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# Magnetic phases of quasi-two-dimensional antiferromagnet on triangular lattice $\text{CuCrO}_2$

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We have carried out  $^{63,65}\text{Cu}$  NMR spectra measurements in magnetic field up to about 45 T on single crystal of a multiferroic triangular antiferromagnet  $\text{CuCrO}_2$ . The measurements were performed for magnetic fields aligned along the crystal  $c$ -axis. Field and temperature evolution of the spectral shape demonstrates a number of phase transitions. It was found that the 3D magnetic ordering takes place in the low field range ( $H \lesssim 15$  T). At higher fields magnetic structures form within individual triangular planes whereas the spin directions of the magnetic ions from neighboring planes are not correlated. It is established that the 2D-3D transition is hysteretic in field and temperature. Lineshape analysis reveals several possible magnetic structures existing within individual planes for different phases of  $\text{CuCrO}_2$ . Within certain regions on the magnetic H-T phase diagram of  $\text{CuCrO}_2$  a 3D magnetic ordering with tensor order parameter is expected.

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## I. INTRODUCTION

The problem of an antiferromagnet on a triangular planar lattice has been intensively studied theoretically.<sup>1-5</sup> The ground state in the Heisenberg and XY models is a “triangular” planar spin structure with three magnetic sublattices arranged  $120^\circ$  apart. The orientation of the spin plane is not fixed in the exchange approximation in the Heisenberg model. For the simplest semiclassical model of triangular structure with single antiferromagnetic exchange interaction between nearest neighbors the applied static field does not remove the degeneracy of the spin configurations. Therefore the usual small corrections such as quantum and thermal fluctuations, and relativistic interactions in the geometrically frustrated magnets play an important role in the formation of the equilibrium state.<sup>2,5,6</sup> Interests in triangular antiferromagnets are fueled by a rich variety of exotic phases which can be realized in such systems. Such model systems can be tested experimentally in three-dimensional (3D) crystals, where magnetic ions are located in the triangular lattice sites of crystallographic planes. If the in-plane interactions strongly exceed inter-plane interactions we can expect that such quasi-two-dimensional (quasi-2D) magnet will demonstrate the features typical for 2D models. Various realizations of quasi-2D antiferromagnets on triangular lattice are discussed in reviews (Refs. 7,8).

$\text{CuCrO}_2$  is an example of quasi-2D antiferromagnet ( $S = 3/2$ ) with triangular lattice structure. Early neutron scattering experiments reveal that the electronic spin structure in  $\text{CuCrO}_2$  is in a planar  $120^\circ$ -degree configuration below  $T_c \approx 24$  K,<sup>9</sup> with a disorder caused by the frustration of the inter-plane exchange bonds. More recently, neutron scattering investigations<sup>10</sup> in  $\text{CuCrO}_2$  single crystals detected a 3D planar magnetic order with incommensurate wave vector that slightly differs from the wave vector of a commensurate  $120^\circ$ -degrees structure.

The magnetic ordering is accompanied by a simultaneous crystallographic distortion<sup>11</sup> of the regular triangular lattice and by the appearance of an electrical polarization. According to neutron scattering experiments<sup>12</sup> the interaction between nearest  $\text{Cr}^{3+}$  ions within triangular plane is strongest. This in-plane interaction is more than 20 times larger than the frustrated inter-plane interaction. Thus,  $\text{CuCrO}_2$  can be considered as an example of quasi-2D antiferromagnet.

We present a NMR study of the low temperature magnetic structure of  $\text{CuCrO}_2$  in fields up to 45 T aligned along the crystallographic  $c$ -axis. Such field direction corresponds to orientation within the spin plane of the spiral structure in low field range. The highest field in our experiments is about  $1/6$  of the saturation field which can be estimated using susceptibility value as  $\mu_0 H_{\text{sat}} \approx 280$  T. Analysis of temperature and field evolution of NMR spectral shape reveals the magnetic H-T phase diagram of  $\text{CuCrO}_2$  and suggests the realized magnetic phases. In most respects, the main features of the observed phase diagram are consistent with the phase diagram obtained from electric polarization measurements measured in pulsed magnetic fields.<sup>13,14</sup> The observed spectra at low magnetic field ( $\mu_0 H \lesssim 15$  T) can be well described by a 3D magnetic structure as detected by neutron experiments at zero field,<sup>12</sup> whereas the NMR spectra observed at higher fields indicate the loss of the 3D magnetic ordering of  $\text{CuCrO}_2$ . In this case the magnetic state of  $\text{CuCrO}_2$  can be modeled as a number of randomly stacked independently ordered 2D triangular magnetic layers. The transition from 3D to 2D state exhibits hysteretic behavior in both field and temperature. Surprisingly, the magnetic phase identified with NMR as 2D state at the same H-T region also demonstrates magnetically driven electric polarization.<sup>13</sup> These facts indicate that the high field magnetic structure is, in fact, a 3D-polar phase with tensor order parameter, akin to

## II. CRYSTAL AND MAGNETIC STRUCTURE

The structure  $\text{CuCrO}_2$  consists of magnetic  $\text{Cr}^{3+}$  ( $3d^3$ ,  $S = 3/2$ ), nonmagnetic  $\text{Cu}^+$ , and  $\text{O}^{2-}$  triangular lattice planes, which are stacked along  $c$ -axis in the sequence Cr-O-Cu-O-Cr (space group  $R\bar{3}m$ ,  $a = 2.98 \text{ \AA}$ ,  $c = 17.11 \text{ \AA}$  at room temperature<sup>10</sup>). The layer stacking sequences are  $\alpha\gamma\beta$ ,  $\beta\alpha\gamma$ , and  $\beta\beta\alpha\alpha\gamma\gamma$  for Cr, Cu and O ions, respectively. The crystal structure of  $\text{CuCrO}_2$  projected on the  $ab$ -plane is shown in Fig.1a. The distances between the nearest planes denoted by different Greek letters for copper and chromium ions and the pairs of planes for oxygen ions are  $c/3$ , whereas the distance between the nearest oxygen planes denoted by the same letters is  $(1/3 - 0.22)c$  (Ref. [10]). No structural phase transition has been reported at temperatures higher than Néel ordering temperature ( $T > T_c \approx 24 \text{ K}$ ). In the magnetically ordered state the triangular lattice is distorted, so that one side of the triangle becomes slightly smaller than the two other sides:  $\Delta a/a \approx 10^{-4}$  (Ref. [11]).

The magnetic structure of  $\text{CuCrO}_2$  has been in-

tensively investigated by neutron diffraction experiments.<sup>9,10,16–18</sup> It was found that the magnetic ordering in  $\text{CuCrO}_2$  occurs in two stages.<sup>18,19</sup> At the higher transition temperature  $T_{c1} = 24.2 \text{ K}$ , a transition to a 2D ordered state occurs, whereas below  $T_{c2} = 23.6 \text{ K}$ , a 3D magnetic order with incommensurate propagation vector  $\mathbf{k}_{ic} = (0.329, 0.329, 0)$  along the distorted side of triangular lattice planes<sup>11</sup> is established. The magnetic moments of  $\text{Cr}^{3+}$  ions can be described by the expression

$$\mathbf{M}(\mathbf{r}_{i,j}) = M_1 \mathbf{e}_1 \cos(\mathbf{k}_{ic} \mathbf{r}_{i,j} + \Theta) + M_2 \mathbf{e}_2 \sin(\mathbf{k}_{ic} \mathbf{r}_{i,j} + \Theta), (1)$$

where  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are two perpendicular unit vectors determining the spin plane orientation with the normal vector  $\mathbf{n} = \mathbf{e}_1 \times \mathbf{e}_2$ ,  $\mathbf{r}_{i,j}$  is the vector to the  $i, j$ -th magnetic ion and  $\Theta$  is an arbitrary phase. The spin plane orientation and the propagation vector of the magnetic structure are schematically shown at the bottom of Fig.1. For zero magnetic field  $\mathbf{e}_1$  is parallel to  $[001]$  with  $M_1 = 2.8(2) \mu_B$ , while  $\mathbf{e}_2$  is parallel to  $[1\bar{1}0]$  with  $M_2 = 2.2(2) \mu_B$  (Ref. [18]). The pitch angle between the neighboring Cr moments corresponding to the observed value of  $\mathbf{k}_{ic}$  along the distorted side of triangular lattice planes is equal to  $118.5^\circ$  which is very close to  $120^\circ$  expected for regular triangular lattice planes structure.

Owing to the crystallographic symmetry at  $T > T_c$  in the ordered phase ( $T < T_c$ ) we can expect *six* magnetic domains. The propagation vector of each domain can be directed along one side of the triangle and can be positive or negative. As reported in Refs. [17,20,21], the distribution of the domains is strongly affected by the cooling history of the sample. For field aligned along  $[001]$  axis all six domains are equivalent.

Inelastic neutron scattering data<sup>12</sup> has shown that  $\text{CuCrO}_2$  can be considered as a quasi-2D magnet. The spiral magnetic structure is defined by the strong exchange interaction between the nearest  $\text{Cr}^{3+}$  ions within the triangular lattice planes with exchange constant  $J_{ab} = 2.3 \text{ meV}$ . The inter-planar interactions are at least one order of magnitude weaker than the in-plane interaction and frustrated.

Results of the magnetization, electric polarization, ESR and NMR experiments<sup>20–22</sup> have been discussed within the framework of the planar spiral spin structure at fields studied experimentally:  $\mu_0 H < 14 \text{ T} \ll \mu_0 H_{sat}$ . ( $\mu_0 H_{sat} \approx 280 \text{ T}$ ). The orientation of the spin plane is defined by the biaxial crystal anisotropy. One *hard* axis for the normal vector  $\mathbf{n}$  is parallel to the  $c$  direction and the second axis is perpendicular to the direction of the distorted side of the triangle. The anisotropy along  $c$  direction dominates with anisotropy constant approximately hundred times larger than that within  $ab$ -plane resulting from the distortions of the triangular structure. A magnetic phase transition was observed for the field applied perpendicular to one side of the triangle ( $\mathbf{H} \parallel [1\bar{1}0]$ ) at  $\mu_0 H_c = 5.3 \text{ T}$ , which was consistently described<sup>17,20,22</sup> by the reorientation of the spin plane from  $(110)$  ( $\mathbf{n} \perp \mathbf{H}$ ) to  $(1\bar{1}0)$  ( $\mathbf{n} \parallel \mathbf{H}$ ). This spin reorientation to “umbrella like” phase happens due to the weak susceptibility anisotropy

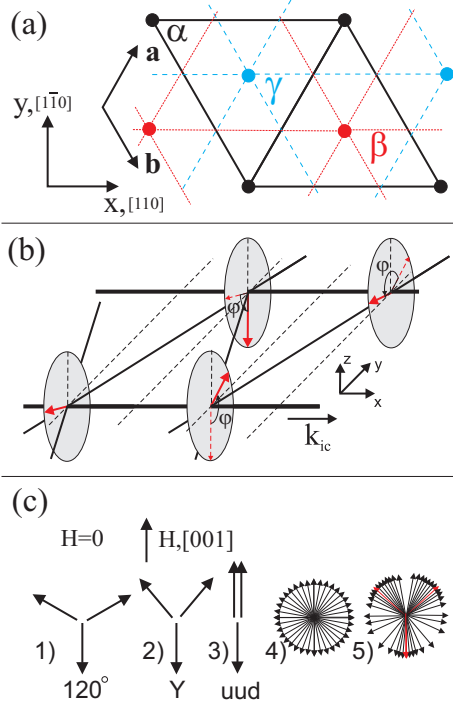


FIG. 1: (color online) (a) Crystal structure of  $\text{CuCrO}_2$  projected on the  $ab$ -plane. The three layers,  $\alpha\beta\gamma$ , are the positions of  $\text{Cr}^{3+}$  ions. (b) Schema of the spin structure within one triangular plane at zero field (solid red arrows). The gray circles show the orientation of the spin plane  $(110)$ .  $\varphi = 118.5^\circ$  is a pitch angle of the structure, see text. The incommensurate wavevector  $\mathbf{k}_{ic}$  is collinear with the base of the triangle (thick line). (c) Schema of spin configurations for regular and weakly distorted 2D-triangle structures at low fields.

of the spin structure  $\chi_{\parallel} \approx 1.05\chi_{\perp}$ , where  $\parallel$  and  $\perp$  refer to fields parallel and perpendicular to  $\mathbf{n}$ , respectively. Further increase of applied field does not result to any additional phase transitions up to fields  $\approx 60$  T.<sup>13,14</sup>

For fields directed parallel to  $c$  axis the magnetic phase diagram is much more complex. According to electric polarization studies in  $\text{CuCrO}_2$ , at fields up to 92 T<sup>13,14</sup> the low temperature magnetic structure undergo a number of transitions. The phases realized during the magnetization process are not yet identified and shall be discussed in this paper.

### III. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The sample we used in this experiment is the same as described in Ref. [21]. Measurements were taken on a superconducting Cryomagnetics 17.5 T magnet, a 30 T resistive magnet and 45 T hybrid magnet at the National High Magnetic Field Laboratory. All magnets were field sweepable. For technical reasons zero field cooling of the sample could not be performed while using 45 T magnet.  $^{63,65}\text{Cu}$  nuclei (nuclear spins  $I = 3/2$ , gyromagnetic ratios  $^{63}\gamma/2\pi = 11.285$  MHz/T,  $^{65}\gamma/2\pi = 12.089$  MHz/T) were probed using pulsed NMR technique. The spectra were obtained by summing fast Fourier transforms (FFT) or integrating the averaged spin-echo signals as the field was swept through the resonance line. NMR spin echoes were obtained using  $\tau_p - \tau_D - 2\tau_p$  pulse sequences, where the pulse lengths  $\tau_p$  were 1-3  $\mu\text{s}$ , the times between pulses  $\tau_D$  were 15  $\mu\text{s}$ . Measurements were carried out in the temperature range  $2 \leq T \leq 40$  K stabilized with a precision better than 0.1 K.

### IV. EXPERIMENTAL RESULTS

The crystal cell of  $\text{CuCrO}_2$  contains single copper ion. As a result the  $^{63,65}\text{Cu}$  NMR spectra for the paramagnetic states consist of two sets of triplets, corresponding to  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  isotopes. Each triplet corresponds to quadrupolar split transitions: a central line ( $m_I = +1/2 \leftrightarrow -1/2$ ) and two quadrupole satellite transitions ( $m_I = \pm 3/2 \leftrightarrow \pm 1/2$ ).<sup>21</sup> Below the magnetic ordering temperature, the narrow NMR line transforms into a broad spectrum characteristic of incommensurate magnetic structure. The shape of NMR spectrum is defined by the distribution of local magnetic fields on the copper nuclei within the sample. The observed shapes of NMR spectra depend on field, temperature and cooling history. For different lines in the triplet the spectra measured at the same conditions were found to be of the same shape. So, we chose the lines which were well distanced from neighbours to avoid overlapping.

In order to facilitate the discussion connecting the magnetic structure to the NMR spectra, we shall refer extensively to the schematic phase diagram of  $\text{CuCrO}_2$

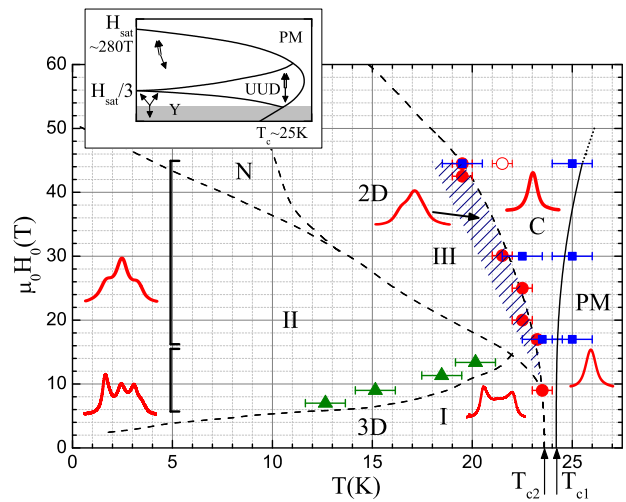


FIG. 2: (color online) H-T magnetic phase diagram of  $\text{CuCrO}_2$ . The dashed lines are the boundaries of magnetic phases possessing electric polarization from Ref.13. Symbols mark the boundaries between different phases obtained from temperature evolution of  $^{63,65}\text{Cu}$  NMR spectra. Red circles and green triangles represent fields where transformations of NMR spectra shapes were observed. Solid red circles denote the points at which the spectral shape is transformed from the paramagnetic phase when the sample is cooled in field. Open red circle corresponds to the spectra taken as the temperature increases. Blue squares show positions of kink like anomalies in temperature dependencies of spin-lattice relaxation rate  $T_1^{-1}(T)$ . Solid line is guide to the eyes. NMR spectra observed in different areas are marked schematically on the phase diagram. Inset is the sketch of phase diagram taken from Ref. [23]. Shaded areas cover the experimental H-T region within which this work was performed.

shown in Fig.2. The phase transitions observed in Refs.[13,14] as anomalies on field dependencies of electric polarization are marked with dashed lines. The two-step transition from paramagnetic state to the ordered phase at zero field are marked with arrows.<sup>18,19</sup>

The temperature evolutions of  $^{63}\text{Cu}$  NMR spectra measured at frequencies 105.81 MHz, 498 MHz cooled in field from the paramagnetic state are shown in the Fig.3. The spectra shown in Fig.3a ( $\mu_0H \approx 9$  T) is typical for spectra measured at fields below 15 T. At high temperatures,  $T > T_{c2}$ , each spectrum is characterized by a single peak, as expected for paramagnetic phase. On the other hand, below  $T_{c2}$ , the spectra demonstrate a two-horn pattern characteristic of incommensurate structure, with a low-field peak more intense than the high-field peak. At temperatures below 20 K the two-horn spectrum becomes distorted: an additional maximum at the middle of the NMR spectrum appears and the high field maximum splits into two.

For fields above 15 T (and up to 45 T), the typical temperature evolution of the spectra is shown in Fig.3b (showing data for  $\mu_0H = 42.5$  T). The spectra evolves from a single-peak line for  $T \gtrsim 20$  K to an asymmetric

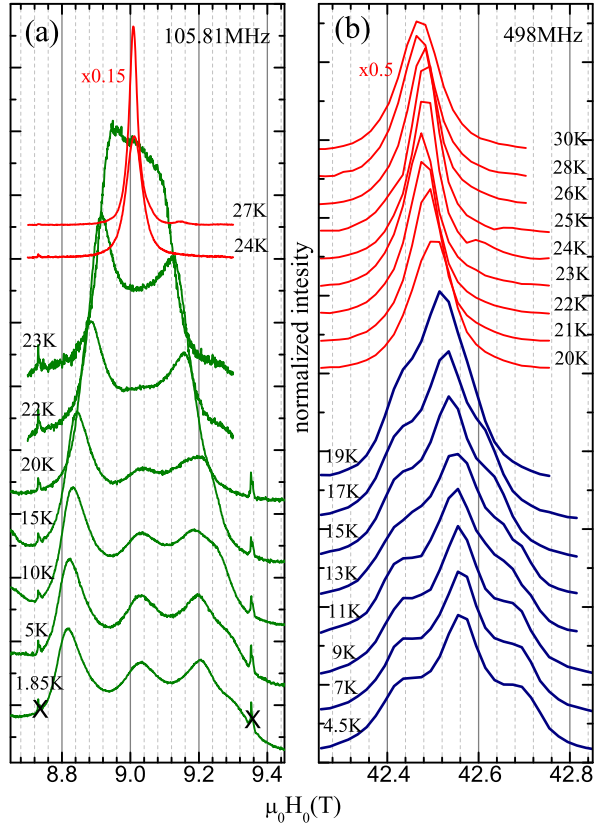


FIG. 3: (color online) Typical temperature evolution of  $^{63}\text{Cu}$  NMR spectra ( $m_I = +1/2 \leftrightarrow -1/2$  transition) for field cooled samples. Data are taken at frequencies a) 105.81 MHz and b) 498 MHz. Color reference to the spectral lineshape as described in the text: red - single peak, green - double horn pattern (both distorted and undistorted), and blue - helmet shape (symmetric and asymmetric). The peaks marked with crosses are spurious  $^{63,65}\text{Cu}$  NMR signals from the probe.

helmet-shaped line which becomes more symmetric as the temperature is lowered. In the main panel of Fig.2, the cross-hatched region in the phase diagram indicates where the asymmetric helmet lineshape was observed.

Fig.4 shows NMR spectra measured at  $T = 20$  K and 5 K at different fields. All spectra were measured while the sample is cooled in field (FC). The spectra in Figs.3,4 are differentiated by different colors: spectra with single peaks are red colored, two-horn and distorted two-horn shaped spectra are green colored. NMR spectra with helmet shape or distorted helmet shape spectra are blue colored. The spectrum transformation from single-peaked line-shape to two-horn or helmet-like one is sharp (see Fig.3). These transitions are marked on the phase diagram by red circles. The error bars at these points are defined by the temperature step between measured spectra.

The transition from the single-peak line to a broad line is hysteretic at high fields. At 44.5 T, the transition temperature upon cooling differs from the transition upon heating by 2 K. The open red circle on the phase dia-

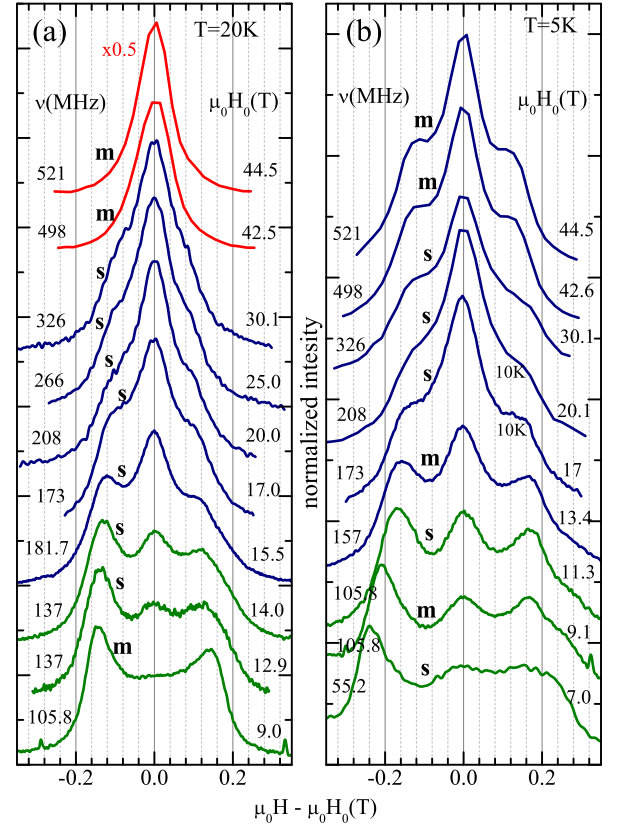


FIG. 4: (color online) Field evolution of  $^{63}\text{Cu}$  NMR spectra measured at temperatures a) 20 K and b) 5 K after field cooling. The spectra are shifted by the values  $\mu_0 H_0$  indicated to the right of each line. Color identifiers are the same as in Fig.3. Symbols  $m$  and  $s$  correspond to the main ( $m_I = +1/2 \leftrightarrow -1/2$ ) and high-field satellite ( $m_I = +3/2 \leftrightarrow +1/2$ ) transitions, respectively.

gram at 44.5 T corresponds to the transition observed while warming up. At fields below 17 T, the difference in the transition temperatures between cooling and warming is not more than the temperature steps at which the data were taken.

The shapes of the NMR spectra at low temperatures depend on the field at which the sample was cooled. Spectra measured at 105.8 MHz and  $T = 5$  K after field cooling from 40 K to 5 K is shown in the Fig.5a.

As elaborated in Ref.[21] the “double-horn” and “helmet” shaped NMR spectra in  $\text{CuCrO}_2$  are specific for incommensurate magnetic structures within triangular planes with inter-plane order and disorder respectively. Green triangles on the phase diagram denotes the boundary between H-T regions where double-horn spectra (i.e. 3D order) is realized independently on cooling procedure and the region where the NMR spectra (or out of plane ordering) depends on the cooling history. The region with hysteresis is marked with II on the phase diagram. The green points were obtained with the experimental procedure demonstrated in Fig.5b. First, the system was prepared by cooling the sample from  $T = 40$  K to  $T = 5$  K at

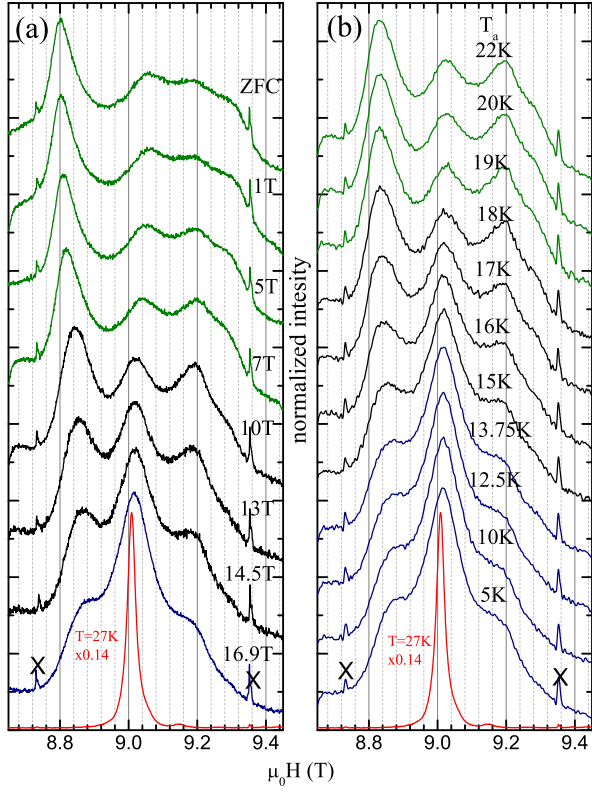


FIG. 5: (color online)  $^{63}\text{Cu}$  NMR spectra ( $m_I = +1/2 \leftrightarrow -1/2$  transition),  $\nu = 105.81$  MHz,  $T = 5$  K. The peaks marked with crosses are spurious  $^{63,65}\text{Cu}$  NMR signals from the probe. Color identifiers are the same as in Fig.3. The black lines demonstrate the spectra which can be considered as a combination of low field distorted two-horn shaped spectrum and high field helmet-like shaped spectrum. (a) Series of spectra obtained after cooling in different fields from 40 K to 5 K. (b) Series of spectra with different annealing temperatures. The first spectrum at the bottom was measured after cooling the sample from 40 K to 5 K in the field  $H = 16.9$  T. Before other measurements the sample was first annealed at temperature  $T_a$  and field  $H = 9$  T during 10 minutes then the temperature was set back to 5 K and the spectrum was obtained.

a fixed field of 16.9 T and then reducing the field to 9 T. A typical spectrum obtained after such procedure has a helmet shape demonstrated by the lowest blue spectrum in both Fig.5a (labeled “16.9 T”) and Fig.5b (labeled “5 K”). While keeping the field at 9 T, the temperature of the sample is then raised to some temperature  $T_a$  where it is annealed for 10 minutes before cooling back down to 5 K, at which point the spectrum is again obtained. Fig.5b shows the evolution of the 5 K spectrum as the annealing temperature is increased. It is evident that at 9 T, the 2D-3D transition, indicated by a transition from helmet to distorted double-horn lineshape, takes place at  $T_a = 15 \pm 1$  K. This transition point is represented by a green triangle on the phase diagram.

Not all phases can be differentiated by the shape of NMR spectra. So, within the high temperature phase

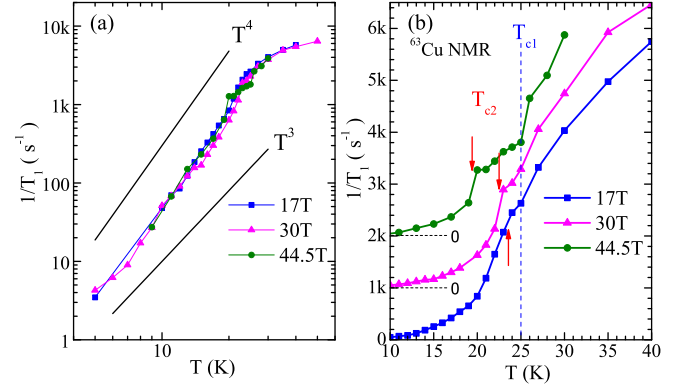


FIG. 6: (color online) Temperature dependence of  $^{63}\text{Cu}$  spin-lattice relaxation rate at fields 17, 30 and 44.5 T.

between  $T_{c1}$  and  $T_{c2}$  single line shaped spectra were observed, as in the paramagnetic phase. To determine this transition we measured the temperature dependence of spin-lattice relaxation rate at fields 17, 30 and 44.5 T from 40 K to 5 K, shown in Fig.6.  $T_1$  was extracted using multi exponential expression.<sup>24</sup>

The temperature dependence of the relaxation rate  $T_1^{-1}$  at  $T < T_{c2}$  approximately follows a power law behavior with an exponent equal to  $3.5 \pm 0.5$  (Fig.6a). In Fig.6b, anomalous discontinuities in the behavior of  $T_1^{-1}$  (positions marked with arrows) are observed and they are plotted with blue squares in Fig.2. Note that at temperatures below  $T_{c2}$  we did not find any singularity corresponding to the transition to the low temperature high field phase observed in pulse field experiments<sup>13</sup> identified as phase N in Fig.2.

From these experimental observations and referring to Fig.2, we summarize the phase diagram as follows: 1) There are two regions, identified as C and PM where the NMR spectra are single peaked. 2) Two regions, I and III, are identified with either two-horn or helmet shaped spectra. These phases are separated by 3) a broad region II, where the spectra demonstrate hysteretic behavior. The spectral shape in this region is a subtle combination of those in I and III and is determined by cooling history. This large hysteresis was also observed in pulsed fields experiments.<sup>13</sup>

## V. DISCUSSION

The dominant interactions, which govern the magnetic state of  $\text{CuCrO}_2$ , are exchange interactions within triangular  $ab$ -plane.<sup>12</sup> The intra-plane exchange interaction between spins of nearest chromium ions is at least 20 times larger than the frustrated inter-plane exchange interactions. We shall first discuss the magnetic phases within the model of a 2D antiferromagnet on the regular triangular lattice. For such a model, in the limit of large spins, the magnetic ground state is expected to be planar three-sublattice 120-degree structure. The spin plane

orientation in exchange approximation is arbitrary. This degeneracy may be lifted by taking into account the relativistic interactions with the crystal environment. The orientation of the spin plane in  $\text{CuCrO}_2$  in the ordered state, i.e. along (110), is defined by two “easy” axes of anisotropy: a strong axis [001] perpendicular to triangular planes and another weak axis within the triangular planes [110]. This model can be described by the model Hamiltonian:

$$H = \sum_{i,j} J \mathbf{S}_i \mathbf{S}_j + \sum_i \left( \frac{1}{2} A_z S_{i,z}^2 + \frac{1}{2} A_y S_{i,y}^2 \right), \quad (2)$$

where the exchange integral between nearest spins:  $J \simeq 26.6$  K,<sup>12</sup> and the anisotropy parameters are:  $A_z \simeq -0.8$  K,  $A_y \simeq -0.0075$  K.<sup>20,25</sup>

The in-plane anisotropy parameter is less than 1 % of that of the out-of-plane anisotropy. That means, that the model with one “easy” axis can be a good approximation. The ground magnetic state in such a model is the so-called three sublattice Y-phase, see Fig.1c1.<sup>5,23</sup> This phase possesses spontaneous magnetic moment and at  $H = 0$  two domains are allowed. The spontaneous magnetization of three-neighbor magnetic moments is evaluated from the exchange and anisotropy parameters of  $\text{CuCrO}_2$  as  $3 \cdot 10^{-3} \mu$ , where  $\mu$  is magnetic moment of chromium ion.<sup>5,23</sup> The application of magnetic field along anisotropy axis removes the degeneracy. The magnetization of the sample grows monotonically with field up to 1/3 of the saturated magnetization. Such value of magnetization is expected to be maintained in some field range in the vicinity of the value  $1/3 H_{sat}$ . In this field range the collinear up-up-down (UUD) phase is expected. The field range of UUD phase is stabilized by uniaxial anisotropy and thermal fluctuations. The thermal fluctuations in the vicinity of  $T_N$  for anisotropic model can stabilize UUD phase even at zero field.<sup>23</sup> This fact probably explains the two-stage transition from paramagnetic to ordered phase in  $\text{CuCrO}_2$ .

The H-T phase diagram of 2D Heisenberg antiferromagnet on the triangular lattice from Ref. [23] is shown as insert to Fig.2. The field range studied in our experiments is shaded. The field axis was scaled using the value of exchange integral  $J = 26.6$  K, which corresponds to  $\mu_0 H_{sat} \approx 280$  T. Thus within the 2D regular triangular antiferromagnetic model for field range  $H < 45$  T we can expect Y-phase at low temperature, collinear UUD phase and paramagnetic phase at higher temperatures. Note, that the magnetic ordering temperature of  $\text{CuCrO}_2$  ( $\approx 24$  K) is in a good agreement with  $T_N = 0.51 JS(S+1) \approx 25$  K, evaluated within 2D XY-model of triangular antiferromagnet.<sup>26</sup>

According to Ref. [27] the main properties of antiferromagnetic  $\text{CuCrO}_2$  have natural explanation based on Dzyaloshinski-Landau theory of magnetic phase transitions. Firstly, let us consider the properties of  $\text{CuCrO}_2$  which can be explained by strongest exchange couplings. The crystal structure of  $\text{CuCrO}_2$  allows for the Lifshitz

invariant which couples spins of neighboring triangular planes and explains the helicoidal spin structure with incommensurate wave vector. The proximity of the wave vector of magnetic structure for  $\text{CuCrO}_2$ , (0.329,0.329,0), to the wave vector of a simple 120-degree structure (1/3,1/3,0) demonstrates the smallness of Lifshitz invariant compared with intra-plane exchange interaction. The difference of the pitch angle of the spins of the neighboring magnetic ions versus 120 degrees causes a nonzero magnetic moment on every triangle of the structure rotating within spin plane along the wave vector direction with period approximately equal to hundred sides of triangle structure (see Eq.1). The value of noncompensated rotated moment for every three neighbor magnetic ions is calculated to be  $0.045\mu$ , where  $\mu$  is the magnetic moment of chromium ion. This value is approximately 15 times larger than the magnetic moment expected due to uniaxial anisotropy. The applied magnetic field will distort the triangles so that the total magnetic moments are aligned along energetically preferable field direction. We can expect that the magnetic field can induce the nonharmonic distortion of magnetic structure which stabilizes the preferable Y-like configuration because of its energetic favorability. At high enough fields a transition to commensurate phases is expected.

The inter-plane interaction in  $\text{CuCrO}_2$  is strongly frustrated and as a result, 3D magnetic ordering with the propagation vector (0.329,0.329,0) observed in the experiment can not be established due to usual exchange interactions between two spins of neighbor triangular planes. 3D ordering can be established, according to Ref.[27], due to the symmetry invariants with at least six spin operators of ions originating from two or three neighbor triangular planes. At the same time, 3D ordering of vector  $\boldsymbol{\eta} = \mathbf{M}(\mathbf{r}_{i,j}) \times \mathbf{M}(\mathbf{r}_{i+1,j})$  (see Eq.1) can be caused by other invariants with a smaller number of spin operators (namely four). Due to this fact it is possible that the vector  $\boldsymbol{\eta}$  will be ordered at a temperature higher than the usual 3D spiral magnetic ordering temperature. The magnetic structure with order parameter  $\boldsymbol{\eta}$  can be described by Eq.1 with random phases  $\Theta$  for different triangular planes.

Symmetry analysis of relativistic interactions in  $\text{CuCrO}_2$  explains the existence of electric polarization proportional to vector  $\boldsymbol{\eta}$  of magnetic structure.<sup>27</sup> For 3D-ordered spiral phase such polarization was observed experimentally.<sup>22,28</sup> It is important that the electric polarization is expected also for magnetic phase with tensor order parameter  $\boldsymbol{\eta}$ .<sup>27</sup>

To identify the magnetic phases occurring in  $\text{CuCrO}_2$ , NMR spectra for different model structures were calculated. In our calculation we assume that the local magnetic field at Cu sites is the sum of the long-ranged dipole field  $\mathbf{H}_{dip}$  and the transferred hyperfine contact field produced by the nearest  $\text{Cr}^{3+}$  moments. The details of this calculation can be found in our previous study.<sup>21</sup> Below we shall list the model phases that we used to explain the observed shapes of the NMR spectra of  $\text{CuCrO}_2$  at

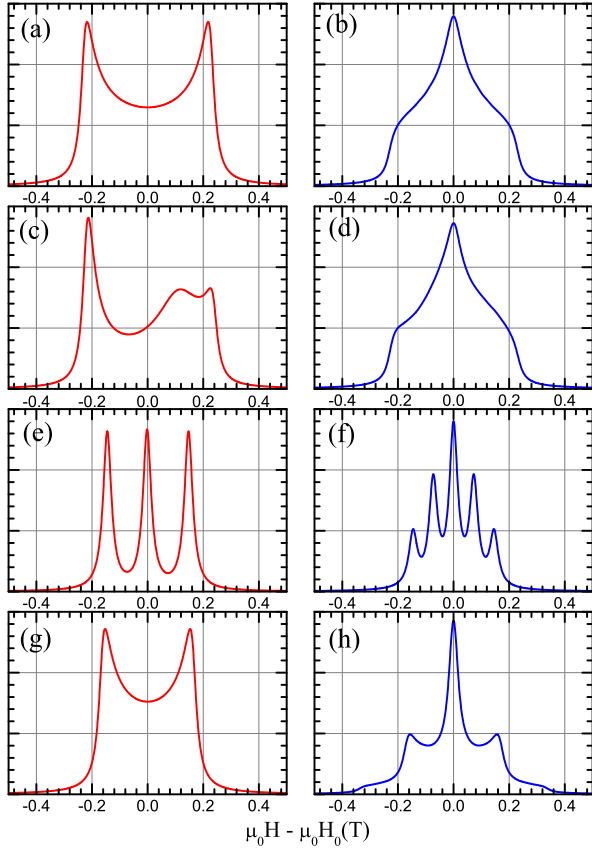


FIG. 7: (color online) Simulated NMR spectra corresponding to different models discussed in the text,  $M_1 = M_2 = 3\mu_B$ , individual linewidth  $\delta = 18$  mT. (a),(b),(c),(d),(e),(f) spiral plane (110); (g),(h) spiral plane (001); (a) 3D incommensurate structure; (b) 3D-polar and 2D incommensurate structures; (c) 3D incommensurate structure with distortion ( $C = 0.04$ ); (d) 3D-polar and 2D incommensurate structures with distortion ( $C = 0.01$ ); (e) 3D commensurate Y structure; (f) 2D commensurate Y structure; (g) 3D and 3D-polar incommensurate spin-flopped structures; (h) 2D incommensurate spin-flopped structure.

fields aligned along [001].

#### 1. Paramagnetic and collinear UUD structures.

Effective fields generated by magnetic environment on each copper ion are identical. As a result, one single peaked NMR spectrum is expected. The position of the line is defined by the total magnetization.

#### 2. 3D commensurate Y structure.

This is described by Eq.1 with propagation vector  $(1/3, 1/3, 0)$ . The initial phase  $\Theta$  measured from  $\mathbf{e}_1 \parallel \mathbf{z}$  can be equal to  $60^\circ$ ,  $180^\circ$  or  $300^\circ$ . The choice of  $\Theta$  determines one of three possible magnetic domains. The computed spectrum for such 120-degree Y structure (see Fig.1c1) is given in Fig.7e. The commensurate 120-degree Y phase can be deformed due to applied field: the moments of two of three sublattices are tilted towards field direction (Fig.1c2). In this case simulated spectrum consists of three lines of equal intensity as for 120-degree

Y structure.

#### 3. 2D commensurate Y structure.

This is described by Eq.1 with 2D propagation vector  $(1/3, 1/3)$ . The magnetic domain which is established within every  $ab$ -plane was chosen arbitrary. This was achieved by random selection of  $\Theta$  among the values  $60^\circ$ ,  $180^\circ$ ,  $300^\circ$ . The computed spectrum consists of 5 lines, see Fig.7f.

#### 4. 3D incommensurate structure.

This is described by Eq.1 with propagation vector  $(0.329, 0.329, 0)$ , see Fig.1c4. The initial phase  $\Theta$  can be any, but the same for all triangular planes. The result is shown in Fig.7a. Such shape with two maxima at the boundaries is typical for incommensurate structures.

#### 5. 3D incommensurate distorted structure.

For this structure we introduced in Eq.1 a small nonlinearity in phase:

$$\Phi = (\mathbf{k}_{ic} \mathbf{r}_{i,j} + \Theta) + C \cdot \sin(3(\mathbf{k}_{ic} \mathbf{r}_{i,j} + \Theta)), \quad (3)$$

where  $0 < C < 0.35$  defines the amplitude of unharmonicity. Such unharmonicity tilts the spins within spiral towards to the Y phase (phase angles  $60^\circ$ ,  $180^\circ$ ,  $300^\circ$  measured from  $\mathbf{e}_1 \parallel \mathbf{z}$ ) in contrast to upside down Y phase (phase angles  $0^\circ$ ,  $120^\circ$ ,  $240^\circ$ ), see Fig.1c5. The result is shown in Fig.7c.

#### 6. 3D-polar and 2D incommensurate structures.

The incommensurate phases, distorted and undistorted, were simulated for two types of disorder. In the first case parameters  $\Theta$  in all triangular planes of the structure were chosen arbitrarily (see Eqs.1,3), whereas the direction of the rotation of spins within the triangular planes and, therefore, the sign of vector  $\boldsymbol{\eta}$ , was set to be the same. We shall assign this phase as 3D-polar ordered phase with order parameter  $\boldsymbol{\eta}$ . For the second type of disorder both  $\Theta$  and sign of  $\boldsymbol{\eta}$  for all triangular planes were arbitrary. We shall assign this phase as 2D-ordered phase. The 2D long range order is possible only at zero temperature. Nevertheless, because the NMR experiment is sensitive only to the nearest magnetic neighborhood of the nuclei, we can expect that the spectra obtained within this model will also describe the magnetic structure with short ranged spiral correlations with different signs of  $\boldsymbol{\eta}$ , which are expected for 2D triangular structure.<sup>29</sup> The shapes of simulated spectra for both types of disorder were identical. The result for undistorted 3D-polar and 2D phases is in Fig.7b, for distorted ones is in Fig.7d. The characteristic feature of spectra from the magnetic structure with partial disorder is the presence of strong central maximum on the spectra.

#### 7. Spin-flopped umbrella-like structures.

This is described by Eq.1 with  $\mathbf{n} \parallel \mathbf{z}$  for 3D, 3D-polar and 2D phases. 3D and 3D-polar structures both resulted in an identical double horn pattern (Fig.7g). 2D structure resulted in a spectrum with 5 characteristic maxima (Fig.7h).

From comparison of experimental data with the models' simulations we can exclude from consideration incommensurate and spin-flopped structures (Fig.7e,f,g,h).

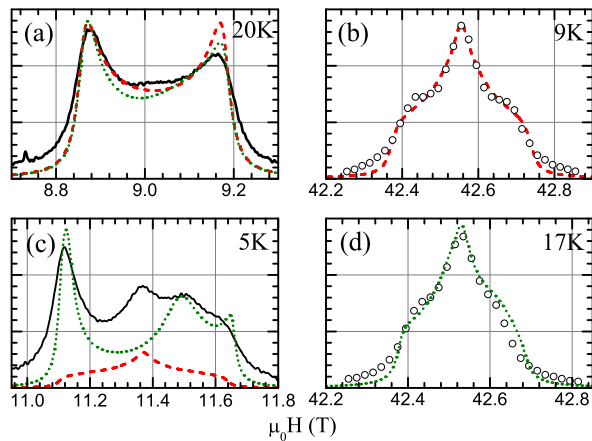


FIG. 8: (color online) Fitting of NMR spectra (black lines and circles) within 3D and 2D incommensurate magnetic structures: (a) - 3D, undistorted ( $C = 0$ , red dashed line) and distorted ( $C = 0.013$ , green dotted line),  $M_1 = M_2 = 2.1\mu_B$ ; (b) - 2D, undistorted ( $C = 0$ ),  $M_1 = M_2 = 2.4\mu_B$ ; (c) - 3D, distorted ( $C = 0.06$ , green dotted line) and 2D, undistorted ( $C = 0$ , red dashed line),  $M_1 = M_2 = 3.5\mu_B$ ; (d) - 2D, distorted ( $C = 0.015$ ),  $M_1 = M_2 = 2\mu_B$ . Individual linewidth  $\delta = 18$  mT.

These phases were suggested from microscopic model studied numerically in Ref. [14]. The spectra with 3 and 5 maxima were not observed in experiment. Double horn shaped spectra were observed only at low fields, where the umbrella-like structure with  $\mathbf{n} \parallel \mathbf{c}$  is certainly not realized.

As a result of modeling we suggest the following magnetic structures realized within the studied H-T region. In all fields below  $H \approx 45$  T at temperatures below the red solid symbols on the phase diagram an incommensurate spiral phase is established within individual planes. In region I the system is 3D ordered. At higher fields (region III) the 3D-polar or 2D structure is established. Within the broad region II on the phase diagram the spectra exhibits hysteresis where the inter-plane ordering essentially depends on cooling history. At high temperatures  $T \gtrsim 20$  K the transition from I to III has no field hysteresis. The field hysteresis grows drastically at lower temperatures.

The area on phase diagram bounded by two lines between  $T_{c1}$  and  $T_{c2}$  can be considered as collinear UUD phase. The NMR spectra within this phase has single-peaked shape. The phase boundaries for this phase marked on the phase diagram were obtained from the anomalies on the temperature dependencies of spin lattice relaxation time  $T_1$ . The temperature range of exist-

tence of this phase increases with field, consistent with theoretical expectations.<sup>23</sup>

The fits to the experimental NMR spectra using suggested models are shown in Fig.8. The NMR spectra measured in regions I and III can be fitted satisfactorily by 3D and 2D incommensurate magnetic structures. The observed asymmetry of the spectra can be described by the unharmonicity of helical structure discussed above (Fig.8a,d). The complicated shape of spectra observed within the hysteretic region II of the phase diagram can be fitted by superposition of the spectra from 2D and 3D incommensurate structures (Fig.8c). The shape of NMR spectra is also dependent on the differences in spin-spin relaxation time  $T_2$  along the spectrum lines. However, the measured  $T_2$  along a spectrum for sampling spectra show that the  $T_2$  correction of the spectra can change the relative intensity by not more than 15 %.

Finally, we note that the local field on the nucleus measured by NMR experiment is formed by neighboring magnetic ions of few coordination spheres. It means that similar spectral shapes can also be obtained in the presence of corresponding short range correlations, static during the NMR experiment ( $\gtrsim 1$  ms).<sup>30</sup>

## VI. CONCLUSIONS

The magnetic phase diagram of  $\text{CuCrO}_2$  is studied with Cu NMR for  $\mathbf{H} \parallel \mathbf{c}$ . NMR experiments revealed the H-T regions where 2D/3D-planar spiral, UUD and paramagnetic phases are realized. The 2D-planar spiral phase realized in region III is very unusual. On one hand, according to NMR the usual 3D order is absent, but at the same time this phase possesses electric polarization.<sup>13</sup> Symmetry analysis of magnetic properties of  $\text{CuCrO}_2$ <sup>27</sup> allows one to explain these observations by a realization of 3D magnetic state with tensor order parameter. This phase can be classified as a polar nematic phase.

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