THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

Part XI. The Sodium Salts

By Sir C. V. Raman

(*Memoir No.* 131 *of the Raman Research Institute, Bangalore* 6)

Received June 30, 1962

The atomic vibration spectra of all the alkali halides, each consisting of a set of nine discrete frequencies, were computed and listed in Part VI of this memoir. The calculations which were made took into account the two force-constants α and β expressing the interactions between adjoining metal and halogen atoms in the structure. α and β refer respectively to the longitudinal and transverse displacements of the two atoms relative to each other and are very simply related to the bulk-modulus and shear-modulus respectively of the crystal. They are, therefore, readily evaluated from the results of ultrasonic measurements of the elastic constants.

In the case of the four sodium halides, the highest of the nine frequencies expressed as a wave-number, came out respectively for the fluoride, the chloride, the bromide and the iodide as 281 cm.$^{-1}$, 187 cm.$^{-1}$, 152 cm.$^{-1}$ and 131 cm.$^{-1}$ The progressive diminution of the frequency is to some extent a consequence of the increasing atomic weight of the halogen, but it is chiefly the result of the diminishing strength of the binding between the metal and halogen atoms in the series. Expressed as infra-red wavelengths in microns, the corresponding figures are $35 \cdot 6\,\mu$, $53 \cdot 5\,\mu$, $65 \cdot 8\,\mu$ and $76 \cdot 3\,\mu$ respectively. These wavelengths agree with the positions in the spectrum of the maximum reflecting power for infra-red radiation reported in the literature for sodium fluoride and sodium chloride respectively, while no determinations of the rest-strahlen wavelength have been reported for the bromide or the iodide.

The vibration frequencies which we shall adopt for the calculation of the atomic heats for the four halides of sodium are listed below in Table I. There are certain differences between these figures and the frequencies computed and listed in Part VI of the memoir. The justification for these changes will be stated later. The details of the computation of the atomic heat are exhibited in Tables II, III, IV and V. The results are graphically exhibited

TABLE I

Atomic Vibration Frequencies

(in $\mathrm{cm.}^{-1}$)

	Degeneracies								
	3	4	8	4	8	6	3	3	6
NaF ..	285	270	260	246	236	240	210	187	144
NaCl	189	179	165	147	124	158	135	116	97
NaBr	163	144	144	77	77	152	144	76	60
NaI ..	140	129	129	55	55	133	129	54	43

in Figs. 1, 2, 3 and 4 below. No determinations of specific heat have been reported for sodium bromide in the temperature range between 0° and 300° K. Accordingly, Fig. 3 shows only the computed atomic heats. In Figs. 1, 2 and 4, the experimental values have been shown alongside the computed curve to exhibit the agreement between theory and observation. It will be seen that this is quite satisfactory and particularly so in the case of sodium iodide where recent and reliable measurements of the specific heats are available:

Amongst the sodium salts, the fluoride stands in a class by itself. Its melting point is the highest, its refractive index the lowest and, excepting lithium fluoride, its aqueous solubility is the lowest and the bulk-modulus and the shear-modulus of elasticity the highest amongst all the sixteen halides. These facts indicate that the structure of sodium fluoride is held together by powerful interatomic forces. Its vibration frequencies should therefore be much higher than those of the corresponding modes of the other halides of sodium. Table I shows this to be the case.

The atomic weights of sodium and fluorine being not very different, the octahedral layers containing the one or the other species of atom alone have comparable frequencies of oscillation, those of the sodium atoms being a little lower. The position is reversed in respect of the other halides, where the halogens have much greater atomic weights. With the increasing mass of the halogen atoms, the oscillations of the layers containing them have progressively lower frequencies. This is shown by the entries on Table I.

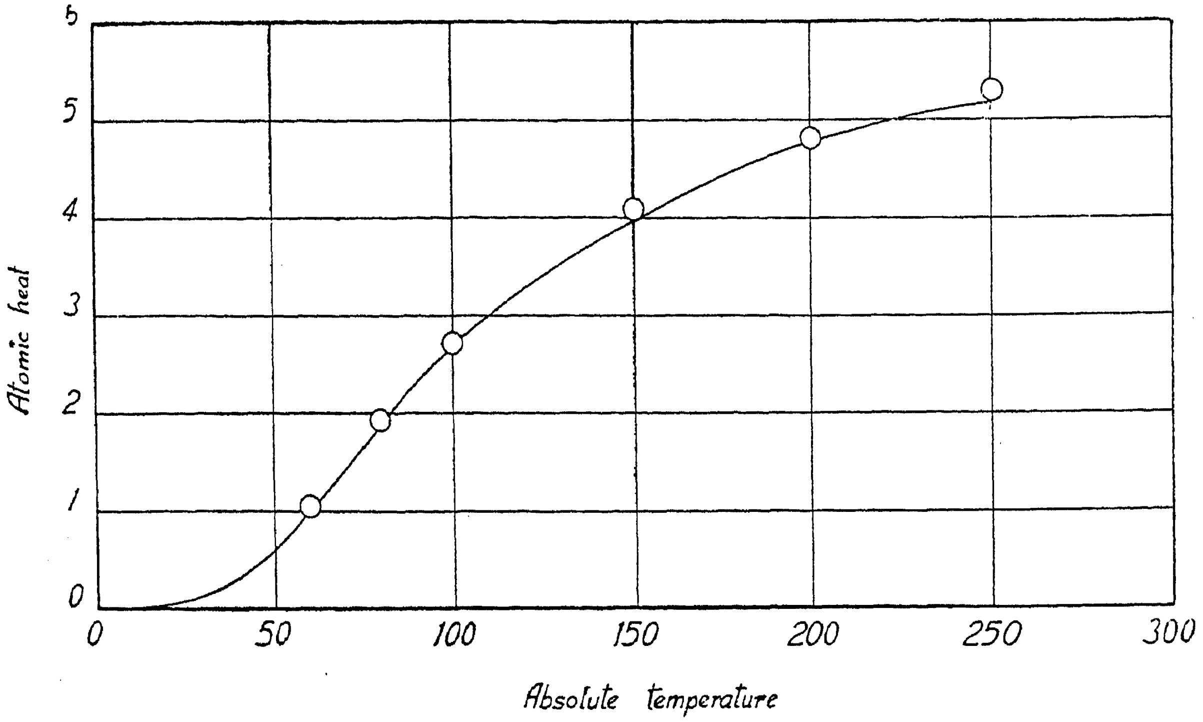

FIG. 1. Atomic Heats of Sodium Fluoride.

C_v Computed values ———

C_p Observed values O O O O

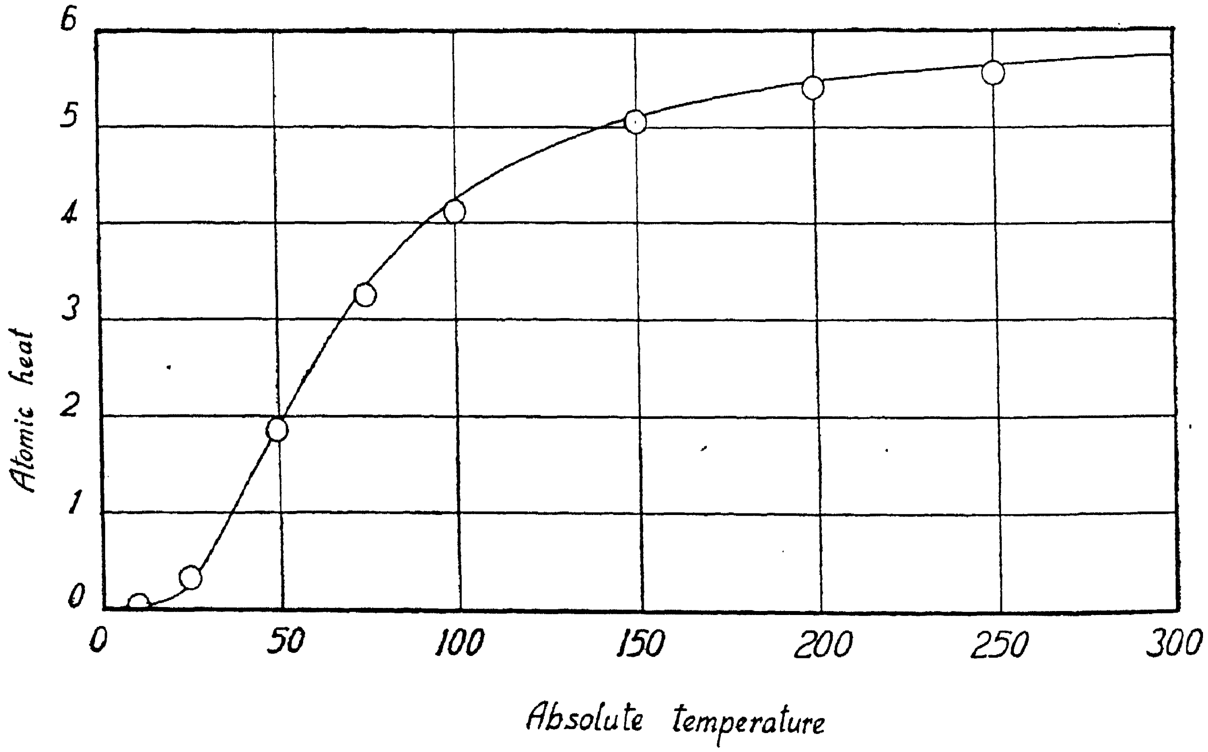

FIG. 2. Atomic Heats of Sodium Chloride.

C_v Computed values ———

C_v Observed values O O O O

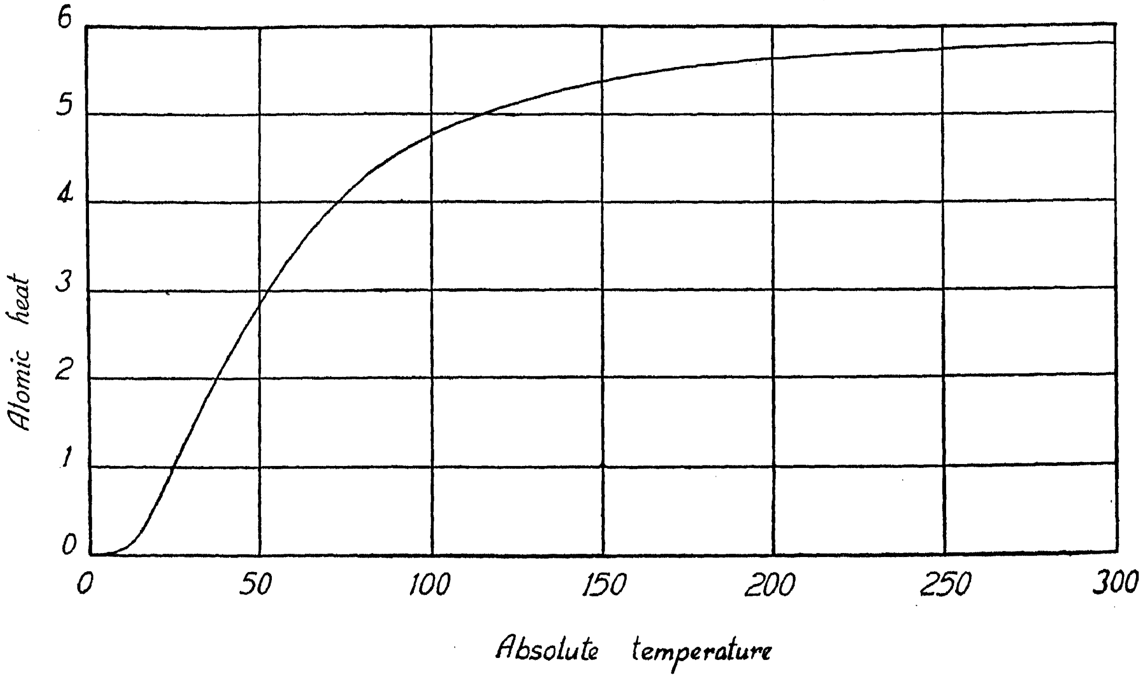

FIG. 3. Atomic Heats of Sodium Bromide (Computed).

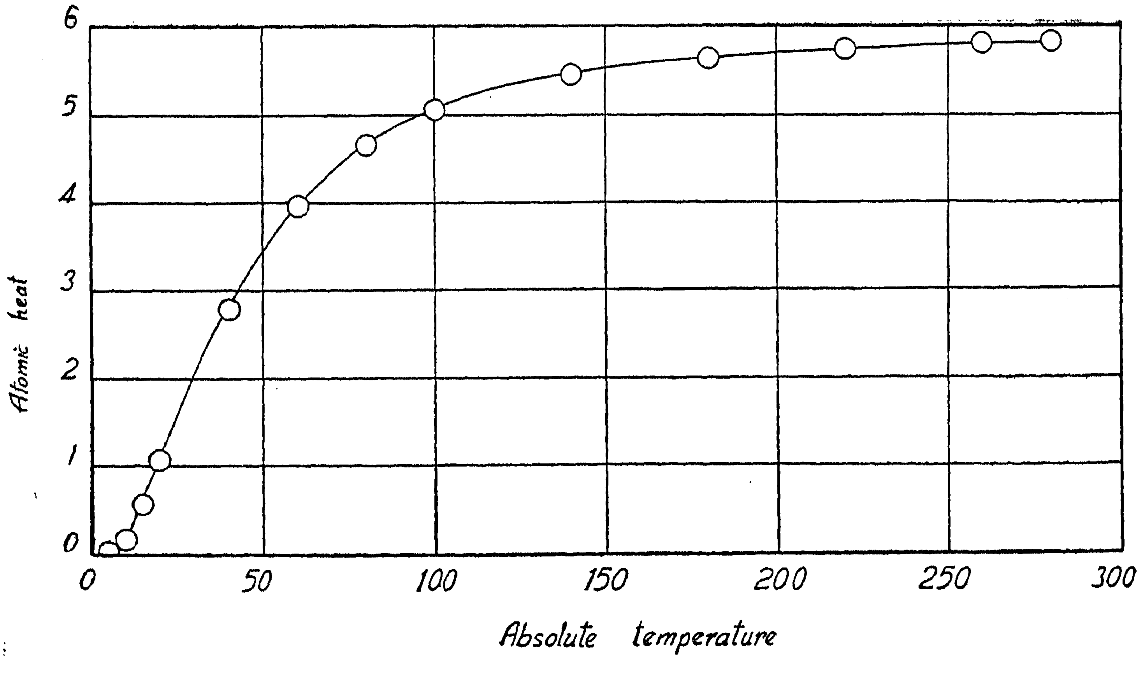

FIG. 4. Atomic Heats of Sodium Iodide.

C_v Computed values ———

C_v Observed values ○ ○ ○ ○

A somewhat similar situation also arises in respect of the two lowest frequencies of coupled oscillation of the atoms in the cubic layers.

TABLE II

Computation of the Atomic Heats of Sodium Fluoride

	20° K.	40° K.	60° K.	80° K.	100° K.	150° K.	200° K.	250° K.
3E (285) ..	..	0·0012	0·0175	0·0561	0·1038	0·2037	0·2628	0·2974
4E (270) ..	..	0·0025	0·0301	0·0890	0·1560	0·2874	0·3629	0·4049
8E (260) ..	..	0·0068	0·0717	0·1983	0·3374	0·5977	0·7413	0·8219
4E (246) ..	..	0·0051	0·0452	0·1149	0·1868	0·3149	0·3827	0·4189
6E (240) ..	..	0·0090	0·0743	0·1836	0·2929	0·3578	0·5805	0·6341
8E (236) ..	..	0·0134	0·1059	0·2562	0·4021	0·6507	0·7804	0·8493
3E (210) ..	..	0·0103	0·0594	0·1239	0·1799	0·2662	0·3075	0·3283
3E (187) ..	0·0001	0·0189	0·0832	0·1530	0·2071	0·2846	0·3199	0·3382
6E (144) ..	0·0023	0·1088	0·2929	0·4312	0·5223	0·6341	0·6805	0·7023
3D (144) ..	0·0246	0·1266	0·2162	0·2697	0·3017	0·3383	0·3525	0·3594
Calc. C_c ..	0·0270	0·3026	0·9964	1·8759	2·6900	3·9354	4·7710	5·1547
Exptl. C_p* ..	..	..	1·065	1·929	2·714	4·089	4·804	5·307

* "Landolt-Bornstein" 6 Auflage, 4 Teil, II Bd., 1961, p. 486.

The forces which determine the atomic vibration frequencies in the alkali halides are *principally* those arising from relative displacements of the metal and halogen atoms attached to each other in the structure. It suffices to take them into account to obtain a good approximation to the actual values of the atomic vibration frequencies. In particular, the highest vibration frequency is correctly given in the cases of LiF, NaF and NaCl where it is known from observational data. The same approximation also suffices as a basis for a computation of the atomic heats of the solids, and the results obtained are not unsatisfactory. But other interatomic forces of lesser magnitude have also to be considered if a complete quantitative agreement with the facts is to be obtained in all cases.

As has been pointed out in earlier parts of the memoir, the interactions between atoms of the same species do not appear in the equations of motion for the mode of vibration having the highest frequency. But they do appear in the expressions for the other modes. In particular, they have a sensible

Table III

Computation of the Atomic Heats of Sodium Chloride

	10° K.	25° K.	50° K.	75° K.	100° K.	150° K.	200° K.	250° K.	300° K.
3E (189) ..	..	0·0007	0·0463	0·1339	0·2029	0·2830	0·3185	0·3377	0·3471
4E (179) ..	..	0·0016	0·0739	0·1972	0·2897	0·3881	0·4312	0·4544	0·4662
8E (165) ..	..	0·0060	0·1902	0·4483	0·6252	0·8057	0·8802	0·9198	0·9417
6E (158) ..	..	0·0063	0·1606	0·3583	0·4863	0·6134	0·6678	0·6941	0·7089
4E (147) ..	..	0·0069	0·1288	0·2617	0·3436	0·4198	0·4523	0·4668	0·4761
3E (135) ..	..	0·0088	0·1170	0·2156	0·2721	0·3234	0·3439	0·3536	0·3591
8E (124) ..	..	0·0374	0·3680	0·6252	0·7611	0·8786	0·9283	0·9510	0·9637
3E (116) ..	..	0·0196	0·1552	0·2474	0·2950	0·3354	0·3506	0·3583	0·3627
6E (97) ..	0·0001	0·0837	0·3974	0·5577	0·6312	0·6920	0·7141	0·7247	0·7311
3D (97) ..	0·0102	0·1107	0·2573	0·3135	0·3373	0·3563	0·3630	0·3663	0·3682
Calc. C_v ..	0·0103	0·2817	1·8947	3·3588	4·2444	5·0957	5·4499	5·6267	5·7248
Exptl. C_v* ..	0·0170	0·3253	1·8620	3·2536	4·1244	5·0490	5·4040	5·5454	..

* Clusius, K., Goldmann, J. and Perlick, A., *Z. Naturforschg.*, 1949, **4 A**, 424–32.

Table IV

Computation of the Atomic Heats of Sodium Bromide

	10° K.	20° K.	40° K.	60° K.	80° E.	100° K.	150° K.	200° K.	250° K.	300° K.
3E (163)	..	0·0004	0·0346	0·1157	0·1872	0·2371	0·3029	0·3308	0·3455	0·3536
6E (152)	..	0·0014	0·0907	0·2650	0·4074	0·5017	0·6224	0·6739	0·6973	0·7115
3E (144)	..	0·0011	0·0544	0·1464	0·2156	0·2611	0·3171	0·3403	0·3511	0·3575
12E (144)	..	0·0045	0·2176	0·5858	0·8623	1·0445	1·2683	1·3610	1·4045	1·4300
12E (77)	0·0025	0·1718	0·8015	1·1219	1·2683	1·3447	1·4213	1·4508	1·4644	1·4732
3E (76)	0·0007	0·0453	0·2037	0·2821	0·3178	0·3369	0·3518	0·3630	0·3664	0·3683
6E (60)	0·0090	0·1836	0·5068	0·6254	0·6764	0·6983	0·7241	0·7328	0·7377	0·7406
3D (60)	0·0408	0·1669	0·2966	0·3354	0·3511	0·3582	0·3661	0·3687	0·3700	0·3707
Calc. C_v	0·0530	0·5750	2·2059	3·4777	4·2861	4·7825	5·3780	5·6213	5·7369	5·8054

TABLE V

Computation of the Atomic Heats of Sodium Iodide

	5° K.	10° K.	15° K.	20° K.	40° K.	60°K.	80° K.	100° K.	140° K.	180° K.	220° K.	260° K.
3E (140)	..	..	0·0001	0·0014	0·0594	0·1537	0·2224	0·2662	0·3127	0·3354	0·3465	0·3536
6E (133)	..	..	0·0003	0·0043	0·1393	0·3331	0·4655	0·5493	0·6355	0·6774	0·6983	0·7106
3E (129)	..	..	0·0002	0·0027	0·0757	0·1736	0·2397	0·2797	0·3213	0·3403	0·3501	0·3566
12E (129)	..	..	0·0008	0·0108	0·3028	0·6944	0·9586	1·1186	1·2852	1·3610	1·4005	1·4265
12E (55)	..	0·0316	0·2043	0·4506	1·0751	1·2852	1·3713	1·4125	1·4495	1·4644	1·4743	1·4797
3E (54)	..	0·0088	0·0544	0·1170	0·2721	0·3234	0·3439	0·3536	0·3627	0·3664	0·3686	0·3702
6E (43)	0·0004	0·0556	0·2053	0·3472	0·6088	0·6805	0·7080	0·7204	0·7322	0·7377	0·7406	0·7414
3D (43)	0·0146	0·0905	0·1775	0·2381	0·3302	0·3525	0·3612	0·3650	0·3685	0·3700	0·3707	0·3712
Calc. C_v	0·0150	0·1865	0·6429	1·1721	2·8634	3·9964	4·6706	5·0653	5·4676	5·6526	5·7496	5·8098
Exptl. C_v*	0·0147	0·1676	0·560	1·060	2·800	3·965	4·650	5·045	5·455	5·645	5·740	5·800

* Berg, W. T. and Morrison, J. A., *Proc. Roy. Soc. (Lond.)*, 1957, **242 A**, 467.

influence on the oscillation frequencies of the atoms appearing in the octahedral layers. The magnitude of the corrections thus arising is known for the particular case of NaCl by reason of the availability of spectroscopic data for all its frequencies. Indeed, the figures for NaCl shown in Table I are based on the observational studies and not those given by the approximate theoretical formulæ.

The density of sodium fluoride is 2·79 and its lattice spacing 4·62 Å, as against 2·17 and 5·63 Å respectively for sodium chloride. There is thus good reason for assuming that the forces of interaction between atoms of the same species in sodium fluoride would influence the oscillation frequencies proportionately to an even greater extent than in the case for sodium chloride. These considerations determine the vibration frequencies of the octahedral layers computed and shown in Table I for sodium fluoride. These are substantially higher than those calculated from the elastic constants and listed in Part VII of this memoir.

The physical properties of sodium bromide and sodium iodide put them in a category different from the two other halides discussed above. Accordingly, their atomic vibration frequencies computed from the elastic constants have been taken over without substantial modifications and entered in Table I above. Corrections have, however, been made to take account of the changes of the atomic vibration frequencies to be expected at the low temperatures covered by the specific heat determinations.

SUMMARY

Computations of the atomic heats of the four sodium halides are presented and compared with the measured values. The spectroscopic data are the basis of the calculations in the case of NaCl and the atomic vibration frequencies determined from the elastic constants in the others. The vibration frequencies for NaF have been corrected to take account of the interactions between atoms of the same species which are strong in that crystal.