Dielectric Behaviour of Hydrated Crystals. II. Potassium Mercury (II) Chloride Monohydrate and Ammonium Mercury (II) Chloride Monohydrate[1]

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Introduction

The water molecule in a salt hydrate crystal, which does not directly coordinate with the metal ion and is situated in an open space in the crystal lattice, will differ to a certain degree from the directly coordinated water molecule in the dielectric behaviour relating to the dipole orientation of the water molecule. In the present paper, potassium mercury (II) chloride monohydrate, $K_2HgCl_4 \cdot H_2O$ and its isomorphous crystal, ammonium mercury (II) chloride monohydrate, $(NH_4)_2HgCl_4 \cdot H_2O$ are dealt with as the typical examples containing the interstitial water of crystallization as confirmed by the X-ray analyses.

Crystal, Specimen and Equipment

A large single crystal of $K_2HgCl_4 \cdot H_2O$ are grown by slow cooling from seed crystal in a slightly supersaturated aqueous solution contained in a glass vessel dipped in a water-thermostat. This solution has been prepared from potassium chloride and mercuric chloride according to the phase diagram. It requires about four or five weeks to obtain a suitable, large, transparent, single crystal.

The crystal of the ammonium salt is obtained in a similar way.

The specimen is made by cutting and grinding, and is inserted directly between silver- or platinum-coated electrodes for the measurement of the capacity and the equivalent resistance of the crystal condenser in a way similar to that described in the previous paper.[2]

Result of Dielectric Measurement

(a) **$K_2HgCl_4 \cdot H_2O$.** The permittivities of this rhombic crystal at a room temperature are as follows: $\epsilon_a = 6.7 \pm 0.3$, $\epsilon_b = 6.1 \pm 0.2$, $\epsilon_c = 17.5 \pm 1.0$ (15°C, at 3 Mc and 5 kc). There is a marked anisotropy between the permittivities parallel and perpendicular to the c-axis. The temperature dependences of the permittivities and the dielectric losses are shown in Fig. 1, and the temperature coefficients $\frac{1}{\epsilon}\left(\frac{d\epsilon}{dT}\right)$ are as follows:

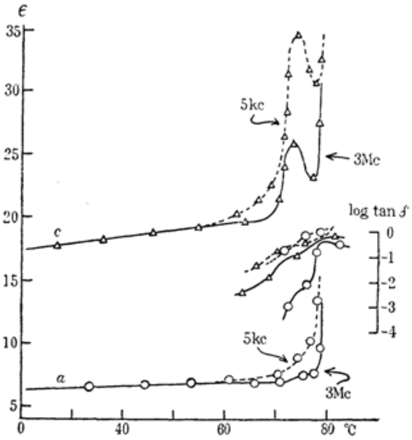

Fig. 1. The temperature dependences of the dielectric behaviour of $K_2HgCl_4 \cdot H_2O$

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[1] Parts of this investigation were separately read before the annual meetings of the Chemical Society of Japan in April 1949 and 1950, the annual meeting of the Crystallographic Society of Japan in May, 1950 and the Second International Congress of Crystallography at Stockholm in July, 1951.

[2] R. Kiriyama and H. Ibamoto, This Bulletin, **27**, 32 (1954).

	-170——$-120°$	-120——$-40°$	-40——$+70°$
a	3×10^{-4}	7×10^{-4}	1×10^{-3}
c	4×10^{-4}	7×10^{-4}	3×10^{-3}

In these measurements, the average rate of heating is 0.2° per minute. The behaviour along the *b*-axis is almost similar to that along *a*. Above 70°C, there is a dispersion between 3 Mc and 5 kc along the *c*-axis, and the permittivity-temperature curve shows a peak at about 110°, while there is no such peak either along the *a*-axis or along the *b*-axis, and the dispersions along these axes are considerably small compared with that along *c*. At about 117°, sudden increases of the permittivities are observed in both *a*-and *c*-directions. When a considerable amount of phosphorus pentoxide powder has been spread at the bottom of the measuring cell, this steep increase at 117° diminishes and a maximum permittivity become measurable, then the ϵ-T curve shows a second peak at certain degrees higher than 117°. Therefore, it may be concluded that the increase at 117° is due to the surface conduction in the adsorbed layer of the dehydrated water molecules on the crystal surface. Similar phenomena were observed in the course of the dielectric measurements of $K_2CuCl_4 \cdot 2H_2O$, $(NH_4)_2CuCl_4 \cdot 2H_2O$ and $Sr(HCO_2)_2 \cdot 2H_2O$ when the dehydration took place suddenly.[2)]

Sometimes we observed a rather rapid increase of ϵ_c at a far lower temperature than that observed in the ordinary case and there arises a terrace on the low temperature side of the peak at 110° in the ϵ_c-T diagram. But this phenomenon is not reproducible and differs somewhat from others. Such a non-reproducible phenomenon may be attributed to some lattice imperfections of the crystal and a qualitative explanation will be given in the next paper of our studies.

For the purpose of making clear the cause of the anomaly at about 110°C, we carried out also the measurement of the time dependence of ϵ_c at constant temperatures, three different points being so chosen out of the temperature region where the anomaly is observed to be of significance from the view point of the results of X-ray experiments. The results are shown in Fig. 2. In the ϵ_c-time diagrams, the curve for 82.5° has two low peaks whereas that for 94° has only one high peak and that for 102.5° has also one high peak which lies nearer to the ordinate axis than that for 94°. After 300–500 hours, these curves seem to tend to an asymptotic value of about 13–15. According to the X-ray experiment mentioned below, the ordinary form transforms gradually into the high temperature form above 82°C. However, the transition velocity from the low temperature form into the high temperature one is so very little above the transition point, that the maximum ϵ_c which corresponds to the peak at about 110°C on the ϵ_c-T curve in Fig. 1 will appear very late as is seen for the appearance of the second peak in the ϵ_c-time curve for 82.5°. And the higher the temperature, the larger the transition velocity, and therefore the corresponding maximum ϵ_c at the higher temperature will appear in the earlier stage of the ϵ_c-time diagram.

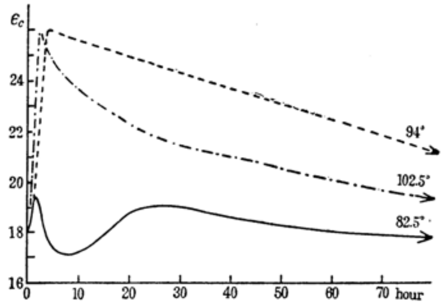

Fig. 2. The time dependences of ϵ_c at constant temperatures for $K_2HgCl_4 \cdot H_2O$

(b) $(NH_4)_2HgCl_4 \cdot H_2O$. The permittivities at 18°C are ϵ_a 7.2, ϵ_b 6.5, ϵ_c 22.3 at 3 Mc. There is also a marked anisotropy observed in the case of the potassium salt mentioned in (**a**). The temperature dependences of the dielectric behaviour are shown in Fig. 3. The sign of the temperature coefficient of the permittivity along each crystallographic axis of the ammonium salt is positive in the neighbourhood of the room temperature, but at lower temperatures the temperature coefficient of ϵ_a becomes negative. It may be

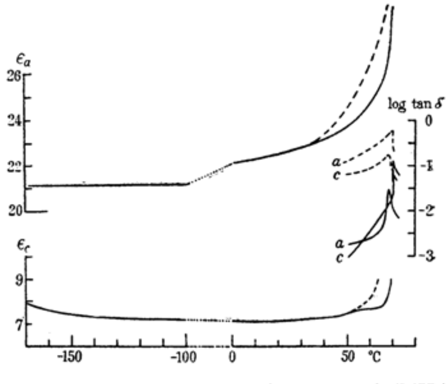

Fig. 3. The dielectric behaviour of $(NH_4)_2HgCl_4 \cdot H_2O$. Samples are sandwiched in two mica foils in these cases. Full line-3 Mc, broken line—5 kc.

worth noticing that the negative sign of the temperature coefficient of the permittivity at low temperatures was also found in another ammonium salt, $(NH_4)_2CuCl_4 \cdot 2H_2O$.[2]

In ϵ-T diagram of this ammonium mercury (II) salt, a peak which is seen in the case of the potassium salt just below the dehydration temperature is not observed. But careful tracing of the ϵ_c-T curve suggests that such a peak may also exist so closely below the dehydration temperature that the peak can not be separated from the steep increase of ϵ_c in the neighbourhood of the dehydration temperature.

Results of X-ray and Thermal Investigations of $K_2HgCl_4 \cdot H_2O$

The change of the crystal structure is investigated by Laue patterns taken with the incident beam parallel to the *b*-axis at various temperatures (Table I). These results show that the crystal lattice is collapsing gradually above about 82°C. The Debye photographs of the initial and the final stages of 300 hours-heating are taken using Cu $K\alpha$ radiation with Ni-filter at various temperatures (Table II).

From these Laue and Debye photographs, it is concluded that the potassium salt gradually transforms from the low temperature form to the high temperature one above 82°C. The indices of the Debye patterns of this high temperature form are determined wholly in reference to the indices of the ordinary low temperature form, notwithstanding that the relative intensities of the Debye patterns of the high temperature form are essentially different from those of the low temperature one (Table V).

TABLE I

STRUCTURE CHANGE OF $K_2HgCl_4 \cdot H_2O$ OBSERVED FROM LAUE PATTERNS

T(°C)	time(hour)	lattice
25	3	low temperature form
55	3	low (no change)
81	3	low (no change)
107	3	low (Laue spots weaken)
125	3	no spots, fiber patterns of KCl
155	(3)	Debye-rings of KCl only

The second column shows the time of exposure at the temperature given in the first column except the last case. The photograph of the last case was taken also for 3 hours-exposure after 300 hours-heating at 155°.

TABLE II

STRUCTURE CHANGE OF $K_2HgCl_4 \cdot H_2O$ OBSERVED FROM DEBYE PHOTOGRAPHS

T(°C)	initial 10 hours	final 10 hours
25	low	low
60	low	low
75	low	low
80	low	—
82	—	low-high (mixed)
85	low	—
91	—	high (broad)
100	high (broad)	high
120	high (broad)	high (sharp)
128	—	high (sharp)
145	—	high (weak), KCl (strong)

Moreover, the dilatometric experiment using toluene as the dilatometer-liquid shows no discontinuity throughout this transition, whereas the case using mercury shows distinct bending of the dilatometric curve at about 82°. These results suggest that the fine powders of the high temperature form produced by the lattice breaking of the low temperature form are easily wetted by mercury but not by toluene, and there must exist a lattice transformation at about 82° without detectable volume change.

Besides these, the thermal analysis curve obtained by S. Seki and H. Chihara in this laboratory shows that there is no appreciable heat absorption at about the transition point but there are two peaks at 115° and 123°. In this experiment, the average rate of heating is 1.6° per minute and this rate is considerably faster than that in the case of the dielectric measurement. Therefore, the two peaks at 115° and 123° in the thermal analysis curve may be attributed to the latent heat of the delayed lattice transformation and those of the vaporization of the water liberated from the collapsing lattice and of the sublimation of mercuric chloride produced by the decomposition of this double salt respectively.

The microscopic observation of the surface after the partial dehydration at 120° shows numerous small pits distributed randomly on the *c*-plane and a few semi-cylindrical swellings along the *c*-axis on the *a*-plane. Moreover, in the course of the observation of the change of the optical properties with a polarizing microscope for the transparent thin plates, some stripes along the *c*-axis appear on the surface of the *a*-plane as the temperature rises and then the crystal collapses gradually, but many nuclei of dehydration are seen at the same time on the *c*-plane, and as the number of the nuclei increase, the crystal plate loses its transparency. By the way, these partly dehydrated specimens are considerably hard and tough and they appear in white unglazed ceramic feature.

Discussion

(a) Anisotropy of the Room Temperature Permittivities. For the purpose of discussing the dielectric polarization of this rhombic crystal in the first place, the permittivity along each crystallographic axis is compared with the square of the refractive index for the corresponding axis (Table III).

TABLE III

REFRACTIVE INDICES FOR NaD3) AND PERMITTIVITIES OF $K_2HgCl_4 \cdot H_2O$

n_a (α) 1.648	n_a^2 2.72	ε_a 6.7
n_b (γ) 1.699	n_b^2 2.89	ε_b 6.1
n_c (β) 1.678	n_c^2 2.82	ε_c 17.5

In this case, the maximum polarization in the optical frequency region is directed along its b-axis while that in the radio-frequency region is along its c-axis.

The crystal structure of the low temperature form of the potassium salt belongs to space group $Pbam-V_h^9$ and has a unit cell of $a=8.27$, $b=11.63$, $c=8.89$ kX containing four formula units.4) There is a mirror plane perpendicular to the c-axis, therefore the dipoles of a pair of water molecules should be cancelling each other in the direction of the c-axis, and this cancellation is confirmed at a room temperature as a fixed four-proton system by the proton nuclear magnetic resonance absorption experiment using single crystals.5) Consequently, the large polarization along the c-axis is mainly due to the atomic polarization of mercury which is surrounded by a less symmetrical chlorine octahedron and may be easily polarizable along the c-axis. In fact, the position of the mercury atom is 0.2 Å apart from the center of gravity of the chlorine octahedron (Fig. 4). Such an atomic polarization is somewhat analogous to that of the titanium atom in the ferroelectric barium titanate crystal.

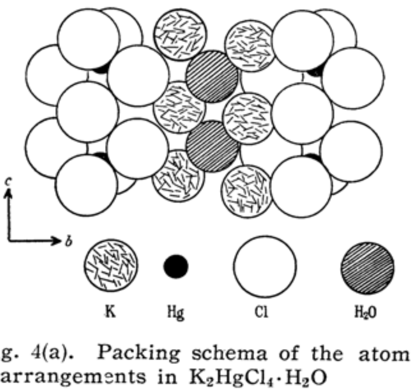

Fig. 4(a). Packing schema of the atomic arrangements in $K_2HgCl_4 \cdot H_2O$

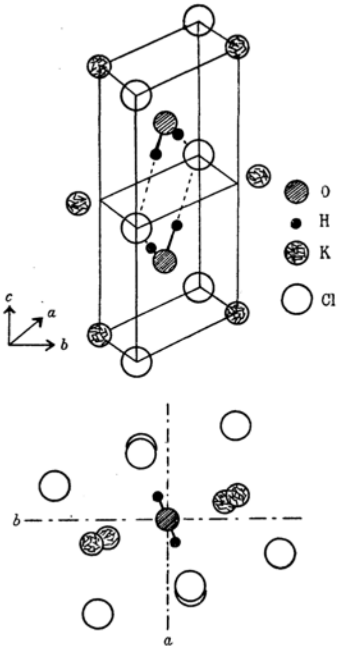

Fig. 4(b). The perspective and projection of the atomic arrangements around the pair of the water molecules in $K_2HgCl_4 \cdot H_2O$

In the case of the ammonium mercury (II) chloride monohydrate, the anisotropy of the permittivities, namely the far larger value of ϵ_c compared to those of ϵ_a and ϵ_b, may be attributed to the same cause as in the potassium salt.

(b) The High Temperature Modification of the Potassium Salt. Based on the facts that no detectable volume change is observed at the transition point, and also that the position as well as the indices of the X-ray reflections of the high temperature form coincide completely with those of the ordinary form, it may be concluded that the unit-cell dimensions of the high temperature form must be the same at the transition temperature as those of the low temperature form.

The analysis of the crystal structure of this high temperature form seems to be too difficult to determine precisely from the known data of the Debye photographs only. Fortunately, there are at least two clues for

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3) P. Groth, "*Chemische Krystallographie,*" Teil **1**, 360 (1906).

4) C. M. MacGillavry, J. H. de Wilde and J. M. Bijvoet, *Z. Krist.*, **100**, 212 (1938).

5) J. Itoh, R. Kusaka, Y. Yamagata, R. Kiriyama and H. Ibamoto, *J. Phys. Soc. Japan*, **8**, 293 (1953).

this crystal structure; one is the above invariableness of the lattice constants at the transition point, and the other the indefinite proportion of the water content in the high temperature form, i.e. the occupation of the possible interstitial positions of the lattice by the water molecules. From these considerations we have tried to determine the atomic arrangement of the high temperature form assuming that the corresponding space group is $Pbnm—V_h^{16}$ and all chlorine atoms are in almost hexagonal close packing. The most probable crystal structure for the present among many possible models is gvien after successive trial and error approximations. The atomic coordinates and the relative intensities $I_{obs.}$, the squares of the structure factors $F^2_{cal.}$ of the Debye-patterns are shown in Tables IV and V respectively.

TABLE IV

ATOMIC PARAMETERS OF THE HIGH TEMPERATURE FORM OF $K_2HgCl_4 \cdot H_2O$6)

$Pbnm—V_h^{16}$, $a=8.3$, $b=11.6$, $c=8.9$ Å, $Z=4$.

		x	y	z
Hg	(4c)	0.40	0.22	0.25
K(I)	(4a)	0.00	0.00	0.00
K(II)	(4b)	0.50	0.00	0.00
Cl(I)	(4c)	0.75	0.06	0.25
Cl(II)	(4c)	0.25	0.44	0.25
Cl(III)	(8d)	0.25	0.19	0.00

The structure principle of the high temperature form is that the mercury atom is surrounded by four chlorine atoms forming a deformed tetrahedron and the potassium atom by slightly deformed chlorine-octahedron. Strictly speaking, such a structure without the water molecule is not a high temperature modification of the monohydrate and the remaining water molecules in the lattice are probably in some interstitial positions. From the existence of the reflection of (110) which is a forbidden reflection for the high temperature space group, it will be concluded that in the high temperature form after the phase transition there remain also in several places the tunnel structures parallel to the c-axis, and the water molecules enclosed in these tunnels may have some chances of forming chain-like associations parallel to the c-axis within an adequate temperature range.

TABLE V

INTENSITY RELATIONS OF DEBYE-PATTERNS OF $K_2HgCl_4 \cdot H_2O$

			low form		high form	
d (kX)		(hkl)	$I_{obs.}$	$F^2_{cal.}$	$I_{obs.}$	$F^2_{cal.}$
6.75		(110)	vs	0.4	m	0.
5.85		(020)	m	0.2	m	0.1
5.38		(111)	—	0.	s	0.7
4.85		(021)	—	0	m	0.1
4.45		(002)	w	0.1	w	0.1
4.35	$HgCl_2$	(001)	—	—	w-s	—
4.15		(200)	m	0.4	—	0.
3.91		(210)	—	0.	m	0.4
3.72		(112)	vs	1.0	—	0.
3.53		(022)	s	0.7	s	0.4
3.52		(130)				
3.38		(220)	vw	0.1	w	0.2
3.26		(131)	w	0.3	w	0.4
3.13	KCl	(200)	—	—	m-vs	—
3.05		(202)	s	1.0	—	0.
3.00	$HgCl_2$	(200)	—	—	vw-w	—
2.94		(212)	m	0.4	vs	1.0
2.93		(040)				
2.76		(041)	—	0.	m	0.4
2.76		(132)	—	0.1		
2.74		(140)	vw	0.2	—	0.1
2.69		(222)	vs	0.9	vw	0.4
2.69		(310)				
2.64		(301)	—	0.	—	0.4
2.58		(311)	—	0.	vw	0.1
2.52		(123)	—	0.	—	0.4
2.50		(320)	vw	0.2	—	0.
2.43		(042)	w	0.5	—	0.
2.40		(321)	—	0.	w	0.6
2.38		(240)	w	0.4	—	0.
2.25		(330)	vs	1.2	vs	1.0
2.23		(150)				
2.23		(004)				
2.23		(223)				
2.21	KCl	(220)	—	—	vw-w	—
2.18		(322)	—	0.	w	0.5
2.17		(151)	—	0.		
2.11		(114)	m	1.2	vvw	0.
2.10		(242)				
2.02		(303)	s	0.7	w	0.7
2.02		(250)				
2.02		(401)				
2.02		(340)				
1.95		(420)	m	0.9	w	0.4
1.94		(060)				

(c) **The Structure of the Ammonium Mercury (II) Chloride Monohydrate, $(NH_4)_2HgCl_4 \cdot H_2O$.** The isomorphism of the ammonium salt and the potassium salt has been confirmed by us structurally by means of X-ray methods. The ammonium salt has a unit cell of the dimensions $a=8.50$, $b=11.97$, $c=9.19$ Å (Cu $K\alpha=1.542$ Å) containing also four formula units. The ammonium salt is so sensitive to moisture that it is difficult to keep the crystal sample without lattice collapsing at just below the dehydration tem-

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6) *cf.* Internationale Tabellen zur Bestimmung von Kristalstrukturen, (1938).

perature for several hours necessary to obtain the Debye photograph. Therefore, it could not be decided whether or not the hign temperature form of $(NH_4)_2HgCl_4 \cdot H_2O$ exists in a temperature range just below the dehydration point.

(**d**) **The Temperature Dependences of the Permittivities.** Now it is to be discussed what is the cause of the anomalous dispersion which appeared in $K_2HgCl_4 \cdot H_2O$ along the c-axis above the transition temperature. The result of the X-ray analysis of the low temperature form shows that there is a characteristic tunnel structure which contains water molecules only. This tunnel is strangulated by the surrounding atoms, consisting of a train of cocoon-shaped spaces with narrow and wide passages alternately. Water of crystallization in such spaces may be looked upon as a zeolitic water, but at room temperatures the fast that the orientations of the water molecules are fixed in the crystal lattice is confirmed. Moreover, there are no marked dispersions in the permittivity-temperature diagrams below the transition point 82° for the practically perfect crystal. Thus it may be concluded that the water molecules in the crystal lattice of the low temperature form are not movable in the whole range of temperatures below the transition point, this water of crystallization being not typically zeolitic.

The phase transition proceeds gradually and the atomic displacements of the chlorines are the smallest and those of the mercuries the largest among the three sorts of atoms, chlorine, potassium and mercury. Besides these, most of water molecules diffuse into the newly constructed lattice and take some suitable interstitial positions, but some of water molecules remain in the remnants of the tunnel structure as described in (**b**). The water molecules confined in these closed capillaries parallel to the c-axis will have some chances of chain-like associations of the water dipoles as the lattice loosens moderately when the temperature is maintained in an adequate range. Thus the high ϵ_c appears in consequence of the formation of chain-like clusters of the water dipoles parallel to the c-axis and not of the independent simple rotation of the water dipoles. The higher the temperature, the more violent the thermal motion and the more such clusters of water molecules will dissociate. Besides these, the dehydration through the collapsing lattice will become remarkable. The dissociation of the dipole clusters and the diminution of the numbers of the water molecules both cause the dielectric polarization to fall down above 110° as the experiment shows.

Based on this consideration, the changes of ϵ_c at three constant temperatures in the anomalous temperature region may be explained as follows. The first peak on the curve at 82.5°C may be due to the chain-like association of the water molecules enclosed in some original tunnel-structures which have probably some sort of lattice defects of their atomic arrangements. As the lattice transformation proceeds slowly at the constant temperature, these original tunnel-structures will be obstructed gradually and then the chance of the association will be diminished. Therefore, the polarization due to such dipole clusters will fall down, giving a peak of maximum polarization as seen in the figure (Fig. 2). However, in the course of the rearrangement of the atoms, the original tunnel-structures may remain in several places containing water molecules. As this newly constructed lattice is loosened gradually again, these water molecules which have had no chance of dipole association up to this stage owing to the original narrow passages of the tunnel-structure will be able to pass through it and may have some chances of association. Therefore, the dielectric polarization along this direction of the tunnel-structure will rise again. However, these enclosed water molecules may escape rather easily through the loosening lattice and then the polarization will diminish gradually in progress of time. Thus there appears the second peak as seen in the figure. The change at 94° or 102.5° may be explained in a similar way. At such higher temperatures, the transition proceeds rather quickly and the two peaks as seen in the process at 82.5° will fuse in one, and the saddle-shaped fall between two peaks will not be observable in either cases at 94° or 102.5°.

In $(NH_4)_2HgCl_4 \cdot H_2O$, the existence of the high temperature form is not certain as mentioned in (**c**). But the analogous feature of the permittivities below the dehydration temperature may be explained in the same way as in the case of the potassium salt.

The dielectric behaviour and the problem of the zeolitic water of crystallization of potassium tin (II) chloride monohydrate, $K_2SnCl_4 \cdot H_2O$, of which structure is similar to the mercury salts dealt with in the present paper, will be reported in the following paper, Part III.

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