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Publication Date
1966-03-01

UCRL-16752

University of California

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Berkeley, California

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Submitted to Journal of Inorganic Chemistry

UCRL-16752

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AEC Contract No. W-7405-eng-48

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March 1966

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

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 $\bar{3}m1$, 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, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, 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 (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 (Å^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 $Bij = \beta_{ij}/4a_i^{*}a_j^{*}$, 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)
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.

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

(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.

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	0 128 123		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*	2 121-134	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									
4 420 435		L FOB FCA	7 6 -4	8 226 228		7 27 -22	3 47 -48		7 126 120	2 21 22									
6 397-428*	H,K= 1, 0	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									
8 232 244	L FOB FCA	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									
10 191-196	2 14 13	2 111 118	10 7 -6	14 97-105	0 41 40	10 0 6	6 7 -11	0 43 -44		5 47 -38									
12 170 174	4 47 -43	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									
14 101-110	6 9 6	4 106-106	12 7 7	H,K= 3, 1	2 27 29		8 0 -1	2 27 29	L FOB FCA	7 31 30									
	8 9 14	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									
H,K= 0, 1	10 0 -4	6 96 -99		0 32 -35	4 47 43	L FOB FCA	10 0 -5	4 15 -14	1 61 63	9 17 -20									
L FOB FCA	12 7 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										
0 24 -23	14 0 -1	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									
2 12 -10		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									
4 58 64	H,K= 1, 1	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									
6 15 -23	L FOB FCA	11 98 103	2 27 30	5 43 -42		4 38 -39	0 95 -95	9 13 -13	6 0 -6	1 29 -29									
8 5 2	0 324-284*		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									
10 0 -1	1 464-426*	H,K= 1, 8	4 25 -26	7 5 8	L FOB FCA	6 30 34	2 86 92			3 31 32									
12 7 -8	2 174 166	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									
	3 483 537*	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									
H,K= 0, 2	4 181-183	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									
L FOB FCA	5 272-305*	2 23 -22	8 0 -2	11 12 16	3 0 -2	10 20 16	6 92 88	1 33 -34	1 29 -26	7 25 24									
0 34 26	6 203 210	3 41 -41	9 24 25	12 7 -13	4 130 134		7 136-136	2 34 -34	2 34 34	8 23 22									
2 40 39	7 232 249	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										
4 38 38	8 129-133	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									
6 19 -21	9 222-228	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									
8 16 18	10 101 100	7 16 -16	13 20 21	L FOB FCA		1 155-154		6 33 -30	6 30 31	0 155 152									
10 26 -31	11 140 142	8 7 14		0 32 34	H,K= 3,10	2 87 88	H,K= 5, 6	7 17 15		1 0 -2									
12 7 15	12 88 -80	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									
14 0 -6	13 107-108	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 49 47		0 134-138	3 39 41	1 8 -13	5 138-139	1 15 -10		0 49 -51	4 146 146									
H,K= 0, 3		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									
L FOB FCA	H,K= 1, 2	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									
0 713 678*	L FOB FCA	0 25 -28	3 253-253	6 26 -28	4 13 -20	8 69 -69	4 45 42	0 166 164		7 13 1									
2 459-477*	0 19 20	1 52 -46	4 123-124	7 24 25		9 94 -95	5 12 -12	1 12 -4	H,K= 8, 0										
4 350 380*	1 31 -28	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									
6 338-357	2 42 -43	3 30 34	6 128 124	9 21 -19	L FOB FCA	H,K= 4, 8	7 7 -4	3 7 -4	2 63 -69	L FOB FCA									
8 221 230	3 36 -39	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									
10 177-182	4 28 34	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									
12 158 158	5 42 44	6 22 22	9 149 148	12 17 19	6 37 37	1 36 36		6 118-123	8 45 43	2 20 19									
14 99-105	6 32 -38	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									
	7 9 3	8 17 -16	11 116-115		10 26 17	3 36 -36	L FOB FCA			4 17 -20									
H,K= 0, 4	8 6 15	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									
L FOB FCA	9 16 17			L FOB FCA		5 34 32	1 48 42	L FOB FCA	L FOB FCA										
0 58 -68	10 0 -1	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									
2 46 48	11 15 -15	L FOB FCA	0 31 32	1 8 -3	L FOB FCA	7 25 -25	3 47 -43	1 23 -26	1 48 46	L FOB FCA									
4 44 44	12 7 -1	1 130-129	1 10 -6	2 364-364	0 173-175		4 17 -16	2 25 24	2 6 -2	0 32 26									
6 20 17	13 0 2	2 71 77	2 54 -51	3 0 -4	1 333-332	H,K= 4, 9	5 37 39	3 17 16	3 44 -44	1 13 -15									
8 24 -20	14 0 2	3 126 124	3 35 43	4 307 311	2 151 149	5 37 -34	6 0 -1	4 17 -20	4 11 13										
10 0 2		4 65 -68	4 34 32	5 12 -2	3 348 340	7 34 -34	7 34 -34	5 23 -22	5 28 23	H,K=10, 0									
12 22 -19	H,K= 1, 3	5 126-126	5 26 -27	6 275-270	4 162-157			6 20 22	6 20 -19	L FOB FCA									
	L FOB FCA	6 60 63	6 37 -37	7 6 1	5 262-251	H,K= 5, 8	H,K= 6, 8		7 37 -36	2 42 34									
H,K= 0, 5	0 32 -35	7 84 97	7 7 5	8 205 199	6 161 153	L FOB FCA	L FOB FCA		8 7 11	4 45 -44									
L FOB FCA	1 67 -69		8 29 30	9 7 2	7 220 214	0 55 -62	0 32 34		4 31 28	6 35 35									
0 28 34	2 15 13	H,K= 1,11	9 19 -23	10 168-160	8 116-114	1 120 119	1 0 -6		10 13 -17	8 22 -20									
2 23 -15	3 16 17	L FOB FCA	10 7 -10	11 0 1	9 105-100	2 101 -98	2 33 -37												
4 62 63	4 55 -56	0 13 13	11 13 12	12 132 131	10 94 89	3 102-108			H,K= 8, 2	H,K=10, 1									
6 27 -31	5 15 -12	1 32 28		13 0 -0	11 132 125	L FOB FCA	H,K= 7, 0		L FOB FCA	L FOB FCA									
8 31 32	6 17 18	2 13 -16	H,K= 2, 7		12 71 -66	4 57 -58	L FOB FCA		0 84 -86	0 62 -66									
10 41 -44	7 33 34	3 21 -27	L FOB FCA	H,K= 3, 4	13 102 -97	2 101 -98	4 61 -59		1 182 183	1 145-147									
12 13 21	8 6 6	4 17 15	0 6 -8	L FOB FCA		4 50 46	H,K= 5, 9		2 83 82	2 68 69									
	9 11 -12	5 25 26	1 58 56	C 53 -59	H,K= 4, 2	6 45 -47	L FOB FCA		3 158-154	3 122 123									
H,K= 0, 6	10 11 8		2 26 29	1 21 -22	L FOB FCA	8 49 49	4 61 -59		4 92 -91	4 76 -76									
L FOB FCA	11 7 9	H,K= 2, 0	3 40 -43	2 44 42	C 10 6	10 14 -13	0 28 26		5 147 142	5 112-112									
0 366 360	12 0 -3	L FOB FCA	4 25 -27	3 9 9	1 23 17	12 11 10	1 17 -15		6 85 79	6 60 62									
2 330-339	13 13 -13	2 114-108	5 38 39	4 16 12	2 10 8				7 140-132	7 103 109									
4 270 274		4 39 41	6 0 6	5 29 -29	3 40 -42	H,K= 5, 1	H,K= 6, 0		8 73 -67										
6 233-241	H,K= 1, 4	6 43 -48	7 40 -41	6 25 23	4 11 8	L FOB FCA	L FOB FCA		9 105 98	H,K=10, 2									
8 191 191	L FOB FCA	8 32 35	8 13 -10	7 11 14	5 55 54	0 27 29	2 325-316	H,K= 7, 1		L FOB FCA									
10 139-145	0 168-175	10 0 -3	9 27 28	8 25 -21	6 17 -20	1 68 66	4 296 293	L FOB FCA		0 13 -15									
12 116 121	1 318-319	12 7 3	10 8 6	9 7 -7	7 18 -14	2 17 18	6 249-239	0 104-107	H,K= 8, 3	1 45 44									
	2 152 156	14 8 -4		10 0 7	8 6 -4	3 53 -52	8 191 181	1 233-231	L FOB FCA	2 13 18									
H,K= 0, 7	3 332 340		H,K= 2, 8	11 13 13	9 24 23	4 14 12	10 157-153	2 107 107	C 43 4C	3 36 -38									
L FOB FCA	4 153-151	H,K= 2, 1	L FOB FCA	12 23 -20	10 0 6	5 14 10	12 114 120	3 209 204	1 7 -5	4 8 -13									
0 54 -62	5 254-259	L FOB FCA	0 83 -86		11 24 -23	6 22 -22		4 118-116	2 58 -53	5 32 33									
2 44 45	6 155 153	0 20 20	1 167 166	H,K= 3, 5	12 C -4	7 46 -43	H,K= 6, 1	5 185-176	3 12 15	6 0 6									
4 13 6	7 204 208	1 82 80	2 84 92	L FOB FCA	13 8 7	8 6 9	L FOB FCA	6 100 99	4 55 51										
6 28 29	8 113-117	2 35 36	3 154-154	0 35 37		9 31 28	0 28 -31	7 170 162	5 C -3	H,K=10, 3									
8 27 -24	9 184-181	3 35 -38	4 80 -82	1 16 -15	H,K= 4, 3	10 19 -20	1 39 -36	8 91 -84	6 38 -39	L FOB FCA									
10 7 8	10 89 87	4 9 -4	5 155 159	2 36 -32	L FOB FCA	11 7 -10	2 29 29	9 130-124	7 C 4	0 31 -34									
12 20 -22	11 132 128	5 9 -5	6 83 80	3 27 28	C 53 -59	12 8 15	3 24 27	10 72 70	8 34 36	1 8 -12									
	12 72 -66	6 13 -13	7 124-121	4 55 52	1 38 -38	13 23 20	4 6 -3	11 103 96		2 32 34									
H,K= 0, 8	13 94 -95	7 37 -35	8 74 -72	5 0 -2	2 21 19		5 52 -47		H,K= 8, 4	3 8 8									
L FOB FCA		8 6 10	9 101 100	6 34 -33	3 9 9	H,K= 5, 2	6 6 8	H,K= 7, 2	L FOB FCA	4 32 -34									
0 41 41	H,K= 1, 5	9 18 17		7 11 12	4 59 -59	L FOB FCA	7 25 23	L FOB FCA	0 C 9										
2 46 -44	L FOB FCA	10 6 -16	H,K= 2, 9	8 32 35	5 17 -20	0 137-138	8 18 -15	0 6 -8	1 43 4C										
4 55 53	0 29 29	11 0 -5	L FOB FCA	9 19 -15	6 39 39	1 280 274	9 13 -17	1 46 43	2 0 7	H,K=11, 0									
6 33 -36	1 16 4	12 0 11	0 26 24	10 44 -40	7 24 24	2 122 124	10 7 10	2 16 19	3 43 -39	L FOB FCA									
8 44 41	2 32 -33	13 13 14	1 21 -19	11 0 3	8 7 -6	3 259-252	11 25 22	3 39 -41	4 7 -2	2 54 -48									
10 32 -40	3 49 -52	14 0 -2	2 38 -32	12 20 22	9 7 -8	4 132-131	12 13 -13	4 0 -8	5 31 33	4 54 50									
	4 16 16		3 28 30	H,K= 3, 6	10 24 20	5 224 213		5 46 44	6 8 -9	6 36 -39									
H,K= 0, 9	5 47 46	H,K= 2, 2	4 28 28	L FOB FCA	11 7 11	6 129 124	H,K= 6, 2	6 7 -5	7 3C -33										
L FOB FCA	6 36 -37	L FOB FCA	5 22 -22	0 256 252	12 13 -14	7 190-185	L FOB FCA	7 33 -29		H,K=11, 1									
0 206 208	7 10 -6	0 218-218	6 23 -26	1 0 -3		8 102 -96	0 33 32	8 16 -11	H,K= 8, 5	L FOB FCA									
2 221-222	8 11 17	1 368 370	7 8 13	2 258-254	H,K= 4, 4	9 153 147	1 37 -38	9 27 24	L FOB FCA	0 13 13									
4 174 177	9 29 26	2 158 160	8 17 21	3 6 -4	L FOB FCA	10 84 77	2 20 -14	10 8 11	0 6C -62	1 34 33									
6 152-153	10 0 1	3 420-411*		4 217 213	C 103-115	11 115-111	3 44 44		1 122 124	2 8 -8									
8 124 139	11 19 -19	4 165-166	H,K= 2,10	5 7 -3	1 239-240	12 59 -57	4 42 35	H,K= 7, 3	2 54 58	3 34 -30									
10 91-103	12 8 5	5 269 279	L FOB FCA	6 184-180	H,K= 5, 3		5 14 -9	L FOB FCA	3 1C6-107	4 8 11									
	13 0 4	6 183 179	0 13 -15	7 12 2	L FOB FCA	H,K= 6, 3	6 29 -28	1 23 -21	4 58 -62	5 28 27									
H,K= 0,10		7 224-230	1 41 40	8 160 155	4 122-122	L FOB FCA	7 31 28	2 36 32	5 94 103										
L FOB FCA	H,K= 1, 6	8 122-123	2 23 25	9 0 2	5 205-198	0 259 252	8 23 23	3 11 8		H,K=11, 2									
0 45 -43	L FOB FCA	9 206 201	3 37 -40	10 120-120	6 105 107	1 6 -3	9 26 -26	4 48 -46	H,K= 8, 6	L FOB FCA									
2 35 35	0 26 -31	10 95 93	4 20 -23	11 0 1	7 166 167	2 252-241	10 32 -30	5 16 -17	L FOB FCA	0 49 -53									
4 19 -16	1 60 -62	11 133-134	5 38 39		8 96 -95	3 6 -4	11 8 8	6 39 39	0 36 34	1 13 -10									
6 20 24	2 28 29	12 79 -73	6 13 12	H,K= 3, 7	9 141-137	4 235 225		7 16 15	1 106 110	2 48 50									
8 20 -21	3 26 28	13 104 102		L FOB FCA	1C 76 73	5 11 -3	H,K= 6, 4	8 7 -7	2 38 -37										
	4 39 -43	14 42 45	H,K= 2,11	11 106 105	6 190-179	L FOB FCA	7 12 2	9 0 -6		H,K= 9, 0									
H,K= 0,11	5 33 -33		L FOB FCA	0 46 -50	12 50 -51	7 158 148	8 158 148	10 25 21	L FOB FCA	2 108-199									
L FOB FCA	6 20 22	H,K= 2, 3	0 49 -53	1 14 -19		9 7 2	4 87 -86		2 252-241	4 195 198									
0 42 42	7 43 41	L FOB FCA	1 96 100	2 36 35	H,K= 4, 5	0 10 14			3 6 -4	H,K= 7, 4									
2 45 -46	8 12 -9	0 32 34	2 52 58	3 7 8	L FOB FCA				4 235 225	L FOB FCA									
4 43 40	9 19 -19	1 18 18		4 15 -12	C 16 14				5 11 -3	0 73 -74									
6 34 -37	10 13 12	2 83 -85	H,K= 3, 0	5 21 -18	1 34 32				6 190-179	8 127 126									
	11 20 19	3 40 41	L FOB FCA	6 28 26	2 0 0				7 12 2	1C 1C9-113									
H,K= 0,12	12 8 -7	4 33 34	2 496-469*	7 7 13	3 44 -46				8 158 148										
				8 22 -20	4 6 1				9 1 2	H,K= 9, 1									
										L FOB FCA