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The Atomic Parameters in the Lanthanum Trifluoride Structure[1]

BY ALLAN ZALKIN, DAVID H. TEMPLETON, AND TED E. HOPKINS

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Crystals of LaF_3 exhibit a structure which is typical of numerous trifluorides of lanthanide and actinide elements. In 1931 Oftedal[2] suggested a structure, based on a study of crystals of the mineral tysonite, with the assumption that the space group is $P6_3/mcm$, but with atomic coordinates which correspond almost to the symmetry $P6_3/mmc$ with a smaller unit cell. The evidence for the larger cell is the presence of weak reflections which may easily escape detection in powder diagrams. Schlyter[3] failed to see these reflections with tysonite crystals, but Templeton and Dauben[4] found them with a synthetic crystal of CeF_3. The atomic positions given by Oftedal give lanthanum a peculiar coordination geometry with five nearest neighbors and six more neighbors at a greater distance.

We were prompted to study LaF_3 again by the availability of excellent synthetic crystals and recent interest in the spectroscopic properties of ions in this structure. When we had nearly finished the determination of the structure, we learned that Mansmann[5] had independently reached the same conclusions concerning the symmetry and assignment of atoms to point sets, without reporting atomic coordinates.

We conclude that Oftedal's cell is correct and that his coordinates for La are quite accurate, but that the crystals are trigonal rather than hexagonal. Because of his failure to recognize this point symmetry, Oftedal did not consider the correct space group, and he misplaced most of the F atoms. In our structure, each La is on a twofold axis and has nine neighbors (a normal number) at nearly equal distances.

Experimental Section

A large crystal of lanthanum trifluoride, purported to be 99.999% pure, was sent to us by Dr. Kenneth Lee of Varian Associates in Palo Alto, Calif. A fragment of this crystal about 0.1 to 0.2 mm in size was glued to the end of a Pyrex fiber with the hexagonal axis parallel to the fiber axis. The crystal was dipped into liquid nitrogen rapidly several times in an attempt to diminish extinction effects by increasing the mosaic spread by thermal shock, but no effect was observed in the intensities before and after the treatment. Diffraction angles and intensities were measured with an Eulerian cradle goniostat equipped with a scintillation counter using Mo $K\alpha$ radiation ($\lambda(K\alpha_1)$ 0.70926 A). The cell dimensions measured at 22° are $a = 7.185 \pm 0.001$ and $c = 7.351 \pm 0.001$ A, in excellent agreement with the values reported by Swanson, *et al.*[6] The density calculated with 6 molecules per cell is 5.938 g/ml.

The diffraction intensities correspond to Laue symmetry $\bar{3}m1$, but there are clear violations of symmetry 6/mmm and 6/m; *i.e.*, $I(hkl) = I(h + k, -k, l)$, but $I(hkl) \neq I(-k, h + k, l)$. Thus, the crystals are trigonal rather than hexagonal (in the strict sense). The failure of previous workers to recognize the lower symmetry may be the result of twinning in their specimens or the result of low accuracy of intensities estimated from films.

We failed to detect any pyroelectric effect when a large crystal fragment, suspended on a thread, was dipped into liquid nitrogen; when withdrawn, the crystal showed no attraction for the side of the dewar. The systematic absences, $(h0l)$ absent if $l = 2n + 1$, correspond to space groups P3c1 and $P\bar{3}c1$. We conclude that the crystals are centric because a reasonable structure is found in space group $P\bar{3}c1$ (D_{3d}^4), No. 165 in the "International Tables."[7]

The intensity measurements included 914 independent reflections (all positive hkl with $2\theta < 90°$) of which 63 were recorded as zero. The data were corrected for the Lorentz-polarization effects. The absorption factor μ was estimated to be ~ 200 cm^{-1}, and the μR for the crystal was estimated to be ~ 2. The data were not corrected for absorption. An empirical extinction correction was made based on an approximation suggested by Zachariasen[8] where $F_c \approx F_o(1.0 + CJ)$, where F is the scaled structure factor, J is the raw observed intensity, and C is an adjustable constant.

The structure given by Oftedal[2] can be fitted to space group $P\bar{3}c1$ by assigning the atoms to point sets as listed in Table I. Prior to the extinction correction, we attempted to refine this structure with a full-matrix, least-squares program, with trial-and-error displacements of various atoms to break the higher symmetry. The first set of refinements went poorly; *i.e.*, the R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, stayed high ($\sim 0.15$) and the temperature factor for the twofold fluorine "blew up." Different trial structures and the use of a noncentric space group (P3c1) gave even worse results. We observed what appeared to be severe extinction effects, and, by deleting some low-angle data which included some of the larger intensities, definite improvement in the refinement resulted. A plot of F_o/F_c (observed and calculated structure factors) *vs.* the intensities showed a very definite extinction-type correlation. From this plot a value for C in the extinction correction was obtained, and then it was adjusted in the least-squares refinement. The extinction was so severe that the two most intense reflections were observed to be one-eighth of their calculated values. In the final refinements the anomalous dispersion factors for La^{3+} were included ($\Delta f' = -0.4$, $\Delta f'' = 2.9$ electrons).[9] An anisotropic temperature factor of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ was applied to lanthanum, with suitable constraints because of the twofold axis, and an isotropic temperature factor of the form $\exp[-(B \sin^2\theta/\lambda^2)]$ was applied to each fluorine. The five most intense reflections and seven of the reflections with the worst

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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(3) K. Schlyter, *Arkiv Kemi*, **5**, 73 (1953).

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(7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1952, p 271.

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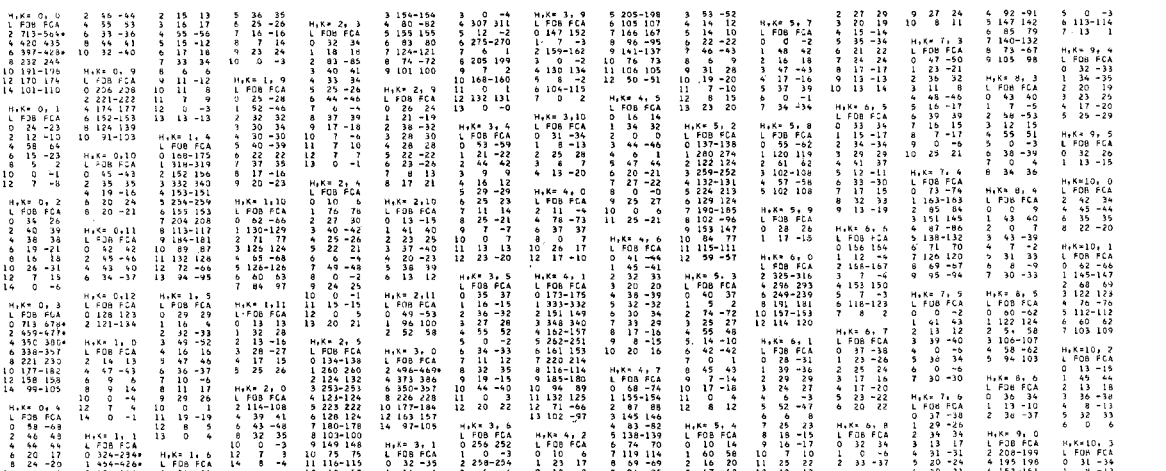
TABLE I

OBSERVED[a] AND CALCULATED STRUCTURE FACTORS (×2.0) FOR LANTHANUM TRIFLUORIDE[b]



[a] The observed FOB = $S\sqrt{JLp}(1.0 + CJ)$, where S is the over-all scaling factor from least squares of 10.826, J is the raw intensity corrected for background, Lp is the Lorentz-polarization correction, and C is the extinction correction factor of 0.000464. [b] The asterisked data in the FCA column are those given zero weighting in the least-squares calculation.

TABLE II

POSITIONAL PARAMETERS IN LANTHANUM TRIFLUORIDE

No.	Atom	Point symmetry	Positions and postional parameters
6	La	2	$\pm(x, 0, 1/4;\ 0, x, 1/4;\ \bar{x}, \bar{x}, 1/4)$ $x = 0.3401 \pm 0.0005$
12	F(1)	1	$\pm(x, y, z;\ \bar{y}, x - y, z;\ y - x, \bar{x}, z;$ $\bar{y}, \bar{x}, 1/2 + z;\ x, x - y, 1/2 + z;$ $y - x, y, 1/2 + z)$ $x = 0.312 \pm 0.002$ $y = -0.005 \pm 0.002$ $z = 0.581 \pm 0.002$
4	F(2)	3	$\pm(1/3, 2/3, z;\ 1/3, 2/3, 1/2 + z)$ $z = 0.313 \pm 0.002$
2	F(3)	32	$\pm(0, 0, 1/4)$

TABLE III

TEMPERATURE FACTORS (A^2)[a] IN LANTHANUM TRIFLUORIDE

Atom	Temp factors		
La	$B_{11} = 0.6 \pm 0.2$	$B_{22} = 0.6 \pm 0.2$	$B_{33} = 0.8 \pm 0.2$
	$B_{12} = 0.3$[b]	$B_{13} = -0.025$[b]	$B_{23} = -0.05 \pm 0.01$
F(1)	$B = 1.3 \pm 0.4$		
F(2)	$B = 1.0 \pm 0.4$		
F(3)	$B = 1.7 \pm 0.7$		

[a] Anisotropic $B_{ij} = \beta_{ij}/4a^*_i a^*_j$, where a^*_i is the ith reciprocal axis length. [b] Symmetry considerations force $B_{22} = 2B_{12}$ and $B_{23} = 2B_{13}$.

agreement were deleted from the final refinements. The final R factor was 0.052. The observed and calculated structure factors are shown in Table I.

Results

Tables II and III show the final positional and thermal parameters, respectively. The standard deviations shown in Tables II and III are estimates by the authors rather than the results of the least squares and in all cases are considerably larger than the calculated values. These estimates resulted from a study of the parameters as conditions of the refinement were modified. The parameters changed considerably more

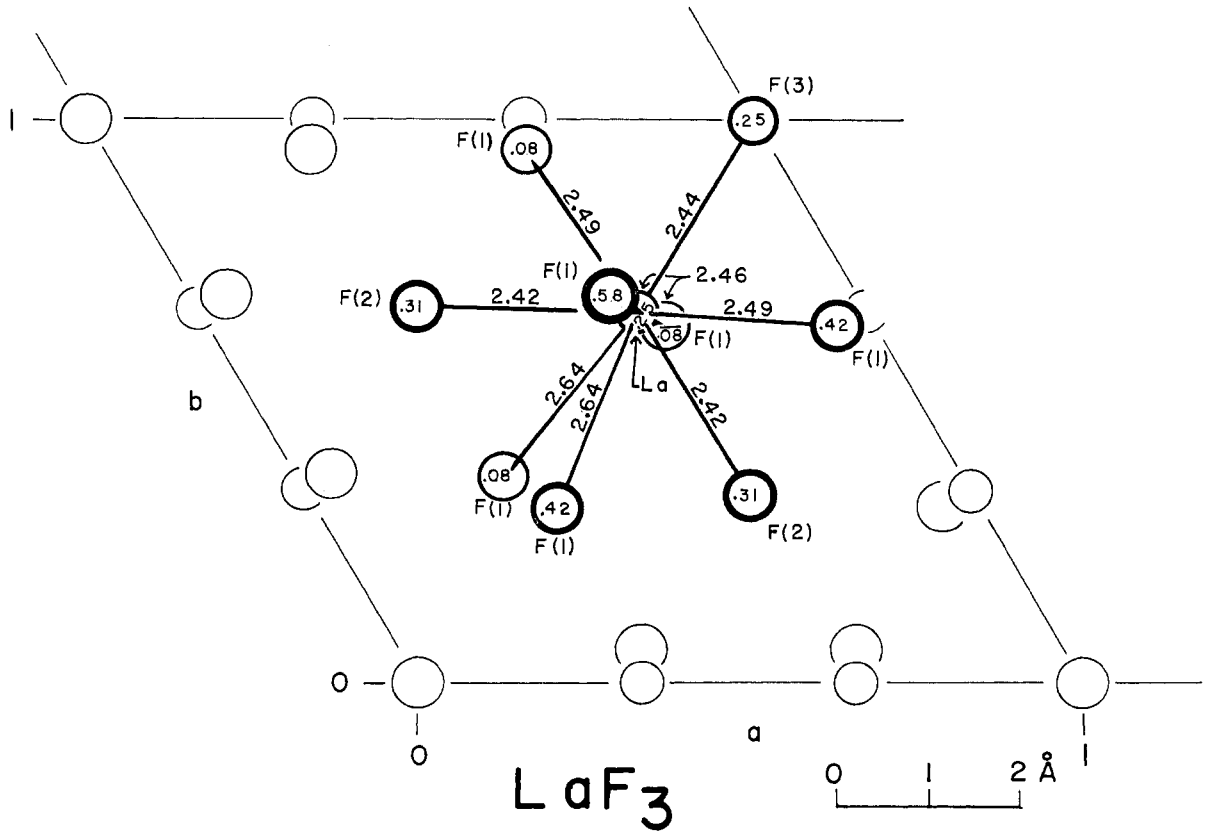


Figure 1.—The ninefold coordination of lanthanum in lanthanum trifluoride as viewed down the *c* axis.

TABLE IV
INTERATOMIC DISTANCES OF LESS THAN 3 A IN LANTHANUM TRIFLUORIDE

Atoms	Distance, A	Atoms	Distance, A
La-2F(2)	2.416 ± 0.003	F(1)-1F(2)	2.69 ± 0.02
La-1F(3)	2.443 ± 0.004	F(1)-2F(1)	2.74 ± 0.02
La-2F(1)	2.46 ± 0.02	F(1)-1F(3)	2.76 ± 0.01
La-2F(1)	2.49 ± 0.01	F(1)-1F(2)	2.79 ± 0.01
La-2F(1)	2.64 ± 0.01	F(1)-1F(2)	2.87 ± 0.02
La-2F(1)	3.01 ± 0.01	F(2)-3La	2.416 ± 0.003
F(1)-1La	2.46 ± 0.02	F(2)-3F(1)	2.69 ± 0.02
F(1)-1La	2.49 ± 0.01	F(2)-3F(1)	2.79 ± 0.01
F(1)-1La	2.64 ± 0.01	F(2)-3F(1)	2.87 ± 0.02
F(1)-1La	3.01 ± 0.01	F(3)-3La	2.443 ± 0.004
F(1)-1F(1)	2.57 ± 0.03	F(3)-6F(1)	2.76 ± 0.01
F(1)-1F(1)	2.68 ± 0.03		

than the calculated standard deviations when just high-angle data were used or when the extinction correction was introduced. Our estimates of the standard deviations bracket these fluctuations more realistically, and, because of the highly nonrandom nature of the errors here, the authors believe that an educated guess is preferable to a mathematical fiction. The thermal parameters (other than B_{13} and B_{23}) are systematically lower than the true values, because of neglect of absorption, by an unknown amount which is estimated to be about 0.6 A[2]. This effect is not included in the estimated standard deviations. Table IV shows a list of interatomic distances.

The structure we find has lanthanum in almost exactly the positions reported by Oftedal. The fluorine atoms have been shifted so that of the six second-nearest neighbors of each lanthanum, four have moved closer and two have moved away; thus, lanthanum has a normal coordination number of nine. We have failed to find any simple description for the geometry of these neighbors. Each fluorine has three lanthanum neighbors. A sketch showing the ninefold coordination of lanthanum as viewed down the *c* axis is shown in Figure 1.[10]

(10) NOTE ADDED IN PROOF.—M. Mansmann, *Z. Krist.*, **122**, 375 (1965), has recently reported atomic coordinates for this structure which correspond to our results within 0.06 A in the worst case and with complete agreement concerning the symmetry.

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The Structure of $YbSb_2$, a $ZrSi_2$ Isotype[1]

BY R. WANG, R. BODNAR, AND H. STEINFINK

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In the recent study of the ytterbium–antimony phase diagram,[2] $YbSb_2$ was found to exist as one of the most stable phases in this system. It crystallizes in a pro-

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