Structure Refinement of Ti_5Sb_3 from Single-crystal Data

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In a previous paper, crystallographic data on new arsenides and antimonides of titanium and scandium were presented.[1] It was claimed that the β-Yb_5Sb_3 structure type [2] is represented in the Sc-Sb, Ti-Sb, Ti-As and probably also in the Ti-P systems. The author was then unaware of the work by Steinmetz *et al.*,[3] who, on the basis of powder diffraction data, showed that Ti_5Sb_3 crystallizes with this structure. The present report confirms their findings, but their positional parameters, which were derived from less extensive data, have had to be revised in the light of the single-crystal data.

Experimental. Titanium (Koch-Light Laboratories Ltd., 99.95 %) and antimony (Johnson Matthey Chemicals Ltd., 99.9999 %) were reacted by arc-melting to give a single phase sample.[1] A single crystal fragment was picked from the debris of the crushed alloy for the X-ray intensity measurement.

A Stoe-Philips four-circle diffractometer was used for collecting the data, the $\omega-2\theta$ step scan technique being employed. The reflexions were measured within the intervals $0\leq h\leq 15$, $-9\leq k\leq 12$ and $-8\leq l\leq 10$, corresponding to an upper angular limit of $2\theta=66°$. Three test reflexions were monitored at regular intervals to check the stability. The measurement also included those reflexions systematically absent according to the *Pnma* space-group assignment. The intensities of these reflexions never exceeded two standard deviations, which supports the proposal of *Pnma* symmetry [1,3] and contradicts the suggestion by Kjekshus *et al.*[4]

The crystal used for the data collection was rather small and of an irregular shape. In the course of examination by scanning electron microscopy for obtaining a good geometrical description of it, the crystal was unfortunately lost. Accordingly, no appropriate correction for absorption could be performed. In view of the small size of the crystal – maximum cross section 50 μm – together with a linear absorption coefficient of 192 cm^{-1}, the general effects of neglecting this correction are small. Nevertheless, systematic errors occur, since – owing to the irregular shape of the crystal – some groups of reflexions are likely to be more affected than the average. After the systematically absent reflexions had been rejected, the intensities were averaged and corrected for Lp effects. A series of structure refinements was started, using a full-matrix least-squares method. Space-group symmetry *Pnma* was assumed, supported by a zero moment plot. The positional parameters of β-Yb_5Sb_3 were adopted as starting values for the coordinates. The initial refinement involved 1 scale factor, 14 positional parameters and 6 isotropic temperature factors. The atomic scattering factors [5] were corrected for anomalous dispersion.[6]

The quantity minimized was $\sum w(|F_o^n|-|F_c^n|)^2$ with $n=1$ or $n=2$ for refinement on F and F^2, respectively. The agreement indices found in the text are defined as:

$$R(F^n)=\sum||F_o^n|-|F_c^n||/\sum|F_o^n|$$

and $R_w(F^n)=[\sum w(|F_o^n|-|F_c^n|)^2/\sum w|F_o^n|^2]^{\frac{1}{2}}$; $n=1, 2$.

Here, w denotes the individual weight of each reflexion and is defined by the expression:

$$w^{-1}=\sigma_c^2+(p|F_o^n|)^2.$$

σ_c is the standard deviation of F^n based on counting statistics, while the other term modifies the weight to account for other errors. The value of p was selected to give an even weighting scheme.

The first refinement – on F, to suppress divergence – yielded higher temperature factors than expected. Another disturbing feature was that F_o was consistently lower than F_c for the low-angle reflexions where k was odd. Since the 8*d* atoms give only small contributions to these reflexions when $y\sim 0$, it was considered likely that the effects could be accounted for by thermal anisotropy if the electron density is very different in the *b* direction as compared with that in the *ac* plane. However, the introduction of anisotropic thermal parameters did not create any considerable drop in the R-value.

Another attempt was then made at refining the occupancy of the atoms with the highest temperature factors, the 8*d* titanium and the 4*c* antimony, respectively. The occupancy of the antimony was refined to 92 %, causing a small drop in the R-value. The actual values of the occupancy and the anisotropic thermal parameters probably reflect systematical errors to a great extent. The abnormally high temperature factors as well as the disturbing k-index dependence remained. It is possible that the observed errors are due to the neglect of an absorption correction or to some kind of disorder in the crystal.

The refinement on F cannot cover reflexions with randomly occurring negative values for the intensities, and hence the data tend to be somewhat biased as compared with an F^2 refinement.[7,8] The final refinement on F^2, including all the reflexions, gave the R-values (1205 refl.):

$$R(F^2)=0.087,\ R_w(F^2)=0.12 \text{ and } R(F)=0.088.$$

A ΔR plot gave a fairly straight line for the ranked deviates in the range ± 2 around the

mean. It had a slope of 0.67 and an intercept of −0.03.

The positional parameters were not especially sensitive to the different modes of refinement and are presented in Table 1. The cell dimensions were determined from powder photographs.[1]

Table 1. Crystallographic data of Ti_5Sb_3. Cell dimensions: $a = 10.2173(5)$ Å, $b = 8.3281(5)$ Å, $c = 7.1459(4)$ Å. Space group *Pnma* (No. 62), $Z = 4$.

Atom	Position	*x*	*y*	*z*
Ti(1)	8*d*	0.05705(20)	0.05823(27)	0.20174(28)
Ti(2)	4*c*	0.23539(26)	1/4	0.81717(39)
Ti(3)	4*c*	0.28158(29)	1/4	0.33160(40)
Ti(4)	4*c*	0.00533(23)	1/4	0.52152(38)
Sb(1)	8*d*	0.32279(7)	0.49075(8)	0.06612(9)
Sb(2)	4*c*	0.47625(11)	1/4	0.58965(15)

Table 2. Interatomic distances in Ti_5Sb_3 less than 3.8 Å.

Ti(1)−Sb(2)	2.710(2)		
Sb(2)	2.751(2)	Ti(4)−Sb(2)	2.794(3)
Ti(4)	2.838(3)	2Sb(1)	2.801(2)
Sb(1)	2.912(2)	2Sb(1)	2.809(2)
Sb(1)	2.933(2)	2Ti(1)	2.838(3)
Sb(1)	2.941(2)	Ti(2)	2.989(4)
Ti(3)	2.945(3)	Ti(3)	3.132(4)
Ti(1)	3.194(5)	Ti(2)	3.160(4)
Ti(3)	3.245(3)	2Ti(1)	3.302(3)
Ti(1)	3.258(4)	Ti(3)	3.405(4)
Ti(4)	3.302(3)		
Ti(2)	3.430(3)		
Ti(2)	3.664(4)	Sb(1)−Ti(3)	2.792(2)
		Ti(4)	2.801(2)
Ti(2)−Sb(2)	2.730(3)	Ti(4)	2.809(2)
2Sb(1)	2.825(2)	Ti(2)	2.825(2)
2Sb(1)	2.869(2)	Ti(2)	2.869(2)
Sb(2)	2.949(3)	Ti(1)	2.912(2)
Ti(4)	2.989(4)	Ti(1)	2.933(2)
Ti(4)	3.160(4)	Ti(3)	2.934(2)
2Ti(1)	3.430(3)	Ti(1)	2.941(2)
Ti(3)	3.502(4)	Sb(2)	3.745(1)
2Ti(1)	3.664(3)	Sb(1)	3.746(1)
Ti(3)	3.706(4)		
Ti(3)−Sb(2)	2.712(3)	Sb(2)−2Ti(1)	2.710(2)
2Sb(1)	2.792(2)	Ti(3)	2.712(3)
2Sb(1)	2.934(2)	Ti(2)	2.730(3)
2Ti(1)	2.945(3)	2Ti(1)	2.751(2)
Ti(4)	3.132(4)	Ti(4)	2.794(3)
2Ti(1)	3.245(3)	Ti(2)	2.949(3)
Ti(4)	3.405(4)	2Sb(1)	3.745(1)
Ti(2)	3.502(4)		
Ti(2)	3.706(4)		

Result and discussion. The single-crystal refinement confirms that Ti_5Sb_3 belongs to the β-Yb_5Sb_3 structure type. The positional parameters of Table 1 differ from those reported by Steinmetz *et al.*,[3] and are much more accurate. Owing to the systematical errors encountered in the refinements, the individual thermal parameters are not very reliable and are therefore not presented.

From Table 2, where the interatomic distances are given, it emerges that the 4*c* antimony tends to be surrounded by eight neighbours, while the 8*d* antimony clearly coordinates nine metal atoms. The former arrangement is that of a slightly distorted bisdisphenoid (dodecahedron), and the latter can be described as a triangular prism with one additional atom outside each rectangular face of the prism (tetrakaidecahedron). The coordination of the metal atoms around the non-metal is thus somewhat different from the situation in the isostructural compounds β-Yb_5Sb_3,[2] Ca_5Sb_3,[9] and Ca_5Bi_3.[10] In these compounds, the coordination number is seven for the 4*c* non-metal atom and eight or seven for the 8*d*. It would be very interesting to compare the coordination numbers within the series Ti_5As_3,[1] γ-V_5As_3 [11] and Cr_5As_3,[11] but no data are yet available for any of these compounds. The situation in Yb_5Bi_3 [12] is probably similar to that in β-Yb_5Sb_3.

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