# Low temperature magnetic structure of MnSe

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**Abstract.** In this paper we report low temperature neutron diffraction studies on MnSe in order to understand the anomalous behaviour of their magnetic and transport properties. Our study indicates that at low temperatures MnSe has two coexisting crystal structures, high temperature NaCl and hexagonal NiAs. NiAs phase appears below 266 K and is antiferromagnetically ordered at all temperatures while the NaCl phase orders antiferromagnetically at 130 K.

## 1. Introduction

Manganese chalcogenides, MnS, MnSe and MnTe are antiferromagnetic compounds with transition temperatures increasing with molecular weight [1,2]. In the case of MnS and MnSe the stable crystal structure is a cubic NaCl type and these are wide gap insulators [3–5]. On the other hand, MnTe crystallizes in the hexagonal NiAs type structure [6] and is one of the few semiconductors among the 3d transition metal compounds.

The magnetic susceptibility of MnSe shows certain anomalies as well as hysteresis effects over a wide range of temperatures centered around 160 K [2,7]. The presence of these anomalies has been attributed to a structural transition to hexagonal NiAs phase, which coexists with the high temperature cubic phase [8–11]. These crystallographic and magnetic transition below 300 K, have led to contradictory interpretation of results. Neutron diffraction studies indicate that the hexagonal phase has stacking faults with ferromagnetic sheets perpendicular to the c-axis, stacked antiferromagnetically, with spin direction within the sheets [9] or spin direction parallel to the sheets [10]. Whereas the Mössbauer studies show that the spin arrangement in NaCl form is multiaxial while in the hexagonal NiAs modification the spins are along the $\langle 2\,1\,0 \rangle$ direction [12].

In this paper we report the results of the study of crystal and magnetic structure of MnSe at low temperatures. Neutron diffraction studies in the temperature range
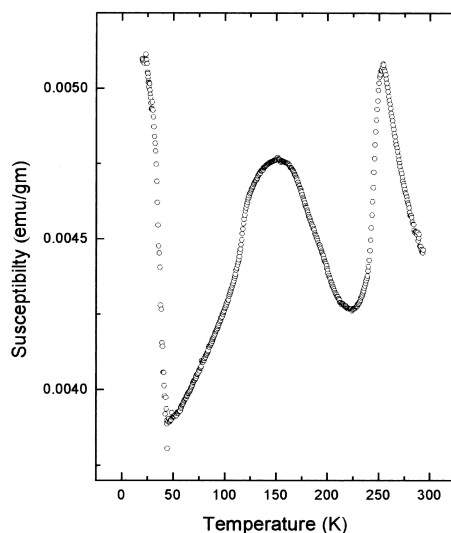
**Figure 1.** Magnetic susceptibility of MnSe as a function of temperature.

10–300 K were carried out to understand the anomalies and to elucidate the low temperature crystal and magnetic structure of these compounds.

## 2. Experimental

The samples were prepared by mixing stoichiometric amounts of finely powdered Mn, Se, and Te and then palletized and sealed in evacuated quartz ampoule below $10^{-6}$ Torr and subsequently given an appropriate heat treatment. MnSe was slowly heated to 650°C, annealed for 20 h and furnace-cooled. The sample was characterized by X-ray diffraction and the sample was found to be single phase crystallizing in NaCl-type structure. Magnetic susceptibility measurements were performed using a Faraday balance in the temperature range 30–300 K in a field of 100 Oe. Neutron diffraction experiments were carried out in the temperature range 10–300 K using the profile analysis diffractometer at Dhruva.

## 3. Results and discussion

A plot of DC susceptibility for MnSe during the warm-up cycle is shown in figure 1. Susceptibility exhibits a broad hump between 130–170 K and a sharp peak at 270 K. These anomalies can be broadly described as due to magnetic ordering of cubic and hexagonal phases [11] of MnSe, respectively. A new feature of the susceptibility curve is a sharp rise below 50 K. Such a feature has not been reported earlier. It should be mentioned here that very few reports [13] on susceptibility measurements down to 10 K on MnSe exist in literature.
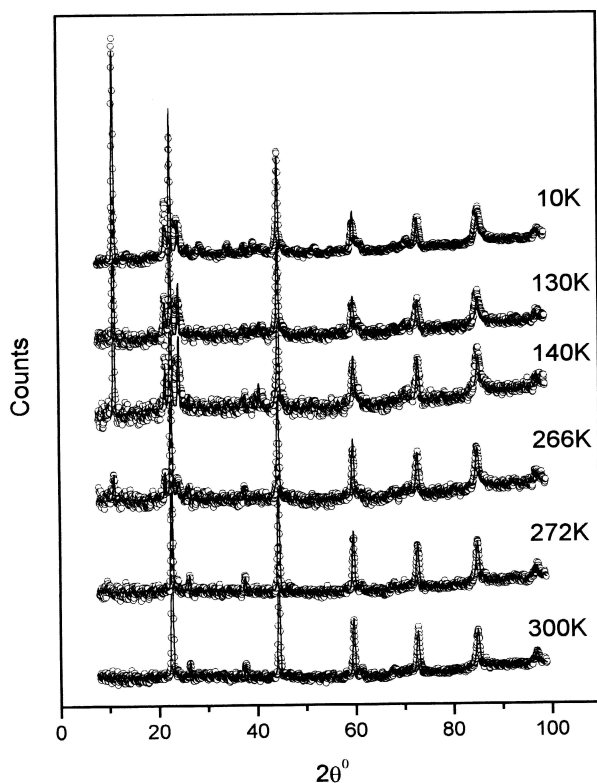
**Figure 2.** Neutron diffraction plots of MnSe at different temperatures. Solid line is the Rietveld fit to the data.

In order to understand the origin of these anomalies neutron diffraction patterns were recorded during the warm-up cycle from 10 to 300 K at several temperatures using a closed cycle refrigerator. Rietveld refinements of the neutron diffraction data were done using Fullprof (FP2K) program [14] and are presented in figure 2. The 300 K pattern shows MnSe to be cubic (NaCl-type) with a lattice constant of 5.45 Å. Diffraction peaks indexable to NiAs-type hexagonal phase start appearing between 272 K and 266 K (refer to figure 2). This phase is antiferromagnetically ordered as indicated by $(0\,0\,2)$ magnetic reflection at about $2\theta = 10°$. The peak around 250 K in susceptibility coincides well with the appearance of this magnetic Bragg reflection. The spin alignment in this phase is ferromagnetic in the basal plane and these ferromagnetic sheets are stacked antiferromagnetically along the *c*-axis. Additional reflections and sudden increase in the intensity of $(0\,0\,2)$ magnetic reflection that coincides in position with $(1\,1\,1)$ magnetic reflection of cubic NaCl phase below 140 K indicates antiferromagnetic ordering of the high temperature cubic phase. The susceptibility also shows a sharp fall at around this temperature. The broad hump in susceptibility between 270 and 150 K can then be ascribed to a competition between decreasing contribution to susceptibility from antiferromagnetic NiAs phase and increasing paramagnetic contribution from cubic NaCl phase.
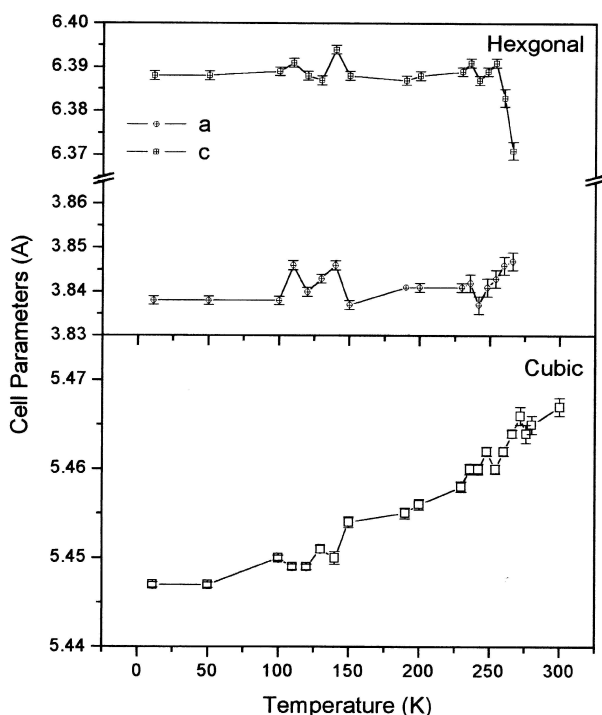
**Figure 3.** Variation of cell parameters with temperature.

Variation of cell parameters and the magnetic moment per Mn ion as a function of temperature for both cubic and hexagonal phases, estimated from our analysis are presented in figures 3 and 4 respectively. The diffraction patterns, however, give no indication of another phase transition to explain the rise in susceptibility below 50 K. In figure 5 we plot weight% composition of cubic and hexagonal phases as obtained from Rietveld refinements. It can be seen that about 30% by weight of the sample is converted to hexagonal phase and this remains nearly constant in the 210–10 K region. This is in good agreement with the result of Jacobson and Fender [10] who obtained a maximum of 38% of hexagonal phase. It may be observed that some of the hexagonal reflections are anomalously broad compared to others. The anomalous widths of these peaks could be assigned to the presence of stacking faults along the *c*-axis [9,10]. These faults occur due to an incomplete structural transition that MnSe undergoes.

## 4. Conclusions

1. MnSe has cubic NaCl-type structure at room temperature (300 K).
2. It undergoes a structural transition to NiAs-type hexagonal phase at about 266 K. Up to 30% of the sample by weight gets converted to hexagonal phase and the remaining 70% is cubic.
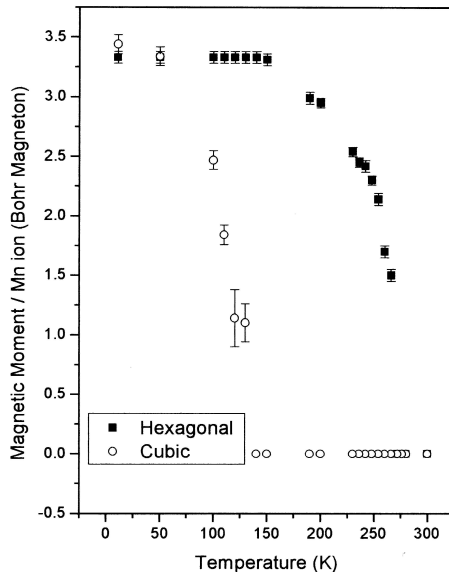
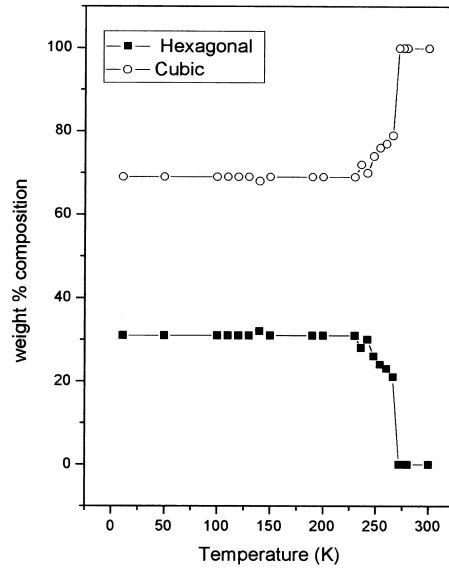**Figure 4.** Variation of magnetic moment of Mn in MnSe.



**Figure 5.** Weight% composition of the two phases in MnSe.

3. The hexagonal phase is antiferromagnetically ordered at the temperature it appears. The spin alignment is ferromagnetic in the basal plane with antiferromagnetic stacking of such planes along the *c*-axis.

4. The high temperature cubic phase also orders antiferromagnetically at about 130 K and the ordering is MnO-type.

5. The hexagonal phase has stacking faults as evidenced by the broadening of some reflections.

## Acknowledgements

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