Evidence for orthorhombic distortions in the ordered state of ZnCr$_2$O$_4$: A magnetic resonance study

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We present an elaborate electron-spin resonance study of the low-energy dynamics and magnetization in the ordered phase of the magnetically frustrated spinel ZnCr$_2$O$_4$. We observe several resonance modes corresponding to different structural domains and found that the number of domains can be easily reduced by field-cooling the sample through the transition point. To describe the observed antiferromagnetic resonance spectra it is necessary to take into account an orthorhombic lattice distortion in addition to the earlier reported tetragonal distortion which both appear at the antiferromagnetic phase transition.

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I. INTRODUCTION

The intriguing physics of spinel compounds is in the focus of current solid-state research. The current hot debates on the origin of exotic phenomena and ground states in magnetic spinels concern, e.g., the Verwey transition in Fe$_3$O$_4$, heavy-fermion formation in LiV$_2$O$_4$, colossal magnetoresistance in Cu doped FeCr$_2$S$_4$, gigantic Kerr rotation and the orbital glass state in FeCr$_2$S$_4$, the spin-orbital liquid in FeSc$_2$S$_4$, the colossal magneto-capacitive effect in CdCr$_2$S$_4$ and HgCr$_2$S$_4$, the negative thermal expansion and strong spin-phonon coupling in ZnCr$_2$Se$_4$ and ZnCr$_2$S$_4$, the spin dimerization in CuIr$_2$S$_4$ and MgTi$_2$O$_4$, and the spin-Peierls-like transitions in 3-dimensional solids. The appearance of these fascinating ground states is attributed to the competition of charge, spin and orbital degrees of freedom, which are strongly coupled to the lattice.

Additional complexity in the normal AB$_2$X$_4$ spinels arises from the frustration effects related to the topological constrains of the pyrochlore lattice of corner-sharing tetrahedra of the B-site magnetic ions. In this geometry the exchange interaction alone cannot select a unique ground state. As a result, the magnetic system remains in the disordered state down to temperatures much lower than the scale provided by the exchange interaction. In ZnCr$_2$O$_4$ strong direct antiferromagnetic Cr-Cr exchange is manifested by the Curie-Weiss temperature of about $-400$ K, while magnetic order appears only below 12 K via a first-order phase transition. At this transition the aforementioned degeneracy is lifted by a structural deformation, which is reported to be tetragonal.

Neutron-scattering experiments have proven that non-collinear commensurate antiferromagnetic order is established below the transition temperature. However, the details of the magnetic structure are still under heavy debate. It was speculated that a multi-k structure is formed. Moreover, sample dependent intensities of the magnetic reflections suggest that ZnCr$_2$O$_4$ is critically located close to several spin structures.

In the present paper we report results of a magnetic resonance study in the ordered phase of ZnCr$_2$O$_4$. Earlier ESR studies concentrated on the paramagnetic state above $T_N$ and did not report any resonance absorption signals below $T_N$. We find several gapped resonance modes, spin-reorientation transitions, and evidences for an orthorhombic structural deformation. We observe magnetic resonance signals originating from different structural domains. We demonstrate that these domains can be effectively aligned by field cooling in a moderate magnetic field. The low-energy dynamics can be described qualitatively within the exchange-symmetry theory, indicating that magnetic order in ZnCr$_2$O$_4$ is governed by a single order parameter.

II. EXPERIMENTAL DETAILS

ZnCr$_2$O$_4$ single crystals were grown by chemical transport reactions from polycrystalline starting material prepared by solid-state reactions of stoichiometric binary zinc and chromium oxides of 99.99% purity. Perfect single crystalline samples of octahedral shape and dimensions up to 3 mm on the edge were obtained. X-ray diffraction at room temperature revealed a single-phase material with the cubic spinel structure with a lattice constant $a = 8.332(1)$ Å and an oxygen fractional coordinate $x = 0.263(1)$. The magnetic properties were studied using a commercial SQUID magnetometer (Quantum Design MPMS-5) working at fields up to 50 kOe.

Magnetic resonance measurements in the wide frequency range from 20 to 150 GHz were performed at the Kapitza Institute. For these measurements we have used a set of home-made transmission-type ESR spectrometers equipped with a superconducting cryomagnet. High-sensitivity X-band (9.3 GHz) magnetic resonance
experiments were carried out using a Bruker "Elexsys E500 CW" spectrometer equipped with an Oxford Instruments helium gas-flow cryostat. Magnetic resonance absorption spectra were recorded at different frequencies for three principal orientations of the magnetic field: $H_{\parallel}(001)$, (110), (111). The measurements were mostly done on zero-field cooled samples, the effect of field cooling was checked at certain frequencies.

### III. EXPERIMENTAL RESULTS.

Figure 1 shows the temperature dependence of the magnetic susceptibility of ZnCr$_2$O$_4$ single crystals for the magnetic field applied along all three characteristic directions of the cubic system. The susceptibility is isotropic above the antiferromagnetic (AFM) transition temperature $T_N = 12.5$ K. At high temperatures the susceptibility follows a Curie-Weiss law, but deviates already at about 100 K and develops a broad maximum around 50 K indicative for short-range AFM correlations. At $T_N$ one observes a discontinuous change of the data typical for a first-order transition. In the magnetically ordered regime the magnetic susceptibility of the zero-field-cooled (ZFC) sample shows a pronounced anisotropy with the highest value for measurements along the (001) direction (for the measurements in the field of 10 kOe).

To investigate the anisotropy in more detail, the magnetization was measured dependent on the magnetic field both for zero-field cooling (ZFC) as well as after field-cooling (FC) in 50 kOe. As shown in Fig. 2 the ZFC data manifest a non-linear behavior in small fields (up to 20 kOe) and a linear increase of the magnetization for higher fields. For $H_{\parallel}(100)$ the $M/H$ curve shows a linear increase indicating smooth rotation of the magnetization, while for the two other directions strong non-linearities are observed around 15 kOe, as typical for a spin-flop. Field cooling has only a weak effect for $H_{\parallel}(001)$, but leads to nearly constant $M/H$ for the other two orientations. In the field cooled sample the largest value of magnetic susceptibility is observed for $H_{\parallel}(110)$.

The evolution of the resonance-absorption spectrum with temperature is shown in Figure 3. At high temperatures (in the paramagnetic phase) a single absorption component with a $g$-factor close to 2.0 is observed. The transition to the antiferromagnetically ordered state is clearly marked by the discontinuous transformation of the resonance absorption spectrum: below the Néel temperature $T_N$ the absorption spectrum consists of several components strongly shifted from the paramagnetic resonance position. No hysteresis exceeding the resolution limit of 0.1 K was detected at the transition. On cooling below $T_N$ the resonance lines first show a pronounced shift, but below 5 K the temperature dependence of the resonance positions is negligible.

The shape of the resonance absorption spectra is strongly affected by field cooling. Figure 4 compares the resonance absorption measured on ZFC and FC samples. Here field cooling was performed at the field of 50 kOe.
starting from 20 K. For $\mathbf{H}||\langle110\rangle$ and $\langle111\rangle$ field cooling leads to the disappearance of some of the absorption components. The remaining absorption components are usually slightly shifted from the corresponding absorption component measured on the ZFC sample. The vanishing absorption intensity does not necessarily add to the remaining components: for example, for $\mathbf{H}||\langle110\rangle$ the intensity of the remaining component after field cooling is the same as for the ZFC sample. For $\mathbf{H}||\langle001\rangle$ field cooling effects are less evident — all absorption components are observed in FC samples, field cooling leads only to a slight change of the absorption intensity.

Actually, application of a field of 50 kOe during the cooling seems to be excessive. It is enough to cool the sample at the moderate field of 18 kOe to suppress some of the resonance modes as can be seen in the inset of Figure 3. Especially, the soft modes indicative for spin-reorientation, disappear after field cooling but reappear as the sample is rotated to another crystallographically equivalent position. Note that the nonlinearity of the magnetization curves vanishes after field cooling as well. The stability of the ZFC resonance absorption under prolonged exposure to the magnetic field below $T_N$ was also checked by the high-sensitive X-band measurements. At 4 K the shape of the resonance absorption is reproducible to the finest details. However, at 8 K (which is still below $T_N$) keeping the $\mathbf{H}||\langle110\rangle$-oriented sample at 18 kOe for 90 minutes leads to 30% reduction of the observed resonance absorption.

The entire frequency-field diagrams for the different orientations of the magnetic field are given in Figure 5. These dependences demonstrate the presence of several resonance modes with zero-field gaps of $21 \pm 2$ GHz and $113 \pm 2$ GHz. For $\mathbf{H}||\langle110\rangle$ and $\langle111\rangle$ one of the resonance modes softens in the magnetic field between 10 and 15 kOe. Note that the nonlinearity of the magnetization curves is also observed at $H = 10 \ldots 15$ kOe for these directions (Figure 2). Field cooling reduces the number of the observed resonance modes to two: one for each of the zero-field gaps.

IV. DISCUSSION.

A. Phase transition, domains, field cooling

As documented above, the change of the resonance field at the phase transition is discontinuous. In conventional molecular field approximation, the shift of the antiferromagnetic resonance field with respect to the paramagnetic resonance is proportional to the magnitude of the order parameter, i.e., to the sublattice magnetization. The discontinuous change of the resonance field at the phase transition indicates that the order parameter is not small even just below the transition temperature. This observation is in agreement with the analysis of the order parameter fixed by anisotropic interactions (Figure 6).

The magnetic susceptibility of the paramagnetic phase is isotropic due to its cubic symmetry. Cubic symmetry is lost in the ordered state because of the lattice deformation. The lattice-strain direction can take one of the equivalent crystallographic axes. The susceptibility tensor of the antiferromagnet is anisotropic, the orientation of its principal axes is determined by the orientation of the order parameter fixed by anisotropic interactions with respect to the crystallographic axes. Therefore, the susceptibility tensors of different structural domains are oriented differently and the gain in the Zeeman energy is different for different domains. Thus, the application of magnetic field makes one of the domains more favorable. It provides an obvious mechanism for the observed field-cooling effect and for the instability of the resonance absorption close to $T_N$, described in the previous section. This assumption is in agreement with the increase of the magnetic susceptibility in the field-cooled sample (Figure 2).

The formation of the domain structure in the case of a cubic-to-tetragonal lattice transition is well studied for ferroelastic systems. A complicated domain structure consisting of thin twinned domains is usually formed in ferroelastics (see, for example, recent Refs. 23,24). Twinning allows to avoid strong local strain at the contact of the domains with different directions of deformation axes.
The thickness of twin domains observed in the doped ferroelastic HTSC compound YBa$_2$Cu$_3$O$_7$ is about 10–100 nm. Twinning also leads to a slight tilting (of the order of $\Delta a/a$) of the domain axes from the corresponding crystallographic axes of the high-temperature phase. While the axes tilting is too small ($\Delta a/a \sim 10^{-3}$) to be of importance, small domain thickness could result in excitation of standing spin-waves with $k \sim 1/L$ ($L$ is a domain thickness) instead of a uniform $k = 0$ oscillation. This size effect can be a possible reason for the slight shift of the resonance absorption position in the FC sample. This allows to estimate the thickness of the crystallographic domains. We assume a quadratic spectrum of antiferromagnetic spin-waves

$$E = \sqrt{\Delta_0^2 + \alpha^2 k^2}$$

(1)

here $\alpha \sim J a$. $J$ denotes the exchange coupling constant between nearest-neighbour spins at distance $a$. If $ak \ll \Delta_0$, the effective zero-field gap for the standing spin-waves is larger than for the uniform oscillation by $\delta = \alpha^2 k^2 / (2\Delta_0)$. Consequently, the resonance branches of the monodomain (FC) sample should be shifted downwards (on the $H$-$f$ plane) by $\delta$ with respect to the resonance branches of the multidomain (ZFC) sample: i.e. for the branches rising with the field the remaining absorption component of the FC sample shifts at the given frequency to higher fields with respect to its position in the case of the ZFC sample. This slight shift is observed in the experiment (Figure 4), its magnitude does not exceed the half-width of the absorption line. We estimate $\delta/h$ as 1 GHz ($h$ is the Planck constant). Then, the domain thickness can be estimated as

$$\frac{L}{a} \sim \frac{J}{\sqrt{\Delta_0 \delta}}$$

(2)

which yields (substituting $J = 20$ K$^{27}$ $\Delta_0/h=20$ GHz, ) $L/a \sim 100 \gg 1$.

In further discussion we assume that the domains are thick enough to be considered as bulk antiferromagnet, and that the domain walls do not contribute to the magnetic resonance absorption.

**B. Application of the exchange-symmetry theory**

We use the theory of exchange symmetry$^{25}$ to analyze the experimental results. According to this theory, if the relativistic effects are much smaller than the exchange interaction, the order parameter can be represented by at most 3 unitary orthogonal vectors which transform by irreducible representations of the crystal symmetry group. The number of vectors and these representations define the exchange symmetry of the magnet. This approach allows to describe all symmetry-based properties of a magnet without considering its detailed microscopic structure or any model assumption. For the case of a noncollinear antiferromagnet the order parameter consists of at least two vectors. In case of only two vectors for the sake of simplicity we denote $l^{(i)} = [l^{(i)} \times l^{(j)}]$. We derive the dynamic equations for homogeneous oscillations from the Lagrange function

$$\mathcal{L} = \sum_i I_i \left( l^{(i)} + \gamma [l^{(i)} \times \mathbf{H}] \right)^2 - U_a,$$

(3)

where $\gamma$ is the gyromagnetic ratio of the free electron, the constants $I_i$ are related to the eigenvalues of the susceptibility tensor, and the term $U_a$ includes small relativistic corrections to the main exchange part due to spin-orbital and dipole-dipole effects. These corrections can be expanded by the components of the order parameter. The first order of the $U_a$ expansion is quadratic on $l^{(i)}$. The second order terms can be omitted, because they are $\alpha^2$ times smaller, where $\alpha$ is the fine-structure constant. The Lagrange function must be invariant under all transformations of the crystallographic symmetry group, which results in some relations between the coefficients in $U_a$ expansion. These relations vary for different exchange-symmetry groups.

The dynamic equations are obtained by taking a variational derivative of the Lagrangian$^{26}$ over the rotations of the spin space. These equations should be linearized near the equilibrium position to obtain the eigenfrequencies of small oscillations. In general case, if the magnetic field direction deviates from the eigenvector of the susceptibility tensor, the equilibrium positions cannot be determined analytically. To model the observed frequency-field dependences, we perform numerical calculations of the oscillation eigenfrequencies. We use standard minimization routines to find an equilibrium orientation of the order parameter. This modeling procedure is combined with a fitting algorithm using the constants $I_i$ and the coefficients of the $U_a$ expansion as fit parameters.

When performing the expansion of the relativistic corrections, it is necessary to take into account that in the case of ZnCr$_2$O$_4$ the magnetic unit cell is larger than the crystallographic one$^{22,28}$. Therefore some components of the order parameter are not invariant under some of the translational elements of the crystallographic symmetry group. Since the crystal-symmetry group $D^{2d}_2$, suggested in Ref.$^{21}$, has a point symmetry $D_{2d}$ in the vertex of the crystallographic cell, we will focus primarily on the point-symmetry subgroup. Note that this special property remains for all subgroups of $D^{2d}_2$. Thus, on discussing the lowering of the lattice symmetry below $T_N$ to $D_2$, we will focus primarily on the point-symmetry subgroup.

Although some representations of $D_{2d}$ allow weak ferromagnetism, the susceptibility measurements do not reveal any spontaneous magnetization. This can be either due to the spontaneous magnetization being too small, or, more likely, there is no weak ferromagnetism for the exchange group in the present case. Therefore, we will not take weak ferromagnetism into account in further discussion.
C. Evidence for orthorhombic distortions below \( T_N \)

Here we will demonstrate that the assumption of the tetragonal lattice symmetry in the ordered phase contradicts the experimental observation described in the previous section and the explanation of the experimental findings requires a further reduction to orthorhombic symmetry.

First, we note that the symmetry of the magnetic structure below \( T_N \) is lower than tetragonal. This statement follows directly from the observation of the distinct field-cooling effect for \( \mathbf{H} \parallel (111) \), since this field orientation is equivalent for all tetragonal domains.

For the tetragonal lattice deformation only three types of different crystallographic domains, differing by the direction of the tetragonal axis \( z \parallel (001) \), \( (010) \), \( (001) \), can be formed at the transition. Since the magnetic symmetry of the ordered phase is lower than the lattice symmetry, two types of magnetic domains with different \( x \) and \( y \) axes can be formed in each crystallographic domain. Here and further on in this paper we will denote \( x \) and \( y \) the directions of the two-fold axes perpendicular to the \( z \) axis (\( S_4 \) axis for the \( D_{2d} \) symmetry). Note that the reduction of the point symmetry from \( O_h \) to \( D_{2d} \) could be done in two ways: (i) by removal of the \( [100] \) and \( [010] \) symmetry axes as well as \( (10) \) mirror planes; (ii) by removal of the \( [110] \) and \( [10-1] \) symmetry axes as well as \( (100) \) and \( (010) \) mirror planes with the former four-fold axes \( (100) \) and \( (010) \) becoming two-fold axes. In the second choice of axes the magnetic field aligned along the \( (111) \) direction would be equivalent for all domains and there would be no reason for the observed field-cooling effects. Thus, the first possibility has to be realized. (Identification \( ^{24}\) of the tetragonal phase as \( \overline{P}4m2 \) also points to the first possibility.) Therefore, \( x \) and \( y \) axes are aligned along the diagonals of the cubic facets.

Now all domains can be classified by the orientation of their "\( xyz \)" basis with respect to the cubic axes of the paramagnetic phase as shown in Table I. Some of these domains appear to be equivalent in the particular experimental conditions (here \( x, y, z \) are the unit vectors in the corresponding directions, trivial cases are combined):

### TABLE I: Classification of the AFM domains with respect to the cubic axes of the paramagnetic phase

| domain | \( x \) | \( y \) | \( z \) |
|--------|--------|--------|--------|
| (a)    | [110]  | [-110] | [001]  |
| (b)    | [1-10] | [110]  | [001]  |
| (c)    | [101]  | [10-1] | [010]  |
| (d)    | [-101] | [101]  | [010]  |
| (e)    | [011]  | [0-11] | [100]  |
| (f)    | [01-1] | [011]  | [100]  |

\( \mathbf{H}\parallel [100] \)
- domains (e),(f): \( \mathbf{H}\parallel z \)
- domains (a), (b), (c), (d): \( \mathbf{H}\parallel x + y \)

\( \mathbf{H}\parallel [110] \)
- domain (a): \( \mathbf{H}\parallel x \)
- domain (b): \( \mathbf{H}\parallel y \)
- domains (c), (f), (d), (e): \( \mathbf{H}\parallel \frac{x+y}{\sqrt{2}} + z \)

\( \mathbf{H}\parallel [111] \)
- domains (a), (c), (e): \( \mathbf{H}\parallel \sqrt{2}x + z \)
- domains (b), (d), (f): \( \mathbf{H}\parallel \sqrt{2}y + z \)

Note that for the \( \mathbf{H}\parallel (111) \) field orientation there are only two types of different magnetic domains. As one can see from the experimental data in Figure 3 we observe five resonance branches in this orientation: two originating from the higher gap, two originating from the lower gap and one in the high-field—low-frequency part of the frequency-field diagram. The observation of this fifth branch indicates the existence of a third zero-field gap which is not observed directly and is less or equal in magnitude than the lowest observed gap of 21 GHz.

To apply the exchange-symmetry theory as described in the previous subsection it is necessary to specify the symmetry of the order parameter. The point symmetry group \( D_{2d} \) has two-dimensional and one-dimensional irreducible representations. If \( \mathbf{l}^{(1)} \) and \( \mathbf{l}^{(2)} \) transform by a two-dimensional representation, then \( \mathbf{l}_1 = \mathbf{l}_2 \) and the relativistic contribution to the Lagrangian \( E \) has the form:

\[
U_a = \frac{1}{2} A \left( \mathbf{l}_1^{(1)} \right)^2 + \frac{1}{2} B \left( \mathbf{l}_2^{(2)} \right)^2 + \frac{1}{2} C \left( \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} + \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} \right) + \frac{1}{2} D \left( \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} \right)^2
\]

(4)

If \( \mathbf{l}^{(1)} \) and \( \mathbf{l}^{(2)} \) transform differently under translations, then \( B = C = 0 \). In the other fundamental case, if \( \mathbf{l}^{(1)} \) and \( \mathbf{l}^{(2)} \) transform by one-dimensional representations, the relativistic contribution reads:

\[
U_a = \frac{1}{2} A \left( \mathbf{l}_1^{(1)} \right)^2 + \frac{1}{2} B \left( \mathbf{l}_2^{(2)} \right)^2 + \frac{1}{2} C \left( \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} - \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} \right)
\]

(5)

or

\[
U_a = \frac{1}{2} A \left( \mathbf{l}_1^{(1)} \right)^2 + \frac{1}{2} B \left( \mathbf{l}_2^{(2)} \right)^2 + \frac{1}{2} C \left( \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} + \mathbf{l}_1^{(1)} \mathbf{l}_2^{(2)} \right)
\]

(6)

Depending on the coefficients of the \( U_a \) expansion, there are two general possibilities: (i) the \( \mathbf{l}^{(1)} \) lie in the \( (xz) \) and \( (yz) \) planes; (ii) the \( \mathbf{l}^{(1)} \) lie in the planes including the \( z \) axis and the bisector of the \( (xy) \) plane (i.e. in the \( D_{2d} \) group mirror planes). \( \text{ZnCr}_2\text{O}_4 \) corresponds
to the first case, since in the second case for $\mathbf{H}||(111)$ the order parameter vectors $l^{(1)}, l^{(2)}, l^{(3)}$ in all magnetic domains form the same angles with the field direction, which should result in the absence of the field cooling effects.

We tried to fit the experimentally observed frequency-field dependences applying the exchange-symmetry theory as described above. However, we did not reach any reasonable agreement of the modeled curves with the experiment. The reason of this disagreement can be explained qualitatively. Namely, it can be proven (see Appendix) that for the tetragonal $D_2d$ point symmetry the domain manifesting a spin reorientation transition becomes indistinguishable from the other domains above the transition field. This is due to the fact that even for a magnetic symmetry lower than tetragonal, the anisotropic contribution $U_a$ reflects the tetragonal crystal symmetry. Thus, after the spin reorientation transition the reoriented domain appears to be in a state with the Zeeman energy lower than before reorientation, but with the same value of the anisotropic term $U_a$. The equivalence of the magnetic domains above the transition should provide the same magnetic resonance frequencies above the spin-flop transition. Moreover, there would be no reason for these domains to split again as the magnetic field is reduced to zero. This, however, contradicts the experimental observation of the specific resonance modes corresponding to the domain undergoing a spin-reorientation above the spin-flop field, as well as to the reproducibility of the low-field domain structure.

The problem can be solved by the assumption that the lattice deformation at $T_c$ involves not only a compression along the $c$-direction, but also a weak in-plane deformation leading to further reduction of the symmetry. There are two options: to exclude mirror planes (which yields $D_2$ point symmetry) or to exclude second-order axes ($C_{2v}$). As we have shown above, the components of the order parameter lie in the $(xz)$ and $(yz)$ planes. This limits our choice to $D_2$ point symmetry (the corresponding space subgroup of $D_{2d}^2$ is $D_2^1 (F222)$) with second-order axes along $001$ directions ($z$), and along $(110)$ directions ($x$ and $y$). This assumption provides inequivalent crystallographic domains differing by the $x$ and $y$ directions. These orthorhombic distortions were not detected in the earlier structural studies, most likely because they are probably smaller than the experimental resolution.

D. Modeling of the AFM resonance frequency-field dependences for the case of orthorhombic distortions

We modeled the antiferromagnetic resonance frequency-field dependences assuming orthorhombic distortions below $T_N$. As was explained above, to write down the expansion of $U_a$ we again will focus on the point-symmetry group. The $D_2$ symmetry group has four one-dimensional representations. There are only four fundamentally different cases, the others can be reduced to them by renaming the axes $x$, $y$ or vectors $l^{(1)}, l^{(2)}$:

$$U_a = \frac{A}{2} \left( l_z^{(1)} \right)^2 + \frac{B}{2} \left( l_z^{(2)} \right)^2 + \frac{C}{2} \left( l_x^{(1)} \right)^2 + \frac{D}{2} \left( l_x^{(2)} \right)^2 + E \left( l_y^{(1)} - l_y^{(1)} \right) + F \left( l_y^{(1)} l_y^{(2)} + l_y^{(2)} l_y^{(1)} \right)$$

$$U_a = \frac{A}{2} \left( l_z^{(1)} \right)^2 + \frac{B}{2} \left( l_z^{(2)} \right)^2 + \frac{C}{2} \left( l_x^{(1)} \right)^2 + \frac{D}{2} \left( l_x^{(2)} \right)^2 + E \left( l_y^{(1)} l_y^{(2)} + l_y^{(2)} l_y^{(1)} \right)$$

$$U_a = \frac{A}{2} \left( l_z^{(1)} \right)^2 + \frac{B}{2} \left( l_z^{(2)} \right)^2 + \frac{C}{2} \left( l_x^{(1)} l_x^{(2)} + l_x^{(2)} l_x^{(1)} \right) + F l_x^{(1)} l_x^{(2)}$$

$$U_a = \frac{A}{2} \left( l_z^{(1)} \right)^2 + \frac{B}{2} \left( l_z^{(2)} \right)^2 + \frac{C}{2} \left( l_x^{(1)} \right)^2 + \frac{D}{2} \left( l_x^{(2)} \right)^2$$

Here we again exclude weak ferromagnetism from the consideration. The first three cases are feasible only if $l^{(1)}$ and $l^{(2)}$ transform in the same way under translations. The third case is feasible if $l^{(1)}$ and $l^{(2)}$ transform by the same one-dimensional irreducible representation.

The low symmetry of the ordered state results in too many free parameters in the equations of spin dynamics (four to six coefficients in the $U_a$ expansion and two of the three $I_i$ constants). By fixing the zero-field gaps of the AFM resonance spectrum we can put only three constraints on these parameters. Other constraints are expected to appear during the fitting of the modeled AFM resonance spectra. This involves too many degrees of freedom for the assumptions on the sort of equilibrium position, the way the spin-flop transition takes, and the correspondence between structural domains and resonance branches. An unequivocal quantitative reproduction of the experimental curves was difficult to achieve, however, a reasonable agreement with the experimentally observed AFM resonance spectra was obtained for different sets of parameters and for the different forms of $U_a$.

Here we present the results of modeling the case of $U_a$ taken in the form $\mathbf{S}$. From Figure $\mathbf{4}$ one can see that the correspondence of model and experiment is fairly good. The correct quantity of resonance branches is obtained. The values of the zero-field gaps are in good agreement with the experimental data. For orientations $\mathbf{H}||(110)$ and $(111)$ the spin-reorientation transitions of certain domains are well reproduced.

Our modeling indicates that the frequency-field dependences can be reasonably reproduced assuming a single type of order parameter and taking into account all possible domains. There are really just two types of discrepancies between the experimental data and modeled curves: first, there are predicted low-frequency modes at
Figure 5: (color online) Frequency-field dependences of the resonance modes for the principal cubic orientations (open symbols—ZFC, closed symbols—FC). The numeric calculations (lines) are based on Eqn. 5. Fit parameters: $\gamma = 2.8$ GHz/kOe, $I_1 = 3.931$, $I_2 = 0.950$, $I_3 = 1.00$, $A = 65523.87$ GHz², $B = 3444.56$ GHz², $C = -6192.39$ GHz², $D = -5664.49$ GHz², $E = -8710.32$ GHz², $F = 0$.

High fields which are not observed; second, for the orientation $H||<110>$ the modes corresponding to the domain with lowest energy $(H||x)$ are far from the experimental data corresponding to the domain stable under field cooling (see the fit curves and experimental data marked by a, a', b, b' in the lower panel of Fig. 5). These discrepancies can be due to the following reasons: at 9 GHz ESR experiments, fields up to only 18 kOe were available, whereas above 18 GHz the frequency-field dependences of the low-frequency modes in question are rather flat. In the case of $I_2 = I_3$ they become field independent which results in a strong broadening of the resonance modes in the experiments at fixed frequency. Thus, these modes cannot be detected in a field scan. Concerning the discrepancy for the $H||x$ domain, note that the modeled curves still demonstrate an "anti-crossing" which can be enhanced, for example, by higher order terms in the energy expansion.

Our modelling demonstrates that the spin-reorientation transition can be realized by a continuous

Figure 6: (color online). Upper frame: Calculated field dependences of the energy difference for various domains. The calculations are done for the same parameters as used for the AFM resonance spectrum shown in Figure 5. Middle frame: Calculated magnetization of the domains with unfavorable orientation. Inset: Calculated field dependences of the Euler angles for the $H||<110>$ y-domain. Lower frame: Calculated magnetization of the domains with favorable orientation of the order parameter.
rotation of the order parameter as shown e.g. for the $y$ domain in the inset of Fig. 4. This explains the absence of a sharp change of the magnetization at the spin-reorientation transition which is simulated in the middle and lower frames of this figure. The field dependence of the magnetization is qualitatively well reproduced: it demonstrates a nonlinear behavior with a characteristic change during the spin-reorientation for the unfavorable domains, which would disappear after field cooling, and an almost linear behavior for the favorable domains which remains after field cooling. The energy difference between different domains shown in the upper frame of this figure explains the observed field-cooling phenomena. The domains corresponding to the modes surviving the field cooling have the lowest energy in the magnetic field. For the orientation $H \parallel \langle 111 \rangle$ the calculated energy difference between the domains is similar and, thus, the field-cooling effect is comparable to the case $H \parallel \langle 110 \rangle$. For $H \parallel \langle 001 \rangle$ this difference is much smaller which can probably explain the much weaker field-cooling effect for this direction. However we have to admit the problem in reproducing the experimentally observed anisotropy of the field-cooled magnetization at low fields: the experimentally highest susceptibility for the monodomain FC sample is observed for $H \parallel \langle 110 \rangle$ (Figure 4), while the modelled curves for the presented parameter set indicate a slightly higher susceptibility for the most favorable domain in the $H \parallel \langle 100 \rangle$ (Figure 0). Note that the modeled difference of the three favorable domains is tiny, thus for low fields some weak effects related to shape anisotropy or surface effect may destroy the stability of the uniform magnetization.

Summarizing the results of our modeling, we conclude that the low-energy dynamics of the ordered phase of ZnCr$_2$O$_4$ can be described by the assumption of a single type of magnetic order below $T_N$. This puts a question mark on the possibility to realize different spin structures in ZnCr$_2$O$_4$ as suggested earlier. We suppose that the complications in the determination of the magnetic structure of ZnCr$_2$O$_4$ by neutron scattering were caused by the unaccounted orthorhombic deformations and effects of multiple domains.

V. CONCLUSIONS

We have performed a detailed study of the low-energy dynamics of the ordered phase of the frustrated antiferromagnetic spinel ZnCr$_2$O$_4$. We have proven directly that multiple domains exist below the transition temperature $T_N$. We have demonstrated that some of these domains are effectively suppressed by field cooling. Spin-reorientation transitions indicated by softening of certain antiferromagnetic resonance modes and by the nonlinear behavior of the magnetization are observed.

These results are incompatible with the earlier proposed symmetry of the distorted lattice. Thus, we conclude that the lattice deformation at the phase transition involves small in-plane distortions besides the tetragonal distortions. We suggest that the actual symmetry of the lattice below $T_N$ corresponds to the orthorhombic $D_2^7$ symmetry.

We have demonstrated that the low-energy dynamics can be reasonably described within the framework of the exchange-symmetry theory, assuming a noncollinear magnetic ordering characterized by a single order parameter.

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**APPENDIX A: INSTABILITY OF THE CERTAIN DOMAINS IN CASE OF THE TETRAGONAL LATTICE SYMMETRY**

Here we will prove that for the $D_{2d}$ point symmetry at the spin-reorientation transition the domain demonstrating this transition becomes indistinguishable from the other domains.

First we consider the case when $l^{(1)}$ and $l^{(2)}$ transform by two-dimensional representation of $D_{2d}$. Minimizing the energy (4) we get the orientation of the order parameter in the absence of magnetic field. For $|B| > |A|$ the solution consists vectors lying in the mirror planes, which is not the case of ZnCr$_2$O$_4$ (see above). For $|A| > |B|$ and $A < 0$ the two solutions are $l^{(1)} || x$, $l^{(2)}$ lying in the (yz) plane and $l^{(2)} || y$, $l^{(1)}$ lying in the (zx) plane. The case of $A > 0$ can be reduced to this one by renaming the axes $x$ and $y$. These solutions define two different magnetic domains. If the susceptibility along $l^{(3)}$ is less than along $l^{(1)}$ and $l^{(2)}$, then for $H || x$ one of the domains is already in its minimum of the Zeeman energy. The other one is not in the minimum and at some value of magnetic field it will undergo a spin-reorientation transition. As it turns out, there is only one possible state for it after the transition, the same as for the first domain. So after the spin-flop these two domains will be indistinguishable. If the susceptibility along $l^{(1)}$ and $l^{(2)}$ is less than along $l^{(3)}$, both domains are not in the minimum of the Zeeman energy when the field is applied along the $x$ axis. Still after the spin-flop both domains again become indistinguishable.

Now we consider case when $l^{(1)}$ and $l^{(2)}$ transform by
one-dimensional representations of $D_{2d}$. To define the orientation of the order parameter we minimize the energy. We get the result that one of the vectors (let it be $l^{(1)}$) is aligned in the $(xy)$ plane, but its orientation in this plane remains arbitrary. To find a solution, it is necessary to take into account the next order terms in the $U_a$ expansion. There is no need to write down all of them, just note that due to the tetragonal symmetry the dependence of $U_a$ on the angle $\phi$ between $l^{(1)}$ and $x$ is $F \cos(4\phi)$. There are two sets of solutions depending on the sign of $F$. For $F > 0$ the solutions are $\phi = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4$, i.e. $l^{(1)}$ lies in the mirror plane, which is not the case of ZnCr$_2$O$_4$. For $F < 0$ the solutions are $\phi = 0, \pi/2, \pi, 3\pi/2$. These solutions define two magnetic domains: for one of them $l^{(1)}||x$ and for the other $l^{(1)}||y$. First, no matter along which $l^{(1)}$ the susceptibility is largest, a spin-reorientation transition is expected for $H||(|x \pm y)$ (i.e. $H||001$). This spin-reorientation is either rotation of the order parameter around the $z$ axis by $\pi/4$ or, in the special case of the largest susceptibility being along the $z$ axis, rotation of the largest susceptibility direction to the $(xy)$ plane. However, such a transition is not observed in our experiments. Second, the spin-flop transition observed at $H||111$ can be caused only by rotation of the order parameter around the $z$ axis, but after this rotation both domains become indistinguishable.

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