Proton Magnetic Resonance in Cupric Formate Tetrahydrate, $Cu(HCO_2)_2\cdot 4H_2O$

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In the preceding paper¹⁾ the results of the dielectric measurement of a single crystal of cupric formate tetrahydrate, $Cu(HCO_2)_2\cdot 4H_2O$, have been described. This substance undergoes a phase transition of the first order at 237°K. The transition is characterized by a sudden increase in the dielectric constant as it passes through the transition region towards higher temperatures. Above the transition point, the crystal exhibits marked dielectric dispersions and absorptions with a large anisotropy. The atomic arrangement in the crystal lattice at room temperature has been determined by X-rays²⁾, except for that of the hydrogen atom. On these bases, it has been concluded that certain types of the orientational motion of the water molecule should occur above the transition temperature.

For the purpose of locating the protons of the water molecules in this crystal below the temperature of the phase transition, and also in order to ascertain the motion of water molecules above that, the proton magnetic resonance (PMR) spectra have been studied as a function of the orientation and the temperature in both single crystal and polycrystalline samples. Some results of the proton magnetic resonance experiment will give additional information on the nature of the transition.

It is to be noted that this crystal contains paramagnetic Cu^{2+} ions which in principle cause the resonance spectra to be broad at very low temperatures. Bloembergen has already examined the proton resonance in a single crystal of cupric sulfate pentahydrate, $CuSO_4\cdot 5H_2O$, both theoretically and experimentally³⁾. With this work in mind, we have

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1) H. Kiriyama, This Bulletin, **35**, 3146 (1962).

2) R. Kiriyama, H. Ibamoto and K. Matsuo, *Acta Cryst.*, **7**, 482 (1954).

3) N. Bloembergen, *Physica*, **16**, 95 (1950).

made an experiment above the temperature of liquid air and at a quite low field of about 1300 gauss. Under these conditions, the expected paramagnetic effect could be almost ignored and the problem could be treated by Pake's method[4] for the water molecule in gypsum, $CaSO_4 \cdot 2H_2O$.

Experimental

The experimental method and the apparatus were almost the same as have already been reported[5]. A Pound-Watkins r. f. spectrometer was used to observe the first derivative of the resonance line. All the experiments herein reported were made at a fixed frequency of about 5.5 Mc./sec., and the magnetic field was slowly swept by a resistance network. The applied magnetic field was modulated with a small amplitude at 60 c./sec., and the derivative of the resonance line was plotted as a function of the applied field by a recording milliammeter, preceded by a phase-sensitive detector and a narrow-band amplifier. The absorption curve was obtained by graphical integration of the derivative.

The powdered sample was prepared by dissolving basic cupric carbonate in formic acid, and the single crystal was grown from the aqueous solution by slow cooling. The single crystal sample used was a cylinder, 8 mm. in diameter and 25 mm. long, cut from large crystals. The axes of three sorts of cylindrical samples were chosen to be parallel to [010], to the normal of (001) and to that of (100) respectively. The crystal was rotated around a given axis perpendicular to the external magnetic field H_0, and the spectra were observed at regular intervals.

The temperature was varied from 110 up to 310°K. Liquid air or dry ice was used as the cooling material, and a heating coil was wound on the probe to obtain a temperature higher than that achieved with the given refrigerant. Temperatures were measured with a copper-constantan thermocouple set close to the sample. Recording was always taken after a steady condition had been reached for a time far longer than the observed time lag.

Preliminary Remarks

The Crystal Structure.—The crystal structure[2] of $Cu(HCO_2)_2 \cdot 4H_2O$ has been studied at room temperature. The crystal is monoclinic holohedral, and the corresponding space group is $C_{2h}^5-p2_1/a$. The unit cell contains two formula units, and its dimensions are $a=8.18$, $b=8.15$, $c=6.35$ Å, $\beta=101°5'$. The water molecules are sandwiched between layers in which two copper ions are bridged by one formate ion to form two-dimensional networks parallel to (001). Each copper ion is surrounded by four oxygen atoms of four formate ions ($Cu-O = 2.00$ and 2.01 Å) in a nearly square configuration and by two water molecules (H_2O-I) above and bolow this planar CuO_4 at a greater distance (2.36 Å). Another water molecule (H_2O-II) is linked not to the copper ion, but to an oxygen atom of formate ion and two oxygens of water molecules (H_2O-I) with hydrogen bond distances of 2.82, 2.78 and 2.74 Å respectively. It is an interesting structural problem that there are four available protons as against three O-O lines capable of forming hydrogen bonds.

Though the crystal structure below the transition temperature has not yet been refined by X-ray studies, as has already been mentioned in the preceding paper[1], some experimental evidence indicates that the low temperature crystal structure is almost the same as the room temperature one, except, of course, for the positions of the hydrogen atoms. Only a small contraction of about 0.1 Å in c, and no appreciable changes in either a or b are found by superimposing Weissenberg photographs taken at 180° on the 300°K photograph.

It is easy to locate the proton of the formate ion in the lattice because the direction and the distance of the C–H bond are known approximately, but this is outside our problem. Therefore, our interest will be confined to the protons of the water molecule.

The Effect of Paramagnetic Ion.—The paramagnetic resonance absorption for a single crystal of this substance was investigated by Shimada et al.[6] in a millimeter wave region. Their conclusion was that there is an exchange interaction between the cupric ions; only one absorption line is observed in every direction, whereas two non-equivalent ions are contained in the unit cell. More recently, Martin and Waterman[7] have measured the temperature variation of the magnetic susceptibility between 80 and 300°K on the polycrystalline sample. According to them, this crystal obeys the Curie-Weiss law of the form $\chi \propto (T-\theta)^{-1}$ where θ, the Weiss constant, has the large value of $-175°$. Although the exchange energy is not known accurately, these results indicate that the exchange interaction between the non-equivalent cupric ions in this crystal is fairly strong. Consequently, the broadening action of cupric ions may be considerably reduced by exchange interaction between them.

The time-averaged magnetic moment $\bar{\mu}_c$ of the cupric ion is given in order of magnitude by Curie's law:

$$\bar{\mu}_c = (\mu_c^2/3\boldsymbol{k}T)H_0 \qquad (1)$$

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[4] G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

[5] T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).

[6] J. Shimada, H. Abe and K. Ono, ibid., **11**, 137 (1956).

[7] R. L. Martin and H. Waterman, *J. Chem. Soc.*, **1959**. 1359.

where μ_c is the magnetic moment of the cupric ion. In an applied field of 1300 gauss at 110°K, which is the lowest temperature of our measurements, the value of $\bar{\mu}_c$ given by Eq. 1 is very small, of the order of 1 nuclear magneton, and it is much smaller still at higher temperatures. The average local field due to cupric ions, therefore, will not produce any further splitting in the proton resonance lines under consideration. The only effect of the paramagnetic ions is a slight shift of the center of the absorption line from the resonance field of liquid water, a shift which amounts to about 0.5 gauss or less, according to the formula of Bloembergen[3].

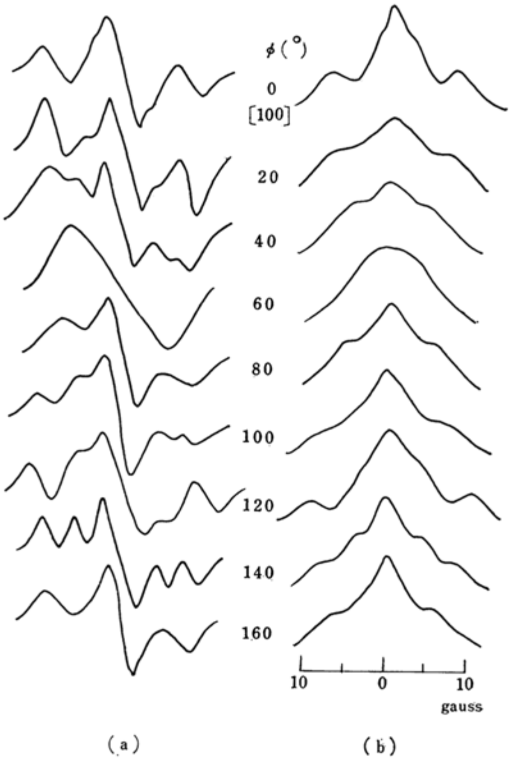
Results and Discussion

Proton Resonance below the Transition Temperature.—The experiment at liquid air temperature was made with the single crystal mounted in such a way that it could be rotated about the b-axis, which was perpendicular to the applied magnetic field, H_0. The derivative curve was recorded at 10° intervals as the crystal was rotated thruogh 180°. Typical traces and the corresponding integral curves are shown in Fig. 1. The absorption curves were almost symmetrical about the center of line, and no distortion due to cupric ions was disclosed within the range of experimental error. Furthermore, the resonance pattern in every orientation remained unchanged from 110° up to about 230°K. These experimental results have given a direct confirmation of the expectation discussed in the previous section. It is, therefore, evident that the fine structure observed in the present study is not to be attributed to the copper-proton interaction but to the proton-proton interaction in each water molecule.

If a proton pair exhibits only dipole-dipole interaction, the displacement of component lines, ΔH in gauss, from the field strength corresponding to free protons is related to the orientation of crystal by the formula given by Pake[4]:

$$\Delta H = \pm\alpha\,[3\cos^2(\phi-\phi_0)\cos^2\delta-1] \qquad (2)$$

Here $\alpha=(3/2)\mu r^{-3}$, in which μ is the proton magnetic moment and r is the pair separation. ϕ is the angle between the external magnetic field, H_0, and a reference axis attached to the crystal that is in the plane of crystal rotation. ϕ_0 is the angle between the projection of the p-p line (let p-p indicate proton-proton) onto the plane of rotation and the reference axis in the crystal, and δ is the angle between the p-p line and the plane of rotation. The effect of the paramagnetic cupric ions should be added to expression 2, but it is very small in this case, less than 0.5 gauss.



(a) (b)

Fig. 1. Resonance patterns with various directions of H_0 in the ac-plane at 110°K, (a) derivatives, (b) integrals.

When the crystal is turned about the two-fold axis b, two resonance doublets and, in addition, a central peak may be expected, because the unit cell would contain only two types of proton pairs of two non-equivalent water molecules and isolated protons of formate ions. At some orientations, the experimental derivative curves obviously displayed up to three peaks on either side of the center. However, owing to the broadening effect of the cupric ions, and also to the interaction between the proton pairs, each component line was quite broad; the overlap of the peaks was serious over part of the range, and the values of the peak displacements had to be derived by a decomposition procedure described later. As may be seen in Fig. 1, near $\phi=0°$ and 120° the outermost peaks of the absorption curves were fairly well (though not completely) resolved. The measured peak displacements, ΔH (after correction for the effect of the paramagnetic ions), are shown as closed symbols in Fig. 2 against ϕ, which is, herein, the angle of H_0 measured from the a-axis in the monoclinic angle β chosen above.

If, however, the shape of each component

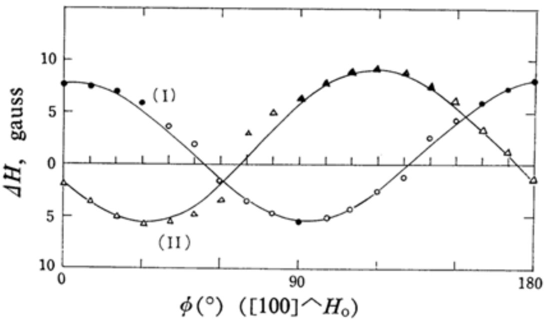
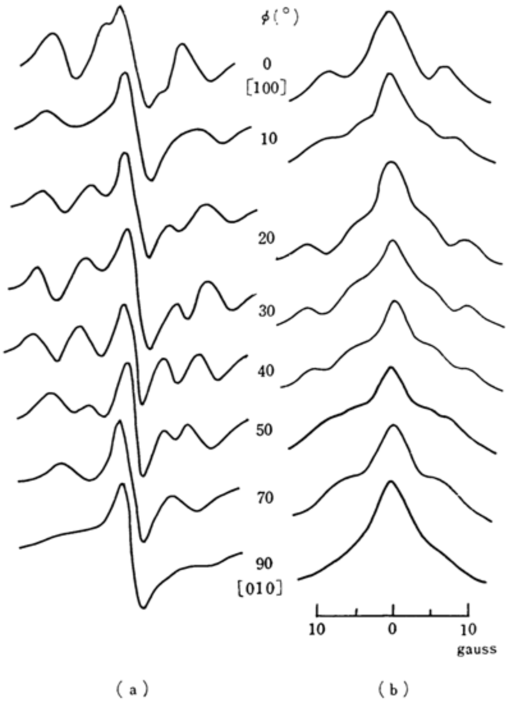


Fig. 2. Angular variation of the peak displacement ΔH in the *ac*-plane at 110°K. Closed symbols represent experimental points and open symbols denote decomposition procedure (see text). Calculated curves: I, $\phi_0=3°$, $\delta=25°$, $\alpha=5.4$ g.; II, $\phi_0=120°$, $\delta=20°$, $\alpha=5.4$ g.

line is assumed to be symmetrical, the area of the outermost peaks on the experimental absorption curves near $\phi=120°$ would amount to roughly half as much as that of the outermost peaks near $\phi=0°$. Thus, near $\phi=0°$ the ratio of the area under these peaks to that under the rest of the curve is close to 2 : 3, whereas near $\phi=120°$ the area ratio is only about 1 : 4 rather than the expected 2 : 3. Such a difference in peak height was an essential feature, because different samples behaved in the same manner because relaxation measurements confirmed that the PMR signals were unsaturated. The near-Gaussian form of the resolved outermost peaks near both $\phi=0°$ and $\phi=120°$, and also the approximate correlation between the areas, suggested the presence of residual proton pairs, but the derivative curves at no setting provided any evidence for it. Instead, it was more plausible that dipole-dipole interaction between the proton and the next nearest protons gave rise to further splitting in the resonance lines; consequently, the shape of the peak might not be symmetrical with respect to its maximum. On this supposition, we tried to resolve the absorption curves. To do this, mean absorption half curves were constructed from at least four experimental half-traces. On each of these, a standard curve, derived from the outer peak at $\phi=0°$, was superimposed at the appropriate peak displacement, and another standard curve, derived from the outer peaks at $\phi=120°$, was shifted along the field axis until the sum of the two standard curves yielded a close approximation to the outer part of the averaged experimental curve; substraction from the total curve left a residue corresponding to the protons of formate ions. The less reliable peak displacements derived from such a decomposition procedure are shown as open symbols in Fig. 2. By fitting the angular variation of the peak displacements to Eq. 2, ϕ_0 was measured to be 3° for one p-p line and 120° for the other, and the δ values were estimated to be about 25° and 20° respectively. Curves I and II in the figure are those calculated from Eq. 2, assuming $2\alpha=10.8$ gauss for all proton pairs.

In order to ascertain the p-p orientations given above, two other axes of rotation were examined. Figure 3 shows representative experimental absorption patterns for the various directions of H_0 in the *ab*-plane at 110°K. The angle ϕ between H_0 and the *a*-axis is stated with each spectrum. The angular dependence of the peak displacement ΔH is given in Fig. 4. As expected from the symmetry of the crystal, the resonance pattern at an angle $-\phi$ was just the same as one for $+\phi$; namely, two orientations of ϕ_0 and $-\phi_0$ for each group of proton pairs were allowed. The Pake curves in the *ab*-plane were calculated from Eq. 2 using the angular dispositions just determined from the peak displacements in the *ac*-plane and are presented in Fig. 4 as curves I (I_1 and I_2) and II (II_1 and II_2) for each of two non-equivalent proton pairs respectively. Since nine component lines were expected usually, a complete analysis of the resonance patterns was more difficult than that in the *ac*-plane.



(a) (b)

Fig. 3. Resonance patterns for various directions of H_0 in the *ab*-plane at 110°K, (a) derivatives, (b) integrals.

However, some additional evidence concerning the orientation of proton pairs may be drawn from this experiment as follows: (i) the maximum peak-to-peak separation, $2\Delta H$, for proton pair I occurs at $\phi=\pm25°$ from the *a*-axis, and both p-p vectors lie very nearly in the *ab*-plane. The maximum separation is 21.6 gauss, corresponding to a p-p distance, *r*, of 1.58 Å. The ratio of the area under these outer peaks to that under the rest of the curve is close to the expected 1 : 4 ; (ii) each resonance spectrum seems always to have some component lines with an ΔH of 2∼5 gauss, so that the other proton pair II may be about 60° out of the *ab*-plane ; (iii) near $\phi=90°$, the absorption curves were unduly broad. This broadening obviously means that some of the protons of adjacent water molecules might be close together in the *b*-axis direction.

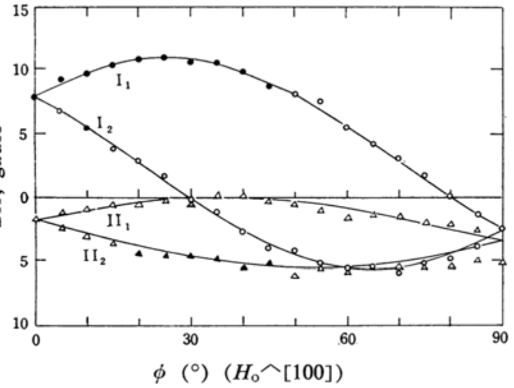


Fig. 4. Angular variation of the peak displacement ΔH in the *ab*-plane at 110°K. Calculated curves : I_1 and I_2, $\phi_o=\pm25.2°$, $\delta=2.5°$, $\alpha=5.4$ g.; II_1 and II_2, $\phi_o=\pm36°$, $\delta=54.5°$, $\alpha=5.4$ g.

The result of the measurement at 110°K with H_o in the *bc*-plane did not contradict that obtained in the case of the *b*-axis rotation. By taking the values of ϕ_o and δ and by using spherical trigonometry, one can compute the direction angles of the p-p lines with respect to the crystallographic axes. They were $\alpha_o=25°$, $\beta_o=65°$ and $\gamma_o=97°$ for proton pair I, while they were $\alpha_o=118°$, $\beta_o=70°$ and $\gamma_o=27°$ for proton pair II. These angles are measured away from the positive sides of the crystallographic axes, *a*, *b* and *c* respectively.

The Position of Protons below the Transition Temperature.—Although the positions of hydrogen atoms can not be determined directly from the results of the present study, it is possible to locate the most likely sites for them within the framework of the heavy atoms. As has been described above, the atomic arrangement in the low temperature form is almost the same as that of the room temperature form and the change in interatomic distances in the transition is negligible. Therefore, there is no trouble in locating the p-p vector based on the structure of the room temperature form. As the water molucule H_2O-I is co-ordinated to the cupric ion directly, it should orient itself by placing two protons opposite the " positive " copper ion. Thus, the direction of the p-p vector in H_2O-I will be nearly parallel to the *ab*-plane. Furthermore, the protons of H_2O-I will not deviate much from the two O-O lines where the hydrogen bonds were predicted by X-rays. It has therefore been concluded that the proton pair I should be assigned to that of H_2O-I and, consequently, the other pair II, to that of H_2O-II.

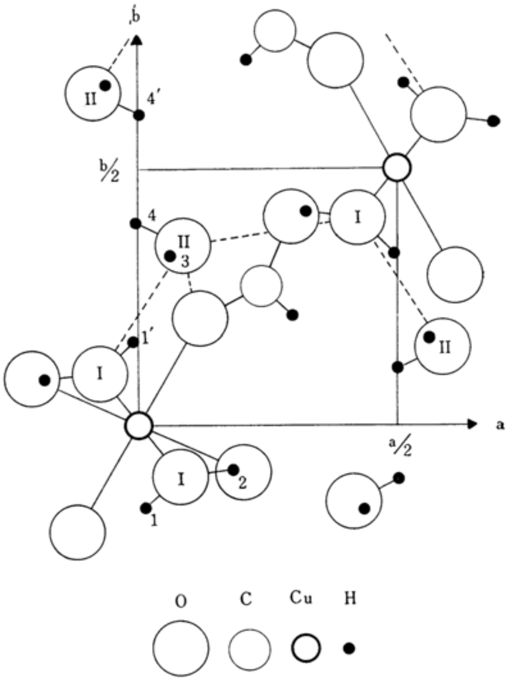


Fig. 5. Projection of the structure of Cu·$(HCO_2)_2\cdot4H_2O$ on the (001) plane. Broken lines represent possible hydrogen bonds.

By using the p-p separations and the orientations of the p-p vectors, and assuming the O–H distance in the water molecule to be 0.96 Å[8], the location of the hydrogen atoms can be obtained. The deduced parameters of water hydrogen atoms are given in Table I. The projections on (001) and (010) are shown in Figs. 5 and 6 respectively. It appears that two protons (H_1 and H_2) of H_2O-I form two non-linear hydrogen bonds with two adjacent

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[8] G. Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules ", Von Nostrand, New York (1945), p. 489.

oxygens of H_2O-II in the same water layer; meanwhile one proton (H_3) of H_2O-II serves to bind the water oxygen to one oxygen of formate ion, and the other proton (H_4) is free from any hydrogen bond. With respect to packing in the *b* direction, hydrogen atoms neighbor each other as expected from the breath of the absorption spectrum. Consequently, some of the hydrogen atoms along the *b*-axis are separated by 1.9∼2.3 Å, a little less than twice the van der Waals radius of 1.2 Å for the hydrogen atom.

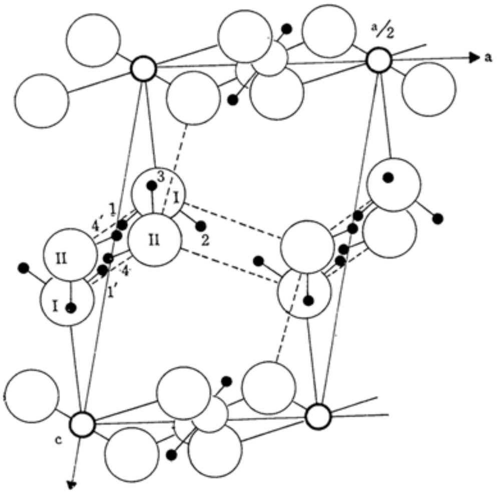


Fig. 6. Projection of the crystal structure on (010).

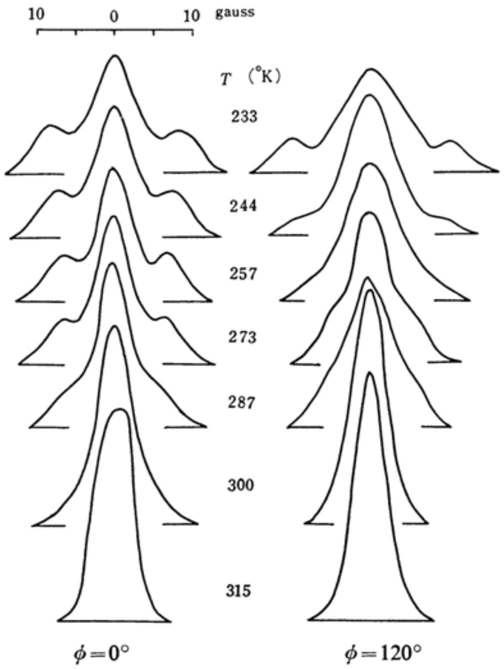
TABLE I. SET OF POSSIBLE COORDINATES FOR PROTONS IN WATER MOLECULES

		x	*y*	*z*
H_1	(H_2O-I)	0.01_2	-0.16_2	0.43_9
H_2	(H_2O-I)	0.18_0	-0.09_2	0.44_7
H_3	(H_2O-II)	0.06_1	0.33_1	0.33_1
H_4	(H_2O-II)	-0.00_6	0.39_3	-0.46_5

The present study is based upon Pake's method, which is applicable to the model of a "two-proton system", but the structure of this substance is much more complex than such an ideal case in two important respects: first, the water molecules lie close to each other, forming a sheet structure, and then the broadening of the fundamental line shape is so great that details are somewhat obscured; second, one must consider the effect of the cupric ions, which prevents one from using the second moment method for the purpose of structure determination. In spite of these difficulties, the positional determination of the proton pair has been fairly successful, since the resonance line shape fortunately retained the characteristic feature of the two-proton system. However, for further refinement of the proton position, a direct method of determination, such as neutron diffraction analysis at low temperatures, would be desirable.

Proton Resonance above the Phase Transition Temperature and Motion of the Water Molecules

The resonance pattern observed at the lowest temperature measured did not significantly change up to 233°K, a few degrees below the phase transition temperature, T_{tr}, 237°K. It is, therefore, certain that the hydrated water molecules are effectively stationary within the crystal lattice of the low temperature phase. When the temperature reached T_{tr}, absorption lines began to narrow with the increasing temperature at all settings of the single crystal. Two typical series of resonance line integrals for various temperatures are shown in Fig. 7, where ϕ is the angle between the applied field H_0 and the *a*-axis in the *ac*-plane. The outer peaks on the absorption curves at $\phi=0°$ and 120° have been assigned just above to the proton pairs of H_2O-I and H_2O-II respectively. In the direction of $\phi=0°$, the peak-to-peak separation, $2\Delta H$, gradually decreased from 16 to 12.5 gauss over a range of about 40° above T_{tr}, and these peaks retained prominent features well until 287°K. Then the outer



$\phi=0°$ $\phi=120°$

Fig. 7. Resonance absorption lines at various temperatures above T_{tr} for two special ϕ's of the single crystal. ϕ is the angle between the *a*-axis and H_0.

peaks started to collapse towards the center of the spectrum, a process which continued until the temperature was 300°K. At 300°K the absorption curve consisted of a single peaks 3.0 gauss wide, the line width being defined as the distance between the points of maximum slope. As the temperature was raised further, this single line then split up, so that at 315°K the spectrum seemed to consist of three peaks. On the other hand, the separation between the well-resolved peaks on the absorption line at $\phi=120°$ decreased much more rapidly than those at $\phi=0°$ in the temperature range 237∼287°K so that prominent features of the outer peaks were barely observable even at 257°K. Then the spectrum showed further narrowing to a single peak 3.3 gauss wide between 300 and 315°K. In this temperature range the proton magnetic resonance curves at particular settings of the crystal are completely resolved into three peaks, as we shall see later.

It is known that the second moment of a resonance spectrum should be theoretically independent of the thermal motion of the nuclei⁹⁾. However, side-spectra on absorption curves developed by thermal motions are usually too weak to be observed. If these side-spectra are neglected, the second moment of the central line would be affected by the motion. The experimental second moments for both single crystal and powdered samples are plotted against temperature in Fig. 8. The contribution of the dipole-interaction between the protons to the total second moment in the rigid state was calculated by Van Vleck's formula¹⁰⁾. This value amounted to about 28.6 gauss^2 for the powder, while the experimental value was 29.0 gauss^2. The apparent change in the second moment extends over a wide temperature range from 235° to 310°K, and its total reduction for the powdered sample was 24 gauss^2. This large change indicates that the reorientation of the water molecules occurs around one axis or even more than one axis.

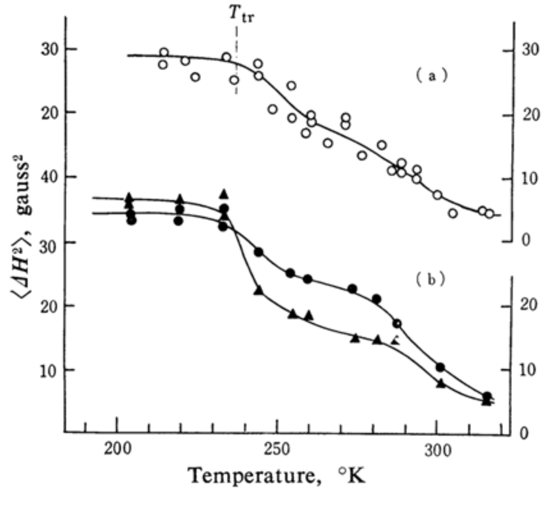


Fig. 8. Second moment as a function of temperature: for the powdered sample, (a); for the single crystal, (b).
○ Powder, ● $\phi=0°$, ▲ $\phi=120°$

In the middle of the line-width transition region, the second moment decreased with the temperature much less rapidly than at the ends of the transition region. The rather discontinuous change in the separation between the peaks or the line width, particularly near $\phi=0°$, was responsible for this stepwise decrease of the second moment. Because of the r^{-6} dependence of the second moment, a 0.2% increase in the c lattice dimension occurring at T_{tr} should produce only a 1% decrease in the second moment; hence it seems unlikely that the change in the second moment near 240°K is only a result of the lattice expansion. A study of the changes in the derivative curves indicates that both kinds of water molecule are set in motion just above the phase transition temperature and that the reorientation becomes sufficiently rapid to collapse the characteristic rigid hydrate spectra at different temperatures for the water molecules at two non-equivalent lattice sites. As is to be expected from the crystal structure, H_2O-I is subjected to a higher energy barrier to rotation than that to which H_2O-II is subjected, this being a main cause of the observed stepwise reduction in the second moment.

If the motion of the water molecule at higher temperatures is rapid rotation or reorientation about an arbitrary axis, as in Fig. 9,

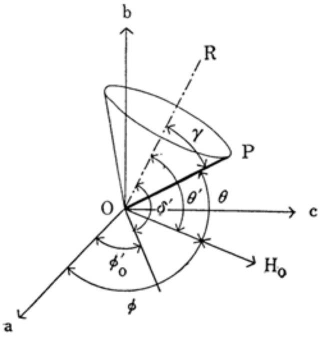


Fig. 9. Diagram showing definition of the angles for the rotating proton pair system.

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[9] E. R. Andrew and R. A. Newing, *Proc. Physic. Soc.*, **72**, 959 (1958).

[10] J. H. Van Vleck, *Phys Rev.*, **74**, 1168 (1948).

then the absorption line should have two component lines, as given by the formula[11].

$$\Delta H = \pm(\alpha/2)(3\cos^2\gamma - 1)(3\cos^2\theta' - 1)$$

Then

$$\Delta H = \pm(\alpha/2)(3\cos^2\gamma - 1) \times [3\cos^2\delta' \cos^2(\phi - \phi_0') - 1] \qquad (3)$$

where γ, θ', δ', ϕ and ϕ_0' are as shown in the figure; OP is the vector r joining the two protons of the water molecule, and OR is the rotation axis making angle θ' with H_0 and angle γ with r.

In the temperature range of 300° to 315°K, the absorption curves with the magnetic field in the *ac*-plane consisted of a central peak and only one double line, whose separation strongly depended on the orientation of the crystal. The central peak was assigned to the proton of the formate ion, and the doublet to the water molecule. Some of the measured derivatives and the angular variation of the line-pair separation, $2\Delta H$, at 310°K are shown in Fig. 10. The extreme separations were 4.5 and 5.3 gauss respectively. Assuming that the peak-to-peak separation of 5.3 gauss corresponds to $\phi - \phi_0 = 90°$ in Eq. 3, and using $r = 1.58$ Å, as given in the previous section, the value of angle γ is computed to be 90° or 35°. Since the water molecule has a symmetry axis perpendicular to the p-p line, the former figure seems to be more acceptable. If, however, γ equals 90° for all p-p vectors, this form of motion of H_2O would not affect the dielectric properties. The large dielectric absorption and the corresponding dispersion found above T_{tr} lead us to postulate that one isolated hydroxyl group, O–H_4, of H_2O-II does reorient about the remaining O–H_3 bond in the same water molecule (see Figs. 5 and 6). On the basis of the nature of the chemical bonds between each water molecule in two different sites and its surroundings as well as of the character of the dielectric anisotropy, it is suggested that the value of γ for H_2O-II should be 35° rather than 90°, whereas the angle γ for H_2O-I has the expected value of 90°.

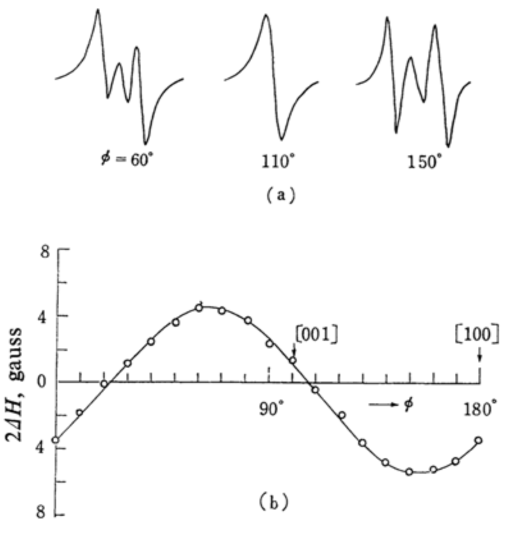

Fig. 10. Resonance patterns as the single crystal is turned about the *b*-axis at 310°K, (a) derivatives in three directions of H_0, (b) angular variation of the peak-to-peak separation.

If the data in Fig. 10 conforms to Eq. 3, the remaining parameters, ϕ_0' and δ', may be estimated from the field splittings at various orientations. The maximum line-pair separation occurs in the region of 60∼70°; this yields a value for ϕ_0' of 65°. The ratio of the extreme separations is 4.5/5.3, and, also, ΔH appears to pass through zero at $\phi = 15°$ and 105°. These results lead to an estimate for projection angle δ of 38°. Thus, a set of plausible values for the parameters in Eq. 3 are $\phi_0' = 65°$, $\delta = 38°$, and $(\alpha/2)(3\cos^2\gamma - 1) = 2.7$ gauss; the continuous line in Fig. 10 indicates the corresponding line-pair separations. It is to be noted that there is no difference between the rotational states of two non-equivalent water molecules over the last few degrees before reaching the dehydration point at 319°K.

Now one can estimate the proton contribution to the second moment for the powdered sample in the rotational state. It may be considered that the component line shown in Fig. 10 owes its width to the inter-molecular broadening. The smallest values of the line width are found from the single crystal data, to be 1.2 gauss for the doublet and 0.8 gauss for the central line, the inter-molecular broadening being estimated to be about 0.4 gauss^2. The rigid lattice second moment of an isolated water molecule is 23 gauss^2 for an H–H distance of 1.58 Å. When the water molecules rotate about an axis making an angle γ of 90° or 35° with the interproton line, the second moment may be reduced to $23/4 = 5.7$ gauss^2. Since the water molecules include 4/5 of the protons in the chemical formula, the total second moment is expected to be 5.0 gauss^2, which is in good agreement with the observed value at 315°K.

Summary

The proton magnetic resonance spectra of $Cu(HCO_2)_2 \cdot 4H_2O$ have been investigated over the range 110° to 315°K, using both single crystal and powdered samples. The water molecules are effectively rigid below the phase transition temperature, 237°K, and the most

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[11] H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

probable positions of the protons of the two non-equivalent water molecules are postulated on the basis of Pake's method.

The narrowing of the absorption line occurs above 237°K; this implies the gradual onset of a certain motion of both kinds of water molecules. The absorption spectra in the higher temperature range of 300∼315°K indicate that the reorientation of the water molecules takes place almost exclusively about one axis.

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