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MAGNETISM AND FERROELECTRICITY

On the Magnetic Phase Diagram of Copper Metaborate

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Abstract—A stepwise transition from one incommensurate state of the spin system of a copper metaborate crystal to another incommensurate state was previously revealed using neutron scattering in an applied magnetic field. In this paper, the new state is interpreted as a combination of a commensurate state of one spin subsystem and an incommensurate state of another spin subsystem of the crystal.

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1. INTRODUCTION

Earlier [1, 2], it was established that a tetragonal crystal of copper metaborate CuB_2O_4 undergoes a magnetic phase transition to an ordered state of the type of a weak ferromagnet at the Néel temperature $T_N \approx 20$ K. This state is commensurate with the crystal lattice, because the magnetic unit cell coincides with the crystal chemical unit cell. At the temperature $T_I \approx 10$ K, the spin system of copper metaborate transforms into an incommensurate helical structure along the tetragonal axis **c**. Experiments on neutron scattering in this crystal have revealed an unusual transition from an incommensurate state to a commensurate state in strong magnetic fields [3, 4]. For example, upon elastic scattering at $T = 4.2$ K in the magnetic field $H_{c1} = 1.3$ T directed along the [1, 1, 0] direction, reflections with $\mathbf{q} \approx [0, 0, 0.14]$ (in units of the reciprocal lattice) disappear abruptly, whereas reflections with $\mathbf{q}_1 = [0, 0, 0]$ and $\mathbf{q}_2 \approx [0, 0, 0.27]$ increase by one order of magnitude. The intensity of reflections with $\mathbf{q}_2$ decreases by a factor of two already after the magnetic field is increased by 0.5 T, i.e., at $H_{c2} \approx 1.8$ T; however, in a magnetic field of 1.3 T, these reflections are observed up to a temperature of 6 K. For inelastic neutron scattering at a temperature of 1.5 K in zero magnetic field, both excitation branches of the spin system have minima at $\mathbf{k} \approx [0, 0, 0.15]$. In contrast to this case, at a temperature of 3 K and in a magnetic field of 2 T in the [1, –1, 0] direction, the excitation energy has a minimum at $\mathbf{k} = [0, 0, 0]$ for the high-energy branch and a minimum at $\mathbf{k} \approx [0, 0, 0.15]$ for the low-energy branch. In this study, we propose a model of the spin system of copper metaborate which allows for the above-described behavior of the system in a strong magnetic field.

2. PHENOMENOLOGICAL MODEL AT ZERO EXTERNAL MAGNETIC FIELD

The structure of copper metaborate is described by the space group $I\bar{4}2d$ with the unit cell parameters $a = 11.528$ Å and $c = 5.607$ Å. Copper ions Cu^{2+} occupy two nonequivalent positions: Cu(*b*) occupies the 2*b* position with point symmetry $S_4(0, 0, 1/2)$, and Cu(*d*) occupies the 4*d* position with point symmetry $C_2(0.0815, 1/4, 1/8)$.

In order to describe the aforementioned phase transitions in zero external magnetic field on the basis of the experimental data [1–4], we restrict our consideration to the modes obtained by the symmetrical analysis [5] as order parameters: $T = T_N \longleftrightarrow \eta_1 = (l_{by}, l_{bx})$, $\mathbf{l}_b = \mathbf{S}_{b1} - \mathbf{S}_{b2}$; $T = T_I \longleftrightarrow \eta_2 = (l_{dx}, l_{dy})$, $\mathbf{l}_d = \mathbf{S}_{d1} - \mathbf{S}_{d2} + \mathbf{S}_{d3} - \mathbf{S}_{d4}$. Both modes are transformed according to the two-component representation Γ_5 [6], and the indexes *b* and *d* denote the positions occupied by ions in the unit cell.

Spins of copper ions are coupled by the antiferromagnetic indirect exchange interaction through the Cu–O–B–O–Cu chains. For this interaction, we introduce the designation $J^{(n)}$, where *n* is the number of fractions **c**/8 in the projection of the vector between the coupled spins onto the **c** axis. The subsystem of *b* spins involves only one type of spin–spin interactions, $J_{bb}^{(2)}$, which is responsible for the formation of a three-dimensional lattice with the commensurate ground state ($\mathbf{q} = 0$, where **q** is the wave vector of the magnetic structure). In the subsystem of *d* spins, the spin–spin interactions can be divided into three types: the interactions $J_{dd}^{(4)}$ and $J_{dd}^{(8)}$, which couple spins into zigzag chains in voids of the aforementioned three-dimensional lattice paral-

lel to the tetragonal axis, and the interaction $J_{dd}^{(2)}$, which provides coupling between the chains. Ferromagnetic ordering inside the chain and antiferromagnetic ordering between the chains with the order parameter η_2 is possible only under the condition $2J_{dd}^{(2)} > J_{dd}^{(4)} + J_{dd}^{(8)}$. By analogy with the ANNY model, the commensurability of the quantities $J_{dd}^{(2)}$, $J_{dd}^{(4)}$, and $J_{dd}^{(8)}$ is responsible for the formation of the incommensurate ground state of the subsystem of d spins ($\mathbf{q} \neq 0$). The interactions $J_{bd}^{(1)}$, $J_{bd}^{(3)}$, and $J_{bd}^{(5)}$ provide the coupling between the subsystems, which is frustrated for copper metaborate in the commensurate phase.

Taking into account the above distribution of exchange interactions, we can write the incomplete thermodynamic potential of the spin system of the crystal in the form

$$\Phi\{\eta\} = \int\left\{\left[\frac{A_{12}(\eta_1\cdot\eta_1)}{2} + \frac{A_{14}(\eta_1\cdot\eta_1)^2}{4} + \frac{D_{12}\eta_1'\cdot\eta_1'}{2}\right]\right.$$
$$\left[\frac{A_{22}(\eta_2\cdot\eta_2)}{2} + \frac{A_{24}(\eta_2\cdot\eta_2)^2}{4} + \frac{D_{22}\eta_2'\cdot\eta_2'}{2} + \frac{D_{22}\eta_2''\cdot\eta_2''}{2}\right]$$
$$\left. + C_{12}(\eta_1\cdot\eta_2' - \eta_1'\cdot\eta_2)\right\}dV, \qquad (1)$$

where $A_{12} = T - T_1$; $A_{22} = T - T_2$; the constants A_{14}, D_{12}, A_{24}, $-D_{22}$, D_{24}, and $-C_{12}$ are positive; $\eta' \equiv \partial\eta/\partial z$; $\eta'' \equiv \partial^2\eta/\partial z^2$; and V is the volume of the crystal. The terms enclosed in the square brackets represent the particular contributions of each of the subsystems, which interact with each other exclusively via the Lifshitz invariant constructed from two two-component order parameters [5]. The invariant $\eta_1 \cdot \eta_2$ is absent because of the aforementioned frustration of the exchange interaction between the subsystems in the commensurate phase.

Since the thermodynamic potential (1) does not contain anisotropic contributions in the basal plane, the solution of the extremum condition $\delta\Phi/\delta\eta = 0$ can be found in the plane-wave representation

$$\eta_1 = (p_{11}\exp(iq_1z) + p_{11}^*\exp(-iq_1z),$$
$$p_{12}\exp(iq_1z) + p_{12}^*\exp(-iq_1z)),$$
$$\eta_2 = (p_{21}\exp(iq_2z) + p_{21}^*\exp(-iq_2z),$$
$$p_{22}\exp(iq_2z) + p_{22}^*\exp(-iq_2z)).$$

There are three such solutions.

(i) $q_1 = q_2 = 0$ is the commensurate state, $\eta_1 = 2p_1(1, 0)$, $p_1 = \mathrm{Re}\{(-A_{12}/A_{14})^{1/2}/2\}$, $\eta_2 = 2p_2(1, 0)$, $p_2 = \mathrm{Re}\{(-A_{22}/A_{24})^{1/2}/2\}$, $\Phi_1 = \{[22A_{12}p_1^2 + 4A_{14}p_1^4] + [2A_{22}p_2^2 + 4A_{24}p_2^4]\}V$.

(ii) $q_1 = q_2 = q \neq 0$ is the incommensurate state, $\eta_1 = 2p_1(\cos(qz), -\sin(qz))$, $\eta_2 = 2p_2(\cos(qz), \sin(qz))$, p_1^2 and p_2^2 are the solutions of the fourth-order polynomials, $\Phi_2 = \{[(2A_{12} + 2D_{12}q^2)p_1^2 + 4A_{14}p_1^4] + [(2A_{22} + 2D_{22}q^2 + 2D_{24}q^4)p_2^2 + 4A_{24}p_2^4] + 8C_{12}qp_1p_2\}V$.

(iii) $q_1 = 0$, $q_2 = (-D_{22}/D_{24})^{1/2}$ is the "semi-incommensurate" state, $\eta_1 = 2p_1(1, 0)$, $p_1 = \mathrm{Re}\{(-A_{12}/A_{14})^{1/2}/2\}$, $\eta_2 = 2p_2(\cos(qz), \sin(qz))$, $p_2 = \mathrm{Re}\{(-A_{22n}/A_{24})^{1/2}/2\}$, $A_{22n} = T - T_{2n}$, $T_{2n} = T_2 + D_{22}^2/(2D_{24})$, $\Phi_3 = \{[2A_{12}p_1^2 + 4A_{14}p_1^4] + [2A_{22n}p_2^2 + 4A_{24}p_2^4]\}V$.

Let us dwell on the last solution. This solution follows from the condition $q_1 \neq q_2$: the contribution of the Lifshitz invariant to the thermodynamic potential becomes negligible, that is,

$$\int C_{12}(\eta_1\cdot\eta_2' - \eta_1'\cdot\eta_2)dV = 0;$$

the interaction between the subsystems throughout the crystal is absent; and each of these subsystems is ordered in accordance with its ground eigenstate. By evaluating the region of the existence of solutions $\Phi_2 < \Phi_1$ at $T < T_2 + 4C_{12}^2/D_{12}$ and $\Phi_3 < \Phi_1$ at $T < T_{2n}$, we can determine the ratio between the coefficients of the incomplete thermodynamic potential at which the spin system of the crystal transforms from the commensurate state into the incommensurate or semi-incommensurate state with decreasing temperature.

3. AN EXTERNAL MAGNETIC FIELD

The coexistence of a commensurate state of one subsystem with an incommensurate state of the other subsystem is highly improbable because the frustration of the exchange interaction is violated. Such a state can exist only in a strong homogeneous magnetic field. In order to describe the interaction of the magnetic field with the spin system of the crystal, it is necessary to add the following terms to the incomplete thermodynamic potential:

$$\Delta\Phi\{\eta\} = \int\left\{\left[\frac{A_{32}\eta_3\cdot\eta_3}{2} + \frac{B_{12}(\eta_1\cdot\eta_1)(\eta_3\cdot\eta_3)}{2}\right]\right. \qquad (2)$$
$$\left. + \left[\frac{A_{42}\eta_4\cdot\eta_4}{2} + \frac{B_{24}(\eta_2\cdot\eta_2)(\eta_4\cdot\eta_4)}{2}\right] - H(p_{3H} + p_{4H})\right\}dV,$$

where the constants A_{32}, B_{13}, A_{42}, and B_{24} are positive and depend on the orientation of the magnetic field H; the parameters B_{13} and B_{24} are responsible for the decrease in $|\eta_1|$ and $|\eta_2|$, respectively, as the order parameters increase with increasing magnetic field [5];

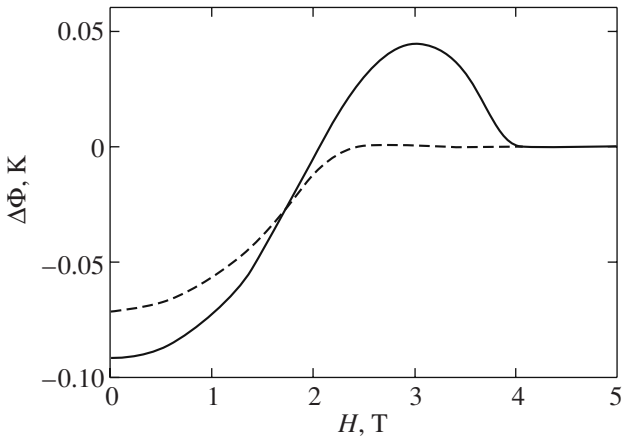

Fig. 1. Simulated field dependences of the thermodynamic potentials Φ_2 (solid line) and Φ_3 (dashed line) reckoned from the potential Φ_1 for the temperature $T = 4$ K.

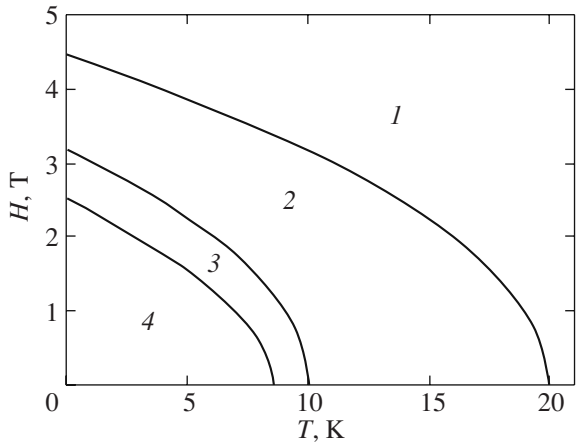

Fig. 2. Simulated H–T magnetic phase diagram: (*1*) paramagnetic phase, (*2*) antiferromagnetic commensurate phase, (*3*) semi-incommensurate phase, and (*4*) incommensurate phase.

H ∥ **c**: $\eta_3 = m_{bz}$ is transformed according to the representation Γ_2,

$$\mathbf{m}_b = \mathbf{S}_{b1} + \mathbf{S}_{b2};$$

$\eta_4 = m_{dz}$ is transformed according to the representation Γ_2,

$$\mathbf{m}_d = \mathbf{S}_{b1} + \mathbf{S}_{b2} + \mathbf{S}_{d3} + \mathbf{S}_{d4};$$

H ⊥ **c**: $\eta_3 = (m_{bx}, -m_{by})$ is transformed according to the two-component representation Γ_5,

$\eta_4 = (m_{dx}, -m_{dy})$ is transformed according to the two-component representation Γ_5;

and p_{3H} and p_{4H} are the components of the parameters η_3 and η_4 along the magnetic field.

Figures 1 and 2 represent the results of the numerical simulation performed for the following coefficients of the thermodynamic potential: $A_{12} = T - 20$, $A_{14} = 100$, $D_{12} = 170$, $C_{12} = -11$, $A_{22} = T - 7$, $A_{24} = 100$, $D_{22} = -100$, $D_{24} = 1600$, $A_{32} = 1$, $B_{13} = 1$, $A_{42} = 1$, and $B_{24} = 1$. It can be seen from Fig. 1 that an increase in the magnetic field can be accompanied by a change in the ratio between the thermodynamic potentials Φ_1, Φ_2, and Φ_3, which leads to the transition of the spin system of the crystal to another state. As a result, we obtain the magnetic phase diagram shown in Fig. 2.

In the temperature range 10–20 K, the d spins are in the paramagnetic state and aligned with the **c** axis due to the Dzyaloshinskii–Moriya weak interaction with the already ordered subsystem of b spins. In order to describe this interaction within the phenomenological approach, it is necessary to take into account the invariants

$$\eta_1 \cdot \eta_5 \quad \text{and} \quad \eta_3 \cdot \eta_5,$$

where $\eta_5 = (S_{d2z} - S_{d4z}, S_{d1z} - S_{d3z})$ is transformed according to the two-component representation Γ_5 [5]. We will restrict our analysis to the case of the orientation minimization

$$\eta_1 = l_b(\sin(\varphi_{lb}), \cos(\varphi_{lb})),$$

$$\eta_3 = m_b(\cos(\varphi_{mb}, -\sin(\varphi_{mb}))), \quad \eta_5 = m_d(2, 2),$$

where η_5 corresponds to ordering of d spins along the [0, 0, 1] axis according to the rule $S_{d1z} + S_{d2z} - S_{d3z} - S_{d4z}$. The first invariant provides alignment of the antiferromagnetically ordered b spins along the [1, 1, 0] axis with $\varphi_{lb} = \pi/4$. The second invariant allows us to describe the canted weakly ferromagnetic system of b spins in the plane with $\varphi_{mb} = -\pi/4$. The agreement between the simulated orientation of the spins and the experimental data obtained at 12 K [2] confirms the observed paramagnetic behavior of the system of d spins above 10 K.

4. DISCUSSION

The anomalously large increase in the magnitude of the wave vector q from zero to ≈0.15 with decreasing temperature below T_I is associated with the change in the ratio between the order parameters η_1 (with the commensurate eigenstate of b spins, $q_b = 0$) and η_2 (with the incommensurate eigenstate of d spins, $q_d \approx 0.27$). As the external homogeneous magnetic field increases, copper metaborate undergoes the following sequence of phase transitions: (i) up to the first critical magnetic field H_{c1}, there exists a stable incommensurate state ($\eta_1 \neq 0, \eta_2 \neq 0$); (ii) at $H = H_{c1}$, the spin system of copper metaborate due to the first-order phase transition transforms into a semi-incommensurate state ($\eta_1 \neq 0, \eta_2 \neq 0$); (iii) at the second critical magnetic field H_{c2}, the d spins collapse ($\eta_1 \neq 0, \eta_2 = 0$); and (iv) at the

third critical magnetic field H_{c3}, the b spins collapse ($\eta_1 = 0$, $\eta_2 = 0$). The critical magnetic fields H_{c1} and H_{c2} for copper metaborate at 4.2 K were determined using elastic neutron scattering [3] and are equal to 1.3 and 1.8 T, respectively. The critical magnetic field H_{c3} can be estimated from the maximum of the high-energy excitation branch obtained for the spin system upon inelastic neutron scattering [4]: 8 meV/($2\mu_B$) ≈ 68 T, where μ_B is the Bohr magneton.

At present, we are analyzing the microscopic model in order to refine the magnetic phase diagram of copper metaborate.

REFERENCES

1. G. Petrakovskii, D. Velikanov, A. Vorotinov, K. Sablina, A. Amato, B. Roessli, J. Schefer, and U. Staub, J. Magn. Magn. Mater. **205**, 105 (1999).
2. B. Roessli, J. Schefer, G. Petrakovskii, B. Ouladdiaf, M. Boehm, U. Staub, A. Vorotinov, and L. Bezmaternikh, Phys. Rev. Lett. **86**, 1885 (2001).
3. J. Schefer, M. Boehm, B. Roessli, G. A. Petrakovskii, B. Ouladdiaf, and U. Staub, Appl. Phys. A: Mater. Sci. Process. **74**, S1740 (2002).
4. M. Boehm, B. Roessli, J. Schefer, B. Ouladdiaf, J. Kulda, and G. A. Petrakovskii, Physica B (Amsterdam) **378–380**, 1128 (2006).
5. M. A. Popov, G. A. Petrakovskii, and V. I. Zinenko, Fiz. Tverd. Tela (St. Petersburg) **46** (3), 478 (2004) [Phys. Solid State **46** (3), 491 (2004)].
6. O. V. Kovalev, *Irreducible and Induced Representations and Corepresentations of Fedorov's Groups* (Nauka, Moscow, 1986) [in Russian].

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