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Magnetic properties of crystalline γ-MnS thin films

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We report temperature dependence of magnetic behavior of MnS thin films. Temperature ranges well below and above the transition point. The obtained magnetic measurements and the theoretical magnetic calculations suggest that the magnetic behavior of γ-MnS is Curie like type at high temperatures. On the other hand in the low temperature region the magnetic arrangement is an ordered antiferromagnetic phase.

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1. Introduction

Diluted magnetic semiconductors (DMS) have received considerable attention due to their observed magnetism [1-3]. This category of semiconductors is in fact alloys of nonmagnetic semiconductors and magnetic elements [4]. The magnetic interaction in II-VI semiconductors, such as CdTe, ZnSe is dominated by the antiferromagnetic exchange, which results in the paramagnetic, antiferromagnetic, or spin-glass behavior of the material [3]. They have been proposed as an approach to spin sensitive electronics, and the possibility of fabricating many semiconductor devices, including cellular phones (microwave transistors), compact disks (semiconductor lasers), and many other applications [5-8]. Manganese sulfide (MnS) which belongs to the family of DMS is extensively studied because of its magneto optical properties [9-12]. MnS thin films or powders can be found in several polymorphic forms: the rock salt type structure (α-MnS) is the most common form, by low temperature growing techniques it crystallizes into the zincblende (β-MnS) or wurzite (γ-MnS) structure [13,14]. Recently, it was demonstrated [15] that MnS clusters can be isolated in ze. In this work we have investigated magnetic behavior of crystalline (γ-MnS) thin films by experimentally and theoretically. Special interest has been focused on the magnetic phase and spin arrangements of thin films at different temperature regions.

2. Experimental details

MnS thin films were deposited on glass substrates using chemical bath deposition CBD method at room temperature (27 °C). The substrates used for the deposition of MnS thin films were commercial glass slides with the size of 76×26×1 mm. The details of experimental system and preperation of thin films has been explained elsewhere [16]. The magnetic moment and susceptibility measurement system is a commercial magnetometer (VSM-7304) which is suitable to collect data at various applied magnetic fields and different temperatures.

3. Results and discussion

Fig. 1 shows XRD pattern of MnS on glass substrate in the range of 2θ angle between 10° to 70°. We observe only one strong peak at $2\theta = 28.26^{\circ}$ (d = 0.3157 nm) which can be attributed to the (002) line of the hexagonal γ-MnS wurtzite phase.

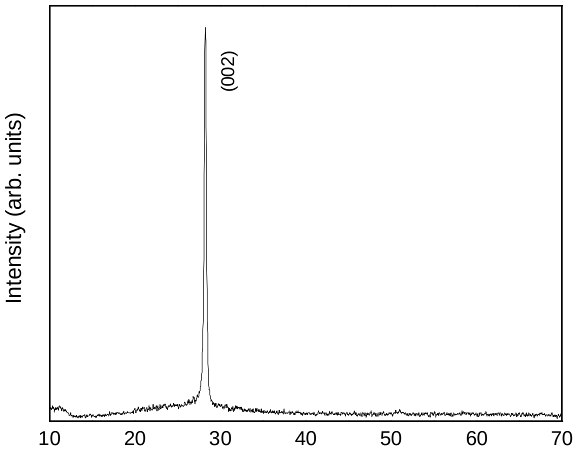

Fig. 1. X-ray diffraction pattern of MnS film deposited on glass substrate at 27 °C.

The deposited MnS thin film grows preferentially along the *c*-axis. As determined from the XRD data, the lattice parameter *c* is estimated to be 0.6315 nm which is consistent with the standard value of 0.6447 nm. It is important to note that we have deposited well ordered MnS thin film on glass substrate at room temperature. This is reported in one of our recent studies [16]. The susceptibility measurement of MnS is shown in Fig. 2 where temperature ranges from 160 to 250 K. Fig. 3 shows magnetic susceptibility in antiferromagnetic phase from 0 to 100 K.

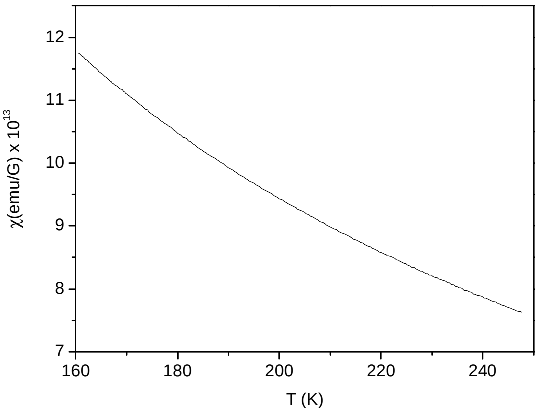

Fig. 2. High temperature susceptibility.

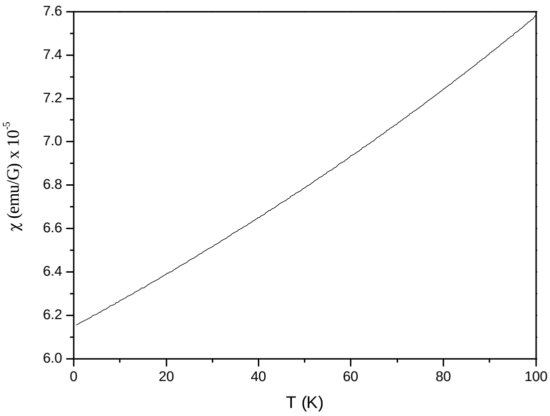

Fig. 3. Low temperature susceptibility.

In Fig. 4 we show sub lattice magnetization. In a magnetic system difficulties arise when the exchange interaction between neighboring ions and long range magnetic order have to be explained. There are many theoretical and experimental studies devoted to this subject [17-19]. For the present research only two extreme cases are considered in order to explain the experimental data, namely, well below and far away from the transition temperature. Since the sample contains magnetic Mn centers in a hexagonal structure, it would be apparent that a Curie type magnetic behavior will emerge in a certain temperature range. It should also be clear that γ-Mn shows a Néel type antiferromagnetic order below the transition temperature [20]. As we have mentioned above we are interested in some particular regions in which either the ordered or a completely disordered phase has already formed.

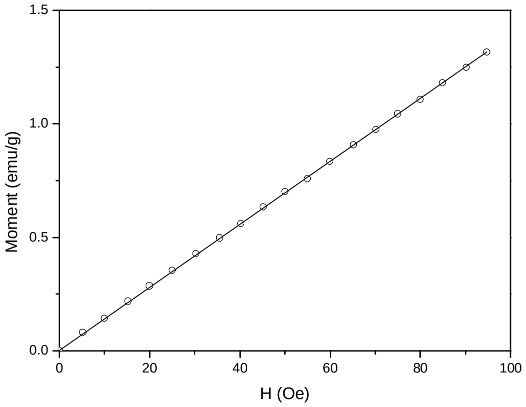

Fig. 4. Sublattice magnetization.

A. Low temperature behavior

Since the system is antiferromagnetic, the expected magnetic moment should be zero at low temperatures. The magnetic centers are aligned in the *z* direction and the relative alignment of each pair is antiparallel to each other at this temperature range. Although this is the expected ordering, the nature may be completely different due to the frustration of neighboring bonds. This is a well known phenomenon and generally occurs in some special crystal types, commonly known as unbipartite lattice [18,21]. For the present research this fact has not been taken into account but we should note that our system is of that type too. For simplicity we assume that the magnetic ordering is a two sublattice type. For an antiferromagnet with sublattices *A* and *B*, the molecular field for the *A* moments is given by *HmA* = *wAAMA* + *wABMB*, where *wAB* is the inter-site interaction coefficient which is negative and usually much larger than the positive intra-site interaction *wAA*. A similar expression can of course be written for the *B* sites. If *wAA* = *wBB* = w_1 and *wAB* = *wBA* = w_2 we end up with

$$\chi = \frac{N\mu_{eff}^2}{3k(T-\theta)} \tag{1}$$

Where

$$\theta = \frac{N\mu_{eff}^2 (w_1 + w_2)}{6k} \tag{2}$$

The critical temperature known as the Néel temperature for such systems is given by

$$T_N = \frac{N\mu_{eff}^2 (w_1 + w_2)}{6k} \tag{3}$$

Where $\mu_{eff}^2 = gJ(J+1)\mu_B$ is called the effective magnetic moment. The variation of the susceptibility for high and low temperature is shown in Fig. 2 and Fig. 3, respectively. It is quite obvious that some Néel type susceptibility exists. The field dependence of the magnetic moment and magnetic susceptibility can be derived from the Zeeman perturbation term as (for one sublattice)

$$M(T,H) = \mu_{eff} JB_j(T,H) \tag{4}$$

and

$$\chi(T,H) = \nabla_H M(T,H) \tag{5}$$

where T is the temperature, $B_j(T,H)$ is the Brillouin function, J is the angular momentum of Mn ions, and H is the applied magnetic field. The variation of these quantities at a particular temperature is shown in Fig. 4. As can be seen from this figure the sublattice magnetization is a linear function of the applied field. It should be remembered that the other sublattice variation is exactly the same as this one but its direction is reversed such that the average magnetic moment is zero. This is again in good agreement with the observed behavior shown in Fig. 5. It is also obvious that the susceptibility is constant for this sublattice. As shown in the Fig. 6 it is constant and that is what one would be expecting. The susceptibility below T_N surely depends on the angle between the applied field and the direction of the sublattice magnetization. The field dependence for an antiferromagnet is free from hysteresis. It usually takes a very large field to reach saturation. This is quite obvious from all the measurements done at all temperatures.

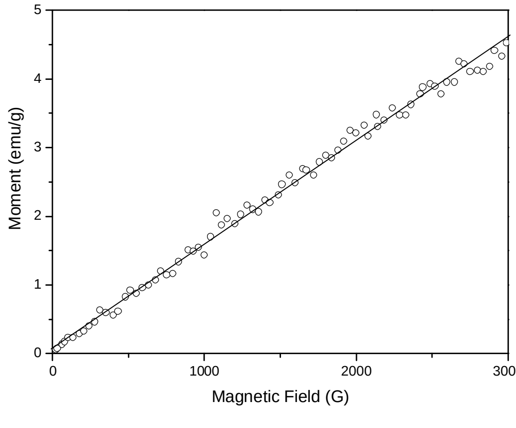

Fig. 5. Magnetization bellow Néel temperature.

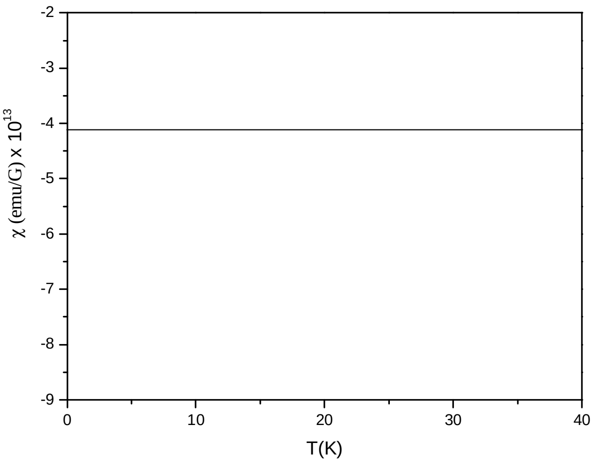

Fig. 6. Susceptibility bellow the Néel temperature.

B. High temperature behavior

It is quite well known that all the ordered magnets above a certain temperature become paramagnetic. In a paramagnetic state the susceptibility becomes field dependent and does not significantly vary with temperature at well above the transition temperatures. The magnetic moment on the other hand shows a linear dependence to the applied field. Each paramagnetic centre behaves independently from its surroundings and tries to align parallel to the applied field. The average magnetic moment then surely will show linear applied field dependence. The susceptibility and average magnetic moment in this ordered temperature independent range can easily be calculated from the well known formula of Van Vleck as

$$\chi(T,B) = \left(\frac{Ng^2\mu_B^2}{3kT} \right) S(S+1) \tag{6}$$

and

$$M(T,B) = 2.828\sqrt{T.\chi(T,B)} \tag{7}$$

The variations of magnetic moment and susceptibility in a low homogeneous applied field are shown in Fig. 7 and Fig. 8. The variation of these quantities with the applied field can easily be evaluated from the Zeeman perturbation term and they are shown Fig. 9 and Fig. 10. It is quite clear that the calculations are well supported by the experimental observations shown in Fig. 2, Fig. 3, Fig. 5, Fig. 7, and Fig. 8.

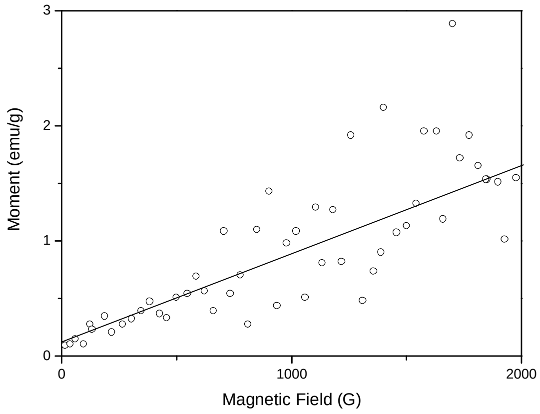

Fig. 7. Magnetization above the Néel temperature.

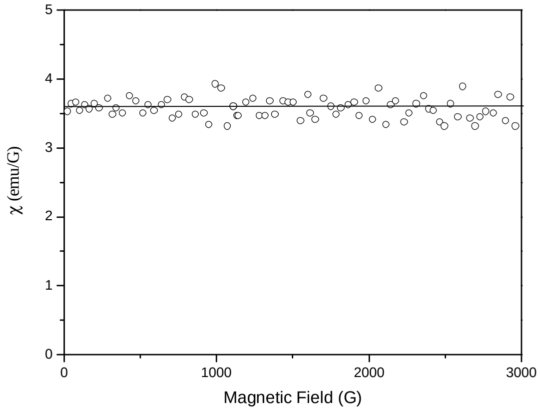

Fig. 8. Susceptibility above Néel point.

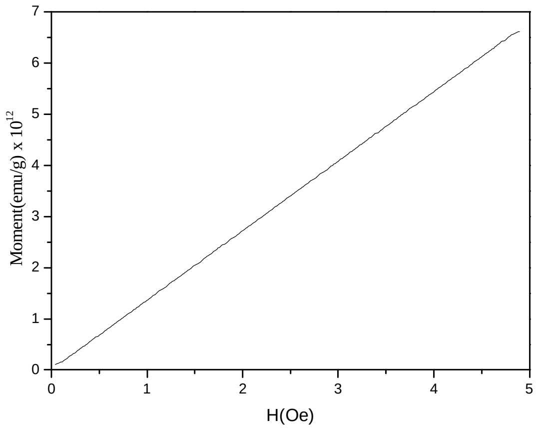

Fig. 9. Magnetization as a function of applied field.

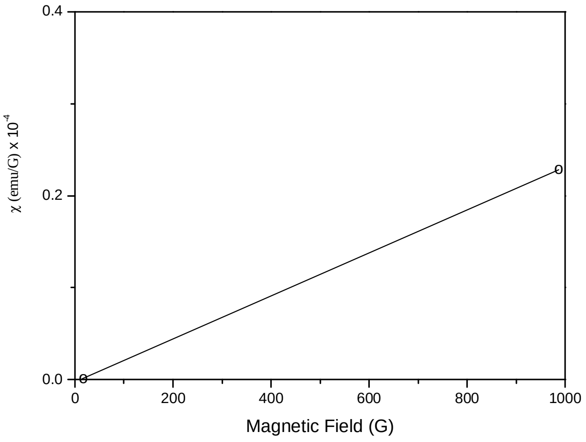

Fig. 10. Susceptibility as a function of applied field.

As a result we can easily say that the magnetic behavior is in good agreement with the literature indicating that the system is antiferromagnetic.

4. Conclusion

We have deposited crystalline γ-MnS thin film on glass substrate at room temperature by using CBD method. The magnetic structure of prepared film was characterized by means of several parameters including magnetic moment and magnetic susceptibility. It is quite obvious from the theoretical calculations and experimental observations that the magnetic behavior is an antiferromagnetic Néel type and it is consistent with the existing literature.

Acknowledgements

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