

## Structure Refinement of $\text{TiSe}_2$ by Neutron Diffraction

C. RIEKEL

*Institut Laue-Langevin, B.P. No. 156, 38042-Grenoble Cédex, France*

Received November 13, 1975

The structure of titanium diselenide ( $\text{TiSe}_2$ ) was refined from single crystal neutron data. The anisotropic thermal parameters were found to be nearly the same as in  $\text{TiS}_2$ . Only very little disorder was found on interstitial places.

### Introduction

The refinement of the  $\text{TiSe}_2$  structure is part of a program to determine accurately the structural parameter of layered dichalcogenides like  $\text{TiS}_2$  (1). This knowledge is indispensable for the discussion of bonding problems and the chemical reactivity of these compounds. A further point of interest was, that on the same crystal of  $\text{TiSe}_2$  acoustic phonons had been measured by neutron scattering (2).

### Experimental Methods

The crystal of titanium diselenide had been grown by standard vapor transport techniques (3) using titanium powder (99.9% Alfa Inorganic Chemicals), selenium (99.999% Research Inorganic Corporation) and iodine as transporting agent. Chemical analysis resulted in a value of  $22.9 \pm 0.4\%$  and  $75.7 \pm 0.6\%$  Se giving an overall Ti/Se ratio of 1:2.00 (5). The crystal selected had the form of a hexagonal plate cut off at one side. The largest diameter of the plate was 5.21 mm and the thickness 0.61 mm. The total crystal volume amounted to  $6.1 \text{ mm}^3$  (calculated as part of the absorption correction).

Laue and Weissenberg techniques ( $\text{MoK}\alpha$ ) showed that the reflection shapes were not distorted as is often observed in platelike crystals. No twinning was observed. The

spacegroup was found to be  $P\bar{3}m1$ . The crystal was mounted for data collection with the  $b^*$  and  $c^*$  axis in the equatorial plane of the diffractometer at  $\chi = 0$ . The data were collected on the automatic four-circle diffractometer D8 at the ILL. The cell parameters were refined from 16 well-centered reflections using a wavelength of 0.9114 (1). Instrumental and crystal data are summarized in Tables I and II.

### Data Collection and Data Reduction

The intensities were measured by the  $\theta/2\theta$  scan technique using an experimentally determined scan length. The step size was varied to obtain 50 points. A total of 564  $hkl$ ,  $\bar{h}kl$ ,  $h\bar{k}l$ , and  $\bar{h}\bar{k}l$  reflections having  $d^* \leq 1.79 \text{ \AA}^{-1}$  and 2 standard reflections every 20 reflections were measured. No significant change in the intensities of the standard reflections during the data collection was observed. The integrated intensities ( $J$ ) were corrected for background using a method (4) which divides peak and background in such a way that  $\delta(J)/J$  is minimized. Squared structure amplitudes ( $F_0^2$ ) were corrected for absorption by the Gaussian integration method (5). The linear absorption coefficient ( $\mu$ ) was calculated from the mass absorption coefficients for Ti and Se (6). Because of the small value of  $\mu$  ( $0.292 \text{ cm}^{-1}$ ) the  $F_0^2$  values were found to be little affected by absorption. For most

TABLE I

INSTRUMENTAL DATA	
Monochromator	Cu (200)
Wavelength	0.9114 (1) Å
Monochromator	
Take-off-angle	28° (2θ)

TABLE II

CRYSTAL DATA	
$a = b = 3.540$ (1) Å	
$c = 6.008$ (3) Å	
$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Vol 65.2 Å <sup>3</sup>	
Absorption coefficient $\mu$ 0.292 (cm <sup>-1</sup> ) $d_{\max}^*$ 1.79 Å <sup>-1</sup>	
Total number of reflections measured: 564	
Number of independent reflections: 375	

reflections the transmission factor was larger than 0.97.

The corrected  $F_0^2$  values were averaged over symmetry-related reflections using Eq. (1):

$$F_{0i}^2 = \left( \sum_i F_{0i}^2 / \sigma_i^2 \right) / \sum_i 1 / \sigma_i^2 \quad (1)$$

where  $\sigma_i^2$  is the variance of  $F_{0i}^2$  from counting statistics. The standard deviations of the averaged  $F_{0i}^2$  values were calculated by Eq. (2):

$$\sigma(F_{0i}^2) = \left[ 1 / \sum_{i=1}^n 1 / \sigma_i^2 \right]^{1/2}. \quad (2)$$

For only 12 of the strongest reflections the difference in the  $\Delta F_0^2$  values of symmetry related reflections proved to be higher than six times  $\sigma(F_0^2)$ . These reflections were also introduced into the refinement as no error in the measurement was found. Finally the  $R_s$ -value of all symmetry related reflections was calculated according to Eq. (3).

$$R_s = \left( \sum_i \Delta |F_{0i}^2| / F_{0i}^2 \right) \cdot 100 \quad (3)$$

$R_s$  amounted to 0.022. For the refinement the standard deviations  $\sigma(F_0^2)$  were modified according to Eq. (4):

$$\sigma_m(F_{0i}^2) = [\sigma^2(F_{0i}^2) + (k_w F_{0i}^2)]^{1/2}. \quad (4)$$

$k_w$  was calculated by Eq. (5):

$$k_w = \left[ \sum_i (F_{0i}^2 - F_{ci}^2)^2 / \sigma_i^2 \right]^{1/2} / \sum_i F_{0i}^4 / \sigma_i^2 \quad (5)$$

and was determined to be 0.014. A total of 375 independent reflections were thus obtained for structure refinement.

### Structure Refinement

For least-squares calculations the "ORX FLS-3" programs was used (8). All other calculations were performed with the programs of the "X-ray system" (7). Starting parameters were taken from the TiS<sub>2</sub> structure (1). Scattering length as determined by the Christians filter technique (8) were used ( $b_{Ti} = -0.333$ ,  $b_{Se} = 0.795$ )  $\times 10^{-12}$  cm). Other scattering length for Se (10) were also tried but resulted in substantially worse refinements. Several cycles of refinement based on  $F_0^2$ , including the positional parameters of Se and the anisotropic thermal parameters of Ti(1) and Se(1) resulted in an  $R_F$ -value (see below) of 0.030. The standard deviation of the observation of unit weight ( $\equiv S$ ) as determined by Eq. (6) was 5.1:

$$S = \left[ \frac{1}{NO - NV} \sum_i w_i (F_{0i}^2 - F_{ci}^2)^2 \right]^{1/2} \quad (6)$$

where  $w = 1/\sigma^2$  and  $F_c$  is the calculated structure factor.  $NO$  is the number of observations while  $NV$  is the number of variables.

A difference Fourier synthesis revealed only little disorder. At the Ti(1) and Se(1) positions a small peak and a small hole appeared with peakheights less than 3% of the corresponding peaks in the Fourier synthesis. A further hole appeared at 0, 0, 0.25, and a peak at 1/3, 2/3, 0.5 with about the same peakheights.

The introduction of an isotropic extinction parameters reduced  $R_F$  to 0.018. No changes in the anisotropic thermal parameters larger than 5  $\sigma$  were observed.  $S$  decreased to 2.5.

It was further tried to improve the refinement by introducing additional Ti(=Ti(2)) at 0, 0, 0.25 and Se ( $\equiv$  Se(2)) at 1/3, 2/3, 0.5. A similar model has been proposed for Zr in nonstoichiometric zirconium diselenide (11) but with Zr atoms substituting Se atoms at 1/3,

TABLE III

FINAL ATOMIC COORDINATES FOR TiSe<sub>2</sub> WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES<sup>a</sup>

	Site	<i>pp</i>	<i>x</i>	<i>y</i>	<i>z</i>	
	Ti(1)	$\bar{3}m$	1.0	0.0(0)	0.0(0)	0.0(0)
	Se(1)	$3m$	1.0	1/3(0)	2/3(0)	0.25504(3)
	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Ti(1)	0.884(20)	0.884(26)	1.196(20)	0.442(10)	0.0(0)	0.0(0)
Se(1)	0.689(10)	0.689(10)	0.776(8)	0.344(5)	0.0(0)	0.0(0)

<sup>a</sup> The *U*<sub>*ij*</sub> (Å<sup>2</sup>) have been multiplied by 100. The expression for the temperature factor is:  $T = \exp [-2\pi^2(U_{11}h^2 a^2 + U_{22}k^2b^2 + \dots)]$ .

2/3, 0.25. Although this reduced *R*<sub>F</sub> to 0.013 and *S* to 1.7, the disorder type will have to be studied on a more imperfect crystal as a constrained model with *pp* Ti(1) = 1 - 0.5 *pp* Ti(2) refined equally well as a second model with *pp* Ti(1) = 1 - *pp* Ti(2) (*pp* ≡ population parameter). For both models *pp* Se(1) = 1 - *pp* Ti(2) was assumed. The second model implies unusually short Ti(1)-Ti(2) bondlength of 1.5 Å which is obviously not possible. The same applies to the zirconium diselenide structure, the refinement of which is currently in progress for the composition ZrSe<sub>1.9</sub>. Final *R* values for the TiSe<sub>2</sub> model are:

$$R_F = \frac{\sum_i |F_{0i} - |F_{ci}||}{\sum_i F_{0i}} = 0.018,$$

$$R_F^2 = \frac{\sum_i |F_{0i}^2 - |F_{ci}|^2|}{\sum_i F_{0i}^2} = 0.034,$$

*R*<sub>w</sub> (*F*<sup>2</sup>)

$$= \left[ \frac{\sum_i \sigma_i^{-2} |F_{0i}^2 - |F_{ci}|^2|}{\sum_i \sigma_i^{-2} F_{0i}^4} \right]^{1/2} = 0.049.$$

In Table III the atomic coordinates and thermal parameters are collected. Interatomic distances and bond angles are given in Table IV.

TABLE IV

INTERATOMIC DISTANCES (Å)  
AND BOND ANGLES (°)

Ti(1)-Se(1)	2.554 (1)
Se(1)-Se'(1)	3.583 (1) (Å)
Ti(1) Se(1) Ti'(1)	87.72 (3) (°)
Se(1) Ti(1) Se'(1)	85.60 (3) (°)

## Discussion

The crystal was stoichiometric according to chemical analysis. Neutron diffraction shows only a small amount of disorder which may be associated with interstitial atoms but which will have to be more thoroughly studied on a more imperfect crystal.

The thermal parameters of Ti(1) and Se(1) are very similar to those of TiS<sub>2</sub>(1). The high stability of the Ti atoms in their octahedral surrounding is furthermore exemplified by the fact that no phase transition was observed for neutron diffraction on TiSe<sub>2</sub> powder at 4.2°K (13). This shows that the larger octahedral cage in TiSe<sub>2</sub> does not produce a "rattling" of the Ti atom but that the bond character changes as described by Gamble (12).

Comparing the unit cell parameter for TiS<sub>2</sub>, TiSe<sub>2</sub>, and TiTe<sub>2</sub> (Table V) one finds a change of 6.7% for the *a*-axis, and 14.0% for the *c*-axis in going from the sulfide to the telluride (13). This reflects the change in octahedral distortion of the TiX<sub>6</sub> (*X* = S, Se, Te) octahedron which gets more flattened as the anion gets larger.

TABLE V

UNIT CELL DIMENSIONS OF TiS<sub>2</sub>, TiSe<sub>2</sub>, AND TiTe<sub>2</sub>

	TiS <sub>2</sub>	TiSe <sub>2</sub>	TiTe <sub>2</sub>
<i>a/b</i>	3.409(1)	3.540(1)	3.778(1) (Å)
<i>c</i>	5.694(1)	6.008(3)	6.493(1)
$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$			

### Acknowledgments

I thank S. Mason for his valuable help during the measurement, B. E. F. Fender for his interest and suggestions, J. D. N. Cheeke for this beautiful crystal specimen.

### References

1. C. RIEKEL AND R. SCHÖLLHORN, *Mat. Res. Bull.* **10**, 629 (1975).
2. W. G. STIRLING, B. DORNER, AND J. D. N. CHEEKE, *Solid State Comm.*, in press.
3. H. SCHÄFER, *Chemical Transport Reactions*, Academic Press, New York (1964).
4. M. S. LEHMANN AND F. K. LARSEN, *Acta Crystallogr.* **A30**, 580 (1974).
5. P. COPPENS, "Crystallographic Computing", pp. 255-270, F. R. Ahmed, Munksgaard, Copenhagen (1970).
6. G. E. BACON, "Neutron Diffraction", Oxford, Clarendon Press (1962).
7. J. M. STEWART, F. A. KUNDEL, AND J. C. BALDWIN, "The X-Ray System", Version 1970, Computer Science Center, Univ. of Maryland.
8. W. R. BUSING, *Acta Cryst.* **A27**, 683 (1971).
9. L. KOESTER AND K. KNOPF, unpublished.
10. A. J. JACOBSON AND B. E. F. FENDER, *J. Chem. Phys.* **52**, 4563 (1970).
11. A. GLEIZES AND Y. JEANNIN, *J. Solid State Chem.* **1**, 180-184 (1970).
12. F. R. GAMBLE, *J. Solid State Chem.* **9**, 358 (1974).
13. C. RIEKEL, unpublished.