Highly Frustrated Magnetism 2008 (HFM 2008) IOP Publishing
Journal of Physics: Conference Series **145** (2009) 012030 doi:10.1088/1742-6596/145/1/012030

Spin dynamics of the ordered phase of the frustrated antiferromagnet $ZnCr_2O_4$: A magnetic resonance study.

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Abstract. We present an elaborate electron-spin resonance study of the low-energy dynamics and magnetization in the ordered phase of the frustrated spinel $ZnCr_2O_4$. 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.

The spinel $ZnCr_2O_4$ is a model system to study geometric frustration [1]. It is also an interesting example (along with the sister compound $CdCr_2O_4$) for the lifting of frustration by lattice distortions. Magnetic ordering at $T_N = 12.5$ K ($\Theta/T_N \approx 30$) is accompanied by a structural phase transition [2, 3] which violates the equivalence of the exchange bonds on the pyrochlore lattice and makes the antiferromagnetic ordering possible. However the magnetic structure of the ordered phase is not deciphered completely yet [3]. It was suggested [3] that even in the tetragonal phase $ZnCr_2O_4$ is critically located close to several spin structures.

Here we present results of a detailed magnetic resonance study of the ordered phase of $ZnCr_2O_4$. Magnetic resonance allows to probe the low-energy excitations of a magnet at energies as low as 0.03 meV. The dynamic properties of the ordered magnet depend strongly on the structure of the order parameter, its orientation, and lattice symmetry. The experiments were performed on high-quality single crystals of $ZnCr_2O_4$ grown by chemical transport reactions from polycrystalline starting material prepared by solid-state reactions of stoichiometric binary zinc and chromium oxides. Electron spin resonance (ESR) absorption spectra were measured at the frequencies 9–150 GHz (corresponding magnon energies 0.03–0.4 meV) at temperatures down to 1.8 K. High frequency (20–150 GHz) ESR experiments were performed using a set of home-made transmission-type spectrometers equipped with a superconducting cryomagnet. High-sensitivity X-band (9.4 GHz) measurements were carried out using a Bruker "Elexsys E500 CW" spectrometer equipped with an Oxford Instruments helium gas-flow cryostat. The

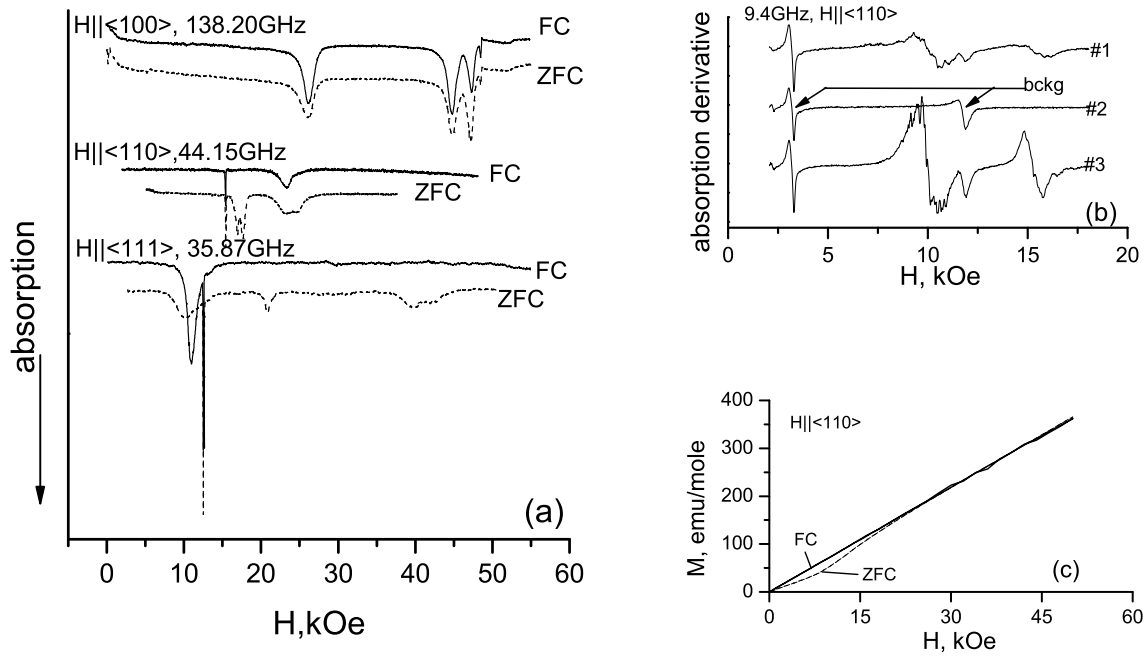

Figure 1. Effect of field cooling on the dynamic and static properties of $ZnCr_2O_4$: (a) Resonance absorption spectra for the field cooled (FC, solid) and zero-field cooled (ZFC, dashed) sample for different orientations at $T = 1.8$ K. The narrow absorption line at $g = 2.00$ is due to a DPPH marker. (b) X-band ESR spectra at $T = 4.2$ K. ♯1 — ZFC sample, ♯2 — same orientation after FC, ♯3 — sample rotated by 90° around $\langle 100 \rangle$ to the equivalent position after FC; (c) Magnetization curves of the ZFC (dashed) and FC (solid) samples at $T = 2.0$ K.

magnetic properties were studied using a commercial SQUID magnetometer (Quantum Design MPMS-5). All experiments have been done on different crystals from the same batch.

We observed strongly orientation dependent resonance absorption signals below T_N (Fig. 1a,b). At the transition temperature the absorption spectrum transforms from a single-component paramagnetic absorption to a multi-component antiferromagnetic resonance absorption. This transformation is discontinuous in agreement with the first-order nature of this phase transition. The low-temperature absorption spectra are found to be completely reproducible even after prolonged exposure of the sample to the high magnetic field.

Field cooling (FC) is found to affect strongly the shape of the resonance absorption. Field cooling effects were tested by cooling the sample through the phase transition in a field of 50 kOe for the high-frequency ESR and magnetization measurements and in a field of 18 kOe for the X-band ESR. The FC effect is orientation sensitive: for the orientations $\mathbf{H}||\langle 110 \rangle, \langle 111 \rangle$ field cooling of the sample completely suppresses certain absorption components, while for $\mathbf{H}||\langle 100 \rangle$ only very slight changes are observed in the intensity of the components (Fig. 1a,b). The magnetization curves are also sensitive to field cooling: the magnetization curves of the zero-field cooled (ZFC) sample demonstrate a nonlinearity around 15 kOe in all principal orientation which vanish after field cooling for $\mathbf{H}||\langle 110 \rangle, \langle 111 \rangle$ (Fig. 1c), while for $\mathbf{H}||\langle 100 \rangle$ the magnetization curve remains unaffected by field cooling.

The frequency-field dependences of the ESR absorption (i.e., the field dependences of the energy of $k = 0$ magnons) are presented in Figure 2. There are several branches, zero-field gaps of about 25 and 115 GHz are clearly observed. Some of the branches tend to soften at a field

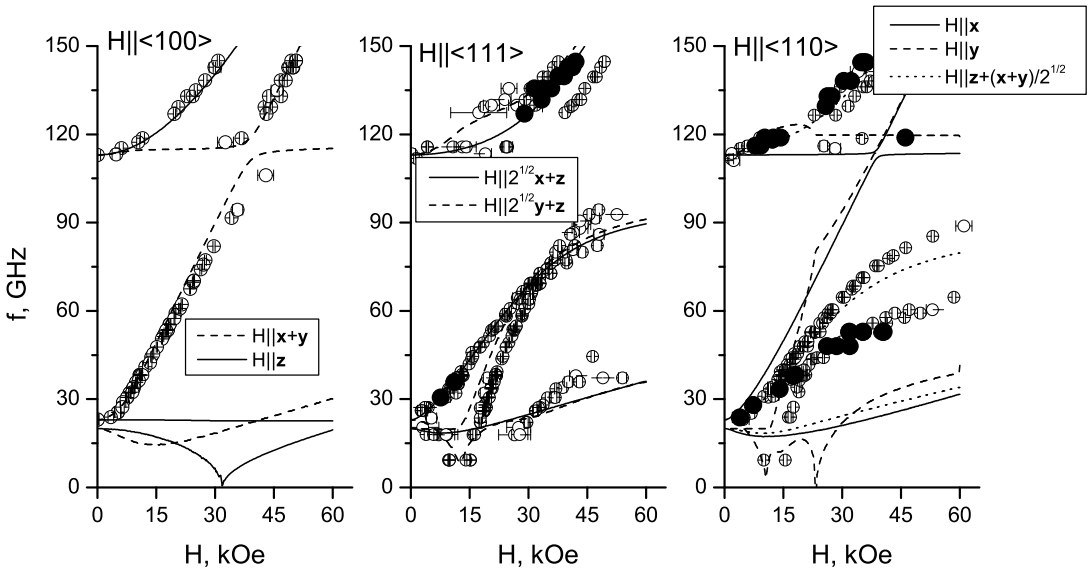

Figure 2. f(H) dependences at $T = 1.8$ K. Circles — experimental data (○ - ZFC, ● - FC), curves (solid, dashed and dotted) — theoretical modelling for different domains. Fit parameters: $\gamma = 2.8$ GHz/kOe, $I_1 = 3.931$, $I_2 = 0.950$, $I_3 = 1.00$, $A = 65523.87$ GHz^2, $B = 3444.56$ GHz^2, $C = -6192.39$ GHz^2, $D = -5664.49$ GHz^2, $E = -8710.32$ GHz^2, $F = 0$.

of about 15 kOe. The softening of resonance branches indicates a spin-reorientation transition, since at the spin-reorientation transition a certain spin-rotation does not cost any energy and the corresponding oscillation mode loses its rigidity. The softening mode disappears after field cooling (Fig. 1b). Note that the nonlinearity of the magnetization is observed in the same field.

The existence of different structural (and magnetic) domains below the transition point provides a plausible reason for the observed field cooling effects. Since the magnetic susceptibility tensor of an antiferromagnet is anisotropic and its orientation with respect to the crystal axes is fixed by anisotropic interactions, some of the domains should have larger magnetic susceptibility. These domains are selected during the field cooling, while in the ZFC sample all possible domains are present.

The $\mathbf{H}||\langle 111\rangle$ orientation of the magnetic field is equivalent for all three possible tetragonal domains (with the strain axis along [100], [010] and [001]). If the magnetic symmetry of the ordered phase would be also tetragonal, all magnetic domains would be equivalent in this case. The existence of different magnetic domains, evidenced by the observation of the field cooling effect in this orientation, indicates that the magnetic symmetry of the ordered state is lower than tetragonal, i.e. at least orthorhombic.

Some of the observed results are not compatible with a tetragonal lattice distortion [4]. There are two possibilities for the reorientation of the order parameter on a tetragonal lattice: either it rotates from the fourth order axis to the plane or it rotates around the fourth order axis. In the first scenario, spin-reorientation should be observed at approximately the same field in all domains with the magnetic field perpendicular to the symmetry axis, including some of the domains in the $\mathbf{H}||\langle 100\rangle$ orientation, which is not the case. In the second scenario, the 90°-

rotation of the order parameter results in a state with the same anisotropy energy but a higher susceptibility, thus, the magnetic domain demonstrating a spin-reorientation transition should be unstable and should disappear after the first field scan, which is not observed — on the contrary, the softening ESR mode is reproducible to the finest details even after prolonged exposure to the magnetic field. The explanation of these facts requires that the ordered phase lattice symmetry should be rather orthorhombic than tetragonal. Note that no orthogonal distortions have been reported so far from the structural studies. The amplitude of these distortions could be too small to resolve the Bragg peaks of domains with different orientation of the in-plane axes experimentally. E.g., splitting of the synchrotron X-ray superlattice peak due to the main (tetragonal) distortion reported in Ref.[3] is just a factor of two larger then the peak width.

We have performed a theoretical modelling of the low-energy dynamics of $ZnCr_2O_4$ assuming a single order parameter, orthorhombic lattice distortions, and taking into account all possible domains. The modelling is done within the framework of exchange-symmetry theory [5]. According to this theory, the order parameter can be represented by at most 3 unitary orthogonal vectors which transform by irreducible representations of the crystal symmetry group. For the case of a noncollinear antiferromagnet the order parameter consists of at least two vectors (in case of only two vectors we denote $\mathbf{l}^{(3)} = [\mathbf{l}^{(1)} \times \mathbf{l}^{(2)}]$). The dynamic equations for homogeneous oscillations are derived from the Lagrange function

$$\mathcal{L} = \sum_{i=1}^{3} \frac{I_i}{2} \left(\dot{\mathbf{l}}^{(i)} + \gamma [\mathbf{l}^{(i)} \times \mathbf{H}] \right)^2 - U_a,$$

where γ 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. U_a reflects lattice and magnetic symmetry. Here we present results for U_a taken in the form

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

As a result we obtained a qualitatively good agreement with the experiment (Figure 2): The modelled curves reproduce zero-field gaps, spin-reorientation transitions and all observed branches of the resonance f(H) dependences.

Summarizing, the low-energy dynamics of the ordered phase of the frustrated antiferromagnet $ZnCr_2O_4$ is studied. Magnetic resonance absorption signals originating from different structural domains are observed. The domain structure is found to be sensitive to field-cooling of the sample: some of the domains vanish after field-cooling. The analysis of the magnetic resonance data indicates an orthorhombic symmetry of the lattice below the antiferromagnetic transition. Low-energy dynamic can be described assuming a single spin structure is formed.

Acknowledgments
The authors thank A.I. Smirnov, S.S. Sosin, V.I. Marchenko, L.E. Svistov, I.N. Khliustikov for their continuous interest and numerous discussions. The work was supported by the RFBR (grant 07-02-00725), the Russian Science Support Foundation, Russian Presidential Grants (6122.008.2 and 3526.2008.2), cooperative grant 08.820.05.038RF(Russia-Moldova) and partially by the Deutsche Forschungsgemeinschaft (DFG) within SFB 484 (Augsburg).

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