Dielectric Behavior of Hydrated Crystals. IV. Cupric Formate Tetrahydrate, $Cu(HCO_2)_2 \cdot 4H_2O$

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As part of the studies of the dielectric properties of salt hydrate crystals[1], a single crystal of cupric formate tetrahydrate, $Cu(HCO_2)_2 \cdot 4H_2O$, has now been examined. The crystal has a predominant layer structure[2] in which two non-equivalent water molecules are sandwiched between $\{Cu(HCO_2)_2\}_\infty$ layers. One kind of water molecule coordinates to a copper atom directly, but the other does not. The results of the structure analysis by X-rays suggest that the two kinds of water molecules are linked together by weak hydrogen bonds. It was considered that the crystal might have characteristic dielectric properties with a large anisotropy because of the peculiar arrangement of the water molecules.

This substance undergoes a solid phase transition at $-36°C$ which is accompanied by a sudden change in the permittivity. The large dielectric dispersion and absorption observed above the transition temperature can be ascribed to the dipole orientation of the water molecules within the crystal lattice. A further absorption at much lower frequencies is also found for one particular direction of the single crystal. It may be suggested that this low frequency absorption is associated with lattice imperfections in the hydrogen-bonded systems.

In respect to the motion of the water molecules, definite information can be obtained from the results of proton magnetic resonance studies[3].

Experimental

The material was prepared by dissolving basic cupric carbonate in a dilute formic acid solution which had been made from cupric chloride and potassium carbonate, while the pure polycrystalline salt was obtained by several recrystallizations from cold aqueous water solution. A large single crystal was grown from a seed crystal in a silightly acidic solution. The crystal was cut into sections about 1.5 mm. thick and $1.5 \times 1.5\ cm^2$ in area; the main faces of the two square plates were parallel to (0 1 0) and (0 0 1) respectively, and the other was 11°5′ (i.e. the monoclinic angle β, 101°5′, minus 90°) out of (1 0 0). Considerable care in cutting and grinding the crystal was necessary because of the perfect cleavage parallel to (0 0 1).

The specimen was inserted directly between the platinum-coated electrodes of a parallel-plate condenser. The condenser was mounted in a cylindrical glass container placed in an acetone bath or liquid nitrogen bath of a large Dewar flask. By the careful addition of powdered dry ice into the acetone bath or by controlling the electric current of a heater wound around the cell, the temperature was kept constant within 0.2°C. Since the crystal was efflorescent, the specimens were usually kept in diffusion pump oil, and on measurements the crystal grains were spead on the bottom of the glass container to obtain the equilibrium water vapor pressure.

1) Part III: R. Kiriyama and H. Ibamoto, This Bulletin, 27, 323 (1954).
2) R. Kiriyama, H. Ibamoto and K. Matsuo, *Acta Cryst.*, 7, 482 (1954).
3) H. Kiriyama, This Bulletin, 35, 1205 (1962).

The frequency range from 30 c./sec. to 10 Mc./sec. was covered. In the audio and radio frequency regions, a wide-range conductance-capacitance bridge (Ando Elec. Co. Type TR-1B), and at the highest frequency of measurement, a commercial Q-meter (Yokogawa Elec. Co.), were used. The value of the permittivity was determined from the ratio of the capacity of the specimen to that of a rock salt plate with the same thickness; a standard value of 5.62 for rock salt was used throughout the measurements.

Results

Permittivities and Dielectric Losses at Room Temperature.—The permittivities ε' and corresponding loss factors ε'' of this monoclinic crystal at 20°C are shown in Table I. The complex dielectric constant ε, $(\varepsilon=\varepsilon'+i\varepsilon'')$, is denoted as follows: ε_a and ε_b mean those with the electric field along the *a*- and the *b*-axis respectively, while ε_c is that with the external field perpendicular to the *c* plane, the cleavage plane. As indicated in Table I, there was a marked dielectric anisotropy, the values of ε_a and ε_b being much larger than that of ε_c. In addition, remarkable dielectric dispersions and absorptions were observed for both the *a* and *b* directions.

TABLE I. PERMITTIVITIES AND LOSS FACTORS AT 20°C AS A FUNCTION OF FREQUENCY

	3 Mc./sec.		3 kc./sec.		0.3 kc./sec.	
	ε'	ε''	ε'	ε''	ε'	ε''
ε_a	6.5	2.2	18.7	7.5	28.0	8.5
ε_b	7.0	3.5	31.6	2.5	33.5	2.8
ε_c	4.8	0.0	6.3	0.3	7.3	1.0

Temperature Dependence of Dielectric Properties. — Figure 1 shows the temperature dependence of the permittivities and ratios $\varepsilon''/\varepsilon'$ $(=\tan\delta)$ for various directions of the applied electric field in the audio frequency range. At the lowest temperature of measurement, −170°C, the value of permittivity was about 4.5 in every direction, a magnitude usually found in ionic solid dielectrics. There was no evidence of dielectric loss at low temperatures, and the permittivity increased slightly with an increase in temperature. When a temperature of −36°C was reached, a distinct change in dielectric character occurred, and remarkable dielectric relaxation phenomena were observed above this temperature. Such discontinuity suggests that this crystal undergoes a phase transition. The measurement of specific heat[4] has shown that the transition of the first order occurs at −36°C. Above the transition temperature, T_{tr}, there were great differences in

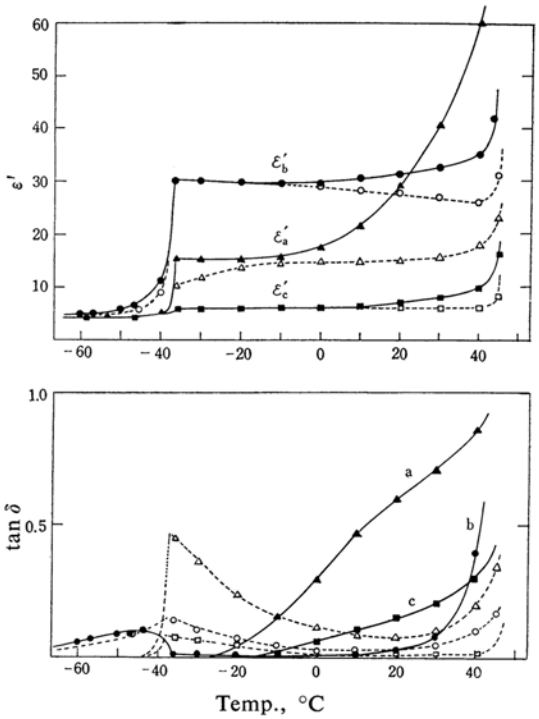

Fig. 1. Temperature dependence of the permittivity and dielectric loss angle at audio frequencies. Hollow symbols represent values obtained at 10 kc. and filled symbols at 0.1 kc.

dielectric properties in the three directions. Thus, just above T_{tr} ε'_b had the largest value among them, ε'_a, about half the value of ε'_b and ε'_c, only 6 at 0.1 kc. Moreover, at higher temperatures another type of dielectric absorption began to appear in different fashions, dependent on the direction of the applied electric field. In the *a* direction, ε'_a and also $\tan\delta_a$ rapidly increased again above about −20°C with a rise in temperature, and an apparent loss maximum was frequently observed at the lowest frequency of measurement, whereas in the *b* direction no such high dielectric losses were observed, while both ε'_b and $\tan\delta_b$ gradually increased up to 30°C. The shapes of the ε'_c-T and $\tan\delta_c$-T curves were rather similar to those in the *b* direction, but the dielectric absorption and dispersion in the former direction were quite small compared with those in the latter.

At the dehydration temperature of 46°C, a sudden increase in the permittivities and corresponding losses were observed in all three directions. Similar phenomenon was always observed in the dielectric measurements for a hydrated crystal when dehydration took place. This may be, therefore, a result of a d.c. conduction in the adsorbed layers of dehydrated water molecules on the crystal surface.

4) The thermal measurement was kindly carried out by Dr. Hiroshi Suga of the Faculty of Science, Osaka University.

Frequency Dependence of Dielectric Constants. —As is shown in Fig. 1, audio frequencies could not cover the dispersion region sufficiently. To obtain full information about the relaxation process, further measurements were made over a wide range from 30 c./sec. to 10 Mc./sec. at several fixed temperatures above the transition point. Representative results of these measurements with the electric field along the *a*- and *b*-axis are shown in Figs. 2 and 3 respectively, in which figures the permittivity and the loss factor are plotted against frequency. The absorption feature with the external field perpendicular to the cleavage plane was similar to that in the *b*-axis direction. In every direction, the absorption in the radio frequency region behaved as a typical relaxational one, and the absorption maxima gradually shifted to higher frequencies as the temperature was increased. The absorption curve in every set of measurements was a little wider than a Debye curve, indicating a spread in relaxation times. Consequently, the experimental maximum value of the loss factor, ε''_{max}, was lower than the value obtained from the term $(1/2)(\varepsilon'_0-\varepsilon'_\infty)$[5] in the Debye expression, where ε'_0 and ε'_∞ were the permittivities respectively below and above the absorption region. According to the method of Cole and Cole[6], ε'' was plotted against ε' in Fig. 4. The plots in the *a*- and the *b*-axis directions at 0°C were circular arcs, the diameters of which made angles of $0.09(\pi/2)$ and $0.16(\pi/2)$ respectively with the ε' axis. These values were rather small as compared with those obtained for a number of solid dielectrics.

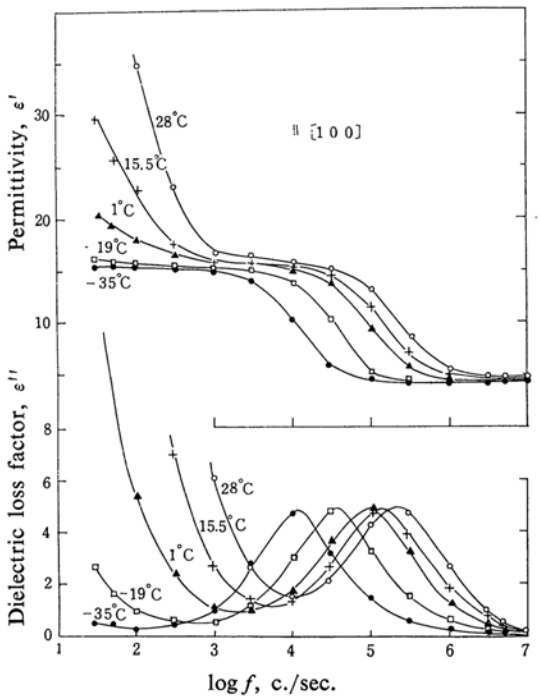

Fig. 2. Dielectric dispersion and absorption with electric field along the *a*-axis at various temperatures above T_{tr}.

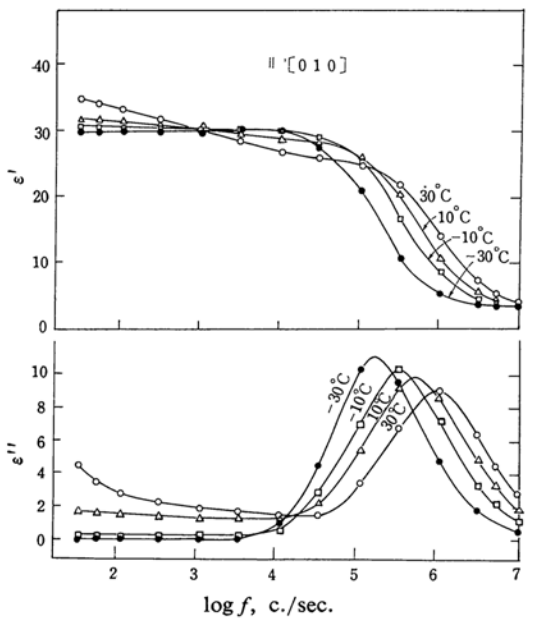

Fig. 3. Dielectric dispersion and absorption with electric field along the *b*-axis above T_{tr}.

The dielectric absorption observed at radio frequencies was ascribed to the dipole orientation resulting from the transition of the dipole from one equilibrium position to another over an energy barrier. The characteristic relaxation time for dipole orientation, τ, was obtained from the frequency of the maximum absorption, f_{max}, according to the relation:

$$\tau = 1/(2\pi f_{max})$$

Then the height H of the energy barrier could be determined from the temperature dependence

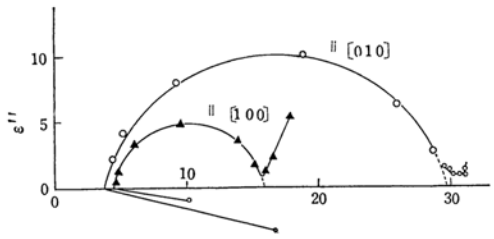

Fig. 4. Cole-Cole plots in two directions of the single crystal at 0°C.

5) For example, see H. Fröhlich, "Theory of Dielectrics", Oxford University Press, London (1949), p. 74.
6) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

of the relaxation time by means of the usual rate law:

$$\log \tau = -\log A + H/(2.3\,RT)$$

where R was the gas constant, T the absolute temperature, and A the frequency factor. Figure 5 shows the variation of $\log \tau$ with $1/T$ for the three cases, and the values of the energy barrier, H, and the frequency factor, A, are listed in Table II.

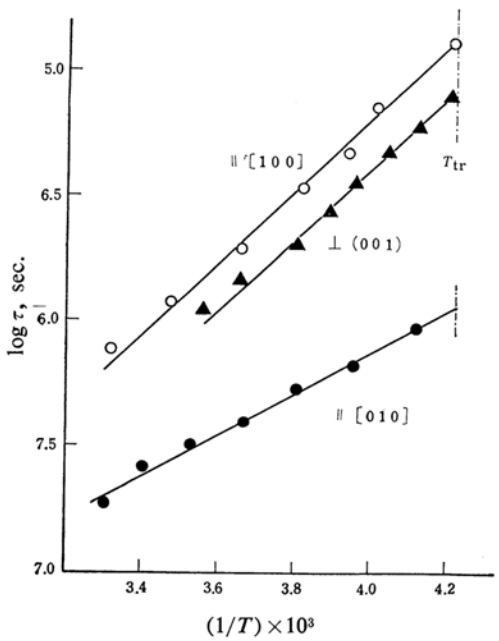

Fig. 5. Plots of $\log \tau$ (sec.) for the high frequency dispersion against reciprocal temperature (°K).

TABLE II. THE VALUES OE THE ENERGY BARRIER AND THE FREQUENCY FACTOR DESCRIBING THE OBSERVED DISPERSIONS

Direction of electric field	A sec^{-1}	H kcal./mol.
∥ [1 0 0]	1×10^{11}	6.7
∥ [0 1 0]	8×10^{9}	4.5
⊥ (0 0 1)	7×10^{10}	6.3

It can be seen in Fig. 2 that a further absorption region, in which the dielectric loss continues to increase with a decrease in frequency, is present at much lower frequencies. This type of absorption was prominent when the electric field was applied along the a-axis as mentioned above. However, the magnitudes of permittivity ε'_a and loss factor ε''_a for the low frequency absorption were somewhat variable from one sample to another, and the values obtained initially for a particular sample could not be reproduced after cooling it to the low-temperature phase and then rewarming it, whereas the results for the radio frequency absorption were quite reproducible in different runs. It would appear that in each run the loss factors of the low frequency absorption do finally attain a region where ε''_a is proportional to $1/f$, this being the evidence of d. c. conductivity.

The Atomic Arrangement in the Crystal Lattice

The crystal structure of the high temperature modification has already been determined by X-rays[2]. The structure projected on the (0 1 0)

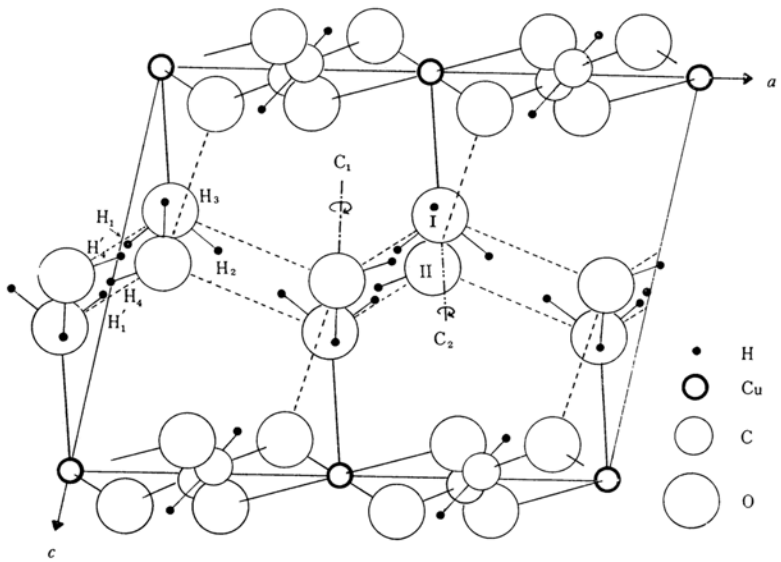

Fig. 6. Projection of the crystal structure on (0 1 0). —— Chemical bonds, ---- Possible hydrogen bonds. C_1 and C_2 represent axes of reorientation of the water molecules.

plane is represented in Fig. 6. A distinct layer structure is formed parallel to the (0 0 1) plane, in which one formate ion is coordinated to two copper atoms and each copper atom is surrounded by four oxygen atoms of four different formate ions in an approximately square configuration. Two non-equivalent water molecules are sandwiched between these layers. One kind of water molecule (H_2O-I) is coordinated to a copper atom with a far longer Cu–O distance, 2.36 Å, than the ordinary covalent Cu–O distance of about 2.0 Å. Another kind of water molecule (H_2O-II) is not linked to any copper atom, but to one oxygen atom of the formated ion and two oxygens of the first kind of water molecule with hydrogen bond distances of 2.82, 2.78 and 2.74 Å respectively.

This crystal has a transition point at −36°C, as has already been mentioned. Though the crystal structure of the low temperature modification has not yet been available, there is no evidence of any significant change in the atomic arrangement above or below the transition point. First, even if the crystal was gradually cooled to the temperature of liquid nitrogen through the transition point, it did not collapse, and the dielectric behavior in the radio frequency region was almost reproducible after such treatment. Moreover, no visible change in optical properties in the neighborhood of T_{tr} was disclosed under a polarizing microscope. Secondly, the heat capacity and volume expansion of the crystal have already been measured by Suga[4], who found that the slight discountinuity at −36°C was due to a transition of the first order. The enthalpy, entropy and volume changes associated with the transition were estimated as follows: $\Delta H=$ 206 cal./mol., $\Delta S=0.87$ e. u., $\Delta V=0.22$ ml./mol. These values are too small to account for a structural change in the transition. Thirdly, a preliminary X-ray study made by superimposing Weissenberg photographs taken at −95°C on the 25°C photographs revealed that the low temperature crystal structure was almost the same as that of room temperature except for a little contraction of about 0.1 Å in *c*.

On the basis of this evidence, the hydrogen atoms of water molecules have been located by the proton magnetic resonance experiment[3]; these results are also included in Fig. 6. Two protons (H_1 and H_2) of the water molecule H_2O-I contribute to form bent hydrogen bonds between the oxygen of its own water molecule and the two nearest oxygens of H_2O-II, whereas one proton (H_3) of H_2O-II makes a rather close approach to one oxygen of the formate ion, where a weak hydrogen bond is also predicted from the X-ray method and the remaining proton (H_4) is free from any hydrogen bond. It should be noted that two folding chains of hydrogen bonds run along the *a*-axis direction. Furthermore, with respect to packing in the *b*-axis direction, some of the hydrogen atoms, H_1', H_4, H_4', H_1, neighbor each other with H–H distances of 1.9∼2.3 Å, these values being smaller than twice the van der Waals radius of 1.2 Å.

Discussion

In the temperature range between −170°C and about −80°C, the permittivities in the three directions are almost independent of the frequencies, and those temperature coefficients which are present are positive and have values found in usual ionic crystals. Above about −80°C, the permittivity with the applied electric field parallel to the *b*-axis increases gradually up to the transition point, and the corresponding dielectric loss appears to be distinctly measurable, while in both directions of the *c*- and the *a*-axis no such dielectric anomalies are observed. It is, therefore, evident that the molecular motion of water within the crystal lattice is almost frozen below the transition point; this is consistent with the result of the proton magnetic resonance experiment. The gradual increase in permittivity in the *b* direction, however, indicates that some sort of reorientational motion of the water molecules has already been excited at several tens of degrees below T_{tr}.

When a temperature of −36°C is reached, the crystal undergoes a phase transition, a process which is associated with a slight volume expansion but without any significant structural change. The transition is also accompanied by a large increase in the permittivities parallel to the cleavage plane and a little increase perpendicular to it. These results indicate that the phase transition does involve freezing and releasing processes of electric dipoles. Thus, the large dielectric absorption and dispersion above T_{tr} must be due to the onset of the rotation of water molecules; this is confirmed by the proton magnetic resonance spectra. Hitherto, we have encountered difficulty in distinguishing the dipole orientation of water molecules from apparent dispersions due to cationic conduction in some hydrated salts, especially in zeolite crystals, for instance, analcite[7] and synthetic zeolites[8]. In the present case, however, there is no possibility of ionic conduction due to the cupric ions

7) R. Kiriyama, H. Ibamoto, M. Koizumi and R. Kitagaki, *Min. J.*, **1**, 313 (1955).
8) R. Kiriyama, H. Kawai and W. Murayama, to be published.

present, referring to the crystal structure and the bond nature. It may, therefore, be inferred that the slight expansion along the *c* direction at T_{tr}, with a little change in the crystalline field but any without fundamental alternation in the structure, is able to give sufficient freedom to the water molecules to permit their reorientation in the external field. The second order transition caused by such sorts of the orientational motion of water molecules was also found in hydrated chromic sulfate, $Cr_2(SO_4)_3 \cdot 18H_2O$[9].

Dielectric absorptions due to the reorientation of water molecules have previously been observed in a number of hydrated crystals, such as $MgPt(CN)_4 \cdot 7H_2O$, $Y_2Pt_3(CN)_{12} \cdot 21H_2O$[10], $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$[11], $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$[12] and pinacol hydrate[13]. The dispersion phenomena in some of these crystals have been explained on the assumption that the water molecules are grouped together in the crystal to form a hydrogen-bonded system similar to that of ice, but from a lack of detailed knowledge of the crystal structure, except for that of alum, definite information about the molecular mechanism of the rate process has not yet been given. For the present case, the atomic arrangements, including also the proton positions, are available; therefore, the large dielectric anisotropy can be elucidated qualitatively on the basis of the individual motion of two kinds of water molecules with different neighbors.

The results of proton magnetic resonance[3] reveal that the axial rotations of both kinds of water molecules are excited in the high temperature phase. If the motion of every water molecule is possible only around the molecular dipole axis, this being a unique two-fold axis C_2 for water molecule, the dielectric properties should then be unaffected by this type of motion. Therefore, to explain the observed dielectric relaxation, the possibility of dipole orientation caused by another type of motion must be considered. In respect to H_2O-I, however, such a type of motion is rather unlikely because of the electrostatic interaction between the cupric ion and the water dipole. The dipole moment of H_2O-II may be easily oriented to the external field, in contrast to that of H_2O-I, because of the weak interactions between it and its surroundings. The permittivity values at a frequency of 30 c./sec. just above T_{tr} were 30, 15 and 6 when the electric field was, respectively, parallel to the *b*- and the *a*-axis and perpendicular to the *c* plane. The remarkable dielectric anisotropy means that the axes about which the water dipoles can rotate are closely bunched around an axis nearly perpendicular to the cleavage plane (referred to as the C_1 axis). Under these circumstances, it is suggested that H_2O-II may rotate about the C_1-axis, whereas H_2O-I rotates most probably about the Cu–O bond; consequently, the effective orientational polarization is mainly due to the dipole orientation of H_2O-II.

The activation energies associated with the dielectric relaxation in the radio frequency absorption are found to be 6.7 for the *a*-direction and 4.5 kcal./mol. along the *b*-axis. These values are much smaller than the values for ice[14] and also for crystalline *n*-primary alcohol[15] and pinacole hydrate[13], in which the dielectric absorptions are associated with the hydrogen bondings of hydroxyl groups. The low energy barrier and the high value of critical frequency suggest that the mechanism of the dielectric relaxation for cupric formate tetrahydrate is of a different nature from those proposed for ice and the others. On the basis of the atomic arrangement in the crystal, it seems that the C_1 axis around which the water molecule H_2O-II can rotate corresponds to the O–H···O bond between H_2O-II and the nearest formate oxygen. A characteristic feature of the arrangement of water molecules is the presence of an isolated hydroxyl group, i. e., $O–H_4$ of H_2O-II. Because of this and the consequent absence of hydrogen bonding, the $O–H_4$ group can easily rotate about the C_1-axis, giving the large dielectric absorption and dispersion with the marked anisotropy. The small distribution of relaxation times may support the proposed mechanism involving the rotation of the hydroxyl group.

The data for the absorption at much lower frequencies are somewhat divergent from sample to sample and also depend on their thermal histories. These structurally sensitive characters suggest that the low frequency absorption is associated with lattice imperfections or ionic impurities. For instance, the origin of hydronium impurity may be considered to be as follows: To obtain a good single crystal, it was necessary to add a few drops of formic acid to the salt solution. In view of this, the crystals used in the present experiments might contain a minute amount of hydronium ions (H_3O^+) replacing water molecules in normal sites. If

9) H. Grayson-Smith and R. F. Sturrock, *Can. J. Phys.*, **30**, 687 (1952).
10) J. Errera and H. Sack, *Trans. Faraday Soc.*, **30**, 687 (1934).
11) R. Guillin, *Compt. rend.*, **213**, 791 (1941).
12) R. Kiriyama and Y. Saito, This Bulletin, **26**, 531 (1953).
13) J. S. Cook and R. J. Meakins, *Trans. Faraday Soc.*, **51**, 1483 (1955).
14) R. Auty and R. H. Cole, *J. Chem. Phys.*, **20**, 1309 (1952).
15) J. S. Dryden, *Australian J. Sci. Res.*, **5**, 661 (1952).

proton conduction starts from such a impurity center, the ionic state can move under the influence of the external field from one molecule to another by the successive transfer of protons along the hydrogen bond. The fact that the conducting effect is predominant only in the *a*-direction may be the most favorable evidence for the proposed mechanism.

Summary

The dielectric properties of single crystals of cupric formate tetrahydrate have been investigated over the range 30 c./sec. to 10 Mc./sec. from the liquid nitrogen temperature to the dehydration point, 46°C. This crystal undergoes a phase transition at −36°C, indicated by a sudden change in the dielectric properties. Above the transition point, large dielectric dispersion and absorptions are present when the applied electric field is along the crystallographic *a*- and *b*-axes, whereas along the normal to (0 0 1) plane, the variations in permittivity and the loss factor with temperature and frequency are quite small.

The results for the radio frequency absorption can be explained on the basis of a molecular mechanism involving the axial reorientation of two water dipoles in the formula unit of $Cu(HCO_2)_2 \cdot 4H_2O$. The energy barrier H(kcal./mol.) and the frequency factor $A(sec^{-1})$ associated with the dipole orientation have been obtained as follows: along the *a*-axis $A=1\times10^{11}$, $H=6.7$; along the *b*-axis $A=8\times10^{9}$, $H=4.5$; and in the direction normal to (0 0 1) $A=7\times10^{10}$, $H=6.3$.

A further absorption at much lower frequencies is remarkable only in the *a*-axis direction. The observed high dielectric loss suggests the possibility of proton transfer in the hydrogen-bonded chains found in this crystal structure.

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