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The crystal structure of $LiHF_2$.

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In 1956 Kruh, Fuwa & McEver (1956) reported 'lithium bifluoride is optically anisotropic and rapidly decomposes in air at room temperature to give hydrogen fluoride and lithium fluoride. Diffraction data are consequently very difficult to obtain, although several attempts to obtain Laue photographs from bits of crystals showed hexagonal symmetry.' Using 1-mil Mylar film in a sealed sample holder (Christ & Champaygne, 1948) to protect a powder sample of anhydrous $LiHF_2$, we have obtained excellent powder diffraction data of this compound. Its synthesis was achieved by stirring finely divided anhydrous LiCl for $2\frac{1}{2}$ hours in liquid anhydrous HF at 15 °C. The resultant $LiHF_2$ was then flushed with dry N_2 at 50 °C. to drive off any excess HF.

Table 1. *Powder diffraction data of* $LiHF_2$

Structure $F5_1$
Hexagonal unit cell: $a = 3{\cdot}003 \pm 0{\cdot}004$, $c = 13{\cdot}186 \pm 0{\cdot}005$ Å
Rhombohedral unit cell: $a = 4{\cdot}725 \pm 0{\cdot}005$ Å, $\alpha = 37°\ 3' \pm 2'$
based on Cu $K\alpha_1 = 1{\cdot}5405$ Å
$(I/I_1)_o$ = observed relative intensity $(I/I_1)_c$ = calculated relative intensity
{*HKL*} hexagonal indices for a given powder reflection
{*hkl*} corresponding rhombohedral indices

{*HKL*}	{*hkl*}	d_o (Å)	d_c (Å)	$(I/I_1)_o$	$(I/I_1)_c$
003	111	4·392	4·395	0·09 ± 0·03	0·095
101	100	2·556	2·552	1·00	1·000
012	110	2·425	2·419	0·44 ± 0·08	0·570
006	222	2·201	2·198	0·28 ± 0·11	0·253
104	211	2·043	2·042	0·10 ± 0·03	0·127
015	221	1·854	1·852	0·34 ± 0·17	0·544
107	322	1·525	1·526	0·08 ± 0·03	0·178
110	10$\bar{1}$	1·502	1·502	0·22 ± 0·10	0·238
009	333	1·465	1·465	< 0·003	0·0001
113	210	(LiF)	1·421	—	0·012
018	332	1·396	1·392	0·003	0·005
021	11$\bar{1}$	1·294	1·294	0·047	0·039
202	200	1·276	1·276	0·031	0·032
116	321	1·239	1·240	0·078	0·090
024	220	(LiF)	1·210	—	0·009
1,0,10	433	1·175	1·176	0·021	0·034
205	311	1·165	1·166	0·039	0·058
0,0,12	444	1·098	1·099	0·021	0·017
0,1,11	443	1·087	1·089	0·021	0·022
027	331	1·070	1·070	0·021	0·033
119	432	—	1·049	—	0·0001
208	422	1·021	1·021	0·001	0·001
211	20$\bar{1}$	0·9801	0·9802	0·013	0·023
122	21$\bar{1}$	0·9718	0·9722	0·009	0·021
1,0,13	544	0·9435	0·9450	0·005	0·007
214	310		0·9420		0·006
0,2,10	442	(LiF)	0·9259	—	0·014
125	320	0·9205	0·9211	0·016	0·050
1,1,12	543	0·8866	0·8867	0·018	0·054
0,1,14	554	—	0·8856	—	0·004
2,0,11	533	0·881	0·8814	0·004	0·012
0,0,15	555	—	0·8791	—	0·001
217	421	0·8716	0·8715	0·009	0·038
300	21$\bar{1}$	0·8667	0·8669	0·006	0·028
303	300	—	0·8505	—	0·001
128	431	—	0·8442	—	0·002
306	411	0·8061	0·8064	0·006 (x_1)	0·016

Table 1 contains the powder diffraction data obtained with filtered Cu $K\alpha$ radiation in a cylindrical G. E. camera (71·6 mm. radius). The pattern of $LiHF_2$ was indexed on the basis of the $F5_1$ structure (Andersen & Hassel, 1926; Frevel & Rinn, 1953; Rinne *et al.*, 1923). Three films of different exposure were measured with a comparison scale to obtain the averaged relative intensities recorded. The sample of $LiHF_2$ as prepared contained approximately 10 wt.% LiF which served as a useful internal standard for film calibration and intensity comparisons. The atomic positions referred to the rhombohedral cell are: Li^+ at (0, 0, 0), H^+ at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, F^- at (u, u, u), and F^- at $(\bar{u}, \bar{u}, \bar{u})$. The structure factors and the intensity expression are given by

$$F_{hkl} = f_{Li^+} + 2f_{F^-} \cos 2\pi(h+k+l) + f_{H^+} \cos \pi(h+k+l)$$

$$I_{hkl} \propto \frac{(1+\cos^2 2\theta)}{\sin^2\theta \cos\theta} j_{hkl} F^2_{hkl} \exp[-2B \sin^2\theta/\lambda^2].$$

For the calculation of the relative intensities, we used the atomic scattering factors of Li^+ by Hurst, Miller & Matson (1958): For F^-, the values of Vand, Eiland & Pepinsky (1957). The temperature factor was arbitrarily taken as $B = 1{\cdot}5$ Å^2, although anisotropic temperature factors are indicated. From a calculation of the relative intensities of the LiF pattern (internal standard) it was ascertained that the absorption correction amounted to less than 10% and thus was not applied. The value of the parameter u was found to be $0{\cdot}414 \pm 0{\cdot}004$, yielding a fluorine–fluorine distance in the $(FHF)^-$ ion of 2·27 Å in good agreement with the value of 2·26 Å in KHF_2 (Helmholtz & Rogers, 1949).

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