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The Structure of LaF_3 – A Single-Crystal Neutron Diffraction Study at Room Temperature

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Abstract

A single-crystal neutron diffraction study at room temperature has been carried out to examine the ambiguity in the space group for LaF_3, which cannot be resolved by neutron powder diffraction. With $P6_3cm$ an R factor of 0·042 (249 unique reflections) was obtained compared with a corresponding value of 0·136 for $P\bar{3}c1$. Marked anisotropy is observed in the thermal parameters of two of the F atoms, which may be correlated with the positions of near-neighbour atoms.

Introduction

The tysonite structure is still not unambiguously established. There have been a number of reports where various space groups have been proposed; these include $P\bar{3}c1$, suggested by Mansmann (1965) and Zalkin, Templeton & Hopkins (1966), $P6_3/mcm$ (Oftedal, 1929, 1931) and $P6_3cm$ proposed by de Rango, Tsoucaris & Zelwer (1966), where the number of molecular units per unit cell (Z) is six. There have also been suggestions for $Z = 12$ in the $P6_3/mcm$ space group by Sher, Solomon, Lee & Müller (1966) from NMR studies, and for $Z = 2$ in $P6_3/mmc$ (Schlyter, 1952) from X-ray diffraction. There are several reasons why it is important to establish the correct structure.

LaF_3 is frequently used as a non-magnetic host for spectroscopic investigations of paramagnetic lanthanide ions and LaF_3 itself is a good ionic conductor with interesting high-temperature properties. Above ~1000 K it has an anomalously high heat capacity (Lyon, Osborne, Flotow & Grandjean, 1978) and one of the highest known ionic conductivities (Chadwick, 1982). In a previous powder neutron diffraction study by

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Cheetham, Fender, Fuess & Wright (1976) the choice of structure was narrowed to the space groups $P\bar{3}c1$ and $P6_3cm$ but the powder diffraction results, although giving a good fit to the data, were unable to distinguish between the two alternatives. Because of a reported absence of piezo- and pyroelectric effects, the centrosymmetric space group $P\bar{3}c1$ appeared the more likely. More recently a single-crystal electron diffraction study by Greis & Bevan (1978) indicates a $Z = 6$ supercell (the observed reflections are the same for the three space groups given above) but they also suggest that LaF$_3$ may sometimes crystallize in the space group $P6_3/mmc$ ($Z = 2$). Our present interest is, in fact, concerned with the high-temperature structure and behaviour of LaF$_3$, but we report here a room-temperature neutron diffraction study which clearly demonstrates that the space group $P6_3cm$, first proposed by de Rango *et al.*, is to be preferred.

Experimental

Data collection

A cylindrical single crystal of LaF$_3$ (height 4 mm, diameter 2 mm), grown by one of us (A. V. Chadwick) at the University of Kent was examined under normal-beam geometry on the D15 diffractometer at the Institut Laue–Langevin. The crystal, one of a batch of similar crystals, was grown by a modified Stockbarger technique using graphite crucibles (Ultra Carbon, UF 4S grade, purity 99·9995%) under argon (BOC Ltd). The starting material was LaF$_3$ powder (Rare Earth Products, purity 99·99%) containing 2% by weight PbF$_2$ (BDH 'Optran' grade), the latter material acting as a 'scavenger' for oxygen. A growth rate of 2 mm h^{-1} was employed and the crucible was cooled directly to room temperature following the growth without any high-temperature annealing. The crystals were optically clear with no evidence of translucence indicating an oxide content of less than 20 p.p.m. (Garton & Walker, 1978). Chemical analyses were not performed on the grown crystals but electrical-conductivity measurements indicated that the growth procedures had not introduced impurities into the starting material.

The wavelength used was 1·176 Å, obtained from the (331) planes of a Cu monochromator using a take-off angle of 45°. 2θ scans of width 2° with 25 steps of 0·08° were employed and altogether 763 reflections were measured. Absorption was negligible and a careful examination of equivalent reflections demonstrated that the crystal was well centred. For example, seven reflections of the 232 type gave a standard error of 0·6% on the mean structure factor. The $\lambda/2$ component of the primary beam was neglected in subsequent refinements. Multiple-scattering effects are somewhat larger but the combined effects are still small and can be ignored.

Data reduction and refinement

Data reduction was carried out by using the Lehmann & Larsen (1974) method which uses the minimum $\sigma(I)/I$ criterion for judging the extent of the elastically scattered radiation. Reflections of the type $hh\bar{i}l$ with l odd were systematically absent – as expected for $P\bar{3}c1$ and $P6_3cm$ – and were not included in the refinement which was based on 249 unique reflections. Refinements were carried out using the Cambridge Crystallographic Sub-routine Library (Matthewman, Thompson & Brown, 1982) with scattering lengths for La and F of 8·3 and 5·65 fm respectively. The residual, R, is defined as: $R = \sum||F_o| - |F_c||/\sum |F_o|$.

Results and discussion

Space group $P\bar{3}c1$ or $P6_3cm$?

We used the neutron powder results of Cheetham *et al.* to eliminate the space group $P6_3/mcm$. Taking the lattice parameters of Zalkin *et al.* ($a = 7{\cdot}185$, $c = 7{\cdot}351$ Å), full-matrix least-squares refinements with anisotropic temperature factors were carried out for both the space groups unresolved by the powder neutron diffraction data. The starting parameters for $P6_3cm$ were derived from de Rango *et al.* and those for $P\bar{3}c1$ from Cheetham *et al.* With the strongest 20 reflections which were strongly affected by extinction omitted, the former refined to an R value of 0·06, the latter to 0·20, demonstrating unambiguously that the space group at room temperature is not $P\bar{3}c1$.

An isotropic-extinction correction [Becker & Coppens (1974) type I, Lorentzian model] was made using all reflections. The domain radius was fixed at 100 μm and the (isotropic) mosaic spread allowed to refine with the atomic parameters and scale factor to give a final R factor in $P6_3cm$ of 0·045.* The use of weights inversely proportional to the variance of F_{hkl} caused no significant change in the value of the residual so unit weighting was retained. At convergence all shifts were zero. A similar extinction correction applied in the space group $P\bar{3}c1$ gave an R factor no better than 0·136.

Atomic parameters

The final atomic parameters are presented in Table 1 for the structure given in Fig. 1. The positions of the La and four F atoms are quite close to those observed

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38745 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters in* $P6_3cm$

La: z parameter fixed at 0·25 to define origin; B parameters in Å². T.F. = $\exp(-\frac{1}{4}\sum_i\sum_j B_{ij}h_ih_ja_i^*a_j^*)$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
La	0·6742 (2)	0	0·25	0·53 (3)	0·41 (4)	0·66 (4)	$0{\cdot}5B_{22}$	0·01 (3)	0
F(1)	0	0	0·3209 (7)	B_{22}	0·62 (6)	0·63 (10)	$0{\cdot}5B_{22}$	0	0
F(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·2187 (7)	B_{22}	0·73 (5)	4·6 (3)	$0{\cdot}5B_{22}$	0	0
F(3)	0·2857 (4)	0	0·0810 (6)	1·40 (6)	1·97 (9)	0·51 (7)	$0{\cdot}5B_{22}$	−0·01 (7)	0
F(4)	0·3724 (3)	0	0·4185 (6)	1·43 (6)	3·9 (2)	0·57 (8)	$0{\cdot}5B_{22}$	0·23 (7)	0

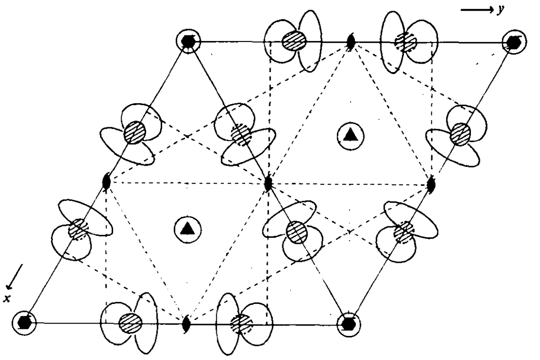

Fig. 1. The LaF_3 structure in $P6_3cm$. Hatched ellipses represent La atoms, and those enclosed by broken lines indicate La atoms obscured by F atoms. The F(1) atoms lie on the $\bar{6}_3$ axis, the F(2) atoms on the threefold axis; the F(3) and F(4) atoms lie on the mirror plane, F(3) atoms being represented by the more isotropic of the ellipses. The principal axes of the ellipsoids (also in Figs. 2–6) have lengths equal to $3{\cdot}0\,(\langle u_i^2\rangle)^{1/2}$, $i = x, y, z$; that is, equal to three times the r.m.s. displacements along the principal axes.

by de Rango *et al.* The present study allows, however, a full analysis of the thermal parameters and the results indicate a strong anisotropy of thermal motion parallel to the z axis for the atom F(2) and a similar large anisotropy parallel to the xy plane for F(4). These anisotropies are illustrated in Figs. 4 and 6. Fig. 2 shows the F coordination of a La atom, and Figs. 3–6 inclusive how the near-neighbour positions around the four F atoms. Examination of the chemical environments of F(1) (Fig. 3) and F(2) (Fig. 4), both of which lie in tunnels defined by La atoms and neighbouring F atoms, shows that F(2) is less restrained in the z direction than is F(1) (see Fig. 7), and this provides a plausible explanation for the relatively large thermal motion in the z direction. It is less easy to account for the large B_{22} parameter of the F(4) atom but it is certainly possible that this motion normal to z is correlated with the large B_{33} parameter of F(2). Although we can only speculate at present, it is likely that the large thermal motions are associated with the unusually high room-temperature mobility of the F^- ion.

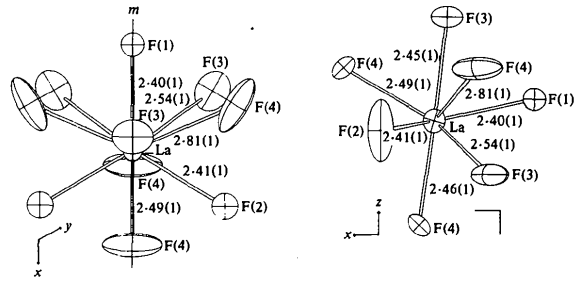

Fig. 2. Environment of the La atom (distances in Å).

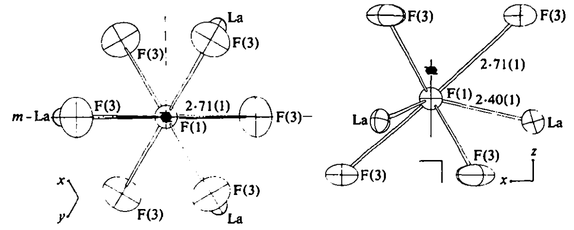

Fig. 3. Environment of the F(1) atom (distances in Å).

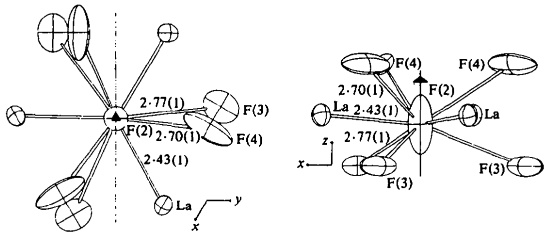

Fig. 4. Environment of the F(2) atom (distances in Å).

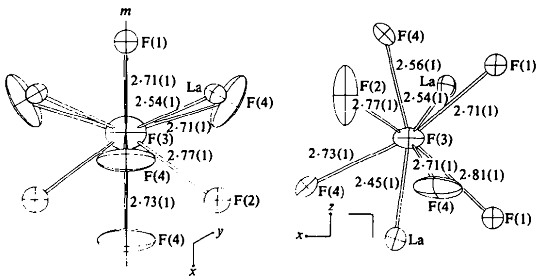

Fig. 5. Environment of the F(3) atom (distances in Å).

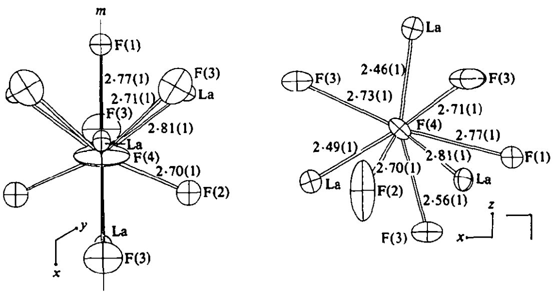

Fig. 6. Environment of the F(4) atom (distances in Å).

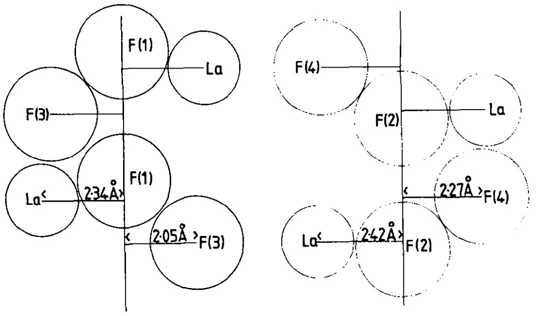

Fig. 7. View of channels for F(1) and F(2) in the xy plane.

Table 2. *Interatomic potentials used in lattice-energy calculations* [*potential of the form* $V = A \exp(-r/\rho) - C/r^6$]

(*a*) Interaction

	A (eV)*	ρ (Å)	C (eV Å^6)*
La···La	53317·72	0·22068	0·0
La···F	6686·86	0·26055	0·0
F···F	7236·47	0·28028	148·853

(*b*) Shell parameters

	Charge (e)	Spring constant (eV Å^{-2})*
La	6·58698	105·496
F	−2·380	101·200

* 1 eV ≡ 1·60 × 10^{-19} J.

Lattice-energy calculations

One of the puzzling features of the LaF$_3$ structure is the inability of powder diffraction experiments to distinguish between space groups $P\bar{3}c1$ and $P6_3cm$. This suggests a similarity of atom spacings which ought to be reflected in similar lattice energies.

The lattice energies of the two structures have been calculated, therefore, using methods which have been described elsewhere (Catlow & Norgett, 1976; Catlow & Mackrodt, 1982). Details of their application to LaF$_3$, including defect-energy calculations, are available separately (Cormack, Walker & Catlow, 1983). In essence, the Born model of the solid is used with appropriate short-range potentials which are given in Table 2. Table 3 summarizes the results of these calculations.

Table 3. *Lattice energies of different* LaF$_3$ *structures*

Positional parameter employed (space group)	Lattice energy (eV)*
Oftedal ($P6_3mcm$)	307·4
de Rango *et al.* ($P6_3cm$)	307·7
This paper ($P6_3cm$)	308·2
Zalkin *et al.* ($P\bar{3}c1$)	308·4

* 1 eV = 1·60 × 10^{-19} J.

Table 4. *Predicted positional parameters for the* LaF$_3$ *structure*

From Cormack, Walker & Catlow (1983). See text for method of calculation.

	x	y	z
La	0·6740	0	0·2500
F(1)	0	0	0·3218
F(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·2094
F(3)	0·2717	0	0·0806
F(4)	0·3900	0	0·4286

The surprising conclusion is that the lattice energies of the two different structures are indeed *very* close. We note, however, that with the original de Rango parameters the lattice energy is significantly smaller, presumably reflecting the slightly less accurate positional parameters in this earlier study. Finally, we record that the high-symmetry $P6/mcm$ structure proposed by Oftedal is less stable and that beginning with this structure and allowing the atoms to relax from the ideal sites until the minimum-energy configuration is attained leads to the $P6_3cm$ structure.

In this case the positional parameters are determined solely by the interatomic potentials and are indeed close to those reported above, as shown in Table 4. We note that the predicted stability of the $P6_3cm$ structure over $P\bar{3}c1$ is, however, very small, and may be within the errors associated with the choice of atomic potentials.

Conclusions

The present studies show that a single-crystal examination is essential for LaF$_3$. It is also evident that, because the differences between the various models are associated with the F positions, neutron diffraction is a valuable, indeed necessary, method for the very accurate determination of the F parameters. The scattering-length ratio of La:F is 1·5:1 for neutrons but 5·4 : 1 for X-rays, so the F positions are much more easily located by neutrons. Of the earlier crystallographic studies which give three different types of F, the studies of Oftedal (1929, 1931), Mansmann (1965) and Zalkin, Templeton & Hopkins (1966) were by X-rays only, but de Rango, Tsoucaris & Zelwer (1966) used neutrons as well as X-rays to make the space-group assignment which has four different crystallographic F atoms. There remains a puzzle as to why Schlyter (1952) with X-rays and Greis & Bevan (1978) with electrons have observed at least a few crystals with $Z = 2$, *i.e.* without the superlattice reflections associated with $Z = 6$. It is possible that the more disordered structure is associated with a different level of chemical impurity or as a frozen-in high-temperature form. However, to at least 923 K we have shown that the space group $P6_3cm$ is retained (unpublished results).

Can we then be certain that $P6_3cm$ is the correct space group for room-temperature LaF_3? A small uncertainty remains until the anisotropic temperature factors are measured over a range of temperatures. Until we have this temperature dependence, the possibility that the observed high B values for F(2) and F(4) atoms mask a very small distortion of the $P6_3cm$ structure cannot be entirely ruled out. The presence of multiple-scattering effects precludes a straightforward search for extremely weak reflections forbidden in $P6_3cm$. A more serious criticism of the choice of this noncentrosymmetric space group is the reported absence of a piezoelectric effect (Mansmann, 1965). We have also, therefore, tried to measure a piezoelectric coefficient but like Mansmann find no evidence for a positive effect. We note, however, that the effect is likely to be small and could easily be masked by the relatively high room-temperature conductivity of the crystals we examined.

We thank Mr J. Broomfield of AERE Harwell for making the piezoelectric measurements.

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