The specific heats of the alkali halides and their spectroscopic behaviour—Part XII. The potassium and rubidium salts

SIR C V RAMAN

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Table 1 below reproduces the atomic vibration frequencies of the halides of potassium and rubidium calculated by the approximate method set out in part V of the memoir. Only two force-constants α and β appear in the formulae; α is a measure of the resistance to a change of bond-lengths and β to a change of the bond-angles in the crystal structure. The figures in table 1 are the same as those listed in part VI of the memoir but they are arranged in a slightly different manner. The highest frequency appears first, then the four frequencies of vibration of the octahedral layers and finally the frequencies of the four modes of coupled vibration of the atoms in the cubic layers. By reason of the neglect of all other atomic interactions except the two referred to above, the tangential and perpendicular modes of vibration of the octahedral layers appear in the table with identical frequencies. To this degree of approximation, they are both derivable from the highest frequency in a simple manner, being determined respectively by the masses of the two species of atoms in the structure as compared with the reduced mass which determines the highest frequency.

Table 1. The atomic vibration frequencies (cm^{-1})

				Degeneracies					
	3	4	8	4	8	6	3	3	6
KF	202	166	166	116	116	182	167	114	87
KCl	133	96	96	92	92	119	102	85	60
KBr	105	86	86	60	60	96	88	58	43
KI	90	79	79	44	44	84	80	42	32
RbF	167	151	151	71	71	158	152	69	55
RbCl	103	87	87	56	56	95	89	53	39
RbBr	78	56	56	54	54	71	63	47	33
RbI	64	49	49	40	40	59	53	36	26

As has been shown in part IV of the memoir, the two force-constants ϕ and ψ which express the interactions of the atoms of the same species with each other (metal and halogen respectively) do not appear in the formula for the highest frequency of vibration. Accordingly, we may expect the values for those frequencies shown in table 1 to correspond fairly closely with the observed behaviour of the respective crystals. Earlier in this memoir, it has been shown that this is the case for those halides of lithium and of sodium for which we have the necessary experimental data. We may therefore expect the same to be the case also for the halides of potassium and rubidium.

The infra-red wavelengths corresponding to the highest frequencies shown in table 1 are $50\,\mu$, $75\,\mu$, $95\,\mu$ and $111\,\mu$ respectively for the four halides of potassium and $60\,\mu$, $97\,\mu$, $128\,\mu$ and $156\,\mu$ for the four halides of rubidium. No studies appear to have been published on the infra-red behaviour of either potassium fluoride or rubidium fluoride. The reported results of the observations made with the six other halides on the reflections by their surfaces and on the absorption by thin films are not inconsistent with the figures given above. It should be remembered in this connection that studies of absorption and reflection in the region of such great wavelengths are beset with experimental difficulties and that the influence of the subsidiary modes has also to be taken into account in the interpretation of the observed effects.

In the preceding part of the memoir it was shown that the reported measurements of the atomic heats of sodium iodide from the absolute zero of temperature up to $270°\,K$ are faithfully represented by the theoretical computations based on the approximate formulae for the atomic vibration frequencies. Such a close agreement is presumably the result of the atomic weight of iodine being much greater than that of sodium. We may, therefore, reasonably expect that the thermal behaviour of lithium chloride, lithium bromide and lithium iodide and perhaps also of sodium bromide would likewise be faithfully represented by computations made on the same basis. Unfortunately, however, no experimental data on their specific heats have been reported for these same four halides.

The thermal behaviours of potassium fluoride and of potassium chloride may be expected to resemble those of sodium fluoride and sodium chloride respectively. In other words, it would be necessary to amend the approximate formulae for the vibration frequencies by taking into account the interactions between the atoms of the same species in their structures. Alternatively, it would be necessary to proceed on the basis of spectroscopic determinations of the atomic vibration frequencies. Potassium fluoride would be a difficult case to study by the available techniques. But the three other halides of potassium are distinctly more promising, since in their cases, the Rasetti technique for recording the doubled frequency shifts in light-scattering is available. Precise investigations of KCl, KBr and KI using that technique should enable a complete correspondence to be established between their thermal and spectroscopic behaviours.

Measurements of the specific heats of KCl, KBr and KI have been reported over a range of temperatures extending down to very low values. The measured values give the specific heats at constant pressure and need to be corrected to derive the specific heats at constant volume. These corrections are negligible at low temperatures but increase in importance with rising temperature. The values of the atomic heat thus corrected are exhibited in figure 1, the curves marked (1), (2) and (3) referring respectively to the iodide, bromide and chloride of potassium. The uncorrected values for potassium fluoride are shown in the curve marked (4). It will be seen that the values for potassium fluoride lie well below those of the other three halides and that the gaps between the curves (1), (2), (3) and (4) increase progressively, as is to be expected in view of the differences between the atomic vibration frequencies of the four halides shown in table 1.

As has already been remarked, we cannot expect the atomic heats of the potassium salts computed on the basis of the approximate frequencies listed in table 1 to fit the experimentally determined values in a perfect manner. Nevertheless, it appeared useful to make such computations and to present the results side by side with the atomic heats as measured and reported in the most recent investigations. Tables 2, 3, 4 and 5 exhibit the results respectively for the four potassium salts. It may be remarked that throughout the range of temperature covered by these tables, the computed atomic heats for the four halides follow each other in the same order as the observed values viz., KI > KBr > KCl > KF. When the computed values are represented graphically, they
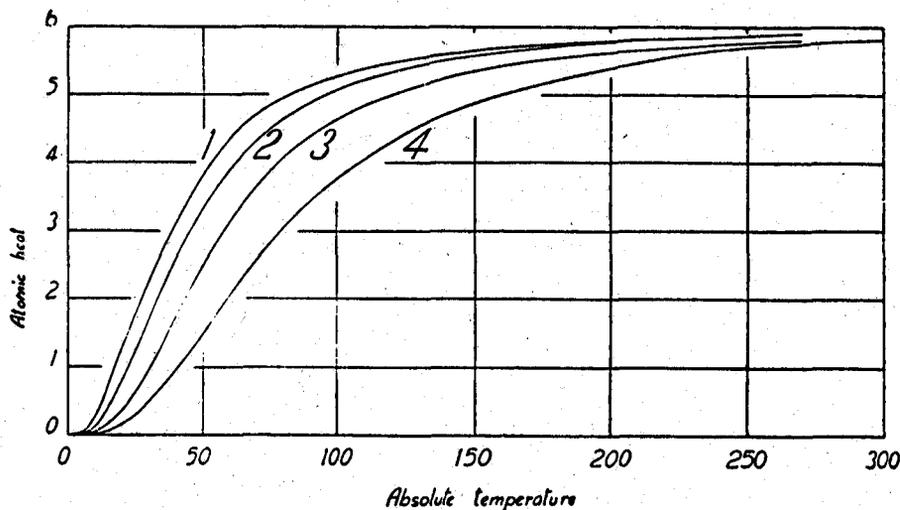

Figure 1. Experimental values of the atomic heats. (1) KI, (2) KBr, (3) KCl and (4) KF.

Table 2. Comparison of the computed and observed values of the atomic heats of potassium fluoride

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K	300° K
Calculated C_v	0·0145	0·0591	0·172	1·299	2·620	3·724	4·255	5·094	5·442	5·621	5·721
Experimental C_p	—	0·0377	0·139	0·946	2·089	3·044	3·776	4·863	5·398	5·698	5·858

Experimental values of C_p from Westrum Jr., E F and Pitzer, K S, *J. Am. Chem. Soc.*, **71**, 1940 (1949) as "Landolt–Bornstein" 6 Auflage, II Band, 4 Teil., p. 486.

Table 3. Comparison of the computed and observed values of the atomic heats of potassium chloride

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K
Calculated C_v	0·0506	0·215	0·552	2·582	3·969	4·702	5·105	5·557	5·726	5·808
Experimental C_v	0·0402	0·151	0·357	1·779	3·157	4·079	4·657	5·355	5·619	5·761

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

Table 4. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
Calculated C_v	0·171	0·611	1·233	3·491	4·611	5·139	5·408	5·703	5·813
Experimental C_v	0·116	0·390	0·802	2·650	3·934	4·663	5·076	5·572	5·771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

Table 5. Comparison of the computed and observed values of the atomic heats of potassium iodide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
Calculated C_v	0·441	1·158	1·901	3·833	4·933	5·340	5·548	5·769	5·853
Experimental C_v	0·288	0·792	1·356	3·165	4·373	4·957	5·284	5·656	5·795

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

appear as a family of non-intersecting curves similar to those for the experimental values shown in figure 1. They approach the axis of the abscissae at approximately the same temperatures and tend towards the maximum or limiting value in the same temperature range as the curves representing the experimental data. However, it is evident from tables 2, 3, 4 and 5 that the computed atomic heats are definitely larger than the observed ones. The percentage difference varies from halide to halide and also with the temperatures at which the two sets of values are compared.

The reason why the computed values are higher than the observed ones is not far to seek. Fully twenty-four out of every forty-eight degrees of dynamic freedom are manifested as the four modes of vibration of the atoms in the octahedral layers. These modes have, according to table 1, frequencies appearing in the middle range of the spectrum of each halide and hence they make the principal contribution to the atomic heat in the temperature range where it increases most rapidly. The neglect of the force-constants ϕ and ψ results in assigning to these modes frequencies which are distinctly less than the actual values. In consequence also, their computed contributions to the atomic heat are greatly exaggerated. It is not surprising that in these circumstances, the computed atomic heats exceed the observed values by large percentages.

By reason of the high atomic weights of both metal and halogen and the weakness of the binding between them, the vibration frequencies of rubidium bromide and rubidium iodide are quite low, as is seen from table 1. The position, however, is somewhat different in the cases of rubidium fluoride and rubidium chloride. These two halides are of special interest by reason of the great disparity between the atomic weights of the metal and the halogen which are their constituents. Unfortunately, however, no specific heat measurements are available for them.
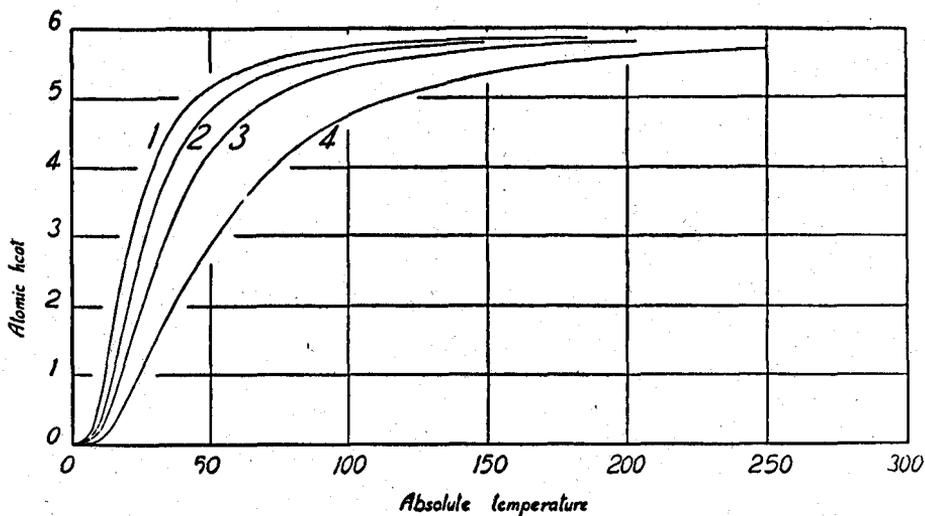

Figure 2. Computed values of the atomic heats. (1) RbI, (2) RbBr, (3) RbCl and (4) RbF.

The atomic heats of all the four rubidium salts have been computed on the basis of the frequencies listed in table 1 and are represented graphically in figure 2 above. The curves (1), (2), (3) and (4) marked in the figures refer respectively to RbI, RbBr, RbCl and RbF. The curves (3) and (4) are well separated from each

other and so also curves (2) and (3), though less conspicuously, while (1) and (2) fall close to each other. For reasons already explained, we cannot hope to find that the atomic heats thus computed for RbBr and RbI give a good fit with the experimental data available for these two halides. The comparison between the computed and observed atomic heats presented in tables 6 and 7 for the two cases indeed exhibits notable differences. The atomic heat falls so steeply in a narrow range of temperature in these cases that such differences are only to be expected.

We may here make a few remarks of a general nature. For some of the alkali halides, measurements of the elastic constants made at low temperatures are available. It is evident that the bulk-modulus and shear-modulus as determined at such temperatures and not those found by room-temperature measurements would be the proper basis for a computation of the atomic vibration frequencies from which the specific heats at low temperatures could be evaluated. The corrections to the frequencies needed on this account vary from halide to halide. In all cases, however, they do not exceed a few per cent, and in some cases, e.g., lithium fluoride, they are negligible.

Table 6. Comparison of the computed and experimental values of the atomic heats of rubidium bromide

	10·5° K	15·4° K	22·2° K	30·3° K	42·8° K	60·5° K	81·5° K	105·3° K	148·4° K
Calculated C_v	0·44	1·21	2·41	3·51	4·50	5·16	5·49	5·67	5·812
Experimental C_v	0·32	0·73	1·52	2·57	3·80	4·73	5·25	5·47	5·87

Table 7. Comparison of the computed and experimental values of the atomic heats of rubidium iodide

	12° K	16·3° K	20·3° K	27·3° K	39·8° K	68·6° K	129° K	189·5° K
Calculated C_v	1·15	2·09	2·84	3·84	4·79	5·52	5·83	5·87
Experimental C_v	0·78	1·27	1·85	2·85	4·08	5·27	5·79	5·90

Experimental values of the atomic heats of RbBr and RbI from Clusius K, Goldmann, J and Perlick, A Z. *Naturforsch.*, A4, 424 (1949).

Table 8. Computed values of the atomic heats of rubidium fluoride

Temperature °K	10	15	20	40	60	80	100	150	200	250
Calculated C_v	0·074	0·316	0·705	2·285	3·474	4·254	4·752	5·358	5·610	5·730

Table 9. Computed values of the atomic heats of rubidium chloride

Temperature °K	10	15	20	40	60	80	100	150	200
Calculated C_v	0·231	0·738	1·379	3·585	4·658	5·164	5·427	5·712	5·820

Summary

The atomic heats of the potassium and rubidium halides are computed on the basis of the table of vibration frequencies given in part VI and compared with the observed values in the cases for which these are available. The differences noticed are explained as arising from the octahedral modes having been assigned frequencies lower than the actual ones in the calculation.