

# Crystal Structure of $\text{ScCl}_3$ Refined from Powder Neutron Diffraction Data

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The crystal structure of  $\text{ScCl}_3$  has been refined from high-resolution powder neutron diffraction data. The structure is of the  $\text{BiI}_3$  type, and consists of two-dimensional  $\text{ScCl}_3$  layers. A slight deformation of the  $\text{ScCl}_6$  coordination octahedron is rationalized on the basis of the different surroundings of the faces of the octahedron. The interatomic distances are discussed in light of crystal structure data for reduced scandium chlorides.

The layered  $M\text{Cl}_3$  trichlorides ( $M = 3d$  element or main group III or V element) crystallize with somewhat different structure types. For instance,  $\text{CrCl}_3$  exists in two modifications: at low temperatures with an h.c.p.-based  $\text{BiI}_3$ -type structure, and at high temperature with the c.c.p.-based  $\text{YCl}_3$ -type structure. Furthermore,  $\alpha\text{-TiCl}_3$ ,  $\text{VCl}_3$  and  $\text{FeCl}_3$  take the  $\text{BiI}_3$ -type structure, whereas the Sc, Y and La trichlorides take, respectively, the  $\text{BiI}_3$ -,  $\text{YCl}_3$ - and  $\text{UCl}_3$ -type structures.

The atomic coordinates describing the structure for  $\text{ScCl}_3$  have not yet been refined from diffraction data, and the assumption of isostructurality between  $\text{ScCl}_3$  and  $\text{FeCl}_3$  is based on rather poor Debye–Scherrer powder diffraction photographs.<sup>1</sup> On the other hand,  $\text{FeCl}_3$  itself has been extensively studied with respect to structural and magnetic properties,<sup>2–5</sup> and also intercalated  $\text{FeCl}_3$  in graphite has been structurally characterized.<sup>6,7</sup> No further attention has later been devoted to  $\text{ScCl}_3$ . On the other hand, several reduced scandium chlorides (viz.  $\text{ScCl}$ ,  $\text{Sc}_5\text{Cl}_8$ ,  $\text{Sc}_7\text{Cl}_{10}$  and  $\text{Sc}_7\text{Cl}_{12}$ ) have more recently been synthesized by chemical transport reactions from mixtures of Sc and  $\text{ScCl}_3$  (with probably  $\text{ScCl}_2$  as the transporting species).<sup>8–11</sup> Their crystal structures have been determined from single-crystal X-ray diffraction data. A common feature for these reduced scandium chlorides is that they contain either metal atom clusters or metal atom chains.<sup>8–11</sup>

The present report provides crystal structure data for  $\text{ScCl}_3$  as determined from high-resolution powder neutron diffraction data. The structure is discussed in relation to structural features for other  $\text{BiI}_3$ -type compounds and for reduced scandium chlorides.

## Experimental

Anhydrous, crystalline  $\text{ScCl}_3$  was synthesized by reductive chlorination of purified scandium oxide.<sup>12</sup> A finely homogenized mixture of  $\text{Sc}_2\text{O}_3$  and carbon black (5N, Pramet Šumperk Co., Czechoslovakia; in 50% excess with respect to stoichiometry) was placed in a corundum boat and heated in a stream of dried chlorine in a silica tube furnace. Upon increasing the temperature to about 900 °C, chlorination started and large  $\text{ScCl}_3$  crystals were obtained at the cold zone of the tube. Subsequent handling of the product took place in a dry bag with an argon protection atmosphere.

The product obtained was phase pure according to powder X-ray diffraction (PXRD) data (Guinier–Simon camera,  $\text{CuK}\alpha_1$  radiation, Si as internal standard; sample kept inside closed glass capillaries). Some reflections were clearly broadened, and thus unit-cell dimensions were deduced from the profile refinement of powder neutron diffraction (PND) data.

PND data were collected at room temperature between  $2\theta = 6$  and  $154^\circ$  in steps of  $0.025^\circ$  with the D2B instrument at ILL, Grenoble. The wavelength was  $1.5938 \text{ \AA}$ . Owing to its extreme sensibility towards oxygen and moisture, the  $\text{ScCl}_3$  sample was kept inside a closed, cylindrical aluminium sample holder under an inert atmosphere. Seven regions with additional reflections stemming from the aluminium were excluded prior to the profile refinements.

The profile refinements were performed using the Hewat version of the Rietveld program<sup>13,14</sup> modified for measurement points in integer steps of  $10^{-3}$  deg. The scattering amplitudes  $b_{\text{Sc}} = 12.29$  and  $b_{\text{Cl}} = 9.579 \text{ fm}$  were used.<sup>15</sup> The refinements were conducted for the hexagonal setting of the space group  $R\bar{3}$ . One scale factor, three

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Table 1. Refined atomic coordinates for  $\text{ScCl}_3$  from powder neutron diffraction data. Space group  $R\bar{3}$ , hexagonal setting.<sup>a</sup>

Atom	Site	x	y	z
Sc	6c	0	0	0.3333(3)
Cl	18f	0.6543(8)	0.9990(10)	0.0791(2)

<sup>a</sup>Calculated standard deviations in parentheses.

halfwidth parameters, two unit-cell dimensions, zero point, preferred orientation parameter, four atomic coordinates and two isotropic temperature factors (or eight anisotropic ones) were refined: altogether 14 (or 20) free variables entered into the final least-squares refinements.

## Results and discussion

No systematic absences were identified in the observed PXD and PND patterns of  $\text{ScCl}_3$ . The diffraction data are hence consistent with the space group  $R\bar{3}$  earlier adopted in the structure description of  $\text{FeCl}_3$ .<sup>3</sup> The profile refinements followed the hexagonal setting of this space group. The refined unit-cell dimensions are  $a = 6.3775 \pm 0.0003$  and  $c = 17.790 \pm 0.005$  Å, which correspond to  $a_{\text{rh}} = 6.979 \pm 0.002$  Å and  $\alpha = 54.362 \pm 0.010^\circ$  for the rhombohedral cell. 237 reflections and 5500 data points entered the profile refinements, and the statistically expected profile  $R$ -factor was  $R_{\text{exp}} = 28.9\%$ . A significantly improved fit was obtained by the introduction of a preferred orientation parameter to account for orientation effects of the plate-like crystallites.

The refined atomic coordinates and anisotropic tem-

perature factors are listed in Tables 1 and 2 ( $R_{\text{N}} = 17.4\%$  and  $R_{\text{P}} = 32.8\%$ ). Refinements where an isotropic temperature factor description was used gave  $B_{\text{Sc}} = 1.88 \pm 0.08$  Å<sup>2</sup> and  $B_{\text{Cl}} = 2.44 \pm 0.06$  Å<sup>2</sup>, although with a significantly less good fit. The observed, calculated and difference PND patterns are shown in Fig. 1. There are only minor discrepancies between the observed and calculated diffraction patterns.

The layered  $\text{BiI}_3$ -type structure is described in terms of pseudo-hexagonally closely packed chlorine atoms ( $AB$  stacking sequence) with metal atoms occupying 1/3 of the octahedral voids in an ordered way. Layers with composition  $\text{ScCl}_3$  are arranged perpendicular to the three-fold axis with the Sc atoms occupying 2/3 of the available octahedral sites within a given layer. One such  $\text{ScCl}_3$  layer (viz. the one through  $z = 0.00$ ) is shown in Fig. 2. The layer can be considered as built of  $\text{ScCl}_6$  octahedra sharing three edges. The octahedron itself is shown in Fig. 3. Despite the distortion of the layers, the six Sc–Cl bond lengths should be considered as equal. The calculated distances are 2.528(8) and 2.515(8) Å for the lower and upper halves of the octahedron, respectively.

Considering the octahedron, the shared Cl–Cl edges are the shortest ones, somewhat reminiscent of the poly-center bonding in  $\text{Al}_2\text{Cl}_6$ . The other edges differ in length according to whether the neighbouring face belongs to the empty  $\text{Cl}_6$  octahedron (intermediate edge) or opens towards the next layer (longest edge). These features are generally found for  $\text{BiI}_3$ -type compounds. If the close packing were ideal, simple relationships would exist between the unit-cell dimensions and the edge of the regular octahedron ( $r$ );  $a_{\text{h}} = \sqrt{3}r$ ;  $c_{\text{h}} = 6r\sqrt{2}/\sqrt{3}$  and  $c_{\text{h}}/a_{\text{h}} = \sqrt{8} \approx 2.828$ . For  $\text{ScCl}_3$ ,  $c_{\text{h}}/a_{\text{h}} = 2.789$ .

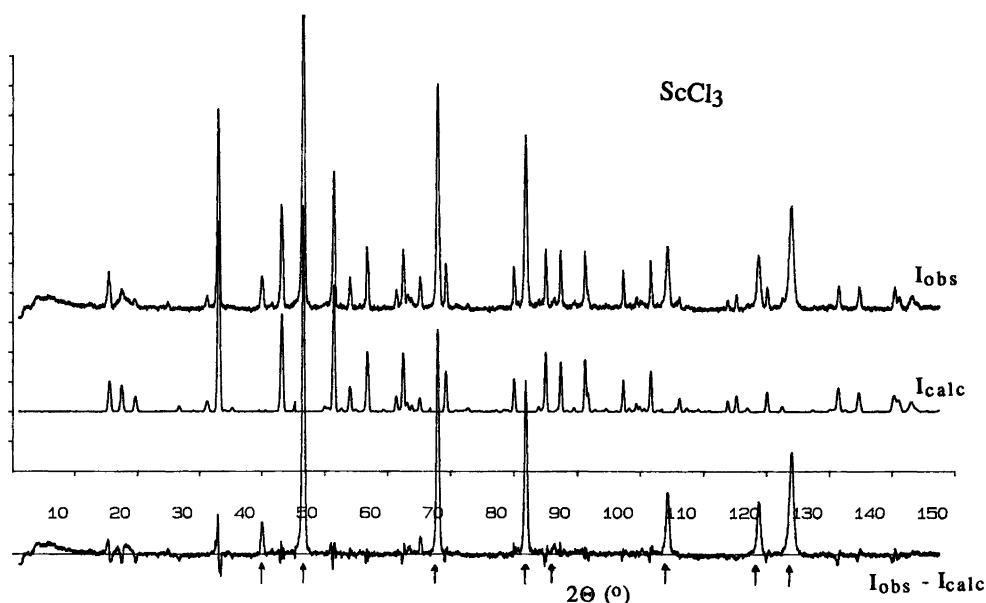


Fig. 1. Observed, calculated and difference powder neutron diffraction diagram for  $\text{ScCl}_3$  (D2B at ILL,  $\lambda = 1.5938$  Å). Arrows indicate reflections from the Al sample holder.



Table 4. Calculated interatomic distances (in Å) in ScCl<sub>3</sub>, and selected interatomic distances (or ranges) in reduced scandium chlorides.

Phase	Cl/Sc	d(Sc–Cl)	d(Cl–Cl) <sup>a</sup>	d(Sc–Sc)	Ref.
ScCl <sub>3</sub>	3.00	2.52	3.44	3.68	This work
Sc <sub>7</sub> Cl <sub>12</sub>	1.71	2.54–2.75	3.47	3.20–3.23	8
Sc <sub>5</sub> Cl <sub>8</sub>	1.60	2.53–2.67	3.48	3.02–3.23	9
Sc <sub>7</sub> Cl <sub>10</sub>	1.43	2.44–2.69	3.44	3.15–3.41	10
ScCl	1.00	2.59	3.47	3.22, 3.47	11
Sc	–	–	–	3.26, 3.31	16

<sup>a</sup>Shortest Cl–Cl separation.

For FeCl<sub>3</sub>, the single-crystal study had to account for the existence of different twins (caused by different stacking variants with respect to the Fe-distribution between the Cl layers) within the crystal.<sup>3</sup> For the temperature factors, a significant difference was found for the (in-plane)  $B_{\parallel}$  and (plane-normal)  $B_{\perp}$  for the iron atoms, being, respectively, 1.2 and 1.75 Å<sup>2</sup>. Significant anisotropy was also found in the present powder diffraction study of ScCl<sub>3</sub> (Fig. 3). The unusually large  $B_{1,1}$  for Cl (Table 2) may possibly be caused by the asymmetric environment around the Cl atoms (two filled and one vacant Sc site).

In the reduced scandium chlorides, different surroundings for the Sc atoms are frequently found. For example, in Sc<sub>7</sub>Cl<sub>12</sub> there exist Sc<sub>6</sub>Cl<sub>12</sub><sup>3-</sup> clusters with a central Sc octahedron.<sup>8</sup> In addition, Sc<sup>III</sup> cations are found in octahedral interstices between the clusters with a Sc<sup>III</sup>–Cl bond distance of 2.549 Å.<sup>8</sup> In Sc<sub>5</sub>Cl<sub>8</sub> there exist two types of infinite chains. One consists of edge-sharing Sc octahedra, the other of edge-sharing Sc<sup>III</sup>Cl<sub>6</sub> octahedra.<sup>9</sup> A comparison of the interatomic separations listed for various Sc compounds in Table 4 should be made, while at the same time considering relevant details of the atomic arrangement. For the ScCl<sub>6</sub> octahedron in Sc<sub>5</sub>Cl<sub>8</sub>, the Sc–Cl distances of 2.538 and 2.563 Å are in good agreement with the present values for ScCl<sub>3</sub>. In the more metal-rich compound Sc<sub>7</sub>Cl<sub>10</sub>, which contains infinite double chains of edge-sharing Sc octahedra, there also exist 'isolated' Sc<sup>III</sup> atoms (viz. not bonded to other Sc atoms), with Sc–Cl distances of 2.502 and 2.566 Å in the octahedral coordination polyhedron.<sup>10</sup> In the most metal-rich compound, ScCl, there exist no 'isolated' Sc<sup>III</sup> atoms.<sup>16</sup> For all these compounds, the shortest non-bonding Cl–Cl distance is around 3.45 Å. Generally, as the portion of metal–metal bonding interactions increases from ScCl<sub>3</sub> to ScCl, the Sc–Cl bond strength decreases. Analogous correlations have been made recently for a completely metallic system of manganese carbides.<sup>17</sup>

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