

The Crystal Structure of MnIn_2Se_4 , a Ternary Layered Semiconductor

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Single crystals of MnIn_2Se_4 have been grown by the chemical vapour phase transport technique using AlCl_3 as the transporting agent. The structure was refined to $R = 0.064$, $R_w = 0.059$ for 609 reflections. MnIn_2Se_4 ($R\bar{3}m$, hexagonal axes $a = 4.051(1)$, $c = 39.464(2)$ Å, $c/a = 9.74$, $Z = 3$) crystallizes with a nearly close-packed layered structure (sequence of the Se layers $ABCA|CABC|BCAB$) with M_{oct} ($= 0.56 \text{ Mn} + 0.44 \text{ In}$) in octahedral coordination ($M_{\text{oct}}\text{-Se} = 6 \times 2.721(1)$ Å) and M_{tet} ($= 0.78 \text{ In} + 0.22 \text{ Mn}$) in tetrahedral coordination ($M_{\text{tet}}\text{-Se} = 1 \times 2.527(2)$ and $3 \times 2.593(1)$ Å). The overall layer sequences is $A\beta B\alpha C\gamma A|C\alpha A\gamma B\beta C|B\gamma C\beta A\alpha B$.

The semiconductor MnIn_2Se_4 has an energy gap of $E_g = 1.38$ eV [1] which is suitable for photovoltaic applications. Furthermore, the plate-like habit and easy cleavage of MnIn_2Se_4 point to a quasi-two-dimensional layered structure, which may influence the magnetic properties.

From X-ray powder diffraction measurements [2] a rhombohedral unit cell was found for this material. The lattice constants ($a = 4.05(6)$ and $c = 39.4(9)$ Å) are similar to that of MgIn_2Se_4 [3]. Therefore, by analogy to MgIn_2Se_4 , the crystal structure was proposed [2] to be of the ZnIn_2S_4 type [4]. The distribution of the Mn and In atoms over the octahedral and tetrahedral sites could not be determined due to texture effects existing in the powder samples. The present paper describes the results of a single-crystal structure refinement.

Plate-like single crystals of MnIn_2Se_4 with a size of up to 1 cm^2 could be grown by the chemical vapour phase transport technique using AlCl_3 as the

transporting agent [2]. A crystal with approx. dimensions $0.4 \times 0.4 \times 0.06$ mm was used for the data collection on an Enraf-Nonius CAD4 diffractometer ($\text{MoK}\alpha$, $\lambda = 0.71073$ Å, graphite monochromator in incident beam). An EDX analysis made on the same crystal after data collection showed Mn, In and Se to be present in the approximate ratio 1:2:4. No traces of the transporting agent could be detected. The result of the structure analysis finally confirmed the composition MnIn_2Se_4 . Lattice parameters were refined from 2θ values of 25 carefully centered reflections in the range $6.4 \leq \theta \leq 14.4^\circ$. Intensities were measured for $2 \leq \theta \leq 50^\circ$ in $\omega-2\theta$ scan mode, scan width $(1.0 + 0.35 \tan\theta)^\circ$. Three standard reflections showed only small random fluctuations and indicated no loss of intensity throughout data collection. Merging of the 3939 collected intensities ($\sin\theta_{\text{max}}/\lambda = 1.1 \text{ \AA}^{-1}$; $-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $0 \leq l \leq 85$) gave 869 unique reflections ($R_{\text{int}} = 0.054$), of which 609 with $I > 3\sigma(I)$ were considered as observed and used for the calculations.

Possible space groups are $R\bar{3}m$, $R3m$ or $R32$. Statistical tests strongly suggested the presence of a centre of inversion and consequently the centrosymmetric space group $R\bar{3}m$.

The structure was solved by inspection of Patterson syntheses, followed by successive difference-Fourier syntheses. In the least-squares refinement $|F|$ magnitudes were used to refine an overall scale factor, positional parameters, occupation factors for the cations and isotropic thermal parameters. After the last isotropic refinement cycle a numerical correction for absorption was applied to the original data set (program DIFABS [5]). The anisotropic refinement of 15 variables (including an extinction parameter) confirmed the centric space group $R\bar{3}m$, resulting in $R = 0.064$, $R_w = 0.059$ and a ratio shift to error < 0.001 in the final refinement cycle. The maximum features in the final difference-Fourier synthesis were $+3.7$, -2.3 e\AA^{-3} near the heavy atoms, obviously resulting from insufficient correction for absorption. Final atomic coordinates and equivalent isotropic temperature factors are given in Table I*, derived bond distances and angles in Table II.

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* Lists of structure factors, positional and anisotropic thermal parameters, bond distances and bond angles have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2. Copies may be obtained by quoting the depository number CSD 55380, the name of the authors and literature citation.



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Table I. Crystallographic data for MnIn_2Se_4 *. Rhombohedral, space group $R\bar{3}m$ (No. 166), hexagonal axes $a = 4.051(1)$, $c = 39.464(2)$ Å, $c/a = 9.74$, $V = 560.7(4)$ Å³, $Z = 3$, $D_x = 5.33$ g·cm⁻³.

Atomic positions and thermal parameters				
Atom	x/a	y/b	z/c	U_{eq} [Å ²]**
M_{oct} (0.56 Mn + 0.44 In)	0	0	0	0.0128(4)
M_{tet} (0.78 In + 0.22 Mn)	0	0	0.23404(3)	0.0103(1)
Se(1)	0	0	0.12764(3)	0.0091(3)
Se(2)	0	0	0.29807(3)	0.0086(3)

* Here, and in the following table, the e.s.d.'s of the last significant figure are given in parentheses.

** The equivalent isotropic thermal parameters U_{eq} are defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structure of MnIn_2Se_4 (Fig. 1) comprises slabs, each consisting of four selenium layers with a sequence ABCA. The cations are situated between the Se layers in octahedral and tetrahedral holes. There is some cation disorder on octahedral ($M_{\text{oct}} = 0.56 \text{ Mn} + 0.44 \text{ In}$) and tetrahedral ($M_{\text{tet}} = 0.78 \text{ In} + 0.22 \text{ Mn}$) sites. The cation-anion distances ($M_{\text{oct}}\text{-Se} = 6 \times 2.721(1)$; $M_{\text{tet}}\text{-Se} = 1 \times 2.527(2)$ and $3 \times 2.593(1)$ Å, $\langle M_{\text{tet}}\text{-Se} \rangle = 2.576$ Å) agree well with those found in $\text{Mn}_2\text{In}_2\text{Se}_5$ [6]. The Se- M_{tet} -Se- M_{oct} -Se- M_{tet} -Se slabs are stacked along the c -axis according to the rhombohedral symmetry, resulting in an overall layer sequence $A\beta B\alpha C\gamma A | C\alpha A\gamma B\beta C | B\gamma C\beta A\alpha B$. The slabs are bound together by van der Waals interactions only (Se(1)-Se(1) = 3.867(1) Å). This explains the plate-like habit of the crystals and the cleavage plane parallel (001).

It should be noted that in spite of the close similarity of the crystal structures of MnIn_2Se_4 and MgIn_2Se_4 [3] the latter was described in the acentric space group $R3m$. All attempts, however, to refine the structure of MnIn_2Se_4 in $R3m$ failed completely. During the refinement poor convergence, strong correlations and irregular behaviour of even the isotropic thermal parameters have been

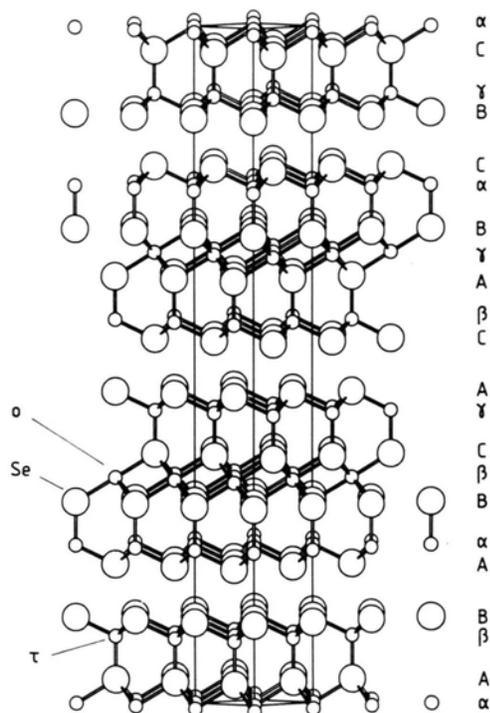


Fig. 1. Structure of $\text{Mn}_2\text{In}_2\text{Se}_4$ (Schakal plot). The layer sequence of anions (Se), M_{oct} (o) and M_{tet} (τ) is indicated by roman capitals and small greek letters, respectively.

observed. These are typical symptoms when a centrosymmetric structure is refined in a non-centrosymmetric space group. It will be shown elsewhere [7] that space group $R\bar{3}m$ is indeed the correct one for MgIn_2Se_4 as well as for the analogous compound MgAl_2Se_4 . Because the centric space group implies not only equal coordination but also equal occupancy of the tetrahedral sites, the term "ZnIn₂S₄ structure" should be avoided for the group of compounds mentioned here.

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$M_{\text{oct}}\text{-Se}(2)$	2.721(1)	6 ×	$\text{Se}(2)\text{-}M_{\text{oct}}\text{-Se}(2)$	96.19(2)	6 ×
$M_{\text{tet}}\text{-Se}(2)$	2.527(2)	1 ×		83.81(2)	6 ×
$\text{-Se}(1)$	2.593(1)	3 ×			
$\text{Se}(1)\text{-}M_{\text{tet}}$	2.593(1)	3 ×	$\text{Se}(2)\text{-}M_{\text{tet}}\text{-Se}(1)$	115.56(3)	3 ×
$\text{-Se}(1)$	3.867(1)	3 ×	$\text{Se}(1)\text{-}M_{\text{tet}}\text{-Se}(1)$	102.75(4)	3 ×
$\text{Se}(2)\text{-}M_{\text{tet}}$	2.527(2)	1 ×			
$\text{-}M_{\text{oct}}$	2.721(1)	3 ×			
$\text{-Se}(2)$	3.635(1)	3 ×			

Table II. MnIn_2Se_4 : Selected interatomic distances [Å] and bond angles [°].

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