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LOW FREQUENCY ANTIFERROMAGNETIC RESONANCE IN COPPER CHLORIDE DIHYDRATE AND PHASE TRANSITIONS

V. G. BAR'YAKHTAR, A. A. GALKIN, S. N. KOVNER, and V. A. POPOV

Donets Physico-technical Institute, Ukrainian Academy of Science;
Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

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Antiferromagnetic resonance in a $CuCl_2{\cdot}2H_2O$ single crystal is investigated at the frequencies 5.2, 3.0, 1.1, and 0.65 GHz. The temperature dependence of resonant fields corresponding to frequencies 3 and 0.65 GHz is measured at temperatures between 1.52 and 4.2°K. The resonant field corresponding to the frequency 0.65 GHz and the larger of the resonant fields corresponding to the frequency 3 GHz vary with temperature, within the experimental errors, just as the turning field of the sublattice magnetic moments does. The homogeneous oscillation frequencies of the magnetic moment in an antiferromagnet separated into domains are calculated. A phase equilibrium diagram is proposed for $CuCl_2{\cdot}2H_2O$ in a magnetic field parallel to the "easy" axis. The temperature dependence of the lability fields is calculated in the spin-wave-theory approximation.

1. INTRODUCTION

THERE have been many experimental and theoretical investigations of antiferromagnetic resonances (AFMR) in copper chloride dihydrate. The $CuCl_2 \cdot 2H_2O$ crystals have rhombic symmetry with lattice parameters a = 7.38 Å, b = 8.04 Å, and c = 3.72 Å, the a axis being the "easy" axis, along which the antiferromagnetism axis 1 is aligned in the absence of an external magnetic field.

The dependence of the AFMR frequencies $\omega_{1,2}$ on the external magnetic field H, which is directed along the "easy" axis a, may have for this type of crystal (in accordance with the properties of the magnetic-anisotropy energy) the form of the curve shown either in Fig. 1a or in Fig. 1b (see [1,2]). The difference in the behavior of the AFMR frequencies is connected with the difference in the transition from the phase $\Phi_{\parallel}$ with vector 1 parallel to the a axis, to the phase $\Phi_{\perp}$ with vector 1 perpendicular to the a axis. (This transition takes place in $CuCl_2 \cdot 2H_2O$ at H_{tr} = 6.5 kOe.) Namely, the transition with continuous rotation of the vector 1 from the direction $1 \parallel a$ to the direction $1 \perp a$ corresponds to the behavior of the resonant frequencies in Fig. 1b, while the transition in which the vector 1 changes the direction abruptly by $\pi/2$ at $H = H_{tr}$ corresponds to the behavior of the resonant frequencies in Fig. 1a.

The data on AFMR in $CuCl_2 \cdot 2H_2O$, previously obtained at the high frequencies 32 and 9.4 GHz, and also at 3.5 MHz (see [2,3-5]) are insufficient for the identification of this transition. To establish which type of transition from the phase $\Phi_{\parallel}$ to the phase $\Phi_{\perp}$ takes place in $CuCl_2 \cdot 2H_2O$, investigations of AFMR were made at low frequencies 5.2, 3, 11, and 0.65 GHz in a field $H \parallel a$.

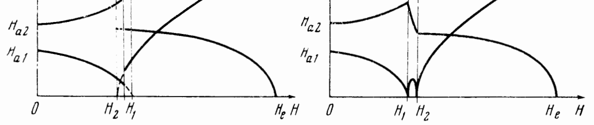

FIG. 1. Resonant frequencies: a – for first-order phase transitions, b – for two second-order phase transitions (for a sample with infinite dimensions).

If the magnetic anisotropy properties in $CuCl_2 \cdot 2H_2O$ correspond to continuous rotation of 1 during the transition from the phase $\Phi_{\parallel}$ to the phase $\Phi_{\perp}$, i.e., to a transition through a phase $\Phi_{<}$, then, according to the theory, four resonant absorption lines should be observed at low frequencies and in fields much weaker than the exchange field H_e.

On the other hand, if they correspond to rotation of 1 jumpwise by $\pi/2$, then, according to the theory, two resonance lines should be observed at $H \ll H_e$ (see Figs. 1a and b). In the present investigation, we did not observe four resonant fields at any of the investigated frequencies. It was observed that the large resonant fields at frequencies 0.65 and 3 GHz coincide, within the limits of experimental error.

A similar effect was observed earlier in [2,6] in investigations of AFMR in $CuCl_2 \cdot 2H_2O$ at high frequencies, and was called "orientational" resonance. These data suggest that at temperatures T > 1.5°K the properties of the magnetic anisotropy of $CuCl_2 \cdot 2H_2O$ correspond to a phase transition in which the direction of the vector 1 changes jumpwise (see Fig. 5 below, which shows schematically the phase diagram of a biaxial antiferromagnet at $H \parallel a$).

The existence of the "orientational" resonance at low frequencies (as well as its observation at high frequencies) is attributed by us to singularities in the absorption of the microwave field by the antiferromagnet, which breaks up into domains[7] when the field H is close to H_{tr}.

Of great importance is an investigation of the temperature dependence of the resonant fields, since it yields information on the interaction between the spin waves, and also provides additional information concerning the "orientational" resonance. The temperature dependence of the resonant fields at frequencies 9.4, 3.5, and 32 GHz has already been investigated.[3,5,6] The resonant field at the frequency 3.5 MHz (see [5], Fig. 4) and the smaller of the resonant fields at 9.4 GHz increase with increasing temperature. On the other hand, the temperature dependence of the larger of the resonant fields at the frequency 9.4 GHz has a more complicated character (see [4], Fig. 3): up to $T \lesssim 2.2°K$ the position of the line does not depend on the temperature, and at higher temperatures its dependence is similar to the temperature of the critical field H_{tr} (see [3], Fig. 3).

We have investigated the temperature dependence of the resonant fields at the frequencies 3 and 0.65 GHz in the interval $T = 1.52-4.2°K$. The observed temperature dependences of the resonant fields coincide, within the limits of experimental accuracy, with the temperature dependence of the critical field H_{tr}. These temperature dependences are compared with the calculated temperature dependences of the resonant fields, and also with the $H_{tr}(T)$ dependence calculated in the framework of spin-wave theory.

We have calculated the resonant frequencies of an antiferromagnet broken up into domains.

2. EXPERIMENTAL PROCEDURE

Single crystals of $CuCl_2 \cdot 2H_2O$ with $T_N = 4.33°K$, used in the present measurements, were grown from a saturated aqueous solution of copper chloride at room temperature for 15–20 days. They had the form of elongated prisms with rhombic cross sections and yielded a perfect cleavage along the c plane. The volume of the investigated samples ranged from 1 to 3 mm^3. The crystals were selected with the aid of a polarization microscope, and oriented by using the pleochroism of $CuCl_2 \cdot 2H_2O$.

To observe the AFMR in the frequency range 0.65–5.2 GHz, we used a radio spectroscope with a transmission type resonator. Its block diagram is shown in Fig. 2a. The resonators,[8] a drawing of which is shown in Fig. 2b, were placed vertically in a cryostat, and the magnetic field H was produced with the aid of a standard electromagnet. A holder inside the resonator made it possible to vary the inclination of the sample relative to the vertical plane. By rotating the electromagnet in the horizontal plane, the field **H** could be oriented along the crystal axes. The microwave power was provided by standard generators, and the external magnetic field was modulated at a frequency of 50 Hz. The resonant signal was amplified by a narrow-band amplifier and observed at the output on an oscilloscope or else plotted with an automatic recorder. The resonant fields were measured with the aid of proton resonance using standard apparatus, and their measurement accuracy was ± 10 Oe. The frequency of the generators was determined with the aid of a resonant wave meter accurate to 0.0001%, and was monitored by measuring the field of an absorption signal from a standard free radical placed in the resonator. The sample temperature ranged from 1.52 to 4.2°K and was determined from the vapor pressure of the helium bath.

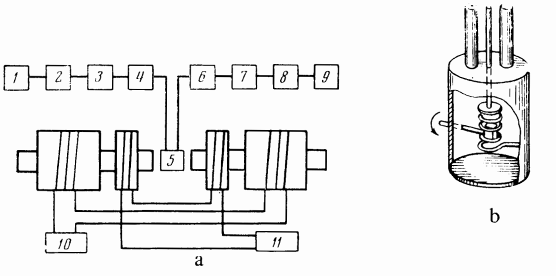

FIG. 2. Block diagram of decimeter-band radio spectroscope: a) 1 – generator power supply, 2 – generator, 3 – attenuator, 4 – matching device, 5 – resonator, 6 – detector, 7 – amplifier, 8 – synchronous detector, 9 – automatic plotter, 10 – electromagnetic power supply, 11 – modulator. b) Drawing of resonator.

3. EXPERIMENTAL RESULTS

The resonant properties of antiferromagnetic $CuCl_2 \cdot 2H_2O$ were investigated at the frequencies $\nu_1 = 5.2$, $\nu_2 = 3$, $\nu_3 = 1.1$, and $\nu_4 = 0.65$ GHz. Two resonant lines were observed at each of the frequencies ν_1, ν_2 and ν_3, but only one resonant line was observed at ν_4.

The dependence of the position of the resonant fields on the temperature in the interval $T \approx 1.52-4.2°K$ was investigated at the frequencies ν_2 and ν_4 and is shown in Fig. 3. Measurement at $T = 1.52°K$ and at the frequency ν_1 yield $H_1^{res} = 6.12$ kOe and $H_2^{res} = 6.73$ kOe, while at ν_3 we have $H_1^{res} = 6.63$ kOe and $H_2^{res} = 6.65$ kOe. To exclude the influence of the shape of the sample, measurements of any one sample were made at fixed experimental conditions. As seen from Fig. 3, the two resonant lines at ν_2 and the one resonant line at ν_4 exhibit a systematic shift towards higher resonant fields with increasing temperature.

At $T \approx 1.52-2.5°K$, the two resonant fields at the frequency $\nu_2 = 3$ GHz change, practically remaining at the same distance from each other. Their variation with temperature duplicates the variation of the magnetic field H_{tr} at which the phase $\Phi_{\parallel}$ $(l \parallel a)$ and the phase $\Phi_{\perp}$ $(l \perp a)$ are in equilibrium.

In the interval $T \approx 2.5-4.2°K$, the larger resonant fields shifts with increasing temperature, duplicating the variation of $H_{tr}(T)$, whereas the shift of the weaker resonated field slows down and its distance from the larger field increases.

The only resonant field obtained at the frequency $\nu_4 = 0.65$ GHz duplicates in the entire temperature interval $T \approx 1.52-4.2°K$ the shift of the larger resonant field at the frequency ν_2 with increasing frequency, and coincides with it within the limits of experimental accuracy. The agreement between the resonant field at the fre-

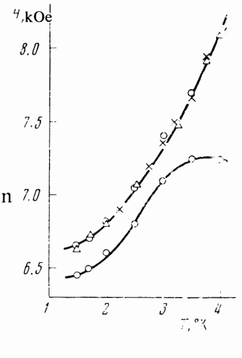

FIG. 3. Temperature dependence of the resonant fields at the frequencies: ○ – ν_2 = 3 GHz, Δ – ν_4 = 0.65 GHz, X – the transition field A_{tr}.

quency ν_4 with the value of the larger resonant field at ν_2 and with the value of H_{tr} in the entire temperature interval indicates that both resonant lines correspond to the so-called "orientational" resonance. From the fact that in the temperature interval from 1.52 to 2.5°K both resonant fields shift parallel to each other at the frequency ν_2, we can conclude that the temperature dependences of the critical field $H_{tr}(T)$ and of the lability field, which limits the region of stability of the phase with $l \parallel a$, are the same.

4. THEORY

A. Resonant Frequencies

As seen from Fig. 1, in the case of a transition from the phase $\Phi_{\parallel}$ ($l \parallel a$) to the phase $\Phi_{\perp}$ ($l \perp a$) through an intermediate phase $\Phi_{<}$, there exists a narrow magnetic-field interval $H_2 < H < H_1$ in which the larger of the resonant frequencies changes strongly with changing magnetic field H. Therefore the independence of the large resonant field of the frequency at high frequencies ($\nu \approx 32$ GHz at temperatures $T \gtrsim 1.5$°K) could be interpreted, at first glance, as a result of absorption of microwave power in the phase $\Phi_{<}$ and, consequently, as evidence that the transition from the phase $\Phi_{\parallel}$ to the phase $\Phi_{\perp}$ goes via the phase $\Phi_{<}$.

The agreement of the values of the larger resonant field at low frequencies ($\nu_2 = 3$ GHz and $\nu_4 = 0.65$ GHz at $T > 1.52$°K, see Sec. 3), observed in the present investigation, contradicts such an interpretation. We shall show that the agreement between the values of the larger of the resonant fields at high and at low frequencies can be attributed to absorption of microwave power in a sample broken up into domains.

It can be assumed that the absorption of the energy of the high-frequency field at $H = H_{tr}$ is connected with heterophase fluctuations and is manifest in the form of resonant absorption only because the magnetic field H determines simultaneously the AFMR frequencies and the phase transition. This assumption, however, is contradicted by the data of [4], where absorption at $T < 2.2$°K and at a frequency $\nu = 9$ GHz was observed at $H_1^{res} < H_{tr}$ and $H_2^{res} < H_{tr}$, and no noticeable absorption was observed at $H = H_{tr}$. When the temperature was larger than 2.2°K, absorption was observed at $H_1^{res} < H_{tr}$ and $H_2^{res} \approx H_{tr}$ at the same frequency. This indicates that the transition from the phase $\Phi_{\parallel}$ into the phase $\Phi_{\perp}$ behaves like a first-order phase transition, at least at $T > 1.5$°K.

To calculate the resonant frequency, we start from the following expression for the Hamiltonian of the antiferromagnet:

$$\mathscr{H} = \sum_{fg} (I_{fg}\mathbf{S}_f\mathbf{S}_g + \beta\mathbf{S}_f\mathbf{S}_g + \rho_{fg}\mathbf{S}_f\mathbf{S}_g) + \frac{1}{2}\sum_{f_1f_2} (\beta_{f_1f_2}S_{f_1}^xS_{f_2}^x + \rho_{f_1f_2}S_{f_1}^yS_{f_2}^y)$$
$$+ \frac{1}{2}\sum_{g_1g_2} (\beta_{g_1g_2}S_{g_1}^xS_{g_2}^x + \rho_{g_1g_2}S_{g_1}^yS_{g_2}^y) - \mu H\left(\sum_f S_f^z + \sum_g S_g^z\right), \quad (1)$$

where I_{fg} is the exchange integral, the quantities β and ρ describe the magnetic anisotropy, S_f is the spin of the atom in the f-th site of the lattice, and summation over f is carried out over the sites of the first magnetic sublattice, and over g over the sites of the second magnetic sublattice, and μ is double the Bohr magneton. The z axis is oriented along the a axis, and the x axis along the c axis in the crystallographic cell.

It is convenient to represent S_f and S_g in the form

$$\mathbf{S}_f = \mathbf{e}_{1\zeta}(f)S_{f\zeta} + \mathbf{e}_{1\eta}(f)S_{f\eta} + \mathbf{e}_{1\xi}(f)S_{f\xi},$$
$$\mathbf{S}_g = \mathbf{e}_{2\zeta}(g)S_{g\zeta} + \mathbf{e}_{2\eta}(g)S_{g\eta} + \mathbf{e}_{2\xi}(g)S_{g\xi}, \quad (2)$$

where $\mathbf{e}_{1\zeta}$ and $\mathbf{e}_{2\zeta}$ are unit vectors along the quantization axis of the first and second sublattice, respectively, and the unit vectors $\mathbf{e}_{1\eta}$ and $\mathbf{e}_{2\eta}$ are directed along the x axis, and finally, the spin operators are connected with the Holstein-Primakoff operators by the relations

$$S_f^+ = S_{f\xi} + iS_{f\eta} \approx \sqrt{2S}a_f^+, \quad S_g^+ = S_{g\xi} + iS_{g\eta} \approx \sqrt{2S}a_g^+,$$
$$S_f^- = S_{f\xi} - iS_{f\eta} \approx \sqrt{2S}a_f, \quad S_g^- = S_{g\xi} - iS_{g\eta} \approx \sqrt{2S}a_g, \quad (3)$$
$$S_{f\zeta} = S - \overset{+}{a}_f a_f, \quad S_{g\zeta} = S - \overset{+}{a}_g a_g.$$

Using formulas (2) and (3), we can represent the Hamiltonian $\mathscr{H}$ in the form

$$\mathscr{H} = E(S^2) + \mathscr{H}_1(S^{3/2}) + \mathscr{H}_2(S), \quad (4)$$

where E and $\mathscr{H}_1$ are respectively equal to

$$E = S^2\sum_{fg}[I_{fg}\cos(\theta_f - \theta_g) + \rho_{fg}\sin\theta_f\sin\theta_g]$$
$$+ \frac{1}{2}S^2\sum_{f_1f_2}\rho_{f_1f_2}\sin\theta_{f_1}\sin\theta_{f_2} + \frac{1}{2}S^2\sum_{g_1g_2}\rho_{g_1g_2}\sin\theta_{g_1}\sin\theta_{g_2}$$
$$- \mu SH\left[\sum_f\cos\theta_f + \sum_g\cos\theta_g\right], \quad (5)$$

$$\mathscr{H}_1 = \sum_f F_fS_{f\eta} + \sum_g F_gS_{g\eta} = \sum_f\Big\{\mu H\sin\theta_f + \cos\theta_f\Big[\sum_g S\rho_{fg}\sin\theta_g$$
$$+ \sum_{f'}S\rho_{ff'}\sin\theta_{f'}\Big] + S\sum_g I_{fg}\sin(\theta_g - \theta_f)\Big\}S_{f\eta}$$
$$+ \sum_g\Big\{\mu H\sin\theta_g + \cos\theta_g\Big[\sum_f S\rho_{fg}\sin\theta_f + \sum_{g'}S\rho_{gg'}\sin\theta_{g'}\Big]$$
$$+ S\sum_f I_{fg}\sin(\theta_f - \theta_g)\Big\}S_{g\eta}. \quad (6)$$

In these expressions θ_f and θ_g are the angles between the z axis and the unit vectors $e_{1\zeta}(f)$ and $e_{2\zeta}(g)$, respectively, and

$$S_{f\eta} \approx i(a_f - a_f^+)(S/2)^{1/2}, \quad S_{g\eta} \approx i(a_g - a_g^+)(S/2)^{1/2}. \quad (7)$$

We note that

$$F_f = \delta E/\delta\theta_f, \quad F_g = \delta E/\delta\theta_g. \quad (8)$$

Therefore the equations $F_f = 0$ and $F_g = 0$ determine the angles θ_f and θ_g as functions of the field H in the ground state.

The expression for $\mathscr{H}_2(4)$ is

$$\mathscr{H}_2 = \sum_{f_1f_2}\Big[A_{f_1f_2}a_{f_1}^+a_{f_2} + \frac{1}{2}B_{f_1f_2}(a_{f_1}a_{f_2} + a_{f_1}^+a_{f_2}^+)\Big]$$
$$+ \sum_{g_1g_2}\Big[A_{g_1g_2}a_{g_1}^+a_{g_2} + \frac{1}{2}B_{g_1g_2}(a_{g_1}a_{g_2} + a_{g_1}^+a_{g_2}^+)\Big]$$
$$+ \sum_{fg}[A_{fg}(a_f^+a_g + a_g^+a_f) + B_{fg}(a_fa_g + a_f^+a_g^+)], \quad (9)$$

where

$$A_{f_1f_2} = \frac{1}{2}S(\beta_{f_1f_2} + \rho_{f_1f_2}\cos\theta_{f_1}\cos\theta_{f_2}) + S\delta_{f_1f_2}\Big[\sum_g (I_{f_1g}\cos(\theta_{f_1} - \theta_g)$$

$$+\rho_{f_1 g}\sin\theta_{f_1}\sin\theta_g)+\sum_{f_3}\rho_{f_1 f_3}\sin\theta_{f_1}\sin\theta_{f_3}-\mu H\cos\theta_{f_1}\Big], \quad (10)$$

$$A_{g_1 g_2}=\frac{1}{2}S(\beta_{g_1 g_2}+\rho_{g_1 g_2}\sin\theta_{g_1}\sin\theta_{g_2})+S\delta_{g_1 g_2}\Big[\sum_f (I_{fg_1}\cos(\theta_f-\theta_{g_1})$$
$$+\rho_{fg_1}\sin\theta_f\sin\theta_{g_1})+\sum_{g_3}\rho_{g_1 g_3}\sin\theta_{g_1}\sin\theta_{g_3}-\mu H\cos\theta_{g_1}\Big], \quad (11)$$

$$B_{g_1 g_2}={}^1\!/_2 S(\beta_{g_1 g_2}-\rho_{g_1 g_2}\sin\theta_{g_1}\sin\theta_{g_2}), \quad (12)$$
$$B_{f_1 f_2}={}^1\!/_2 S(\beta_{f_1 f_2}-\rho_{f_1 f_2}\sin\theta_{f_1}\sin\theta_{f_2}), \quad (13)$$

$$A_{fg}=SI_{fg}\cos^2(\theta_f-\theta_g)+{}^1\!/_2 S(\beta_{fg}+\rho_{fg}\cos\theta_f\cos\theta_g), \quad (14)$$
$$B_{fg}=SI_{fg}\sin^2(\theta_f-\theta_g)+{}^1\!/_2 S(B_{fg}-\rho_{fg}\cos\theta_f\cos\theta_g), \quad (15)$$

$$\delta_{f_1 f_2}=\begin{cases}1, & f_1=f_2\\ 0, & f_1\neq f_2\end{cases}.$$

The equations of motion for the operators a_f and a_g are

$$\dot{a}_{f_1}=-i\frac{\delta\mathscr{H}}{\delta a_{f_1}}=-i\sum_{f_2}[A_{f_1 f_2}a_{f_2}+B_{f_1 f_2}a_{f_2}^{+}]-i\sum_g[A_{f_1 g}a_g+B_{f_1 g}a_g^{+}],$$

$$\dot{a}_{g_1}=-i\frac{\delta\mathscr{H}}{\delta a_{g_1}}=-i\sum_{g_2}[A_{g_1 g_2}a_{g_2}+B_{g_1 g_2}a_{g_2}^{+}]-i\sum_f[A_{fg_1}a_f+B_{fg_1}a_f^{+}]. \quad (16)$$

It is also necessary to add to these equations two Hermitian-adjoint equations for the operators a_f^{+} and a_g^{+}.

We are interested in the frequency of the homogeneous oscillations. Accordingly, we assume that the quantities a_f and a_g do not depend on f and g, and denote them respectively by a_1 and a_2. Then the equations of motion can be represented in the form

$$i\dot{a}_1=A_{11}a_1+B_{11}a_1^{+}+A_{12}a_2+B_{12}a_2^{+},$$
$$i\dot{a}_2=A_{22}a_2+B_{22}a_2^{+}+A_{12}a_1+B_{12}a_1^{+}. \quad (17)$$

The quantities A and B, which enter in these equations, are equal to

$$A\equiv A^{\parallel}\xi+A^{\perp}(1-\xi), \qquad B\equiv B^{\parallel}\xi+B^{\perp}(1-\xi), \quad (18)$$

where $A^{\parallel}$ and $B^{\parallel}$ are obtained from formulas (10)–(15) by putting $\theta_f = 0$ and $\theta_g = \pi$. $A^{\perp}$ and $B^{\perp}$ are obtained from (10)–(15) by putting $\theta_f = \theta$ and $\theta_g = -\theta$ ($\cos\theta = \mu H(2I_0+\rho_0'-\rho_0)^{-1}$), and ξ is the amount of matter in the phase $\Phi_{\parallel}$. In deriving (17), we have neglected the influence of the domain walls, in which the angles θ_f and θ_g change strongly. Therefore Eq. (17) and the frequencies corresponding to them are the more accurate, the better the condition $d \gg x_0$ is satisfied (d—domain thickness, x_0—thickness of domain wall)[1].

Assuming that the quantities a have a time variation $a_1, a_2 \sim e^{-i\omega t}$ we can obtain from (17) the following expressions for the frequencies:

$$\omega^2=\frac{1}{2}\{A_{11}^2+A_{22}^2+2A_{12}^2-B_{11}^2-B_{22}^2-2B_{12}^2$$
$$\pm[4(A_{12}(A_{11}+A_{22})-B_{12}(B_{11}+B_{22}))^2$$
$$-4(B_{12}(A_{22}-A_{11})-A_{12}(B_{22}-B_{11}))^2+(A_{11}^2-A_{22}^2-B_{11}^2+B_{22}^2)]^{1/2}\} \quad (19)$$

Using formulas (10)–(15) and (18), we obtain

$$\omega_{1,2}^2=\{A^2+(\xi\mu H)^2+A_{12}^2-B_{11}^2-B_{12}^2\pm[4(AA_{12}-B_{11}B_{12})^2$$
$$+4(\xi\mu H)^2(A^2-B_{12}^2)]^{1/2}\}, \quad (20)$$

where

$$A=S[I_0+{}^1\!/_2(\beta_0+\rho_0)]\xi+S[I_0+\rho_0'-{}^1\!/_2\rho_0\sin^2\theta+{}^1\!/_2\beta_0-{}^1\!/_2\rho_0](1-\xi),$$
$$A_{12}={}^1\!/_2 S(\beta_0'-\rho_0')\xi+S[I_0\cos^2\theta+{}^1\!/_2\beta_0'-{}^1\!/_2\rho_0'\cos^2\theta](1-\xi),$$
$$B_{11}=B_{22}={}^1\!/_2 S(\beta_0-\rho_0)\xi+{}^1\!/_2 S[\beta_0-\rho_0\cos^2\theta](1-\xi),$$
$$B_{12}=S[I_0+{}^1\!/_2(\beta_0'-\rho_0')]\xi+S[I_0\sin^2\theta+{}^1\!/_2(\beta_0'-\rho_0'\cos^2\theta)](1-\xi),$$

$$I_0=\sum_f I_{fg}, \quad \rho_0=\sum_{f_2}\rho_{f_1 f_2}=\sum_{g_2}\rho_{g_1 g_2}, \quad \rho_0'=\sum_f\rho_{fg};$$

$$\beta_0=\sum_{f_2}\beta_{f_1 f_2}=\sum_{g_2}\beta_{g_1 g_2}, \qquad \beta_0'=\sum_g\beta_{fg}.$$

The upper sign in (19) and (20) corresponds to ω_1 and the lower sign to ω_2.

If the antiferromagnet is in the form of a plate perpendicular to the orientation of the external magnetic field, then when $H > \mu_{\perp}H_{tr}$ ($\mu_{\perp}$ is the transverse magnetic permeability) it is necessary to put in formula (20) $\xi = 0$,[7] and we arrive at the resonant frequencies in the phase $\Phi_{\perp}$:[1]

$$(\omega_1^{\perp}(H))^2=S[\beta_0-\beta_0'-\rho_0+\rho_0']H_e\left(1-\frac{H^2}{H_e^2}\right)=(\mu H_a)^2\left(1-\frac{H^2}{H_e^2}\right),$$

$$(\omega_2^{\perp}(H))^2=\frac{(2I_0-\rho_0+\rho_0'+\beta_0+\beta_0')(2I_0+\rho_0+\rho_0')}{(2I_0-\rho_0+\rho_0')^2}[(\mu H)^2-(\mu H_2)^2]. \quad (21)$$

Here

$$(\mu H_2)^2=(\mu H_e)^2\frac{\rho_0-\rho_0'}{2I_0+\rho_0+\rho_0'}, \qquad \mu H_e=S(2I_0+\rho_0'-\rho_0).$$

If $H < \mu_{\parallel}H_{tr}$ ($\mu_{\parallel}$ is the longitudinal magnetic permeability), then we must put $\xi = 1$ in formula (20)[7] and we arrive at the resonant frequencies in the phase $\Phi_{\parallel}$:[1]

$$(\omega_{1,2}^{\parallel})^2=\mu^2\{H^2+{}^1\!/_2(H_{a1}^2+H_{a2}^2)\pm[(H^2+{}^1\!/_2(H_{a1}^2+H_{a2}^2))^2$$
$$-(H_1^2-H^2)(H_{12}^2-H^2)]^{1/2}\}.$$

Here

$$H_{a1}^2=S^2(2I_0+\beta_0+\beta_0')(\rho_0-\rho_0'), \qquad H_{a2}^2=S^2(2I_0+\rho_0+\rho_0')(\beta_0-\beta_0'),$$

$$H_{12}^2=S^2(2I_0+\beta_0+\beta_0')(\beta_0-\beta_0'), \qquad H_1^2=S^2(2I_0+\rho_0+\rho_0')(\rho-\rho_0'),$$
$$H_{tr}^2=H_1H_2. \quad (22)$$

We note that we consider the case when $\rho_0 > 0$, $\beta_0 - \beta_0' > 0$, $\rho_0 - \rho_0' > 0$, $\beta_0 - \beta_0' > \rho_0 - \rho_0'$, corresponding to a jumpwise rotation of l through an angle $\pi/2$ on going from phase $\Phi_{\parallel}$ to phase $\Phi_{\perp}$.

Finally, the change of the AFMR frequencies in the field interval $\mu_{\parallel}H_{tr} < H < \mu_{\perp}H_{tr}$ is described by formula (20), in which we put formally $H = H_{tr}$, and the dependence of the AFMR frequencies on the external field H is taken into account with the aid of the quantity

$$\xi=(\mu_{\perp}H_{tr}-H)(\mu_{\perp}-\mu_{\parallel})^{-1}H_{tr}^{-1}.$$

We see therefore that expression (20), derived with allowance for the subdivision of the antiferromagnet into domains, describes the continuous variation of

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[1] In the case of small deviations of the magnetic moments from their equilibrium values at $H \approx H_{tr}$, it can be readily seen that these deviations, which correspond to the homogeneous natural oscillations in the phases $\Phi_{\parallel}$ or $\Phi_{\perp}$, are not homogeneous for a sample broken up into domains. Homogeneous oscillations in a sample broken up into domains correspond to a certain superposition of the oscillations of the magnetic moments in the phases $\Phi_{\parallel}$ and $\Phi_{\perp}$; we have considered this superposition above. Our averaging is analogous to the well known averaging of the microscopic equations in the derivation of the macroscopic equations of electrodynamics.

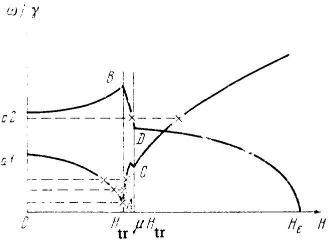
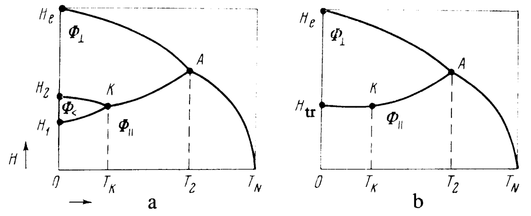


FIG. 4. Dependence of the resonant frequencies ω on the field H in a first-order phase transition in a sample of finite dimensions (X – schematic position of the experimental points).



a b

FIG. 5. Phase diagrams.

the resonant frequencies with changing magnetic field (compare Figs. 1a and 4). This means that formula (20) explains the nature of the resonant absorption of the microwave field energies at $H = H_{tr}$ at both high and low frequencies.

We present finally an expression for the frequencies ω_1 and ω_2 in two limiting cases. If $\xi \ll 1$, then

$$\omega_1^2 = (\omega_1^\perp(H_{tr}))^2 + 2S^2\xi I_0(\rho_0 - \rho_0'),$$

$$\omega_2^2 = (\omega_2^\perp(H_{tr}))^2 + 2S^2\xi I_0(\rho_0 - \rho_0'). \tag{23}$$

If $|1 - \xi| \ll 1$, then

$$\omega_1^2 = (\omega_1^\parallel(H_{tr}))^2 - (1 - \xi)\frac{S^2I_0(\rho_0 - \rho_0')[34(\rho_0 - \rho_0') + 14(\beta_0 - \beta_0')]}{3(\rho_0 - \rho_0') + (\beta_0 - \beta_0')}$$

$$\omega_2^2 = (\omega_2^\parallel(H_{tr}))^2 + 2(1 - \xi)\frac{S^2I_0(\rho_0 - \rho_0')(\beta_0 - \beta_0' - \rho_0 + \rho_0')}{3(\rho_0 - \rho_0') + (\beta_0 - \beta_0')} \tag{24}$$

The AFMR frequencies have a similar form also for an arbitrary ellipsoidal sample, and the field interval in which ξ changes from 1 to 0 depends on the demagnetizing coefficients. Since $\chi \ll 1$, the field interval from $\mu_\parallel H_{tr}$ to $\mu_\parallel H_{tr}$ is very small. Therefore the temperature dependence of the resonant fields corresponding to the intersection of the line ω = const with the resonance curves $\omega = \omega_{1,2}(H)$ in the interval $\mu_\parallel H_{tr} < H < \mu_\perp H_{tr}$ will duplicate the temperature dependence of the field $H_{tr}(T)$, as was indeed observed in our experiments.

B. Phase Transitions

Let us consider the phase diagram of an antiferromagnet in a magnetic field parallel to the "easy" axis. As already noted, the AFMR data point to the existence of a first-order phase transition between the phases $\Phi_\parallel$ and $\Phi_\perp$ at T > 1.5°K. On the phase diagram of Fig. 5, this transition corresponds to the curve AK. The curves AH_e and AT_N separate the phases $\Phi_\perp$ and $\Phi_\parallel$ respectively from the phase with $l = 0$ (paramagnetic phase).

It is of interest to consider the question of the continuation of the equilibrium curve AK to the region of lower temperatures. Two variants of the phase diagram are possible: either the first-order phase transition curve extends continuously down to T = 0°K, terminating at $H = H_{tr}$ (Fig. 5b), or at some point K it branches into two second-order phase transition lines KH_2 and KH_1 (Fig. 5a). The variant of the phase diagram of Fig. 5a takes place if $H_2 < H_1$. On the other hand, if $H_2 > H_1$, then the variant of the phase diagram of Fig. 5a takes place. The difference between H_2 and H_1 can be determined from data on the resonant frequencies. Using formulas (21) and (22), we find that

$$H_{a2}^2(H_1 - H_2)H_1^{-1} = H_{a2}^2 - H_a^2 - H_{tr}^2. \tag{25}$$

It follows therefore that $H_2 > H_1$ if $H_{tr} > \sqrt{H_{a2}^2 - H_a^2}$.

According to [2] 2), H_{tr}, H_{a2}, and H for $CuCl_2 \cdot 2H_2O$ have the following values at T = 0°K: $H_{tr} = 6.5 \pm 0.05$ kOe, $H_{a2} = 11.2 \pm 0.05$ kOe, and $H_a = 9.2 \pm 0.05$ kOe. Using these values, we can verify that $H_2 - H_1 > 0$. Thus, according to these data, the crystal $CuCl_2 \cdot 2H_2O$ corresponds to the phase diagram of Fig. 5a. The transition from the curves H_2K and H_1K to the first-order phase transition curve AK is connected with the fact that with increasing temperature the values of the fields H_1 and H_2 increase and decrease, respectively. To illustrate this circumstance, we present the result of the calculation of the corrections to H_1 and H_2, necessitated by the interaction of the spin waves with one another (in the calculation of the dependences of H_1 and H_2 on T we have assumed for simplicity that the crystal is uniaxial, i.e., we put $\rho = \beta$):[9]

$$\tilde{H}_1 = H_1\left[1 + \frac{2}{3S}\left(\frac{T}{SI_0}\right)^2\right], \quad \tilde{H}_2 = H_2\left[1 - \frac{2}{3S}\left(\frac{T}{SI_0}\right)^2\right]. \tag{26}$$

Although these results are valid formally in the temperature region $\mu H_{tr} \ll T \ll T_N$ (which in fact does not hold for $CuCl_2 \cdot 2H_2O$, inasmuch as $\mu H_{tr} \approx 0.9$°K and T_N = 4.33°K), they still describe correctly the character of variation of $\tilde{H}_1$ and $\tilde{H}_2$ with changing temperature.

If it is assumed that the formulas in (26) describe correctly the monotonic variation of $\tilde{H}_1$ and $\tilde{H}_2$ with increasing temperature, then at a certain temperature T_1 the fields $\tilde{H}_1$ and $\tilde{H}_2$ are equal, and when $T > T_2$ the field $\tilde{H}_1$ becomes larger than the field $\tilde{H}_2$ and the transition from the phase $\Phi_\parallel$ into the phase $\Phi_\perp$ will be of first order.

We have investigated experimentally the first-order phase transition (curve AK of the diagrams of Fig. 5a). We note that the data concerning the curve AK, i.e., the dependence of H_{tr} on T, given in [2,5] agree with our data. The dependence of the field H_{tr} on the temperature can be calculated from spin-wave theory. This dependence is given by the formula

$$H_{tr}(T) = H_{tr}\left[1 + \frac{2}{3S}\left(\frac{T}{SI_0}\right)^2\right] \tag{27}$$

at $\mu H_{tr} \ll T \ll T_N$.

The phase diagram in Fig. 5a, strictly speaking, holds in a field H ∥ a. At an arbitrarily small inclination of the field H to the "easy" magnetization axis, the points H_1 and H_2, being points at which the symmetry of the magnetic field changes jumpwise, vanish. In the entire interval $0 < H < H_e(\psi)$, where $H_e(\psi)$ is the field in which the vector l vanishes and ψ is the angle between the easy-magnetization axis and the field H,

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2) The symbols used in [2] for the quantities H_{tr}, H_{a2}, and H_a are respectively H_c, H_b, and H_a.

the stable phase is $\Phi_<$. If the angle ψ is sufficiently small, it is possible to separate, as before, a relatively narrow interval of values of the field H, of the order of $H_2 - H_1$, in which a continuous rotation of the vector l takes place from a direction almost parallel to the "easy" axis to a direction almost perpendicular to it.

Taking into account the foregoing remarks, we can conclude that at an angle $\psi \neq 0$ the sections H_1K and H_2K of the phase diagram of Fig. 5 become meaningless as phase equilibrium curves, and the section AK—the first-order phase transition curve—terminates at the point K, which can be regarded as the critical point. On the curve AK, the phase transition itself is now accompanied by a jump of the angle θ between the vector l and the "easy" axis, but not from 0 to $\pi/2$, but from a value θ_1 in the phase $\Phi_<$, which exists in the region below the curve AK, to the value θ_2 in the phase $\Phi_<$ existing in the region above this curve.

C. Dependence of the Fields H^0_{res} and H_{tr} on the Temperature

We have seen (see Fig. 4) that the resonant fields H^0_{res} corresponding to the frequencies of the "orientational" resonance are quite close to the field H_{tr}. Therefore, measurement of the temperature dependence of H^0_{res} should yield information concerning the temperature dependence of H_{tr}. The closer the resonance frequencies to the points A and B (see Fig. 4), the closer the temperature dependence of H^0_{res} to $\tilde{H}_{\text{tr}} = H_{\text{tr}}(T)$. The frequency intervals BD and AC, at which the "orientational" resonance takes place, are of the order of

$$\Delta\omega^{n} = \omega_2{}^{\perp}(\tilde{H}_{\text{tr}}) - \omega_2{}^{\parallel}(\tilde{H}_{\text{tr}})$$
$$\approx \mu(\tilde{H}_1{}^2 - \tilde{H}_{\text{tr}}{}^2)^{1/2}\left[1 - \frac{(\tilde{H}_{a2}{}^2 - \tilde{H}_{\text{tr}}{}^2)^{1/2}}{(2\tilde{H}_{\text{tr}}{}^2 + \tilde{H}_{a1}{}^2 + \tilde{H}_{a2}{}^2)^{1/2}}\right];$$

$$\Delta\omega_1 = \omega_1{}^{\parallel}(\tilde{H}_{\text{tr}}) - \omega_1{}^{\perp}(H_{\text{tr}}) \approx \mu[(2\tilde{H}_{\text{tr}}{}^2 + \tilde{H}_{a1}{}^2 + \tilde{H}_{a2}{}^2)^{1/2} - (\tilde{H}_{a2}{}^2 - \tilde{H}_{a1}{}^2)^{1/2}], \tag{28}$$

where $\tilde{H}_a$ and $\tilde{H}_{\text{tr}}$ are certain functions of the temperature, corresponding to the section AK of the diagram; $\omega_1^{\parallel}(H_{\text{tr}})$, $\omega_1^{\perp}(H_{\text{tr}})$, $\omega_2^{\parallel}(H_{\text{tr}})$, and $\omega_2^{\perp}(H_{\text{tr}})$ are the values of the resonant frequencies at $H = H_{\text{tr}}$ in the phases $\Phi_{\parallel}$ and $\Phi_{\perp}$, respectively.

Let us estimate the position of the point C of the frequency interval AC. According to (21), the frequency $\omega_2^{\perp}(H)$ at $H = \tilde{H}_{\text{tr}}$ is given by

$$\omega_2{}^{\perp}(\tilde{H}_{\text{tr}}) = \mu(\tilde{H}_{\text{tr}}{}^2 - \tilde{H}_2{}^2)^{1/2} = \mu\left[H_{\text{tr}}{}^2 - H_2{}^2 + \frac{8}{3S}H_{\text{tr}}{}^2\left(\frac{T_N}{SI_0}\right)^2\left(\frac{T}{T_N}\right)^2\right]^{1/2}, \tag{29}$$

where $\tilde{H}_{\text{tr}}$ and $\tilde{H}_2$ are defined by formulas (27) and (26). Using (25) and the formula

$$H_1(H_1 - H_2) = \frac{H_1{}^2}{H_{\text{tr}}{}^2}(H_{\text{tr}}{}^2 - H_2{}^2), \tag{30}$$

we find that at $H_{a2} = 11.2$ kOe, $H_a = 9.2$ kOe, and $H_{\text{tr}} = 6.5$ kOe we get $H^2_{\text{tr}} - H^2_2 = -\frac{2}{3}\,\text{kOe}^2$. Putting $2SI_0 \approx \mu H_e$ and using $H_e \approx 1.2 \times 10^5$ Oe,[10] we get $SI_0 \approx 8$°K. Assuming $T_N = 4.33$°K and $S = \frac{1}{2}$, we get

$$\omega_2{}^{\perp}(\tilde{H}_{\text{tr}}) = \mu\left[67\left(\frac{T}{T_N}\right)^2 - \frac{2}{3}\right]^{1/2} \tag{31}$$

From this we find that at T = 1.5°K, we have $\nu_2^{\perp}(\tilde{H}_{\text{tr}}) \approx 1$ GHz. This value, obtained by an approximate calculation, is in good agreement with the values of the frequencies of the "orientational" resonance, obtained both in the present paper and in papers by others.[4] Putting $\omega_2^{\perp}(\tilde{H}_{\text{tr}}) = 0$, we get from (31) $T_1 \approx (T_N/10) \approx 0.4$°K. This value of T_1 can be regarded as a rough estimate of the position of the point T_K (see Fig. 5a). Since $T_1 = 0.4\text{°K} < \mu H_{\text{tr}} \approx 0.9$°K, it can be assumed that $T_K \sim \mu H_{\text{tr}}$. It is of interest to investigate experimentally the temperature dependence of the position of the point C and to determine the temperature T at which $\omega_2^{\perp}(\tilde{H}_{\text{tr}})$ vanishes.

Let us compare the temperature dependence of $\tilde{H}_{\text{tr}}$, given by formula (27), with the experimental data for the larger resonant field at the frequencies $\nu_2 = 3$ GHz and $\nu_4 = 0.65$ GHz. Using $H_{\text{tr}} = 6.5$ kOe, we rewrite (27) in the form

$$\tilde{H}_{\text{tr}} = 6.5 + aT^2\ [\text{kOe}]. \tag{32}$$

The value of a can be determined by using $H_{\text{tr}} = 6.66$ kOe at T = 1.52°K, which yields a = 0.07 kOe/deg². At this value of a, formula (32) agrees well with the experimental data for the larger values of the resonant field at frequencies ν_1 and ν_4 and T < 2°K. The same value for a is obtained by putting in (27) $S = \frac{1}{2}$ and $SI_0 = 11$°K. The value $SI_0 = 11$°K constitutes 0.8 of the value of SI_0 determined from the data on the exchange field ($H_e = 200$ kOe[11]).

5. CONCLUSION

The results obtained in the study of the temperature dependence of the resonant fields, and the calculation of the dependence of the AFMR frequencies on the magnetic field, lead to the conclusion that:

a) the transition from the phase $\Phi_{\parallel}$ to the phase $\Phi_{\perp}$ in copper chloride dihydrate at T > 1.52°K is of first order;

b) in such a transition the antiferromagnet breaks up into domains of the phases $\Phi_{\parallel}$ and $\Phi_{\perp}$, as shown theoretically in [7];

c) the transition from the phase $\Phi_{\parallel}$ into the phase $\Phi_{\perp}$ at T < 1°K is apparently a result of two second-order phase transitions.

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