

# X-Ray Powder Profile Refinement of the Structure of Pseudo-tetragonal Sc<sub>3</sub>As<sub>2</sub>

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Phase-analytical work on the Sc-As system<sup>1,2</sup> has revealed the occurrence of ScAs, Sc<sub>5</sub>As<sub>3</sub>, Sc<sub>2,3</sub>As and two polymorphs of the approximate composition Sc<sub>3</sub>As<sub>2</sub>. X-Ray single-crystal diffraction data are so far available only for Sc<sub>2,3</sub>As (Sc<sub>7</sub>As<sub>3</sub>), the structure of which has recently been solved.<sup>3</sup> The structure types of the others have been determined on the basis of X-ray powder-film data.

In a previous paper,<sup>1</sup> it was reported that the diffractogram of one polymorph of Sc<sub>3</sub>As<sub>2</sub> could be indexed to a high degree of precision with a tetragonal cell. However, evidence was later presented to show that the symmetry is in fact orthorhombic.<sup>2</sup> The compound is isostructural with Hf<sub>3</sub>P<sub>2</sub>,<sup>4</sup> and the *a* and *c* axes are equal to within 0.02%. This paper presents the results of a refinement of the structural parameters using X-ray powder-profile data from Hagg-Guinier films.

*Powder profile refinement.* The net effect of the pseudo-tetragonality is that all reflexions on a powder diffractogram suffer from overlap, except those of the forms *hk0*, *0kl* and *hkh*. There are too few of these, however, to facilitate a satisfactory refinement of the orthorhombic axes<sup>2</sup> or to form the basis for a structure refinement. Since no single crystal was available, it was considered worthwhile to apply the powder-profile refinement technique, where the contributions of the individual reflexions to the observed overlapped intensity material could be taken into account. Moreover, a recent modification<sup>5</sup> of the Rietveld full-profile analysis provides the possibility to include a second phase in the refinement.

The specimen contained Sc<sub>3</sub>As<sub>2</sub> and ScAs together with traces of Sc<sub>2</sub>O<sub>3</sub> and Sc<sub>5</sub>As<sub>3</sub>. Since the profile refinement program permitted simultaneous refinement of only two phases, regions of the film containing lines from Sc<sub>2</sub>O<sub>3</sub> and Sc<sub>5</sub>As<sub>3</sub> were omitted from the subsequent refinement. The equipment for recording the powder profiles has been described earlier.<sup>6</sup>

CuKα<sub>1</sub> radiation was used, and the diffracted intensity was filtered through aluminium foil to reduce the fluorescence background. A correction for the absorption in the foil was applied to the intensity data.

The following parameters were refined: an overall scale factor, an overall "occupancy factor", *θ*-zero-point, individual temperature factors (5 for Sc<sub>3</sub>As<sub>2</sub> and 2 for ScAs), half-width parameters (3 for each phase), asymmetry parameters (1 for each phase), cell constants (3 for Sc<sub>3</sub>As<sub>2</sub> and 1 for ScAs) and positional parameters (10 for Sc<sub>3</sub>As<sub>2</sub>).

The refinement converged to the following R-values:

$$R_p = \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum_i y_i(\text{obs})} = 0.217$$

$$R_{wp} = \left\{ \frac{\sum w_i [y_i(\text{obs}) - y_i(\text{calc})]^2}{\sum w_i y_i^2(\text{obs})} \right\}^{1/2} = 0.300$$

$$R_I = \frac{\sum_k |I_k(\text{obs}) - I_k(\text{calc})|}{\sum_k I_k(\text{obs})} = 0.180$$

$$R_F = \frac{\sum_k \left| \sqrt{I_k(\text{obs})} - \sqrt{I_k(\text{calc})} \right|}{\sum_k \sqrt{I_k(\text{obs})}} = 0.118$$

For details of the refinement procedure and the definitions of the symbols used above, see Refs. 5 and 6.

The positional parameters of Sc<sub>3</sub>As<sub>2</sub> are presented in Table 1. The approximate character of the absorption correction makes the thermal vibration parameter values obtained very uncertain; therefore, these are not included in the table. A list of interatomic distances is given in Table 2.

*Results and discussion.* Despite the extensive overlap among the reflexions, the profile refinement converged satisfactorily and clearly confirmed the idea that the pseudo-tetragonal Sc<sub>3</sub>As<sub>2</sub> is isostructural with Hf<sub>3</sub>P<sub>2</sub>. Other representatives of this structure type are Hf<sub>3</sub>As<sub>2</sub>,<sup>7</sup> Zr<sub>3</sub>As<sub>2</sub><sup>8</sup> and Sc<sub>3</sub>P<sub>2</sub>.<sup>2</sup> The general structural features of the type have been described previously and need not be discussed again in this context. However, some additional comments based on structural comparisons may be given.

Table 1. Structure data for Sc<sub>3</sub>As<sub>2</sub> (Hf<sub>3</sub>P<sub>2</sub> type). Space group: *Pnma* (No. 62), *a* = 10.3754(3) Å, *b* = 3.8063(2) Å, *c* = 10.3754(3) Å (Ref. 2). All atoms in 4(c) positions. Standard deviations are given in parentheses.

Atom	Positional parameters ( <i>y</i> = 1/4)	
	<i>x</i>	<i>z</i>
Sc(1)	0.0489(11)	0.1304(12)
Sc(2)	0.3742(11)	0.0646(12)
Sc(3)	0.2224(10)	0.7935(9)
As(1)	0.3167(6)	0.4938(6)
As(2)	0.4877(6)	0.8224(7)

Table 2. Interatomic distances (Å) and coordination in  $\text{Sc}_3\text{As}_2$ . Distances shorter than 4.0 Å are listed. Standard deviations in parentheses.

Sc(1)–As(1) 2.732(13)	As(1)–Sc(1) 2.732(13)
–2As(1) 2.752(10)	–2Sc(1) 2.752(10)
–2As(2) 2.781(10)	–2Sc(2) 2.844(10)
–Sc(2) 3.444(16)	–2Sc(3) 2.847(8)
–2Sc(1) 3.460(21)	–Sc(3) 3.259(11)
–2Sc(3) 3.481(13)	–2As(1) 3.806(0)
–2Sc(3) 3.489(13)	–As(2) 3.843(9)
–Sc(2) 3.646(17)	–As(2) 3.910(9)
–2Sc(1) 3.806(0)	As(2)–2Sc(2) 2.655(9)
–Sc(3) 3.931(16)	–Sc(3) 2.716(12)
Sc(2)–2As(2) 2.655(9)	–Sc(3) 2.769(12)
–As(2) 2.775(14)	–Sc(2) 2.775(14)
–2As(1) 2.844(10)	–2Sc(1) 2.781(10)
–2Sc(3) 3.204(13)	–2As(2) 3.806(0)
–Sc(3) 3.223(16)	–As(1) 3.843(9)
–Sc(1) 3.444(16)	–As(1) 3.910(9)
–2Sc(2) 3.498(20)	
–Sc(1) 3.646(17)	
–2Sc(2) 3.806(0)	
Sc(3)–As(2) 2.716(12)	
–As(2) 2.769(12)	
–2As(1) 2.847(8)	
–2Sc(2) 3.204(13)	
–Sc(2) 3.223(16)	
–As(1) 3.259(11)	
–2Sc(1) 3.481(13)	
–2Sc(1) 3.489(13)	
–2Sc(3) 3.806(0)	
–Sc(1) 3.931(16)	

A histogram analysis<sup>9</sup> of the interatomic distances reveals that the two arsenic atoms in  $\text{Sc}_3\text{As}_2$  both coordinate seven metal atoms, but As(1) has an eighth metal neighbour 15% further away. The weighted averages of the seven Sc–As distances are 2.80 and 2.73 Å for As(1) and As(2), respectively. These values lie close to the sum of the CN 12 Goldschmidt metal radius of scandium (1.60 Å) and the tetrahedral covalent radius of arsenic (1.18 Å). The distribution of Hf–P distances in  $\text{Hf}_3\text{P}_2$  shows similar features. The shortest Sc–Sc distance corresponds to a normal metal–metal contact.

For the transition-element arsenides and phosphides of the general composition  $\text{Me}_3\text{X}_2$  (Me = metal, X = P, As) three structure types have been reported, namely  $\text{Hf}_3\text{P}_2$ ,  $\text{Cr}_3\text{C}_2$ <sup>10</sup> and  $\text{V}_3\text{As}_2$ .<sup>11</sup> Lundström suggested<sup>4</sup> that the  $\text{Cr}_3\text{C}_2$  type has a tendency towards lower coordination about the X atom than the  $\text{Hf}_3\text{P}_2$  type. He also alluded to spatial considerations so as to indicate that the

$\text{Cr}_3\text{C}_2$  might occur for smaller  $r_X/r_{\text{Me}}$  radius ratios than the  $\text{Hf}_3\text{P}_2$  type. Similar ideas, although in a slightly different context, were brought forward by Brink Shoemaker.<sup>12</sup> However, the two types of structures co-exist in the Sc–P and Sc–As systems,<sup>2</sup> and it is likely that phosphorus and arsenic can accommodate more metal neighbours than can carbon in  $\text{Cr}_3\text{C}_2$ . The radius ratio between carbon and chromium (0.60) lies close to the “ideal” value of 0.53, when all metal atoms of a regular trigonal prism form metal contacts. The central non-metal atom can achieve a higher coordination number only if the Me–Me distances increase. For larger radius ratios ( $r_P/r_{\text{Sc}}=0.69$  and  $r_{\text{As}}/r_{\text{Sc}}=0.74$ ), the triangular prism structure becomes more “open”, allowing extra atoms outside the quadrilateral prism faces to coordinate the central atom. In  $\text{V}_3\text{As}_2$ ,<sup>11</sup> with  $r_{\text{As}}/r_{\text{V}}=0.87$ , pronounced seven- and eight-coordinations occur.

Contrary to spatial expectations, the tendency for pure seven-coordination in the isostructural  $\text{Sc}_3\text{As}_2$  and  $\text{Hf}_3\text{P}_2$  is slightly greater for the compound with the larger  $r_X/r_{\text{Me}}$  radius ratio. This is clearly indicated in the histogrammic representation.

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