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The Crystal Structure of Sc_7As_3 as Determined by Direct Methods

ROLF BERGER,* BENGT I. NOLÄNG and LARS-ERIK TERGENIUS

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structure of Sc_7As_3 has been determined by direct methods applied to single-crystal diffractometer data. The symmetry is tetragonal, space group *I4/mcm*, and the lattice parameters are $a=14.3751$ Å and $c=8.0281$ Å. The structure constitutes a new structure type with 8 formula units to the cell.

Structural data from a phase analysis study of the Sc–As system were reported in a series of papers.[1-3] Attention was given to the metal-rich part only, and the study revealed similarities between the Sc–As and the Sc–P systems[2] as regards the crystal structures adopted. However, differences occur for the most metal-rich compositions. Rundqvist and Nyarko (quoted in Ref. 1) found a phase denoted $Sc_{2.3}As$, and a renewed investigation suggested that its composition might be Sc_7As_3, with 80 atoms to the tetragonal unit cell.[4] This paper presents a complete single-crystal structure determination which confirms this hypothesis.

EXPERIMENTAL

Preparation. Equimolar amounts of scandium (Rare Earths Prod., claimed purity 4N) and arsenic (Koch-Light Ltd., claimed purity 6N) were brought to reaction in a silica-tube synthesis. The product formed – predominantly ScAs – was subsequently melted together with additional metal in an argon-arc furnace. Since this specimen exposed fuzzy powder lines, it was heat-treated for 10 min under argon at approximately 1200 °C in an induction furnace, with the specimen resting in a water-cooled copper crucible. Only the superficial part of the alloy button showed crystals with prominent morphology, and from there a single crystal was picked for the intensity data recordings.

X-Ray powder investigations. The powder photographs were recorded by a Guinier-Hägg focusing camera equipped with strictly monochromatic $CuK\alpha_1$ radiation. The accompanying fluorescence background effects were successfully taken care of by the introduction of an aluminium foil next to the film. The powder pattern from a bulk sample of the heat-treated specimen showed very sharp lines of Sc_7As_3, together with a handful of very weak lines belonging to Sc_5As_3,[2] which was obviously present in minute amounts.

Although the specimen had probably experienced a large temperature gradient, the excellent quality of the Sc_7As_3 lines indicated homogeneity. There was thus no reason to suspect that the composition and cell dimensions of the single crystal would deviate appreciably from those of the bulk.

Silicon ($a=5.431065$ Å)[5] was used as an internal calibration standard, and the lattice dimensions obtained from a least-squares refinement on Q ($=d^{-2}$) were $a=14.3751(2)$ Å and $c=8.0281(2)$ Å. Individual weighting of the observations was applied. The standard deviations reflect the precision only, and no corrections for refraction were made.

Single-crystal diffractometry. Preliminary Weissenberg photographs showed sharp spots, although each with a very weak satellite. The crystal, mainly of a needle form, had the approximate dimensions $35\times45\times130$ μm. The exact form had to be approximated to some extent.

The equipment and data collecting procedure have been described elsewhere.[6] The reciprocal space covered was limited by $0\leq h\leq 25$, $-25\leq k\leq 20$ and $0\leq l\leq 14$, corresponding to a maximum in 2θ of 78°. The instrumental stability was monitored by

* Present address: Instituut voor anorganische chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, Nederland.

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remeasuring three standard reflexions at regular intervals. The intensity of these showed a general decrease, and the continuous measurement was interrupted by a power supply failure. The change could be described fairly well by a linear function of time, common to all three test reflexions. Another linear intensity correction had to be applied to the data recorded after the instrumental breakdown. The setting of the crystal was rechecked after the conclusion of the measurement and was found to coincide with the initial one. Alloy structures of this type are generally stable towards radiation damage, so the effects are probably due to a device error. The intensity data are thus, to some extent, marred by systematic errors, for the applied corrections are still rather approximate. This is also true for the absorption correction.

Numerical calculations. All calculations were performed on NORD 100 and IBM 370/158 computers. The intensity data were corrected for Lp and absorption effects, the latter by using a Gaussian grid method. The minimum and maximum transmission factors obtained were respectively 0.43 and 0.56 for a calculated linear absorption coefficient of 172 cm^{-1} using the mass absorption coefficients given in Ref. 7. The intensity values of equivalent reflexions were averaged yielding an internal consistency factor (analogous to the conventional agreement factor) of 6.5 %. The crystallographic programs used are to be found in Ref. 8.

STRUCTURE DETERMINATION

The preliminary Weissenberg and oscillation photographs obtained from rotation of the crystal around the *a* and *c* axes showed systematic absences for *hkl* and *hhl* reflexions corresponding to the space-groups *I*4/*mcm*, *I*4*cm* or $I\bar{4}$-*c*2. These absences were substantiated from the intensity measurements. The very strong (004) reflexion indicated that the atoms ought to be confined essentially to planes *c*/4 apart, which favoured the *I*4/*mcm* alternative.

In the beginning of the structure determination all intensity values were converted to normalized structure factors, from which 113 reflexions with E-values over 1.0 were selected, together with 50 weak reflexions, and fed into the *MULTAN 78* program.[9] The solution of the highest probability for *I*4/*mcm* was used for calculating *E*-maps of parallel layers at and about $z=0$ and $z=1/4$. Peaks corresponding to some As and Sc atoms were identified, and the rest were found from subsequent F_o-syntheses. The ultimate structure proposal seemed reasonable as regards coordination and interatomic distances. A series of least-squares refinements was then started, at first based on *F* but later on F^2 to maintain the normal distribution. The (004) reflexion was deleted from the refinements because of extinction and the (110) reflexion because of interference by the primary beam stop. The atomic scattering factors, including anomalous dispersion corrections, were taken from Ref. 7.

The full-matrix refinements converged satisfactorily, but it was noted that the isotropic temperature factor of Sc(4) was exceptionally high, and the conversion to an anisotropic model gave an unreasonably large component in the *z*-direction. Difference Fourier maps through 0, 1/2, 1/4 indicated that the electron density of Sc(4) was considerably smeared out from $z=1/4$. Therefore, the

Table 1. Structure data for Sc_7As_3 from refinement based on F^2 assuming space group *I*4/*mcm* (No. 140). $a=14.3751(2)$ Å and $c=8.0281(2)$ Å, $V=1658.95$ Å^3; $Z=8$. The anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2+U_{22}k^2+2U_{12}hk)a^{*2}-2\pi^2(U_{13}hl+U_{23}kl)a^*c^*-2\pi^2U_{33}c^{*2}]$. Standard deviations within parentheses.

					$U_{ij}\times10^4$ (Å^2)					
Atom	Position	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sc(1)	16 *l*	0.33176(7)	*x*+1/2	0.1956(2)	173(3)	U_{11}	71(5)	27(5)	−5(3)	U_{13}
Sc(2)	16 *k*	0.32822(10)	0.01939(10)	0	216(6)	180(6)	94(5)	−120(5)	0	0
Sc(3)	16 *k*	0.11902(9)	0.12547(9)	0	103(6)	102(6)	103(4)	−16(4)	0	0
Sc(4)	8 *g*[a]	0	1/2	0.2223(5)	83(6)	U_{11}	208(32)	−30(20)	0	0
Sc(5)	4 *a*	0	0	1/4	70(5)	U_{11}	146(10)	0	0	0
As(1)	16 *j*	0.19499(4)	0	1/4	46(2)	89(3)	46(2)	0	0	16(3)
As(2)	8 *h*	0.22006(6)	*x*+1/2	0	123(3)	U_{11}	20(3)	80(4)	0	0

[a] 50 % occupation.

original choice of the 4*b* position was changed into 8*g* with 50 % occupation. This operation yielded reasonable anisotropic temperature factors, compatible with those of the other metal atoms. The *R*-values (F^2) dropped very slightly from 8.0 to 7.8 % (1284 reflexions). The highest residual peak in the difference Fourier maps was equivalent to 3 % of an arsenic peak in a corresponding F_o synthesis.

In order to check whether the result was due to an erroneous symmetry model, another refinement was made in *I4cm*, where Sc(4) was assigned the corresponding fourfold position and given $z=0.22$ from the centrosymmetric model as a start value. The *z*-coordinate of Sc(2) was locked at zero to define the origin, but all the other positional and thermal parameters were allowed to refine according to the non-centrosymmetric conditions. However, the input atomic parameters hardly changed, at the most 1.2σ, and the *R*-value dropped to 7.7 %.

The space group $I\bar{4}c2$ does not give any additional information about the Sc(4) atoms because in this space group these occupy an eightfold position as in *I4/mcm*. Due to the increased number of refined parameters a refinement in $I\bar{4}c2$ ended at a slightly lower $R(F^2)$-value of 7.6 % without changing the atomic parameters significantly.

We do not find the results of the alternative refinements very conclusive and therefore choose to present the structure with the centrosymmetric description as given in Table 1. In that model, however, we encounter the problem of how the Sc(4) atoms are distributed among the crystallographically equivalent sites. For instance, there can be complete ordering within each "channel" along the *c*-axis, so that the metal atoms are situated at *z* and $z+1/2$ but with different *z*-values $(1/2\pm\delta)$ per channel. This pseudo-ordering would yield constant Sc–Sc distances ($=1/2\ c$). But the disorder can also occur within each channel, a situation which is not discernible from the other one from these data, and that would give two alternative intermetallic distances depending on which side of the mirror plane the Sc(4) atom is situated compared with its next neighbour. The Sc–Sc distance of 0.45 Å ($=2\delta c$) as read from Table 2 is an artifact which, of course, does not appear in *I4cm*.

Table 2. Interatomic distances (Å) in Sc_7As_3 less than 4 Å. Standard deviations within parentheses. For distances to Sc(4), see text for comments.

Sc(1)–	As(2)	2.661(1)	Sc(4)–	Sc(4)	0.445(9)
	As(2)	2.761(1)		4Sc(2)	3.059(3)
	2Sc(2)	3.122(2)		4Sc(2)	3.339(3)
	Sc(1)	3.141(3)		2Sc(1)	3.427(1)
	2As(1)	3.147(1)		2Sc(1)	3.483(1)
	2Sc(2)	3.248(2)		Sc(4)	3.569(9)
	Sc(4)	3.427(1)			
	2Sc(3)	3.429(2)			
	Sc(1)	3.437(2)	Sc(5)–	4As(1)	2.803(1)
	Sc(4)	3.483(1)		8Sc(3)	3.195(1)
	2Sc(3)	3.963(2)			
			As(1)–	2Sc(2)	2.788(1)
Sc(2)–	2As(1)	2.788(1)		Sc(5)	2.803(1)
	As(2)	2.967(2)		2Sc(3)	2.820(1)
	2Sc(4)	3.059(3)		2Sc(3)	2.911(1)
	Sc(2)	3.098(3)		2Sc(1)	3.147(1)
	2Sc(1)	3.122(2)		2As(2)	3.940(1)
	2Sc(1)	3.248(2)		2As(1)	3.964(1)
	2Sc(4)	3.339(3)			
	Sc(3)	3.372(2)			
	Sc(3)	3.529(2)	As(2)–	2Sc(1)	2.661(1)
	Sc(2)	3.886(3)		2Sc(3)	2.683(2)
				2Sc(1)	2.761(1)
				2Sc(2)	2.967(2)
Sc(3)–	As(2)	2.683(2)		4As(1)	3.940(1)
	2As(1)	2.820(1)			
	2As(1)	2.911(1)			
	2Sc(5)	3.195(1)			
	Sc(2)	3.372(2)			
	2Sc(1)	3.429(2)			
	2Sc(3)	3.516(2)			
	Sc(2)	3.529(2)			
	2Sc(1)	3.963(2)			

STRUCTURAL DESCRIPTION AND DISCUSSION

To our knowledge, the Sc_7As_3 structure constitutes a new structure type, and in view of its metallic lustre and composition, the compound is likely to be metallic. The main features presented in Fig. 1*a* reveal resemblances with other early transition-metal arsenides or phosphides. For instance, the star-like complex made of a metal "body-centred" unit with triangular prisms linked to it can be found in other structure types represented in similar systems, say V_3As_2,[10] Nb_7P_4[11] and $Nb_5Ni_4P_4$[12]. Another body-centred unit is found for Sc(4), which has still more metal neighbours as in an element b.c.c. structure, but the arrangement is heavily distorted. A similar arrangement is found in the W_5Si_3 type.

The units discussed are interlinked by bisdisphenoids sharing edges in à similar manner as in the Y_5Bi_3 and β-Yb_5Sb_3 types, as illustrated for com-

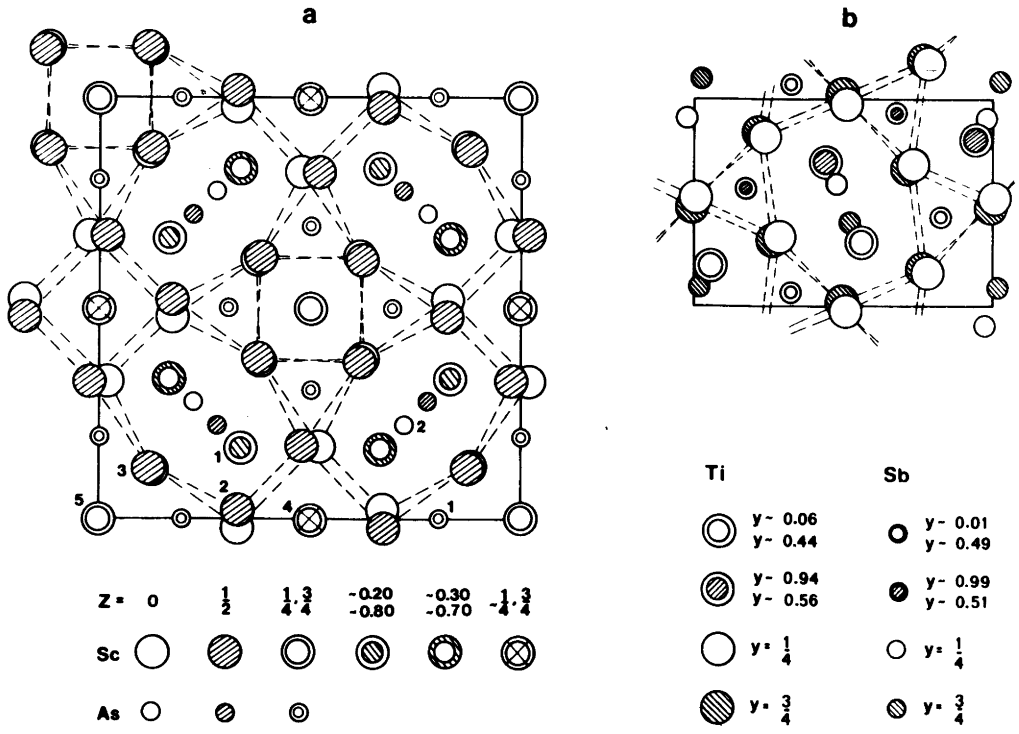

Fig. 1. (a) The structure of Sc_7As_3 projected on (001), and (b) the structure of Ti_5Sb_3 (β-Yb_5Sb_3 type) projected on (010).

parison by Ti_5Sb_3[13] in Fig. 1*b*. The connections between adjacent bisdisphenoids (trapezoids in the projection) are, however, different, probably since Sc_7As_3 must accommodate relatively more metal atoms.

As stated above, various degrees of distortion from the idealized geometry occur, but it is especially difficult to explain why the Sc(4) atom would prefer the irregular coordination polyhedron created by its moving out from the $z=1/4$ mirror plane. With the atom in the originally chosen 4*b* site, metal contacts of 3.20 Å would be obtained, compatible with the scandium atomic radius of 1.60 Å (Goldschmidt CN 12).

The Sc–As distances found are more in line with expectations. They are collected around the mean of the radius sum (taking the tetrahedral covalent radius of 1.18 Å for arsenic). A histographic analysis[4] of the distances to As(1) shows a slight tendency for coordinating 7 rather than 9 metal neighbours (Fig. 2). The As(2) atom in the bisdisphenoid coordinates 8 metal atoms, where, in

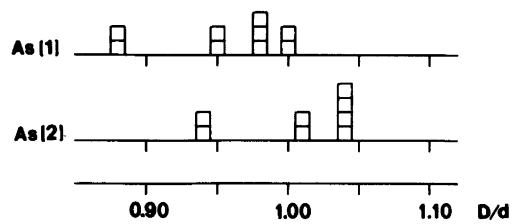

Fig. 2. Histographic representation of the coordination around the As atoms in Sc_7As_3. Each square corresponds to one interatomic distance.

the set corresponding to one of the distorted tetrahedra, the Sc–As distances are up to 5% shorter than the radius sum. The same tendency is found in the bisdisphenoidal arrangements in the β-Yb_5Sb_3 compounds.[4]

The composition Me_7X_3 has also been found in the Sc–P system,[2] where the corresponding compound is of the Ru_7B_3 structure type.[14]

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