Incommensurate magnetic structure in copper metaborate

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Abstract

The results on the magnetic susceptibility, magnetization, specific heat, neutron scattering and μSR of the tetragonal copper metaborate single crystal are presented. The easy plane magnetic commensurate structure with the spontaneous moment was determined in the temperature range $21\div10$ K. The incommensurate magnetic ground state of this crystal was observed at the temperatures below 10 K until 0.15 K. It is shown the existence of a third magnetic transition below 1.8 K. The external magnetic field induces the phase transition from the incommensurate to commensurate structure. A phenomenological theory of the incommensurate magnetic structure was developed.

Key words: magnetic phase transitions; magnetic soliton lattice

Iincommensurate magnetic structures are known to appear most often as a result of competition of exchange interactions not having any limitations on crystal structures. Less frequently, incommensurate structures are formed as a result of relativistic interactions. In this case the physical reason is the so-called Dzyaloshinskii-Moria antisymmetric exchange interaction This interaction forms incommensurate structures only in crystals that have no center of symmetry. In this paper we give the results of the experimental and theoretical investigations of copper metaborate magnetic structure.

According to X-ray and neutron diffraction studies, CuB_2O_4 forms tetragonal crystal, space group $I\bar{4}2d$ (D_{2d}^{12}) with lattice parameters a = 11.528 $\AA$ and c = 5.607 $\AA$. The unit cell contains 12 formula units. Copper ions are situated in two non-equivalent positions, namely Cu(b) - site $4b$, point symmetry group S_4 (0,0,0.5), and Cu(d) - site $8d$, point symmetry group C_2 (0.0815,0.25,0.125).

Peculiarities in temperature dependencies of magnetic susceptibility obtained on a SQUID magnetometer appeared at T_A = 20 K and T_B = 10 K. For a magnetic field applied in the basal plane of the crystal, a susceptibility jump was observed at T_A. Then susceptibility rapidly increased as temperature decreased. At T_B susceptibility decreased in a jump by approximately one order of magnitude and then monotonically increased down to 4.2 K. For a magnetic field applied parallel to the tetragonal axis of the crystal, the temperature dependence of susceptibility was smooth in the whole temperature range.

The magnetic susceptibility anomalies described above were accompanied by singularities of the temperature dependence of heat capacity. In addition, the heat capacity temperature dependence contained an anomaly in the form of a broad maximum near 4 K.

Muon spin relaxation (μSR) data on the temperature dependence of the depolarization rate confirmed the conclusion of magnetic transformation at T_A and T_B. The measurements at temperatures down to 0.06 K revealed the occurrence of an additional magnetic transformation close to 1 K.

Neutron diffraction studies of copper metaborate were performed for single crystal that contained the ^{11}B isotope to decrease absorption of neutrons. The

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magnetic structure in the temperature range 10÷20 K was found to be commensurate and a weak ferromagnetic. The value of magnetic moment at 12 K was about 1 μ_B for ions Cu(b) and 0.25 μ_B for Cu(d). The magnetic moment of Cu(d) ion rapidly increased as temperature lowered below T_B and equaled 0.7 μ_B at 2 K.

At temperatures below T_B two magnetic satellites appeared symmetrically with respect to reciprocal lattice points of the commensurate phase. The magnetic structure became incommensurate along the tetragonal axis of the crystal and was described by a spin density wave with phase modulation. The spin modulation wave vector continuously increased from $q = (0, 0, 0)$ at 10 K to $q \approx (0, 0, 0.15)$ at 1.8 K. The temperature dependence of wave vector obeyed the power law $q(T) \sim (T_B - T)^{1/2}$. Below 1.8 K we observed a constancy of q.

In a small temperature range near T_B higher magnetic satellite harmonics appear in the neutron diffraction spectrum which is the signature of the formation of magnetic solitons.

Strong diffuse neutron scattering was superimposed on the Bragg peaks for the Q_0 neutron scattering vector along the [001] direction. The intensity of diffuse scattering increased as temperature rised from 1.8 K and reached a maximum close to T_B.

At the application of a magnetic field B along the [110] direction, the wave vector decreased according to $q(B) = q(0) - 0.0039 \cdot B^2$, where B was measured in Tesla. Above the critical field $B_c = 1.3T$ the wave vector decreased in a jump to zero at the temperature 4.2 K. The diffraction measurements at 4.2 K and the magnetic field 1 T along [110] direction had not shown $3q$-satellites. However for B > 0 we observed supplementary $2q$-satellites which may be related to a deformation of the magnetic structure helix. In contrast to the zero-field case where magnetic satellites of index $3q$ appeared close to the temperature of the commensurate-incommensurate phase transition, harmonicas of index $2q$ were visible at all temperatures for $B = 1T$. Whereas q-satellites disappeared above $Bc \approx 1.3T$, the intensity of the second-order harmonicas abruptly increased indicating the appearance of a first-order magnetic phase transition. This new magnetic phase is characterized by a wave vector $q_i = (0, 0, 0.22)$ and is characterized by the coexistence of an incommensurate modulation of the magnetic structure together with magnetic intensity at the commensurate position $q_0 = (0, 0, 2)$. Whereas at $B = 1.3T$ the q_i-satellite decreased with increasing temperature and vanished at $T \approx 6K$, the intensity of the q_0-peak increased in this temperature range.

At a magnetic field decreasing the temperature of transition from the incommensurate to commensurate magnetic structure increased steadily until it reached T_B for $B = 0T$ in accordance with static magnetic and resonance measurements data. Close to the phase transition there was the region of temperatures where a central peak appeared in the incommensurate phase. This peak was not observed in zero magnetic field. On the other hand, when the magnetic field was removed the diffraction spectrum was characterized by the superposition of diffuse scattering and magnetic satellites. The application of magnetic field tended to suppress the diffuse scattering.

A phenomenological analysis of such properties as temperature dependencies of wave vector q and thermal capacity was fulfilled. The thermodynamic potential was presented as a functional of two-component order parameters η_A and η_B. Both parameters transform on the same two-dimensional representation and differ by linear combinations of magnetic modes. The parameter η_A was corresponded to the transition at T_A. The description of helix magnetic ordering lower T_B was obtained by accounting of Lifshits invariant allowed by copper metaborate symmetry and constructed on the η_B parameter. The result of the analysis is that in the temperature range $T_A \div T_B$ the order parameter η_B is small compared with η_A and rapidly increases at $T < T_B$. A similar increase of q coincides with that observed experimentally but qualitatively differs from the latter in that $q \neq 0$ already at temperatures below T_A. As for thermal capacity the fluctuation contribution with a maximum intrinsic to a second-order phase transition dominates at T_A. In the experimental curves the singularity at T_B had the form of a step. This peculiarity is related to a rapid growth of the η_B parameter. The field induced by the bilinear interaction between subsystems suppresses thermal fluctuations in the second subsystem. The step at T_B was observed against the background of a broad maximum that increased as temperature decreased. This maximum can be assigned to a Schottky-type anomaly. The deviation of the experimental dependence from the calculation results at $T < 3.5K$ is caused by the approach to the phase transition at 1.8 K.

The sharp decrease of intensity of magnetic peaks (3,3,±q) at 1.8 K and subsequent constancy of q at lowering temperature can be connected with lock-in transition in a commensurate phase. Such a transition is accompanied by jump appearance of a gap in the spectrum of excitations transversal to order parameter and appropriate decrease of correlation functions.

The transformation of a magnetic spiral to soliton lattice and corresponding appearance of higher-order harmonicas happens at combined action of Lifshits invariant and an invariant of anisotropy as $\eta^n \cos(n\varphi)/n$. The application of a magnetic field in the tetragonal plane induced such anisotropy with $n = 1$. Therefore appearance on neutron diffraction pattern of magnetic peaks of index $2q$ is quite natural.