Cryst. Res. Technol.	**31**	1996	S	635–638

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CRYSTALLINE STRUCTURE AND SPIN CORRELATIONS IN $(AgIn)_{0.5}MnTe_2$ AND $(CuIn)_{0.5}MnTe_2$ ALLOYS.

Polycrystalline samples of $(AgIn)_{0.5}MnTe_2$ and $(CuIn)_{0.5}MnTe_2$ alloys were prepared by a melt and annealing technique, followed by different heat treatments (annealing at 600°C and quenched to room temperature or annealing at 300°C and slow cooled to room temperature) in order to get different degrees of crystal and magnetic order. However neutron powder diffraction data of these samples revealed the same disordered zinc-blende structure for all of them (High Resolution Powder Diffraction at T = 300 K). No long range magnetic order is obtained (T = 1.2 K) in any of these alloys. However spin correlations are evidenced at low temperature by the presence of broad lorentzian shaped magnetic Bragg peaks in the neutron diffraction data. These peaks can be labelled as (1 1/2 0), (1 3/2 0) and (2 1/2 1), and correspond to a type III antiferromagnetic order AFM-III (fcc crystal unit cell). From the value of their full width at half maximum (FWHM) a magnetic correlation length is deduced. These results have also been analysed as a function of temperature in the frame of a model developed by HOLDEN et al. for $Zn_{1-z}Mn_zTe$ alloys.

1. INTRODUCTION

Diluted magnetic semiconductors (DMS) are semiconducting alloys whose lattice is made up in part of substitutional magnetic atoms. The most extensively studied and most thoroughly understood materials of this type are the $A^{II}_{1-z}Mn_zB^{VI}$ alloys in which a fraction of the group II sublattice is replaced at random by Mn. However, similar alloys can be produced by introducing manganese into the equivalent ternary compounds, the tetrahedraly coordinated $A^IB^{III}C_2^{VI}$ chalcopyrites; e.g. $(CuIn)_{1-z}Mn_{2z}Te_2$, etc. In these quaternary alloys, it has been shown that, depending upon heat treatment, a given material can show two different sets of magnetic and band-gap behaviour. This fact has been correlated with positioning of the manganese atoms in the cation lattice (LAMARCHE et al.), although in all cases the magnetic behaviour is spin-glass, indicating a random

distribution of manganese on some sub-lattice (WOOLLEY et al.). In the way of studying the influence of heat treatment on the crystal and magnetic structures we have undertaken a neutron diffraction characterization of $(AgIn)_{0.5}MnTe_2$ and $(CuIn)_{0.5}MnTe_2$ samples prepared with different annealing conditions.

2. EXPERIMENTAL

Alloy samples of $(AgIn)_{0.5}MnTe_2$ and $(CuIn)_{0.5}MnTe_2$ were prepared by the standard melt and annealing technique as described in (QUINTERO et al.). Two set of samples of each system were prepared with different heat treatments: i) annealing at 600°C and quenching to room temperature (in the following AgIn600 or CuIn600); ii) annealing at 300°C and slow cooling to room temperature (in the following AgIn300 or CuIn300). The powder samples with a volume of about 1.5 cm^3 were packed in cylindrical cans (I.D. 6 mm, length 50mm) and mounted in a variable temperature cryostat permitting measurements to be made between 1.2 K and 300 K.

Neutron powder diffraction experiments were performed with the 3T-2 high resolution powder diffractrometer at the Orphée reactor in Saclay. A neutron beam monochromatized from a Ge (335) single crystal was passing through a collimator system giving a wavelength of λ = 1.2268 Å and a neutron intensity of 5 x 10^6 cm^{-2} S^{-1} at the sample position. In a second series of measurements the $(AgIn)_{0.5}MnTe_2$ diffraction patterns at several temperatures were collected with the G4-3 spectrometer (λ = 2.662 Å).

The intensity data was evaluated with the Rietveld method. Atomic coordinates in space group F $\bar{4}$ 3 m and lattice parameter values, previously reported (NEAL et al.), were used as starting parameters in the least-squares refinements.

3. THEORETICAL MODEL

The total neutron scattering from alloys such as $(AgIn)_{0.5}MnTe_2$ and $(CuIn)_{0.5}MnTe_2$ consists of several components: i) coherent elastic (Bragg) scattering; ii) thermal diffuse inelastic coherent scattering; iii) incoherent scattering and iv) magnetic diffuse scattering. The first three components involve neutron scattering by the nuclei in the crystal, while the last one arises from the magnetic electrons of the Mn ions interacting with the neutron magnetic moment. The expressions to describe these four components, for the case of unpolarized neutrons scattered from a polycrystalline powdered sample, and further details on the model can be found in the paper of HOLDEN et al.

4. RESULTS AND DISCUSSION

Figure 1 shows the neutron diffraction patterns, obtained at room temperature. The neutron diffraction patterns corresponding to the AgIn600 and AgIn300 samples are practically identical. All the reflections were indexed on the space group F $\bar{4}$ 3 m with very similar lattice parameters values (a = 6.3693(2) Å for AgIn600, and a = 6.3722(2) Å for AgIn300).

Similar measurements were made for the $(CuIn)_{0.5}MnTe_2$ (a = 6.2629(2) Å for CuIn600, and a = 6.2648(3) Å). In this case values of the lattice parameter a were again very similar for both CuIn600 and CuIn300 samples. These results revealed the same disordered zinc-blende structure for both systems. It is clear that both AgIn300 and CuIn300 samples are as expected β' phase (QUINTERO et al.). However, with the AgIn600 and CuIn600 samples, the results are much less clear. This is perhaps to be expected, since the samples were prepared in 5 gm pieces, and we have seen that it is extremely difficult to quench this amount quickly enough to retain the β phase (QUINTERO et al.).

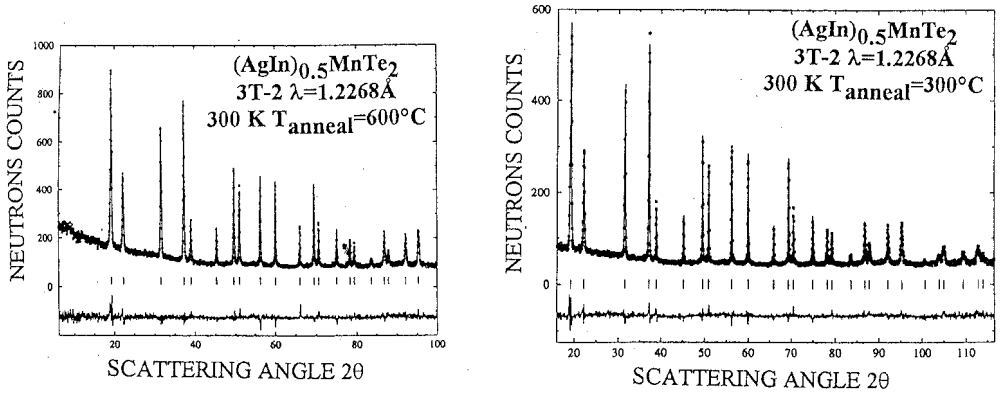

Fig.1: Rietveld refinement pattern of both: a) Ag600 and b) Ag300 samples at room temperature.

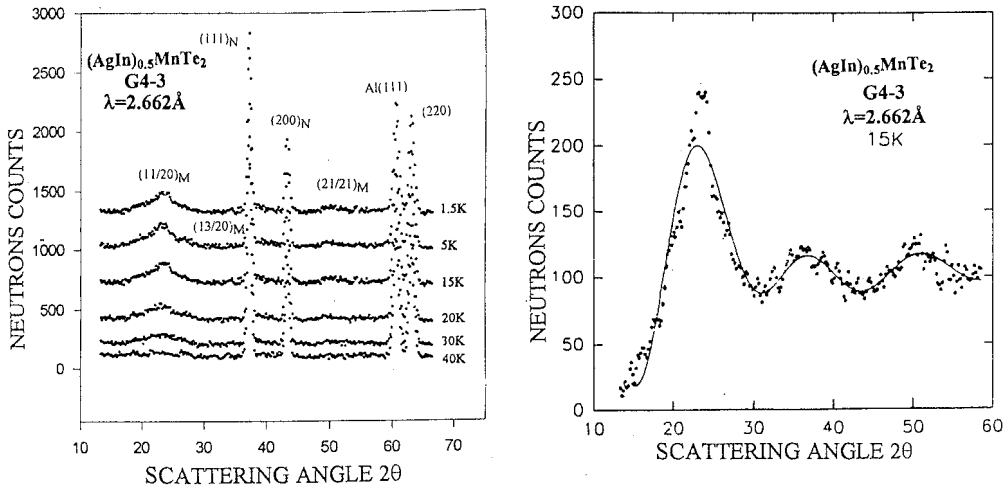

Fig.2: a) Temperature dependence of ND patterns; b) Analysis of the magnetic scattering at 15K.

The temperature dependence of the low angle part of the neutron diffraction patterns of AgIn600 is shown in fig. 2.a. We see the expected pattern of zinc-blende nuclear Bragg peaks, superimposed on a diffuse scattering background. The main feature of the diffuse scattering is a broad magnetic peak centered on 23°, which may be indexed as (1 1/2 0) in the ZB structure. This peak is an indication of correlations between Mn spins which are more intense at low temperature and which broaden and weaken with increasing

temperature. Two other diffuse peaks are identifiable; that near 38°, which is partly overlaid by the adjacent (111) nuclear peak, may be indexed as (1 3/2 0) and the other, near 52° may be indexed as (2 1/2 1). Similar diffraction patterns were also observed for CuIn samples. As demonstrated in the reference cited above (HOLDEN et al.), the position of the diffuse peaks are a signature of AFM-III order. The width of the diffuse magnetic peaks are always much greater than those of the Bragg peaks, implying that the above antiferromagnetic order is only short range.

Table I. $(AgIn)_{0.5}MnTe_2$ at 15 K. Correlation coefficients A_1 - B_1, spin S of Mn^{++} ions, and k the inverse of the correlations length.

$A_1 - B_1$	$A_2 - B_2$	$A_3 - B_3$	$A_4 - B_4$	S [μ_B]	k [$Å^{-1}$]
-2.5±0.1	+1.6±0.1	+2.8±0.2	-0.3±0.2	2.32±0.02	0.1008±0.0003

The observed diffraction patterns over the range 10° to 60° scattering angle after subtraction of the nuclear Bragg component, were fitted to the theory developed by HOLDEN et al. for correlations between the central spin and successive shells of neighbours. As an example, the corresponding fit at 15 K is shown in fig. 2.b. This fitting is quite satisfactory at moderate to high temperature; as the extend of the magnetic short range order increased the fits became less satisfactory. This occurs because the sharpness of the experimental peak can not be simulated with a limited number of shell terms. The parameters of the fits at 15 K are collected in Table I. The shell correlations reproduce the sign sequence of correlations calculated for the type III antiferromagnet.

4. CONCLUDING REMARK

The spin correlation results are in good agreement with previous work made on $Zn_{1-z}Mn_zTe$ alloys system. No difference was found between the ND patterns for samples with different heat treatments, indicating that in the present materials, the same arrangement of Mn^{2+} ions was obtained in all cases.

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