

## Short Communications

### New Metal-rich Phases in the Scandium – Phosphorus System

ROLF BERGER \*

Institute of Chemistry, University of Uppsala,  
Box 531, S-751 21 Uppsala, Sweden

An introductory phase-analytical study by means of X-ray powder diffraction of the metal-rich part of the Sc – P system has been performed, some results of which have already been published.<sup>1</sup> Silica-tube syntheses in similar systems often yield inhomogeneous products, and a repetitive technique of grinding, compacting and annealing must be used in order to promote homogenization. In some cases, as in the Ti – P system, the most metal-rich phases do not form at all owing to kinetic hindrance by another phosphide occurring as a superficial layer on the metal grains. However,  $Ti_3P$  could be obtained by arc-melting the inhomogeneous phosphide – metal products followed by annealing.<sup>2</sup> Moreover, heat-treatment of scandium compounds in a silica tube may lead to the formation of elemental silicon accompanied by  $Sc_2O_3$ , as observed for  $Sc_5Ga_3$  (at 1200 °C)<sup>3</sup> and for scandium arsenides (at 900 °C in the presence of

iodine).<sup>4</sup> Therefore, the synthetic method of arc-melting ScP together with scandium was adopted, optionally followed by silica-tube heat-treatment. Two orthorhombic modifications of  $Sc_3P_2$  were synthesized in this manner.<sup>1</sup> The method failed to give good results for the more metal-rich compositions, partly owing to unfavourable formation conditions of the intermediate phases, and partly owing to uncontrollable losses of phosphorus in the process. As a consequence, it was nevertheless decided to try the silica-tube method. Two new scandium phosphides could be characterized, the crystallographic data of which are presented in Table 1.

*Experimental details.* The X-ray equipment and methods of phases analysis have been described in a earlier report.<sup>1</sup>

One specimen of 70 at% scandium was prepared by compacting a mixture of scandium filings and ScP (performed in silica tube) and heat-treating it in a silica tube. After one week at 950 °C the specimen gave a very complex powder pattern. It was obviously far from equilibrium; the already known phases ScP,  $Sc_3P_2$  ( $Cr_3C_2$  type) and Sc (possibly with dissolved phosphorus) were identified, but the multitude of lines left over indicated the presence of at least one unknown intermediate phase. The specimen was ground and recompact and was treated for another week at the same temperature. The resulting powder photograph showed marked changes. The ScP and Sc phases had disappeared, indicating a step further towards equilibrium. The  $Sc_3P_2$  lines had become weak, but all the more

\* Present address: Laboratory of Inorganic Chemistry, University of Groningen, Nijenborgh 16, NL-9747 AG Groningen, The Netherlands.

Table 1. Crystallographic data of phases characterized in the present study (further details may be obtained from the author). Cell dimensions in Å units with standard deviations in parentheses. Silicon was used as internal standard.

Phase	Space group	Structure type	Cell dimensions	No. of reflexions in the refinement
$Sc_7P_3$	$P6_3mc$	$Ru_7B_3$	$a = 8.9340(2)$ $c = 5.7349(2)$	48
$Sc_3P$	$Pnma$	$Fe_3C$	$a = 6.7540(5)$ $b = 8.4449(5)$ $c = 5.7662(3)$	54

important for the interpretation, the relative intensities of the rest had changed so that two distinct sets of lines could be discerned. Each one of these, in the form of  $\sin^2 \theta$  values, were fed into the TREOR indexing program<sup>5</sup> (version 2; as modified by L.-E. Tergenius at this Institute) which provided a highly probable solution in each case.

The phase dominating the specimen after the repeated homogenization treatments was assigned a hexagonal cell, the powder pattern of which had already been tentatively interpreted from metal-rich arc-melted alloys, although with lines of extremely bad quality.<sup>1</sup> The weaker set of lines – also found in arc-melt powder patterns – was ascribed to a primitive orthorhombic cell. Taking the average atomic volumes into consideration, it was deduced that the hexagonal cell should contain 20–21 and the orthorhombic cell 16–17 atoms. A search in Structure Reports<sup>6</sup> using the appropriate Pearson symbols<sup>7</sup> suggested that the new Sc–P phases ought to be isostructural with  $\text{Ru}_7\text{B}_3$ <sup>8</sup> (*hP*20) and  $\text{Fe}_3\text{C}$ <sup>9</sup> (*oP*16), respectively. Indeed, another similar synthesis at 75 at% scandium gave the cementite type phosphide as the predominant phase present in the sample. Not even after another week's heat-treatment, now at 1050 °C, were the specimens homogeneous single phase. On the contrary, the prolonged heating and grinding procedures without any special precautions introduced  $\text{Sc}_2\text{O}_3$  as a contaminant. The Sc–P specimens, bar ScP, are fairly sensitive to atmospheric moisture and decompose.

$\text{Sc}_3\text{P}_3$ . The structure proposal was checked by an intensity calculation which gave an excellent agreement with the observed powder pattern intensities. The positional parameters of  $\text{Ru}_7\text{B}_3$  as given by Aronsson<sup>8</sup> were used. They give, however, rather short Sc–P distances, and more reasonable ones may be obtained if the coordinates are somewhat altered. The true situation might correspond to an increase in coordination number as compared to  $\text{Ru}_7\text{B}_3$  from six to eight. The coordination geometry about the non-metal atom is essentially trigonal prismatic (see Ref. 8 for details).

$\text{Sc}_3\text{P}$ . An intensity calculation using the  $\text{Fe}_3\text{C}$  positional parameters<sup>9</sup> left no doubt as to the correct assignment of structure. The known representatives of this structure type allow a range of positional parameters wide enough to make it difficult to optimize the parameter values to give reasonable interatomic distances without a proper structural refinement. The  $\text{Fe}_3\text{C}$  parameters yield Sc–P distances some 5% shorter than the radius sum of 2.70 Å and Sc–Sc distances of the magnitude of 3.20 Å. Also in this structure the scandium–phosphorus interactions conform to a trigonal–prismatic coordination description with a coordination number of six or eight.

*Discussion.* It must be emphasized that the results were not obtained under equilibrium conditions. It is likely, however, that the new phases synthesized do belong to the stable binary system.

As can be inferred from the previous report<sup>1</sup> the Sc–P and Sc–As systems have structure representatives in common, a working hypothesis which led to the unravelling of the pseudo-tetragonal  $\text{Sc}_3\text{As}_2$  structure.<sup>10</sup> The direct structural correspondence fails for the most metal-rich compositions. This difference between the two scandium systems might partly reflect the effect of the radius ratio; the  $r_{\text{P}}/r_{\text{Sc}}$  ratio of 0.69 is small enough to favour structure types with relatively low coordination numbers otherwise adopted by transition-metal carbides and borides. Anti-types where a rare earth enters the non-metal sites are known for  $\text{Cr}_3\text{C}_2$  and  $\text{Hf}_3\text{P}_2$  (sulfides) and for  $\text{Fe}_3\text{C}$  (fluorides) illustrating the importance of the relative atomic sizes. The  $\text{Ru}_7\text{B}_3$  and  $\text{Fe}_3\text{C}$  types are also known for rare-earth intermetallics where a Group VIII metal enters the non-metal sites. Since no detailed structural data are available for any one of the new phases, a strict analysis of the coordination is impossible. However, as suggested above, phosphorus may in  $\text{Sc}_7\text{P}_3$  coordinate six (less likely eight) scandium atoms to be compared with the tetragonal  $\text{Sc}_7\text{As}_3$  where the two arsenic atoms have 8 (bisdisphenoid) and 7+2 (trigonal prism) near neighbours, respectively.<sup>11</sup>

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