

# Ferromagnetic resonance and magnetic structure of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$

S. O. Demokritov, N. M. Kreĭnes, V. I. Kudinov, S. V. Petrov, and A. V. Chubukov

*S. I. Vavilov Institute of Physics Problems, Academy of Sciences of the USSR, Moscow*

(Submitted 30 April 1988)

Zh. Eksp. Teor. Fiz. **94**, 283–292 (December 1988)

The ferromagnetic resonance spectrum was determined for a quasi-two-dimensional ferromagnet  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  with the easy-plane anisotropy. The experimental results are explained by an unusual magnetic structure in which the difficult magnetic anisotropy axes have different directions in neighboring planes.

## 1. INTRODUCTION

In a short letter we reported earlier<sup>1</sup> that the ferromagnetic resonance (FMR) spectra of a quasi-two-dimensional ferromagnet  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  cannot be described by the usual model of an easy-plane ferromagnet. We shall therefore give the results of a more detailed investigation of the FMR in this compound.

Copper chloride complexes with the general formula  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ , where  $n = 1, 2, \dots, 10$  (Refs. 2 and 3) occupy a special place among compounds which can be quite justifiably regarded as two-dimensional ferromagnets. Divalent copper ions ( $S = \frac{1}{2}$ ) are distributed between planar  $\text{CuCl}_4$  layers separated by two layers of organic molecules  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)$ . In each layer the copper ions are in an octahedron of Cl atoms and they form an almost regular square lattice. As  $n$  is increased, the separation between  $\text{CuCl}_4$  layers increases, which reduces the interaction between the planes (at least in the range  $n \gg 3$ ). In the whole of this class of compounds the exchange interaction in the copper layers is ferromagnetic ( $J \approx 20$  K) and it is several orders of magnitude stronger than the exchange  $J'$  between the layers ( $J' \sim J \times 10^{-4}$ ).<sup>3,4</sup>

We investigated magnetic properties of the compound  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  ( $n = 1$ ) by the FMR method. We selected this compound from the rest in the same class for the following reasons: firstly, the interplanar (interlayer) exchange constant  $J'$  is small; secondly, in contrast to compounds with higher values of  $n$ , the exchange in question is of ferromagnetic nature. It has been assumed earlier that the behavior of this compound can be described by a simple model of an easy-plane ferromagnet. This model is capable of providing a fairly simple interpretation of the resonance spectra and identifying the characteristics of the magnetic properties associated with the two-dimensional nature of the system. However, it has been found that the magnetic ordering of the selected compound is more complex (see below).

At room temperature the compound  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  has a face-centered orthorhombic cell (symmetry group  $D_{2h}^{15}$ ) with the parameters  $a = 7.38$  Å,  $b = 7.29$  Å, and  $c = 18.66$  Å (Refs. 5 and 6). At temperatures  $T \lesssim 250$  K this symmetry decreases to monoclinic (monoclinic angle  $92.3^\circ$ ).<sup>5</sup> The unit cell contains four formula units and, consequently, four magnetic  $\text{Cu}^{2+}$  ions. The ferromagnetic exchange interaction between the magnetic  $\text{Cu}^{2+}$  ( $S = \frac{1}{2}$ ) ions is nearly of the Heisenberg nature with  $J = 19.2$  K (and the corresponding exchange field is  $H_E = 550$  kOe).<sup>3,5,7</sup> A slight anisotropy (representing  $\sim 1\%$  of the exchange interaction) tends to align the spins in the basal

plane; the corresponding easy-plane anisotropy field is  $H_A \approx 1.5$  kOe (Ref. 4). A very weak uniaxial anisotropy in the plane of the layers ( $H_a \approx 80$  Oe) reported in Ref. 4 and a weak ferromagnetic exchange between the spins in the neighboring planes ( $H_e \approx 50$  Oe), also reported in Ref. 4, ensure that below  $T_c = 8.9$  K (Ref. 3) the crystal is ferromagnetically ordered. Electron spin resonance measurements<sup>8</sup> give the following values of the  $g$  factor:  $g_{\parallel} = 2.05$  (along the  $c$  axis) and  $g_{\perp} = 2.27$  (along the layer plane).

Our  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  crystals were grown from a solution of this compound in ethyl alcohol at  $50^\circ\text{C}$  by the evaporation method (Refs. 5 and 6). Samples were in the form of disks with their plane perpendicular to the crystallographic  $c$  axis. Experiments carried out on ten crystals yielded similar results. We shall give the results obtained for a sample with a diameter 2.1 mm and 0.15 mm thick; the demagnetization coefficients were  $N_{\perp} = 0.894$  and  $N_{\parallel} = 0.053$ ; hence, the demagnetizing fields in the plane of the sample and along the  $c$  axis had the following values at  $T = 0$  K:  $4\pi N_{\parallel} (g_{\parallel}/2)M_0 = 26.5$  Oe and  $4\pi N_{\perp} (g_{\perp}/2)M_0 = 450$  Oe, where  $M_0 = \mu_B/\nu_0 = 40$  Oe is the average saturation magnetization.

We investigated the dependence of the FMR frequency of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  on an external magnetic field in the frequency range 100–4500 MHz at the lowest temperature  $T = 1.3$  K achieved in our apparatus. At this temperature we could ignore the fluctuation effects and the resonance spectra were determined simply by the magnetic structure of the investigated compound. Measurements were deliberately carried out at low frequencies and correspondingly low fields, when the FMR spectra could be used to find readily the magnetic properties (anisotropy field, gap in zero field, etc.) of this ferromagnet.

The FMR spectra were recorded on the basis of absorption of high-frequency power. A crystal was placed directly either in a strip or a helical line. This made it possible to carry out measurements in a wide frequency range (100–4500 MHz) in the same experiment. The hf power supplied to the sample was less than 1 mW and the absorption at the resonance amounted to a few percent. An oscillatory magnetic field  $h$  in high-frequency lines was directed along the plane of a sample and at right-angles to an external field  $H$ . A horizontal magnetic field was created by an electromagnet and a helium Dewar was placed inside the gap. Rotation of the magnet relative to the vertical axis through any angle and rocking by  $\pm 4^\circ$  relative to the horizontal axis made it possible to orient the field along any direction. The magnetic field was measured with a Hall sensor. The width of the

FMR line expressed in terms of the field was no more than 1 Oe; this was evidence of the high quality of the investigated samples.

## 2. MAGNETIC STRUCTURE

As pointed out above, following the published results<sup>4,5</sup> we can describe  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  by a model of a ferromagnet with an easy-plane anisotropy. Applying the classical theory at  $T = 0$  K, we find that the anisotropic part of the energy of such a system is<sup>9</sup>

$$E = \frac{A}{2} M_z^2 - \frac{a}{2} M_x^2 - (\mathbf{H}\mathbf{M}) + 2\pi\mathbf{M}\vec{N}\mathbf{M}, \quad (1)$$

where  $E$  is the energy per unit volume,  $A > 0$  is the easy-plane anisotropy constant,  $a > 0$  is the easy-axis anisotropy constant in the planes of the layers;  $N_{ij}$  is the tensor representing the demagnetization coefficients. The directions of the coordinates  $x$ ,  $y$ , and  $z$  in Eq. (1) are identical with the directions of the axes  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ . The effective fields corresponding to the anisotropy constants are as follows:

$$H_A = [A + 4\pi(N_z - N_y)] M_0 g_{\perp} / 2, \quad (2a)$$

$$H_a = [a + 4\pi(N_y - N_x)] M_0 g_{\parallel} / 2 \approx a M_0 g_{\parallel} / 2. \quad (2b)$$

If a magnetic field is applied along the difficult magnetization axis  $\mathbf{c}$ , then in a field  $H = H_A + H_a$  we should observe a reorientational phase transition corresponding to the establishment of a magnetic moment along the field. The FMR frequency then vanishes. A similar reorientation transition occurs also for  $\mathbf{H} \parallel \mathbf{b}$ , when an increase in the field causes rotation of the magnetic moment  $\mathbf{M}$  from the  $\mathbf{a}$  to the  $\mathbf{b}$  axis and then in fields  $H \gg H_a$  the moment again becomes aligned exactly along the field. The resonance spectrum of an easy-plane ferromagnet can be described by the following expressions which apply to the three selected magnetic field directions (see, for example, Ref. 9):

for  $\mathbf{H} \parallel \mathbf{c}$ , then

$$\nu = \gamma (H_a (H_a + H_A))^{1/2} \left[ 1 - \left( \frac{H_z}{H_A + H_a} \right)^2 \right]^{1/2}, \quad H_z \leq H_A + H_a, \quad (3a)$$

$$\nu = \gamma [(H_z - H_A)(H_z - H_A - H_a)]^{1/2}, \quad H_z > H_A + H_a; \quad (3b)$$

for  $\mathbf{H} \parallel \mathbf{b}$ , then

$$\nu = \gamma (H_a (H_a + H_A))^{1/2} [1 - (H_y / H_a)^2]^{1/2}, \quad H_y < H_a, \quad (4a)$$

$$\nu = \gamma [(H_y - H_a)(H_y + H_A)]^{1/2}, \quad H_y > H_a; \quad (4b)$$

for  $\mathbf{H} \parallel \mathbf{a}$ , then

$$\nu = \gamma [(H_x + H_a)(H_x + H_a + H_A)]^{1/2}. \quad (5)$$

Here,  $\gamma = 2.82$  GHz/kOe is the gyromagnetic ratio;  $\tilde{H}_z = H_z g_{\perp} / 2$ ;  $\tilde{H}_{x,y} = H_{x,y} g_{\parallel} / 2$ ;  $\tilde{H}_A = H_A g_{\perp} / 2$ ;  $\tilde{H}_a = H_a g_{\parallel} / 2$ . For simplicity, we shall in future omit the tilde sign in the case of fields.

When  $\mathbf{H}$  is oriented along the  $\mathbf{c}$  and  $\mathbf{b}$  axes, the FMR frequency vanishes in fields  $H = H_A + H_a$  and  $H = H_a$ , respectively, providing a natural method for determination of the anisotropy constants. In fields  $H > H_A + H_a$  at a given frequency the resonance field is maximized if  $\mathbf{H}$  is parallel to the difficult magnetization axis  $\mathbf{c}$ . This allows us to orient the magnetic field exactly at right-angles to the easy plane. How-

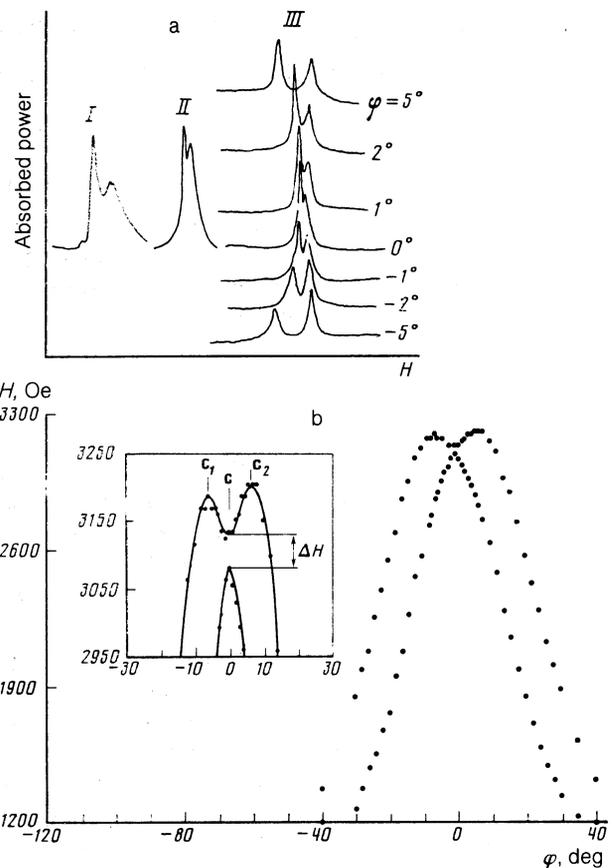


FIG. 1. a) Profiles of the FMR lines obtained at different microwave field frequencies  $\nu$ : I) 1.2 GHz; II) 2.0 GHz; III) 4.0 GHz. Direction of an external magnetic field  $\mathbf{H}$  is represented by the angle  $\varphi$  between  $\mathbf{H}$  and the  $\mathbf{c}$  axis ( $\varphi = 0^\circ$  corresponds to  $\mathbf{H} \parallel \mathbf{c}$ ). b) Dependence of the resonance field of two FMR modes at  $T = 1.3$  K when  $\nu = 4.0$  GHz. The inset shows the region near  $\varphi = 0$  on an enlarged scale.

ever, a study of the FMR spectra of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  revealed that the behavior of the system is more complex and cannot be described by a simple model of an easy-plane ferromagnet.<sup>1</sup>

Figure 1 gives the experimentally determined dependence of the resonance field on the direction of the magnetic field in the  $cb$  plane at  $\nu = 4000$  MHz. We can see from this figure that two resonances were observed and their positions varied with the direction of the field relative to the  $\mathbf{c}$  axis (angle  $\varphi$ ). There were three special directions of the magnetic field (Fig. 1b):  $\varphi = 0$  ( $\mathbf{H} \parallel \mathbf{c}$ ), when the fields at both resonances were closest, and  $\varphi \approx \pm 5^\circ$  ( $\mathbf{H} \parallel \mathbf{c}_1, \mathbf{c}_2$ ), when the field of one of the resonances reached a maximum. When the magnetic field direction approached  $\varphi = 0$  (Fig. 1a), both resonances began to interact on approach to one another: the lines became narrower and stronger. However, we were unable to ensure full coincidence of the lines for any direction of the magnetic field. The resonance lines remained split (Fig. 1b) and the splitting decreased as a function of temperature and frequency.

The dependence of the FMR frequencies of both lines on the magnetic field obtained for the  $\varphi = 0$  direction at  $T = 1.3$  K is plotted in Fig. 2. In a magnetic field  $H < H_A^*$  we recorded only one resonance line and the second could not be detected. The resonance spectra  $\nu(H)$  could not generally be described by means of the expressions in Eq. (3). In particu-

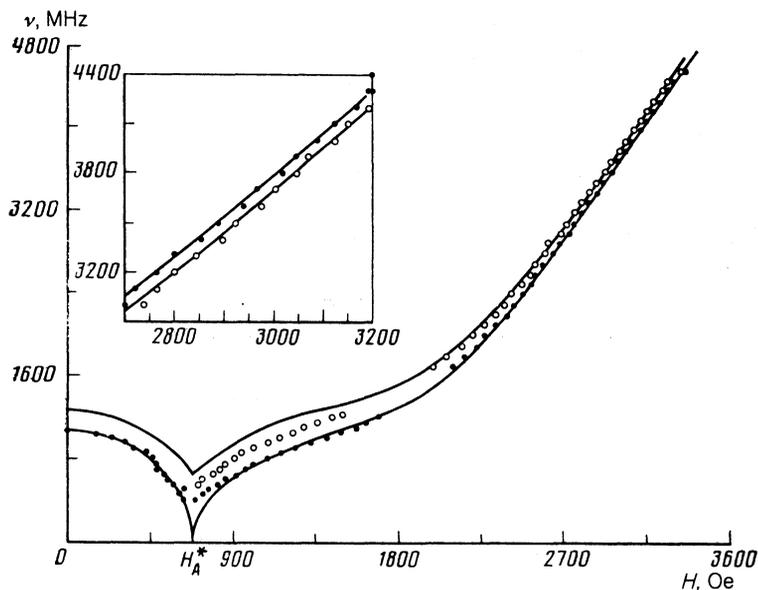


FIG. 2. Ferromagnetic resonance spectra for the field direction  $\mathbf{H} \parallel \mathbf{c}$  at  $T = 1.3$  K. The points are the experimental results obtained for two modes and the continuous curves are the results of calculation based on Eqs. (9)–(12). The inset shows in greater detail the hf part of the spectrum.

lar, when the field was oriented exactly along the  $\mathbf{c}$  axis ( $\varphi = 0$ ), the FMR spectrum became “softer” in a field  $H_A^*$  much lower than the easy-plane anisotropy field  $H_A$  which was found by extrapolation of the hf part of the spectrum ( $\nu \approx 3$  GHz) using the dependence  $\nu \approx \gamma(H - H_A)$  (Ref. 1). However, it was found that the expressions in Eq. (3) described the experimental results well if the angle between the field and the  $\mathbf{c}$  axis was  $\varphi = \pm 5^\circ$  (the direction  $\varphi = 0^\circ$  was the symmetry axis of the system). In fact, in this case we found (Fig. 3) that there were two different FMR modes and the field dependence of one of the modes (curve 1 in Fig. 3) fully obeyed the classical expressions. The behavior of the second mode will be described later.

The results obtained can be explained on the assumption that the investigated compound contains two weakly

interacting systems of ferromagnetically ordered ions with the easy-plane anisotropy. In each system the normal to the easy planes makes an angle of  $\psi \approx \pm 5^\circ$  with the  $\mathbf{c}$  axis (Fig. 4). When the field is oriented at the angle  $\varphi = \psi = 5^\circ$  (or  $-5^\circ$ ), then for one of the systems the field is exactly parallel to the difficult axis  $\mathbf{c}_1$  characterized by  $\varphi_1 = 0$  (or  $\mathbf{c}_2$ ), whereas for the other system it is oriented at an angle  $\varphi_2 = 2\psi = 10^\circ$  to the difficult axis  $\mathbf{c}_2$  ( $\mathbf{c}_1$ ). The two resonance modes in Fig. 3 then correspond to a resonance in each of these systems. When the magnetic field  $\mathbf{H}$  is parallel to the crystallographic axis  $\mathbf{c}$  (this represents the symmetric direction  $\varphi = 0$  in Fig. 1), the two systems are in equivalent positions. Then, if we ignore the interaction between the systems, the resonance spectra should be the same for both systems. However, we were unable to ensure coincidence of the two FMR modes in our experiments for any direction of the magnetic field (inset in Fig. 1b). Splitting of the resonance line

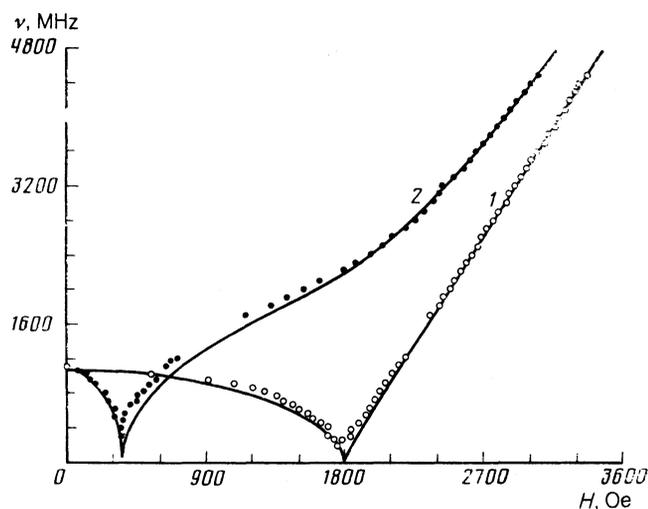


FIG. 3. Ferromagnetic resonance spectrum for the  $\mathbf{H} \parallel \mathbf{c}_1, \varphi = 5.35^\circ$  direction at  $T = 1.3$  K: 1) resonance mode corresponding to a system of planes (layers) for which the external field  $\mathbf{H}$  in this geometry is directed along the difficult axis  $\mathbf{c}_1$ , i.e.,  $\varphi_1 = 0^\circ$ ; 2) resonance mode corresponding to a second system of planes (layers) for which the field  $\mathbf{H}$  is oriented at an angle  $\varphi_2 = 10.7^\circ$  to the difficult anisotropy axis  $\mathbf{c}_2$ . The continuous curves are calculated using Eqs. (13) and (14).

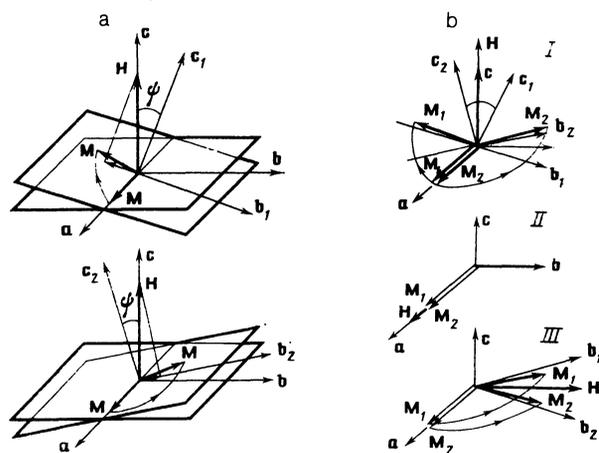


FIG. 4. a) Relative orientations of the magnetic easy planes in the neighboring layers of copper: the crystallographic plane  $ab$  correspond to the copper ion layers;  $ab_1$  and  $ab_2$  are the magnetic easy planes formed as a result of the magnetic anisotropy; the  $\mathbf{c}$  axis is the crystallographic one; the directions  $\mathbf{c}_1$  and  $\mathbf{c}_2$  correspond to the difficult magnetic anisotropy axes tilted relative to the  $\mathbf{c}$  axis by angles  $\pm \psi$ . The tilt of the magnetic moments is also shown when the external magnetic field  $\mathbf{H}$  is parallel to the  $\mathbf{c}$  axis. b) Reorientation of the magnetic moments in the neighboring layers for three directions of an external field: I)  $\mathbf{H} \parallel \mathbf{c}$ ; II)  $\mathbf{H} \parallel \mathbf{a}$ ; III)  $\mathbf{H} \parallel \mathbf{b}$ .

into two modes even when for  $\mathbf{H} \parallel \mathbf{c}$  demonstrated that the systems in question interacted with one another. Hence, we concluded that  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  consists of alternate magnetic layers of copper with the difficult magnetization axes rotated by  $\pm \psi$  relative to the crystallographic axis  $\mathbf{c}$  in the  $bc$  plane (Fig. 4).

This magnetic structure appears for the following reasons: it is known (see, for example, Ref. 10) that materials with the orthorhombic symmetry group  $D_{2h}^{15}$  admit the existence of an invariant  $M_{1y}M_{1z} - M_{2y}M_{2z}$ , where  $M_1$  and  $M_2$  are the magnetic moments of the neighboring layers. The presence of such a term had been confirmed experimentally<sup>10,11</sup> for  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ , which is a compound with a structure similar to that of the material investigated by us. Including an additional invariant, we can represent the energy of a ferromagnet including not only the relativistic terms, but also a weak exchange along the  $\mathbf{c}$  axis:

$$E = \frac{A}{2}(M_{1z}^2 + M_{2z}^2) - \frac{a}{2}(M_{1x}^2 + M_{2x}^2) - d(M_{1y}M_{1z} - M_{2y}M_{2z}) - H(M_1 + M_2) - J' \left[ M_{1z}M_{2z} \left( \frac{2}{g_{\perp}} \right)^2 + (M_{1x}M_{2x} + M_{1y}M_{2y}) \left( \frac{2}{g_{\parallel}} \right)^2 \right]. \quad (6)$$

This expression for the energy makes it necessary to introduce not only  $H_A$  and  $H_a$  but also two additional fields:  $H_D = dM_0(g_{\parallel}g_{\perp})^{1/2}/2$  and  $H_e = J'M_0$ .<sup>1)</sup> We recall that in our case we have  $H_A \gg H_a, H_D$ .

As pointed out already, if  $d = 0$  and the external field is oriented exactly along the  $\mathbf{c}$  axis, an increase of the field rotates the spins in the  $ac$  plane and when the field reaches a critical value  $H = H_A + H_a$ , the spins become oriented along the field. However, for  $d \neq 0$ , the situation is radically different. Elementary calculations show that the presence of an additional anisotropic term which has opposite signs for the neighboring layers (planes) results in the  $H_D^2 \ll H_A H_a$  case in an effective separation of the directions of the difficult axes  $\mathbf{c}_1$  and  $\mathbf{c}_2$  in the neighboring layers by angles  $\pm \psi$ , where

$$\sin \psi \approx H_D/H_A. \quad (7)$$

The easy planes rotate similarly. We shall denote their new positions by  $ab_1$  and  $ab_2$ . In the absence of the field the complexity of the structure of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  is not manifested because the magnetic moments in the neighboring layers are parallel to the common easy axis  $\mathbf{a}$ .

However, in a magnetic field applied exactly along the  $\mathbf{c}$  axis, reorientation occurs in a manner completely different from that in the  $d = 0$  case: since the magnetic field has finite projections along the  $\mathbf{b}_1$  and  $\mathbf{b}_2$  axes in the easy planes (Fig. 4), the spins are tilted out of the  $ab_1$  and  $ab_2$  planes and at the same time become reoriented within the easy planes, so that in a field

$$H_A^* \approx (H_A + H_a) \left[ 1 + \sin^2 \psi \left( \frac{H_A}{H_a} \right) \left( \frac{H_A + 2H_a}{H_a} \right) \right]^{-1/2} \approx H_A \left[ 1 + \sin^2 \psi \left( \frac{H_A}{H_a} \right)^2 \right]^{-1/2} \quad (8)$$

the  $x$  component of the magnetization disappears. We can

easily show that in this case the whole macroscopic magnetization disappears in the  $xy$  plane, since the  $y$  components of the magnetic moments in the neighboring layers are directed opposite to one another. At the transition point the  $z$  component of the magnetic moment is  $M_z \approx M_0(g_{\perp}/2)(H_A^*/H_A)$ . A further increase of the field causes continuous rotation of the spins toward the  $z$  axis. The most important point in our case is that  $H_A \gg H_a$  and, therefore, even for a small angle  $\psi$  the shift of the critical field is very considerable: for  $\psi = 5^\circ$ , we have  $H_A^* \sim 0.4H_A$ . The results of our measurements indicate that  $H_D = 160$  Oe for  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ ; for comparison we can mention that in the case of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  ( $n = 2$ ) the corresponding value is  $H_D = 119$  Oe (Refs. 10 and 11).

Therefore, using the above model we cannot, strictly speaking, regard  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  as a ferromagnet since the neighboring planes containing magnetic ions are inequivalent. However, splitting of this system into ferromagnetic planes with different directions of the difficult axes seems to us a clearer interpretation than introduction of the ferromagnetic and antiferromagnetic vectors  $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2$  and  $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$ , where  $\mathbf{M}_1$  and  $\mathbf{M}_2$  are moments in the neighboring planes. It should be pointed out that the tilt of the difficult axes  $\psi$  is independent of temperature (within the limits of the experimental error).

Naturally, when the directions of the anisotropy axes in the neighboring layers are not identical, the excitation spectrum will have two branches. For the field directed exactly along the  $\mathbf{c}$  axis, the resonance frequencies are as follows:

if  $H < H_A^*$ , then

$$\nu_1^2 = \gamma^2 H_a (H_A + H_a) \left[ 1 - \left( \frac{H}{H_A^*} \right)^2 \right], \quad (9)$$

$$\nu_2^2 = \gamma^2 \left\{ H_a (H_A + H_a) \left[ 1 - \left( \frac{H}{H_A^*} \right)^2 \right] + H_e \frac{H_A^2 - H^2}{H_A} \right\};$$

if  $H > H_A^*$ , then

$$\begin{aligned} \nu_1^2 &= \gamma^2 (H \cos \theta - H_A \cos 2\theta + 2H_D \sin 2\theta) \\ &\times (H \cos \theta - H_A \cos^2 \theta - H_a + H_D \sin 2\theta - H_e \sin^2 \theta), \\ \nu_2^2 &= \gamma^2 (H \cos \theta - H_A \cos^2 \theta - H_a + H_D \sin 2\theta + H_e \cos^2 \theta) \\ &\times (H \cos \theta - H_A \cos 2\theta + 2H_D \sin 2\theta + H_e \cos 2\theta), \end{aligned} \quad (10)$$

where the value of the angle  $\theta$  ( $M_z = \frac{1}{2} g_{\perp} M_0 \cos \theta$ ) can be found from the following equation:

$$H \sin \theta = H_D \cos 2\theta + (H_A - H_a) \sin \theta \cos \theta, \quad (11)$$

whereas the exact (deduced using the model in question) value of the critical field is

$$H_A^* = (H_A + H_a) \left[ 1 + \left( \frac{H_D}{H_a + H_e} \right)^2 \right]^{-1/2} \times [1 - H_D^2 (H_a + H_e)^{-1} (H_A + H_a)^{-1}]. \quad (12)$$

For  $\mathbf{H} \parallel \mathbf{c} \parallel \mathbf{z}$ , the difference between the frequencies is clearly due to the existence of the exchange interaction  $H_e$  between the planes (layers). It follows from Eqs. (9)–(11) that one of the frequencies ( $\nu_1$ ) vanishes in the critical field  $H = H_A^*$ . At the same point we have  $\nu_2^2 = \gamma^2 H_e (H_A^2 - H_A^{*2})/H_A$ , and since the investigated substance is characterized by  $H_e$

$\sim H_a$ , it follows that the upper branch of the oscillations does not demonstrate explicit softening in the vicinity of the critical point (field). In higher fields  $H \gg H_A^*$  the difference between the frequencies is practically constant:  $\Delta\nu \approx \gamma H_e$ .

It follows from Eqs. (9)–(12) that inclusion of the exchange interaction is important only if the field direction is practically coincident with the  $\mathbf{c}$  axis; if the field is directed at an angle  $\varphi$  to the  $\mathbf{c}$  axis, then the mismatch of the anisotropy fields in the neighboring layers makes the frequencies  $\nu_1$  and  $\nu_2$  different even in the absence of the interlayer interaction (for one of the frequencies the angle between the field and the true anisotropy axis is  $\varphi + \psi$ , and for the other frequency it is  $\varphi - \psi$ ). Ignoring terms  $\sim H_D^2/H_A H_a$  (when it is possible to reduce the effect of the additional invariant to rotation of the anisotropy axis) and  $H_e/H_A$ , we find that the expression for the resonance frequency is as follows when the direction of the field is inclined at an angle  $\chi$  to the true anisotropy axis:

$$\nu = \gamma \left[ H_a (H_A + H_a) \left( 1 - \left( \frac{H}{H_A^*} \right)^2 \right) \right]^{1/2}, \quad H < H_A^*(\chi),$$

$$\nu = \gamma [H \cos(\beta - \chi) - H_a - H_A \cos^2 \beta]^{1/2} \quad (13)$$

$$\times [H \cos(\beta - \chi) - H_A \cos 2\beta]^{1/2}, \quad H > H_A^*(\chi),$$

and the angle  $\beta$  is found from the condition

$$2H \sin(\beta - \chi) = H_A \sin 2\beta. \quad (14)$$

In particular, when the external field is directed along one of the  $\mathbf{c}_1$  or  $\mathbf{c}_2$  axes (i.e.,  $\varphi = \pm \psi$ ) then for one of the modes we have  $\chi = 0$  and the expressions in Eq. (13) reduce naturally to Eq. (3), whereas for the second mode we have  $\chi = 2\psi$ . The experimental and calculated spectra for the  $\mathbf{H} \parallel \mathbf{c}_1$  geometry are shown in Fig. 3. We find the exact values  $\psi = 5.35^\circ$ , and the anisotropy fields  $H_A = 1740$  Oe and  $H_a = 68$  Oe, and the field  $H_D = 160$  Oe were determined from the condition of the best match between the experimental results (at  $T = 1.3$  K) and the theory. Allowance for the demagnetizing field yielded the following values of the anisotropy constants at  $T = 1.3$  K:  $AM_0 = 1320$  Oe and  $aM_0 = 68$  Oe.

We must mention once again that when the FMR frequencies in the neighboring planes are very different, the resonances are completely independent and the weak interlayer interaction can be ignored. If the frequency of an oscillatory field is identical with the resonance frequency in one plane, then the magnetic moments in the neighboring plane are not in resonance and are not excited by the hf field.

If the magnetic field is directed along the crystallographic  $\mathbf{c}$  axis, it is equivalent for all the magnetic layers (Fig. 4):  $\varphi_1 = \varphi_2 = \psi = 5.35^\circ$ . In this case the FMR frequencies of both systems of planes should coincide if there is no interaction:  $\nu_1 = \nu_2$ . However, a weak exchange interaction between them lifts the degeneracy so that we have  $\nu_1 \neq \nu_2$  (Fig. 1). The initially independent oscillations of the moments in the neighboring planes are now coupled and this can be deduced from the change in the resonance line profile when  $\mathbf{H}$  approaches the  $\mathbf{c}$  axis (Fig. 1a). The resonance spectrum then reveals the presence of two modes (Fig. 2): one mode corresponds to phase-locked oscillations of the mo-

ments, whereas the moments in the other mode oscillate in antiphase. The continuous curves in Fig. 2 are the results of calculations based on Eqs. (9)–(12). We can see that, in general, the agreement between the theory and experiment is reasonable. Some difference between the theoretical and experimental curves in the range of fields close to  $H_A^*$  is clearly associated with the fact that the weak interlayer interaction can be due not only to the exchange but also, for example, to the dipole forces and, therefore, can depend on the magnetic field. At frequencies  $\nu > 3$  GHz the splitting is practically constant and amounts to  $\Delta H = 35$  Oe (inset in Fig. 1b and Fig. 2). This is in agreement with the interlayer exchange field  $H_e = 45$  Oe obtained in Ref. 4.

Our explanation is, generally speaking not the only one possible. In particular, the transition to the monoclinic phase may be accompanied by thinning of a crystal, i.e., by the formation of macroscopic domains with rotate anisotropy axes. Clearly, allowance for this effect will have practically the same consequences as inclusion of the invariant  $M_{1y} M_{1z} - M_{2y} M_{2z}$ . The only difference is that in the case of twinning the interaction between two resonance modes may be due to the dipole forces and, in order to ensure that the interaction exists, in reality, the shape of the domains should differ considerably from that of a plate. This seems to be unlikely so that we shall consider a model with an additional invariant, especially as a similar invariant with a close value of  $H_D$  had been confirmed experimentally for  $(C_2H_5NH_3)_2 CuCl_4$  which with respect to the crystal structure resembles the material under investigation.<sup>10,11</sup>

We must stress nevertheless that the direct proof of the validity of the proposed model would be discovery, for example by the method of neutron diffraction, of an antiferromagnetic moment induced by an external field  $\mathbf{H} \parallel \mathbf{c}$ . In fact, when a field is applied exactly along the  $\mathbf{c}$  axis, as the spins rotate in the  $ab_1$  and  $ab_2$  planes (Fig. 4) the antiferromagnetic vector  $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$  appears and increases with the field (here,  $\mathbf{M}_1$  and  $\mathbf{M}_2$  apply to the neighboring layers); this vector is directed along the  $\mathbf{b}$  axis. At the transition point when the field is  $H_A^*$  the antiferromagnetic vector reaches its maximum value ( $L \approx 0.85M_0$ ) and decreases smoothly as the field increases further.

The magnetic structure described above should have practically no effect on the FMR spectra in the case when the magnetic field is directed in the  $ab$  plane, i.e.,  $\mathbf{H} \perp \mathbf{c}$ . Figure 5a shows the experimental FMR spectra obtained for two directions of the field at  $T = 1.3$  K: 1)  $\mathbf{H} \parallel \mathbf{a}$  with the field along the easy axis in the plane of the layers; 2)  $\mathbf{H} \parallel \mathbf{b}$ , i.e., perpendicular to the easy axis in the plane of the layers. The continuous curves are plotted on the basis of Eqs. (4) and (5) applicable to an easy-plane ferromagnet. In fact, the agreement between the experimental and calculated curves is good. This is due to the fact that in the  $\mathbf{H} \perp \mathbf{c}$  geometry the tilt of the magnetic difficult axes (Fig. 4) has less effect on the static and dynamic properties of the system than in the  $\mathbf{H} \parallel \mathbf{c}$  geometry described above.

If the field  $\mathbf{H}$  is directed along the easy axis  $\mathbf{a}$  common to all the magnetic layers (i.e., if  $\mathbf{H} \parallel \mathbf{a}$ ) and consequently, it is directed along the magnetization in a crystal, the sample is a collinear ferromagnet. For  $\mathbf{H} \parallel \mathbf{b}$ , then in a weak field  $H < H_a$  the magnetic moments are rotated in each layer plane. In a field  $H = H_a$  the moments in some layers are directed along

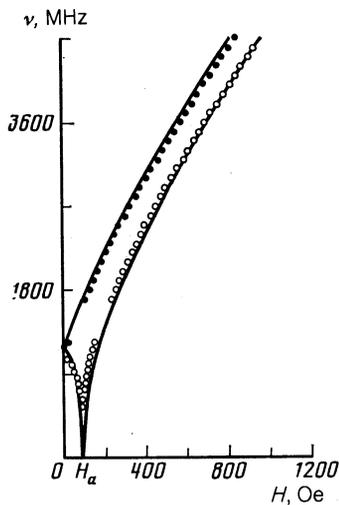


FIG. 5. Ferromagnetic resonance spectrum for two directions of the field  $\mathbf{H}$  in the  $ab$  plane at  $T = 1.3$  K:  $\bullet$   $\mathbf{H} \parallel \mathbf{a}$ ;  $\circ$   $\mathbf{H} \parallel \mathbf{b}$ . The continuous curves are calculated using standard expressions given by Eqs. (4) and (5) for a ferromagnetic resonance in an easy-plane ferromagnet.

$\mathbf{b}_1$  and along  $\mathbf{b}_2$  in other layers, as shown in Fig. 4 ( $H_a \ll H_A$ ). In this case the corrections to  $H_a$  due to the tilt of the difficult anisotropy axes are very small. Softening of the resonance should occur not in the field  $H_a$ , but in a very similar field  $H \approx H_a / \cos \psi = 0.996 H_a$ . The angle between  $\mathbf{b}_1$  and  $\mathbf{b}_2$  amounts to  $2\psi = 10.7^\circ$ , as already mentioned. Therefore, a weak tilt of the moments in the neighboring layers appears in a crystal and a weak antiferromagnetic moment  $L \approx 2M_0 \sin \psi \leq 0.2M_0$  is induced. In view of the smallness of the angle  $\psi$  the induced antiferromagnetic moment is more difficult to detect in the  $\mathbf{H} \parallel \mathbf{b}$  geometry than in the  $\mathbf{H} \parallel \mathbf{c}$  case (described above). Theoretically distinguishable directions of the difficult magnetic anisotropy axis in neighboring layers, deduced allowing for the interaction between the layers, should give rise to two resonance modes for any direction of the external field [even zero field, where  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  is a collinear ferromagnet]. However, in reality in the

$\mathbf{H} \parallel \mathbf{c}$  geometry the second mode (antiphase oscillations of the moments in neighboring planes) is excited weakly and it is much more difficult to detect it than in the  $\mathbf{H} \parallel \mathbf{c}$  geometry. It is clear from Fig. 5 that in both geometries for  $\mathbf{H} \parallel \mathbf{c}$  there is only one resonance mode and no splitting. The FMR frequency does not vanish entirely for any direction of the field. In the  $\mathbf{H} \parallel \mathbf{b}$  geometry the residual splitting of the spectrum is estimated to be  $\approx 500$  MHz at  $T = 1.3$  K (Fig. 5); the value decreases on increase in temperature. The reason for this splitting is not clear.

The authors are grateful to A.S. Borovik-Romanov, V.L. Pokrovskii, and G.V. Uimin for valuable discussions, and to A. N. Bazhan for measurements of the magnetization.

<sup>1)</sup>In connection with our comments after Eqs. (3)–(5), note that we shall omit the tilde symbol also in the case of  $\tilde{H}_D = H_D (g_{\parallel} g_{\perp})^{1/2} / 2$  and  $\tilde{H}_c \equiv H_c$ .

<sup>2)</sup>S. O. Demokritov, N. M. Kreines, V. I. Kudinov, and S. V. Petrov, *Pis'ma Zh. Eksp. Teor. Fiz.* **46**, 105 (1987) [*JETP Lett.* **46**, 128 (1987)].

<sup>3)</sup>L. J. de Jongh and A. R. Miedema, *Adv. Phys.* **23**, 1 (1974).

<sup>4)</sup>A. R. Miedema, P. Bloembergen, J. H. P. Colpa, F. W. Gorter, L. J. de Jongh, and L. Noordermeer, *Proc. Nineteenth Annual Conf. on Magnetism and Magnetic Materials*, Boston, 1973, in: *AIP Conf. Proc. No. 18*, 806 (1974).

<sup>5)</sup>H. Yamazaki, *J. Phys. Soc. Jpn.* **41**, 1911 (1976).

<sup>6)</sup>J. J. M. Steijger, E. Frikkee, L. J. de Jongh, and W. J. Huiskamp, *Physica B + C (Utrecht)* **123**, 271, 284 (1984).

<sup>7)</sup>R. D. J. Willett, *J. Chem. Phys.* **41**, 2243 (1964).

<sup>8)</sup>Yu. S. Karimov, *Zh. Eksp. Teor. Fiz.* **65**, 261 (1973) [*Sov. Phys. JETP* **38**, 129 (1974)].

<sup>9)</sup>R. J. H. Wong, R. D. Willett, and J. E. Drumheller, *J. Chem. Phys.* **74**, 6018 (1981).

<sup>10)</sup>E. A. Turov, *Physical Properties of Magnetically Ordered Crystals*, Academic Press, New York (1965).

<sup>11)</sup>P. Bloembergen, P. J. Berkhout, and J. J. M. Franse, *Int. J. Magn.* **4**, 219 (1973).

<sup>12)</sup>V. N. Vasyukov, A. V. Zhuravlev, S. N. Lukin, Yu. G. Pashkevich, V. L. Sobolev, and V. T. Telepa, *Fiz. Tverd. Tela (Leningrad)* **26**, 1297 (1984) [*Sov. Phys. Solid State* **26**, 790 (1984)].

Translated by A. Tybulewicz