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# Atomic Substitution in Cd$_{1-x}$Mn$_x$Te for 0·1 ≤ x ≤ 0·4

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**Abstract.** Cadmium manganese telluride, Cd$_{1-x}$Mn$_x$Te with $x = 0\cdot10$, $0\cdot25$ and $0\cdot40$ has $M_r = 234\cdot25$, $225\cdot63$ and $217\cdot02$, respectively. Each composition is cubic, $F\bar{4}3m$, $a_{0.10} = 6\cdot4531$ (20), $a_{0.25} = 6\cdot4396$ (10), $a_{0.40} = 6\cdot4163$ (22) Å, $V_{0.10} = 268\cdot7$ (5), $V_{0.25} = 267\cdot0$ (4), $V_{0.40} = 264\cdot2$ (5) Å$^3$, $Z = 4$, $D_m^{0.10} = 5\cdot91$ (5), $D_m^{0.40} = 5\cdot49$ (3) g cm$^{-3}$, $D_x^{0.10} = 5\cdot790$, $D_x^{0.25} = 5\cdot612$, $D_x^{0.40} = 5\cdot457$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha_1, \alpha_2) = 0\cdot709319$, $0\cdot713609$ Å, $\mu_{0.10} = 1\cdot806$, $\mu_{0.25} = 1\cdot767$, $\mu_{0.40} = 1\cdot734$ cm$^{-1}$, $T = 294$ (1) K. $R(F_m) = 0\cdot0108$ for $x = 0\cdot10$, $0\cdot0259$ for $x = 0\cdot25$ and $0\cdot0117$ for $x = 0\cdot40$, based upon 214, 188 and 205 independent averaged structure factors at the three respective compositions. Mn completely substitutes for Cd in the range $0\cdot1 \le x \le 0\cdot4$. The randomly distributed Cd and Mn atoms at the Cd site in the zinc-blende structure, and the Te atom, each undergo significantly anharmonic displacements that increase with increasing Mn content. The anharmonicity at both sites probably originates in static atomic displacements along the unit-cell body diagonals that conserve the ~0·05 Å difference between average Te—Cd and Te—Mn interatomic distances. The lattice constant follows Vegard's rule in the range $0 \le x \le 0\cdot4$.

**Introduction.** The semimagnetic semiconducting properties of Cd$_{1-x}$Mn$_x$Te have led to numerous recent studies of this system (see, for example, Giebultowicz, Lebech, Buras, Minor, Kepa & Galazka, 1984). Pajaczkowska (1978) gave lattice constants for the resulting zinc-blende structure that ranged from

6·479 (1) Å with $x = 0\cdot05$ to 6·378 (2) Å with $x = 0\cdot7$. Triboulet & Didier (1981) confirm that solid solutions with zinc-blende structure form between $x = 0$ and 0·75. The distribution coefficient of Mn in the composition range $0\cdot1 \le x \le 0\cdot4$ is found to be close to unity (Bridenbaugh, 1985). Since large single crystals are readily grown throughout the stability range and the lattice constant can be chosen at will between 6·37 and 6·47 Å (Balzarotti, Motta, Kisiel, Zimnal-Starnawska, Czyzyk & Podgorny, 1985), Cd$_{1-x}$Mn$_x$Te has become an attractive choice of substrate crystal for the epitaxic overgrowth of Hg$_{1-x}$Cd$_x$Te and related (II)–(VI) compositions in the fabrication of infrared detectors. The growing importance of this system of materials led us to study the nature of the substitution that takes place as $x$ is varied, with results as presented below.

**Experimental.** Large single-crystal boules of Cd$_{1-x}$Mn$_x$Te were grown by the vertical Bridgman method using a multizone furnace. The temperature profiles in the hot and cold zones varied less than ±1 K over their entire length and were separated by a 5 cm long unheated loss section that created a thermal gradient of 25 K cm$^{-1}$ at the growth interface. The growth rate varied from 1 to 2 cm h$^{-1}$. The ampoule used was 16 mm ID fused quartz; the inner surface was coated with pyrolytic graphite to prevent reaction by Mn and Cd. The first and last 20% of each growth boule, with compositions that correspond to $x = 0\cdot10$, 0·25 and 0·40, was discarded. The densities for compositions with $x = 0\cdot10$ and 0·40 were measured pycnometrically on samples with masses greater than 20 mg. A sphere of each composition was ground, with radius as in Table 1, and mounted in arbitrary orientation on a CAD-4 diffractometer. Radiation used was Mo $K\alpha$

Table 1. *Experimental data for* $Cd_{1-x}Mn_xTe$ *at* 294 K

| $x$ | 0.10 | 0.25 | 0.40 |
|---|---|---|---|
| Lattice-parameter measurements | | | |
| Number of reflections | 25 | 25 | 25 |
| $\theta$ range (°) | 12·8–22·5 | 12·8–22·5 | 12·8–22·5 |
| Structural measurements | | | |
| Crystal radius (mm) | 0·191 (3) | 0·181 (3) | 0·243 (4) |
| Transmission factors: | | | |
|   min., max. (%) | 1·88, 7·49 | 2·30, 8·21 | 1·09, 5·90 |
| $(\sin\theta)/\lambda$ max. ($Å^{-1}$) | 1·15 | 1·15 | 1·15 |
| Range of $h$, $k$ and $l$ | $\pm14, \pm14, \pm14$ | $\pm14, \pm14, \pm14$ | $\pm14, \pm14, \pm14$ |
| Number of standard reflections | 6 | 6 | 6 |
| Variation in experiment (%) | $\pm2\cdot6$ | $\pm2\cdot6$ | $\pm3\cdot8$ |
| Linear decline $[I_t = (1 + nt)]$ $(10^7 n)$ | 4·0 | 0·2 | 1·2 |
| Total exposure ($t$ h) | 143 | 148 | 338 |
| Number of reflections measured | 3686 | 3486 | 6451* |
| $R_{int}$ | 0·0203 | 0·0254 | 0·0215 |
| Number of unobserved reflections | 0 | 0 | 0 |
| Number of reflections used in | | | |
|   refinement $[\geq 3\sigma(F_m^2)]$ | 214 | 188 | 205 |
| Number of parameters refined | 7 | 6 | 7 |
| $R$ | 0·0108 | 0·0259 | 0·0117 |
| $wR$ | 0·0139 | 0·0293 | 0·0157 |
| $S$ | 0·888 | 1·791 | 0·907 |
| $w\dagger$ | $1/\sigma^2(F_m^2)$ | $1/\sigma^2(F_m^2)$ | $1/\sigma^2(F_m^2)$ |
| $(\Delta/\sigma)_{max}$ | $10^{-3}$ | 0·3 | $10^{-4}$ |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e $Å^{-3}$) | 0·86, −0·44 | 1·51, −0·71 | 1·19, −0·42 |
| Extinction, spherulitic radius ($\mu$m) | 3·0 (1) | 4·2 (2) | 3·1 (1) |
| Extinction, mosaic distribution | 0·046 (6) | 0·12 (17) | 0·047 (8) |
| Slope of $\delta R$ plot | 0·75 | 1·83 | 0·78 |
| Intercept ($\sigma$) | 0 | 0·2 | 0 |

\* Each reflection measured twice.
† See text for evaluation of $\sigma^2(F_m^2)$.

$[\lambda(K\alpha_{1,2}) = 0.709319$, $0.713609$ Å (Deslattes & Henins, 1973)] from a graphite monochromator.

Intensities were measured at 295 K by the $\theta$, $2\theta$ step-scan technique with $\Delta2\theta = 0.85° + 0.35°$ tan$\theta$ for the $x = 10$ and 25% compositions and with $\Delta2\theta = 1.80° + 0.35°$ tan$\theta$ for the 40% composition. Enraf–Nonius (1980) control software was used with a PDP 11/24-8e minicomputer. With a maximum of 48 symmetry-equivalent reflections in a form, the averaged value of intensities, after correction for absorption, Lorentz and polarization effects, is regarded as subject to unusually small systematic errors. Each reflection was measured for as long as 240 s, for a counting-statistical (c.s.) standard deviation objective $\sigma_{c.s.}(I)/I \leq 0.02$.

The variance in $F_m^2$ [*i.e.* $\sigma^2(F_m^2)$] was taken as the larger of $V_1$ or $V_2$, where $V_1$ is the variance derived from counting statistics, absorption, attenuation factor and variation in the standards, and $V_2$ is calculated from differences within each equivalent form; see Abrahams, Bernstein & Keve (1971).

In $AB$ binary compounds with the zinc-blende structure, atom $A$ is located at 000 and atom $B$ at $\frac{111}{444}$ in space group $F\bar{4}3m$. The wide composition range reported for $Cd_{1-x}Mn_xTe$ leads to the obvious postulate that Mn substitutes uniquely for Cd. Less obvious possibilities include the formation of polytypes or defect structures [*cf.* Balzarotti *et al.* (1985) and Wu & Sladek (1982)]. No violation of either the stated unit-cell repeat or of the face-centering condition was detected, thus eliminating the possibility of long-range chemical ordering at the $B$ atom site. The initial model for the

composition with $x = 0.10$ placed the Te atom at 000 and a composite atom consisting of 0·9 Cd, 0·1 Mn at $\frac{111}{444}$.

Least-squares refinement of the three-parameter model with isotropic temperature factors and the scale factor as sole variables, using a modified version of the *ORFLS* program (Busing, Martin & Levy, 1973) with $Cd^{2+}$, $Mn^{2+}$ and $Te^{2-}$ atomic form factors and corresponding $f'$ and $f''$ anomalous scattering corrections taken from *International Tables for X-ray Crystallography* (1974), led immediately to $R(F_m) = 0.041$, $wR = 0.038$ and $S = 1.38$. The pronounced extinction present was readily corrected, on the basis of Becker & Coppens' (1974) formalism, by adding a parameter for both spherulitic radius and mosaic spread in the extinction model. Finally, the only third-order tensor displacement coefficient allowed each atom by symmetry was also varied in a modified Gram–Charlier expansion of the probability density function. Although the addition of fourth-order tensor coefficients improved the agreement significantly, some elements in the correlation matrix approached unity resulting in unsatisfactory convergence, hence these four coefficients were not included in the final least-squares refinement.

The final model for $Cd_{0.9}Mn_{0.1}Te$, with seven parameters and 214 $F_m^2$, gave the refinement indicators listed in Table 1. The sensitivity of these indictors to the assumed composition was examined in a parallel series of refinements in which $x$ was taken as 0·075, 0·125 and 0·150, with corresponding indicators that thereupon became $R = 0.0125$, 0·0099 and 0·0104; $wR = 0.0172$, 0·0133 and 0·0167. The diffraction evidence hence suggests that the composition with nominal formula $Cd_{0.9}Mn_{0.1}Te$ may be closer to $Cd_{0.885}Mn_{0.115}Te$. It is expected that more than 99% of the melt must crystallize in order to reach the composition with $x = 0.115$, based on the distribution coefficient of 0·966 (5) reported by Bridenbaugh (1985). The values of the refined parameters for the nominal formula are given in Table 2.

Refinement of the comparable model with nominal composition $Cd_{0.6}Mn_{0.4}Te$ proceeded smoothly, based upon the $F_m$ determined for that composition; the final parameters derived for the composition $Cd_{0.9}Mn_{0.1}Te$ were taken as input parameters. However, refinement of the model with nominal composition $Cd_{0.75}Mn_{0.25}Te$ resulted in a correlation matrix coefficient between $u_{123}(Cd, Mn)$ and $u_{123}(Te)$ of nearly unity. It may be noted that $R_{int}$ for this composition is significantly larger than for the two other compositions; see Table 1.* Intensity measurement of spheres ground from

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\* Lists of structure factors for each composition have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51548 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Second-* $(\times 10^5\ \text{Å}^2)$ *and third-order* $(\times 10^5\ \text{Å}^3)$
*displacement coefficients in* $Cd_{1-x}Mn_xTe$ *at* 294 K

| $x$ | 0·10 | 0·25 | 0·40 |
|---|---|---|---|
| $u_{11}$ $(Cd_{1-x}Mn_x)$ | 2320 (6) | 2314 (10) | 2291 (8) |
| $u_{123}$ | 49 (9) | 59* | 68 (8) |
| $u_{11}$ (Te) | 1737 (5) | 1823 (11) | 1811 (6) |
| $u_{123}$ | 25 (9) | 38 (5) | 45 (7) |

\* See text: for $u_{123}(\text{Te}) = 35 \times 10^{-5}\ \text{Å}^3$, then $u_{123}(\text{Cd, Mn}) = 52\ (5) \times 10^{-5}\ \text{Å}^3$.

earlier boules with this composition gave even higher values of $R_{int}$. Setting $u_{123}(\text{Cd, Mn})$ to $59 \times 10^{-5}$, *i.e.* midway between the coefficient values derived for $x = 0·10$ and 0·40 (see Table 2), gave $u_{123}(\text{Te}) = 38\ (5) \times 10^{-5}\ \text{Å}^3$ which is close to the mid-value of that coefficient for the two other compositions. Similarly, if $u_{123}(\text{Te})$ were set to $35 \times 10^{-5}\ \text{Å}^3$, the resulting value of $u_{123}(\text{Cd, Mn}) = 52\ (5) \times 10^{-5}\ \text{Å}^3$ would be obtained. The agreement indicator, $wR = 0·0293$, for either six-parameter model (*i.e.* with one $u_{123}$ coefficient not varied), is slightly less than the $wR = 0·0296$ for the seven-parameter model with both $u_{123}$ coefficients varied, hence the six-parameter model with values as given in Tables 1 and 2 is regarded as acceptable. Final indicators for each composition are included in Table 1 and the refined values of all parameters are presented in Table 2.

Normal probability $\delta R$-plots (Abrahams & Keve, 1971) for each composition give rather linear arrays with zero intercepts for $x = 0·10$ and 0·40, but form a slightly $S$-shaped array with much larger slope and a small intercept for $x = 0·25$; see Table 1. It is hence apparent that preparation of the 25% Mn composition material is less satisfactory than that of the other compositions.

**Discussion.** The composition CdTe was reported by Williams, Tomlinson & Hampshire (1969) to have a cubic lattice constant $a = 6·4910\ (20)\ \text{Å}$ at 305 K. More recent determinations report 6·483 (5) Å (Brun del Re, Donofrio, Avon, Majid & Woolley, 1983) and 6·469 (3) Å (Balzarotti *et al.*, 1985) at room temperature. The former give 6·469 (5), 6·456 (5) and 6·422 (5) Å respectively for compositions with $x = 0·10, 0·25$ and 0·40 in $Cd_{1-x}Mn_xTe$, whereas the latter give 6·455 (3), 6·436 (3) and 6·416 (3) Å respectively, where these values are interpolated from graphical representations of lattice constant *vs* composition. The present results are not significantly different from those of Balzarotti *et al.* (1985) and both sets of lattice constants show that Vegard's law holds in the composition range $0 \le x \le 0·4$ for $Cd_{1-x}Mn_xTe$.

The present results are entirely consistent with a random distribution of Cd and Mn atoms at the $\frac{111}{444}$ site in the zinc-blende structure. Balzarotti *et al.* (1985) have made EXAFS measurements of $Cd_{1-x}Mn_xTe$ compositions over the range $0 \le x \le 0·7$ and report an

average Te—Cd distance of 2·80 (1) Å that is nearly independent of $x$ and an average Te—Mn distance that decreases from 2·76 to 2·74 (1) Å with increasing $x$. They assume that the cations $Cd^{2+}$ and $Mn^{2+}$ are located without distortion at $\frac{111}{444}$ and that the $Te^{2-}$ anion occupies locations around 000 such that the two distances observed are satisfied.
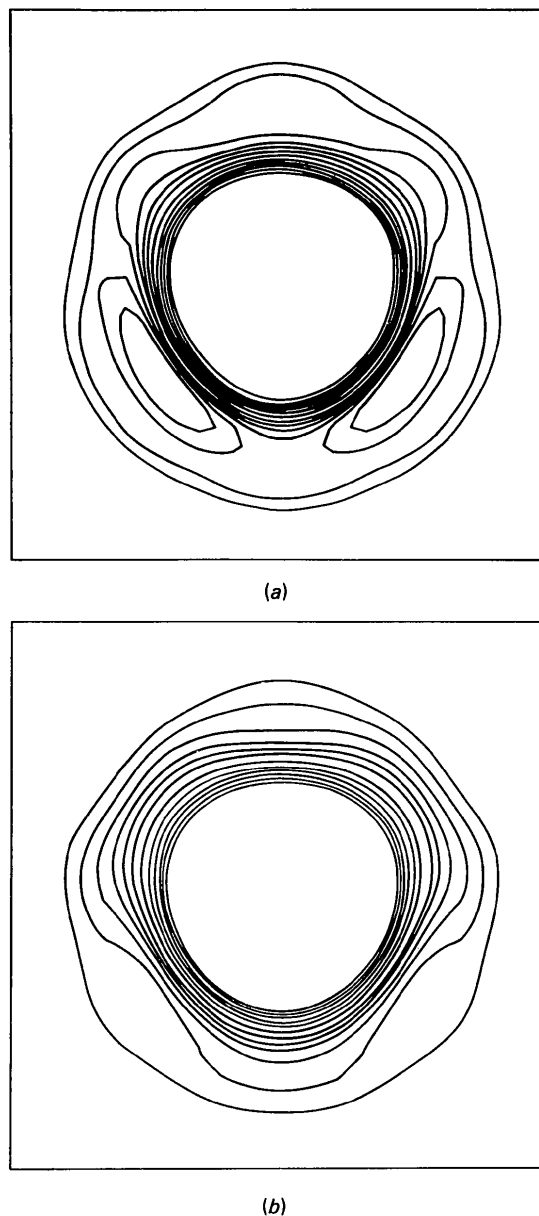


(a)



(b)

Fig. 1. (a) Electron-density distribution in $Cd_{0.6}Mn_{0.4}Te$ through the Te atom site located at the origin, with [001] vertical and [110] horizontal in this and the following section. Contours are at intervals of 3 e Å$^{-3}$ to the 18 e Å$^{-3}$ level and thereafter at intervals of 6 e Å$^{-3}$. Both sections extend 3 × 3 Å. (b) Electron-density distribution through the Cd, Mn atom site at $\frac{111}{444}$ with contour intervals as in (a).

Table 2 shows that the harmonic amplitude of thermal displacement $u_{11}$ increases significantly for Te as the Mn content increases, whereas the corresponding $u_{11}$(Cd, Mn) amplitude remains rather constant with composition. The absolute magnitude of $u_{11}$(Cd, Mn) however significantly exceeds $u_{11}$(Te). The anharmonic displacement coefficient $u_{123}$ for both atomic sites increases with increasing Mn content, with the absolute magnitude of $u_{123}$ for the composite Cd, Mn atom exceeding that for Te at all three compositions. In view of the results of Balzarotti *et al.* (1985), it is likely that the anharmonicity present originates in static, rather than thermal, atomic displacements. In this case, the Mn atom is not located exactly at $\frac{111}{444}$, in accordance with Balzarotti *et al.* (1985), but is distributed several hundredths of an ångström distant along each body diagonal from the Cd site. The smaller $u_{123}$(Te) magnitudes suggest that Te is similarly distributed but over smaller displacements about the unit-cell origin. The electron-density distribution in the (110) plane through the Te atom site, shown in Fig. 1(*a*), exhibits small maxima along the body diagonals with somewhat reduced maxima also observable in the corresponding section through the Cd, Mn atom site, shown in Fig. 1(*b*). An experimental test of the static displacements proposed may be made by undertaking a thermal dependence study. As pointed out by a referee, analysis of any diffuse scattering that may subsequently be found near reciprocal-lattice points, in terms of possible short-range order at the atomic sites, would also be informative.

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# Structure of NaMnF₃ at Room Temperature

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**Abstract.** Manganese sodium fluoride, $NaMnF_3$, $M_r = 134.92$, orthorhombic, *Pnma*, $a = 5.751$ (4), $b = 8.008$ (6), $c = 5.548$ (4) Å, $V = 255.5$ (5) Å³, $Z = 4$, $D_x = 3.51$ Mg m⁻³, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 5.41$ mm⁻¹, $F(000) = 252$, $T = 298$ (1) K, final $R = 0.043$ for 347 observed reflexions. The Mn²⁺ ions are surrounded by six F⁻ ions forming a distorted octahedron with Mn—F distances between 2.105 (2) and 2.123 (2) Å. The model obtained has been analysed from the point of view of distortion from the ideal cubic perovskite-type arrangement.

**Introduction.** The structure of $NaMnF_3$ is closely related to the ideal cubic perovskite structure, characteristic of the crystal of general formula $AMX_3$. For $NaMnF_3$ at room temperature a distortion from the ideal cubic symmetry is observed. This distortion can be caused by various components such as: (i) tilting of the anion octahedra, (ii) distortion of the octahedra and (iii) displacements of the cations (Glazer, 1972).

In earlier studies on the crystal structure of Na-$MnF_3$, lattice parameters were obtained by the X-ray powder method (Simanov, Batsanova & Kovba, 1957)