Crystallographic Data on New Scandium Arsenides and Phosphides

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In a previous paper some preliminary data were given on the phase occurrence in the Sc–As system.[1] As the result of further synthetic and phase-analytical work, previous data have now been partly revised and two new phases have been characterized. Some preliminary results from a survey of the Sc–P system are also given.

Methods of characterization. The phase analyses were based on X-ray powder diffraction using Guinier-Hägg cameras, the radiation being Cu$K\alpha_1$. An aluminium filter reduced the background due to fluorescence. The primary calibration standards were silicon ($a = 5.431065$ Å)[2] or germanium ($a = 5.657906$ Å).[3] In some cases where either of these substances would cause overlap, phases already present in the sample, such as ScAs ($a = 5.4640$ Å)[1] or ScP ($a = 5.3088$ Å),[4] served the same purpose. These latter secondary standards cannot compete with silicon or germanium in accuracy, and the cell dimensions obtained may therefore be affected by minor systematic errors.

None of the compounds in the investigated systems were obtained as a single phase and no chemical analyses were therefore performed. In order to establish probable approximate compositions, the concept of average atomic volumes was used for estimating the number of atoms in the unit cell. The structure type was then deduced from space-group assignments and comparison with similar chemical systems.

The Sc–P system. The phase occurrence in this system has previously not been known, except for ScP.[4,5] A cursory survey was made by Zachrisson.[6] Some of the scandium phosphides are very sensitive to moisture and give off fumes of phosphine with the simultaneous formation of Sc_2O_3. These alloys remain undecomposed for a long period when stored in a desiccator.

Many of the alloy samples showed diffuse X-ray patterns. This fact, and the presence of interfering oxide lines, made the phase analysis difficult. Moreover, the exact composition of a phase could not be determined from the nominal composition owing to the reactions with air.

In this investigation of the Sc–P system, two new compounds have been identified. They seem to to be of approximately equal composition, since their unit-cell volumes differ by less than 1 %, as inferred from Table 1. They were both indexed on orthorhombic cells of a magnitude corresponding to 20 atoms.

A single crystal of poor quality of one of the compounds was found and it showed systematic absences for (*hk*0) and (0*kl*) reflexions in concordance with the space groups *Pnma* or $Pn2_1a$. From this observation, combined with the estimated cell content and the axial ratios, it appeared probable that the compound is of the Cr_3C_2 type,[7] and thus an anti-type to Gd_2S_3.[8] No intensity data were collected from the crystal, but powder intensity calculations using the positional parameters of Cr_3C_2 showed an extremely good fit with the observations.

The other compound of similar composition was obtained as the main product besides scandium when a partly decomposed alloy of *nominal* composition $Sc_{0.67}P_{0.33}$ had been treated in a silica tube for two days at 1000 °C. Scandium oxide was also present. The cell parameters and cell content suggested that this phosphide is of the Hf_3P_2 structure type.[9] No single-crystal data were available in this case, but powder intensity calculations using Hf_3P_2 parameters agreed very well with the observed data.

The Cr_3C_2 and Hf_3P_2 structures contain similar building blocks, arranged in different ways, as pointed out by Lundström[9] and discussed by Brink-Shoemaker.[10] The interatomic distances calculated for the two scandium phosphides are quite reasonable. with Sc–P distances of the order of 2.7 Å and Sc–Sc distances longer than 3.1 Å, the positional parameters of the parent structure-type compounds being used.

In some metal-rich alloys, extra lines were found which could be indexed on a hexagonal cell ($a = 8.921$ Å, $c = 5.732$ Å). The corresponding compound has not been identified, but the cell volume suggests a content of 20 atoms.

The Sc–As system. By a reaction of the elements in the atomic ratio 3:2 in a silica tube at 1000 °C, a phase mixture was obtained which partly contained ScAs. Except for a handful of very weak lines, the remaining ones were indexed on an orthorhombic cell, the content of which corresponded to 20 atoms. Powder intensity calculations showed that another representative of the Cr_3C_2 structure type had been obtained.

A tetragonal phase of approximately the same composition, prepared by arc-melting ScAs, was previously reported.[1] The similarity in unit cell dimensions to those of V_3As_2[11] had suggested that these two compounds were isostructural. This preliminary hypothesis must now be discarded due to new evidence.

0302-4377/80/030231-03$02.50

The fact that two structure types for Sc_3P_2 had been found, one of which was also represented in the Sc–As system, and that phosphide and arsenide systems of the transition metals are often very similar in phase occurrence, led to the idea that the previously reported Sc_3As_2 was in fact pseudo-tetragonal. Indeed, powder intensity calculations, based on positional parameters from the orthorhombic Hf_3P_2 prototype, gave an excellent fit with the experimental data.

The previous mistake in the powder indexing is quite understandable, since the *a*- and *c*-axes must be equal within 0.02 %.

Due to the extensive overlap, it is very difficult to perform a proper cell-parameter refinement from powder-film data. Even at the high-angle limit of the Guinier film, the line splitting is only of the order of 0.01 mm. Non-overlapped reflexions of the types (*hk*0), (0*kl*) and (*hkh*) for the *Pnma* setting provide very limited data, and the numerical results of refinements based on this material are critically affected by the individual weights assigned to the reflexions. Accordingly, only the results of a pseudo-tetragonal refinement of the cell parameters are reported in Table 1.

The second new phase in the Sc–As system was obtained, together with ScAs and the pseudo-tetragonal Sc_3As_2, when the elements in the atomic ratio 5:3 had been brought to react in a silica-tube synthesis. Its powder lines were indexed on an orthorhombic cell of dimensions corresponding to a content of ~30 atoms. The new phase, isostructural with Yb_5Sb_3,[12] explains the additional weak lines mentioned above. Sc_5As_3 has also been found together with $Sc_{2.3}As$.[1]

The survey[13] of phases of the Yb_5Sb_3 type can now be supplemented with Sc_5As_3 and Sr_5Bi_3.[14] Intensity calculations showed that the positional parameters of Sc_5As_3 lie close to those of Ca_5Sb_3,[15] for example, rather than of Ti_5Sb_3.[16] These two latter phases represent different coordination numbers, as demonstrated by a histographic analysis and indicated by the unit-cell axis ratio b/a.[13,17]

The compound designated by the formula $Sc_{2.3}As$, found by Rundqvist and Nyarko (quoted in Ref, 1), was reproduced by arc-melting ScAs together with scandium, followed by heat-treating in an induction furnace at approximately 1200 °C to improve the powder-line quality. The refined cell parameters are in excellent agreement with the previous values. However, the preliminary space-group assignment must be revised to *I*4/*mcm* according to single-crystal data.[13]

Acknowledgements. The author wishes to thank Professor Stig Rundqvist for his interest in this investigation and Dr. Folke Zachrisson for the use of his Sc–P specimens. Parts of this study were performed at the Department of Inorganic Chemistry, University of Groningen, The Netherlands, where Professor Frans Jellinek kindly put the requisite facilities at the author's disposal. Grants

Table 1. Crystallographic data of phases characterized in the present study. Cell dimensions in Å units with standard deviations in parentheses.

Approximate composition	Space group	Structure type	Cell dimensions	Internal standard	No. of refined reflexions
Sc_5As_3	*Pnma*	Yb_5Sb_3	$a=10.7038(4)$ $b=8.1418(3)$ $c=7.2272(3)$	ScAs	75
Sc_3As_2	*Pnma*[a]	Hf_3P_2[a]	$a=c=10.3754(3)$[b] $b=3.8063(2)$	Si,ScAs	71
Sc_3As_2	*Pnma*	Cr_3C_2	$a=7.1423(3)$ $b=3.8698(2)$ $c=14.7073(5)$	ScAs	91
$Sc_{2.3}As$	*I*4/*mcm*[a]	–	$a=14.3751(2)$ $c=8.0281(2)$	Si	110
Sc_3P_2	*Pnma*	Hf_3P_2	$a=10.1075(6)$ $b=3.6944(2)$ $c=10.1793(6)$	Si	48
Sc_3P_2	*Pnma*	Cr_3C_2	$a=6.9781(18)$ $b=3.7570(6)$ $c=14.3655(22)$	ScP	15

[a] Revised data from Ref. 1. [b] Tetragonal refinement.

from the Swedish Institute and from the Netherlands Ministry of Education and Science, together with financial support from the Swedish Natural Science Research Council, are gratefully acknowledged.

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Received December 12, 1979.