

Cerium Scandium Sulphide: Structure Refinement by Powder Neutron Diffraction

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Abstract. CeScS₃, orthorhombic, *Pnma*, $a = 7.1618$ (3), $b = 9.5621$ (4), $c = 6.5065$ (3) Å, $Z = 4$. The structure has been refined by profile analysis of powder neutron diffraction data at room temperature. [$R_{\text{nuclear}} = 2.64$, $R_{\text{profile}} = 6.14$, $R_{\text{weight}} = 6.85$.] It is a distorted perovskite of the GdFeO₃ type.

Introduction. The investigation of the crystal structure of the title compound forms part of a research programme on the structural relations of compounds ABX_3 , where A represents an alkaline or an alkaline-earth metal, B a transition metal and X a halogen or sulphur (Lelieveld & IJdo, 1978, 1980; van Loon, 1974). The lattice parameters of LnScS₃ (Ln = La to Er) were reported by Rodier, Laruelle & Flahaut (1969). From their powder X-ray data they concluded that the compounds are isostructural with YScS₃, which has been the subject of a single-crystal X-ray structure determination (Rodier & Laruelle, 1970). In both cases the space group assumed was *Pna*2₁. The lattice parameters and the crystal structure of YScS₃ revealed that these compounds are possibly isostructural with CaZrS₃ (Lelieveld & IJdo, 1980) which has the GdFeO₃ structure (Table 1).

We prepared CeScS₃, the most suitable compound for powder neutron diffraction, by firing an appropriate mixture of the binary sulphides in a stream of hydrogen sulphide at 1473 K for several days in an induction furnace with carbon crucibles. The compound was annealed for another day at 1073 K. No single crystals were available, so we decided to use the neutron powder profile-refinement technique (Rietveld, 1969) in order to obtain precise structural information. The neutron diffraction diagrams were collected at 300 K on the powder diffractometer at the

Petten High-Flux Reactor as described by van Laar, Rietveld & IJdo (1971). A wavelength of 2.5849 (3) Å from the (111) planes of a Cu monochromator was used. The complete range of data obtained ($5.4^\circ < 2\theta < 138.6^\circ$, in steps of 0.144°) was used in the refinement. Absorption and extinction effects were small and no corrections were made.

We used the structure of CaZrS₃ as the trial model: space group *Pnma* with atomic positional parameters as follows: Ce in 4(c): $x, \frac{1}{2}, z$; Sc in 4(b): $0, 0, \frac{1}{2}$; S(1) in 4(c) and S(2) in 8(d): x, y, z . The variables in the refinement were: a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic temperature factors and an asymmetry parameter below $2\theta = 40^\circ$. The coherent scattering lengths assumed were: Ce 4.8, Sc 11.8, S 2.8 fm (Bacon, 1972). The Rietveld program minimizes the function $\chi^2 = \sum_i w_i [y_i(\text{obs.}) - (1/c) \times y_i(\text{calc.})]^2$, where $y(\text{obs.})$ and $y(\text{calc.})$ are the observed and calculated profile data points, w is the statistical weight allotted to each data point and c is the scale factor. The following R factors were calculated:

$$R_{\text{nuclear}} = 100 \frac{\sum |I(\text{obs.}) - \frac{1}{c} I(\text{calc.})|}{\sum I(\text{obs.})} = 2.64,$$

$$R_{\text{profile}} = 100 \frac{\sum |y(\text{obs.}) - \frac{1}{c} y(\text{calc.})|}{\sum y(\text{obs.})} = 6.14,$$

$$R_{\text{weight}} = 100 \frac{\sum w |y(\text{obs.}) - \frac{1}{c} y(\text{calc.})|^2}{\sum w |y(\text{obs.})|^2} = 6.85,$$

where $I(\text{obs.})$ and $I(\text{calc.})$ are the observed and calculated integrated intensities of each reflection.

Atomic positional parameters are given in Table 2, and the agreement between the observed and calculated profiles is shown in Fig. 1. Refinement was also attempted in *Pn*2₁*a*. No improvement in the agreement between observed and calculated profiles was seen and the atomic positional parameters refined effectively to the symmetry-equivalent positions in *Pnma* within two e.s.d.'s.

Table 1. Lattice parameters (Å)

	a	b	c	References
CeScS ₃ *	7.15	9.55	6.51	Rodier <i>et al.</i> (1969)
YScS ₃ *	7.00	9.46	6.36	Rodier & Laruelle (1970)
CeScS ₃ †	7.1618 (3)	9.5621 (4)	6.5065 (3)	This work, neutron diffraction
CaZrS ₃ †	7.0300 (4)	9.5896 (6)	6.5366 (3)	Lelieveld & IJdo (1980)

* b and c axes interchanged.

† Standard errors in the lattice parameters do not include errors in the neutron wavelength.

Table 2. Atomic parameters

CeScS ₃ (present work)				
	x	y	z	B (Å ²)
Ce	0.0958 (4)	0.25	0.0371 (8)	0.30 (11)
Sc	0	0	0.5	0.65 (5)
S(1)	-0.0334 (11)	0.25	0.6232 (10)	0.68 (20)
S(2)	0.1881 (7)	-0.0607 (6)	0.8219 (8)	0.50 (15)
CaZrS ₃ (Lelieveld & IJdo, 1980)				
	x	y	z	B (Å ²)
Ca	0.0903 (4)	0.25	0.0333 (7)	1.35 (11)
Zr	0	0	0.5	0.69 (7)
S(1)	-0.0345 (9)	0.25	0.6252 (9)	0.84 (17)
S(2)	0.1897 (6)	-0.0626 (4)	0.8185 (6)	0.73 (11)

Table 3. Interatomic distances (Å) and angles (°)

Distances marked with an asterisk occur in pairs. The distances are in the same sequence as those of CaZrS₃, SrZrS₃ and BaZrS₃ (Lelieveld & IJdo, 1980).

Ce-S(1)	2.847 (8)	Sc-S(1)*	2.533 (2)	S(1)-S(2)*	3.590 (8)
	2.853 (9)	-S(2)*	2.557 (5)		3.638 (8)
Ce-S(2)*	3.351 (6)		2.583 (5)	S(2)-S(2)*	3.566 (4)
	2.872 (6)	S(1)-S(2)*	3.608 (7)		3.701 (3)
	3.018 (6)		3.597 (7)		
Sc-S(1)-Sc	141.4 (3)	S(1)-Sc-S(2)	90.3 (2)	S(2)-Sc-S(2)	92.1 (1)
Sc-S(2)-Sc	140.5 (2)		90.7 (2)		

respectively, and the ionic radii for Sc³⁺ and Zr⁴⁺ for six-coordination, 0.73 and 0.72 Å respectively (Shannon & Prewitt, 1969).

There is no evidence for the statement of Rodier & Laruelle (1970) that YScS₃ has the space group *Pn2₁a*. It seems that two of their S atoms are not independent, given the fact that they do not give e.s.d.'s. As a result the space group *Pnma* cannot be excluded. The same feature was found for UCrS₃ (Noël, Padiou & Prigent, 1975) which has the GdFeO₃ structure. For the same reason these authors concluded that the space group is *Pnma*.

From the work of Rodier, Laruelle & Flahaut (1969) and the facts above, it is likely that the whole series LaScS₃ to ErScS₃, including YScS₃, has the distorted perovskite structure of the GdFeO₃ type.

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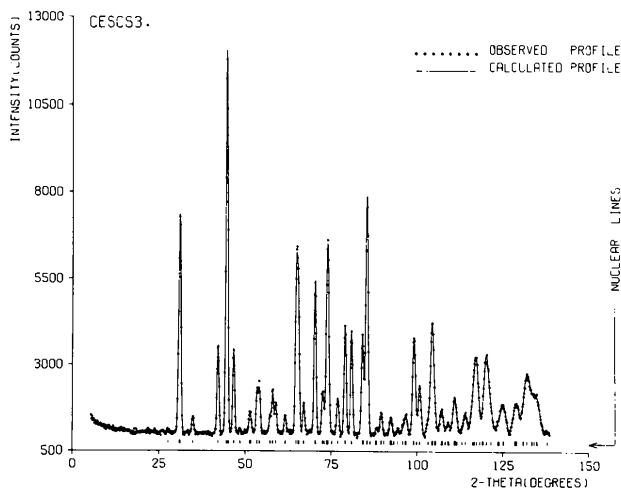


Fig. 1. Observed (dots) and calculated (full line) neutron intensity profile for CeScS₃. $N - P = 660$, where N is the number of statistically independent observations, and P the number of least-squares parameters.

Discussion. Lattice parameters of CeScS₃ and CaZrS₃ are given in Table 1 and the atomic parameters for both compounds in Table 2. Bond angles and distances for CeScS₃ are given in Table 3.

From the data given in the tables it can be seen that the structure of CeScS₃ is indeed a distorted perovskite of the GdFeO₃ type, as has already been shown to be the case for CaZrS₃ (Lelieveld & IJdo, 1980). The structural details of CeScS₃ and CaZrS₃ are very similar. This is consistent with the ionic radii for eight-coordination for Ce³⁺ and Ca²⁺, 1.14 and 1.12 Å