

THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

Part I. Introduction

BY SIR C. V. RAMAN

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

Received June 4, 1962.

THE compounds of the alkali metals with the halogen elements are crystalline solids which are of great interest alike from the theoretical and experimental standpoints. Sixteen of them, *viz.*, the compounds of lithium, sodium, potassium and rubidium respectively with fluorine, chlorine, bromine and iodine possess crystal structures similar to each other, the typical case being rock-salt or NaCl. The elucidation of the thermal properties of the alkali halides in relation to their spectroscopic behaviour is the subject of the present memoir. Since the halides of caesium possess a different structure, they will be left out of consideration in our discussions.

Though all the sixteen halides are cubic crystals having a common structural pattern, they nevertheless exhibit a wide range of physical behaviour. The fluorides, in particular, have distinctive properties. Their melting points are notably higher than those of the corresponding chlorides, bromides and iodides, thereby indicating a stronger binding between the metal and halogen atoms. This is also very clearly shown by a comparison of the elastic behaviours of all the sixteen halides, the determinations of which by the ultrasonic diffraction method have been recently published (Reference 1). Table I below reproduces the data reported by the authors quoted, except that instead of the compressibility, the table shows the bulk-modulus K which is its reciprocal and is taken equal to $(C_{11} + 2C_{12})/3$.

A study of the figures appearing in Table I is instructive. It will be seen that the elastic constants diminish rapidly in the sequence of the alkali metals lithium, sodium, potassium and rubidium and even more rapidly in the sequence of the halogens, fluorine, chlorine, bromine and iodine. The fall in passing from the fluorides to the chlorides is particularly striking. It is also noteworthy that the shear-modulus C_{44} is of the same order of magnitude as the bulk modulus K in the case of the lithium halides. But it is much the smaller of the two in the case of the halides of the other alkali metals.

TABLE I

Lattice spacings and elastic moduli(Elastic moduli in 10^{11} erg/cm.²: Lattice constant in Å: Temperature 22° C)

Substance	C_{11}	C_{12}	C_{44}	K	Lattice constant
LiF ..	11.35	4.80	6.35	6.99	4.01
LiCl ..	4.94	2.26	2.49	3.15	5.14
LiBr ..	3.94	1.88	1.91	2.56	5.49
LiI ..	2.85	1.47	1.35	1.89	6.00
NaF ..	9.71	2.43	2.80	4.85	4.62
NaCl ..	4.93	1.31	1.275	2.52	5.627
NaBr ..	4.02	1.15	0.99	2.11	5.94
NaI ..	3.035	0.90	0.72	1.61	6.46
KF ..	6.58	1.49	1.28	3.18	5.33
KCl ..	4.08	0.69	0.635	1.82	6.28
KBr ..	3.49	0.58	0.51	1.55	6.578
KI ..	2.775	0.47	0.38	1.24	7.052
RbF ..	5.7	1.25	0.91	2.73	5.63
RbCl ..	3.645	0.61	0.475	1.62	6.571
RbBr ..	3.185	0.48	0.385	1.38	6.868
RbI ..	2.585	0.375	0.281	1.11	7.325

The rock-salt structure is one of exceptional simplicity. The characteristic modes of free vibration of the atoms in it can therefore be readily established and described completely in terms related to the geometry of the structure. The frequencies of the free vibrations would naturally depend on the masses of both the metal and halogen atoms and also on the strength of the binding between them which, as is indicated by the figures in Table I, would be very different in the different cases. It follows that the spectrum

of the characteristic frequencies would vary from halide to halide in a distinctive fashion.

It will be shown in this memoir that the spectrum of frequencies of atomic vibration can be evaluated for all the sixteen halides by making use of the data shown in Table I and that on the basis of such evaluation, the specific heats of each halide can be determined in terms of the temperature over the entire range from the absolute zero upwards.

The evaluation of the modes and frequencies of atomic vibration enables us to go further and predict the spectroscopic behaviour of the halides. We are here concerned with two different problems which will be considered separately. The first is the absorption, reflection and dispersion of infra-red radiation incident on the crystal. The second problem concerns the frequency shifts observed when monochromatic light of sufficient intensity traverses the crystal and the scattered radiations are investigated spectroscopically.

As the object of the memoir is to demonstrate the power and success of the theoretical approach which has been adopted, we shall naturally proceed to compare the results to which it leads with the facts of observation in those cases in which the necessary data are available.

We may conclude this introductory part of the memoir by tabulating some further physical data of interest for each of the sixteen alkali halides. Table II exhibits for each halide the following physical constants:

(*a*) the density, (*b*) the refractive index in the visible spectrum, (*c*) the refractive index in the ultra-violet, (*d*) the melting point, and (*e*) the solubility in water at room temperature.

We may draw attention to some significant features noticeable in Table II. There is a large drop in density when we pass from the fluoride to the chloride in each case. This is in striking contrast with the increases in the density in passing from the chloride to the bromide and then to the iodide. This increase in density is a clear indication of the great strength of the binding between the metal and the halogen atoms in the fluorides. As has already been remarked, the same feature is conspicuous from the data for the elastic moduli listed earlier in Table I.

The refractive index of the fluorides is invariably lower than that of the other halides, and it is noteworthy that this feature appears despite the high density of the fluorides. The dispersive power of the fluorides as indicated by the difference of the refractive indices in the visible and ultra-violet is also

TABLE II

Some physical constants

Substance	Density	Refractive index (589 m μ)	Refractive index (254 m μ)	Melting point	Solubility (in 100 parts)
LiF ..	2.6	1.3915	1.4179	870° C.	0.27
LiCl ..	2.07	1.662	..	613° C.	45
LiBr ..	3.46	1.784	..	547° C.	143
LiI ..	4.06	1.955	..	446° C.	151
NaF ..	2.79	1.3258	1.37	992° C.	4.2
NaCl ..	2.17	1.544	1.653	801° C.	36
NaBr ..	3.20	1.6412	1.8323	755° C.	80
NaI ..	3.67	1.7745	..	651° C.	159
KF ..	2.48	1.361	..	880° C.	92
KCl ..	1.98	1.490	1.588	790° C.	28
KBr ..	2.75	1.5596	1.7181	730° C.	54
KI ..	3.13	1.6674	2.0169	723° C.	127
RbF ..	2.88	1.3960	..	760° C.	130
RbCl ..	2.76	1.4936	1.5905	715° C.	77
RbBr ..	3.35	1.5528	..	682° C.	98
RbI ..	3.55	1.6474	..	652° C.	138

small. *Per contra*, it is conspicuously large for the other halides and particularly so in the cases of the bromides and iodides.

The solubility in water of the alkali halides shows large variations in the different cases. Lithium fluoride is only sparingly soluble, in striking contrast with the behaviour of the other halides of lithium. The sodium salts exhibit a regular sequence in their solubilities. But this is not so in

the case of the halides of potassium and rubidium, their fluorides being actually more soluble than the chlorides and bromides.

SUMMARY

The sixteen alkali halides which form the subject of the memoir, *viz.*, the fluorides, chlorides, bromides and iodides of lithium, sodium, potassium and rubidium all possess the rock-salt structure but exhibit a remarkable diversity in their physical properties. Especially notable are the values of their elastic constants, the published determinations of which indicate striking differences in the nature and strength of the binding between the metal and the halogen atoms in the various cases.

REFERENCE

1. Spangenberg, K. and Haussühl, S. *Zeitschrift für Kristallographie*, 1957, Bd. 109, S. 422-37.