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Reinvestigation of $MnSn_2$

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Key indicators

Single-crystal X-ray study
T = 157 K
Mean σ(Mn–Mn) = 0.003 Å
R factor = 0.016
wR factor = 0.030
Data-to-parameter ratio = 26.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of manganese distannite, $MnSn_2$, known from X-ray powder diffraction data, has been refined based on single-crystal data. This intermetallic compound crystallizes in the tetragonal $CuAl_2$ structure type. Mn atoms (4*a* position) form chains parallel to the *c* axis and each Mn atom is surrounded by eight Sn atoms in a square antiprism. Each Sn atom (8*h* position) has four Mn near neighbors from two neighboring Mn chains forming Mn_4Sn rectangular prisms.

Comment

$MnSn_2$, a $CuAl_2$-type compound, has been extensively studied due to its unusual magnetic behavior (Corliss & Hastings, 1968; Kouvel & Jacobs, 1968: Kouvel & Hartelius, 1961), and because of its use as an anode material for secondary non-aqueous lithium batteries (Beaulieu & Dahn, 2000; Larcher *et al.*, 2000; Sato *et al.*, 2001; Negi *et al.*, 2002) and as an erasable optical recording medium (Kobayashi *et al.* 1987). However, the crystal structure and lattice parameters were reported with limited precision from powder diffraction data containing a β-Sn impurity (Havinga *et al.*, 1972; Kouvel & Hartelius, 1961; Kouvel & Jacobs, 1968). Here, we report the single-crystal structure of the title compound and confirm the basic structural features determined from powder diffraction, as well as presenting more precise structural information.

$MnSn_2$ crystallizes in the body-centered tetragonal $CuAl_2$ structure type, as shown in Fig. 1(*a*). Mn and Sn atoms are located at special positions 4*a* (0, 0, $\frac{1}{4}$) and 8*h* ($-x + \frac{1}{2}$, x, 0), respectively. The structure can be described as alternating layers of Mn and Sn perpendicular to the crystallographic *c* axis. Alternatively, as is shown in Fig. 2, this structure can also

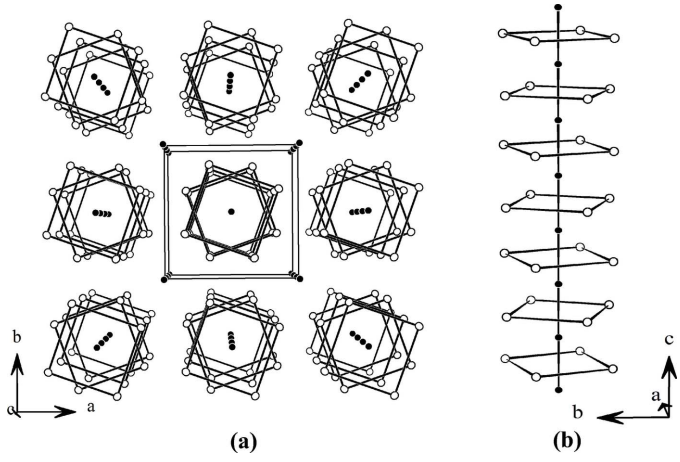

Figure 1
(*a*) The crystal structure of $MnSn_2$. (*b*) An individual Mn-centered Sn square-antiprism chain. Black circles are Mn atoms and open circles are Sn atoms. Displacement ellipsoids are drawn at the 90% probability level.

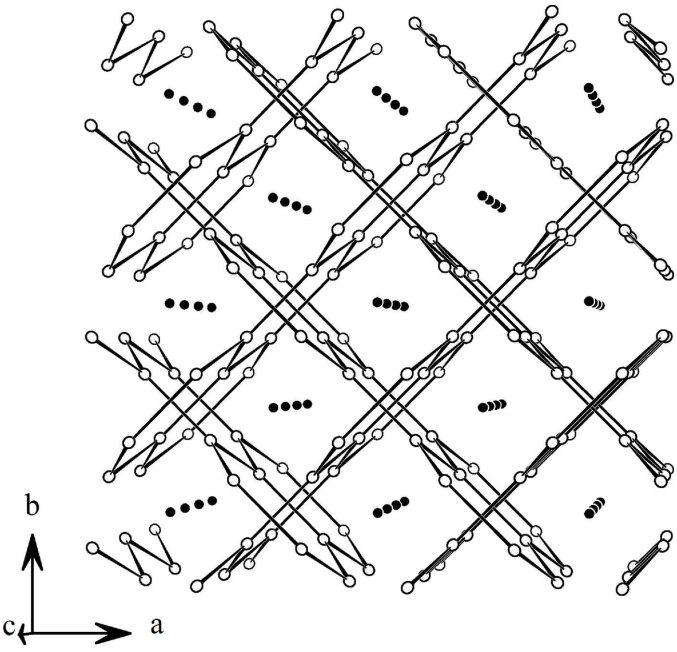

Figure 2
A perspective view of the interpenetrating Sn graphite-like network. Atoms are represented as in Fig. 1.

be described as two interpenetrating graphite-like Sn layers that form a network structure with one-dimensional channels along the *c* axis. Mn atoms are located in these channels. Mn atoms are surrounded by eight Sn atoms in a square antiprism to form one-dimensional chains sharing square faces along the [001] direction (Fig. 1*b*). Each chain shares the four common corners to form a three-dimensional network with square channels. Nearest-neighbor Mn atoms are separated by a distance of 2.7103 (3) Å in the chain direction. The interchain Mn distance is 4.6979 (2) Å. Each Sn atom is bonded to Mn atoms from two neighboring Mn chains at an Sn—Mn distance of 2.8366 (1) Å, forming the base of a rectangular prism. The Sn atoms are 0.8328 Å above the Mn rectangle. The shortest Sn···Sn distance [3.0335 (4) Å] is between Sn atoms in neighboring squares of the same Sn layer. This distance is very similar to that in β-Sn (3.022 Å; Cullity, 1978) and somewhat larger than that in α-Sn (2.810 Å; Cullity, 1978). The next shortest Sn···Sn distances are 3.1805 (3) and 3.4564 (3) Å between squares in a chain and 3.5242 (2) Å in the square.

Experimental

In an attempt to prepare chalcogenonitrides, the compound $MnSn_2$ was obtained by the reaction of NaN_3, Mn and Se with an Sn flux. The starting materials of NaN_3 (0.0975 g; Aldrich, 99%), Mn (0.0257 g; CERAC, 99.95%), Se (0.0395 g; CERAC, 99.999%) and Sn (0.1187 g, metal rod; JohnsonMatthey) were placed into an Nb tube which was made by welding one end of an Nb tube in an argon atmosphere, using a Centorr Associates arc furnace. The atomic ratio of Na:Mn:Se:Sn was 3:1:1:2. After the remaining end had been welded closed, the Nb tube was put into a silica tube and sealed under vacuum to protect it from oxidation during heating. The reaction tube was heated gradually to 993 K over 24 h and held at this temperature for 96 h. The tube was cooled to 453 K at 3 K h^{-1}. Thereafter, the furnace was turned off and the reaction tube cooled to room temperature. After opening the Nb tube in an inert-atmosphere glove box, we observed metallic black fibrous needle-shaped crystals and a light gray mass. A powder X-ray diffraction pattern with a Scintag 2000 θ/θ diffractometer using Cu $K\alpha$ radiation showed that the dominant phases were Na_2Se and Sn. A microprobe analysis of the black needles was made with an EDAX-equipped (Thermonoran) scanning electron microscope (Jeol JXA-8900R). Analysis of these crystals showed only the presence of Mn and Sn; no other elements were detected. To prevent decomposition of the samples, the title compound was transferred from an Ar-filled glove box to the microprobe using a specially designed portable antechamber (Ehrlich, 1995).

Crystal data

$MnSn_2$	Mo $K\alpha$ radiation
M_r = 292.32	Cell parameters from 907 reflections
Tetragonal, $I4/mcm$	θ = 6.1–39.3°
a = 6.6438 (3) Å	μ = 25.48 mm^{-1}
c = 5.4206 (6) Å	T = 157.0 (1) K
V = 239.27 (3) $Å^3$	Needle, black
Z = 4	0.08 × 0.02 × 0.02 mm
D_x = 8.115 Mg m^{-3}	

Data collection

Bruker X8 APEX II 4K CCD area-detector diffractometer	209 independent reflections
	199 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.034
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	θ_{max} = 39.3°
	$h = -10 \rightarrow 7$
T_{min} = 0.346, T_{max} = 0.630	$k = -11 \rightarrow 11$
1402 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.016	$\Delta\rho_{max}$ = 1.21 e $Å^{-3}$
$wR(F^2)$ = 0.030	$\Delta\rho_{min}$ = −1.44 e $Å^{-3}$
S = 1.22	Extinction correction: *SHELXL97* (Sheldrick, 1997)
209 reflections	
8 parameters	Extinction coefficient: 0.0143 (8)
$w = 1/[\sigma^2(F_o^2) + (0.0047P)^2 + 0.2469P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Mn—Mn^{i}	2.7103 (3)	Sn—Sn^{ii}	3.0335 (4)
Mn—Sn	2.83663 (14)	Sn—Sn^{iii}	3.1805 (3)
Sn^{iii}—Mn—Sn^{i}	145.880 (7)	Sn—Mn—Sn^{iv}	76.807 (3)
Sn^{iii}—Mn—Sn	68.197 (6)	Sn^{iii}—Mn—Sn^{v}	75.070 (7)
Sn^{i}—Mn—Sn	122.925 (6)	Mn^{iii}—Sn—Mn^{i}	145.880 (7)
Sn^{iii}—Mn—Sn^{iv}	135.569 (7)	Mn^{iii}—Sn—Mn	111.803 (6)
Sn^{i}—Mn—Sn^{iv}	76.807 (3)	Mn^{i}—Sn—Mn	57.075 (6)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x+1, -y, -z$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $y, -x, -z$; (v) $-y, x, z$.

In this structure type, there is only one free positional parameter, x, which determines the Sn position. We find x = 0.16143 (2), a more precise value than that of 0.1623 (17) (Havinga *et al.*, 1972) estimated from powder diffraction. The highest peak and deepest hole are located 0.65 and 1.09 Å, respectively, from atom Sn.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

DIAMOND (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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