LECLAIRE, A., BENABBAS, A., BOREL, M. M., GRANDIN, A. & RAVEAU, B. (1989). *J. Solid State Chem.* **83**, 245–254.
MAGNELI, A. (1953). *Acta Chem. Scand.* **7**, 315–323.
SHANNON, J. & KATZ, L. (1970). *Acta Cryst.* **B26**, 105–109.

Acta Cryst. (1992). **C48**, 1747–1749

Structure Refinement of the Semi-Metallic Oxide $SrTl_2O_4$: a Neutron Diffraction Study

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Abstract. Strontium thallium oxide, $SrTl_2O_4$, $M_r = 559.4$, orthorhombic, *Pnam*, $a = 10.0451$ (2), $b = 11.6905$ (2), $c = 3.40860$ (4) Å, $V = 400.28$ (2) Å^3, $Z = 4$, $D_x = 9.28$ Mg m^{-3}, powder neutron diffraction data, $\lambda = 1.594$ Å, $T = 293$ K, 457 reflections, $R_p = 0.048$, $R_{wp} = 0.064$, $R_i = 0.046$. The lattice belongs to the $CaFe_2O_4$-type structure; it is built up from double ribbons of edge-sharing TlO_6 octahedra, linked through their corners. Comparison is made with Tl—O distances in other oxides and especially with high T_c superconductors. The JCPDS File No. for $SrTl_2O_4$ is 43-1497.

Introduction. Recent developments of the high T_c thallium cuprates suggest that the thallium–oxygen layers are not inert for superconductivity (Raveau, Michel & Hervieu, 1989) but that they can play the role of hole reservoirs for the superconductive copper–oxygen layers. This viewpoint is supported by electronic structure calculations (Yu, Massida & Freeman, 1988; Kasowksi, Hsu & Herman, 1988; Hamann & Mattheiss, 1988; Jung, Whangbo, Herron & Torardi, 1989). Consequently, it appears that the knowledge of the chemical bond and also of the electronic properties of pure thallium(III) oxides, without copper, is important for the understanding of the role of thallium in superconductivity. Recently, a new phase, $SrTl_2O_4$, with semi-metallic properties, was isolated (Michel, Hervieu, Raveau, Greaney, Fine, Potenza & Greenblatt, 1991). It was shown to be isotypic with the $CaFe_2O_4$ structure (Hill, Peiser & Rait, 1956). Although the structure was correctly established from X-ray data, it did not allow the oxygen positions to be determined with accuracy. We report here on the refinement of the structure of this phase from neutron diffraction data.

Experimental. About 10 g of $SrTl_2O_4$ were synthesized from mixtures of Tl_2O_3 and SrO_2 in the ratio 1/1. The mixed powders were divided in five parts. Each part was pressed in the form of bars which were heated in evacuated silica ampoules at 1173 K for 6 h. After thermal treatment, the bars were crushed and the purity of the preparation was checked by X-ray diffraction.

Symmetry was established with systematic reflections: $0kl$, $k + l = 2n$; $h0l$, $h = 2n$; space group *Pnam*. Powder neutron diffraction data were collected on a D2B diffractometer [$\lambda = 1.594$ Å; Ge monochromator; 64 counters (^{3}He, 506.6 kPa)] at ILL (Grenoble); angular range $10 \leq 2\theta \leq 156°$ with increment of 0.05° (2θ).

Profile refinement used the computer program *DBW*3.2 (Wiles & Young, 1981). Scattering lengths were 0.5805, 0.702, 0.8785 (in 10^{-12} cm) for O, Sr and Tl respectively. Starting parameters were those previously refined from powder X-ray data (Michel *et al.*, 1991). Successive refinements of background, profile and cell parameters and then of positional parameters and isotropic thermal factors were made. Calculations were performed on 457 *hkl*. $R_p = 0.048$, $R_{wp} = 0.064$, $R_i = 0.046$. Further refinement details are given in Table 1. Experimental and calculated diffraction patterns are plotted in Fig. 1. Atomic parameters, compared to those obtained from X-ray diffraction, are given in Table 2.†

Discussion. These results do not differ dramatically from the X-ray data (Table 2) with respect to the positions of the metallic elements, whereas the difference between the O-atom positions is larger.

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† A list of primary diffraction data has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55180 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Refinement data for* $SrTl_2O_4$

Reflection profile representation	Gaussian
Background	Refined simultaneously with functions $Y_{bi} = \sum B_m(2\theta_i/90 - 1)^m$ $(0 \leq m \leq 5)$; $B_0 = 77.7$ (3); $B_1 = 33.8$ (9); $B_2 = -19$ (1); $B_3 = -53$ (2); $B_4 = 0.0$; $B_5 = 0.0$
Preferred orientation	No
Omitted region	None
Absorption correction	None
Resolution (FWHM) of material	0.4° 2θ at 60° 2θ, calculated with function $[\mathrm{FWHM}]^2 = U\tan^2\theta + V\tan\theta + W$ (in $2\theta^2$) with $U = 0.092$ (2), $V = -0.193$ (6), $W = 0.254$ (3)

Table 2. *Comparison of X-ray diffraction and neutron diffraction studies*

All atoms are located in site 4(*c*) (x, y, $\frac{1}{4}$) of space group *Pnam*.

	X-ray*			Neutron†		
	$a = 10.0411$ (2), $b = 11.6975$ (5), $c = 3.40906$ (5) Å, $R_p = 10.3$, $R_{wp} = 13.5$, $R_i = 6.2\%$			$a = 10.0451$ (2), $b = 11.6905$ (2), $c = 3.40860$ (4) Å, $R_p = 4.85$, $R_{wp} = 6.40$, $R_i = 4.60\%$.		
	x	y	B (Å^2)	x	y	B (Å^2)
Tl(1)	0.4225 (3)	0.6080 (2)	1.53 (7)	0.4225 (2)	0.6090 (1)	0.64 (2)
Tl(2)	0.4215 (2)	0.1096 (2)	1.01 (6)	0.4212 (2)	0.1093 (1)	0.53 (2)
Sr	0.7536 (5)	0.6254 (4)	1.33 (8)	0.7534 (2)	0.6504 (2)	0.86 (3)
O(1)	0.2140 (25)	0.1690 (20)	0.7 (6)	0.2110 (2)	0.1772 (2)	0.87 (4)
O(2)	0.1298 (23)	0.4721 (21)	0.6 (6)	0.1256 (2)	0.4777 (2)	0.77 (4)
O(3)	0.5354 (25)	0.7792 (21)	0.5 (6)	0.5188 (2)	0.7790 (2)	0.83 (4)
O(4)	0.4186 (25)	0.4223 (19)	0.0 (5)	0.4136 (2)	0.4254 (2)	0.82 (4)

* Michel *et al.* (1991).
† This work.

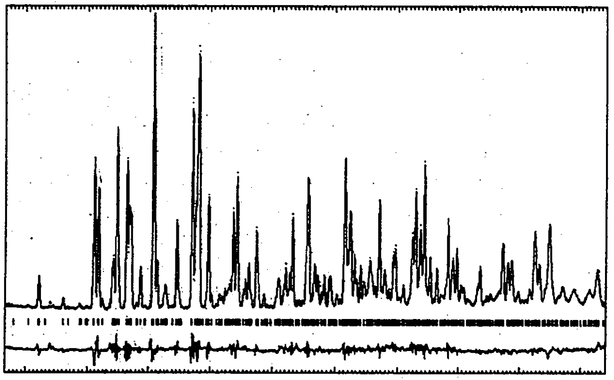

Fig. 1. Experimental (dotted line), calculated and difference (solid lines) neutron diffraction patterns of $SrTl_2O_4$.

Thus it is confirmed that the structure of this phase (Fig. 2) is built up from double ribbons of edge-sharing TlO_6 octahedra, labelled Tl(1) and Tl(2), running along **c**. Laterally, these ribbons share the corners of their octahedra, forming pentagonal tunnels where the Sr ions are located. The interatomic Tl—O distances (Table 3) clearly establish the existence of two sorts of octahedral ribbons. The Tl(2) ribbons exhibit an almost regular octahedral configuration with Tl—O distances ranging from 2.23 to 2.34 Å, whereas the Tl(1) ribbons exhibit strongly distorted octahedra with Tl—O distances ranging from 2.15 to 2.40 Å. Both types of octahedra exhibit similar mean Tl—O distances of 2.30 Å for Tl(1) and 2.28 Å for Tl(2). The environment of Sr is classical; it can be described as a bicapped prismatic trigonal coordination, with the trigonal prism 'O_6' built from the O atoms O(1), O(2) and O(4) exhibiting six nearly equivalent Sr—O distances of 2.55–2.66 Å (Table 3).

Table 3. *Interatomic distances* (Å)

Tl(1)—O(1)	2.311 (2) × 2	Sr—O(1)	2.664 (2) × 2
Tl(1)—O(3)	2.210 (3) × 1	Sr—O(2)	2.574 (2) × 2
Tl(1)—O(4)	2.148 (3) × 1	Sr—O(3)	2.795 (3) × 1
Tl(1)—O(4)	2.404 (2) × 2	Sr—O(3)	2.791 (3) × 1
Tl(2)—O(1)	2.256 (3) × 1	Sr—O(4)	2.550 (2) × 2
Tl(2)—O(2)	2.344 (2) × 2		
Tl(2)—O(2)	2.291 (3) × 1		
Tl(2)—O(3)	2.230 (2) × 2		

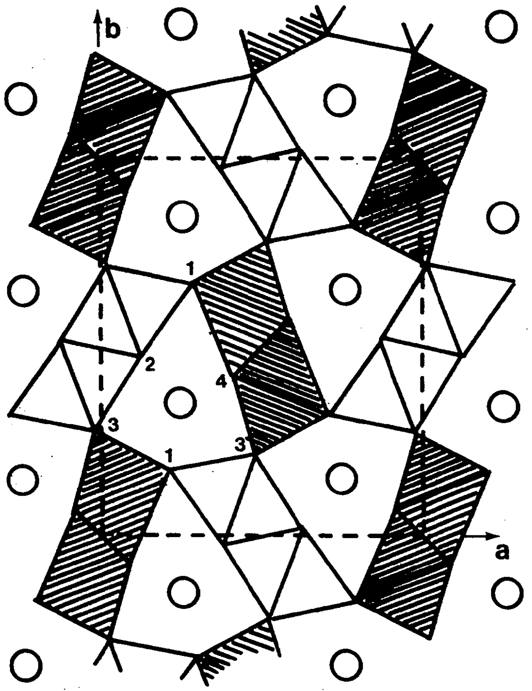

Fig. 2. Projection onto the (001) plane of the structure of $SrTl_2O_4$. $Tl(1)O_6$ octahedra are hatched, open circles symbolize Sr atoms, numbers refer to O atoms.

The data obtained for this phase are important since the Tl—O distances can be used as a reference for Tl in octahedral coordination. Indeed, up to now very few data were available for Tl—O distances in trivalent Tl oxides. The neutron diffraction data on Tl_2O_3, which show Tl—O distances ranging from 2.13 to 2.47 Å, are obtained from only 14 reflections (Papamantellos, 1968). From the single-crystal X-ray data for $Ba_2Tl_2O_5$ (Schenk & Müller-Buschbaum,

1974) distorted TlO_6 octahedra are also observed with distances ranging from 2.16 to 2.4 Å, besides distorted TlO_4 tetrahedra characterized by Tl—O distances of 2.13–2.21 Å. The single-crystal X-ray study of $Sr_4Tl_2O_7$ (Schenk & Müller-Buschbaum, 1973) shows a curious 2 + 2 coordination of Tl with two Tl—O distances of 2.08 Å and two others of 2.50 Å. The recent results obtained for the high T_c superconductor $Tl_2Ba_2CuO_{6+\delta}$ (Shimakawa, Kubo, Manako, Igarashi, Izumi & Asano, 1990) from neutron diffraction data suggest a very different behaviour of Tl^{III} in the superconductors, since the TlO_6 octahedra are characterized in that case by two abnormally short apical Tl—O distances (1.98–2.03 Å) orthogonal to the $[TlO]_\infty$ layers, two intermediate Tl—O distances of 2.526 Å and two abnormally long distances of 2.968 Å in the basal plane. It is also worth pointing out that for this oxide the intermediate Tl—O distances are even superior to the larger Tl—O distances encountered not only in $SrTl_2O_4$ but in the three other thallium oxides.

References

Hamann, D. R. & Mattheiss, L. F. (1988). *Phys. Rev. B*, **38**, 5138–5141.

Hill, P. M., Peiser, H. S. & Rait, J. R. (1956). *Acta Cryst.* **9**, 981–986.

Jung, D., Whangbo, M. H., Herron, N. & Torardi, C. C. (1989). *Physica C*, **160**, 381–390.

Kasowski, R. V., Hsu, W. Y. & Herman, F. (1988). *Phys. Rev. B*, **38**, 6470–6477.

Michel, C., Hervieu, M., Raveau, B., Li, S., Greaney, M., Fine, S., Potenza, J. & Greenblatt, M. (1991). *Mater. Res. Bull.* **26**, 123–128.

Papamantellos, P. (1968). *Z. Kristallogr.* **126**, 143–146.

Raveau, B., Michel, C. & Hervieu, M. (1989). *Congress of Reactivity of Solids*, (*Princeton, June* 1988), *Reactivity of solids*, edited by M. S. Wittingham, pp. 1035–1042. Amsterdam: North-Holland.

Shenk, R. V. & Müller-Buschbaum, Hk. (1973). *Z. Anorg. Allg. Chem.* **396**, 113–122.

Shenk, R. V. & Müller-Buschbaum, Hk. (1974). *Z. Anorg. Allg. Chem.* **405**, 197–201.

Shimakawa, Y., Kubo, Y., Manako, T., Igarashi, H., Izumi, F. & Asano, H. (1990). *Phys. Rev. B*, **42**, 10165–10171.

Wiles, D. B. & Young, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.

Yu, J., Massida, S. & Freeman, A. J. (1988). *Physica C*, **152**, 273–282.

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Redetermination of the Structure of Potassium Tetranitropalladate(II)

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Abstract. $K_2Pd(NO_2)_4$, $M_r = 368.58$, monoclinic, $P2_1/c$, $a = 9.254$ (5), $b = 12.747$ (3), $c = 7.805$ (2) Å, $\beta = 96.43$ (2)°, $V = 914.9$ Å^3 [from setting angles for 14 $0kl$ and 12 $h0l$ data, $2\theta = 18$–$34°$, λ(Mo $K\alpha$) = 0.71073 Å], $Z = 4$, $D_x = 2.676$ Mg m^{-3}, $\mu = 2.95$ mm^{-1}, $F(000) = 704$, $T = 295$ K, $R = 0.031$ for 2327 unique observed reflections. There are two crystallographically independent $Pd(NO_2)_4^{2-}$ ions, each square planar with symmetry $\bar{1}$ (C_i); Pd—N distances are in the range 2.018 (2)–2.047 (2) Å.

Introduction. As part of a broad investigation of the O-transfer chemistry of coordinated O-rich anions such as NO_2^- and NO_3^-, in both solution and the solid state, we have undertaken a detailed analysis of the crystal and molecular structures of a wide range of nitro and nitrato complexes of the transition metals. We have been directly concerned with those complexes of metals with an established catalytic activity.

The structure of the title compound was originally determined by Poraj-Košic (1947). Since the structure was not refined, and various constraints were used, including the unlikely value of 136° for the O—N—O angles, we have redetermined this structure. The fact that the Pd atoms contribute to only one quarter of the data makes it possible to determine the geometry of the nitro groups particularly precisely.

Experimental. The commercial product (Johnson Matthey plc) was recrystallized from water. A yellow tablet, 0.25 × 0.3 × 0.35 mm, was mounted about [100] on a STADI-2 two-circle diffractometer. Data collection used graphite-monochromated Mo $K\alpha$ radiation, at $T = 295$ K, with ω scans with ω range $(1.0 + 0.5\,\sin\mu/\tan\theta)°$. 2616 unique reflections were collected ($2\theta_{\max}$ 60°, h $0 \rightarrow 12$, k $0 \rightarrow 17$, l $-10 \rightarrow 10$) and 2327 with $F \geq 4\sigma(F)$ were used in all calculations. No significant crystal decay or movement was

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