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BRIEF COMMUNICATIONS

Thermal Parameters for Lithium Halides

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The thermal parameters for LiF, LiCl, LiBr, LiI have been determined using a high-resolution neutron powder diffractometer (λ = 1.500 Å), and found to be 1.17(5), 0.73(3); 2.39(7), 1.18(2); 3.16(8), 1.46(3); 4.08(11), 1.84(5) Å^2, respectively, for (Li, X) at 294 K.

Introduction

In 1965, Phillips and Williams (*1*) proposed a 6:6 structure for lithium iodide where the regular octahedral symmetry would be distorted by electrostatic repulsions of the large neighboring iodide ions. Their calculations indicated that a greater lattice energy would result if the small lithium ions moved away from the central anionic positions. Precise location of these ions would be very difficult experimentally using X-ray diffraction as the iodide atoms would dominate the scattering. Consequently the structure of LiI was sought using neutron powder diffractometry. As these results showed that the temperature factor for Li was more than twice that for I, thermal parameters for other lithium halides were determined to see if this result was an isolated event. This work adds new experimental data not recorded in the literature.

Experimental

The materials used were packed under dry helium into a 12-mm-diameter vanadium can, filled to a height of 5 cm, and sealed with an indium "O"-ring. The can was rotated at the center of the Australian High Resolution Powder Diffractometer (*2*) at 294(1) K. The present instrument has eight detectors 6° apart [germanium monochromator, plane (117), λ = 1.376 Å; plane (335), λ = 1.500 Å], and uses the 6HB hole of the Australian Atomic Energy Commission's HIFAR (DIDO-type) 10-MW reactor. Data were corrected for absorption (*3*) with background being found by a 12-point interpolation. The diffractometer was calibrated with Al_2O_3 (a = 4.758, c = 12.991

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TABLE I

SUMMARY OF RIETVELD REFINEMENT ON LITHIUM HALIDES

Compound	Experimental λ (Å)	B_{Li}	B_X	Calculated[a] B_{Li}	B_X (Å)^2
LiF	1.377	1.14(4)	0.75(2)	0.905	0.613
LiF	1.500	1.17(5)	0.73(3)		
	X Ray[b]				
LiF	0.7107	1.011(6)	0.683(3)		
LiCl	1.500	2.39(7)	1.18(2)	1.813	1.334
LiBr	1.500	3.16(8)	1.46(3)	2.208	1.561
LiI	1.500	4.08(11)	1.84(5)	3.366	1.845

Li at (½, 0, 0) etc. and X at (0, 0, 0), etc.

	μRs Expt	Calc	R_p	R_w	R_B
LiF	1.394	1.374	5.7	7.2	1.9
LiF			5.8	7.6	1.0
LiF					3.0
					Single crystal
LiCl	0.765	0.748	4.6	6.1	0.7
LiBr	0.513	0.458	5.0	6.2	0.8
LiI	0.289	0.336	5.1	6.4	0.9

Note. R_p, the pattern R factor = $100[\Sigma|y_i - y_{ci}|/\Sigma y_i]$; R_w, the weighted pattern R factor = $100[\Sigma w(y_i - y_{ci})^2/\Sigma w y_i]$; $w = 1/\sigma^2_{y_i}$ when background refined; $R_B = 100\Sigma|I_{obs} - I_{calcd}|/\Sigma I_{obs}$.

[a] Gupta (6).

[b] Howard and Khadake (7).

Å). Each diffraction pattern was analyzed using a local version of a computer program (4) based on the Rietveld method (5) with scattering lengths for Li, F, Cl, Br, and I of −2.03, 5.65, 9.579, 6.79, and 5.28 fm^{-1}, respectively.

The 6 : 6 structure for lithium iodide was verified by attempting to use the zinc blende structure. After five cycles, the Li at (¼, ¼, ¼) etc., refined to give a negative occupancy factor, R = 29.2%. A second attempt included Li atoms at (¼, ¼, ¼) etc., and (½, 0, 0) etc. The tetrahedral site refined to give zero occupancy in six cycles, while the octahedral one was at full occupancy, R = 1.3%.

The high thermal parameter for Li [B, 4.08(11), $(\overline{U}^2)^{1/2}$ 0.227(3) Å^2] for Li compared to I [B, 1.84(5), $(\overline{U}^2)^{1/2}$ 0.153(2) Å^2] do indicate that the small lithium ion is able to move away from its octahedral site. This relative difference in thermal parameters was found for all lithium halides with B_{Li}/B_X being 1.60, 2.02, 2.16, 2.22 compared to the theoretical 1.48, 1.36, 1.41, 1.82 for X = F, Cl, Br, I. The results are listed in Tables I and II and indicate that the theoretical values of Gupta (6) are always low for B_{Li}. However, our thermal parameters could be subject to some degree of systematic error due to extinction and thermal diffuse scattering. Because iodide was granular and hygroscopic, it was difficult to powder without altering its purity, and as little was known about its particle size, no correction was made for extinction. The geometry of the HRPD minimized errors due to thermal diffuse scattering. It is encouraging to note that the thermal parameters for LiF are comparable to single crystal X-ray data of Howard and Khadake (7) as shown in Table I.

Acknowledgments

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TABLE II

DATA FOR LITHIUM HALIDES [λ = 1.500 Å][a]

(*hkl*)	Multiplicity	LiF		LiCl		LiBr		LiI	
		I_{obs}	I_{calcd}	I_{obs}	I_{calcd}	I_{obs}	I_{calcd}	I_{obs}	I_{calcd}
111	8	2963(18)	2973	3992(21)	4010	3215(23)	3231	1961(14)	1961
002	6	477(6)	452	1028(9)	1021	594(7)	587	258(4)	253
022	12	502(6)	518	1027(10)	1025	597(7)	585	258(4)	254
113	24	3142(19)	3111	3140(19)	3121	2359(16)	2350	1365(12)	1360
222	8	232(4)	236	453(6)	442	253(4)	247	110(2)	105
004	6	177(3)	177	260(4)	261	141(2)	146	63(1)	63
133	24	2405(16)	2407	1746(13)	1747	1221(11)	1219	659(7)	667
024	24	695(7)	702	850(9)	853	456(6)	467	203(3)	201
224	24	750(9)	728	705(8)	712	374(5)	377	159(3)	158
333 } 115 }	8 + 24			1661(13)	1645	1041(10)	1047	536(7)	533
044	12			306(4)	307	151(2)	153	59(1)	62
135	48			2100(15)	2111	1177(11)	1181	544(6)	552
244	24			604(6)	590	280(4)	273	104(2)	106
006	6			155(2)	151	72(1)	71	27(1)	28
026	24			634(8)	647	273(4)	271	99(2)	101
335	24					512(6)	503	205(3)	200
226	24					264(4)	266	93(2)	90
444	8					98(2)	97	28(1)	28
155	24							178(2)	174
117	24							178(2)	174
046	24							88(1)	88
246	48							173(3)	177

[a] These intensities were obtained from the Rietveld refinement.