

THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

Part X. The Lithium Salts

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A DISTINGUISHING feature of the lithium halides is the great disparity between the atomic weights of the metal and halogen atoms which are their constituent elements. Noteworthy also is the strength of the chemical bonds holding the structure together which is indicated by the magnitudes of the force-constants. As a consequence of these features, five of the atomic vibration frequencies have high values, while the other four frequencies are much lower. The vibration spectrum thus consists of two distinct sectors. This is reflected in the thermal behaviour of the crystals. The atomic heat rises rather steeply in the lower ranges of temperature, and this is followed by a much less rapid increase towards the limiting value at higher temperatures.

The manner of computation of the atomic heats has already been explained in Part VII of this memoir. The computation is based on the frequencies of the free modes of atomic vibration and their respective degeneracies. The frequencies now made use of for each case are shown in Table I below. The details of the computation are set out in Tables II,

TABLE I

Atomic Vibration Frequencies (in cm.^{-1})

	Degeneracies								
	3	6	3	4	8	4	8	3	6
LiF ..	508	417	384	435	435	263	263	210	210
LiCl ..	367	343	336	336	336	148	148	147	130
LiBr ..	325	315	312	312	312	92	92	92	80
LiI ..	280	274	273	273	273	64	64	64	56

III, IV and V appearing in the succeeding pages. The results have been graphically represented as functions of the absolute temperature in Figs. 1 and 2 appearing below in the text. Fig. 2 exhibits the computed atomic heats for all the four halides to facilitate their comparison with each other.

Neither spectroscopic studies nor any measurements of specific heats have been reported for lithium chloride, lithium bromide and lithium iodide. The only specific heat data available are those for lithium fluoride. The spectroscopic behaviour of lithium fluoride in the infra-red has been the subject of a detailed investigation by the present writer.¹ The characteristic frequencies determined from that investigation have been shown in Table I and made use of in the computations set out in Table II. The experimental values have been plotted in Fig. 1 in order to exhibit the agreement of the experimental data with the theoretical computations.

The highest frequency of 508 cm.^{-1} appearing in Table I is precisely determined from the spectrophotometer records of absorption by the thinnest cleavage plates of lithium fluoride which exhibit a very pronounced and sharply defined absorption maximum at 9.84μ , the wavelength corresponding to the octave of that frequency. The frequencies of 435 cm.^{-1} and 263 cm.^{-1} of the inactive octahedral modes were deduced from the frequency of 508 cm.^{-1} by a simple calculation based on the individual masses of the lithium and fluorine atoms respectively as compared with the reduced mass which determines the highest frequency. The frequencies of the four active cubic modes 417 cm.^{-1} , 384 cm.^{-1} , 210 cm.^{-1} , 210 cm.^{-1} are observational values derived from the spectrophotometer records which exhibit the absorptions of the second order due to the corresponding modes. Thus, the computations are based exclusively on the spectroscopic observations. In the circumstances, the agreement of the computed results with the observed thermal behaviour over the entire range of temperature exhibited in Fig. 1 forms an impressive demonstration of the validity of the ideas on which the computations are based.

It will be noticed from Table I that the atomic vibration frequencies listed in it fall into two groups. The frequencies in each group differ but little from each other, and indeed in the cases of lithium bromide and lithium iodide, they are practically identical. The frequencies of both the groups diminish with the increasing atomic weight of the halogen, the fall being proportionately more rapid for the second group. As a consequence, the atomic heats of the lithium halides exhibit their greatest differences in the lower ranges of temperature.

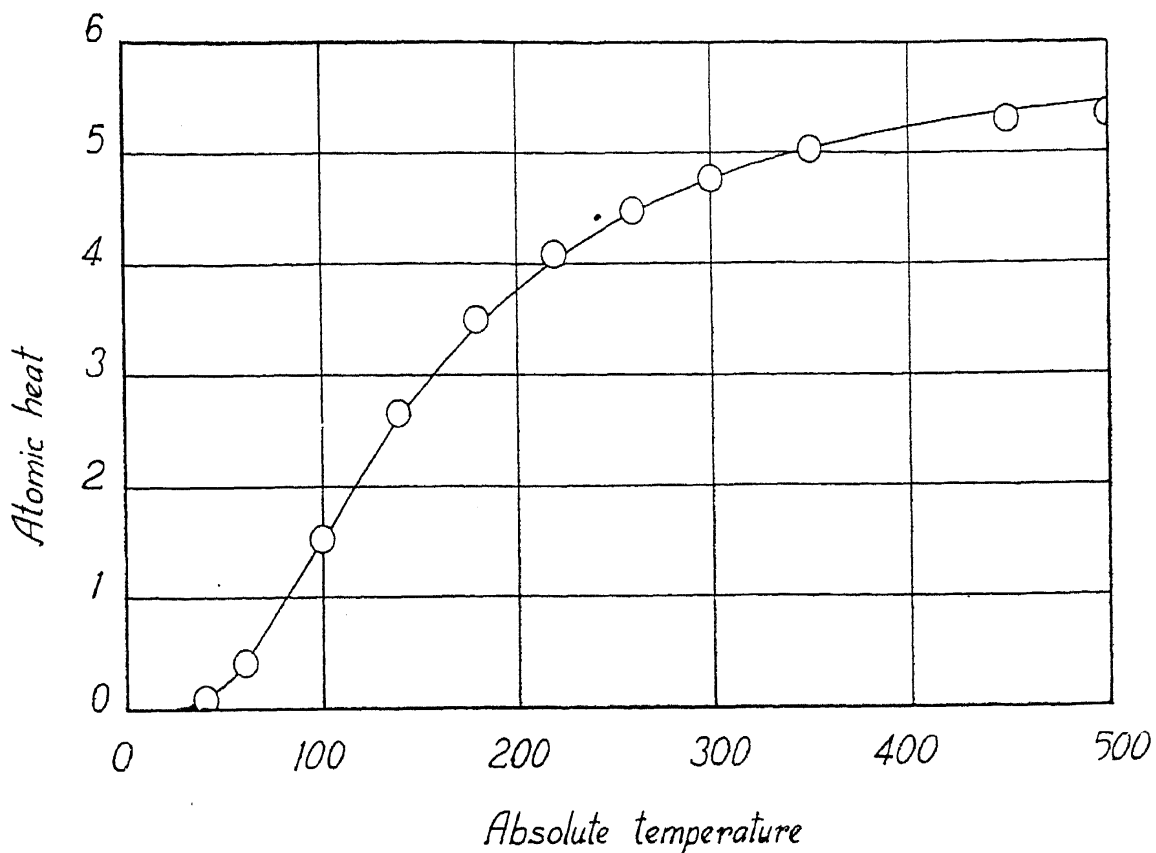


FIG. 1. Atomic Heats of Lithium Fluoride
 Computed values ———.
 Observed values ○○○○.

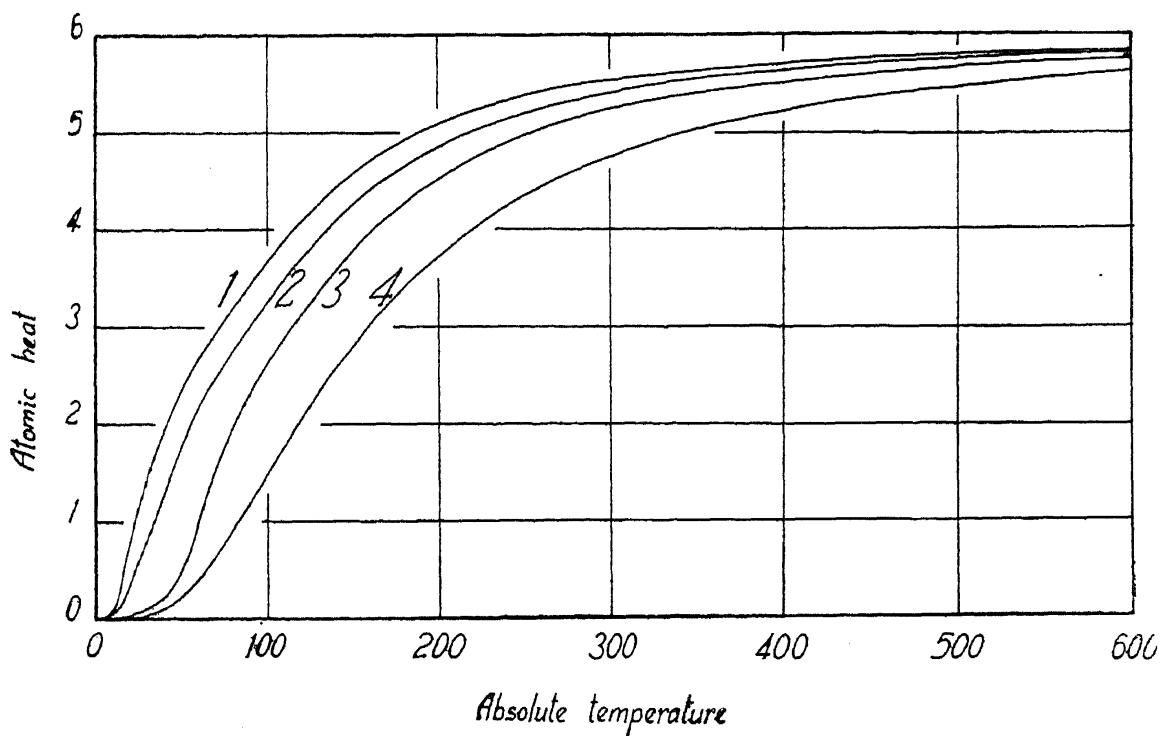


FIG. 2. Computed Atomic Heats of (1) LiI, (2) LiBr, (3) LiCl, (4) LiF.

TABLE II. *Computation of the Atomic Heats of Lithium Fluoride*

Temperature	20° K.	40° K.	60° K.	100° K.	140° K.	180° K.	220° K.	260° K.	300° K.	350° K.	400° K.	450° K.	500° K.
3E (508)	0.0003	0.0124	0.0530	0.1061	0.1559	0.1971	0.2293	0.2594	0.2821	0.2982	0.3112
12E (435)	..	0.0001	0.0042	0.0154	0.3368	0.5773	0.7784	0.9275	1.0377	1.1117	1.2116	1.2653	1.3036
6E (417)	0.0030	0.0033	0.1868	0.3104	0.4074	0.4611	0.5342	0.5821	0.6165	0.6412	0.6578
3E (384)	..	0.0001	0.0028	0.0435	0.1133	0.1760	0.2224	0.2568	0.2805	0.3021	0.3171	0.3277	0.3362
12E (263)	..	0.0094	0.1025	0.4932	0.8250	1.0342	1.1642	1.2449	1.3013	1.3508	1.3798	1.4025	1.4178
9E (210)	..	0.0309	0.1782	0.5398	0.7603	0.8828	0.9533	0.9948	1.0254	1.0474	1.0633	1.0748	1.0830
3D (210)	..	0.0081	0.0574	0.2430	0.2966	0.3236	0.3387	0.3470	0.3536	0.3582	0.3614	0.3638	0.3655
Calc. C_v	..	0.0082	0.0979	1.5006	2.5718	3.4104	4.0203	4.4498	4.7620	5.0417	5.2318	5.3735	5.4751
Exptl. C_v^*	..	0.0086	0.1030	1.5250	2.6650	3.5080	4.0760	4.4550	4.7724	5.0245	5.1908	5.2951	5.3496

* (1) K. Clusius, J. Goldmann and A. Perlick .. *Z. Naturforsch.*, 1949, 4 A, 424-32.
 (2) Douglas, T. B. and Denver, J. L. .. *Jour. Am. Chem. Soc.*, 1954, 76, 4826-29.

TABLE III. Computation of the Atomic Heats of Lithium Chloride

	25° K.	50° K.	75° K.	100° K.	100° K.	100° K.	200° K.	250° K.	300° K.	350° K.	400° K.	450° K.	500° K.	550° K.	600° K.
3E (367)	..	0.0009	0.0151	0.0511	0.1415	0.2113	0.2577	0.2879	0.3075	0.3213	0.3308	0.3392	0.3444	0.3486	
6E (343)	..	0.0063	0.0422	0.1271	0.3164	0.4534	0.5393	0.5932	0.6297	0.6542	0.6739	0.6856	0.6952	0.7033	
15E (336)	..	0.0097	0.1153	0.3378	3.8175	0.1550	1.3649	1.4988	1.5853	1.6414	1.6910	1.7194	1.7431	1.7606	
15E (148)	0.0246	0.4750	0.9729	1.2799	1.5707	1.6936	1.7506	1.7831	1.8030	1.8168	1.8263	1.8333	1.8388	1.8429	
6E (130)	0.0217	0.2531	0.4482	0.5560	0.6530	0.6909	0.7098	0.7204	0.7267	0.7311	0.7339	0.7361	0.7382	0.7393	
3D (130)	0.0587	0.1992	0.2759	0.3129	0.3443	0.3560	0.3617	0.3650	0.3669	0.3682	0.3690	0.3696	0.3701	0.3704	
Calc. C.	0.1050	0.9412	1.8696	2.6648	3.8434	4.5602	4.9840	5.2484	5.4191	5.5330	5.6249	5.6832	5.7298	5.7651	

TABLE IV. *Computation of the Atomic Heats of Lithium Bromide*

	25° K.	50° K.	75° K.	100° K.	150° K.	200° K.	250° K.	300° K.	350° K.	400° K.	450° K.	500° K.	550° K.	600° K.
3E (325)	..	0.0025	0.0269	0.0744	0.1720	0.2379	0.2780	0.3037	0.3206	0.3308	0.3403	0.3455	0.3501	0.3536
6E (316)	..	0.0064	0.0611	0.1615	0.3699	0.4880	0.5655	0.6149	0.6468	0.6678	0.6836	0.6941	0.7023	0.7089
15E (312)	..	0.0173	0.1593	0.4161	0.9115	1.2286	1.4230	1.5411	1.6206	1.6732	1.7115	1.7380	1.7581	1.7744
15E (92)	0.2521	1.0560	1.4353	1.6065	1.7431	1.7933	1.8108	1.8305	1.8402	1.8450	1.8509	1.8523	1.8536	1.8544
6E (80)	0.1550	0.4828	0.6104	0.6647	0.7080	0.7241	0.7311	0.7355	0.7388	0.7406	0.7411	0.7416	0.7420	0.7423
3D (80)	0.1525	0.2881	0.3306	0.3480	0.3612	0.3661	0.3682	0.3694	0.3702	0.3707	0.3710	0.3713	0.3715	0.3716
Calc. C _p	0.5596	1.8537	2.6236	3.2712	4.2557	4.8380	5.1830	5.3951	5.5372	5.6287	5.6984	5.7428	5.7776	5.8052

TABLE V. *Computation of the Atomic Heats of Lithium Iodide*

	25° K.	50° K.	75° K.	100° K.	150° K.	200° K.	250° K.	300° K.	350° K.	400° K.	450° K.	500° K.	550° K.	600° K.
3E (280)	..	0.0070	0.0480	0.1085	0.2079	0.2662	0.2998	0.3199	0.3324	0.3418	0.3476	0.3521	0.3558	0.3588
6E (274)	..	0.0161	0.1084	0.2265	0.4261	0.5393	0.6043	0.6440	0.6693	0.6856	0.6973	0.7063	0.7124	0.7173
15E (273)	0.0001	0.0409	0.2618	0.5724	1.0650	1.3623	1.5144	1.6100	1.6732	1.7141	1.7431	1.7656	1.7831	1.7953
15E (64)	0.6526	1.4024	1.6384	1.7327	1.8030	1.8277	1.8415	1.8496	1.8523	1.8540	1.8549	1.8557	1.8564	1.8568
6E (56)	0.3270	0.5395	0.6764	0.7043	0.7267	0.7344	0.7388	0.7409	0.7416	0.7421	0.7424	0.7427	0.7429	0.7430
3D (56)	0.2301	0.3272	0.3511	0.3600	0.3669	0.3692	0.3702	0.3709	0.3713	0.3716	0.3717	0.3718	0.3718	0.3719
Calc. C _p	1.2098	2.2931	3.0791	3.7044	4.5956	5.0891	5.3690	5.5353	5.6401	5.7092	5.7570	5.7942	5.8224	5.8426

It would obviously not be quite correct to base the computations of the atomic heat at low temperatures on the atomic vibration frequencies as determined by spectroscopic observations made at room temperature, since they would be a little different at the lower temperatures. Likewise, it would not be strictly correct to make use of the elastic constants measured at room temperatures for a computation of the atomic vibration frequencies effective at low temperatures. Hence, certain corrections are necessary. Their magnitudes are not the same in all the cases. They are small enough to be ignored in the case of LiF, but are sensible for the three other halides. The necessary corrections to the vibration frequencies have been made in Table I.

SUMMARY

The great disparity between the atomic weights of the constituent metal and halogen atoms has a notable influence on the character of the vibration spectra as also on the thermal behaviour of the lithium halides. The atomic heat rises rather steeply in the lower ranges of temperature and this is followed by a relatively slow increase towards the limiting value at higher temperatures.

REFERENCE

1. Raman, C. V. . . . *Proc. Ind. Acad. Sci.*, 1962, 55 A, 133-52.