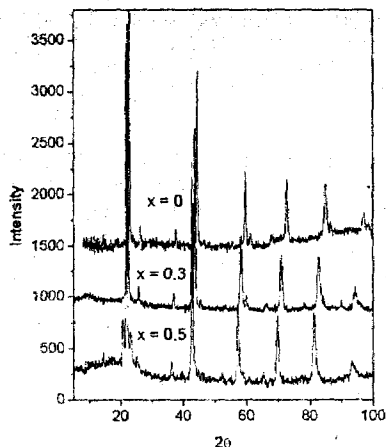


Fig 1. Neutron Diffraction Plots of $\text{MnSe}_{1-x}\text{Te}_x$ at R.T.

It is known that the NiAs type structure can easily be fitted in a NaCl unit cell and the lattice parameters are related as $a_{\text{hexa}} = a_{\text{cubic}}/\sqrt{2}$ and $c_{\text{hexa}} = \sqrt{3} a_{\text{cubic}}/\sqrt{2}$ (as shown in Fig. 2). These relations are better satisfied in $\text{MnTe}_{0.5}\text{Se}_{0.5}$ with $a_{\text{hexa}} = 3.967 \pm 0.003 \text{ \AA}$ and $c_{\text{hexa}} = 6.932 \pm 0.008 \text{ \AA}$ rather than in MnSe where the hexagonal cell parameters are $a = 3.840 \pm 0.001 \text{ \AA}$ and $c = 6.389 \pm 0.001 \text{ \AA}$. Here c is distinctly less than the expected value. This is perhaps the reason for stacking faults found in MnSe that result in broadening of certain hexagonal reflections. It must be mentioned that such a broadening is not seen in $\text{MnSe}_{0.5}\text{Te}_{0.5}$.

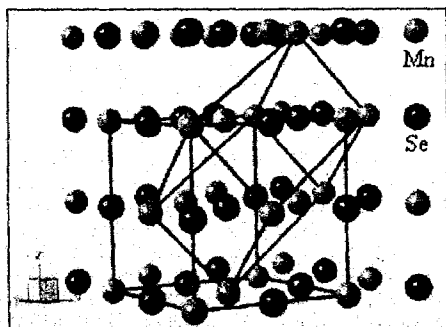


Fig 2. Hexagonal unit cell generated within the NaCl structure.

All the compounds order antiferromagnetically. The NiAs phase in all compounds is type I antiferromagnet

with moments ferromagnetically aligned in the basal plane and stacked antiferromagnetically along c -axis. The ordering temperature of this phase in both MnSe and $\text{MnSe}_{0.5}\text{Te}_{0.5}$ is 270K. The parent cubic phase also orders antiferromagnetically at lower temperature and it decreases with increasing Te content. In MnSe it orders at 130K which decreases to 100K in $x = 0.3$ and further to 70K in $x = 0.5$ sample.

Thus it is clear that as the Te concentration is increased the cubic phase weakens magnetically. Structurally also the lattice expansion is such that at higher Te concentration NiAs phase is more favourable and this would happen at that concentration of Te where the relations between lattice parameters of cubic and hexagonal phase are exactly satisfied. The absence of NiAs phase down to 10K in $\text{MnSe}_{0.7}\text{Te}_{0.3}$ is however not clear.

CONCLUSIONS

1. Crystal and Magnetic structures of Se rich $\text{MnSe}_{1-x}\text{Te}_x$ have been studied using Neutron diffraction. The $x = 0.5$ sample is close to R.T. structural phase transition boundary.
2. NiAs phase also appears in MnSe at low temperatures but such a phase transition is surprisingly absent in $\text{MnSe}_{0.7}\text{Te}_{0.3}$.
3. Both the phases order antiferromagnetically. The NiAs phase orders at 270K in both the compositions while the Neel temperature of cubic phase decrases from 130K in MnSe to 70K in $\text{MnSe}_{0.5}\text{Te}_{0.5}$.

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