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On some Dielectric Properties of a few Solids having "Hydrogen Bond" in their Crystal Structures

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Dielectric constants of boric acid (pressed powder), oxalic acid dihydrate (single crystal), and others were measured by the method of alternating field of about 3×10^6 cycles/sec. in frequency.

The results were discussed qualitatively from atomic structural standpoints. In these hydrate compounds it seems that the rotational effect is more powerful to explain the results than the effect of movement of proton H.

§ 1. Introduction

Theoretical discussions in respect to the dielectric constant ϵ , which is an important physical quantity determining dielectric properties of matter, have been published by CLAUSIUS, MOSSOTTI, DEBYE, ONSAGER, and others. For many gasses and liquids it seems at first sight to be possible to survey their dielectric behaviors systematically³⁾.

From the conceptions of those scholars' theories the properties of some sorts of solids can be explained. But when solids in general are examined, it is not possible to derive any successful and general explanations from those theories.

In contrast to gasses and liquids, in the solids, especially in the case of polar substances, molecules are not interchanged by spheres, and in respect to the molecular field LORENTZ'S or ONSAGER'S theory cannot give a sufficiently good approximation³⁾. In other words, molecules are not treated as independent of each other and are not considered to from their distinct isolations. The forces among them are not weak; molecular rotations will be hindered or impossible, and previously held concepts must be reconsidered. The polarization mechanisms are various and complicated, and the temperature dependency of dielectric constant shows various types

in connection with the second order transitions. These facts eventually seem to be derivable by dealing with them taking into consideration the crystal structures and the atomic bonding natures.

Hydrogen bonds have much smaller bonding energy than that of polar or ionic bonds. The fact that these intermediate bonding forces supply many interesting dielectric properties, will be obvious when one considers the effect of the hydrogen bonds⁽⁶⁾ of such materials as Ice, or Rochelle salt and KH_2PO_4 , the typical ferro electric substances.

Many other solids are known in which hydrogen bonds exist⁽⁷⁾. But in dielectric measurements in conclusive results seem to have been obtained. Accordingly, the writer has measured the dielectric constants of a few solids having hydrogen bonds and has tried to consider the polarization mechanism from the atomic standpoints.

§ 2. Experimental Arrangement and Procedure

Measurements were made by the resonance method. The field was about 3×10^6 cycles in frequency and about 2 volts of resonance voltage. A sample condenser was made with special attention to the temperature dependency of the capacity of sample.

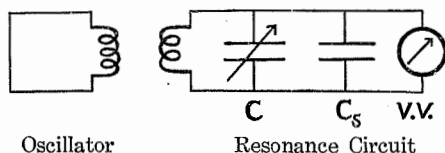


Fig. 1. Schematic principle of measurement.

Fig. 1. shows the principle of the measurements. The oscillator is an ordinary L. C. HARTLEY circuit. Resonance circuit is composed of two coils, a standard condenser C (about 50 p.f.), a sample condenser C_s , and a valve voltmeter v. v.

The sample condenser C_s is a parallel plate type and its capacity is about 20 p.f. when a sample is put in. Fig. 2. shows its construction. For the purpose of controlling temperature, a nichrome wire was wound around a porcelain core, and a hole was made at the bottom to introduce cooled air. By this method temperature was controlled with in the range of -150°C to 300°C .

After being covered with tinfoil pasted with vaseline, the sample is set on the copper plate of about 5 cm^2 in area. The alternating field was applied by holding a terminal pole against one of the tin

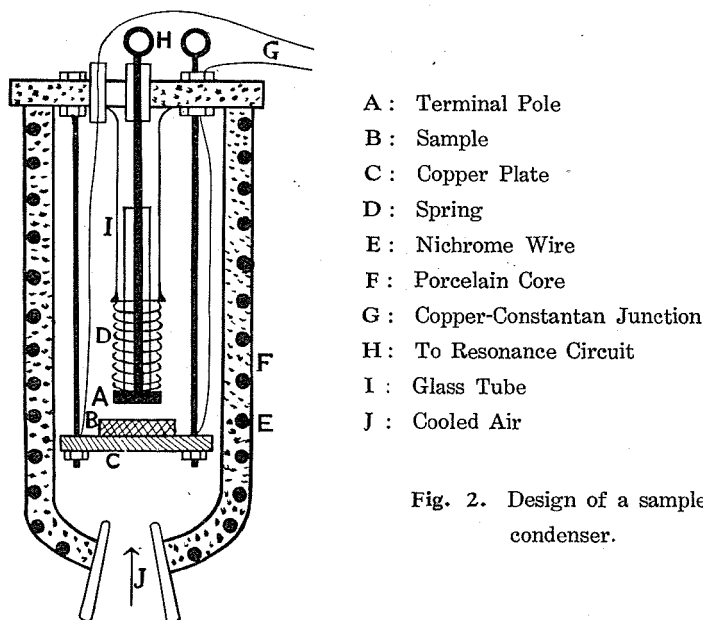


Fig. 2. Design of a sample condenser.

foils. By drawing up the terminal pole we can regard the procedure to be the same as removing the sample condenser. The temperature measurement was made by a copper-constantan thermo junction fixed on the copper plate.

Now to make the measurements, first set the oscillator to work at a certain frequency, and then read the capacity C_0 p.f. of standard condenser when the sample was removed. Similarly C_1 p.f. can be read when the sample is set in. Then the capacity of the sample is $C_s = C_0 - C_1$. If the thickness of sample D in cm. is known and the effective area of the electrodes S in cm^2 , then the dielectric constant of the sample at the temperature $t^\circ\text{C}$ is given by the equation:

$$\epsilon_t = \frac{(C_0 - C_1)}{(S/4\pi D)} \cdot \frac{9}{10} = 11.3 (C_0 - C_1) D/S.$$

Next read the capacity C'_1 p.f. of standard condenser setting the sample at the temperature $t'^\circ\text{C}$. The variation of ϵ is

$$\Delta\epsilon = 11.3 (C_1 - C'_1) D/S, \text{ so one gets}$$

$$\epsilon_{t'} = \epsilon_t + \Delta\epsilon = 11.3 [(C_0 - C_1) + (C_1 - C'_1)] \cdot D/S.$$

By reading C'_1 continuously at various temperatures $\epsilon \sim t$ curve of the sample can be obtained.

§ 3. Part of Hydrogen-bond in Dielectric Polarization

The contribution of hydrogen-bond was investigated recently for liquid phase, (water, alcohol, acetic acid, etc) with results which remarkably deviate from ONSÄGER's theory, and for solid phase, (ice or some ferro electric substances) which are very special. Opinions about their polarization mechanism are not always fixed and different views do seem to be possible⁶⁾. However, outside these special substances, when one investigates and examines the polarization mechanism of general hydrogen-bonding solids, it will be possible to contribute to the opinions about these special substances and to help to make clear their peculiar dielectric behaviors.

To state the matter briefly, the state of affairs in liquid is the effect of polymerisation of molecules.⁶⁾ And the qualitative explanations are based upon a consideration of the rotation of the polymer as a whole. But generally in the case of solids the rotation of molecule or polymer as a whole is more difficult to conceive. Here the investigator meets the fact that the hydrogen-bonding energy amounts nearly several k cal. per mol. and this is of the order of ten times kT of ordinary temperature. So the bonds are thought to have the possibility of being cut off with comparative ease.

Based on this fact, the following two mechanisms have been considered as powerful for some sort of solids. The first is as following. A proton is conceived to be going backward and forward in vibration between two stable points existing between two electro-negative atoms. And being affected by the external electric field, the proton comes to have more chances of becoming fixed in one of these points. This bias setting of proton will contribute to the polarization. However, the second idea as to the mechanism indicates that it is easy to explain the polarization by considering the rotation of a part of the molecule⁷⁾ (atoms or radicals). Actually there are not a few molecular crystals in which these rotations are expected.¹⁾ From the above points of view the writer proposes

to summarize his experimental results with a few substances.

§ 4. Experimental Results and Considerations about them

(i) Boric Acid H_3BO_3

(a) Sample and Experiment Results.

As it was not possible to get a big single crystal, it was necessary to use a pressed powder disk (0.17 cm. in thickness, pressed by 1000 kg/cm² pressure).

Fig. 3 shows the results. The symbol $\circ$ represents the point of experimental accuracy.

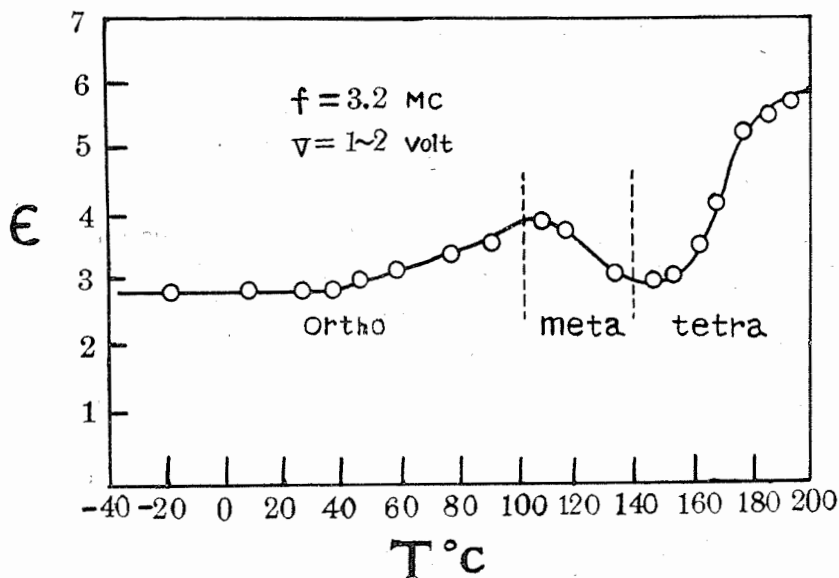


Fig. 3. Dielectric constant of boric acid (pressed powder).

From $-120^\circ C$ to $40^\circ C$, ϵ is almost constant, but the curve shows some rise at $40^\circ C$ and then slightly increases up to about $100^\circ C$. Beyond $100^\circ C$ it begins to decrease, from $150^\circ C$ it somewhat increases again, then the curve seems to become flat.

(b) Discussion of the Result.

Boric acid is a triclinic crystal whose structure has already

been analyzed by ZACHARIAZEN (1935). Fig. 4. shows its atomic configuration. The atoms of the molecule lie in one plane, and molecules form in relation to one other the mesh of hydrogen bonds

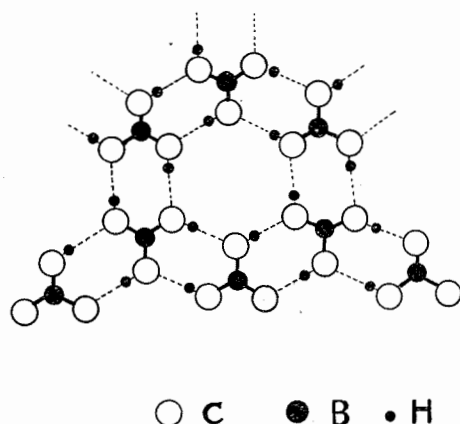


Fig. 4. Atomic arrangement of H_3BO_3 crystal in a Hydrogen-bonding mesh plane.

in the plane. Lying one upon another, these meshes construct the crystal having a scale-like cleavage. Now respecting one free molecule, it possesses no permanent dipole and is treated as a nonpolar substance. Known values of squares refractive index n^2 are 1.80, 2.12, and 2.13, for three axes. ϵ of this experiment has a value of 3 at temperature below 100°C . So the contribution of atomic polarization may be considered. But to explain some temperature dependency of the result, another mechanism must be considered. This is true, because, in general, atomic polarization is almost independent of temperature. Though the result is a certain mean value of ϵ for three axes so the real mechanism is not clearly detectable, still it may be possible to think that the mobility of the semi-ionic B atom perpendicular to molecular plane contributes to the atomic polarization.

On the other hand, to discuss about other axes and also to explain the temperature dependency it must be necessary to consider another mechanism which has temperature dependency. Upon this, thinking on the transition of boric acid, it becomes meta boric acid HBO_2 shown in Fig. 5. at 100°C , and

in the plane. Lying one upon another, these meshes construct the crystal having a scale-like cleavage.

Now respecting one free molecule, it possesses no permanent dipole and is treated as a nonpolar substance. Known values of squares refractive index n^2 are 1.80, 2.12, and 2.13, for three axes. ϵ of this experiment has a value of 3 at temperature below 100°C . So the contribution of atomic polarization may be considered. But to explain some temperature

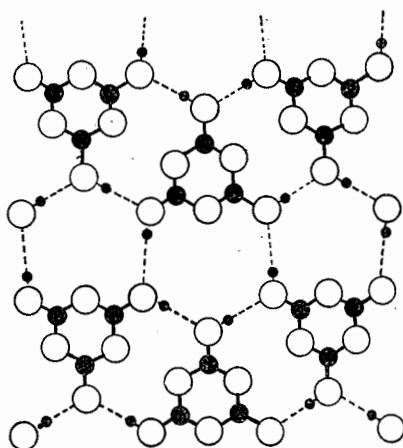
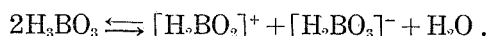


Fig. 5. Atomic arrangement of meta boric acid HBO_2 .

then glassy tetraboric acid $H_2B_4O_7$ at $140^\circ C$. These processes are eventually equivalent to dehydration. These represent the cuttings of the B-O bonds and also these of the O-H bonds by thermal energy. As evidence of this, PAULING¹ advanced the resonance structure between homopolar B-O bond and ionic B-O bond.

H proton has two stable positions between the oxygen atoms and it is going back and forward between these positions. Then it may possibly occur that two protons are bound homopolarly to one oxygen atom and compose H_2O molecule breaking the B-O bond consequently. This is shown by



This H_2O becomes able to rotate and contributes to ϵ . H_2O molecules will increase with temperature, and at the transition temperature to metaboric acid they should amount to one per H_3BO_3 molecule. From the energy consideration it may be more easy to conceive the contribution of the rotational effect than that of the movement of proton caused by the external field.

Also $[H_2BO_2]^+$ and $[H_2BO_3]^-$ come to have dipole moments. But these rotations may not occur because of their large restrations. Moreover the above considerations coincide with the dielectric loss which affected the apparatus at $100^\circ C$.

In respect to the decrement of ϵ above $100^\circ C$, it should be considered that by thermal agitation the rotation of H_2O contributes to the decrement of ϵ as shown in DEBYE's formula. Somewhat remarkable increasing of ϵ , which in the rang $150^\circ C$ to $170^\circ C$, may be due to the rotation of H_2O which occurs similarly to that in the case of H_3BO_3 but more remarkably. Upon the materials becoming glassy tetraboric acid, the dehydration ceases a while and $\epsilon \sim t$ curve becomes flat. Beyond about $200^\circ C$ the dehydration is like to begin its last step of action.

(ii) Oxalic Acid Dihydrate $(COOH)_2 \cdot 2H_2O$

(a) Sample and Results.

Oxalic acid dihydrate is a monoclinic crystal. It was possible to get a single flawless crystal of about $15 \times 10 \times 5 \text{ mm}^3$ in dimension from saturated aquaous solution. Three plates were cut off per-

pendicular to each axis, polished and pasted with tin-foil electrodes with a little vaseline. Their thickness was about 0.3 mm. and the area of the electrode was about 0.3 cm².

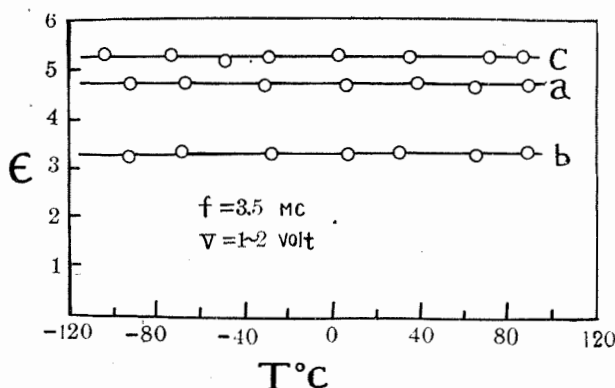


Fig. 6. Dielectric constants of oxalic acid dihydrate single crystal.

Fig. 6. shows the results. From -120°C to 95°C , values of ϵ about three axes were almost independent of temperature. From about 95°C the measurement of ϵ suddenly became impossible. It is known that at 100°C $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ becomes $(\text{COOH})_2$.

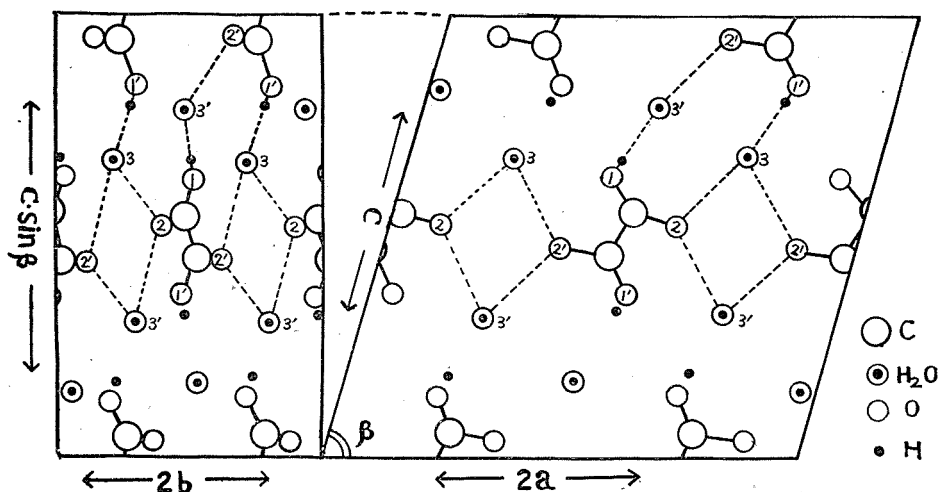
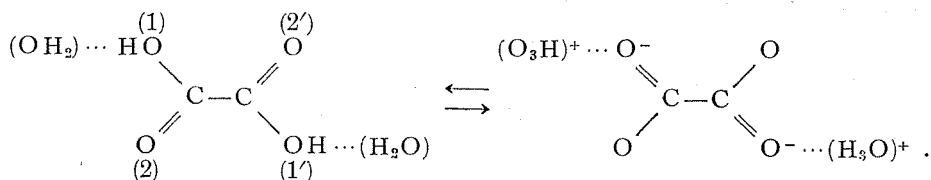
(b) *Discussion of Results.*

The projections of this crystal structure along the b and a axes are shown⁹⁾ in Fig. 7. The atoms of the molecule lie nearly in one plane, but make an angle about 29° with the plane of the projection (010). It should be especially noted that the molecules are not bound together in sheets by hydrogen and hydroxyl bonds. The quadrilateral formed by the atoms $\text{H}_2\text{O}(3)-\text{O}(2')-\text{H}_2\text{O}(3')-\text{O}(2)$, shown by the dotted lines in Fig. 7, forms a closed circuit. However, the octagon formed by the atoms $\text{C}-\text{O}(1)-\text{H}_2\text{O}(3')-\text{O}(2')-\text{C}'-\text{O}(1')-\text{H}_2\text{O}(3)-\text{O}(2)$ is not a closed circuit. It leads back to a molecule on translation further along the b axis above the original molecule.

Thus spiral chains of those bonds including hydrogen-bonds, exist along the b axis. But along this axis, the dielectric constant does not show any peculiarity. So it may be considered that the movement of the proton does not propagate along the b axis. This should be explained more in detail.

BRILL, HARMAN, and PETERS (1940) advocated the resonance

structure shown by



Projection along a axis.

Projection along b axis.

Fig. 7. Atomic arrangement of oxalic acid dihydrate $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$.

This may be based on the idea that to some extent the proton can move between two oxygen atoms. The distance between these two oxygen atoms concerned in the hydrogen bond is $2.51 \text{ \AA}$. This value is the smallest one among many data of hydrogen-bond length. So the idea may be reasonable. The distance between the oxygen of H_2O and $\text{O}(2)$ or $\text{O}(2')$ is $2.8 \text{ \AA}$ or more, and between them no hydrogen-bond is concerned. And $(\text{H}_3\text{O})^+$ being formed the proton may not be combined with $\text{O}(2)$ or $\text{O}(2')$. That is, the hydrogen bond of $-\text{C}-\text{O}(2) \cdots \text{H}-\text{O}$ type is not possible. Consequently even

$(\text{H}_3\text{O})^+$ is formed by the movement of proton of $\text{O}(1)$ or $\text{O}(1')$, it exerts attraction only on $\text{O}(2)$ or $\text{O}(2')$, i.e., it supplies hydroxyl bond. The bond $\text{O}(2)=\text{C}$ or $\text{O}(2')=\text{C}$ is not affected by it.

Concerning the movement of the proton, it is doubtful whether

it is caused or not by the external field, But testing by comparison the experimental values of ϵ , 4.67, 3.36, 5.14 and the known values of the square refractive index n^2 , 2.07, 2.18, 2.64, protons or hydrogen-bonds may contribute to atomic polarization.

In the above the rotation of H_2O was ignored. For H_2O molecule fastens the neighbouring oxalic acid groups $(COOH)_2$ together, and the configuration of H_2O is thought to be an important factor holding together the crystal structure. However, it may be sure that the rotation occurs at about $100^\circ C$, and that above $100^\circ C$ after the dehydration is completed the crystal is transformed into the crystal of dehydrated oxalic acid $(COOH)_2$.

(iii) Additional Work

In addition to the above substances, there are many other ones which are known or expected to have hydrogen-bonds. Especially in the cases where H_2O of hydrate compounds is participating in the crystal construction, hydrogen-bonds do exist. And the dehydrating mechanisms of hydrate compounds may also proceed in the same way as discussed above. In this case, within a certain temperature range in which the rotation of H_2O occurs, sometimes attending on the phase transition, the dielectric dispersion or loss may be in general remarkable.

Besides above mentioned substances, measurements were made for several other substances. But nothing much can be said about them. For some showed remarkable dielectric loss or dispersion at a certain temperature range and measurements became impossible. Others were not obtained in their single crystal form, so any considerations based upon the results are loose or of no significance.

§ 5. Conclusion

The writer offers consider about on the mechanism of polarization in some solid dielectrics having hydrogen-bonds. For the hydrate solid compounds, he would consider the rotational effect of H_2O as important rather than the contribution of H proton movement.

Rochelle salt and KH_2PO_4 include hydrogen-bond in their structures and show very special properties. But, only from the con-

sideration of hydrogen-bond, it is not sufficient or appropriate in general to expect such special properties.

In conclusion, to make the results more complete, it may be necessary to examine the dielectric loss, the specific heat, the spectral or X-ray analysis, and so on. Also by the development of crystal growth technique, many experiments may be made on the interesting solids.

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