SHORT COMMUNICATIONS

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Acta Cryst. (1977). B**33**, 2347–2348

Refinement of the crystal structure of $TiSi_2$ and some comments on bonding in $TiSi_2$ and related compounds.

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(*Received* 10 *February* 1977; *accepted* 26 *February* 1977)

The structure of $TiSi_2$ was refined from counter data to $R = 0{\cdot}035$ for 217 independent structure factors. Lattice constants are $a = 8{\cdot}2671$ (9), $b = 4{\cdot}8000$ (5), $c = 8{\cdot}5505$ (11) Å. None of the interatomic distances differ by more than 0·05 Å from the values of the determination by Laves & Wallbaum [*Z. Kristallogr.* (1939), **101**, 78–93]. A rigid band model accounts well for the electrical properties of the $TiSi_2$- and $CrSi_2$-type compounds and for the valence-electron rules governing the defect-$TiSi_2$ related structures.

The structure of $TiSi_2$ (Laves & Wallbaum, 1939) consists of close-packed hexagonal layers of composition $TiSi_2$, stacked on top of each other in such a way that Ti atoms of adjacent layers avoid close contact. Four such layers form a translation period (stacking sequence *ABCD*). In the $CrSi_2$- and $MoSi_2$-type structures, which are built up in a similar way, three or two layers, respectively, complete a translation period (stacking sequences *ABC* and *AB*). The occurrence of these three structure types is governed by valence-electron rules (Nowotny, 1963). Similar rules (Jeitschko & Parthé, 1967) were also found for the extended series of defect-$TiSi_2$ related structures (Nowotny, 1970), the first member of which, $Mn_{11}Si_{19}$, was described by Schwomma, Preisinger, Nowotny & Wittmann (1964). Because of the importance of the $TiSi_2$ structure for the understanding of these phases we refined it from single-crystal counter data.

A sample of $TiSi_2$ was prepared from the elemental components (purity >99·9%) by arc melting and subsequent rapid cooling. Single crystals, isolated from the crushed sample, were examined with Mo $K\alpha$ radiation in a precession camera. They showed the extinctions typical for space group *Fddd* plus the extinctions of the special point positions of the $TiSi_2$-type structure. Lattice constants were refined from Guinier–Hägg data with high-purity KCl ($a = 6{\cdot}2931$ Å) as standard: $a = 8{\cdot}2671$ (9), $b = 4{\cdot}8000$ (5), $c = 8{\cdot}5505$ (11) Å.

A small irregular crystal (50 × 70 × 80 μm) was used for collecting the intensities on a four-circle diffractometer (Zr-filtered Mo radiation, θ–2θ scans up to $2\theta = 90°$). To account for absorption the crystal shape was approximated to a sphere. The structure was refined by full-matrix least squares (Finger, 1969) with scattering factors for neutral atoms (Cromer & Mann, 1968) corrected for anomalous dispersion (Cromer & Liberman, 1970). Weights were assigned according to counting statistics. The final R is 0·035 for 217 structure amplitudes greater than three standard deviations. R is 0·069 for all 355 F values, including a large number of reflections which are absent because of the special point positions of the $TiSi_2$ structure. These reflections, which are allowed for models with anisotropic thermal parameters, were practically all too weak to be observed under the given experimental conditions.‡

The structure of $TiSi_2$ has only one adjustable positional parameter. From packing considerations, this parameter was assigned by Laves & Wallbaum (1939) the ideal value (transformed to the present setting) of $x = \frac{1}{8} + \frac{1}{3} = 0{\cdot}4583$, which is quite close to the value found in the present investigation (Table 1). Thus none of the interatomic

Table 1. *Atomic coordinates and thermal parameters for* $TiSi_2$

Thermal parameters (×10⁴) are of the form $\exp(-\Sigma\Sigma h_ih_jb_{ij})$. Equivalent isotropic B values (Å²) are also given.

	Ti	Si
Space group *Fddd**	8(*a*)	16(*e*)
x	$\frac{1}{8}$	0·4615 ± 0·0001
y	$\frac{1}{8}$	$\frac{1}{8}$
z	$\frac{1}{8}$	$\frac{1}{8}$
b_{11}	9 ± 1	21 ± 1
b_{22}	26 ± 2	54 ± 3
b_{33}	6 ± 1	12 ± 1
$b_{12} = b_{13}$	0	0
b_{23}	0	7 ± 2
B	0·23	0·48

* Setting with origin at center of symmetry.

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† Contribution No. 2468.

‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32537 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *in* $TiSi_2$

All distances shorter than 3·8 Å are given. Standard deviations are all less than 0·001 Å.

Ti–4Si	2·554	Si–2Ti	2·554
4Si	2·754	2Ti	2·754
2Si	2·782	1Ti	2·782
4Ti	3·206	2Si	2·533
		1Si	2·703
		2Si	2·794
		4Si	3·206

distances (Table 2) differ by more than 0·05 Å from the values of the original determination (multiplied by 1·002 to convert to the presently accepted Å unit), and most agree much better than that.

Bonding in compounds with $TiSi_2$-, $CrSi_2$-, and $MoSi_2$-type structures is not well understood. Both the transition-metal and the Si atoms have large coordination numbers of 10 or 14, depending on whether atoms at about 3·2 Å are counted as neighbors. Also the shortest Si–Si distances are considerably greater than the single-bond distance of 2·35 Å. Thus two-electron bonds, a dominant feature of many transition-metal diphosphides (Jeitschko & Donohue, 1973), can certainly be excluded in these disilicides.

While $CrSi_2$ is semiconducting (Nishida, 1972, and references therein), VSi_2 (with the $CrSi_2$-type structure) and $TiSi_2$ have metallic conductivity (Robins, 1958). The relative arrangement of the near-neighbors up to 4 Å is the same for the $CrSi_2$- and $TiSi_2$-type structures (for instance for an atom in a layer *B* the near-neighbors are the same in stacking sequences *ABC* and *ABCD*). Exact interatomic distances for $CrSi_2$ are not known. The structure was determined from powder data (Borén, 1933) and the only adjustable parameter was obtained from packing considerations. However, the structure of $NbSi_2$ ($CrSi_2$ type) was recently refined (Kubiak, Horyń, Broda & Łukaszewicz, 1972). In this structure all near-neighbor distances agree well with the corresponding ones in $TiSi_2$.

The great similarity of near-neighbor environments in the $TiSi_2$- and $CrSi_2$-type compounds suggests similar band structures. Since $CrSi_2$ is semiconducting, it has no partially filled bands, *i.e.* 14 valence electrons per formula unit are needed for band filling. In the metallic conductors $TiSi_2$ and VSi_2, with 12 and 13 valence electrons per formula unit, the top band apparently is only partially filled. On the other hand, the $TiSi_2$-type compounds $RuAl_2$ (Schwomma, Nowotny & Wittmann, 1963) and $RuGa_2$ (Jeitschko, Holleck, Nowotny & Benesovsky, 1963) should be semiconductors or semimetals, since they, like $CrSi_2$, have 14 valence electrons per formula unit. Recent results (Chen, 1975) show that $RuAl_2$ is indeed semiconducting. Thus a rigid band model seems to account well for the conducting properties of the closely related $TiSi_2$- and $CrSi_2$-type compounds.

In the defect-$TiSi_2$ related structures, also called Nowotny chimney ladder structures (Pearson, 1970), the composition is controlled by valence-electron concentrations in such a way that the number of valence electrons per transition-metal site (*i.e.* $TiSi_2$-like subcell) practically never exceeds the 'magic' number 14 (Jeitschko & Parthé, 1967); the same number is associated with semiconductivity in $CrSi_2$ and $RuAl_2$. This suggests that the band structures of the Nowotny chimney ladder structures are similar to those of the $TiSi_2$- and $CrSi_2$-type compounds, and that additional valence electrons per *T* site would need to be accommodated in destabilizing bands. Since the building principle of these phases allows for a variation of the composition, the most stable composition is adjusted in such a way that no valence electrons have to be accommodated in these destabilizing (antibonding) bonds. The exact level ordering of the band structure remains of course to be determined.

I am indebted to Dr H.-Y. Chen for the sample of $TiSi_2$ and to Mr E. P. Moore for help with the crystallographic work.

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