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The Dependence of the Lattice Parameter and Density of $Zn_{1-x}Mn_xTe$ on Composition

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The lattice parameter of the diluted magnetic semiconductor $Zn_{1-x}Mn_xTe$ has been determined as a function of composition. This material crystallizes in the zinc-blende structure for values of x below about 0.75. The results show that for this range of composition the lattice parameter satisfies Vegard's law and is given by $a(x) = (6.103 + 0.237x)$ Å. This result corrects earlier published values of $a(x)$ for this material (Juza *et al., Z. anorg. allg. Chem.* **285**, 61 (1956)), which are in considerable error. Because of its rather pronounced dependence on x, the lattice parameter provides an excellent method for determining sample composition. By extrapolating the expression of $a(x)$ to $x = 1$, the results also provide a value of 6.340 ± 0.005 Å for the lattice parameter of the hypothetical zinc-blende phase of pure MnTe. The strong dependence of the lattice parameter of $Zn_{1-x}Mn_xTe$ on x is responsible for most of the variation of its density with composition.

$Zn_{1-x}Mn_xTe$ belongs to the group of materials known as "diluted magnetic semiconductors," which have recently been the subject of extensive studies because of their important semiconducting as well as magnetic properties (*1*). This ternary system crystallizes in the zinc-blende structure in the composition range $x \leq 0.75$, the Mn^{2+} ions replacing Zn^{2+} at random lattice sites. Since MnTe itself crystallizes in the NiAs structure, the incompatibility of this crystal structure with the zinc-blende phase imposes an upper limit on x.

In the course of our own studies on $Zn_{1-x}Mn_xTe$, we needed to have a simple and convenient means of determining x. Since the dimension of the unit cell is known to vary with x in ternary compounds of this type (*2*), we considered using X-ray measurements of the lattice parameter as a means of determining composition. On inspecting the literature, however, we noted that the only available data (*3*) on the dependence of the lattice parameter of $Zn_{1-x}Mn_xTe$ on composition is suspect: its extrapolated value for $x = 0$ is in serious disagreement with the value established for ZnTe in other studies (*4*). This has moti-

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vated us to conduct a systematic investigation of the dependence of the $Zn_{1-x}Mn_xTe$ lattice parameter on x over the range of compositions presently available.

The samples of $Zn_{1-x}Mn_xTe$ used in this study were prepared by either Bridgman growth or by sintering, using in both instances individual elements as starting materials. The lattice parameter was determined at room temperature by X-ray powder diffraction, using a Guinier camera and the $K\alpha_1$ line of copper ($\lambda = 1.54060$ Å). Typically 10 diffraction lines were used in determining the lattice parameter for each powder sample, corresponding to 2θ from 24 to 82°. An internal standard (Si, $a = 5.43088$ Å) was admixed into the $Zn_{1-x}Mn_xTe$ powder sample.

The chemical composition x of the samples was determined by both inductively coupled plasma atomic emission spectroscopy and by Auger analysis. The latter was performed in a Physical Electronics Inc. Model 590 System, operated in the derivative mode using a 5 keV, 0.5 μA electron beam. Calibration was based on standards of ZnTe and a series of $Cd_{1-x}Mn_xTe$ of known composition. Both standards and unknowns were given a minimal sputter with 2 keV xenon ions to remove surface carbon contamination and an oxide layer (ca. 20 Å thick) which developed spontaneously on the freshly cleaved surfaces. Compositions quoted represent the average of several analyses obtained within 1 mm of each other and also within 1 mm of the X-ray powder measurements, thus minimizing the error which could arise due to segregation in the Bridgman ingots.

TABLE I

Sample	Nominal x	x from chemical analysis	Lattice parameter a (Å)	Method of preparation
ZMT-3	0.003	0	6.1028 ± 0.0005	Bridgman
ZMT-9	0.05	0.045 ± 0.01	6.1153 ± 0.0005	Bridgman
441	0.064	0.067 ± 0.01	6.1214 ± 0.0010	Bridgman
ZMT-2	0.10	0.132 ± 0.02	6.1293 ± 0.0023	Bridgman
303	0.20	0.138 ± 0.01	6.1431 ± 0.0023	Sintered
ZMT-1	0.20	0.190 ± 0.02	6.1431 ± 0.0010	Bridgman
304	0.30	0.295 ± 0.02	6.1800 ± 0.0010	Sintered
285	0.50	0.37 ± 0.02	6.1906 ± 0.0017	Bridgman
ZMT-6	0.60	0.52 ± 0.02	6.2230 ± 0.0018	Bridgman
148	0.60	0.595 ± 0.02	6.2424 ± 0.0028	Bridgman
453	0.55	0.67 ± 0.02	6.2637 ± 0.0010	Bridgman
442	0.76	0.695 ± 0.03	6.2682 ± 0.0010	Bridgman

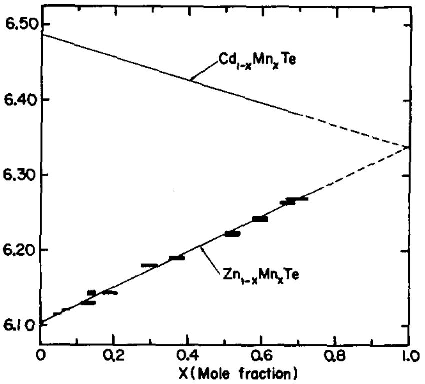

FIG. 1. The dependence of the room temperature lattice parameter $a(x)$ of $Zn_{1-x}Mn_xTe$ on composition x. The black rectangles are experimental data from Table I, indicating error limits for each sample. The solid line is the least squares fit given by Eq. (1). Also shown in the figure is the dependence of $a(x)$ on x for $Cd_{1-x}Mn_xTe$, as stated in Ref. (5). The dashed portion of either line represents an extrapolation beyond the range of the zinc-blende phase for both ternaries. Note that both extrapolations converge on one value, corresponding to the hypothetical zinc-blende form of MnTe.

The results of the analysis are listed in Table I. The table also indicates the "nominal composition" (i.e., the atomic fraction of Mn in the *starting* materials which were mixed together for crystal growth). The lattice parameter $a(x)$ from Table I is plotted in Fig. 1 as a function of x determined by the chemical analysis. The dependence of the lattice parameter on composition appears to follow Vegard's law (linear dependence of a on x), within the error limits of the measurements, yielding the analytical expression

$$a(x) = (6.103 + 0.237x)\ \text{Å}, \qquad (1)$$

obtained by a least-squares fit, with a standard deviation of ±0.001 on the intercept and ±0.004 on the slope. The error in the analysis arises predominantly from the determination of composition, as can be seen from the error limits given in the graph and the table.

The rather pronounced rate of change of $a(x)$ with x suggests the use of the lattice parameter as a reliable means of determining the composition of $Zn_{1-x}Mn_xTe$ crystals. We note that in the case of very good monocrystals, such as the $x = 0$ specimen, the error can be expected to remain below ±0.0005 Å, which corresponds to a determination of the atomic fraction x to within ±0.002, i.e., ±0.2 at.%. It is likely that the increase in the uncertainty in the lattice parameter with increasing x seen in the present data is to be ascribed, at least in part, to the finite distribution of x about an average value.

As was already pointed out, $Zn_{1-x}Mn_xTe$ has been reported (*2*, *3*) to form in a single zinc-blende phase up to about $x \lesssim 0.8$. In the present study, however, our X-ray data indicated that all samples examined with compositions in excess of $x \approx 0.7$ showed some presence of other crystal phases (particularly $MnTe_2$). Samples with $x = 0.68$ and 0.69 showed only very minute traces of these phases, and we have included them in Table I and Fig. 1. At higher concentrations X-ray diffraction of alien crystal phases became very pronounced, and we have excluded such data from the present analysis. However, *all* samples below $x > 0.6$ revealed consistently only the zinc-blende crystal structure.

Although $Zn_{1-x}Mn_xTe$ does not form homogeneous zinc-blende crystals over the entire range $0 < x < 1.0$ (because MnTe itself crystallizes in the NiAs structure), we can, nevertheless, infer the lattice parameter of the hypothetical zinc-blende phase of MnTe by extrapolating our data to $x = 1.0$, as shown by the dotted line in Fig. 1. This yields the value of

$$a(x = 1) = 6.340 \pm 0.005 \text{ Å}. \quad (2)$$

In Fig. 1 we have also plotted the literature value for the variation of $a(x)$ vs x for $Cd_{1-x}Mn_xTe$, which likewise forms zinc-blende crystals only up to $x \lesssim 0.75$, and whose lattice parameter is reported to vary as (*5*)

$$a(x)_{CdMnTe} = (6.487 - 0.149x) \text{ Å}. \quad (3)$$

It is interesting that in the limit of $x = 1$, Eq. (3) for the lattice parameter of $Cd_{1-x}Mn_xTe$ gives

$$a_{MnTe} = 6.338 \text{ Å},$$

which is in remarkably good agreement with the value obtained by extrapolation of the $Zn_{1-x}Mn_xTe$ data, as shown in the figure.

Having the value of $a(x)$ for $Zn_{1-x}Mn_xTe$, we can now calculate its density $d(x)$ as a function of x. Using Eq. (1), we obtain

$$d(x) = \frac{5.6394\,(1 - 0.0541x)}{(1 + 0.0388x)^3} \text{ g/cm}^3. \quad (4)$$

Figure 2 shows a graph of $d(x)$ vs x. It is interesting to note that, in spite of the close values of the atomic weights of Zn and Mn,

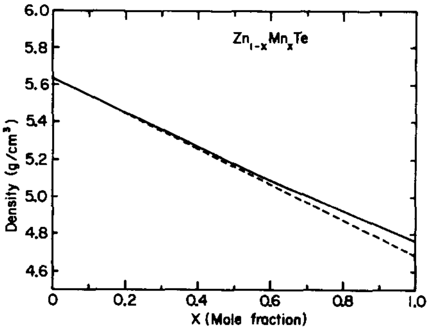

FIG. 2. The dependence of the density of $Zn_{1-x}Mn_xTe$ on composition. The solid curve is calculated with Eq. (4). The dashed line is the linear approximation, Eq. (5), which becomes increasingly inaccurate as x increases, due to cubic terms in x. The composition dependence of the lattice parameter accounts for about two thirds of the variation of $d(x)$ with x in $Zn_{1-x}Mn_xTe$.

the density of $Zn_{1-x}Mn_xTe$ *does* vary rather significantly with composition. The reason for this is the rather pronounced variation of $a(x)$ with x, which in fact accounts for over two thirds of the change in the density. One must therefore be cautioned that if one were to attempt to determine the value of x from the density of $Zn_{1-x}Mn_xTe$ while using the lattice parameter of ZnTe (as might appear justified for small values of x), one would automatically obtain a value of x erroneous by a factor of about 3. The density is linear in x for small x,

$$d(x) = 5.6394\,(1 - 0.1706x)\ \mathrm{g/cm^3}, \quad (5)$$

but this expression is reliable only for $x \lesssim 0.2$, as can be seen from Fig. 2.

We remark parenthetically that the increase of $a(x)$ with x in $Zn_{1-x}Mn_xTe$ and the decrease of $a(x)$ with x for $Cd_{1-x}Mn_xTe$, shown in Fig. 1, suggest certain interesting possibilities for the quaternary compound $Cd_{1-x-y}Zn_xMn_yTe$, recently successfully prepared by Woolley *et al.* (*6*). For example, it should be possible in such a system to vary the separation of Mn^{2+} ions while keeping fixed their atomic fraction, thus enabling studies of such aspects as the influence of exchange interaction between Mn^{2+} on ion separation at *constant x*. It should also be possible in such quaternary systems to vary independently the lattice parameter and the Mn content over a very significant range.

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References

1. See, e.g., J. K. FURDYNA, *J. Appl. Phys.* **53**(11), 7637 (1982).

2. A. PAJACZKOWSKA, *Progr. Crystal Growth Charact.* **1**, 289 (1978).

3. R. JUZA, A. RABENAU, AND G. PASCHER, *Z. anorg. allg. Chem.* **285**, 61 (1956).

4. H. E. SWANSON, M. C. MORRIS, AND L. ULMAR, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards, Monograph 25, Sec. 3, (1964).

5. N. BOTTKA, J. STANKIEWICZ, AND W. GIRIAT, *J. Appl. Phys.* **52**, 4189 (1981).

6. J. C. WOOLLEY, J. E. AVON, R. BRUN DEL RE, T. DONOFRIO, J. MAJID, AND A. MANOOGIAN, *Bull. Amer. Phys. Soc.* **27**, Abstract KE 13 (1982).