Domain-wall phase transitions induced by an external magnetic field in the rhombic antiferromagnet $(C_2H_5NH_3)_2CuCl_4$

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A theoretical and experimental study is made of the spin reorientation in the domain walls of the rhombic antiferromagnet $(C_2H_5NH_3)_2CuCl_4$ as a function of the magnitude and direction of the external magnetic field. The structure of the domain walls is determined both for a magnetic field parallel to the easy axis and for a magnetic field deviating toward the intermediate axis. A symmetry classification of the domain walls is constructed.

1. INTRODUCTION

Rhombic antiferromagnets have been shown[1] to have domain-wall phase transitions induced by an external field. Depending on the relationship between the internal parameters (primarily that between the exchange and anisotropic interactions) and on the magnitude and direction of the external magnetic field, different types of domain walls can exist in magnetically ordered structures.[2] Importantly, these domain walls can have different symmetries.[3,4] Because of this, it is possible to have phase transitions involving the rearrangement of the domain-wall structure. Because the internal parameters which determine the type of domain walls in the magnet depend on the temperature, pressure, etc., a phase transition in the domain walls can occur when these variables change. Restructuring of the domain walls as a function of temperature was first observed[5] in the orthoferrite $DyFeO_3$. Another possibility for a change in the type of domain wall is afforded by the influence of a magnetic field on a magnet with a domain structure. A domain-wall phase transition induced by an external magnetic field was first considered in Ref. 1, where it was shown that a rhombic antiferromagnet in a magnetic field stronger than field of the spin-flop transition has a phase transition involving a restructuring of the domain walls separating antiferromagnetic domains with antiparallel directions of the antiferromagnetism vector $\mathbf{L}$ ($\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$; $\mathbf{M}_1$ and $\mathbf{M}_2$ are the sublattice magnetizations), and the results of an observation of such a transition in $CuCl_2 \cdot 2H_2O$ were reported.

In Ref. 1 a study was made of rhombic antiferromagnets with no Dzyaloshinskiĭ interaction. In this case, so-called "kinetic domains," separated by 180-degree domain walls, can occur throughout the entire existence region of the state with $\mathbf{L} \neq 0$ and for arbitrary directions of the external magnetic field; the onset of these domains is due to transitions to the magnetically ordered state.[6] Rhombic antiferromagnets which admit a Dzyaloshinskiĭ interaction belong to another important type. Unlike the former, the latter, because of the presence of a weak ferromagnetic moment, can have a thermodynamically stable domain structure in fields above the spin-flop field. In addition, if the magnetic field deviates from the easy axis there can be domains with non-180° walls.

The present paper is devoted to a theoretical and experimental study of how the spin-reorientation in the domain walls of antiferromagnets which admit a Dzyaloshinskiĭ interaction depends on the magnitude and direction of the external magnetic field. The experimental studies were done on single crystals of ethyl ammonium tetrachlorocuprate—$(C_2H_5NH_3)_2CuCl_4$ (Néel temperature $T_N = 10.2$ K).

In a magnetic field $\mathbf{H} \| \mathrm{EA}$ (EA is the axis of easy magnetization) at $T = 4.2$ K, a phase transition is observed in the domain walls of the spin-flop phase at $H^* = 966$ Oe $\approx 0.7 H_E$ (H_E is the field of the spin-flip transition; the field of the spin-flop transition is $H_t = 290$ Oe). When the magnetic field deviates from the easy axis, a splitting of the line of phase transitions is observed. The domain-wall structure is determined theoretically both in a magnetic field parallel to the easy axis and in a magnetic field deviating toward the intermediate axis. The field H^* of the spin reorientation in the domain walls of the spin-flop phase is calculated, and a symmetry classification of the domain walls is constructed.

2. DOMAIN-WALL STRUCTURE

Let us consider a two-sublattice rhombic antiferromagnet with the $2_x(+)$ structure in the Turov classification.[7] We write the energy density of such a magnet in the standard form[7]

$$E=\lambda \mathbf{M}_1\mathbf{M}_2-H(\mathbf{M}_1+\mathbf{M}_2)-d(M_{1y}M_{2z}-M_{1z}M_{2y})-d'(M_{1y}M_{1z}-M_{2y}M_{2z})+(\beta_y/2)(M_{1y}^2+M_{2y}^2)+\beta_y' M_{1y}M_{2y}+(\beta_z/2)(M_{1z}^2+M_{2z}^2)+\beta_z' M_{1z}M_{2z}, \quad (1)$$

where λ is the intersublattice exchange interaction constant, $\beta_y, \beta_y', \beta_z, \beta_z'$, and d' are the anisotropy constants, and d is the Dzyaloshinskiĭ interaction constant. For

$$\lambda+{}^1/_2(\beta_y+\beta_y')+{}^1/_2(\beta_z-\beta_z')-\{[\lambda+{}^1/_2(\beta_y+\beta_y')-{}^1/_2(\beta_z-\beta_z')]^2+(d-d')^2\}^{1/2}>\lambda+{}^1/_2(\beta_z+\beta_z')+{}^1/_2(\beta_y-\beta_y')-\{[\lambda+{}^1/_2(\beta_z+\beta_z')-{}^1/_2(\beta_y-\beta_y')]^2+(d+d')^2\}^{1/2}>0$$

the X axis is the easy axis and the Z axis is the hard axis.

In a magnetic field $\mathbf{H} \| \mathrm{EA}$ the following ground state are possible.[8]

1. An antiferromagnetic phase, $0 < HM_0^{-1} < H_t$:

$$\mathbf{M}=0, \quad L_y=L_z=0, \quad L_x=\pm 2M_0.$$

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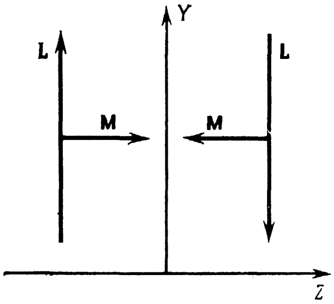

FIG. 1.

2. A spin-flop phase, $H_t < HM_0^{-1} < H_E$:

$$M_x=2H/H_E,\quad M_y=0,\quad M_z=H_{a1}[1-H_{a2}]^{-1/2}L_y,$$
$$L_x=L_z=0,\quad L_y=\pm 2M_0H_{a1}H_{a2}.$$

3. A spin-flip phase, $HM_0^{-1} > H_E$:

$$\mathbf{L}=0,\quad M_y=M_z=0,\quad M_x=2M_0,$$

where

$$\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2,\quad |\mathbf{M}_1|=|\mathbf{M}_2|=M_0,\quad H_t^2=\lambda^2-[\lambda-H_E]^2,$$
$$H_E=H_2+[H_1^2+(d+d')^2]^{1/2},$$
$$H_1=\lambda-{}^1/_2(\beta_y-\beta_y')+{}^1/_2(\beta_z+\beta_z'),$$
$$H_2=\lambda-{}^1/_2(\beta_y-\beta_y')-{}^1/_2(\beta_z+\beta_z'),\qquad H_{a1}=1-H^2/H_E^2M_0^2,$$
$$H_{a2}={}^1/_2[1-H_1/(H_E-H_2)].$$

In the antiferromagnetic phase the ground state is doubly degenerate. This degeneracy in the antiferromagnetic phase is known to give rise to the formation of domains with antiparallel directions of the vector **L**, separated by 180-degree domain walls.[6] Clearly, such domain walls have the lowest energy only when **L** turns in the plane formed by the easy and intermediate axes (in the XY plane).

In the spin-flop phase the ground state is also doubly degenerate. Importantly, here there is degeneracy with respect to **M** also (states with $\pm M_z$). Therefore, in samples with a finite shape factor the formation of domains is energetically favorable, since it will lead to a decrease in the energy of the demagnetizing fields.[9] Thus, unlike the domains of the antiferromagnetic phase and unlike the domains of the spin-flop phase in antiferromagnets with no Dzyaloshinskiĭ interaction,[1] in the present case a thermodynamically stable domain structure is expected to form.

Let us consider the possible types of domain walls between the domains of the spin-flop phase. The ground states of the magnet are illustrated in Fig. 1. For convenience we have shown only the projections of the vectors **L** and **M** onto the YZ plane. The transition from one stable state to the other can occur through a rotation of **L** in either the XY plane (a type-I domain wall, or DW I) or the YZ plane (a type-II domain wall, or DW II). Clearly, in both types of domain walls, there are two energetically equivalent rotations of **L**, differing in the direction of rotation of **L**, i.e., in a field **H**||EA, DW II are twofold degenerate (the structure of DW I and DW II are discussed in more detail in Sec. 4).

Let us calculate the energy of DW I and DW II for the case of plane domains walls. If the structure of the domain wall is described by a single configuration variable θ (in this case θ is the angle between **L** and the easy axis), then the energy density E_{DW} of the domain walls is given by the expression[2]

$$E_{\mathrm{DW}}=(\alpha M_0^4)^{1/2}\int_{\theta_1}^{\theta_2}(E(\theta)-E_\infty)^{1/2}\,d\theta, \tag{2}$$

where α is the inhomogeneous exchange interaction constant, θ_1 and θ_2 are the values of the independent variable θ corresponding to the states of the magnet in the adjacent domains, and E_∞ is the energy of the homogeneous state.

Introducing ΔE, the height of the potential barrier separating the states θ_1 and θ_2, we can write expression (2) as

$$E_{\mathrm{DW}}=(\alpha M_0^4\Delta E)^{1/2}|\theta_2-\theta_1|\xi, \tag{3}$$

where ξ is a constant of the order of unity [in particular, $\xi=1$ for potential (1)]. For DW I the height of the potential barrier ΔE^{I} is equal to the energy difference of the antiferromagnetic and spin-flop phases. Near the field of the spin-flop transition ($H \gg H_t$) one has[10]

$$\Delta E^{\mathrm{I}}\approx E_A^{XY}H_t^2/H_E^2\ll E_A^{XY}$$

(E_A^{XY} is the anisotropy energy in the XY plane). The potential barrier ΔE^{II} (for DW II) is equal to the energy difference between the state with **L**||Z and the spin-flop phase, i.e., ΔE^{II} is determined by the anisotropy in the basal plane:

$$E_A^{YZ}=(\beta_y-\beta_y')L^2\approx(\beta_y-\beta_y')M_0^2.$$

Assuming that E_A^{XY} and E_A^{YZ} are of the same order of magnitude, we find that $\Delta E^{\mathrm{I}} \ll \Delta E^{\mathrm{II}}$ in the region of the spin-flop transition, i.e., DW I is energetically favored. In the region of the spin-flip transition ($H\approx H_E$) one has $|\mathbf{M}| \gg |\mathbf{L}|$. Here

$$\Delta E^{\mathrm{II}}=(\beta_y-\beta_y')L^2\ll(\beta_y-\beta_y')M_0^2,$$

and rotation in the XY plane is energetically unfavorable, since it entails a substantial decrease in the magnetization vector **M** ($M_x \sim M_0$ in the domains, while at the center of a domain wall $M_x=0$). Thus DW II is energetically favored in fields $H\approx H_E$. Hence, it necessarily follows that at a certain field H^* ($H_t < H^* < H_E$) there will be a phase transition involving a rearrangement of the domain-wall structure from DW I to DW II (as to the nature of the phase transition, see Sec. 4). The value of the field H^* is determined from the equation $\Delta E^{\mathrm{I}}=\Delta E^{\mathrm{II}}$ and is equal to

$$H^*=\{\lambda^2-[(H_3^2+(d-d')^2)^{1/2}-{}^1/_2(\beta_y+\beta_y')-{}^1/_2(\beta_z-\beta_z')^2\}^{1/2}M_0, \tag{4}$$

where

$$H_3=\lambda+{}^1/_2(\beta_y+\beta_y')-{}^1/_2(\beta_z-\beta_z').$$

For $d-d'=0$, relation (4) goes over to the expression obtained in Ref. 1. For λ much greater than $\beta_y+\beta_y'$, $\beta_z-\beta_z'$, and $d-d'$, expression (4) simplifies to

$$H^*=[(\beta_z-\beta_z')[2\lambda-(\beta_z-\beta_z')]-(d-d')^2]^{1/2}M_0. \tag{5}$$

Domain walls of the spin-flop phase, like ferromagnetic domain walls, can have Bloch lines—regions of a domain

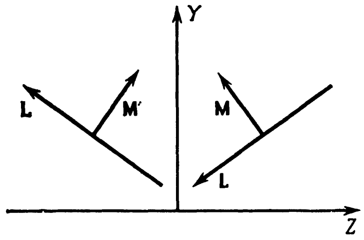

FIG. 2.

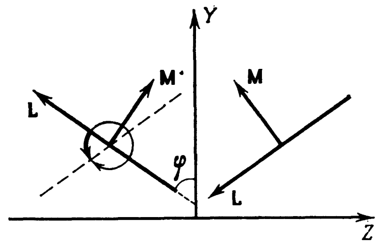

FIG. 3.

wall which separate adjacent segments having opposite directions of rotation of the vector **L**. Significantly, the spin configurations at the center of the Bloch line correspond to those at the center of the alternative domain wall. Therefore, for the spin-reorientation phase transition in the domain walls, the center of a Bloch line acts as a nucleus of the new domain wall.

When **H** is inclined to the X axis in the XY plane, the ground state remains twofold degenerate, with the vector **L** deviating from the Y axis and the vector **M** leaving the XZ plane. The stable states differ in the sign of the components M_z and L_y:

$$\mathbf{L}_{1,2}=(L_x, \pm L_y, L_z), \quad \mathbf{M}_{1,2}=(M_x, M_y, \pm M_z).$$

Figure 2 shows the projections of **L** and **M** onto the YZ plane (**H** is in the XY plane). In DW II the degeneracy is lifted: the vector **L** is rotated by an angle $\pi - 2\varphi$ in one of the type-II domain walls and by $\pi + 2\varphi$ in the other; here φ is the angle between the projection of **L** onto the YZ plane and the Y axis (see Fig. 3, where the dashed line shows the position of the vector **L** in the adjacent domain, the heavy line shows the rotation of **L** in the wall by an angle $\pi - 2\varphi$, and the light line shows a rotation by $\pi + 2\varphi$). Clearly, a domain wall in which **L** is rotated by a smaller angle has a lower energy. With increasing field the angle φ increases monotonically, and in the field of the second-order phase transition II to the symmetric phase ($\mathbf{L}\|Z$) the angle φ becomes equal to $\pi/2$. Then the rotation of the vector **L** becomes equal to zero in one of the type-II domain walls and to 2π in the other, i.e., the first of the type-II domain walls undergoes a transition to a homogeneous state, while the second type-II domain wall is converted into a 360-degree domain wall of the symmetric phase. At the transition from the symmetric phase on decreasing **H**, the 360-degree domain walls are sources of both kinds of type-II domain walls, with $\Delta\varphi < \pi$ and $\Delta\varphi > \pi$, where $\Delta\varphi$ is the angle of rotation of the vector **L** in the domain wall. It can be shown that on the average, each of the 360-degree domain walls of the symmetric phase leads to the formation of two type-II domains walls (in one of them $\Delta\varphi < \pi$, while in the other $\Delta\varphi > \pi$). Thus, on the transition from the symmetric phase, the number of type-II domain walls is restored.

In an oblique magnetic field the vector **L** in the type-I domain walls describes a complicated spatial trajectory. The symmetry analysis carried out below shows that the twofold degeneracy of the type-I domain walls is preserved in a magnetic field tilted into the XY plane.

3. EXPERIMENTAL RESULTS

Our experimental study of the spin reorientation in the domain walls of the spin-flop phase was done on antiferromagnetic single crystals of $(C_2H_5NH_3)_2CuCl_4$. This crystal belongs to the rhombic system, space group $\mathbf{D}_{2h}^{15}$ (Ref. 11). Its magnetic properties were studied in detail in Refs. 12–16.

The ethyl ammonium tetrachlorocuprate crystals were grown from an aqueous solution by the temperature-reduction method. Thin slabs with dimensions of $10\times5\times0.5$ mm^3 were used in the experiment. The crystalline axis **c** (the axis of hard magnetization) was orthogonal to the plane of the slab. The direction of the axis of easy magnetization was determined to within 1° on the basis of the maximum value of the magnetic susceptibility measured (in arbitrary units) at the spin-flop transition. The experiment was done in magnetic fields ranging from the antiferromagnetic to the paramagnetic phases (0–5 kOe) at temperatures from 2 to 4.2 K. The temperature was determined to within $5\cdot10^{-3}$ K.

H||EA. Detailed studies of the magnetic susceptibility χ of the crystal in a magnetic field have revealed[12,13,15] the characteristic features peculiar to the H–T magnetic phase diagram of an easy-axis antiferromagnet, in particular, at $T = 4.2$ K in fields $H \approx 300$ Oe (the first-order, spin-flop phase transition) and $H \approx 1250$ Oe (the second-order, spin-flip phase transition).

The present study of the dependence of the susceptibility on the magnetic field **H** has shown that $\chi(H)$ also has an anomaly at $H^* = 966$ Oe ($T = 4.2$ K). Figure 4 shows the experimental field dependence of the magnetic susceptibility. The behavior of $\chi(H)$ in fields near H^* is reminiscent of that near the spin-flop field, but $\chi(H^*) = 10^{-3}\chi(H_t)$. The behavior of $\chi(H)$ at H^* was similar over a wide range of frequencies (5–35 MHz). Consequently, the observed anomaly of the susceptibility χ at the field H^* can be due

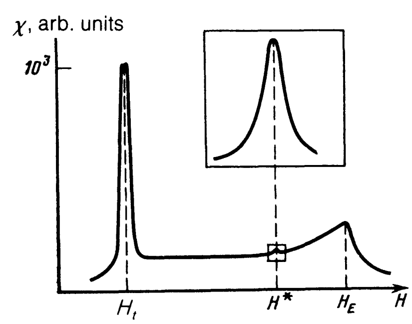

FIG. 4.

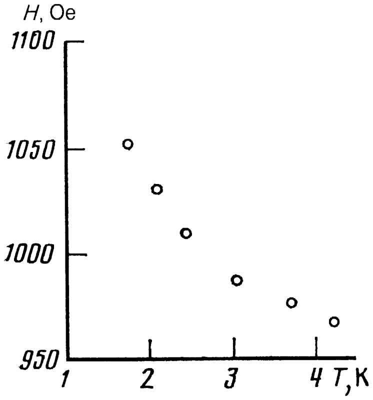

FIG. 5.

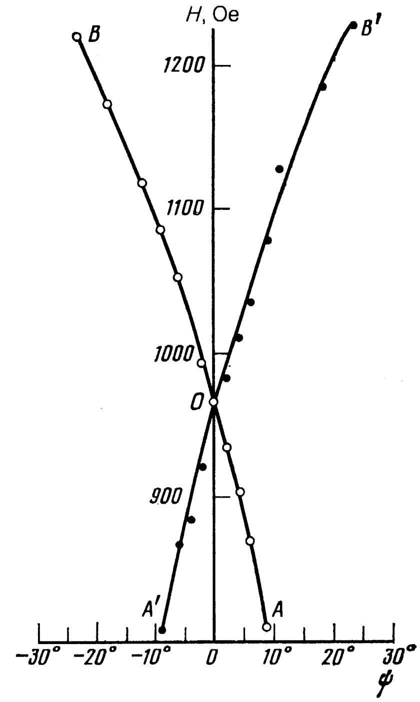

FIG. 6.

neither to an antiferromagnetic resonance of the homogeneous state (AFMR), since the anomaly is found outside the frequency-field curve[14,16] of the AFMR of $(C_2H_5NH_3)_2CuCl_4$, nor a magnetic resonance of the nuclei located in the domains, since for such nuclei the resonance frequency characteristically exhibits a linear dependence on the magnetic field. Analysis of the phenomenological potential (1) shows that spin-reorientation transitions between homogeneous states of this magnet cannot occur in the given field range $H_t < H < H_E$. Therefore, it is natural to suppose that the change in the susceptibility at the field H^* is due to a phase transition in the domain walls of the spin-flop phase. This conjecture is supported by the low intensity of the signal: the spin-reorientation transition occurs in a small part of the sample—in the domain walls. Furthermore, it has been shown[1] that a spin reorientation in the domain walls of the spin-flop phase should be expected at fields near the crossing field H' of the AFMR frequencies of the spin-flop phase. For $(C_2H_5NH_3)_2CuCl_4$ the field H' is[14,16] approximately 850 Oe, i.e., H^* corresponds to the region of the first-order phase transition in the domain walls of the spin-flop phase. When the temperature decreases the field H^* increases monotonically (Fig. 5). To get a more precise idea of the nature of the signal in the field H^*, we carried out experiments in an oblique field.

H in the XY plane. When **H** was directed at an angle to the easy axis there was a splitting of the signal (Fig. 6). Observation of the shape of the signals (Fig. 7) in an oblique field permitted the conclusion that at $\psi = 0$ there is a crossing of two lines. In Fig. 6 the position of one of the lines (AB) is denoted by open dots and the other ($A'B'$) by filled dots. At high fields these lines terminate at the line of second-order phase transitions to the symmetric phase with $\mathbf{L} \| Z$ (points B and B'). On segment $BA(B'A')$, as the field **H** changes from point $B(B')$ to point $A(A')$, the amplitude of the signal falls off monotonically, and at point $A(A')$ it can no longer be distinguished from the background of instrument noise. At the same time, the half-width of the signals shows a monotonic increase. On the H-ψ phase diagram the position of the lines AB and $A'B'$ are symmetric with respect to the H axis (Fig. 6). For $T = 4.2$ K points B and B' have the coordinates $H = 1240$ Oe, $\psi = \pm 23°$, while A and A' are at $H = 809 \pm 10$ Oe, $\psi = \pm 9°$. We note that no signals of any kind were detected above the line of second-order phase transitions to the symmetric phase.

As we mentioned in the previous section, a deviation of **H** from the easy axis lifts the degeneracy in the type-II domain walls: in one of them the vector **L** is rotated by an angle $\Delta\varphi_1 = \pi - 2\varphi$, while in the other $\Delta\varphi_2 = \pi + 2\varphi$; these domain walls exchange places when ψ changes sign. Since the energy of the domain wall in which $\Delta\varphi$ has the smaller value is lower than the energy of the domain wall with the larger $\Delta\varphi$, one expects that in an inclined field a phase transition would occur from the twofold degenerate type-I domain walls to the type-II domain walls in which $\Delta\varphi < \pi$. In this case the H-ψ phase diagram would have only the lower parts of the lines: AO and $A'O$. The presence of the high-field branches means that the domain-wall phase transition occurs in two stages. In the lower field only a fraction of the type-I domain walls undergo a transition to DW II ($\Delta\varphi < \pi$). The remaining type-I domain walls undergo a transition to DW II ($\Delta\varphi > \pi$) only when the upper phase-

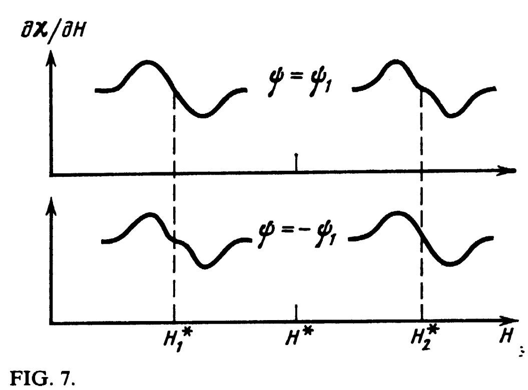

FIG. 7.

transition field is reached. It can be assumed that the transition of all the type-I domain walls in the lower field is hindered on account of the topological inequivalence of the degenerate DW I states.

The measurements were made both on increasing external field and on the reverse path from the existence region of the symmetric phase. To within the accuracy of the experiment we detected no changes in the position of the lines or their amplitudes. In one of the versions of the experiment the sample was cooled from room temperature to liquid-helium temperature in an external field $H = 5$ kOe $> H_E$ ($\psi \neq 0$). As the field was decreased we observed two signals of equal intensity at the same values of the field as before. However, the intensity was lower by a factor of 5 than in the previous case, and the intensity of the signals did not change on a decrease of the magnetic field to zero and a return to the symmetric phase.

This fact is one of the important arguments for the idea that the signal is due to the rearrangement of the domain walls. In fact, it is natural to assume that the intensity of the signals is proportional to the number of domain walls in the sample. Consequently, the decrease of the signal intensity when the sample cools in a magnetic field means that in this case the number of domain walls is considerably smaller than in a sample cooled at $H = 0$. Such a dependence of the number of domain walls in the crystal on its magnetic history implies that in this case the conditions for thermodynamic stability of the domain structure are not satisfied. In fact, if a thermodynamically stable domain structure were present in the sample, the period of this structure (and consequently, the number of domain walls) would be determined solely by the values of the external variables—the magnetic field **H** and temperature T—and would not depend on the path of transition to this state. It can be assumed that the presence of defects hinders the motion of the walls and prevents the establishment of thermodynamic equilibrium. Under such conditions the number of domain walls will be determined by the manner of transition to the ordered state: on cooling in zero field, by the number of 180-degree domain walls of the antiferromagnetic phase; on cooling in an external field, by the number of 360-degree domain walls of the symmetric phase. The reasons for the formation of 180-degree domain walls of the antiferromagnetic phase have been rather well studied.[6,7,17,18,19] As to the formation of the 360-degree domain walls of the symmetric phase, we note the following. At high temperatures ($T > T_N$) the external magnetic field induces a net magnetization vector **M**. In turn, owing to the Dzyaloshinskiĭ interaction, the components M_y and M_z of the net magnetization vector give rise to components of the antiferromagnetism vector L (L_z and L_y, respectively). Because of the nonuniformity of the internal field and the inhomogeneity of the sample, the distribution of the vector L over the volume of the sample is inhomogeneous; this can be a source of 360-degree domain walls.

4. SYMMETRY ANALYSIS OF THE DOMAIN WALLS

A calculation of the domain-wall energy in an oblique field presents certain mathematical difficulties, and we shall therefore confine ourselves to a study of the qualitative behavior of the vectors **L** and **M** in the domain walls purely on considerations of symmetry. For this we use the method of symmetry analysis developed in Refs. 3 and 4.

The symmetry group $\mathbf{G}_{pm}$ of the paramagnetic phase[11] of $(C_2H_5NH_3)_2CuCl_4$ is $\mathbf{D}_{2h}^{15} + \mathbf{D}_{2h}^{15} \cdot 1'$, where $1'$ is the operation of time reversal. When an external magnetic field **H** is imposed along the easy axis of the crystal the order of the group $\mathbf{G}_{pm}$ is lowered. Let us denote the symmetry group of the crystal in an external magnetic field by $\mathbf{B}_{pm}^{H}$. Clearly, $\mathbf{G}_{pm}^{H}$ is a subgroup of the group $\mathbf{G}_{pm}$. Starting from $\mathbf{G}_{pm}$, one can easily construct the group $\mathbf{G}_{pm}^{H}$, which consists of the following elements:

$$1,\ 2_x(+),\ 2_y'(-),\ 2_z'(-),\ \bar{1},\ \bar{2}_x(+),\ \bar{2}_y'(-),\ \bar{2}_z'(-), \qquad (6)$$

where $\bar{1}$ is the inversion operation, and the symbols + and − indicate the parity of the elements according to Turov.[7]

Since the samples under study were thin slabs with normal vectors parallel to the Z axis, it makes sense to consider the two possible orientations of plane domain walls in the crystal: $\mathbf{n} \| Y$ and $\mathbf{n} \| X$, where **n** is the normal to the wall. Let us turn to a study of the symmetry properties of such domain walls in the spin-flop phase.

A. N‖Y

In accordance with Refs. 3 and 4, let us construct the symmetry group $\mathbf{G}_{bc}$ of the boundary conditions, i.e., the symmetry class of a magnet with an isolated domain wall, without allowance for the actual structure of this domain wall. The group $\mathbf{G}_{bc}$ contains the elements

$$1,\ 2_x(+),\ \ 2_y'(-),\ \ 2_z'(-). \qquad (7)$$

The possible symmetry groups $\mathbf{G}_c$ of a crystal containing domain walls are subgroups of $\mathbf{G}_{bc}$. For the group $\mathbf{G}_{bc}$ in (7) there are 5 such subgroups. Below, we list all these groups $\mathbf{G}_c$ and indicate the qualitative form (invariant with respect to each group) of the coordinate dependence of the components of the vectors **L** and **M**:

$\mathbf{G}_1$:	1	L_x	L_y	L_z	M_x	M_y	M_z
$\mathbf{G}_2$:	$1, 2_x$	S	A	A	S	A	A
$\mathbf{G}_3$:	$1, 2_y'$	–	S, A	–	S, A	–	S, A
$\mathbf{G}_4$:	$1, 2_z'$	A	A	S	A	S	A
$\mathbf{G}_5$:	$1, 2_x, 2_y', 2_z'$	–	A	–	–	–	A

The symbols S and A indicate that the function has parts which are symmetric and antisymmetric, respectively, with respect to the substitution $y \to -y$. A prime indicates that the component is zero. The groups $\mathbf{G}_3$ and $\mathbf{G}_5$ describe domain walls in which the vector **L** varies in modulus only (pulsates). Such domain walls can exist only in a narrow neighborhood of T_N. Group $\mathbf{G}_1$ corresponds to a domain wall of general form. Group $\mathbf{G}_2$ describes the symmetry of DW I, and $\mathbf{G}_4$ that of DW II. The index of the subgroup $\mathbf{G}_c$ of group $\mathbf{G}_{bc}$ indicates the degeneracy of the state defined by $\mathbf{G}_c$. It follows that for $\mathbf{H} \|$ EA, the type-I and type-II domain walls are twofold degenerate. This degeneracy is associated with the possibility of different directions of rotation of **L** and **M** in the domain wall.

Thus, in the spin-flop phase there are domain walls of different symmetry which are described by the groups $\mathbf{G}_2$ (DW I) and $\mathbf{G}_4$ (DW II), which are not related to each other by a subgroup relationship. Therefore, the transition from DW I to DW II can occur as a first-order phase transition or as two second-order phase transitions involving the formation of a domain wall having the symmetry of group $\mathbf{G}_1$, which is a subgroup of both $\mathbf{G}_2$ and $\mathbf{G}_4$. Here the situation is analogous to the spin-reorientation transitions between homogeneous states of a magnet.

B. $\mathbf{n}\|X$

In this case the symmetry group $\mathbf{G}_{bc}$ of the boundary conditions consists of the following elements: 1, $2_z'(-)$, $\bar{2}_x(+)$, and $\bar{2}_y'(-)$. The possible types of walls are:

G_1:	1	L_x	L_y	L_z	M_x	M_y	M_z
G_4:	$1, 2_z'$	A	A	S	A	S	A
G_6:	$1, \bar{2}_x$	S	A	A	S	A	A
G_7:	$1, 2_y'$	S, A	–	–	S, A	–	S, A
G_8:	$1, 2_z', \bar{2}_x, \bar{2}_y'$	–	A	–	–	–	A

The interesting groups are $\mathbf{G}_4$, which describes DW II, and $\mathbf{G}_6$ which describes DW I. As before, the degeneracy of DW I and DW II is two.

We see from the table that aside from the dependence of the direction of the normal vector $\mathbf{n}$ of the wall, the symmetry groups of DW II consist of the same elements. The qualitative behavior of the vectors $\mathbf{L}$ and $\mathbf{M}$ is also the same. This indicates that in the general case the normal to the domain wall is of the form

$$\mathbf{n}=(a^2+b^2)^{1/2}(a\mathbf{i}+b\mathbf{j}),$$

where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors along the axes X and Y, respectively, i.e., a type-II domain wall does not have to lie along crystallographic planes. For the low-field type-I walls such a conclusion cannot be drawn. Although the qualitative form of $\mathbf{L}$ and $\mathbf{M}$ is the same for $\mathbf{n}\|Y$ and $\mathbf{n}\|X$, their groups are substantially different. Therefore, the type-I domain walls lie only along crystallographic planes.

In an oblique magnetic field (i.e., for $\mathbf{H}$ in the XY plane) the symmetry group $\mathbf{G}_{pm}^H$ of the crystal is also a subgroup of $\mathbf{G}_{pm}$. In this case the group $\mathbf{G}_{bc}$, both for $\mathbf{n}\|Y$ and for $\mathbf{n}\|X$, is the same as $\mathbf{G}_{pm}^H$ and contains only two elements: 1 and $2_z'(-)$. The possible symmetry groups describing DW I and DW II in this case are clearly subgroups of the corresponding groups considered in parts A and B of this section. We therefore find that DW I corresponds to the group $\mathbf{G}_1$, while DW II corresponds to the group $\mathbf{G}_4$. Domain wall DW I remains twofold degenerate, but in DW II the degeneracy is lifted. We recall that for $\psi\neq 0$, $\mathbf{L}$ is rotated by an angle $\Delta\varphi<\pi$ in one of the type-II domain walls, while in the other $\Delta\varphi>\pi$. We should point out that in Sec. 2 we assumed that only the components L_x and L_y varied in DW I, while a symmetry analysis shows that, generally speaking, even for $\mathbf{H}\|$EA, all of the components of the vector $\mathbf{L}$ vary in the domain walls. It can be shown that the appearance of a nonzero component L_z in DW I is due to the presence of a term $L_xL_yL_zM_x$ in the system energy. This invariant is associated with the fourth-order anisotropy energy. It is clear that allowance for this term would not change H^* significantly.

The results of the symmetry analysis permit the following conclusion. When the external magnetic field $\mathbf{H}$ is oriented strictly along the easy axis, two types of domain walls can exist in the spin-flop phase of the $(C_2H_5NH_3)_2CuCl_4$ crystal: DW I and DW II, both twofold degenerate. When $\mathbf{H}$ deviates from the easy axis in the XY plane, the degeneracy in DW I remains, but that in DW II is lifted, i.e., there will exist two type-II domain walls, both described by the group $\mathbf{G}_4$ but having different energies: in one of them the vector $\mathbf{L}$ is rotated through an angle $\Delta\varphi<\pi$, while in the other $\Delta\varphi>\pi$. This occurs because of the presence of terms containing d and d' in the system energy. For $d=d'=0$ the states with antiparallel directions of $\mathbf{L}$ are energetically equivalent, and in this case only 180-degree domain walls occur in an oblique field.

5. CONCLUSION

The theoretical and experimental investigations carried out in this study have shown that a domain-wall phase transition occurs in a rhombic antiferromagnet in a field H^* above the field of the spin-flop transition. In a magnetic field inclined from the easy axis toward the intermediate axis there are two domain-wall phase transitions, in fields $H_1^*<H^*$ and $H_2^*>H^*$. This is because there are two energetically inequivalent type-II domain walls in an inclined field. At the fields H_1^* and H_2^* the phase transition occurs from the twofold degenerate type-I domain walls to one of the type-II domain walls.

Because of the presence of a nonzero net magnetic moment in a field above the spin-flop field, rhombic antiferromagnets with the Dzyaloshinskiĭ interaction should have a thermodynamically stable domain structure. At the same time, the experimental results on $(C_2H_5NH_3)_2CuCl_4$ show that here the domain walls are basically of kinetic origin.

Finally, we call attention to a general pattern. As the spin-reorientation transition is approached, the difference between the energies of the competing phases decreases sharply, i.e., there is a sharp decrease in the height of the potential barrier separating the stable states in the plane of rotation. This, in turn, implies a decrease in the energy of the domain wall in which $\mathbf{M}_1$ and $\mathbf{M}_2$ are rotated in the same way as at the spin-reorientation transition. If a different type of domain wall exists far from the spin-reorientation transition, one expects a restructuring of the domain walls as this transition is approached. In this regard it can be said that the phase transitions in the domain walls accompany transitions in the volume of the magnet: as the spin-reorientation transition is approached, the structure of the domain walls changes in such a way that the rotations of $\mathbf{M}_1$ and $\mathbf{M}_2$ in the walls correspond to the direction of the impending reorientation.

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