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Space Group, Crystal Structure and Twinning of Lanthanum Trifluoride*

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Dedicated to Professor A. Rabenau on the occasion of his 60th birthday

Abstract

Crystal-structure investigations of LaF_3 crystals twinned by merohedry have been carried out with X-ray and neutron diffraction data. The twin law can be described by any one of the additional symmetry elements of point group $6/mmm$ compared to $\bar{3}m1$. The superimposed intensities were used for structure refinements. Structure parameters as well as the volume ratios for the two twin domains were determined. These structure refinements resulted in $R(I) = 0{\cdot}092$ for 666 neutron data and $R(I) = 0{\cdot}059$ for 964 X-ray data for the superimposed and observed $[I \geq 3\sigma(I)]$ intensities. Twin-volume ratios ranged from 1:1 (crystal ∅ 280 μm) to 1·7:1 (∅ 85 μm). The single-crystal domains have a centre of symmetry and crystallize in space group $P\bar{3}c1$. Similar results were found for PrF_3. Inspection of earlier structure investigations of LaF_3 crystals in the light of our results makes it very probable that these investigations have been carried out with twinned crystals with different twin-volume ratios. Furthermore, it is shown that a recently published structure refinement of LaF_3 based on a hexagonal structure model is incorrect because the diffraction data were measured from a LaF_3 twin with balanced volume ratio.

Introduction

The mineral LaF_3, the most remarkable representative of rare-earth trifluorides with the tysonite structure, exhibits a very high F^- conductivity (Schoonman, Oversluizen & Wapenaar, 1980). This has stimulated considerable interest in the refinement of its crystal structure.

A large number of rare-earth trifluorides of composition LnF_3 (Ln: La-Sm) crystallize in the tysonite structure type. Various papers are devoted to structural investigations of these minerals resulting in discrepancies in the space group. Thus, Schlyter (1952) investigated the crystal structure of the natural mineral (La,Ce)F_3 in space group $P6_3/mmc$ (D^6_{3h}) with the unit-cell dimensions $a = b = 4{\cdot}15$, $c = 7{\cdot}35$ Å with two formula units per elementary cell. Other authors (Oftedal, 1929, 1931; Mansmann, 1965; Zalkin, Templeton & Hopkins, 1966) report a larger unit cell ($a' = a\sqrt{3}$, $c' = c$, H cell) with six formula units per cell due to weak additional reflections. The transformation matrix between the two cells can be described by $(a, b, c) = (\frac{1}{3}, -\frac{1}{3}, 0; \frac{1}{3}, \frac{2}{3}, 0; 0, 0, 1)(a', b', c')$. The large elementary cell and space group $P6_3/mcm$ (D^3_{6h}) were used for the interpretation of NMR data (Afanasiev, Habuda & Lundin, 1972; Goldman & Shen, 1966). Andersson & Proctor (1968) as well as de Rango, Tsoucaris & Zelwer (1966) used the space group $P6_3cm$ (C^3_{6v}) for some tysonite-like structures including LaF_3.

The trigonal space group $P\bar{3}c1$ (D^4_{3d}) was used in structure investigations based on X-ray diffraction with a LaF_3 crystal (Mansmann, 1965; Zalkin, Templeton & Hopkins 1966). These authors gave an explanation of the weak superstructure reflections: the arrangement of the La atoms is very close to the small elementary cell (a, c) and to the corresponding space group $P6_3/mmc$. This pseudosymmetry of the La atoms is strongly violated by the arrangement of the F atoms. Therefore the X-ray diffraction pattern of LaF_3 is subdivided into strong main reflections mainly caused by La atoms with their high X-ray scattering power and weak additional reflections mainly caused by the F atoms with their weak X-ray scattering power. This X-ray diffraction effect disappears in neutron-diffraction experiments (see below). This trigonal LaF_3 structure model was confirmed in a structure refinement with neutron powder data (Cheetham, Fender, Fuess & Wright 1976). Johansson & Proctor (1968) assumed twinning of LaF_3, but found no way to confirm this supposition. Recently Gregson, Catlow, Chadwick, Lander, Cormack &

* *Editorial note:* Two previous papers by the present authors on LaF_3 were originally submitted and are summarized here for brevity. Both papers have been deposited in full, see deposition footnote. The reader's attention is also drawn to the following paper by Zalkin & Templeton (1985).

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Fender (1983) published a structure refinement of LaF_3 based upon the hexagonal structure model of de Rango *et al.* (1966). The discrepancy in the results obtained from these several structure investigations served as an impetus for carrying out the present work.

Reflection symmetry

2505 X-ray data ($\sin\theta/\lambda \le 1{\cdot}0$ Å^{-1}, $\lambda = 0{\cdot}56$ Å, crystal-sphere diameter 85 μm) and 2169 neutron data ($\sin\theta/\lambda \le 0{\cdot}89$ Å^{-1}, $\lambda = 0{\cdot}92$ Å, crystal-sphere diameter 280 μm) were measured from LaF_3 crystals on four-circle diffractometers. Details of the intensity measurements and data treatment are deposited. The 'main reflections' $h-k=3n$ showed hexagonal symmetry $6/mmm$ for the neutron as well as the X-ray measurements. This was in contrast to the reflections with $h-k\neq 3n$, when only the neutron data obeyed $6/mmm$. For the X-ray data the reflection symmetry had to be lowered to $\bar{3}m1$. Neutron and X-ray data were averaged with the Laue symmetry $\bar{3}m1$.

Structure investigations

The structure investigations were started with the trigonal structure model of Mansmann (1965) and Zalkin *et al.* (1966) despite the fact that the neutron data obeyed perfect hexagonal $6/mmm$ symmetry and the X-ray data revealed only weak deviations from this symmetry. However, the structure refinements failed. They resulted in $R = 0{\cdot}20$ for neutron data and $R = 0{\cdot}075$ for X-ray data (calculated with F_{hkl} not with intensity values!). In both cases some refined parameters were physically meaningless; for example, occupation probabilities were much larger than one.

The failure of the structure refinements as well as the discrepancy between the trigonal LaF_3 structure model and the hexagonal diffraction symmetry compelled us to assume a twinning process, involving an increase of the Laue symmetry from $\bar{3}m1$ to $6/mmm$ without changing the lattice constants. This can happen if the twin symmetry element belongs to the symmetry elements of the lattice, but not to the Laue group of the crystal. Such twinning by merohedry has been investigated by Donnay & Donnay (1974), Catti & Ferraris (1976), Klapper & Hahn (1979), Hahn (1981) and Rees (1982). In our case the lattice symmetry and the Laue symmetry are equal to $6/mmm$ and $\bar{3}m1$, respectively.

For LaF_3, only two orientations of twin domains are generated independently of the twin symmetry element applied. Reflections not related by Laue symmetry $\bar{3}m1$ are superimposed by application of the twin elements on the diffraction pattern. The superimposed reflections change their intensity as a function of the ratio V_1/V_2 of the twin domains 1 and 2. The Laue symmetry $\bar{3}m1$ is kept for $V_1/V_2 \neq 1$. It changes to $6/mmm$ for $V_1/V_2 = 1$.

However, *hk*.0 and *hh.l* reflections are not falsified by the twinning. Therefore these reflections were used for a standard least-squares refinement. Now all refined parameters were physically meaningful. The refinements converged with anisotropic temperature factors at $R = 0{\cdot}023$ for neutron data and at $R = 0{\cdot}021$ for X-ray data. This confirms the suggested twin law of the LaF_3 crystals.

The structure investigations were continued with a least-squares program for twinned crystals. This program (Perenthaler, 1980) minimizes $\Delta I^2 = (I_o - I_c)^2$, where I_o are the observed superimposed intensities and I_c the calculated superimposed intensities. The program refined the coordinates (xyz), an isotropic B for each atomic position and the volume parts V_1 and V_2. Final R values and V_1/V_2 ratios are listed in the *Abstract*.

The superimposed intensities were then transformed into single-crystal intensities by means of the refined V_1/V_2 ratio. The data sets so obtained were used for standard crystal-structure refinements with anisotropic temperature factors using the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). Weights were calculated from the $\sigma(I)$ of the superimposed intensities by means of the refined volume ratios. The final reliability values based on all F values were $R = 0{\cdot}034$, $R_w = 0{\cdot}038$ for X-ray data and $R = 0{\cdot}051$, $R_w = 0{\cdot}057$ for neutron data. Atomic parameters* and magnitudes and orientations of the thermal vibrational ellipsoids derived from the neutron data are listed in Tables 1 and 2. The coordinates differ by less than three pooled standard deviations from those of Zalkin & Templeton (1985).

Finally, we have carried out structure investigations on another batch of LaF_3 crystals and also on a PrF_3 crystal. Both crystals were twinned with twin ratios 1·3 and 3·8, respectively. Therefore, we conclude that the possibility of LaF_3 microtwinning is not something unique but is inherent in the whole class of tysonite-like compounds. Mansmann (1965) carried out his structure investigation with a twinned crystal as his published structure factors show. A similar

* The following material has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39742 (59 pp.): Extended versions of this manuscript, lists of the measured detwinned structure factors and calculated structure factors (X-ray and neutron diffraction), the coefficients of the corresponding anisotropic temperature factors, the results of structure refinements with the hexagonal structure model and the corresponding lists of structure factors for the complete data sets of observed neutron-diffraction data and calculated twin intensities, structure parameters and lists of structure factors for refinements of the observed *hk*0 and *hhl* neutron data with the hexagonal and trigonal structure model. Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structure parameters from neutron data (with standard deviations in parentheses)*

	Occupation probability	x	y	z	B(Å^2)
La	1·00	0·66018 (8)	0	$\frac{1}{4}$	0·43 (1)
F(1)	0·98 (1)	0·3659 (1)	0·0537 (2)	0·0814 (1)	1·06 (2)
F(2)	0·97 (2)	$\frac{1}{3}$	$\frac{2}{3}$	0·1867 (2)	0·75 (2)
F(3)	0·98 (2)	0	0	$\frac{1}{4}$	1·09 (2)

comparison makes it very probable that Zalkin *et al.* (1966) used a single crystal with a twin ratio V_1/V_2 greater than 10.

The hexagonal LaF_3 structure model

The interpretation of LaF_3 crystal diffraction data by Gregson *et al.* (1983) is in clear contradiction to our interpretation although the R values are reasonable in both cases. We have hence continued our structure investigation to find the reason for this behaviour.

All reflection intensities in common measured by Gregson *et al.* (1983) and in this study were placed on the same scale. The resulting $R(I_o) = \sum |\Delta I| / \sum I_o = 0{\cdot}06$ shows that both groups have used similar material for their diffraction experiments.

The *hk*0 and *hhl* reflections are not influenced by twinning (see above): Therefore only these reflections allow a distinction between the hexagonal and trigonal structure model without considering the effects of twinning. The hexagonal structure model gave $R(F) = 0{\cdot}043$ and $R_w(F) = 0{\cdot}047$ for 100 reflections and 25 parameters. These R values have to be compared with $R(F) = 0{\cdot}023$ and $R_w(F) = 0{\cdot}025$ for only 20 structure parameters of the trigonal structure model. The Hamilton (1965) test shows that for 100 reflections, $R_w(F) = 0{\cdot}025$ for 20 structure parameters is significantly better than $R_w(F) = 0{\cdot}047$ for 25 parameters.

Using our trigonal structure parameters we calculated structure factors $F(hkl)$ with $h, k \geq 0$ in a model calculation with all structure factors used by Gregson *et al.* (1983); we superimposed them to give

$$F^2_{\text{twin}}(hkl) = [F^2_c(hkl) + F^2_c(hk\bar{l})]/2.$$

In this way the symmetry of the calculated reciprocal space changed from $\bar{3}m1$ to $6/mmm$. The superimposed structure factors correspond to a crystal twinned by merohedry with equal volume for each twin arrangement. Each ordered twin domain crystallizes in $P\bar{3}c1$. These F_{twin} were now considered as observed structure factors and the single-crystal structure model of Gregson *et al.* (1983) refined with these twin data. The scale factor was kept fixed and no extinction correction was used. The refinement converged at $R(F) = 0{\cdot}041$, as compared with $R(F_o) = 0{\cdot}045$ for the same refinement of Gregson *et al.* (1983) with the observed intensities. Good agreement was also found for the structure parameters from both refinements which deviate by a maximum from each other of four standard deviations.

Table 2. *Main axes of the thermal vibrational ellipsoids and their orientation referred to crystallographic axes (with standard deviations in parentheses)*

Estimated error of the angles: 10°.

	R.m.s. amplitude (Å)	Orientation referred to crystallographic axes (°) a	b	c
	0·066 (2)	90	97	6
La	0·071 (2)	180	60	90
	0·083 (2)	90	30	82
	0·104 (2)	106	47	44
F(1)	0·106 (3)	126	44	130
	0·135 (2)	139	99	77
F(2)	0·085 (3)	—	—	90
	0·118 (2)	90	90	0
F(3)	0·099 (3)	—	—	90
	0·147 (3)	90	90	0

The above results show unambiguously that LaF_3 crystallizes in the trigonal structure model proposed by Mansmann (1965) and Zalkin *et al.* (1966) and that LaF_3 strongly tends to twin.

Centre of symmetry

Physical measurements make it very probable that LaF_3 crystallizes in a centrosymmetric space group: The crystals do not possess a piezoelectric effect (Oftedal, 1931). Second harmonics cannot be generated (Haussühl, 1984). We have also tried to answer with our data the question of the centre of symmetry in this structure. All structure refinements above assume the centrosymmetric space group $P\bar{3}c1$. Three anisotropic temperature factor coefficients refined to rather large values: U_{33}[F(3)], U_{33}[F(2)] and U_{11}[F(1)] > 0·02 Å^2. We could not exclude the possibility that a part of these coefficients may be artificially caused by using a centrosymmetric space group and have therefore tried to reduce the space-group symmetry to $P3c1$. The large coefficients U_{ij} of F(1), F(2) and F(3) can be used to calculate appropriate magnitudes and directions of shifts to destroy the centre of symmetry. This results in four noncentrosymmetric structure models. Each was refined with the *hk*0 and *hhl* data and isotropic temperature factors, but none gave any hint in support of a noncentrosymmetric space group.

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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 LaF_3 [Gregson, Catlow, Chadwick, Lander, Cormack & Fender (1983). *Acta Cryst.* B**39**, 687-691] are refined in space group $P\bar{3}c1$ with a model which accounts for the effects of twinning. $R = 0{\cdot}026$ 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° 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* LaF_3 (*Zalkin, Templeton & Hopkins*, 1966)

hkl	*F*(*hkl*)		*F*(*khl*)	
	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.

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