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Crystal Structure of $Mn_3Si_2Te_6$

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The synthesis, magnetic, and electrical properties of a new silicon manganese telluride, semiconducting and ferrimagnetic, has been previously reported. The X-ray determination of the crystal structure of this compound was achieved by means of direct methods and three-dimensional Fourier syntheses. The final least-squares R_w factor of the refinement is $R_w = 0.035$. According to this study the chemical formula is $Mn_3Si_2Te_6$ with $Z = 2$, the trigonal unit cell is $a = 7.029(2)$, $c = 14.255(3)$ Å, the space group is $P\bar{3}1c$. The crystal structure can be described as one of a layer-type compound. Along the c-axis direction, we observe a fully occupied layer of Mn or Si pairs octahedra, then a partially occupied layer of ordered Mn octahedra, and so on. The surroundings of Si atoms are similar to the one found in Si_2Te_3, and the fully occupied layer of octahedra may be compared to the one found in $Fe_2P_2Se_6$.

Introduction

In the manganese telluride family, only the binary compounds MnTe and $MnTe_2$ have been extensively studied. Both compounds are antiferromagnetic. Very few ternary Mn tellurides have been studied up to now (*1*, *2*). The series MnA_2Te_4 with A = Al, Ga, In have been synthesized; these compounds, with a tetragonal crystal structure, are paramagnetic down to 1.3 K (*3*, *5*).

In an attempt to prepared a high-temperature phase of $MnAl_2Te_4$ in a silica cell, a new compound has been obtained. This compound was found to be hexagonal, semiconducting, and ferrimagnetic below 82 K (*6*). The chemical formula was found by microprobe analysis to be close to $Mn_{1.3}SiTe_3$. We decided to prepare single crystals and to determine their structure.

Crystal Growth

Single crystals have been grown by the vapor phase transport technique from a mixture of the elements with a slight excess of tellurium and with iodine as the transport agent; the thermal gradient was from 800 to 720°C. Complete reaction was not achieved after 8 days; in the cooler zone, we found thin, roughly hexagonal, shiny dark platelets with typical dimensions 2 × 2 × 0.1 mm.

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TABLE I

POSITIONAL AND THERMAL PARAMETERS (U_{ij} IN Å^2 × 10^4)

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupation
Mn(1)	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.00068(8)	158(6)	158(6)	242(7)	079(3)	0	0	1
Mn(2)	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	184(5)	184(5)	200(6)	092(3)	0	0	0.966(3)
Si	$4e$	0	0	0.08153(13)	096(7)	096(7)	168(9)	048(4)	0	0	1
Te	$12i$	0.65869(3)	0.00361(3)	0.12788(2)	122(1)	125(1)	188(2)	068(1)	030(1)	024(1)	1

Crystal Structure Determination

According to precession photographs, the cell is hexagonal with parameters a = 7.029(2) Å, c = 14.255(3) Å. The c axis is perpendicular to the platelet, and the a axis is parallel to the edges. The hhl reflections with $l = 2n + 1$ are absent; the possible space groups are $P6_3mc$, $P\bar{6}2c$, $P6_3/mmc$ or $P3_1c$, $P\bar{3}_1c$, if the true symmetry is trigonal.

A triangular prismatic crystal of 0.016 cm width and 0.012 cm thickness was set on a four-circle diffractometer. The intensities of a total of 4503 reflections were collected in the ω-scanning mode, using Ag$K\alpha$ radiation up to a 25° Bragg angle in half the Ewald sphere. An absorption correction was performed, considering a sphere of equivalent volume ($\mu R = 0.6$).

Investigation of equivalent reflections shows that the true symmetry is trigonal and averaging in the $\bar{3}1m$ Laue class lead to 832 independent reflections. Wilson statistic giving a centric distribution of the E-normalized structure factors, we applied the direct methods in $P\bar{3}1c$ space group. Because of the absence of the $h\ k\ 2n + 1$ reflections among the 200 larger E's, the origin couldn't be fixed. Nevertheless, the absence of this reflection class shows that the two halves of the unit cell are almost identical in the c axis direction. Direct methods and Fourier synthesis were then performed in the $P\bar{3}1m$ space group corresponding to the a, b, $c/2$ unit cell, after reindexing of the reflections. The Te, Mn, and Si atoms could be located, respectively, in the $6k$, $2c$, $2e$ positions of the $P\bar{3}1m$ space group.

Returning to the true unit cell, a Fourier difference synthesis showed the presence of one more Mn atom in the $2c$ position of the $P\bar{3}1c$ space group. Including the Te, Mn, Si atoms previously located in the $12i$, $4f$, and $4e$ positions of $P\bar{3}1c$, the true chemical formula is $Mn_3Si_2Te_6$ with $Z = 2$. Using reflections with $F > 2\sigma$ and allowing the anisotropic temperature factors and site populations to vary, a least-squares refinement gave the parameters listed in Table I. The $R(F)$ and $R_w(F)$ factors are, respectively, 0.0412 and 0.035. The weighting scheme used is $w(F) = 1/\sigma(F)^2$ with $\sigma(F) = 1/2((\sigma(I) + (0.02I)^2)/I)^{1/2}$ where $\sigma(I)$ is the standard deviation of the observed intensity I.

Structure Description

Along the c-axis layers of the Te atoms conform to hexagonal close packing, with each layer of Te atoms being of distance $c/4$ from the following one. The Mn atoms or pairs of Si atoms are situated in octahedral sites.

Octahedra containing Mn(1) atoms ($z \approx 0$, or $z \approx \frac{1}{2}$) are surrounded by 3 octahedra containing Mn atoms and with 3 octahedra containing pairs of Si atoms. Each Si pair octahedron is surrounded by 6 Mn octahedra (Fig. 1). Mn(2) octahedra ($z \approx \frac{1}{4}$ or $\frac{3}{4}$) are surrounded by 6 empty octrahedra (Fig. 2). Along the c axis the following sequence

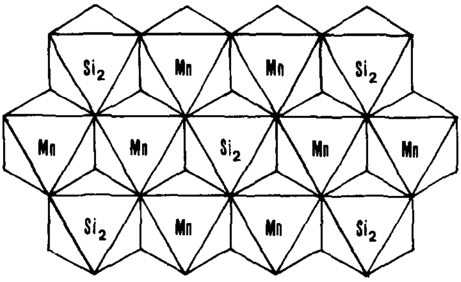

FIG. 1. Fully occupied layer of Mn(1) or Si pairs octahedra.

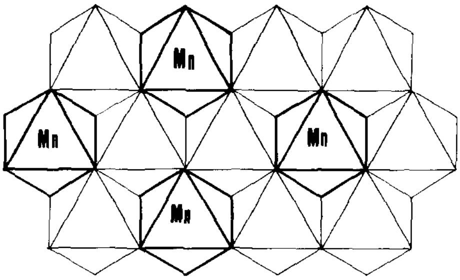

FIG. 2. Partially occupied layer of Mn(2) octahedra.

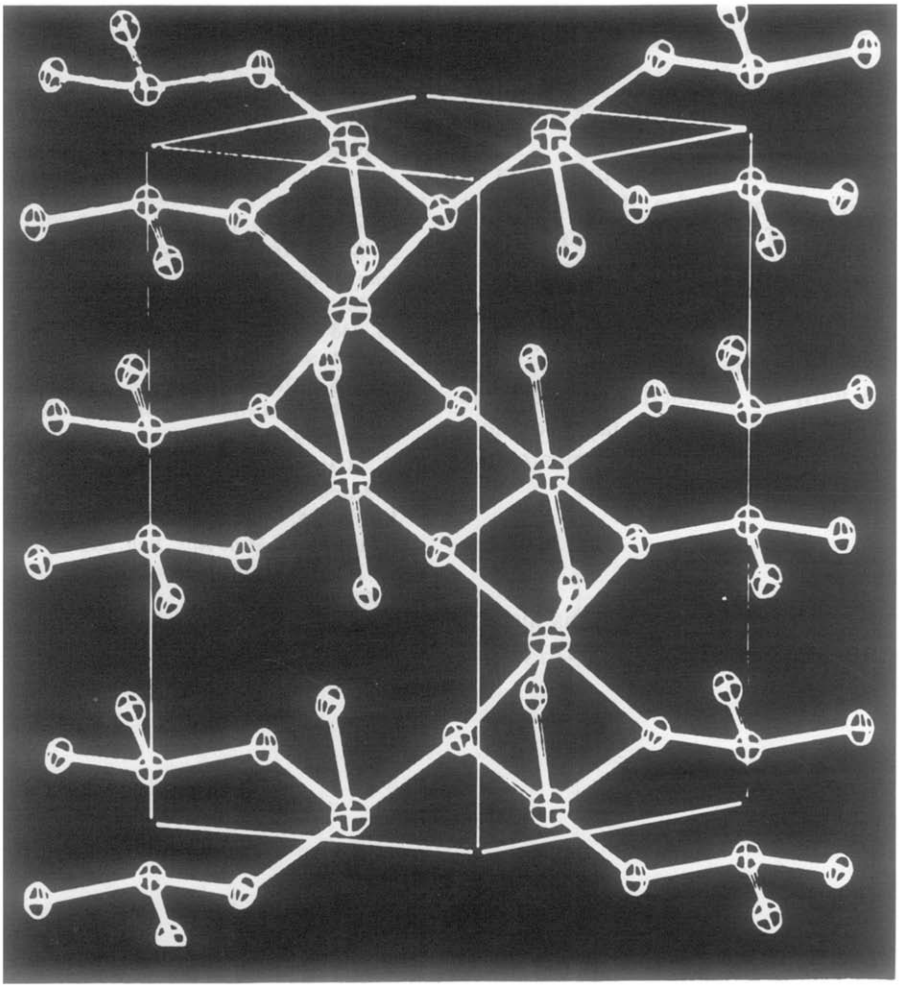

FIG. 3. Sequence of fully and partially occupied layers along the *c* axis.

TABLE II

BOND DISTANCES IN $Mn_3Si_2Te_6$

Mn(1) octahedron			
Mn(1)–Te	2.9331(7) ×3	Te–Te	3.9666(5) ×3
	2.9514( ) ×3		4.0335(5) ×3
			4.2613(5) ×3
			4.3714(5) ×3
Mn(2) octahedron			
Mn(2)–Te	2.9074(3)	Te–Te	4.0335(5) ×6
	2.9075(3)		4.1214(5) ×3
			4.2572(5) ×3
Si–Si octahedron			
Si–Te	2.5007(5) ×3		
Si–Si	2.3244(12)	Te–Te	4.1775(5) ×6
Si–Te	2.5007(5) ×3		4.3714(5) ×6
Te–Si–Te	113.29°		

may be observed: a fully occupied layer of Mn(1) or Si pairs octahedra, then a partially occupied layer of Mn(2) octahedra, again a fully occupied layer of Mn(1) or Si pairs octrahedra followed by a partially occupied layer of Mn(2) octahedra and so on.

A fully occupied layer octahedron shares one edge with six octahedra of the same layer. A partially occupied layer octahedron shares one face with the ones of the upper or lower layer (Fig. 3).

Discussion

The arrangement of the Si atoms may be compared to the one found in Si_2Te_3 (*7*). In this compound octahedra containing two Si atoms are observed. Si–Si bond lengths (2.269 to 2.345 Å), Si–Te bond lengths (2.451 to 2.662 Å), and Te–Si–Te angles (113.50° to 116.85°) (*7*) are comparable with those in Table II. Si_2 pairs with comparable interatomic distances are also observed in $Na_6Si_2Te_6$ and in $K_6Si_2Te_6$ (*8*). The fully occupied layer arrangement is similar to the one found in $Fe_2P_2Se_6$ (*9*). In this selenide, we observe octahedra containing P_2 units. Each P_2 octahedron is surrounded by 6 Fe octahedra, and each Fe octahedron is surrounded by 3 octahedra containing Fe atoms and 3 octahedra containing pairs of P atoms, as in $Mn_3Si_2Te_6$.

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