Title

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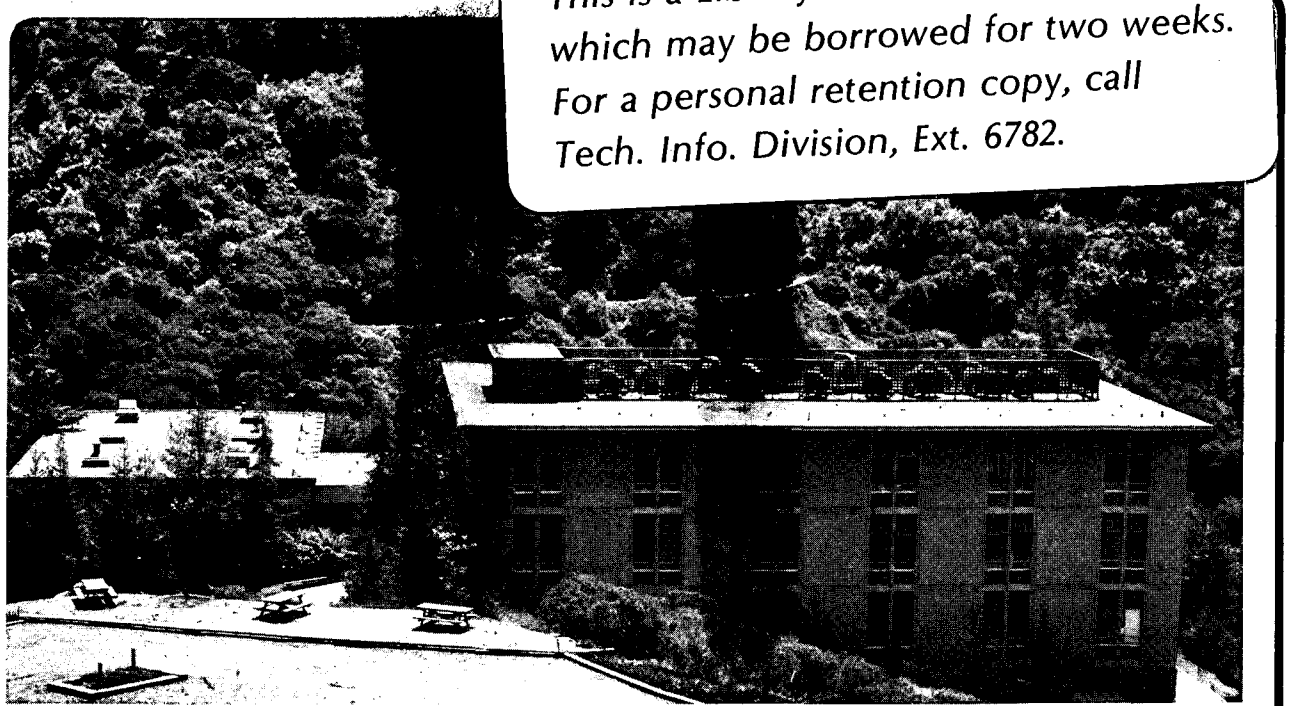

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ABSTRACT

Neutron diffraction data for LaF_3 [Gregson, et al. (1983). Acta Cryst. B39, 687-691] are refined in space group $P\bar{3}c1$ with a model which accounts for the effects of twinning. R = 0.026 for 243 reflections. The results agree with previous and less precise determinations of this crystal structure and disprove the assertion that these neutron data rule out the trigonal structure.

INTRODUCTION

Trigonal crystals of lanthanum trifluoride are prone to twinning with c as the twin axis (rotation of 180° about c), a twin law which does not affect the macroscopic optical properties, the angular conditions for diffraction, nor the rules for systematic absences. Often this twinning has escaped notice in work with large "single crystals" and has lead to incorrect conclusions about the symmetry of the crystal structure. A recent example is a neutron diffraction report by Gregson, Catlow, Chadwick, Lander, Cormack and Fender (1983, hereafter cited as GCCLCF). These authors assert that their data demonstrate that the space group at room temperature is not $P\bar{3}c1$. We show here that in fact these data are in excellent agreement with the trigonal crystal structure, and we report the results of a refinement of the structure in that space group.

Independent X-ray diffraction studies by Mansmann (1965) and by Zalkin, Templeton and Hopkins (1966) showed decisively that the Laue symmetry is $\bar{3}m1$ and reached similar values for the atomic coordinates in space group $P\bar{3}c1$.* A typical sample of structure factor magnitudes in Table 1 gives an indication of the lack of equality of values for reflections hkl and khl when measured with a single crystal. The twinning superimposes these reflections and leads to 6/mmm as the Laue symmetry when the two orientation contribute equally.

*In Zalkin, et al. (1966) the y coordinate of F(1) is in error; it should be -0.055.

In neutron diffraction experiments with larger crystals Rango, Tsoucaris and Zelwer (1966) and Boutin and Choi (1967) observed 6/mmm as the symmetry of the diffraction patterns. It seems that GCCLCF did the same. Their deposited structure factors, which are restricted to reflections independent in 6/mmm, consist of averages of up to four observations for each unique reflection. The reflections averaged are not identified specifically, but it is plausible that hkl and khl type reflections were merged. Such merging would make each datum an average of the two twin orientations even if the twinning were not exactly 50-50.

EXPERIMENTAL

The $P\bar{3}c1$ structure was refined using the structure factors of GCCLCF assuming equality of twinning. Thus $[(F^2(hkl) + F^2(khl))/2]^{1/2}$ was used in place of F(hkl) for the calculated magnitude, and appropriate changes were made in the calculation of the derivatives. Lacking values of the standard deviations we used unit weights, as did GCCLCF. Statistics of the final results indicate that very strong and very weak reflections were overweighted somewhat. We lacked information for a valid extinction correction for the strongest reflections, and six were omitted. An approximate empirical isotropic extinction correction for the remaining 243 reflections increased each F_o by 20 percent or less. Refined on F with anisotropic thermal parameters (21 parameters including scale and extinction), scattering lengths as in GCCLCF, maximum shift/error 10^{-5}, R = 0.026, wR = 0.032, local unpublished programs. Final parameters are listed in Table 2.*

*A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

DISCUSSION

This calculation shows that the neutron diffraction data are explained well by twinning of the trigonal structure. The R = 0.026 for $P\bar{3}c1$ (243 reflections and 21 parameters) is significantly less than R = 0.042 (249 reflections, 25 parameters) for $P6_3cm$. Since R calculated for the six extra reflections in the hexagonal data set is 0.020, inclusion of them is not the reason for the larger value of R. A byproduct of this analysis is a more precise description of the crystal structure (Table 2) than is given by earlier studies. The shortest La-F distances are given in Table 3. There is no significant disagreement with the x-ray results of Zalkin, et al. (1966) nor the neutron powder diffraction analysis of Cheetham, Fender, Fuess and Wright (1976). The thermal parameters indicate large amplitudes in the z direction for F(2) and especially F(3), the atoms which lie in the channels between the lanthanum atoms. For the other atoms the thermal motion is relatively small and less anisotropic. The only previous report of all these parameters (Mansmann, 1965) suffers from incorrect constraints on the lanthanum parameters and gives some amplitudes for fluorine which are zero within experimental error.

Spectroscopic and magnetic resonance data also support the trigonal structure, even though several authors have ignored twinning and have drawn the opposite conclusion. For example, NMR tensors measured with "single crystals" require hexagonal symmetry in the absence of twinning. Difficulties in fitting these data to the site symmetries in $P6_3cm$ prompted proposals of other hexagonal space groups and larger unit cells which are incompatible with the diffraction data regardless of twinning.

Andersson and Johansson (1968) explained how all these data are consistent with a model of twinning of the trigonal structure. A study of the infrared spectra of crystals by Jones and Satten (1966) gives results which also fit the site symmetries of $P\bar{3}c1$ and which cannot be reconciled with those in $P6_3cm$. This latter technique has the advantage that it is not affected by twinning.

We believe that the symmetry of LaF_3 was shown to be $P\bar{3}c1$ many years ago. We hope that the present note will help convince others that this crystal structure has been solved.

ACKNOWLEDGMENT

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Table 1. Sample of X-ray structure factors for LaF_3.
(Zalkin, Templeton and Hopkins, 1966)

hkl	F(hkl)		F(khl)	
	obs.	calc.	obs.	calc.
314	33	37	55	56
324	50	47	33	34
404	78	73	44	44
414	162	157	153	151
424	11	8	25	26
434	59	59	16	12

Table 2. Atomic parameters in $P\bar{3}c1$. Cell dimensions are a = 7.185(1), c = 7.351(1) Å, Zalkin, et al. (1966).

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
La	0.3402(1)	0	1/4	0.43(2)	0.44(3)	0.38(2)	$B_{22}/2$	$B_{23}/2$	-0.06(2)
F(1)	0.3123(2)	-0.0536(2)	0.5813(2)	0.89(3)	1.19(3)	0.69(3)	0.16(3)	0.13(3)	0.16(3)
F(2)	1/3	2/3	0.3141(3)	0.55(3)	B_{11}	1.61(6)	$B_{11}/2$	0	0
F(3)	0	0	1/4	0.63(4)	B_{11}	3.18(14)	$B_{11}/2$	0	0

Table 3. La-F distances, Å

La-2F(2)	2.417(1)
La-F(3)	2.444(1)
La-2F(1)	2.458(1)
La-2F(1)	2.489(1)
La-2F(1)	2.638(1)
La-2F(1)	3.002(1)

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Supplementary Material

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Neutron diffraction data for LaF_3 [Gregson, et al. (1983). Acta Cryst. B39, 687-691] are refined in space group P3c1 with a model which accounts for the effects of twinning. R = 0.026 for 243 reflections. The results agree with previous and less precise determinations of this crystal structure and disprove the assertion that these neutron data rule out the trigonal structure.

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (ALL X11.0)
LAF3 F(0,0,0) = 1667

FOB AND FCA ARE THE OBSERVED AND CALCULATED STRUCTURE FACTORS.
SG = ESTIMATED STANDARD DEVIATION OF FOB. DEL = /FOB/ - /FCA/.
* INDICATES ZERO WEIGHTED DATA.

H	FOB	SG	DEL	H	FOB	SG	DEL	H	FOB	SG	DEL	H	FOB	SG	DEL	H	FOB	SG	DEL
K,L=	1,	0		-2	316	11	4	K,L=	7,	2		K,L=	0,	4		-3	63	11	13
0	56	11	2	-1	437	11	3	-3	200	11	6	0	437	11	14	-2	360	11	10
K,L=	2,	0		K,L=	6,	1		-2	68	11	-33	K,L=	1,	4		-1	399	11	6
-1	321	11	-7	-3	63	11	15	-1	68	11	11	0	449	11	3	K,L=	7,	5	
0	32	11	9	-2	402	11	5	0	245	11	4	K,L=	2,	4		-3	210	11	4
K,L=	3,	0		-1	453	11	2	K,L=	8,	2		-1	61	11	16	-2	566	12	11
-1	108	11	8	K,L=	7,	1		-4	95	11	38	0	190	11	6	-1	304	11	6
K,L=	4,	0		-3	213	11	5	-3	496	11	-0	K,L=	3,	4		K,L=	8,	5	
-2	235	11	6	-2	566	12	2	-2	445	11	3	-1	213	11	5	-4	523	12	10
-1	82	11	4	-1	310	11	5	-1	107	11	2	0	532	12	8	-3	149	11	-0
0	281	11	-4	K,L=	8,	1		0	454	11	6	K,L=	4,	4		-2	266	11	2
K,L=	5,	0		-4	531	12	13	K,L=	9,	2		-2	95	11	14	-1	579	12	5
-2	54	11	15	-3	151	11	2	-4	231	11	-7	-1	546	12	1	K,L=	9,	5	
-1	64	11	12	-2	293	11	1	-3	1017	13	20	0	723	12	-26	-4	265	11	4
0	98	11	2	-1	596	12	10	-2	194	11	-7	K,L=	5,	4		-3	83	11	14
K,L=	6,	0		K,L=	9,	1		-1	277	11	-1	-2	225	11	6	-2	234	11	3
-2	213	11	3	-4	295	11	3	0	996	13	0	-1	152	11	-4	K,L=	10,	5	
-1	227	11	2	-3	79	11	7	K,L=	10,	2		0	315	11	2	-5	576	12	-34
K,L=	7,	0		-2	242	11	-1	-5	56	11	16	K,L=	6,	4		-4	238	11	-27
-3	296	11	-0	-1	278	11	6	-4	68	11	6	-3	664	12	11	K,L=	1,	6	
-2	45	11	13	K,L=	10,	1		-3	62	11	19	-2	287	11	8	0	214	11	7
-1	53	11	24	-5	635	12	17	-2	127	11	-1	-1	99	11	8	K,L=	2,	6	
0	359	11	-4	-4	260	11	1	K,L=	3,	3		0	708	12	2	-1	874	12	3
K,L=	8,	0		-3	156	11	2	-1	126	11	3	K,L=	7,	4		0	292	11	5
-4	238	11	6	-2	615	12	-5	K,L=	4,	3		-3	627	12	-2	K,L=	3,	6	
-3	91	11	1	-1	246	11	-11	-1	71	11	8	-2	160	11	-1	-1	332	11	4
-2	84	11	16	K,L=	11,	1		K,L=	5,	3		-1	413	11	8	01	279	13	8
-1	184	11	6	-5	82	11	9	-2	253	11	-1	K,L=	8,	4		K,L=	4,	6	
0	147	11	-4	-4	507	12	-29	-1	950	13	-47	-4	258	11	-7	-2	772	12	7
K,L=	9,	0		K,L=	0,	2		K,L=	6,	3		-3	314	11	2	-1	181	11	7
-4	311	11	-1	0	579	12	-49	-3	102	11	6	-2	205	11	7	K,L=	5,	6	
-3	982	13	25	K,L=	1,	2		-2	57	11	8	-1	252	11	-5	-2	290	11	2
-2	226	11	3	0	87	11	8	-1	263	11	-2	K,L=	9,	4		-1	598	12	7
-1	192	11	5	K,L=	2,	2		K,L=	7,	3		-4	202	11	5	0	205	11	2
0	852	12	16	-1	268	11	12	-3	161	11	2	-3	761	12	20	K,L=	6,	6	
K,L=	10,	0		0	463	11	-11	-2	644	12	10	-2	273	11	2	-3	846	12	-3
-5	48	11	25	K,L=	3,	2		-1	166	11	1	-1	130	11	1	-2	392	11	-0
-4	246	11	3	-1	297	11	2	K,L=	8,	3		K,L=	10,	4		-1	413	11	1
-3	297	11	-2	0	710	12	-46	-4	658	12	4	-5	152	11	-1	0	729	12	24
-2	111	11	16	K,L=	4,	2		-3	276	11	0	-4	304	11	-8	K,L=	7,	6	
-1	49	11	15	-2	212	11	13	-2	345	11	-1	-3	391	11	-21	-3	155	11	8
K,L=	11,	0		-1	78	11	12	-1	540	12	6	K,L=	2,	5		-2	540	12	2
-5	48	11	40	0	282	11	4	K,L=	9,	3		-1	235	11	17	-1	201	11	8
-4	279	11	-14	K,L=	5,	2		-4	172	11	11	K,L=	3,	5		K,L=	4,	6	
K,L=	2,	1		-2	533	12	-6	-3	142	11	5	-1	316	11	10	0	131	11	6
-1	266	11	3	-1	87	11	-21	-2	27	11	20	K,L=	4,	5		K,L=	7,	6	
K,L=	3,	1		0	577	12	-7	-1	234	11	4	-2	355	11	10	0	201	11	5
-1	355	11	0	K,L=	6,	2		K,L=	10,	3		-1	255	11	9	K,L=	8,	6	
K,L=	4,	1		-3	897	12	-17	-5	315	11	1	K,L=	5,	5		-4	288	11	2
-2	376	11	2	-2	189	11	-6	-4	193	11	-8	-2	279	11	2	-3	172	11	0
-1	282	11	7	-1	379	11	-2	-3	119	11	-5	-1	422	11	8	-2	278	11	6
K,L=	5,	1		0	941	12	-26	-2	316	11	-11	K,L=	6,	5		-1	319	11	-1

STRUCTURE FACTORS CONTINUED FOR
LAF3

H	FOB	SG	DEL
K,L=	9,		6
-4	442	11	-15
-3	427	11	-5
K,L=	2,		7
-1	322	11	11
K,L=	3,		7
-1	336	11	12
K,L=	4,		7
-2	383	11	2
-1	256	11	10
K,L=	5,		7
-2	287	11	7
-1	420	11	3
K,L=	6,		7
-3	46	11	8
-2	367	11	7
-1	419	11	10
K,L=	7,		7
-3	180	11	11
-2	505	11	-2
-1	266	11	9
K,L=	8,		7
-4	464	11	-1
-3	125	11	5
-2	258	11	-1
-1	491	11	-30
K,L=	1,		8
0	218	11	0
K,L=	2,		8
-1	281	11	12
0	287	11	3
K,L=	3,		8
-1	147	11	5
0	179	11	-5
K,L=	4,		8
-2	317	11	8
-1	263	11	4
0	427	11	-0
K,L=	5,		8
-1	403	11	17
0	429	11	2
K,L=	6,		8
-3	371	11	-0
-2	55	11	19
-1	164	11	6
0	445	11	4
K,L=	5,		8
-2	350	11	13
K,L=	7,		8
-3	345	11	-5
-2	377	11	-2
-1	156	11	-0
K,L=	8,		8
-4	467	11	-21
-3	359	11	-39
K,L=	3,		9
-1	115	11	6
K,L=	4,		9
-2	970	13	-11
-1	61	11	7
K,L=	5,		9
-2	208	11	4
-1	843	12	-4
K,L=	6,		9
-3	82	11	6
-2	58	11	0
-1	215	11	-4
K,L=	2,		10
0	354	11	9
K,L=	3,		10
-1	200	11	3
0	339	11	-7
K,L=	4,		10
-1	139	11	6
0	299	11	6
K,L=	5,		10
-2	383	11	-18
-1	291	11	-11

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