

Effect of crystal structure on the magnetic properties of semiconducting $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$

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Single crystals of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for $0.17 \leq x \leq 0.70$ display a cusp in the susceptibility. Films of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ were deposited by sputtering at temperatures ranging from 77 to 1100 K. Films deposited at 300 K and above consist of a mixture of cubic and hexagonal phases. Such films are characterized by a susceptibility cusp at 25 K which is higher than the corresponding single-crystal value (≈ 15 K) although the values of the susceptibility at 4.2 K are very close (4.2×10^{-5} emu/g). The most striking result is observed on films deposited at 77 K. These latter films are amorphous semiconductors with an enhanced susceptibility at 4.2 K (as high as 3×10^{-4} emu/g) and there is no susceptibility cusp above 4.2 K. The interesting conclusion is that crystallinity is essential to the presence of the susceptibility peak, which is consistent with a recent suggestion that $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ is not a canonical spin-glass and is better described by cluster freezing.

I. INTRODUCTION

The magnetic properties of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ single crystals have been investigated by several authors¹⁻³ who all reported a cusp in the susceptibility for $x > 0.17$. While two studies^{1,2} attributed the cusp to a spin-glass transition, one study³ concluded that the cusp is more typical of a mictomagnet than a spin-glass, i.e., the cusp results from cluster freezing. The spin-glass transition is thought to occur^{1,2} as a result of the random distributions of Cd^{2+} and Mn^{2+} ions on fcc sublattice. It was suggested theoretically^{4,5} that such a disordered frustrated system should exhibit a spin-glass transition. However, there is also some evidence that $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ may not be a canonical spin-glass. The number of Mn clusters is larger than statistically predicted,^{1,2} which is to be expected from the fact that the single crystals are slowly cooled after solidification. There is evidence³ for superparamagnetism arising from frozen antiferromagnetic clusters at temperatures well above the temperature at which the susceptibility cusp occurs. Furthermore, the scaling law for the magnetization as a function of concentration x is not obeyed² because the clustering changes as a function of x . Since the magnetic properties of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ mixed crystals seem to be crucially related to clustering, one would expect these magnetic properties to depend on the method of preparation which will be the subject of the present study.

II. EXPERIMENTAL PROCEDURE

$\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ is a semiconductor with a large gap⁶ (2.1 eV) and as a result is not amenable to dc sputtering. It is usual in such cases to resort to rf sputtering, but a different and novel solution was used here. The target, which consisted of a block of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ obtained by melting the components in a graphite crucible inserted in an evacuated quartz tube, was surrounded by a helically wound tungsten heater. The heater was positioned as close as possible to the $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ target so as to provide maximum heating without touching the target. This last point is crucial since the heater is electrically floating while the target is connected to the high negative sputtering voltage. The heater raises the temperature of the target, thus decreasing its resistivity until dc sputtering becomes possible. The heating of the target is accomplished by both radiation and conduction through the Ar sputtering gas and it is therefore best to use a high Ar pressure (0.1 Torr). In order to establish that the deposition process is sputtering, and not evaporation resulting from heating the target, the target was heated at the same power and for the same length of time used during sputtering and no deposit was observed in the absence of sputtering voltage. A typical sputtering rate was 500 Å/min for a sputtering power of 2 W (2000 V, 1 mA). For deposition at 77 K, it was necessary to cement the sapphire substrates onto the

liquid-nitrogen-cooled copper table with Air Products thermal grease in order to avoid heating by the target heater. Film thickness ranged from 300 Å for resistivity measurements up to 75 μm for susceptibility measurements.

Although the composition of the films was not established absolutely, x-ray fluorescence analysis established that it was equal within experimental error to the composition of the target. Furthermore, the composition of the target remained unchanged at the end of the experiments (330 h of sputtering), thus ruling out the possibility of preferential evaporation of the most volatile component (Cd) as a result of target heating.

The ac susceptibility of the films was measured at 10 kHz with a modulating field of 4 Oe with a push rod susceptibility holder⁷ by warming up the samples in helium gas from 4.2 K. The dc susceptibility was obtained by using a SQUID susceptometer with a measuring field of 3 Oe. The structure of the films was ascertained by x-ray diffraction.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Structure

The change of structure as a function of increasing deposition temperature (T_D) is described in Figs. 1–3. The most important result of the present study was obtained on films deposited at 77 K which as shown by the bottom trace of Fig. 1 are amorphous. When T_D is between 77 and 300 K the films are hexagonal with a strong basal plane (002) preferred orientation (top trace of Fig. 1). The degree of preferred orientation changes from film: Sometimes, contrary to the example shown in Fig. 1, it is the (101) peak which is much stronger than the (100) peak while other times one only observes a strong (002) peak surrounded by weak shoulders at the (100) and (101) diffraction angles.

Films deposited at and above 300 K always consist of a mixture of cubic and hexagonal phases (Fig. 2). Such films are characterized by a strong close-packed plane preferred orientation as shown by the strong cubic (111) and hexagonal (002) diffraction peaks. These two peaks are always accompanied by the presence of a much weaker superlattice line (004) (Fig. 2 and bottom trace of Fig. 3). Although such a superlattice line could be labeled (004) or (222), it is clear from the top trace of Fig. 2, where the double peaks are measured with great accuracy, that it should be (004) since that line has exactly half the d spacing of the (002) line. The separation between (111) and (002) peaks, which is 0.3° (top trace of Fig. 2), which is much larger than that observed in CdTe films,⁸ may be caused by an uneven distribution of

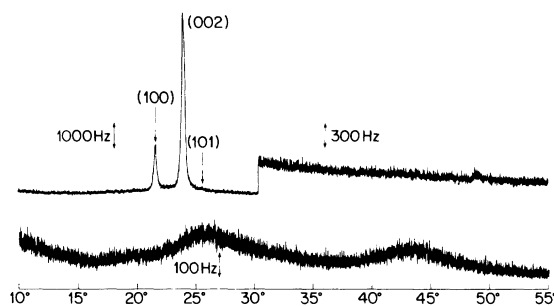


FIG. 1. X-ray diffractometer traces for a - $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ no. 1 deposited at 77 K (bottom trace) and $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ no. 2 deposited at 77 K $< T < 300$ K.

Mn between the two phases. This assumption will find further support in the discussion of the magnetic properties. One further observes that the (111)-(002) preferred orientation becomes more pronounced as T_D is increased. Indeed, while other cubic and hexagonal diffraction lines such as the (110) or (220) are clearly visible for $T_D = 300$ K (Fig. 2, bottom trace), they are essentially missing for $T_D = 400$ K (Fig. 2, top trace) and for $T_D = 900$ K (Fig. 3, bottom trace). The increasing T_D also affects the superlattice line which for $T_D = 900$ K has a d spacing intermediate between half the d spacings of the (111) and (002) diffraction lines.

Finally, when $T_D = 1000$ K the films are cubic as shown by the diffraction trace in the top of Fig. 3. These films, similar to the bulk material, are transparent to visible light with a deep red color. The change from hexagonal to cubic as T_D increases is consistent with the fact that bulk material obtained from the melt is cubic and with the previous observation⁸ that excess Te gives only the cubic form in CdTe. At high T_D , one may expect the most volatile element (Cd) to be reemitted by evaporation, thus leading to excess Te and the cubic form.

One should also mention that the various structural forms are not obtained with equal ease. While at $T_D = 77$ K films thinner than $10 \mu\text{m}$ are always amorphous and for $300 \text{ K} \leq T_D < 1000$ K films are always a mixture of cubic and hexagonal phases, the conditions for the pure cubic and pure hexagonal are not as reproducible. In other words, when $77 \text{ K} < T_D < 300 \text{ K}$ and $T_D = 1000$ K films may not always be single-phase (respectively hexagonal and cubic) but more often turn out to be two phase.

B. Electrical properties

Although the major interest in the present study is magnetic properties, the electrical properties will

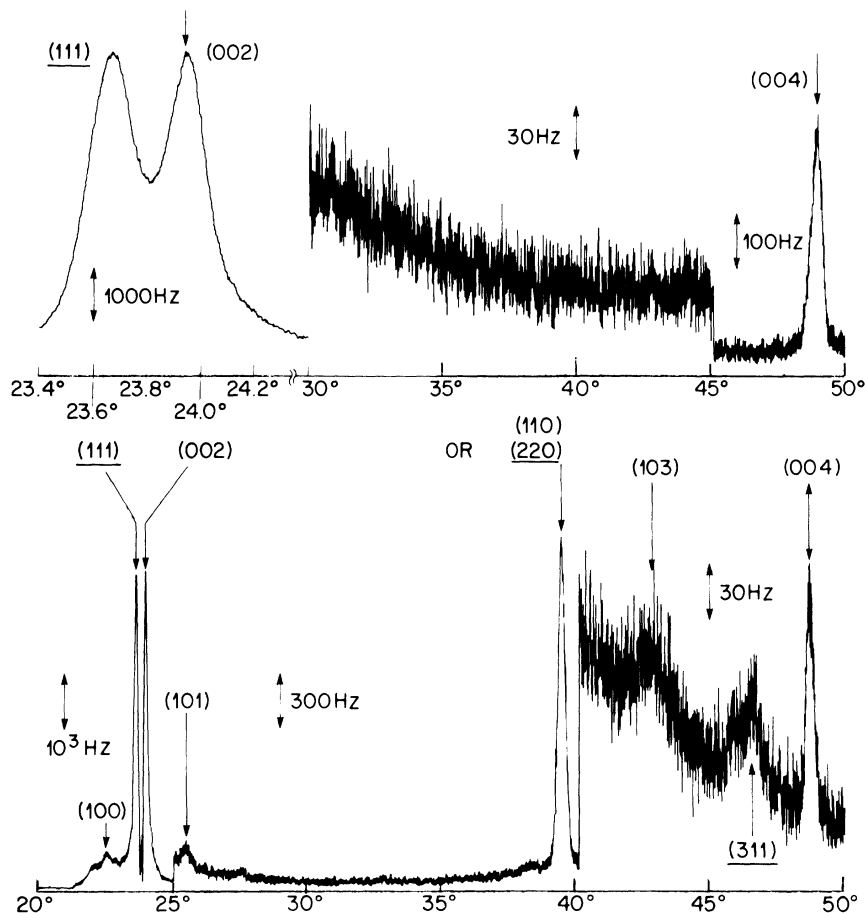


FIG. 2. X-ray diffractometer traces for $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ no. 3 deposited at 300 K (bottom trace) and no. 4 deposited at 400 K (top trace). The indices of the cubic diffraction lines are underlined, those of the hexagonal ones are not. The vertical arrow close to the (002) peak in the top trace indicates the d spacing corresponding to twice the d spacing of the (004) peak.

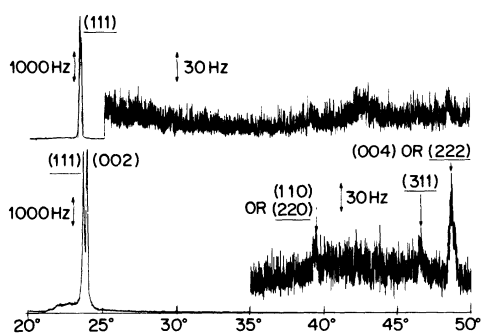


FIG. 3. X-ray diffractometer traces for $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ no. 5 deposited at 900 K (bottom trace) and no. 6 deposited at 1000 K.

be briefly examined because of their relationship to the structural properties. Indeed, as shown in Table I, the room-temperature resistivity of amorphous films deposited at 77 K is several orders of magnitude smaller than crystalline films. Furthermore, even crystalline films deposited at low temperatures (300 K) have a relatively low room-temperature resistivity as compared to films deposited at high temperatures (≥ 900 K) which display bulk resistivity. The lower resistivity of films deposited at low temperatures is undoubtedly caused by the disorder which introduces defect states within the energy gap. This is supported by the data shown in Fig. 4 for an amorphous film deposited at 77 K. Although such a film does not display any sign of variable range hopping as shown by the continuous upward curving of the $T^{-1/2}$ plot, the activation energy (0.2

TABLE I. Properties of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ films.

Sample no.	Thickness (μm)	Rate ($\text{\AA}/\text{min}$)	T_D (K)	Structure	$\rho(300\text{ K})$ ($\Omega\text{ cm}$)	$\chi(4.2\text{ K})$ (10^{-5} emu/g)
1	4.2	230	77	Amorphous		
2	2.6	408	< 300	Hexagonal		
3	4.5	750	300	Hex + cubic	2×10^6	
4	74.6	497	400	Hex + cubic		4.02
5	5	840	900	Hex + cubic	3×10^8	
6	3.3	550	1000	Cubic		
7	0.33	330	77	Amorphous	1.3×10^3	
8	22.5	567	300	Hex + cubic		4.33
9	32.1	181	900	Hex + cubic		4.25
10	17.4	373	1000	Hex + cubic		3.91
11	11.2	75	77	Amorphous + hex		28.3
12	12.6	76	77	Amorphous + hex		24.1
13	65.5	203	77	Amorphous + hex		16.5
14	1.1	64	77	Amorphous		19.4
15	3.5	116	77	Amorphous		30.2

eV) is much smaller than the 2.1-eV band gap of the bulk material.

C. Magnetic properties

The magnetic properties of the crystalline films will be examined first since they are closest to those observed on bulk. As shown in Fig. 5 and Table I, the susceptibility of such films is approximately 4×10^{-5} emu/g at 4.2 K and goes through a broad

maximum in the vicinity of 25 K. This is quite close⁹ to the susceptibility of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ single crystals (solid line in Fig. 6) except for the sharpness and the lower temperature of the susceptibility maximum (15 K). Both differences may be attributed to the uneven distribution of Mn between the cubic and hexagonal phases which was previously mentioned in the structural discussion. Indeed, one would expect that the mixed phases present in the crystalline films would tend to break up the homogeneous clustering which exists in the single crystals. It is also clear from Fig. 6 that any disorder tends to broaden and eventually eliminate the susceptibility peak: Chips of the polycrystalline target still display a peak around 15–20 K, but when those chips are ground into a powder the peak disappears completely. On the other hand, the polycrystalline chips

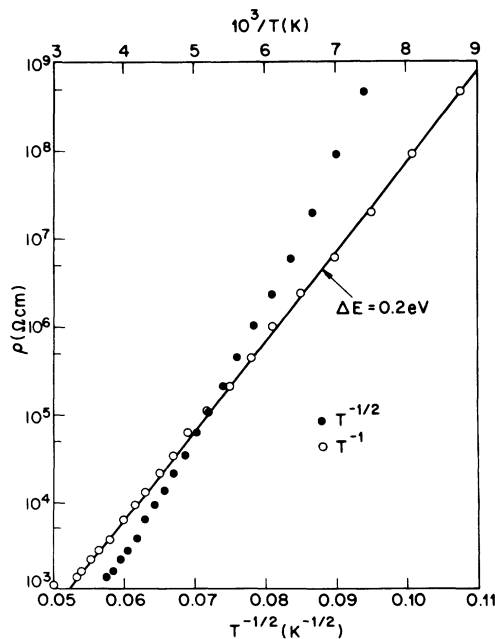


FIG. 4. Temperature dependence of the resistivity of $a\text{-Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ no. 7 deposited 77 K.

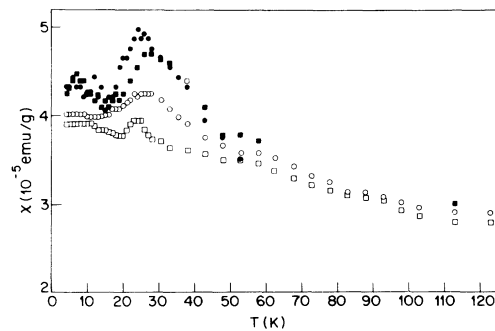


FIG. 5. Temperature dependence of the ac susceptibility of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ films with a mixed hexagonal cubic structure: no. 4, open circles, no. 8, solid circles, no. 9, solid squares, and no. 10, open squares.

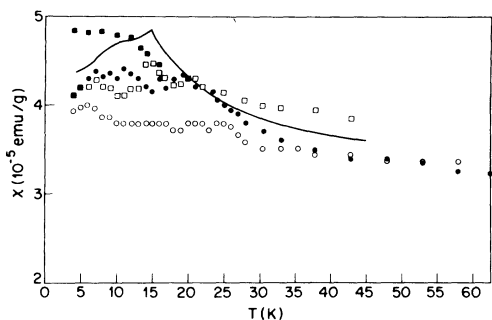


FIG. 6. Temperature dependence of the susceptibility χ of bulk $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$: solid line, χ_{dc} of Galazka *et al.*¹; solid circles, χ_{ac} for target chips; open squares, zero-field-cooled χ_{dc} for target chips; solid squares, 3-Oe field-cooled χ_{dc} for target chips; open circles, χ_{ac} for powder.

display the same "spin-glass" behavior that was previously ascribed to the single crystals,¹ namely, the peak in the dc susceptibility observed in samples cooled in zero field (open squares in Fig. 6) is eliminated by field cooling (solid squares in Fig. 6). Since the small differences between crystalline films and bulk single crystals have been ascribed to disorder, this suggests examining films with maximum disorder, i.e., amorphous films.

The disorder of amorphous films is revealed structurally by the two broad peaks shown in Fig. 1 and by a low resistivity and low activation energy (Fig. 4). As shown in Table I and Fig. 7, this disorder causes a pronounced change in the magnetic properties. First of all, the value of the susceptibility is about an order of magnitude larger than that of the crystalline films. This is even true for films which are too thick to be completely amorphous ($> 10 \mu\text{m}$) which indicates that the hexagonal microcrystals present in such films only represent a small volume fraction of the film. Second, and most important, the peak in the susceptibility is completely absent in fully amorphous films¹⁰ (data for no. 15 in Fig. 7). Films consisting of a mixture of amorphous and microcrystalline material (nos. 11–13) are quite interesting too: They possess the high susceptibility characteristic of amorphous films, but

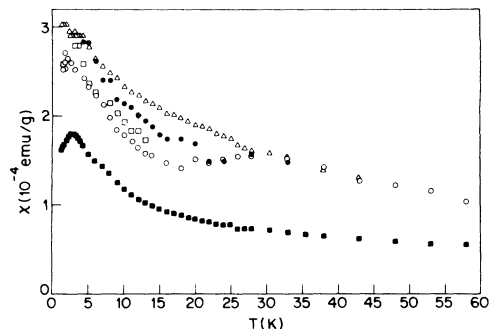


FIG. 7. Temperature dependence of the ac susceptibility of $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ films deposited at 77 K: no. 11, solid circles, no. 12, open circles, and no. 13, solid squares, are amorphous with some microcrystallinity; no. 14, open squares and no. 15, triangles, are fully amorphous.

display a very broad maximum around 25-K-like crystalline films (Fig. 7). Furthermore, film no. 13 (solid squares in Fig. 7), which has the largest microcrystallinity as a result of its greatest thickness, displays the lowest susceptibility for an amorphous film. The peak in the susceptibility around 2.5 K, although more convincing than that displayed by no. 12, may or may not be real since its magnitude is within experimental error.

One may therefore summarize this study by stating that the susceptibility peak in $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ depends on the conditions of preparation. More specifically, amorphous films prepared at 77 K which are expected to have the most random distribution of Mn atoms and therefore the least amount of clustering do not display a susceptibility peak. This result suggests that the susceptibility peak observed in single crystals^{1–3} is not characteristic of a canonical spin-glass but is better described by cluster freezing.³

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⁹The susceptibility is determined with an accuracy of $\pm 5\%$ as a result of the small amount of material used (30 mg maximum even for bulk material).

¹⁰The data on no. 14 could not be extended above 13 K because of insufficient sensitivity resulting from the thinness of the film.