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## Refinement of the Trigonal Crystal Structure of Lanthanum Trifluoride with Neutron Diffraction Data

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### Abstract

Neutron-diffraction data for  $\text{LaF}_3$  [Gregson, Catlow, Chadwick, Lander, Cormack & Fender (1983). *Acta Cryst.* **B39**, 687–691] are refined in space group  $P\bar{3}c1$  with a model which accounts for the effects of twinning.  $R = 0.026$  for 243 reflections. The results agree with previous and less precise determinations of this crystal structure and disprove the assertion that these neutron data rule out the trigonal structure.

### Introduction

Trigonal crystals of lanthanum trifluoride are prone to twinning with  $c$  as the twin axis (rotation of  $180^\circ$  about an axis parallel with  $c$ , or any of several other rotations or reflections which give the same result). This twin law does not affect the macroscopic optical properties, the angular conditions for diffraction, or the rules for systematic absences. Often this twinning has escaped notice in work with large 'single crystals' and has led to incorrect conclusions about the symmetry of the crystal structure. A recent example is a neutron-diffraction report by Gregson, Catlow, Chadwick, Lander, Cormack & Fender (1983, hereafter cited as GCCLCF). These authors assert that their data demonstrate that the space group at room temperature is not  $P\bar{3}c1$ . We show here that in fact these data are in excellent agreement with the trigonal crystal structure, and we report the results of a refinement of the structure in that space group.

Table 1. Sample of X-ray structure factors for  $\text{LaF}_3$  (Zalkin, Templeton & Hopkins, 1966)

<i>hkl</i>	<i>F(hkl)</i>		<i>F(khl)</i>	
	Obs.	Calc.	Obs.	Calc.
314	33	37	55	56
324	50	47	33	34
404	78	73	44	44
414	162	157	153	151
424	11	8	25	26
434	59	59	16	12

Independent X-ray diffraction studies by Mansmann (1965) and by Zalkin, Templeton & Hopkins (1966) showed decisively that the Laue symmetry is  $\bar{3}m1$  and reached similar values for the atomic coordinates in space group  $P\bar{3}c1$ .\* A typical sample of structure-factor magnitudes in Table 1 gives an indication of the lack of equality of values for reflections  $hkl$  and  $khl$  when measured using a single crystal. The twinning superimposes these pairs of reflections and leads to  $6/mmm$  as the Laue symmetry when the two orientations contribute equally.

In neutron-diffraction experiments with larger crystals de Rango, Tsoucaris & Zelwer (1966) and Boutin & Choi (1967) observed  $6/mmm$  as the symmetry of the diffraction patterns. It seems that GCCLCF did the same. Their deposited structure factors, which are

\* In Zalkin *et al.* (1966) the  $y$  coordinate of F(1) is in error; it should be  $-0.055$ .

Table 2. Atomic parameters in  $P\bar{3}c1$ Cell dimensions are  $a = 7.185$  (1),  $c = 7.351$  (1) Å (Zalkin *et al.*, 1966).The temperature factor is given by  $\exp(-\frac{1}{4}\sum_i \sum_j B_{ij} h_i h_j a_i^* a_j^*)$  with  $B_{ij}$  in Å<sup>2</sup>.

	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
La	0.6598 (1)	0	$\frac{1}{4}$	0.43 (2)	0.44 (3)	0.38 (2)	$B_{22}/2$	$B_{23}/2$	0.06 (2)
F(1)	0.3659 (2)	0.0536 (2)	0.0813 (2)	1.76 (4)	1.19 (3)	0.69 (3)	1.03 (3)	-0.03 (3)	-0.16 (3)
F(2)	$\frac{1}{2}$	$\frac{2}{3}$	0.1859 (3)	0.55 (3)	$B_{11}$	1.61 (6)	$B_{11}/2$	0	0
F(3)	0	0	$\frac{1}{4}$	0.63 (4)	$B_{11}$	3.18 (14)	$B_{11}/2$	0	0

restricted to reflections independent in  $6/mmm$ , consist of averages of up to four observations for each unique reflection. The reflections averaged are not identified specifically, but it is plausible that  $hkl$  and  $khl$  type reflections were merged. Such merging would make each datum an average of the two twin orientations even if the twinning were not exactly 50-50.

### Experimental

The  $P\bar{3}c1$  structure was refined using the observed structure factors of GCCLCF assuming equality of twinning. Thus  $\{[F^2(hkl) + F^2(khl)]/2\}^{1/2}$  was used in place of  $F(hkl)$  for the calculated magnitude, and appropriate changes were made in the calculation of the derivatives. Lacking values of the standard deviations we used unit weights, as did GCCLCF. Statistics of the final results indicate that very strong and very weak reflections were overweighted somewhat. We lacked information for a valid extinction correction for the strongest reflections, and six were omitted. An approximate empirical isotropic extinction correction for the remaining 243 reflections increased each  $F_o$  by 20% or less. Refinement was on  $F$  with anisotropic thermal parameters (21 parameters including scale and extinction), scattering lengths as in GCCLCF, maximum shift/error  $10^{-5}$ ,  $R = 0.026$ ,  $wR = 0.032$ , and local unpublished programs. Final parameters are listed in Table 2.\*

### Discussion

This calculation shows that the neutron-diffraction data are explained well by twinning of the trigonal structure. The  $R$  of 0.026 for  $P\bar{3}c1$  (243 reflections and 21 parameters) is significantly less than the 0.042 (249 reflections, 25 parameters) for  $P6_3cm$ . Since  $R$  calculated for the six extra reflections in the hexagonal data set is 0.020, inclusion of them is not the reason for the larger value of  $R$ . A byproduct of this analysis is a more precise description of the

Table 3. La-F distances (Å)

La-2F (2)	2.417 (1)	La-2F (1)	2.489 (1)
La-F (3)	2.444 (1)	La-2F (1)	2.638 (1)
La-2F (1)	2.458 (1)	La-2F (1)	3.002 (1)

crystal structure (Table 2) than is given by earlier studies. The shortest La-F distances are given in Table 3. There is no significant disagreement with the X-ray results of Zalkin *et al.* (1966) nor with the neutron powder diffraction analysis of Cheetham, Fender, Fuess & Wright (1976). The thermal parameters indicate large amplitudes in the  $z$  direction for F(2) and especially F(3), the atoms which lie in the channels between the lanthanum atoms. For the other atoms the thermal motion is relatively small and less anisotropic. The only previous report of all these parameters (Mansmann, 1965) suffers from incorrect constraints on the lanthanum parameters and gives some amplitudes for fluorine which are zero within experimental error.

Spectroscopic and magnetic resonance data also support the trigonal structure, even though several authors have ignored twinning and have drawn the opposite conclusion. For example, NMR tensors measured for 'single crystals' require hexagonal symmetry in the absence of twinning. Difficulties in fitting these data to the site symmetries in  $P6_3cm$  prompted proposals of other hexagonal space groups and larger unit cells which are incompatible with the diffraction data regardless of twinning. Andersson & Johansson (1968) explained how all these data are consistent with a model of twinning of the trigonal structure. A study of the infrared spectra of crystals by Jones & Satten (1966) gives results which also fit the site symmetries of  $P\bar{3}c1$  and which cannot be reconciled with those in  $P6_3cm$ . This latter technique has the advantage that it is not affected by twinning.

We believe that the symmetry of  $\text{LaF}_3$  was shown to be  $P\bar{3}c1$  many years ago. We hope that the present note will help convince others that this crystal structure has been solved.

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\* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39744 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Twin Boundaries in Perovskite

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## Abstract

The twin behaviour of natural and synthetic perovskite ( $\text{CaTiO}_3$ ) was examined by high-resolution electron microscopy (HREM) and selected-area electron diffraction (SAD). Pseudosymmetric twinning yields domains related to each other by either a  $180^\circ$  or a  $90^\circ$  rotation about an axis perpendicular to  $\{101\}$ . A third type of twin involving a  $180^\circ$  rotation about the normal to  $(121)$  had previously been reported but this was not observed in the present study. The boundaries between twin domains were often complex and consisted of intergrowths on the finest possible scale of the various composition planes. It was confirmed that the most common composition planes were  $\{101\}$ ; however, interface surfaces on  $\{010\}$  and  $\{121\}$  were also observed. For the simpler twin boundaries structural models were proposed and described using the Glazer notation.

## Introduction

The mineral perovskite ( $\text{CaTiO}_3$ ) is the prototype of the important *perovskite* structural family whose generic stoichiometry is  $ABX_3$ . Although initially suggested to be cubic it was soon recognized that  $\text{CaTiO}_3$  possessed lower symmetry (Bowman, 1908, and references therein). Subsequent X-ray crystallographic analyses by Megaw (1946) and Kay & Bailey (1957) revealed it to be orthorhombic *Pcmm* with lattice dimensions  $a = 5.37 (= \sqrt{2}a')$ ,  $b = 7.64 (= 2a')$ ,  $c = 5.44 (= \sqrt{2}a')$  Å. The relation between the supercell

and the pseudocubic subcell is given by

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}.$$

The present transmission-electron-microscope investigation was initiated as part of a study of SYNROC, a titanate phase assemblage designed to immobilize high-level nuclear waste (Ringwood *et al.*, 1981). Perovskite is a major constituent of this waste form.

## Experimental methods

Both natural\* and synthetic perovskites were examined by selected-area diffraction (SAD) and high-resolution electron microscopy (HREM). The synthetic specimens were obtained by either cold pressing and sintering at 1573 K for 16 h in a  $\text{CO}/\text{CO}_2$  atmosphere or hot pressing at 14 MPa and 1583 K for 3 h. Perovskite as a component of SYNROC was argon ion-beam milled and examined as self-supporting foils. All other samples were prepared for study by grinding under ethanol with an agate mortar and pestle. Several drops of the suspension were placed on a holey-carbon film mounted on a copper grid. Crystallites were viewed in  $[010]$  and  $[h0l]$  zones.

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