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Heat Capacities and Some Vibrational Properties of Rubidium Chloride

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Molar heat capacities of RbCl were measured between 3 and 300 K with an adiabatic calorimeter and complete thermodynamic properties of the solids have been obtained. The nature of the lattice vibration spectrum of RbCl is examined in terms of the moments of spectrum. Values derived are $\theta_0=184.9\pm1.3$ K, $\theta_\infty=190.0\pm1.0$ K, E_z(zero-point energy)$=3.43\pm0.01$ kJ mol^{-1}. Those properties depend on the kind of cation rather than on the anion in alkali halides. Anharmonicity in the vibration is also discussed.

Because of their simple nature of crystal structure and atomic forces, alkali halides have been investigated by theory and experiment most extensively of all ionic solids. While the nature of lattice vibrations in these solids has been generally understood, the stability of crystal lattices, particularly the relative stability of structures, NaCl type and CsCl type, remains to be explored in relation to the difference in the vibrational properties.

Rubidium chloride occupies a special position among the alkali halide family because it exists in the two modifications, NaCl structure under ordinary conditions and CsCl structure under applied pressure.[1] The reason for the bimorphism lies in the fact that the ratios of radii of the cation and the anion assumes a value close to the critical value of 0.73 which separates the theoretical stability region of the two structures. Decreased stability of NaCl structure in the case of RbCl is expected to be seen in its vibrational properties.

Several papers[2,3,4] have been published to report the heat capacities of rubidium chloride since our measurements were concluded. However, those results are neither mutually consistent where they may be compared nor complete in that only derived quantities are given.

The purpose of the present paper is two fold: One is to provide complete thermodynamic properties of RbCl to help to understand its vibrational properties and the other is to provide heat capacity values of one of the components in the binary system NH_4Cl–RbCl which has been studied in this laboratory.

Experimental

Materials. Reagent grade rubidium chloride (Nakarai Chemicals, Ltd., stated minimum purity 99.5%) was dried *in vacuo* in a temperature-controlled quartz tube at 300 °C for 14 h. The high sensitivity DTA thermogram and the powder X-ray diffraction pattern showed no indications of trace of water or trace of the CsCl-type structure. Sample weight used for calorimetry was 69.0328 g (*in vacuo*) or 0.57980 mol.

Calorimeter and Cryostat. The calorimeter was of adiabatic type, the description of which has been reported elsewhere.[5,6] Helium exchange gas less then 1.6×10^{-6} mol was put into the calorimeter vessel to aid in thermal equilibration within it. No correction was made for the presence of the exchange gas in computing the heat capactiy values.

Temperature Scales. The working thermometer above 15 K is the Leeds & Northrup platinum resistance thermometer (model 8164), the temperature scale of which was fixed in our laboratory by comparison with another thermometer calibrated at the U. S. National Bureau of Standards, based on the IPTS-48 and the provisional NBS-55 scales. Below 15 K the thermometer was the germanium resistance thermometer (CryoCal, Inc., laboratory designation β), which had been calibrated in our laboratory.[7]

Results

Molar heat capacities at constant pressure are given in Table 1 and Fig. 1. The temperature rise in each measurement was small and therefore no curvature correction was necessary. Precision of the measurements was within 7.6% below 11 K, 1.0% from 11 to 20 K, and 0.6% above 20 K. Our results are compared with the results of Paukov and Khriplovich and Kirkham and Yates in Fig. 2, showing that our values lie intermediate between the two previous ones.

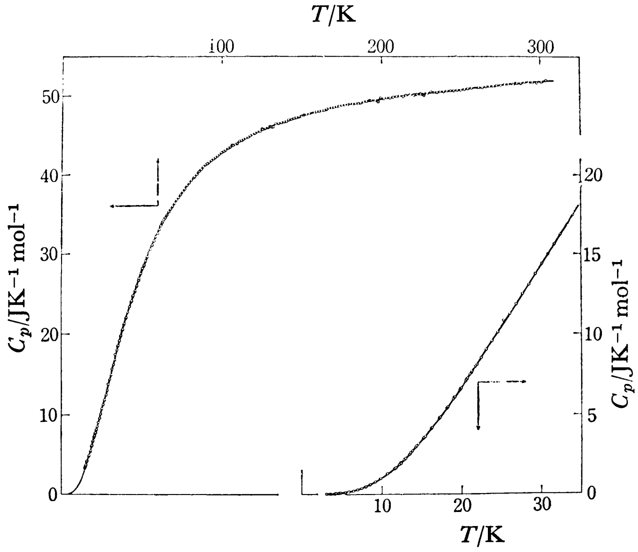

Fig. 1. Molar heat capacity of rubidium chloride.

Thermodynamic functions of rubidium chloride based on the smoothed heat capacity curve are given in Table 2.

Analysis of Experimental Results

Conversion of C_p to C_v and the Debye Temperature. The heat capacity at constant volume C_v was obtained from the heat capacity at constant pressure C_p by help of the standard thermodynamic equation,

$$(C_p-C_v)/C_p = \{1+(\chi_s C_p/\beta^2 VT)\}^{-1}$$

where χ_s is the adiabatic compressibility, β the volume expansion coefficient, V the molar volume, and T the absolute temperature.

TABLE 1. MOLAR HEAT CAPACITIES OF RUBIDIUM CHLORIDE

Weight of specimen 69.0328 g. Molecular weight 120.921, 1948 International Temperature Scales.

T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}
Series I		20.497	7.072	43.807	24.09	Series XI		83.081	39.73
233.073	50.33	21.226	7.604	44.887	24.76	3.070	0.019	84.411	40.01
235.107	50.34	21.929	8.131	45.938	25.36	3.552	0.030	85.815	40.38
237.173	50.43			47.052	26.03	4.101	0.047	87.209	40.63
239.272	50.45	Series V		48.227	26.75	4.644	0.070	88.510	40.93
241.394	50.57	21.016	7.468					89.803	41.16
243.540	50.57	21.724	7.984	Series VIII		Series XII		91.091	41.35
245.739	50.56	22.416	8.504	192.281	49.25	6.918	0.289	92.379	41.57
247.946	50.63	23.098	9.010	196.475	49.30	7.456	0.380	93.668	41.74
250.161	50.65	23.790	9.537	198.090	49.12	7.975	0.475	94.955	41.93
252.399	50.75	24.510	10.09	199.763	49.68	8.536	0.593	96.233	42.14
254.662	50.85	25.261	10.77	201.504	49.54	9.157	0.767	97.503	42.37
256.933	50.92	26.042	11.27	203.402	49.64	9.870	0.993	98.373	42.53
261.400	51.00	26.843	11.87	205.425	49.61	10.687	1.261	100.042	42.70
263.588	50.96	27.646	12.53	207.468	49.75	11.532	1.579	101.311	42.87
265.903	51.10	28.453	13.11	209.529	49.00	12.363	1.927	102.587	43.04
268.266	51.26	29.266	13.78	211.634	49.90			103.868	43.26
270.462	51.17	30.066	14.41	213.776	49.80	Series XIII		105.154	43.42
272.723	51.30	30.870	15.01	215.928	49.99	48.627	27.00	106.542	43.67
275.080	51.26	31.685	15.64	218.092	49.57	49.643	27.57	107.102	43.63
277.447	51.44	32.480	16.24	220.281	50.00	50.650	28.21	108.412	43.77
279.841	51.41	33.262	16.86	222.473	50.08	51.638	28.66	109.725	43.85
282.265	51.47	34.037	17.45	224.662	50.10	52.618	29.16	111.047	44.15
284.710	51.52	34.808	18.01	226.872	49.92	53.596	29.66	112.374	44.25
287.185	51.45	35.583	18.58	229.082	50.28	54.582	30.11	113.716	44.37
		36.399	19.17	231.293	50.42	55.591	30.59	115.080	44.50
Series II		37.280	19.78	235.500	50.38	56.714	31.10	116.464	44.69
283.055	51.42	38.224	20.50			57.860	31.59	117.881	44.83
285.473	51.56	39.256	21.17	Series IX		58.939	32.12		
287.887	51.61	40.406	21.92	135.583	45.74	60.025	32.54	Sersies XVI	
290.302	51.71	41.602	22.71	137.216	46.46	61.114	33.03	125.446	45.57
292.733	51.72	42.757	23.44	138.856	46.58	62.196	33.46	127.137	45.76
295.161	51.63	43.874	24.16	140.476	46.63	63.281	33.88	128.828	45.82
297.853	51.65	44.966	24.83	142.051	46.83	64.370	34.27	130.508	45.96
300.806	51.71	46.036	25.47	143.621	46.91			132.178	45.94
303.746	51.91	47.094	26.07	145.200	47.05	Series XIV		133.840	46.35
		48.152	26.71	146.776	47.16	119.334	45.00	135.497	46.89
Seires III				148.347	47.20	120.826	45.17		
11.731	1.647	Series VI		149.919	47.32	122.361	45.31	Series XVII	
12.318	1.979	11.576	1.611	151.495	47.47	123.941	45.31	165.779	48.24
12.927	2.203	12.173	1.850	153.065	47.52	125.574	45.61	167.241	48.39
13.585	2.586	12.799	2.146	154.631	47.67	127.271	45.76	168.729	48.39
14.345	3.002	13.469	2.492	157.837	47.86	129.049	45.90	170.244	48.42
15.263	3.545	14.252	2.929	159.394	47.89			171.809	48.54
16.284	4.187	15.176	3.466	160.946	47.93	Series XV		173.499	48.61
17.286	4.836	16.225	4.122	162.499	47.99	63.819	34.06	175.258	48.70
18.210	5.438	17.286	4.815	164.054	48.09	64.924	34.46	176.996	48.75
19.060	6.062	18.239	5.440	165.608	48.16	66.036	34.85	178.731	48.78
19.846	6.589	19.106	6.063			67.156	35.25	180.461	48.92
20.580	7.139	19.925	6.634	Series X		68.281	35.59	182.188	48.88
21.270	7.653	20.726	7.225	4.281	0.052	69.413	35.94	183.914	49.00
				4.839	0.088	70.638	36.32	185.636	49.05
Series IV		Series VII		5.348	0.119	71.938	36.73	187.363	49.06
13.821	2.695	35.482	18.50	5.879	0.165	73.225	37.01	189.079	49.17
14.569	3.130	36.361	19.14	6.432	0.220	74.517	37.40	190.791	49.21
15.417	3.597	37.318	19.81	6.958	0.289	75.795	37.79	192.500	49.30
16.286	4.169	38.377	20.53	7.475	0.370	77.116	38.13	194.205	49.32
17.179	4.765	39.470	21.30	8.011	0.475	78.497	38.58		
18.078	5.350	40.562	22.01	8.577	0.601	79.864	38.92		
18.935	5.942	41.659	22.73	9.173	0.763	81.218	39.27		
19.737	6.511	42.729	23.43	9.837	0.967	82.558	39.61		

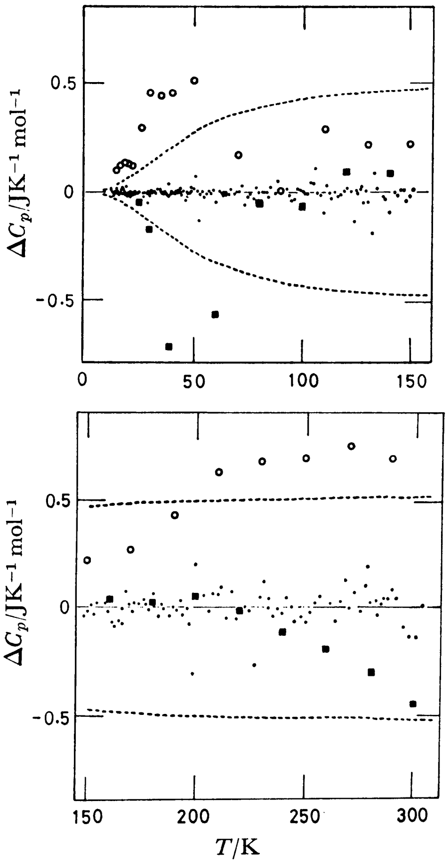

Fig. 2. Deviation plot based on our smoothed values. ----: 1% of C_p, ●: Present results, ■: Kirkham and Yates, ○: Paukov and Khriplovich.

To obtain values of the thermal expansion coefficient, we used Cooper and Yates' results[8] from 30 K to 260 K which were extrapolated to either temperature side in a manner consistent with other alkali halides.[9] Temperature dependence of adiabatic elastic constant of rubidium chloride was taken from the paper by Gluyas *et al.*,[10] because of better accuracy than others.[11,12] The χ_s values below 140 K were obtained by extrapolation. Density below room temperature was also obtained from the published values.[11,12]

The correction C_p-C_v thus evaluated is negligibly small below 50 K, 0.1% of C_p at 100 K, 0.2% at 200 K, and 0.4% at 300 K.

The Debye characteristic temperature $\theta_D(V_T)$ derived from the C_v values depends on the crystal volume at the temperature T. $\theta_D(V_0)$ for the volume at 0 K can be approximated by[13]

$$\theta_D(V_0)/\theta_D(V_T) = (V_T/V_0)^\gamma$$

where γ is the Gruneisen constant. The values of $\theta_D(V_0)$ thus obtained are plotted against T in Fig. 3. The shallow basin at about 90 K is due to the inconsistency inherent in the temperature scale near the normal boiling point of oxygen. The shape of $\theta_D(T)$ curve appears quite normal for an alkali halide crystal with the NaCl-type structure; the rapid decrease at higher temperatures may be attributed to anharmonicity of lattice vibrations. A minimum occurs at about 11 K, showing the deviation of the actual frequency spectrum from the Debye spectrum. Similar minima for sodium chloride and for potassium chloride were explained theoretically by Kellerman[14] and by Jona,[15] respectively, applying the Born-von Karman theory.

Table 2. Thermodynamic functions of rubidium chloride

T	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
K	JK^{-1} mol^{-1}	JK^{-1} mol^{-1}	JK^{-1} mol^{-1}	JK^{-1} mol^{-1}
5	0.091	0.025	0.022	0.003
10	1.017	0.293	0.218	0.075
15	3.380	1.113	0.818	0.294
20	6.712	2.539	1.862	0.677
25	10.47	4.442	3.246	1.196
30	14.35	6.697	4.757	1.940
35	18.15	9.192	6.405	2.787
40	21.65	11.85	8.100	3.754
45	24.84	14.60	9.786	4.810
50	27.76	17.37	11.45	5.920
60	32.58	22.88	14.59	8.288
70	36.12	28.18	17.44	10.75
80	38.96	33.21	19.95	13.25
90	41.15	37.93	22.19	15.73
100	42.70	42.35	24.17	18.18
110	43.98	46.49	25.91	20.58
120	45.06	50.37	27.47	22.90
130	45.97	54.01	28.85	25.16
140	46.69	57.45	30.10	27.35
150	47.35	60.69	31.22	29.46
160	47.95	63.77	32.26	31.51
170	48.43	66.69	33.20	33.50
180	48.84	69.47	34.05	35.42
190	49.19	72.12	34.84	37.28
200	49.48	74.65	35.57	39.09
210	49.75	77.07	36.24	40.84
220	50.01	79.39	36.86	42.53
230	50.26	81.62	37.44	44.18
240	50.49	83.76	37.98	45.78
250	50.72	85.83	38.49	47.35
260	50.94	87.83	38.96	48.87
270	51.17	89.77	39.42	50.35
280	51.39	91.64	39.85	51.79
290	51.61	93.45	40.25	53.20
300	51.82	95.20	40.64	54.57
273.15	51.24	90.36	39.56	50.80
298.15	51.78	94.88	40.57	54.32

The Debye characteristic temperature at 0 K, θ_0, was calculated from the intersection at $T^2=0$ of the C_pT^{-3} *versus* T^2 plot (Fig. 4) to give $\theta_0=18.49\pm1.3$ K. This value is compared with values determined by other measurements and also with the values for other alkali chlorides and rubidium halides in Table 3.

The θ_0 reported by Rallefson and Perssini is 168.5$\pm$2.5 K, some 16 K lower than ours. However, their θ_D curve shows a peculiar behavior below 2 K which obscures the method by which their value was determined. Within the series of chlorides or the series of rubidium salts, it is seen the θ_0 decreases as the mass of constituent ion increases. This tendency agrees with

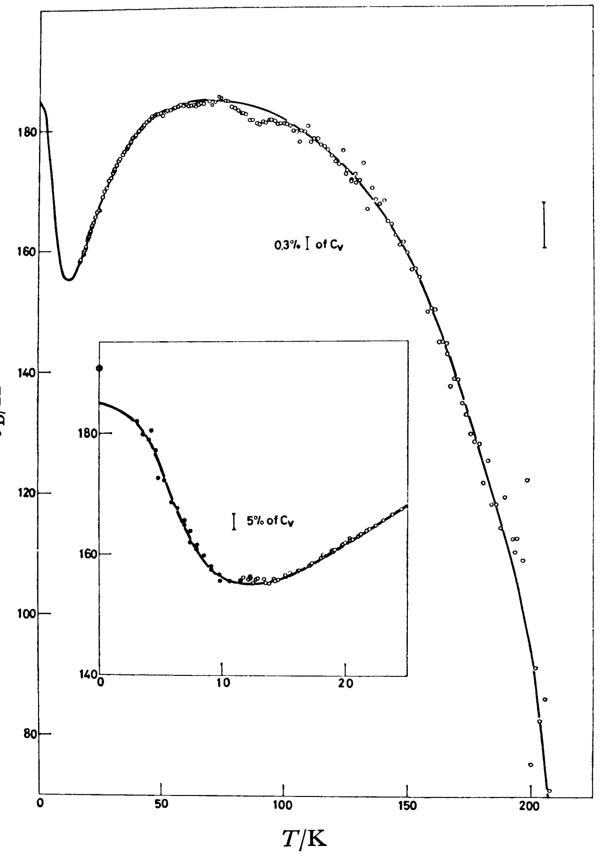

Fig. 3. Temperature dependence of the Debye characteristic temperature, $\theta_D(V_0)$.

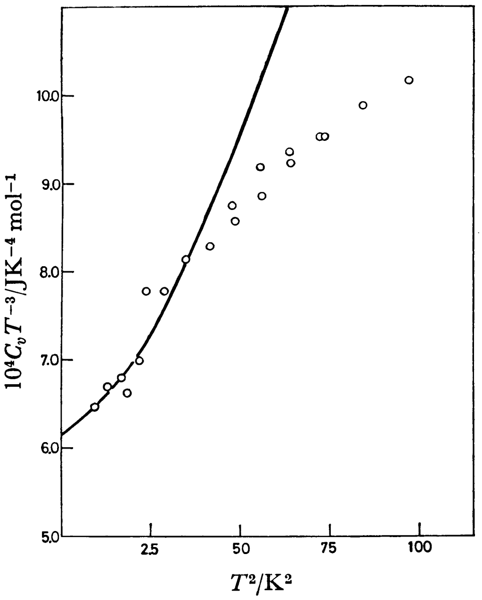

Fig. 4. Determination of θ_0 at 0 K.

the theoretical prediction that the θ_0^2 is inversely proportional to the molecular weight. An interesting feature in this connection is an empirical relation shown in Fig. 5 which is a plot of $\theta_0 \sqrt{M}$ *vs.* $\sqrt{r}$ where M is the molecular weight and r the sum of constituent ionic radii.

Moments of Lattice Vibration Spectrum and Related Thermodynamic Properties. The accuracy with which the heat capacity may be determined for insulators does not permit to deduce the entire lattice vibration spectrum with a reasonable reliability. This was demonstrated by Barron and Morrison in the case of sodium chloride.20) Instead, it is of more practical significance to derive the moments of vibration spectrum which are readier to compare for different alkali halides and which can be directly related to some thermodynamic properties.

The moment values were thus evaluated by using expansion formulae of the Debye temperature, the harmonic thermal energy, the harmonic entropy, and $C_v^{(h)}/T^n$. The results are summarized in Table 4 in the form of the $\nu_D(n)$ function.13)

Now we shall attempt to compare the moment values of the thermodynamic properties derived therefrom with the values from other sources.

TABLE 3. COMPARISON OF θ_0 OF ALKALI CHLORIDE AND RUBIDIUM HALIDES

Alkali halide	Calorimetric	Ultrasonic	Inelastic
LiCl	422±6e)	429±2.2e) 424.7	
NaCl	320.6±1.5f)	321.2±1.6e)	325b) 324a)
KCl	235.1±0.5f)	237.1c)	238b) 240a)
RbCl	168.5±2.5h) 184.9+1.3g)	168.9±0.85e) 168i)	177b) 171a)
RbF		221.0d)	
RbBr	134±2h)	136.5±0.7e)	139i)
RbI	106.5±1.5h)	108.0±0.55e)	

a) Raunio and Rolandson.16) b) Raunio and Rolandson.16) c) Moyer.17) d) Cleavelin, *et al.*18) e) Lewis *et al.*19) f) Barron, *et al.*13) g) Present work. h) Rallefson and Peressini.4) i) Rolandson and Raunio.16)

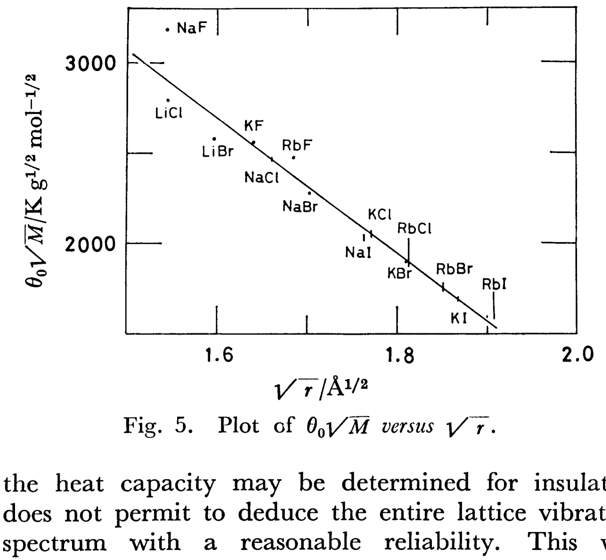

Fig. 5. Plot of $\theta_0\sqrt{M}$ *versus* $\sqrt{r}$.

TABLE 4. VALUES OF $\gamma_D(n)$

n	$\nu_D(n)$/10^{12}Hz	n	$\nu_D(n)$/10^{12}Hz
−3	3.85±0.03	1	3.82±0.02
−2	3.48±0.07	2	3.96±0.03
−1	3.41±0.04	4	4.10±0.04
0	3.62±0.02	6	4.17±0.11

The zero-th moment μ_0 is related to the geometric mean frequency $\nu_g=2.59\pm0.02$ THz, which may be compared with values 4.242 ± 0.013 THz for NaCl[13] and 3.412 ± 0.010 THz for KCl.[13] Similarly the zero point energy E_z decreases as the mass of the constituent ion increases; thus E_z of RbCl derived from the first moment in 3434 ± 10 J mol^{-1}, the smallest value for the alkali chloride having the NaCl structure.

The second moment is related to the high-temperature limit of the Debye temperature, $\theta_\infty=190.0\pm1.0$ K. This value agrees with 191 K obtained from inelastic scattering of neutrons[16] and also with 191 ± 1 K obtained from the Blackman's formula.

$$\theta_\chi = \frac{\hbar}{k}\left(\frac{5r_0}{\chi}\right)^{1/2}\left(\frac{1}{m_+}+\frac{1}{m_-}\right)^{1/2}$$

using the compressibility $\chi=5.54\times10^{-12}$ dynes cm^{-2} and the lattice constant $2r_0=6.581$ Å at 300 K.

Negative moments μ_{-1} and μ_{-2} are related to the Debye-Waller factors at $T=0$ and $T=\infty$ respectively, which appear in the diffraction intensity. However, no such information to compare with is available at the present time.

General shape of the $\nu_D(n)$ curve as shown in Fig. 6 is what one would expect for an ionic crystal although there are some differences in absolute values between ours and those by Cooper and Yates.

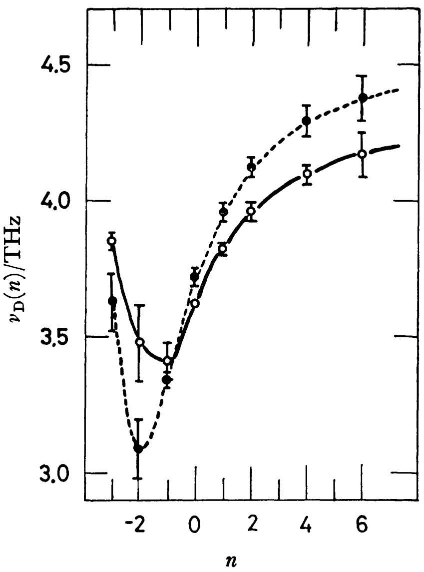

Fig. 6. Comparison of $\nu_D(n)$ function.

The differences come from the fact that Cooper and Yates gave smaller heat capacities than ours in the low temperature region.

Cation Effect and Anharmonicity. Figure 7 compares the reduced characteristic temperature $\theta_D(V_T)/\theta_\infty$ of the alkali chlorides.

It is clearly seen that as the mass of constituent ion increases, the value of θ_D/θ_∞ generally decreases and the temperature at which θ_D/θ_∞ becomes minimum goes lower. Similar tendency is also found in the case of potassium halides[13] although to a much smaller extent: thus this may be called the cation effect.

Blackman[21] showed that the ratio θ_0/θ_∞ should be proportional to $\sqrt{1-\eta^2}$, where $\eta=(m_+-m_-)/(m_++m_-)$. Table 5 suggests that the value of this proportionality constant is not really a constant but depends more critically on the alkali ion than on the halide ion. Barron *et al.*,[13] estimated the constant for RbBr and RbI to be probably within 10% of 0.95, in agreement with the value for RbCl. A simple calculation shows that the magnitude of this constant depends only on the elastic constants. Because the large effect of the alkali metal ion on the magnitude of the elastic anisotropy $c_{44}/(c_{11}-c_{12})$ was shown in Table X of Lewis, Lehoezky, and Briscoe's paper,[19] we may attribute the cation effect that has been demonstrated here also to that appearing in the elastic properties.

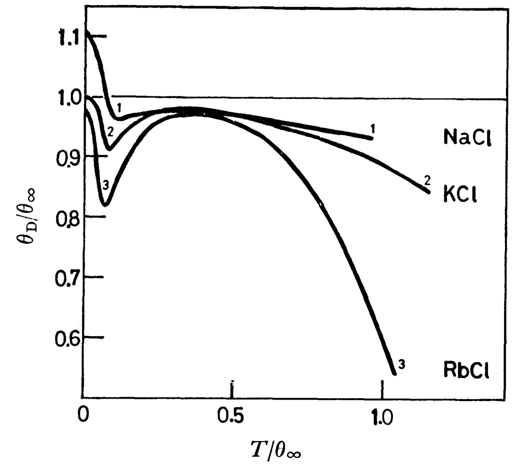

Fig. 7. Comparison of the reduced characteristic temperature.

TABLE 5. DEPENDENCE OF θ_∞/θ_0 UPON MASS RATIO

Salt	θ_∞/θ_0	$\sqrt{(1-\eta^2)}$	$(\theta_\infty/\theta_0)\sqrt{(1-\eta^2)}$
NaCl[a]	0.905	0.977	0.88
NaI[a]	1.188	0.721	0.86
KCl[a]	1.002	0.999	1.00
KBr[a]	1.076	0.939	1.01
KI[a]	1.228	0.849	1.04
RbCl[b]	1.03	0.911	0.94
CsBr[c]	0.8816	0.9685	0.854
CsI[c]	0.8556	0.9997	0.855

a) Barron, *et al.*[13] b) Present work. c) Sorai.[22]

The cation effect also appears in anharmonicity of lattice vibrations. The anharmonic effect comes to be observable in thermodynamic functions such as heat capacity usually at temperatures higher than $(1/2)\theta_\infty$. In the case of RbCl, θ_∞ is 190 K and the maximum of θ_D occurs at 75 K. The magnitude of the anharmonic effect is represented and measured by the anharmonic coefficient A defined by

$$(F-F^h)/6Nk = -\frac{1}{2}AT^2+B+0(T^{-2})$$

or

$$(S-S^h)/6Nk = (C_v-C_v^h)/6Nk=AT$$

for the alkali halides, where $|AT|<1$.

Thus the quantity AT is the leading anharmonic contribution and its coefficient A depends on the volume only. Tosi and Fumi[23] gave more accurate formula for estimating the value of $A(V_0)$;

$$A = \frac{\theta_s - \theta_s^h}{T^2} \frac{d}{d(\theta_s^h/T)} \left(\frac{S^h}{6Nk} \right)$$

where θ_s is the experimental Debye temperature derived from the entropy for the volume at 0 K, θ_s^h the quasiharmonic Debye temperature computed from the ν_g and μ_n, S^h the quasiharmonic entropy, and $T \geqq \theta_\infty$. The coefficient for rubidium chloride was then estimated to be $A = (9.3 \pm 1.7) \times 10^{-5}\ K^{-1}$, using the Tosi-Fumi formula, and this is included in Table 6 for comparison of the anharmonic coefficients of various alkali halides.

Table 6. ANHARMONIC COEFFICIENT $A(V_0)$

Salt	$A(V_0)$ / $10^{-5}\ K^{-1}$	Salt	$A(V_0)$ / $10^{-5}\ K^{-1}$
KF[a]	−2.1±0.5	NaCl[c]	−1.5±0.9
KCl	3±1	NaI[c]	−0.2±0.5
KCl[c]	2.8±0.7		
KBr[b]	2.5±1	RbCl[d]	9.3±1.7
KBr[c]	3.5±1.0		
KI[b]	0.5±0.5	CsBr[e]	−11.4±0.3
		CsI[e]	−9.0±0.3

a) Vieira and Hortal,[24] using a method different from Tosi-Fumi's method. b) Tosi and Fumi.[23]
c) Leadbetter, *et al.*[25] d) Present work. e) Sorai.[22]

The coefficient for rubidium chloride is the largest among the alkali halides having the NaCl-type of structure and the sign and the magnitude of the coefficient is primarily determined by the kind of constituent cation.

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