

Refinement of the Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ Structures and Their Relationship to Nonstoichiometric $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ Compounds

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Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ crystallize in the $\text{Bi}_2\text{Se}_2\text{S}$ structure. The space group is $R\bar{3}m$. The lattice constants for the hexagonal cell at 29°C are: $a = 4.264 \pm 0.001$ and $c = 30.458 \pm 0.007$ Å for Sb_2Te_3 , and $a = 4.188 \pm 0.001$ and $c = 29.937 \pm 0.006$ Å for $\text{Sb}_2\text{Te}_2\text{Se}$. The fractional atom parameters were determined by a one-dimensional Fourier summation and by successive least-squares refinement of the 00 l reflections, after intensity correction for Lorentz and polarization factors. The parameters for Sb_2Te_3 are: $u_{\text{Sb}} = \pm 0.3988$, and $u_{\text{Te}^1} = \pm 0.7869$; those for $\text{Sb}_2\text{Te}_2\text{Se}$ are: $u_{\text{Sb}} = \pm 0.3942$ and $u_{\text{Te}^1} = 0.7854$. The Te^2 or the Se respectively are in 0,0,0. The interatomic distances in Sb_2Te_3 are: $\text{Sb}-\text{Te}^1 = 2.979$, $\text{Te}^1-\text{Te}^1 = 3.736$ and $\text{Sb}-\text{Te}^2 = 3.168$ Å. The corresponding distances for $\text{Sb}_2\text{Te}_2\text{Se}$ are: $\text{Sb}-\text{Te}^1 = 2.975$, $\text{Te}^1-\text{Te}^1 = 3.753$ and $\text{Sb}-\text{Se} = 3.028$ Å. c lattice constant measurements on the $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ series show two regions with almost linear changes represented by the equations $c = -0.529y + 30.465$ for $y \leq 1$ and $c = -0.407y + 30.341$ for $1 \leq y \leq 2$ (y stands for fractional formula unit of selenium). The discontinuity for the composition $\text{Sb}_2\text{Te}_2\text{Se}_1$ suggests that the Se is first substituted into the 0,0,0 positions; after the Te^2 position is filled it goes into the Te^1 position.

Introduction

Considerable interest has been shown in the relation between electronic properties and chemical bonding in the $\text{Sb}_x\text{Bi}_{2-x}\text{Te}_{3-y}\text{Se}_y$ system (Teramoto & Takayanagi, 1960). This interest, in part, is caused by the strong anisotropy in the electrical properties which may vary by as much as a factor of 50 within and perpendicular to the layers of the layer structure (Drabble & Wolfe, 1956; Drabble, Groves & Wolfe, 1958). Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 and, within a wide range of composition, solid solutions of these compounds are believed to be isomorphous with $\text{Bi}_2\text{Te}_2\text{S}$ crystallizing in the tetradymite structure with a rhombohedral cell of the space group $R\bar{3}m$ (Harker, 1939). The corresponding larger hexagonal cell, shown in Fig. 1, consists of 15 layers. For the stoichiometric com-

pounds each layer contains only one kind of atom. The sequence of layers in Sb_2Te_3 is expected to be $\text{Te}^2-\text{Sb}-\text{Te}^1-\text{Te}^1-\text{Sb}$ followed by two identical sequences. The superscripts 1 and 2 denote differently bonded tellurium atoms in the positions 0,0, $\pm u$ and 0,0,0 respectively.

No unequivocal single-crystal X-ray data on Sb_2Te_3 have been available in the past. However, based on the assumption of isomorphism between Sb_2Te_3 and Bi_2Te_3 , Sb and Te^1 atom parameters for Sb_2Te_3 have been calculated from selected area electron-diffraction data (Semiletov, 1956). Ullner (1968) concluded that $\text{Sb}_2\text{Te}_2\text{Se}$ crystallizes with the same structure, except that the Te^2 atoms are replaced by Se. However, his data are inconclusive because of incorrect parameters (based on a uniform distance between layers) for his intensity calculations and an unsatisfactory experi-

Table 1. *Lattice constants of Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$*

Compound	Lattice constant (Å)	X-ray data					Electron diffraction data Semiletov (1956)
		Dönges (1951)	Ullner (1968)	Teramoto & Takayanagi* (1960)	Swanson <i>et al.</i> (1964)	Present paper†	
Sb_2Te_3	a	4.25 Å	2.37 ± 0.008 Å	4.262 Å	4.262 Å	4.264 ± 0.001 Å	4.25 Å
	c	30.35	30.39 ± 0.06	30.45	30.45	30.458 ± 0.007	30.455 ± 0.008 Å
$\text{Sb}_2\text{Te}_2\text{Se}$	a		4.180 ± 0.008	4.190		4.188 ± 0.001	
	c		29.78 ± 0.06	29.950		29.937 ± 0.006	29.930 ± 0.008

* The lattice constants have been deduced from Fig. 5(a) and 5(b).

† Single-crystal diffractometer data at 29°C.

‡ Powder diffractometer data at 25°C.

mental setup. A proper change of parameters affects the intensities more strongly than replacement of the tellurium by selenium in either the Te^1 or the Te^2 position. The substitution of Se into the Te^1 position, however, has been proved for $\text{Bi}_2\text{Te}_2\text{Se}$ (Bland & Basinski, 1961). In conjunction with the selenium substitution into only one of the tellurium positions, deviations of the lattice constants from Vegard's law have been observed (Wiese & Muldower, 1960). They occur for fractional formula units of selenium larger than 1.2. Considering the smallness of the effect, the exact onset of the nonlinearity is hard to determine and it may well be at $\text{Sb}_2\text{Te}_2\text{Se}$.

No deviations from Vegard's law have been reported for $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ (Taramoto & Takayanagi, 1960). Their observation of a linear lattice constant change for $0 \leq y \leq 2$ and of a phase separation of Sb_2Se_3 for compositions with $y > 2$ suggests that the Se may be substituted only into the Te^1 position. Procarione & Wood (1970) suspected this also on account of their optical data while phase-diagram and electronic measurements point to the reverse substitution mechanism (Ullner, 1968).

To resolve the contradiction which results from the existing data, we remeasured the lattice constants for the $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ series and refined the $\text{Sb}_2\text{Te}_2\text{Se}$ structure.

Experimental

Single crystals of $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ were grown from the melt by a modified Bridgman technique (Procarione & Wood, 1970; Wood, Van Pelt & Hyland, 1972). The preparation of sufficiently small crystals for transmission techniques was unsatisfactory because of the resulting crystal deformation. Only cleavage perpendicular to $[001]$ did not affect the crystal quality. Since the parameters of the atom positions can be determined solely from the intensities of the $00l$ reflections, we used 'infinitely' thick cleaved samples in conjunction with a Norelco powder diffractometer for intensity gathering. Thus no absorption corrections had to be made. Small crystals, however, served for the determination of systematic absences by photographic techniques and for lattice-constant determination with a Siemens single-crystal diffractometer. In all cases $\text{Cu } K\alpha$ radiation was used. The powder diffractometer was equipped with a graphite monochromator. All intensities were corrected for Lorentz and polarization factors. The c lattice constants for the $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ series were obtained by step scanning of the $0,0,33$ reflection, and the a and c lattice constants for Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}_1$ by extrapolation from measurements of numerous reflections with the single-crystal diffractometer (Argonne Natl. Lab. Program B-106).

Results

The lattice constants for Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ are listed in Table I. The c lattice constants for other com-

positions of $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ are shown in Fig. 2. If one assumes two regions in which the lattice constants change linearly with composition, one obtains, by a least-square fit, the following equations: $c = -0.529y + 30.465$ for $0 \leq y \leq 1$ and $c = -0.407y + 30.341$ for $1 \leq y \leq 2$. The discontinuity at the composition $\text{Sb}_2\text{Te}_2\text{Se}$ supports the assumption that the Se is first

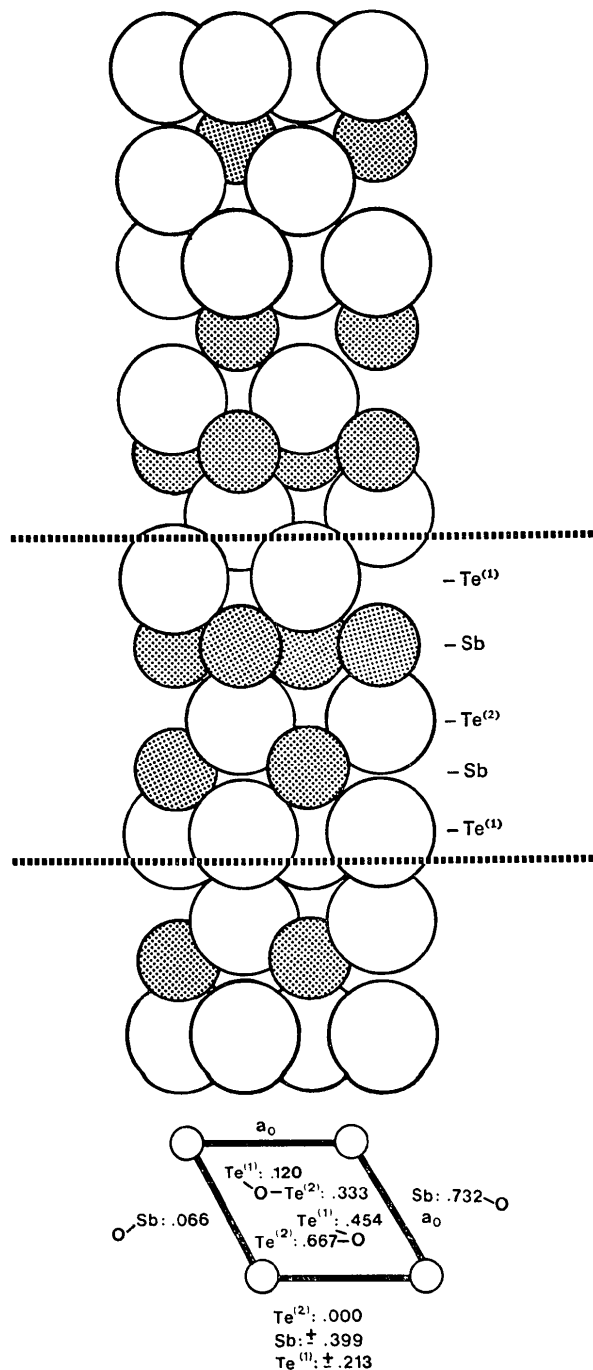


Fig. 1. The crystal structure of Sb_2Te_3 .

substituted into the 0,0,0 position. Laue photographs of the $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ series show continuous changes of relative intensities but no obvious deviation from the hexagonal symmetry. Contrary to previous observations (Ullner, 1968), we detected no systematic line broadening for compounds with $y \leq 1$ but an increasing amount of line broadening with increasing y for $y > 1.2$. It was observed that the difficulty in cleaving samples also followed a similar pattern.

For Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ we observed systematic absences only for reflections with $-h+k+l \neq 3n$ and thus established that they crystallize in the space group $R\bar{3}m$. If one assumes three formula units per

hexagonal unit cell, one obtains an X-ray density of 6.505 g cm^{-3} as compared with the reported density of 6.50 (*Handbook of Chemistry and Physics*, 1967-68) and our measured value of 6.48. The X-ray density and our measured density of $\text{Sb}_2\text{Te}_2\text{Se}$ are 6.327 and 6.30, respectively.

The approximate atom parameters for Te^1 as well as for Sb in the special positions $\pm 0,0,u$ were determined by a one-dimensional Fourier summation after correction of the intensities for Lorentz and polarization factors. The contribution of the 000 reflection was calculated from the number of electrons in each unit cell. The results are shown in Fig. 3. From the change of the electron density around zero and from the change of the bond length to the adjacent Sb peak between Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$, it can be concluded that the Se is substituted into the 0,0,0 position. By using a least-squares refinement program for this configuration (Argonne Natl. Lab. Program 36E7118), we obtained weighted R values of 0.036 and 0.011 for Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$, respectively. A comparison between observed and calculated intensities is given in Table 2. The resulting fractional parameters, isotropic temperature factors, bond lengths and bond distances are listed in Table 3.

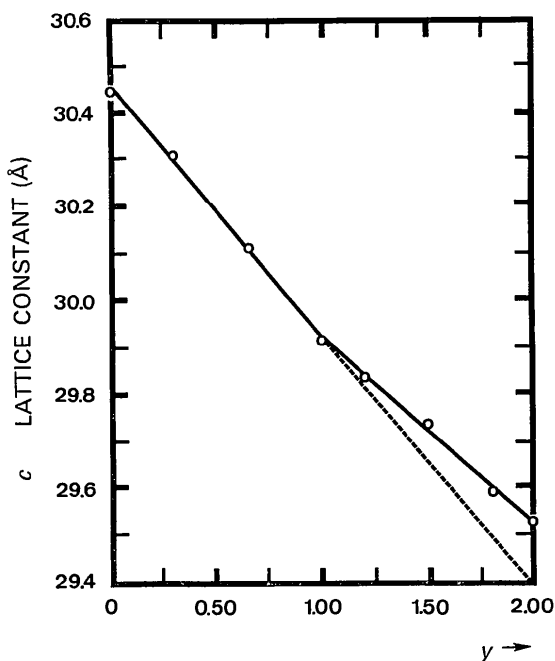


Fig. 2. c lattice constants of $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$, as a function of y .

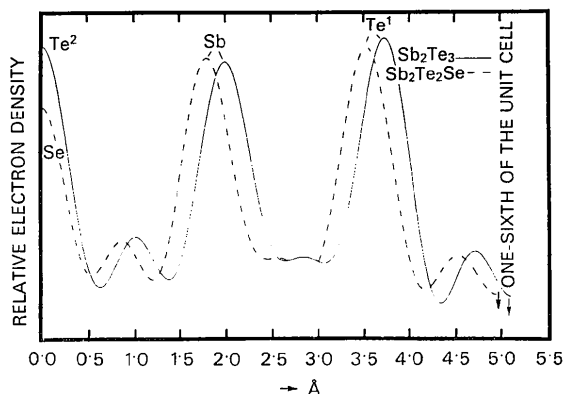


Fig. 3. Fourier synthesis of the 00 l reflections. Because of the centers of symmetry of $z=0$ and $z=\frac{1}{2}$, only one sixth of the unit cell had to be drawn. Although the electron density for each compound is drawn on an absolute scale, the scales for the two compounds vary slightly.

Table 2. Observed and calculated intensities ($\times 10^{-2}$)

	Sb_2Te_3		$\text{Sb}_2\text{Te}_2\text{Se}$	
	Observed	Calculated	Observed	Calculated
003	10.41	7.38	5.90	2.77
006	48.42	39.17	63.03	64.17
009	60.36	61.14	21.06	20.83
0,0,12	13.86	8.47	79.89	70.62
0,0,15	404.04	406.77	207.87	207.70
0,0,18	206.66	205.20	296.31	296.41
0,0,21	119.70	118.12	61.60	60.60
0,0,24	26.60	18.04	0.08	0.02
0,0,27	14.47	19.82	0.56	0.04
0,0,30	23.29	13.50	1.91	2.73
0,0,33	157.41	158.67	135.14	135.42
0,0,36	12.00	11.10	7.48	4.69

We could not achieve any satisfactory refinement for the other two possible configurations: the statistical distribution of Se in both the Te^1 and Te^2 layers and the substitution of the Se into the Te^1 layers only, respectively. If both were allowed to vary, the positional and temperature parameters became completely unrealistic. By fixing the temperature factors to the values in Table 3 (which may be too low for the cases in question) we obtained less unrealistic positional parameters, but R values of 0.485 and 0.898 respectively.

As one can see from the tables, the incorporation of the smaller selenium atoms into the Sb_2Te_3 structure has been achieved by shrinkage of both the a and c lattice constants. In spite of this 1.7 or 1.8% change in a and c , the bond length $\text{Sb}-\text{Te}^1$ has remained approximately

Table 3. *Parameters, temperature factors, bond lengths and bond angles*

		Sb_2Te_3		$\text{Sb}_2\text{Te}_2\text{Se}$	
		From Fourier summation	From least-squares refinement	From Fourier summation	From least-squares refinement
Fractional atom parameters, u_z	Sb	0.398	0.3988	0.394	0.3942
	Te ¹ Te ² or Se respectively	0.788 0	0.7872 0	0.786 0	0.7854 0
Temperature factor, β_{33}	Sb		1.4		1.5
	Te ¹		0.5		0.9
	Te ² or Se respectively		0.8		1.1
Interatomic distances	Sb-Te ¹ and Sb-Te ² , Sb-Se ² respectively		2.979 Å		2.975 Å
	Te ¹ -Te ¹		3.168		3.028
			3.736		3.753
Bond angles	Sb-Te ¹ and Sb-Te ² , Sb-Se ² respectively		91.40°		89.50°
	Te ¹ -Te ¹		84.60		87.51
			69.59		67.84

unchanged and the bond length $\text{Te}^1\text{-Te}^1$ has even increased by about $\frac{1}{2}\%$. This has been achieved by a larger separation of the Sb-Te^1 layers and the $\text{Te}^1\text{-Te}^1$ layers. Only the distance between the Sb-Se layers has decreased (by 9.4%) as compared with the Sb-Te^2 layer distance. The deviation from a regular octahedral surrounding of the selenium atoms by antimony has become smaller than for the corresponding atoms in the Sb_2Te_3 structure.

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