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Structure of $MnIn_2Te_4$-II, an Indium Manganese Telluride High-Pressure Phase

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Abstract. $M_r = 794{\cdot}978$, orthorhombic, *Pnma*, $a = 28{\cdot}279\ (3)$, $b = 4{\cdot}376\ (2)$, $c = 7{\cdot}124\ (2)$ Å, $V = 881{\cdot}59$ Å^3, $Z = 4$, $D_x = 5{\cdot}989$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å (graphite monochromator), $\mu = 199{\cdot}64$ mm^{-1}, $F(000) = 1292$, $T = 296$ K, final $R = 0{\cdot}0267$ for 853 unique reflections. The high-pressure phase $MnIn_2Te_4$-II has been synthesized from $MnIn_2Te_4$-I at a hydrostatic pressure of 1·5 GPa and $T = 1073$ K. The structure comprises layers of $MnTe_6$ octahedra [Mn—Te 2·889 (2)–3·014 (2) Å] stacked along [100] and bridged by chains of $InTe_4$ tetrahedra [In(1)—Te 2·767 (1)–2·794 (1); In(2)—Te 2·756 (1)–2·835 (1) Å].

Introduction. The structure of $MnIn_2Te_4$-I (tetragonal, space group $I\bar{4}2m$, $a = 6{\cdot}191$, $c = 12{\cdot}382$ Å), stable at atmospheric pressure, can be derived from the sphalerite structure (Range & Hübner, 1975). The doubling of one of the three cubic axes of the sphalerite-type unit cell is caused by an ordering of the vacancies as in the $CdGa_2S_4$- and β-Cu_2HgI_4-type structures. However, the different cations are distributed randomly over the occupied tetrahedral sites. The purpose of this study was to achieve an ordered arrangement of the different cations under the influence of high pressure.

Experimental. Experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975) using BN as crucible material. Temperature was varied in the range 973 to 1173 K, pressure in the range 0·5 to 2·0 GPa. Up to 1·0 GPa and 1073 K the phase $MnIn_2Te_4$-I remains stable. After quenching from 1·5 GPa and 1073 K a new phase was obtained, and proved to be homogeneous by Guinier photographs. Therefore, this phase ($MnIn_2Te_4$-II) is a high-pressure phase, metastable under normal conditions. At still higher temperatures and pressures $MnIn_2Te_4$-II becomes unstable again and decomposes.

A silvery crystal fragment (approx. 20 × 30 × 60 μm) used for data collection on an Enraf–Nonius CAD-4 diffractometer; 25 reflections used for measuring lattice parameters; experimental absorption correction (ψ scan, min. correction factor 0·9511, max. 0·9994); intensities measured for $2° < \theta < 25°$; ω–2θ scan technique; $0 \le h \le 33$, $-5 \le k \le 5$, $-8 \le l \le 8$; three standard reflections ($\bar{2}00$, $\bar{1}1\bar{4}$, $\bar{3},0,\bar{1}\bar{2}$) with a total loss of intensity of 3% throughout data collection; 3149 reflections measured, 853 unique ($R_{\text{int}} = 0{\cdot}03$), 210 unobserved [$F < 2\sigma(F)$]. The positional parameters of the first four Te atoms [Te(1)] were determined using direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982); the positions of the remaining Te atoms and of the cations were taken from difference Fourier syntheses (*SHELX*76; Sheldrick, 1976). In least-squares refinement $|F|$ magnitudes were used to refine atomic coordinates, occupation factors and anisotropic temperature factors. $R = 0{\cdot}0267$, $wR = 0{\cdot}0356$ [$w = k/\sigma(F)^2 + |g|F^2$]. $(\Delta/\sigma)_{\max} < 0{\cdot}001$ in final refinement cycle. Final difference Fourier synthesis showed residual electron density of 1·14 (max.) and −2·11 e Å^{-3} (min.). Atomic scattering factors and f', f'' values from *International Tables for X-ray Crystallography* (1974). Bond distances and angles calculated using the program *SADIAN* (Baur & Wenninger, 1969).

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Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1,† bond distances and angles in Table 2.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors*

All atoms in 4(*c*) (x, $\frac{1}{4}$, z); all positions fully occupied.

	x	y	z	B_{eq}*(Å^2)
Te(1)	0·23722 (3)	0·25	0·6626 (1)	1·27
Te(2)	0·89452 (3)	0·25	0·3642 (2)	1·39
Te(3)	0·14644 (3)	0·25	0·0860 (1)	1·19
Te(4)	0·99496 (4)	0·25	0·7408 (1)	1·37
In(1)	0·15159 (4)	0·25	0·4746 (2)	1·37
In(2)	0·04902 (4)	0·25	0·0759 (2)	1·58
Mn	0·30628 (8)	0·25	0·3637 (3)	1·64

* $B_{eq} = \frac{4}{3}\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

$MnTe_6$ octahedra			
Mn—Te(1)	2·889 (2)	Te(1)—Mn—Te(1)	94·45 (6) 2×
—Te(1)	2·890 (1) 2×	—Te(2)	165·58 (9)
—Te(2)	2·977 (2)	—Te(3)	84·99 (5) 2×
—Te(3)	3·014 (2) 2×	Te(1)—Mn—Te(1)	98·41 (7)
		—Te(2)	94·96 (6) 2×
		—Te(3)	177·33 (6) 2×
		—Te(3)	84·24 (2) 2×
		Te(2)—Mn—Te(3)	85·11 (6) 2×
		Te(3)—Mn—Te(3)	93·10 (6)
$InTe_4$ tetrahedra			
In(1)—Te(1)	2·767 (1)	In(2)—Te(3)	2·756 (1)
—Te(3)	2·772 (2)	—Te(4)	2·835 (2)
—Te(2)	2·794 (1) 2×	—Te(4)	2·835 (1) 2×
Te(1)—In(1)—Te(3)	121·96 (5)	Te(3)—In(2)—Te(4)	124·13 (6)
—Te(2)	102·09 (4) 2×	—Te(4)	115·24 (4) 2×
Te(2)—In(1)—Te(2)	103·09 (5)	Te(4)—In(2)—Te(4)	98·70 (4) 2×
Te(2)—In(1)—Te(3)	112·70 (4) 2×	Te(4)—In(2)—Te(4)	101·01 (5)
Edge lengths			
Te(1)—Te(3)	3·961 (1) 2×	Te(1)—Te(2)	4·325 (1) 2×
Te(1)—Te(3)	3·989 (1) 2×	Te(2)—Te(2)	4·376
Te(2)—Te(3)	4·052 (1) 2×	Te(2)—Te(3)	4·634 (1) 2×
Te(1)—Te(1)	4·242 (1) 2×	Te(1)—Te(3)	4·844 (1)
Te(1)—Te(2)	4·325 (1) 2×		
Te(1)—Te(1)	4·376	Te(4)—Te(4)	4·302 (1) 2×
Te(3)—Te(3)	4·376	Te(4)—Te(4)	4·376
		Te(3)—Te(4)	4·722 (1) 2×
		Te(3)—Te(4)	4·939 (1)

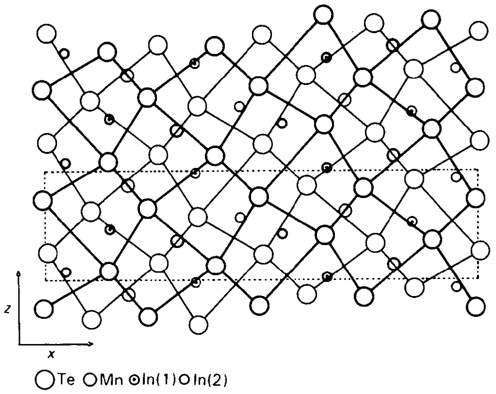

Fig. 1. View of the $MnIn_2Te_4$-II structure along [010]. Thick and thin lines signify atoms and their connections at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ respectively.

The structure of $MnIn_2Te_4$-II can be derived from a body-centred-cubic arrangement of the Te atoms by distortion and filling of some of the tetrahedral and octahedral voids by metal atoms (Fig. 1). Taking the length of the *b* axis of $MnIn_2Te_4$-II (4·376 Å) as the basic dimension for the square nets forming an undistorted b.c.c. packing the following distances between centre and corners of the polyhedra are obtained: octahedra 2 × 2·188 Å* ($=b/2$), 4 × 3·094 Å ($=\sqrt{2}b/2$); tetrahedra 4 × 2·446 Å* ($=\sqrt{5}b/4$). The distances marked with asterisks are too short for voids to be occupied by Mn or In. Therefore, the square nets are distorted.

In order to occupy an octahedral hole it is necessary to stretch the polyhedron. For this reason the corresponding edge in the square net is enlarged. At the same time the opposite edge is contracted. This distortion enlarges all edges of some of the tetrahedral holes, especially the one at the same height *y* as the central atom. Thus the centring atom may be displaced towards this bond. Resulting effects in relation to these tetrahedra are:

–enlargement of the four corner–centre distances;

–enlargement of the angle corner–centre–corner in planes parallel to (010);

–reduction of the angle corner–centre–corner in planes perpendicular to (010);

–adaptation of the residual angles.

This implies that the distortion of the square nets causes the enlargement of some of the holes which can be occupied by cations as a result. Neighbouring sites are reduced at the same time. For this reason an occupation of the anion polyhedra beyond the octahedra:tetrahedra:anions ratio 1:2:4 seems to be possible only with smaller cations.

In contrast to $MnIn_2Te_4$-I, in $MnIn_2Te_4$-II the metal atoms are ordered. Fig. 2 shows the connection of the occupied anion polyhedra in the $MnIn_2Te_4$-II structure. The Mn atoms are coordinated octahedrally by Te atoms, the In atoms tetrahedrally. Both, octahedra and tetrahedra, are distorted (see Table 2). The $MnTe_6$ octahedra share opposite edges with the result that they build chains along [010]. By corner sharing these chains form layers, stacked in the [100] direction, layer sequence *ABAB* ... (see Fig. 2). The $In(2)Te_4$ tetrahedra build zigzag chains in the [010] direction by corner and edge sharing. These chains are bridges between the octahedra layers (see Fig. 2). The $In(1)Te_4$ tetrahedra are connected with five $MnTe_6$ octahedra of

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42159 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

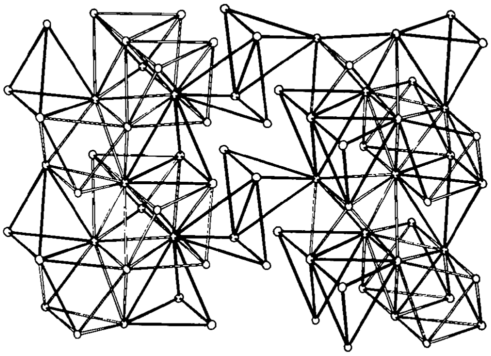

Fig. 2. The connection of occupied octahedra and tetrahedra in $MnIn_2Te_4$-II (*ORTEP*, Johnson, 1965).

one octahedra layer *via* two edges and two corners (see Fig. 2) and strengthen the layer. The bond distances and angles (see Table 2) agree well with the tendencies derived from the distortion of the square nets. The very small angle Te(4)–In(2)–Te(4) 98·70° is a consequence of the edge sharing. An enlargement of the angle would cause an approach of the central atoms.

The resulting structure is more densely packed than that of the normal-pressure modification (decrease of volume 7·1% at the transition $MnIn_2Te_4$-I → $MnIn_2Te_4$-II) and represents a new structure type for AB_2X_4 compounds.

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Structure of Vacancy-Ordered Titanium Heminitride δ'-Ti_2N by Powder Neutron Diffraction

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Abstract. $M_r = 109{\cdot}8$, tetragonal, $I4_1/amd$, $a = 4{\cdot}1493\,(2)$, $c = 8{\cdot}7858\,(5)$ Å, $V = 151{\cdot}26$ Å^3, $Z = 4$, $D_x = 4{\cdot}82$ g cm^{-3}, $\lambda = 1{\cdot}909$ Å, $T = 5$ K, final $R_p = 6{\cdot}1\%$ for 34 reflections. The structure is obtained by ordering N atoms and vacancies in substoichiometric rocksalt structure $TiN_{0.5}$. A shift [by 0·123 (3) Å] of the Ti atoms along the tetragonal axis away from the first neighbour vacancy and towards the first neighbour N was found.

Introduction. Titanium mononitride has the NaCl structure over a wide range of composition ($TiN_{0.42}$ to $TiN_{1.00}$, Ehrlich, 1949), with a random vacancy distribution on the f.c.c. N sublattice. By annealing TiN_x samples (in which $0{\cdot}5 < x < 0{\cdot}6$) at about 773 K a long-range-ordered structure based on the composition Ti_2N is obtained (Lobier & Marcon, 1969; Nagakura & Kusunoki, 1977); this δ'-Ti_2N compound occurs in multidomain twins. From X-ray powder and electron diffraction studies a tetragonal structure with space group $I4_1/amd$ has been suggested (Lobier & Marcon, 1969; Nagakura & Kusunoki, 1977). This is

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