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THE ATOMIC PARAMETERS IN THE LANTHANUM TRIFLUORIDE STRUCTURE

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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 assignement 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:

$$\underline{a} = 7.185 \pm 0.001, \quad \underline{c} = 7.351 \pm 0.001 \text{ Å},$$

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 $\bar{3}$ml, but there are clear violations of symmetry 6/mmm and 6/m; i.e., $I(hk\ell) = I(h+k,-k,\ell)$, but $I(hk\ell) \neq I(-k,h+k,\ell)$. 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 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 951 independent reflections (all positive $hk\ell$ with $2\theta < 90^{\circ}$) 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 Zachariasen[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 $P\bar{3}c1$ 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, $R = \sum||F_o|-|F_c||/\sum|F_o|$, 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 (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) 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 ($\mathring{A}^2$)[a] IN LANTHANUM TRIFLUORIDE

Atom	Temperature Factors		
La	$B11 = 0.6 \pm 0.2$	$B22 = 0.6 \pm 0.2$	$B33 = 0.8 \pm 0.2$
	$B12 = 0.3$[b]	$B13 = -0.025$[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 $B_{ij} = \beta_{ij}/4a_i^*a_j^*$, 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)
La	- 2 F(2)	2.416 ± 0.003
	- 1 F(3)	2.443 ± 0.004
	- 2 F(1)	2.46 ± 0.02
	- 2 F(1)	2.49 ± 0.01
	- 2 F(1)	2.64 ± 0.01
	- 2 F(1)	3.01 ± 0.01
F(1)	- 1 La	2.46 ± 0.02
	- 1 La	2.49 ± 0.01
	- 1 La	2.64 ± 0.01
	- 1 La	3.01 ± 0.01
	- 1 F(1)	2.57 ± 0.03
	- 1 F(1)	2.68 ± 0.03
F(1)	- 1 F(2)	2.69 ± 0.02
	- 2 F(1)	2.74 ± 0.02
	- 1 F(3)	2.76 ± 0.01
	- 1 F(2)	2.79 ± 0.01
	- 1 F(2)	2.87 ± 0.02
F(2)	- 3 La	2.416 ± 0.003
	- 3 F(1)	2.69 ± 0.02
	- 3 F(1)	2.79 ± 0.01
	- 3 F(1)	2.87 ± 0.02
F(3)	- 3 La	2.443 ± 0.004
	- 6 F(1)	2.76 ± 0.01

References

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

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

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(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.

Appendix

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																			
L FOB FCA	L FOB FCA		5 25 -26	4 373 386	9 8 -6	5 47 44	1 60 58	10 131-126	5 138-132	0 25 -28
2 713-564*	0 128 123	H,K= 1, 7	6 44 -46	6 350-357	10 13 13	6 20 -21	2 16 20	11 0 1	6 71 70	1 44 -44
2 121-134	2 121-134	L FOB FCA	7 6 -4	8 226 228		7 27 -22	3 47 -48		7 126 120	2 21 22
4 420 435		0 100-107	8 37 39	10 177-184	H,K= 3, 8	8 0 -0	4 11 -10	H,K= 6, 4	8 69 -67	3 27 32
6 397-428*	H,K= 1, 0	1 213-210	9 17 -18	12 163 157	L FOB FCA	9 25 27	5 32 31	L FOB FCA	9 95 -94	4 7 -16
8 232 264	L FOB FCA	2 111 118	10 7 -6	14 97-105	0 41 40	10 0 6	6 7 -11	0 43 -44		5 47 -38
10 191-196	2 14 13	3 162 205*	11 7 10		1 0 -4	11 25 -21	7 46 -42	1 34 -36	H,K= 7, 5	6 13 13
12 170 174	4 47 -43	4 106-106	12 7 7	H,K= 3, 1	2 44 -44		8 0 -1	2 27 29	L FOB FCA	7 31 30
14 101-110	6 9 6	5 206-192	13 0 -1	L FOB FCA	3 10 16	H,K= 4, 6	9 31 31	3 20 19	0 0 -2	8 13 -14
	8 9 14	6 96 -99		0 32 -35	4 47 43	L FOB FCA	10 0 -5	4 15 -14	1 41 43	9 17 -20
H,K= 0, 1	10 0 -4	7 144 149	H,K= 2, 4	1 16 -6	5 7 -5	0 41 -44	11 17 -20	5 35 -34	2 13 12	
L FOB FCA	12 7 4	8 88 -90	L FOB FCA	2 26 28	6 33 -36	1 45 -41		6 21 22	3 39 -40	H,K= 9, 2
0 24 -23	14 0 -1	9 122-126	0 10 6	3 17 18	7 0 5	2 32 33	H,K= 5, 5	7 24 24	4 0 -6	L FOB FCA
2 12 -10		10 66 65	1 76 78	4 33 37	8 36 39	3 20 20	L FOB FCA	8 17 -17	5 38 34	0 26 24
4 58 64	H,K= 1, 1	11 98 103	2 27 30	5 43 -42		4 38 -39	0 95 -95	9 13 -13	6 0 -6	1 29 -29
6 15 -23	L FOB FCA		3 40 -42	6 5 -4	H,K= 3, 9	5 32 -32	1 190 189	10 13 14	7 30 -30	2 21 -20
8 5 2	0 324-284*	H,K= 1, 8	4 25 -26	7 5 8	L FOB FCA	6 30 34	2 86 92			3 31 32
10 0 -1	1 464-426*	L FOB FCA	5 22 21	8 15 -11	0 147 152	7 33 29	3 165-167	H,K= 6, 5	H,K= 7, 6	4 24 24
12 7 -8	2 174 166	0 23 22	6 6 -4	9 6 -11	1 7 -3	8 17 -16	4 92 -92	L FOB FCA	L FOB FCA	5 22 -19
	3 483 537*	1 24 23	7 49 -48	10 7 3	2 159-162	9 8 -15	5 165 160	0 33 34	0 37 -38	6 27 -22
H,K= 0, 2	4 181-183	2 23 -22	8 0 -2	11 12 16	3 0 -2	10 20 16	6 92 88	1 15 -17	1 29 -26	7 25 24
L FOB FCA	5 272-305*	3 41 -41	9 24 25	12 7 -13	4 130 134		7 136-136	2 34 -34	2 34 34	8 23 22
0 34 26	6 203 210	4 18 15	10 0 -1	13 0 -4	5 8 -2	H,K= 4, 7	8 74 -73	3 29 29	3 13 17	
2 40 39	7 232 249	5 36 35	11 15 -15		6 104-115	L FOB FCA	9 106 106	4 41 37	4 31 -31	H,K= 9, 3
4 38 38	8 129-133	6 25 -26	12 0 5	H,K= 3, 2	7 0 2	0 68 -74	10 54 58	5 12 -11	5 20 -24	L FOB FCA
6 19 -21	9 222-228	7 16 -16	13 20 21	L FOB FCA		1 155-154		6 33 -30	6 30 31	0 155 152
8 16 18	10 101 100	8 7 14		0 32 34	H,K= 3,10	2 87 88	H,K= 5, 6	7 17 15		1 0 -2
10 26 -31	11 140 142	9 23 24	H,K= 2, 5	1 43 -42	L FOB FCA	3 145 146	L FOB FCA	8 32 33	H,K= 7, 7	2 155-149
12 7 15	12 88 -80	10 0 -3	L FOB FCA	2 20 9	0 31 -34	4 83 -82	0 33 34	9 13 -19	L FOB FCA	3 0 -2
14 0 -6	13 107-108		0 134-138	3 39 41	1 8 -13	5 138-139	1 15 -10		0 49 -51	4 146 146
	14 49 47	H,K= 1, 9	1 260 260	4 50 47	2 25 28	6 74 70	2 57 -47	H,K= 6, 6	1 97-103	5 0 -3
H,K= 0, 3		L FOB FCA	2 124 132	5 5 5	3 8 7	7 119 114	3 29 27	L FOB FCA	2 49 58	6 113-114
L FOB FCA	H,K= 1, 2	0 25 -28	3 253-253	6 26 -28	4 13 -20	8 69 -69	4 45 42	0 166 164		7 13 1
0 713 678*	L FOB FCA	1 52 -46	4 123-124	7 24 25		9 94 -95	5 12 -12	1 12 -4	H,K= 8, 0	
2 459-477*	0 19 20	2 32 32	5 223 222	8 20 22	H,K= 4, 0		6 36 -34	2 168-167	L FOB FCA	H,K= 9, 4
4 350 380*	1 31 -28	3 30 34	6 128 124	9 21 -19	L FOB FCA	H,K= 4, 8	7 7 7	3 7 -4	2 63 -69	L FOB FCA
6 338-357	2 42 -43	4 30 -30	7 180-178	10 33 -36	2 11 -4	L FOB FCA	8 36 31	4 153 150	4 60 55	0 32 -33
8 221 230	3 36 -39	5 40 -39	8 103-100	11 0 3	4 78 -73	0 0 9	9 13 -15	5 7 -3	6 42 -43	1 34 -35
10 177-182	4 28 34	6 22 22	9 149 148	12 17 19	6 37 37	1 36 36		6 118-123	8 45 43	2 20 19
12 158 158	5 42 44	7 37 35	10 75 75	13 8 -11	8 0 7	2 0 -3	H,K= 5, 7	7 8 2	10 24 -24	3 23 25
14 99-105	6 32 -38	8 17 -16	11 116-115		10 26 17	3 36 -36	L FOB FCA			4 17 -20
	7 9 3	9 20 -23	12 60 -57	H,K= 3, 3	12 17 -10	4 7 4	0 0 -2	H,K= 6, 7	H,K= 8, 1	5 25 -29
H,K= 0, 4	8 6 15			L FOB FCA		5 34 32	1 48 42	L FOB FCA	L FOB FCA	
L FOB FCA	9 16 17	H,K= 1,10	H,K= 2, 6	0 430 423	H,K= 4, 1	6 8 -13	2 16 18	0 37 -38	0 23 22	H,K= 9, 5
0 58 -68	10 0 1	L FOB FCA	L FOB FCA	1 8 -3	L FOB FCA	7 25 -25	3 47 -43	1 23 -26	1 48 46	L FOB FCA
2 46 48	11 15 -15	0 62 -66	0 31 32	2 364-364	0 173-175		4 17 -16	2 25 24	2 6 -2	0 32 26
4 44 44	12 7 -1	1 130-129	1 10 -6	3 0 -4	1 333-332	H,K= 4, 9	5 37 39	3 17 16	3 44 -44	1 13 -15
6 20 17	13 0 2	2 71 77	2 54 -51	4 307 311	2 151 149	L FOB FCA	6 0 -1	4 17 -20	4 11 13	
8 24 -20	14 0 2	3 126 124	3 35 43	5 12 -2	3 348 340	0 34 -33	7 34 -34	5 23 -22	5 28 23	H,K=10, 0
10 0 2		4 65 -68	4 34 32	6 275-270	4 162-157	1 37 -34		6 20 22	6 20 -19	L FOB FCA
12 22 -19	H,K= 1, 3	5 126-126	5 26 -27	7 6 1	5 262-251	2 36 33	H,K= 5, 8		7 37 -36	2 42 34
	L FOB FCA	6 60 63	6 37 -37	8 205 199	6 161 153	3 23 26	L FOB FCA	H,K= 6, 8	8 7 11	4 45 -44
H,K= 0, 5	0 32 -35	7 84 97	7 7 5	9 7 2	7 220 214	4 23 -25	0 55 -62	L FOB FCA	9 31 28	6 35 35
L FOB FCA	1 67 -69		8 29 30	10 168-160	8 116-114	5 28 -32	1 120 119	0 32 34	10 13 -17	8 22 -20
0 28 34	2 15 13	H,K= 1,11	9 19 -23	11 0 1	9 185-180		2 61 62	1 0 -6		
2 23 -15	3 16 17	L FOB FCA	10 7 -10	12 132 131	10 94 89	H,K= 5, 0	3 102-108	2 33 -37	H,K= 8, 2	H,K=10, 1
4 62 63	4 55 -56	0 13 13	11 13 12	13 0 -0	11 132 125	L FOB FCA	4 57 -58		L FOB FCA	L FOB FCA
6 27 -31	5 15 -12	1 32 28			12 71 -66	2 101 -98	5 102 108	H,K= 7, 0	0 84 -86	0 62 -66
8 31 32	6 17 18	2 13 -16	H,K= 2, 7	H,K= 3, 4	13 102 -97	4 50 46		L FOB FCA	1 182 183	1 145-147
10 41 -44	7 33 34	3 28 -27	L FOB FCA	L FOB FCA		6 45 -47	H,K= 5, 9	2 25 22	2 83 82	2 68 69
12 13 21	8 6 6	4 17 15	0 6 -8	0 53 -59	H,K= 4, 2	8 49 49	L FOB FCA	4 61 -59	3 158-154	3 122 123
	9 11 -12	5 25 26	1 58 56	1 21 -22	L FOB FCA	10 14 -13	0 28 26	6 47 44	4 92 -91	4 76 -76
H,K= 0, 6	10 11 8		2 26 29	2 44 42	0 10 6	12 11 10	1 17 -15	8 14 -9	5 147 142	5 112-112
L FOB FCA	11 7 9	H,K= 2, 0	3 40 -43	3 9 9	1 23 17			10 18 24	6 85 79	6 60 62
0 366 360	12 0 -3	L FOB FCA	4 25 -27	4 16 12	2 10 8	H,K= 5, 1	H,K= 6, 0	12 15 -18	7 14C-132	7 103 109
2 330-339	13 13 -13	2 114-108	5 38 39	5 29 -29	3 40 -42	L FOB FCA	L FOB FCA		8 73 -67	
4 270 274		4 39 41	6 0 6	6 25 23	4 11 8	0 27 29	2 325-316	H,K= 7, 1	9 1C5 98	H,K=10, 2
6 233-241	H,K= 1, 4	6 43 -48	7 40 -41	7 11 14	5 55 54	1 68 66	4 296 293	L FOB FCA		L FOB FCA
8 191 191	L FOB FCA	8 32 35	8 13 -10	8 25 -21	6 17 -20	2 17 18	6 249-239	0 104-107	H,K= 8, 3	0 13 -15
10 139-145	0 168-175	10 0 -3	9 27 28	9 7 -7	7 18 -14	3 53 -52	8 191 181	1 233-231	L FOB FCA	1 45 44
12 116 121	1 318-319	12 7 3	10 8 6	10 0 7	8 6 -4	4 14 12	10 157-153	2 107 107	C 43 4C	2 13 18
	2 152 156	14 8 -4		11 13 13	9 24 23	5 14 10	12 114 120	3 209 204	1 7 -5	3 36 -38
H,K= 0, 7	3 332 340		H,K= 2, 8	12 23 -20	10 0 6	6 22 -22		4 118-116	2 58 -53	4 8 -13
L FOB FCA	4 153-151	H,K= 2, 1	L FOB FCA		11 24 -23	7 46 -43	H,K= 6, 1	5 185-176	3 12 15	5 32 33
0 54 -62	5 254-259	L FOB FCA	0 83 -86	H,K= 3, 5	12 C -4	8 6 9	L FOB FCA	6 100 99	4 55 51	6 0 6
2 44 45	6 155 153	0 20 20	1 167 166	L FOB FCA	13 8 7	9 31 28	0 28 -31	7 170 162	5 0 -3	
4 13 6	7 204 208	1 82 80	2 84 92	0 35 37		10 19 -20	1 39 -36	8 91 -84	6 38 -39	H,K=10, 3
6 28 29	8 113-117	2 35 36	3 154-154	1 16 -15	H,K= 4, 3	11 7 -10	2 29 29	9 130-124	7 0 4	L FOB FCA
8 27 -24	9 184-181	3 35 -38	4 80 -82	2 36 -32	L FOB FCA	12 8 15	3 24 27	10 72 70	8 34 36	0 31 -34
10 7 8	10 89 87	4 9 -4	5 155 155	3 27 28	C 53 -59	13 23 20	4 6 -3	11 103 96		1 8 -12
12 20 -22	11 132 128	5 9 -5	6 83 80	4 55 52	1 38 -38		5 52 -47		H,K= 8, 4	2 32 34
	12 72 -66	6 13 -13	7 124-121	5 0 -2	2 21 19	H,K= 5, 2	6 6 8	H,K= 7, 2	L FOB FCA	3 8 8
H,K= 0, 8	13 94 -95	7 37 -35	8 74 -72	6 34 -33	3 9 9	L FOB FCA	7 25 23	L FOB FCA	0 C 9	4 32 -34
L FOB FCA		8 6 10	9 101 100	7 11 12	4 59 -59	0 137-138	8 18 -15	0 6 -8	1 43 4C	
0 41 41	H,K= 1, 5	9 18 17		8 32 35	5 17 -2C	1 280 274	9 16 -17	1 46 43	2 C 7	H,K=11, 0
2 46 -44	L FOB FCA	10 6 -16	H,K= 2, 9	9 19 -15	6 39 39	2 122 124	10 7 10	2 16 19	3 43 -39	L FOB FCA
4 55 53	0 29 29	11 0 -5	L FOB FCA	1C 44 -40	7 24 24	3 259-252	11 25 22	3 39 -41	4 7 -2	2 54 -48
6 33 -36	1 16 4	12 0 11	0 26 24	11 0 3	8 7 -6	4 132-131	12 13 -13	4 0 -8	5 31 33	4 54 50
8 44 41	2 32 -33	13 13 14	1 21 -19	12 20 22	9 7 -8	5 224 213		5 46 44	6 8 -9	6 36 -39
10 32 -40	3 49 -52	14 0 -2	2 38 -32		1C 24 20	6 129 124	H,K= 6, 2	6 7 -5	7 3C -33	
	4 16 16		3 28 30	H,K= 3, 6	11 7 11	7 190-185	L FOB FCA	7 33 -29		H,K=11, 1
H,K= 0, 9	5 47 46	H,K= 2, 2	4 28 28	L FOB FCA	12 13 -14	8 102 -96	0 33 32	8 16 -11	H,K= 8, 5	L FOB FCA
L FOB FCA	6 36 -37	L FOB FCA	5 22 -22	0 256 252		9 153 147	1 37 -38	9 27 24	L FOB FCA	0 13 13
0 206 208	7 10 -6	0 218-218	6 23 -26	1 0 -3	H,K= 4, 4	10 84 77	2 20 -14	10 8 11	0 6C -62	1 34 33
2 221-222	8 11 17	1 368 370	7 8 13	2 258-254	L FOB FCA	11 115-111	3 44 44		1 122 124	2 8 -8
4 174 177	9 29 26	2 158 160	8 17 21	3 6 -4	C 103-115	12 59 -57	4 42 35	H,K= 7, 3	2 54 58	3 34 -30
6 152-153	10 0 1	3 420-411*		4 217 213	1 239-24C		5 14 -9	L FOB FCA	3 1C6-107	4 8 11
8 124 139	11 19 -19	4 165-166	H,K= 2,10	5 7 -3	2 123 124	H,K= 5, 3	6 29 -28	0 47 -50	4 58 -27	5 28 27
10 91-103	12 8 5	5 269 279	L FOB FCA	6 184-180	3 235 229	L FOB FCA	7 31 28	1 23 -21	5 94 103	
	13 0 4	6 183 179	0 13 -15	7 12 2	4 122-122	0 40 37	8 23 23	2 36 32		H,K=11, 2
H,K= 0,10		7 224-230	1 41 40	8 160 155	5 205-198	1 5 2	9 26 -26	3 11 8	H,K= 8, 6	L FOB FCA
L FOB FCA	H,K= 1, 6	8 122-123	2 23 25	9 0 2	6 105 107	2 74 -72	10 32 -30	4 48 -46	L FOB FCA	0 49 -53
0 45 -43	L FOB FCA	9 206 201	3 37 -40	1C 119-120	7 166 167	3 25 27	11 8 8	5 16 -17	0 36 34	1 106 111
2 35 35	0 26 -31	10 95 93	4 20 -23	11 0 1	8 96 -95	4 55 48		6 39 39	1 13 -10	2 48 50
4 19 -16	1 60 -62	11 133-134	5 38 39		9 141-137	5 14 -10	H,K= 6, 3	7 16 15	2 38 -37	
6 20 24	2 28 29	12 79 -73	6 13 12	H,K= 3, 7	1C 76 73	6 42 -42	L FOB FCA	8 7 -17		H,K=12, 0
8 20 -21	3 26 28	13 104 102		L FOB FCA	11 106 105	7 C 1	0 259 252	9 0 -6	H,K= 9, 0	L FOB FCA
	4 39 -43	14 42 45	H,K= 2,11	0 46 -50	12 50 -51	8 45 43	1 6 -3	10 25 21	L FOB FCA	2 116-119
H,K= 0,11	5 33 -33		L FOB FCA	1 14 -19		9 7 -14	2 252-241		2 208-199	
L FOB FCA	6 20 22	H,K= 2, 3	0 49 -53	2 36 35	H,K= 4, 5	10 17 -18	3 6 -4	H,K= 7, 4	4 195 198	
0 42 42	7 43 41	L FOB FCA	1 96 100	3 7 8	L FOB FCA	11 0 4	4 235 225	L FOB FCA	6 153-151	
2 45 -46	8 12 -9	0 32 34	2 52 58	4 15 -12	C 16 14	12 8 12	5 11 -3	0 73 -74	8 127 126	
4 43 40	9 19 -19	1 18 18		5 21 -18	1 34 32		6 190-179	1 163-163	1C 1C9-113	
6 34 -37	10 13 12	2 83 -85	H,K= 3, 0	6 28 26	2 0 0	H,K= 5, 4	7 12 2	2 85 84		
	11 20 19	3 40 41	L FOB FCA	7 7 13	3 44 -46	L FOB FCA	8 158 148	3 151 145	H,K= 9, 1	
H,K= 0,12	12 8 -7	4 33 34	2 496-469*	8 22 -20	4 6 1	0 10 14	9 7 2	4 87 -86	L FOB FCA	

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