Dielectric Behaviours of Hydrated Crystals I. Strontium Formate Dihydrate, Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate[1]

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Introduction

The investigations of the dielectric behaviours of the hydrated crystals will render some strong clues about the binding state of the water molecules in the crystal lattices. In these measurements, however, it is difficult to obtain reliable data owing to some sorts of lattice imperfections, especially liquid inclusions or efflorescent nuclei, and the surface leakage originated probably from the adsorbed water molecules. For the purpose of avoiding such phenomena, it will be desirable to use large, transparent, single crystals which make it possible to minimize these troublesome effects. In the present paper, the temperature and frequency dependences of the dielectric properties of one rhombic crystal, strontium formate dihydrate, $Sr(HCO_2)_2 \cdot 2H_2O$ and two isomorphous tetragonal crystals, potassium copper (II) chloride dihydrate, $K_2CuCl_4 \cdot 2H_2O$ and ammonium copper (II) chloride dihydrate, $(NH_4)_2CuCl_4 \cdot 2H_2O$ which contain directly coordinated water molecules to the divalent metal ions are reported and the anisotropies of the permittivities of the cupric salts are discussed.

Experimental

Crystals and Specimens of Strontium Formate Dihydrate. As the temperature dependence of the solubility of this anhydrate in water is rather small, a single crystal of this substance can be obtained by slow cooling, together with slow vaporization from the seed crystal placed on the bottom of a glass vessel, filled with a slightly supersaturated aqueous solution, which is kept in an air-thermostat with a regulator of ±1° in the range of 40–30°C.[2] Cutting and grinding these transparent large single crystals perpendicular to three crystallographic axes, we obtain suitable specimens of about 1.5×1.5 cm^2. in area and 1.0–1.5 mm. in thickness in each case. These slices are pasted by tin foils with vacuum grease on both sides. Then this specimen is inserted into the plate condenser mentioned below.

Crystals and Specimens of Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate. These crystals are grown by slow cooling of the supersaturated aqueous solutions by the same process mentioned above. But the temperature dependences of the solubilities being rather steep, it is necessary to regulate the temperature-fluctuation within less than ±0.1°. Consequently, the growing vessels are placed in a water-thermostat and the temperature is carefully controlled. Large crystals thus obtained are cut and ground to form suitable slices which are perpendicular to two crystallographic axes. Among these specimens we select nearly perfect, single crystals which are scarcely optically anomalous and not twinned according to the examination using a polarizing microscope. The slice is directly put between silver-coated brass electrodes forming a crystal condenser in the measuring circuit.

Equipment. The crystal condenser for the measurement at room temperature is a somewhat improved type of the previously used condenser in our laboratory,[3] and the permittivities of the crystal are determined from the ratios of the capacities of the specimens to those of the artificial rock salt of which permittivity is adopted at 5.62 as the standard value.[4] This rock salt was prepared by Stockberger's method in our laboratory.

The cell for the observation of the temperature dependence is also an improved type of that previously reported.[3] The temperature of the specimen in the cell is measured by a copper-constantan couple in the limit of ±1°C. The heating rate is about 0.2°/min. in every case. For the purpose of avoiding the condensation of water vapour upon the crystal surface when the cell is cooled down, a small member of calcium chloride grains have been spread on the bottom of the cell.

The measurements at audio-frequencies are carried out using a capacity-resistance bridge with RC-type oscillator. In these cases, there are no remarkable dispersions between 20 kc–1 kc, thus the measurements are performed mainly at 5 kc.

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[1] This paper was partly presented at the annual meeting of the Crystallographic Society of Japan on May 14, 1950 and partly at the meeting of the Chemical Society of Japan on Sept. 20, 1952 (a symmposium on structural chemistry) and also on Nov. 17, 1952 (a symmposium on complex salt).

[2] R. Kiriyama, Studies on the velocities of crystal growth I. The growth condition of the single crystal of strontium formate dihydrate, *J. Chem. Soc. Japan*, **70**, 260 (1949), in Japanese.

[3] T. Suita, K. Suenaga and I. Nitta, Abstract of the Electrical Engineering Section of the 4th general meeting of Nippon Kogakukai on April, 1940, page 18.

[4] K. Höjendahl, *K. Danske Vidensk. Selskab.*, **16**, No. 2, (1938).

The measurements at radio-frequencies are carried out by a resonance circuit and the dielectric losses are obtained by resistance-substitution. The frequencies used are 600 kc. and 3 Mc. stabilized by quartz oscillators.

Result

Strontium Formate Dihydrate. The permittivities along three crystallographic axes at a room temperature are as follows,

$$\varepsilon_a=5.2,\quad \varepsilon_b=4.9,\quad \varepsilon_c=4.3$$

In these cases, the frequency dependences between 5 kc. and 3 Mc. are not observable, and these values may be more precise than those previously reported by one of the authors.[5]

The temperature dependences between −170°C. and the dehydration point at 3 Mc. are shown in Fig. 1. The temperature coefficients of the permittivities along three axes are very small and it shows a horizontal straight line up to about 70°C. in every case. But the permittivities show slightly decreasing tendencies of at least 1% when the temperature rises above about 70°. However the permittivities increase suddenly at 75° and the crystal collapses, followed by dehydration of the total water of crystallization.

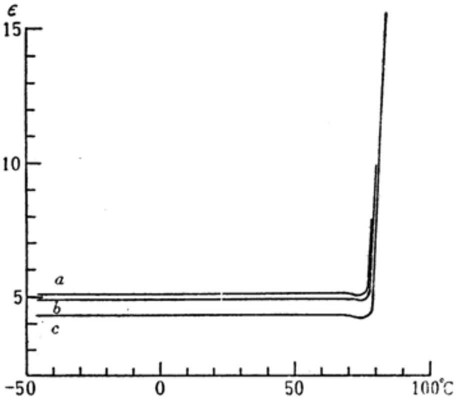

Fig. 1. Strontium formate dihydrate: Anisotropy and temperature dependences of the permittivities along its three crystallographic axes.

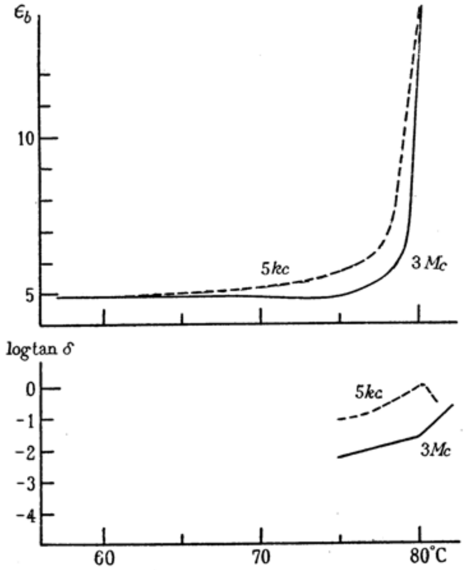

Fig. 2. Strontium formate dihydrate: Dispersion at 3Mc. and 5kc.

The change and dispersion of the dielectric behaviour before and after the dehydration are shown in Fig. 2 in which the curves along b–axis are picked up as an example. The permittivity at 5 kc is higher than that at 3 Mc above 65° and the dielectric loss at 5 kc is also far greater than that at 3 Mc. The cause of such a high dielectric loss will be attributed to the surface conduction of the dehydrated polycrystals. Actually, it is confirmed that the loss diminishes when a thin mica foil has been inserted between the crystal specimen and one of the electrodes.

Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate. The permittivities at room temperature are as follows,

$K_2CuCl_4\cdot 2H_2O$: $\varepsilon_a=8.5,\ \varepsilon_c=5.1$
$(NH_4)_2CuCl_4\cdot 2H_2O$: $\varepsilon_a=7.2,\ \varepsilon_c=5.6$

There are no detectable dispersions between 3 Mc. and 5 kc at room temperature. But, it is remarkable that, in spite of the isomorphous structure, the potassium salt shows greater anisotropy than that of ammonium salt.

The temperature dependences of the permittivities and the losses of both salts are shown in Fig. 3 and 4. The temperature coefficients of the permittivities $\frac{1}{\varepsilon}\left(\frac{d\varepsilon}{dT}\right)$ are obtained from these experimental curves.

$K_2CuCl_4\cdot 2H_2O$: −170 — −20°C. (3 Mc. and 5 kc.)
along a nearly zero; along c 2.2×10^{-4}
$(NH_4)_2CuCl_4\cdot 2H_2O$: −170 — −130°C. (3Mc. and 5 kc.)
along a -7×10^{-4}; along c 9×10^{-4}
−130 — 0°C. (3 Mc. and 5 kc.)
along a nearly zero; along c nearly zero
0 — 100°C. (3 Mc. and 5 kc.)
along a 1.7×10^{-4}; along c 2.2×10^{-4}

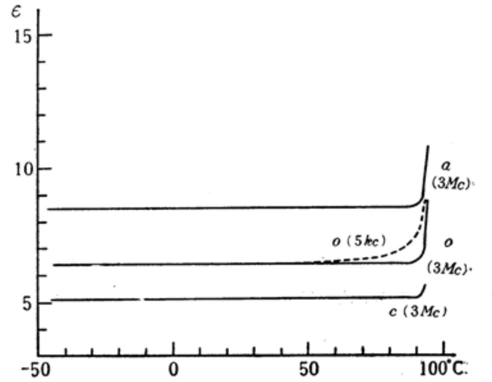

Fig. 3. Potassium copper (II) chloride dihydrate: Temperature dependences of the permittivities and the dispersion perpendicular to o(111) -plane.

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[5] R. Kiriyama, *Kagaku*, **17**, 239 (1947), in Japanese.

100 — 125°C. (3 Mc.)
along a 1.1×10^{-3}; along c 0.6×10^{-3}
100 — 125°C. (5 kc.)
along a 6.5×10^{-3}; along c 6×10^{-3}

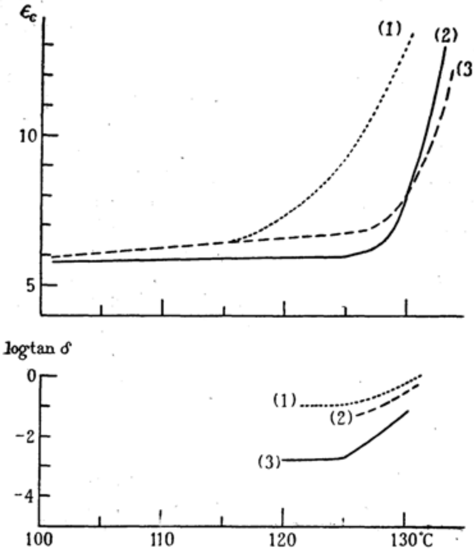

Fig. 4. Ammonium copper (II) chloride dihydrate: Temperature dependences of the permittivities and the dielectric losses; (1) 5kc., direct; (2) 5kc., both sides mica foils; (3) 3Mc., one side mica foil.

Thereupon, in the case of the ammonium salt at low temperatures, we found a rather curious anisotropy of the temperature coefficients which are negative in a–direction and positive in c–direction. The dielectric behaviour of the potassium salt is analogous to that of strontium formate dihydrate which shows no remarkable change up to the dehydration temperature. Especially, in the case of this potassium salt, it shows also a little decreasing tendency at 3 Mc. before the dehydration occurs.

The dehydration of the ammonium salt takes place at a considerably higher temperature than that of potassium salt and this temperature difference will cause some effects originated in the dehydrated water molecules. In the experiments of the ammonium salt, we have often met with the emergence of electrochemical reactions between the specimen and the brass electrodes of which the silver-coating had been perhaps imperfect.

For the purpose of investigating both effects of the surface conduction and the electrode reaction, we have tried to observe the temperature dependences of the specimens in the following ways.

(1) The specimen was directly put between two electrodes.
(2) A mica foil was inserted between the specimen and the lowerside electrode.
(3) Mica foils were inserted between the specimen and two electrodes to separate the effect of d.c. conduction.

Three examples along c–direction of these experiments in the neighbourhood of the dehydration temperature are plotted in Fig. 4.

Discussion

The crystal structure of strontium formate dihydrate was analysed by I. Nitta and K. Osaki[6]. According to their result, one water molecule is coordinated directly to the strontium ion but the other is packed in the lattice surrounded by oxygen atoms and water molecules with hydrogen bond distances. The anisotropy of the permittivities is rather small. This may be expected from the less anisotropic arrangement of the constituent atoms, radical ions and molecules. The negligible smallness of temperature and frequency dependences of permittivities may suggest that there exist fairly strong hydrogen bonds in the lattice and that no rotation-like motions of the water molecules or, unquestionably, of the formate ions will occur up to the collapse of the lattice accompanied with the dehydration of the water of crystallization.

The slight depression of the permittivities immediately below the dehydration temperature at 3 Mc. may be attributed to the loosening of the hydrogen bonds as in the case of the predehydration of copper sulphate pentahydrate[7]. But it is questionable whether the larger value at 5 kc in the same temperature region is a true dispersion caused by some rotation-like motion or originated by slight conduction on the crystal surface.

The abrupt increases of the permittivities due to the surface conduction at the dehydration temperature are analogous to many hydrated salts observed by us.

The crystal structures of both potassium and ammonium copper (II) chloride dihydrates are isomorphous and the perspective is shown in Fig. 5[8]. In this structure, $[CuCl_2(H_2O)_2Cl_2]$ rhombic octahedron is found, but we ought to adopt the planar rhombic $[CuCl_2(H_2O)_2]$ group parallel to c-axis rather than the rhombic planar $[CuCl_2Cl_2]$ group perpendicular to the c-axis as the copper (II)-complex ion in both crystals from the evidences of the atomic distances between the central Cu-atom and the ligands determined by the structure analysis.

Contrary to our expectation based on this isomorphic structure, there is found a larger anisotropy of the permittivities of the potassium salt than of the ammonium salt. The

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[6] I. Nitta and K. Osaki, read before the annual meeting of the Chemical Society ot Japan, April 5, 1947.

[7] R. Kiriyama and H. Ibamoto, This Bulletin, **25**, 359 (1952).

[8] S.B. Hendricks and R.G. Dickinson, *J. Am. Chem. Soc.*, **49**, 2149 (1627); L. Chroback, *Z. Krist.*, **88**, 35, (1934).

most reliable reason for this discrepancy may be due to the atomic polarization of the hydrogen atom of the water molecule which has some different interactions in every lattice of both salts. It has been confirmed that the proton-proton distances were 1.62± 0.02Å in the potassium salt and 1.59 ± 0.02Å in the ammonium salt by means of the proton magnetic resonance experiments[9]. These values are considerably greater than that of the free water molecule, 1.51Å, determined by the spectroscopic method. The larger discrepancy found in the potassium salt may be caused by the fact that there is a stronger interaction between the O-H···Cl system in two neighbouring $[CuCl_2(H_2O)_2Cl_2]$ octahedrons. Moreover, the protonic polarization in the hydrogen bond is larger in the lateral direction of the bond axis than in the direction parallel to the line joining the two electronegative atoms as found in some crystals which contain O-H···O hydrogen bond systems in their crystal lattices[10]. Thus the stronger hydrogen bond of O-H···Cl in the potassium salt causes a larger anisotropy of the permittivity than that of the ammonium salt. Also this effect will clarify the difference of the dichroisms of the potassium and ammonium salts. The fact that one is strong and the other is weak respectively, is due to the difference of the bond strengths between the copper atom and the ligand water molecule. In the potassium salt, the copper-water bond is weaker than that of the ammonium salt owing to the stronger O-H···Cl bond mentioned above, therefore, the rhombic $[CuCl_2Cl_2]$ group on the *c*-plane will have more covalent nature than that of the ammonium salt. This difference of the bond nature, in other words, the polarization of the electron cloud of the chlorine atom will result in a stronger dichroism of the potassium salt than that of the ammonium salt.

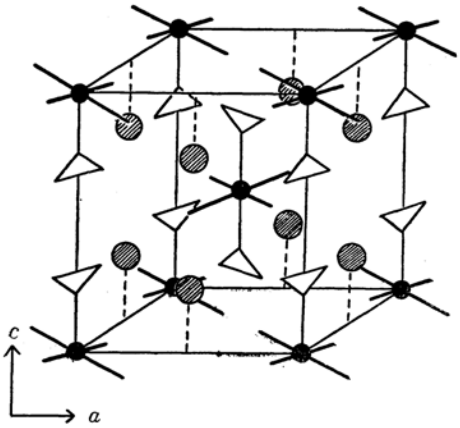

Fig. 5. The crystal structure of $K_2CuCl_4 \cdot 2H_2O$; Cu-black circle; K-hatched circle; H_2O-triangle; Cl is omitted but thick full lines indicate Cl—Cl distances in the orthorhombic octahedron.

The temperature dependences of the permittivities of the potassium salt are very small in a wide temperature range. And the slight dispersion above 50–60°C. may be attributed to the slight orientation of the dipoles of the water molecules occupying disordered lattice points which must often exist in this optically anomalous crystal. And, in this connection, it is noticeable here that there has been no temperature change of the biaxial interference figure of this optically anomalous crystal up to the dehydration temperature, therefore, this optical anomaly is not attributable to the somewhat regular misfit of the water molecules in the lattice. The sudden increase at the dehydration temperature is due to some conductive effects as in the case of the strontium formate dihydrate mentioned above.

In the case of the ammonium salt, the temperature dependences are analogous to that of the potassium salt and the principal explanation of these behaviours will be analogous to that above discussed. The reason for the slight negative temperature coefficient along *a*-axis at low temperatures, is not made clear at present, but it is noticeable that such a tendency is found also in ammonium mercury (II) chloride monohydrate and not in postassium mercury (II) chloride monohydrate[11].

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[9] J. Itoh, R. Kusaka, Y. Yamagata, R. Kiriyama and H. Ibamoto, *Physica*, **19**, 415, (1953).

[10] In gypsum by the authors and in resorsinol and pentaerysritol by S. Yabumoto and R. Kiriyama; These results will be published shortly.

[11] The results of these mercury (II) salts will be published in the following paper shortly.