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THE ATOMIC PARAMETERS IN THE LANTHANUM TRIFLUORIDE STRUCTURE

Allan Zalkin, David H. Templeton, and Ted E. Hopkins

The Atomic Parameters in the Lanthanum Trifluoride Structure[1]

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

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 two-fold 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 per cent pure, was sent to us by Dr. Kenneth Lee of Varian Associates in Palo Alto. 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 Kα radiation ($\lambda(K\alpha_1)$ = 0.70926 Å.). The cell dimensions measured at 22° are:

$\underline{a}$ = 7.185 ± 0.001, $\underline{c}$ = 7.351 ± 0.001 Å,

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) ≠ 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, ($h0\ell$) absent if $\ell = 2n + 1$, correspond

to space groups P3cl and P$\bar{3}$cl. We conclude that the crystals are

centric because a reasonable structure is found in space group P$\bar{3}$cl

(D_{3d}^4), No. 165 in the International Tables[7].

The intensity measurements included 951 independent reflections

(all positive $hk\ell$ with $2\theta < 90°$) of which 65 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 ~2. The data were not corrected for absorption. An empirical

extinction correction was made based on an approximation suggested by

Zacharias en[8] where $F_{corrected} \approx F_{observed}(1.0 + CJ)$, 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$\bar{3}$cl 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 (~0.15) and the temperature factor for the 2 fold fluorine "blew up".

Different trial structures and the use of a non-centric space group (P3cl)

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) versus 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 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 $\exp-(h^2\beta_{11}+k^2\beta_{22}+\ell^2\beta_{33}+2hk\beta_{12}+2h\ell\beta_{13}+2k\ell\beta_{23})$ was applied to lanthanum, with suitable constraints because of the 2-fold 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 agreement were deleted from the final refinements. The final R factor was 0.052. A table of the observed and calculated structure factors is available from the American Documentation Service[10].

Results

Tables I and II show the final positional and thermal parameters respectively. The standard deviations shown in Tables I and II 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 than the calculated standard deviations when just high angle data was used or when the extinction correction was introduced. Our estimates of the standard deviations bracket these fluctuations more realistically and because of the highly non-random nature of the errors here, the authors believe that an educated guess is preferable to a mathematical

TABLE I

POSITIONAL PARAMETERS IN LANTHANUM TRIFLUORIDE

No.	Atom	Point Symmetry	Positions and Positional 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	$\pm(x,y,z;\ \bar{y},x-y,z;\ y-x,\bar{x},z;$
			$\bar{y},\bar{x},1/2+z;\ x,x-y,1/2+z;\ y-x,y,1/2+z)$
			$x = 0.312 \pm 0.002$
			$y = -0.055 \pm 0.002$
			$z = 0.581 \pm 0.002$
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 II

TEMPERATURE FACTORS $(\text{Å}^2)^{\underline{a}}$ IN LANTHANUM TRIFLUORIDE

Atom	Temperature Factors		
La	$B11 = 0.6 \pm 0.2$	$B22 = 0.6 \pm 0.2$	$B33 = 0.8 \pm 0.2$
	$B12 = 0.3^{\underline{b}}$	$B13 = -0.025^{\underline{b}}$	$B23 = -0.05 \pm 0.01$
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 $Bij = \beta_{ij}/4a_i^* a_j^*$, where a_i^* is the ith reciprocal axis length.

[b] Symmetry considerations force B22 = 2B12 and B23 = 2B13.

fiction. The thermal parameters (other than B13 and B23) are systematically
lower than the true values, because of neglect of absorption, by an
unknown amount which is estimated to be about 0.6 $Å^2$. This effect is not
included in the estimated standard deviations. Table III 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 6 second-nearest neighbors of each lanthanum, 4 have moved closer
and 2 have moved away; thus lanthanum has a normal coordination-number
of 9. We have failed to find any simple description for the geometry
of these neighbors. Each fluorine has 3 lanthanum neighbors.

TABLE III

INTERATOMIC DISTANCES OF LESS THAN 3 Å IN LANTHANUM TRIFLUORIDE

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

References

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

(2) I. Oftedal, Z. physik. Chem., Abt. B5; B13, 190 (1931).

(3) K. Schlyter, Ark. Kemi, 5, 73 (1953).

(4) D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 75, 4560 (1953).

(5) Von M. Mansmann, Z. anorg. Chem., 331, 98 (1964).

(6) H. E. Swanson, N. T. Gilfrich, and M. I. Cook, "Standard X-Ray Diffraction Patterns", National Bureau of Standards Circular 539, 7, 21 (1957).

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

(8) W. H. Zachariasen, Acta Cryst., 16, 1142 (1963).

(9) D. T. Cromer, Acta Cryst., 18, 17 (1965).

(10) The table of observed and calculated structure factors has been deposited as Document No. 0000 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $0.00 for photoprints, or $0.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Observed and calculated structure factors (x2.0) for lanthanum
trifluoride. The FOB in this table is derived from the raw intensity J
(corrected for background only) by the formula:

$$FOB = S \times J \times Lp \times (1.0 + C \times J)$$

where S is a scaling factor adjusted by the least squares and has a
value here of 10.826,

Lp is the Lorentz-polarization correction,

and C is the extinction parameter and has the value here of 0.000464.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS (X 2.0) OF LANTHANUM TRIFLUORIDE.

```
H,K= 0, 0        H,K= 1, 7        5 25 -26        H,K= 4, 1        H,K= 5, 5
L FOB FCA        L FOB FCA        6 44 -46        L FOB FCA        L FOB FCA
2 713-564*       0 100-107        7  6  -4        0 173-175        1 190 189
4 420 435        1 213-210                         1 333-332        2  86  92
6 397-428*       2 111 118        H,K= 1, 7        2 151 149        3 165-167
8 232 244        3 162 205*       L FOB FCA        3 348 340        4  92 -92
10 191-196       4 106-106        0 100-107        4 162-157        5 165 160
12 170 174       5 206-192        8  37  39        5 262-251        6  92  88
14 101-110       6  96  99        9  17 -18        6 161 153        7 136-136
                 7 144 149        10  7  -6        7 220 214        8  74 -73
H,K= 0, 1        8  88 -90        11  7  10        8 116-114        9 106 106
L FOB FCA        9 122-126        12  7   7        9 165-180        10 54  58
0 24 -23         10 66  65        13  0  -1        10 94  89
2 12 -10         11 98 103                          11 132 125       H,K= 5, 6
4 58  64                          H,K= 2, 4        12 71 -66        L FOB FCA
6 15 -23         H,K= 1, 8        L FOB FCA        13 102 -97       0 33 34
8  5   2         L FOB FCA        0 10   6                          1 15 -10
10 0  -1         0 23  22         1 76  78         H,K= 4, 2        2 57 -47
12 7  -8         1 24  23         2 27  30         L FOB FCA        3 29  27
                 2 23 -22         3 40 -42         0  6   9         4 45  42
H,K= 0, 2        3 41 -41         4 25 -26         1 23  17         5 12 -12
L FOB FCA        4 18  15         5 22  21         2 10   8         6 36 -34
0 34  26         5 36  35         6  6  -4         3 40 -42         7 37  37
2 40  39         6 25 -26         7 49 -48         4 11   8         8 36  31
4 38  38         8  7  14         8  0  -2         5 55  54         9 13  13
6 19 -21                          9 24  25         6 17 -20
8 16  18         H,K= 1, 9        10  0 -1         7 18 -14         H,K= 5, 7
10 26 -31        L FOB FCA        11 15 -15        8  6   4         L FOB FCA
12  7  15        0 25 -28         12  0  5         9 24  23         0  0  -2
14  0  -6        1 52 -46         13 20 21         10  6  2         1 48  42
                 2 32  32                          11 24 -23        2 16  18
H,K= 0, 3        3 30  34         H,K= 2, 5        12 23 -20        3 47 -43
L FOB FCA        4 30 -30         L FOB FCA                         4 23 -26
0 713 678*       5 40 -39         0 134-138        H,K= 4, 3        5 37  39
2 459-477*       6 22  22         1 260 260        L FOB FCA        6  0  -1
4 350 380*       7 37  35         2 124 132        0 53 -59         7 34 -34
6 338-357        8 17 -16         3 253-253        1 16 -15
8 221 230        9 20 -23         4 123-124        2 36 -32         H,K= 5, 8
10 177-182                        5 223 222        3 27  28         L FOB FCA
12 158 158       H,K= 1,10        6 128 124        4 55  52         0 55 -62
14 99-105        L FOB FCA        7 180-178        5 38 -38         1 120 119
                 0 62 -66         8 103-100        6 22 -22         2 61  62
H,K= 0, 4        1 130-129        9 149 148        7  9   7         3 102-108
L FOB FCA        2 171 177        10 75 -75        8 26  27         4 57 -58
0 58 -68         3 126 124        11 116-115       9  6  -3         5 102 108
2 46  48         4 65 -68         12 60 -57        11 103 96
4 44  44         5 126-126                                          H,K= 5, 9
6 20  17         6 60  63         H,K= 2, 6        H,K= 4, 4        L FOB FCA
8  0   2         7 84  97         L FOB FCA        L FOB FCA        0 28  26
10 0   2                          0 430 423        1 239-240        1  7 -10
12 22 -19        H,K= 1,11        1  8  -3         2 123 124
                 L FOB FCA        2 364-364        3 235 229        H,K= 6, 0
H,K= 0, 5        0 13  13         3  0  -4         4 122-122        L FOB FCA
L FOB FCA        1 32  28         4 307 311        5 205-198        2 325-316
0 28  34         2 13 -16         5 35  43         6 105 107        4 296 293
2 23 -15         3 28 -27         6 275-270        7 166 167        6 249-239
4 62  63         4 17  15         7  6   1         8 96 -95         8 191 181
6 27 -31         5 25  26         8 205 199        9 141-137        10 157-153
8 31  32                          9  7   2         10 76  73        12 114 120
10 41 -44        H,K= 2, 0        10 168-160       11 106 105
12 13  21        L FCB FCA        11  0   1        12 50 -51        H,K= 6, 1
                 2 121-108        12 132 131                         L FOB FCA
H,K= 0, 6        4  39  41        13  0  -0        H,K= 4, 5        0 28 -31
L FOB FCA        6  43 -48                          L FOB FCA        1 39 -36
0 366 360        8  32  35        H,K= 2, 7        0 10  14         2 29  29
2 330-339        10  0  -3        L FOB FCA        1 23  24         3 39 -41
4 270 274        12  7   3        0  6  -8         2 36  35         4  6  -3
6 233-241        14  8  -4        1 58  56         3  7   8         5 52 -47
8 191 191                         2 26  29         4 15 -12         6  6   8
10 139-145       H,K= 2, 1        3 40 -43         5 21 -18         7 43  40
12 116 121       L FCB FCA        4 25 -27         6 16  14
                 0 83 -86         5 38  39         7 13  13         H,K= 6, 2
H,K= 0, 7        1 82  80         6  0   6                          L FOB FCA
L FOB FCA        2 35 -38         7 11  14         H,K= 4, 6        0 33  32
0 54 -62                          8 13 -10        L FOB FCA        1 37 -38
2 44  45         H,K= 2, 2        9 27  28         0 68 -74         2 20 -14
4 13   6         L FCB FCA        10  8  6         1 155-154        3 44  44
6 28  29         0 256 252                          2 87  88         4  0  -8
8 27 -24         1  0  -4         H,K= 2, 8        3 145 146        5 46  49
10 7   6         2 258-254        L FOB FCA        4 83 -82         6  7  -5
12 20 -22        3  6  -4         0 83 -86         5 138-139        7 33 -29
                 4 217 213        1 167 166        6 74  70         8 16 -11
H,K= 0, 8        5  7  -3         2 84  92         7 119 114
L FOB FCA        6 184-180        3  8  13         8 69 -69         H,K= 6, 3
0 41  41         7 12   2         4 80 -82         9 94 -95         L FOB FCA
2 46 -44         8 160 155        5 155 155                         0 259 252
4 55  53         9  0   2         6 83  80         H,K= 4, 7
6 33 -36         10 119-120       7 124-121        L FOB FCA        H,K= 6, 4
8 44  41         11  0   1        8 74 -72         0 41 -44         L FOB FCA
10 32 -40                         9 101 100        1 45 -41
                 H,K= 2, 3                          2 32  33        H,K= 7, 5
H,K= 0, 9        L FCR FCA        H,K= 2, 9        3 20  20        L FOB FCA
L FOB FCA        0 49 -53         L FOB FCA        4 38 -39        0  0  -2
0 206 208        1 96 100         0 18 -15         5 32 -32        1 41  43
2 221-222        2 52  58         1 21 -19         6 30  34        2 13  12
4 174 177                         2 38 -32         7 33  29        3 39 -40
6 152-153        H,K= 3, 0        3 28  30         8 17 -16        4  0  -6
8 124 139        L FOB FCA        4 28  28         9  8 -15        5 38  34
10 91-103        2 496-469*       5 22 -22         10 20 16        6  0  -6
                                  6 23 -26                          7 30 -30
H,K= 0,10                         7  8  13         H,K= 4, 8
L FOB FCA                         8 17  21         L FOB FCA        H,K= 7, 6
0 45 -43                                           0  0  -1        L FOB FCA
2 35  35                          H,K= 2,10        1 36  31        0 37 -38
4 19 -16                          L FOB FCA        2  0  -5        1 15 -17
6 20  24                          0 13 -15         3 35 -34        2 34 -34
8 20 -21                          1 41  40         4  0   6        3 13  17
                                  2 23  25         5 35 -34        4 31 -31
H,K= 0,11                         3 37 -40         6 21  22        5 20 -24
L FOB FCA                         4 20 -23         7 24  24        6 30  31
0 42  42                          5 38  39         8 17 -17
2 45 -46                          6 13  12         9 13 -13        H,K= 7, 7
4 43  40                                           10 13 14        L FOB FCA
6 34 -37                          H,K= 2,11                         2 155-149
                                  L FCR FCA                         3  0  -2
H,K= 0,12                         0 49 -53                          4 146 146
                                  1 96 100                          5  0  -3
                                  2 52  58                          6 113-114
                                                                    7 13   1
                                  H,K= 3, 0
                                  L FOB FCA                         H,K= 8, 0
                                  2 496-469*                        L FOB FCA
                                                                    3  7  -6
                                                                    4 153 150
                                                                    6 42 -43
                                                                    8 45  43
                                                                    9 13 -15
```

H,K= 9, 2 / H,K= 9, 3 / H,K= 9, 4 / H,K= 9, 5 / H,K=10, 0 / H,K=10, 1 / H,K=10, 2 / H,K=10, 3 / H,K=11, 0 / H,K=11, 1 / H,K=11, 2 / H,K=12, 0