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Physica B 318 (2002) 277–281

PHYSICA B

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A neutron scattering and μSR investigation of the magnetic phase transitions of CuB_2O_4

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Abstract

We have investigated the magnetic ground state in CuB_2O_4, copper metaborate, by means of neutron diffraction and μSR measurements. At $T_N = 21$ K CuB_2O_4 undergoes a second-order phase transition from a paramagnetic to an antiferromagnetic commensurate state followed by a second transition at $T^* = 10$ K where the two magnetic sublattices form a soliton lattice, as reported earlier. We give a detailed analysis of the magnetic structure in the commensurate phase which is found to be different from the one published recently. New experimental results are presented which show the existence of a third transition below $T \approx 1.8$ K. The magnetic structure remains incommensurate at very low temperatures, but a re-distribution of the magnetic intensities is observed in the neutron diffraction data set which suggests that the phases between the Cu^{2+} spins are changed. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 75.25.+z; 75.30.Gw; 75.10.Hk

Keywords: Magnetic soliton lattice; Dzyaloshinskii–Moriya interaction; Neutron diffraction; μSR

1. Introduction

Copper-oxide compounds have been the subject of an intense research in the past years as they show a variety of new physical effects like high-T_C superconductivity, spin-Peierls transition or antiferromagnetism associated with very small magnetic moments.

CuB_2O_4 has been synthesized long time ago [1], but it is only recently that the magnetic properties of this compound have been investigated by means of susceptibility, specific heat and μSR measurements. In that paper [2], it was shown that CuB_2O_4 undergoes a magnetic phase transition to a weak-ferromagnetic state at $T_N = 21$ K, followed by a second magnetic transition at $T^* = 10$ K. Later neutron diffraction experiments revealed that below the Néel temperature the magnetic structure of CuB_2O_4 is commensurate associated to the wave vector $\mathbf{k} = (0, 0, 0)$.

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PII: S0921-4526(02)00788-3

At T^* the Cu^{2+} magnetic moments exhibit a particular transition from the commensurate ordered state to an incommensurate one. In a small temperature range near this phase transition, higher harmonics appear in the neutron diffraction spectrum which is the signature of the formation of a magnetic soliton lattice [3], as originally proposed by Dzyaloshinskii [6] and later reconsidered by Izyumov [7].

In the present paper a detailed analysis of the magnetic structure of CuB_2O_4 in the commensurate phase is reported. With the help of the symmetry analysis, we show that the magnetic structure of CuB_2O_4 is non-collinear in the temperature range $10\,K < T < 21\,K$. We obtain a weak ferromagnetic moment per unit cell consistent with the magnetization data, in contrast to the spin arrangement given in Ref. [3]. Moreover, we present neutron scattering experiments and μSR measurements down to $T \approx 0.1\,K$ which show an additional magnetic phase transition below $T = 1.8\,K$.

2. Temperature evolution of the magnetic properties of CuB_2O_4

CuB_2O_4 crystallizes with the tetragonal space group $I\bar{4}2d(D_{2d}^{12})$ [1]. In the commensurate antiferromagnetic ordered state, the magnetic and chemical cells are equivalent.

The chemical cell contains 12 copper atoms in the oxidation state Cu^{2+}. Four of them occupy lattice site 4b with local symmetry ($\bar{4}$ . .), in the following labeled site 'A', and the other eight ions are located on lattice site 8d with local symmetry (.2.), labeled site 'B'.

Using the representational analysis [4] method developed by Bertaut, the decomposition of the magnetic representation Γ_{4b} into the irreducible representations Γ_i ($i = 1-5$) of point group $\bar{4}2m$ yields

$$\Gamma_{4b} = \Gamma_1 + \Gamma_2 + 2\Gamma_5.$$

A similar decomposition for the atoms B at lattice site 8d gives

$$\Gamma_{8d} = \Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + \Gamma_4 + 3\Gamma_5.$$

The one-dimensional magnetic modes Γ_1 and Γ_2 of site 4b correspond to a collinear antiferromagnetic and ferromagnetic ordering along the z-axis, respectively. One of the two-dimensional basis vectors associated with the Γ_5 representation describes a ferromagnetic, the other one an antiferromagnetic magnetic structure in the tetragonal plane. A combination of the vectors yields a canted structure which can have a maximum canting angle of 90 degrees between adjacent Cu(A) moments [3]. From the refinement of a diffraction set of 25 pure magnetic reflections, it was found that the magnetic structure of CuB_2O_4 could be described as a non-collinear 90° arrangement of both the Cu(A) and Cu(B)-spins along the diagonal of the tetragonal plane. The value of the magnetic moment at $T = 12\,K$ was about $1\mu_B$ for atoms Cu(A), and $0.25\mu_B$ for Cu(B). As Cu(A) and Cu(B) magnetic moments did not compensate a spontaneous ferromagnetic moment equal to $0.1\mu_B$ per formula unit (f.u.) was found in the tetragonal plane [3]. However, this value is about two times larger compared to the value of $0.045\mu_B$/f.u. obtained by magnetization measurements [2].

According to symmetry analysis, any linear combination of the two basis vectors associated with the Γ_5 representation for site A gives an allowed magnetic structure. This implies that from arguments based on symmetry analysis alone any tilting angle between the Cu(A) spins in the tetragonal plane is possible. In Fig. 1 we show the calculated quality-of-fit values χ^2 obtained as a function of the tilting angle α and using the neutron data collected in CuB_2O_4 at $T = 12\,K$ on the four-circle diffractometer D10 at ILL. We note that $\alpha = 0$ describes a collinear antiferromagnetic structure whereas for $\alpha = 45°$ the non-collinear structure reported in Ref. [3] is obtained. Any tilting of the spins away from the collinear arrangement results in a net ferromagnetic moment perpendicular to the original spin orientation. The observed magnetic moment of $0.045\mu_B$/f.u. corresponds to a tilting angle of 3°.

Although the corresponding χ^2 is better than for the non-collinear magnetic structure with spins at 90° from each other, the presence of magnetic domains in the sample results in an important systematic uncertainty. Hence, we performed

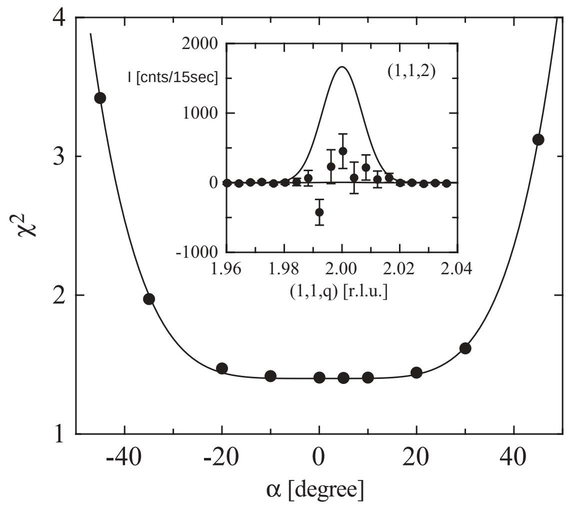

Fig. 1. Quality-of-fit value χ^2 as a function of the tilting angle α out from the collinear alignment for one Cu atom. The inset shows the measured difference $T(12\,K)-T(30\,K)$ of neutron intensities taken at the (1,1,2) Bragg position. The solid line is the expected intensity for a 90° spin arrangement, the broken one for a 3° canting.

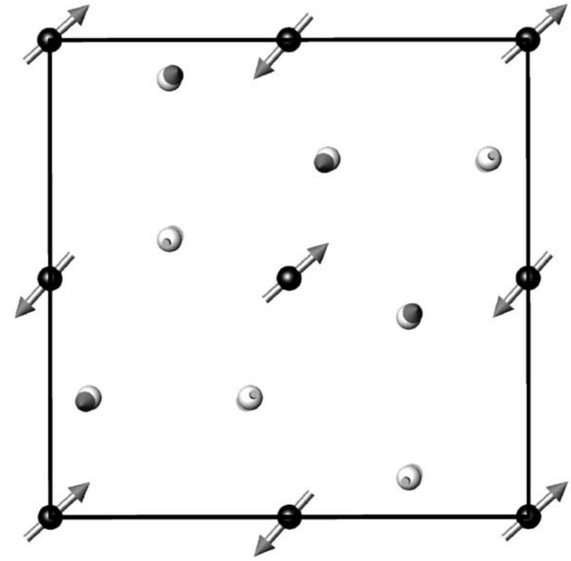

Fig. 2. Antiferromagnetic structure of CuB_2O_4 in the commensurate phase. Cu(A) and Cu(B) positions are represented by black and open symbols, respectively. The arrows mirror the directions of the magnetic moments μ. While Cu(A) moments ($\mu(A) \approx 1\mu_B$) lie in the tetragonal plane, Cu(B) moments ($\mu(B) \approx 0.2\mu_B$) are nearly along the c-axis.

additional neutron experiments to clarify the situation. To that end, the single crystal of CuB_2O_4 was mounted inside a cryomagnet with the magnetic field applied along the [1,1,0] crystallographic direction. With that set up a magnetic field of 400 Oe was sufficient to align the magnetic domains in the scattering plane. Calculations of the expected neutron intensities show that for a 90° canting of the magnetic moments magnetic intensity is expected to be observed at the reciprocal lattice position (1,1,2), while for a 3° tilting the intensity almost vanishes. The scan presented in the inset of Fig. 1 shows that no significant magnetic intensity is observed. Hence, we propose a modified magnetic structure for CuB_2O_4 as shown in Fig. 2. As magnetic moments of the Cu(A) atoms are large compared to Cu(B) moments, the orientation of Cu(B) moments have a larger uncertainty in the fits. Again, the structure shown in Fig. 2 corresponds to our representational analysis with the best goodness-of-fit value. We note that the tilting angle between the Cu^{2+} magnetic moments is due to the relativistic Dzyaloshinskii–Moriya interaction [8], which is allowed by symmetry in copper metaborate.

We probed the local magnetic field in CuB_2O_4 with zero-field μSR measurements. The experiment was performed with the GPS and LTF instruments located on the πM3 beam line of the 600 MeV proton accelerator of PSI (Villigen, Switzerland). As shown in Fig. 3, the slow Gaussian muon depolarization rate observed above 20 K is characteristic of a paramagnetic state where the static internal fields are solely due to nuclear moments. Below 20 K the muon depolarization rate increases by two orders of magnitude, indicating the occurrence of static electronic magnetic moments. The absence of a well-defined spontaneous μ^+-Larmor frequency can be related to the presence of short-range order within the magnetic sublattices [2] producing a wide and apparently Gaussian field distribution at the muon stopping site. Below T^*, the transition into the incommensurate phase is characterized by a sharp reduction of the muon depolarization rate. The subsequent increase observed by further cooling the sample can be linked to an increase of the static moment and/or a gradual change of

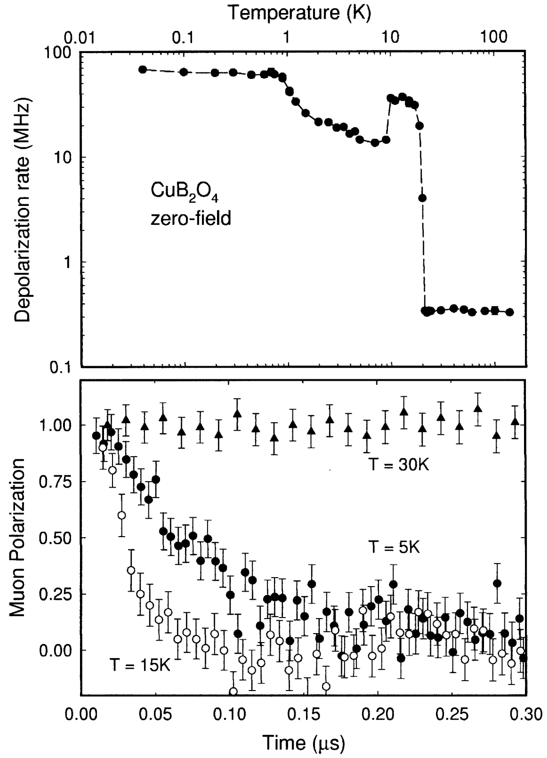

Fig. 3. Temperature dependence of the muon depolarization rate in CuB_2O_4.

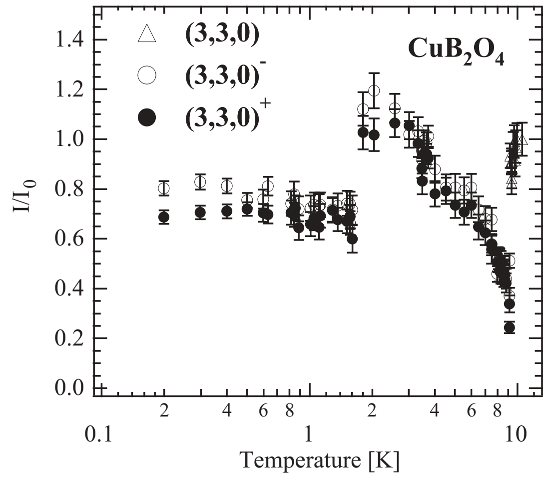

Fig. 4. Temperature evolution of the magnetic intensity (open circles: $(3,3,0)^-$; full circles: $(3,3,0)^+$), as measured with neutron diffraction.

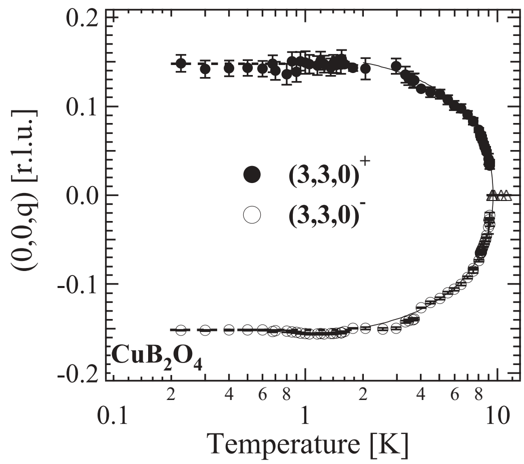

Fig. 5. Temperature dependence of the propagation vector $\mathbf{k_0}$. See text for details.

the ordering vector. At $T = 1\,K$ and below, the muon depolarization shows a clear change.

This experimental result can be related to the neutron diffraction experiments done from $T = 10.3\,K$ to $\approx 300\,mK$ at the four-circle diffractometer D10 at ILL using the four-circle dilution cryostat. Fig. 4 shows the temperature dependence of the magnetic reflections $(3,3,0)^+$ and $(3,3,0)^-$ normalized to the magnetic intensity of the commensurate magnetic peak I_0 at $T = 10.5\,K$. Below T^* the intensity of the satellites starts growing accompanied by a sudden decrease of the central magnetic peak (see triangles in Fig. 4). Satellites and central peak coexist within a small temperature range as already observed in neutron experiments with external magnetic fields [5] and in agreement with the theory for a magnetic soliton lattice [7]. We note that the intensity of the satellites exceeds I_0 with further cooling which can be attributed to the ordering of the Cu(B) moments, as Cu(A) moments are already saturated. Below $T = 1.8\,K$ we observe a sudden decrease in the Bragg intensity of about 40% which is a clear evidence of a change in the magnetic structure.

As shown in Fig. 5 the position of the magnetic satellites can be described by a power law $|\mathbf{k}(T)| \alpha (T^* - T)^{0.5}$ down to $T = 2\,K$. Below that temperature we observe a lock-in of the propagation vector at $\mathbf{k_0} = (0, 0, 0.15)$ (rlu).

3. Conclusion

We investigated the magnetic structure of the commensurate phase in CuB_2O_4 using representational analysis. The obtained structure is shown in Fig. 2.

We performed neutron diffraction and μSR measurements in copper metaborate from $T_N = 21\,K$ down to $T = 60\,mK$. Both experimental methods have revealed a phase transition from a commensurate non-collinear magnetic structure to a helical arrangement of the magnetic moments at $T = 10\,K$. Measurements performed down to 60 mK show that the magnetic structure of CuB_2O_4 remains incommensurate at very low temperatures. Whereas the propagation vector also smoothly increases upon cooling, an abrupt change of the magnetic structure is observed below $T \approx 1.8\,K$. The detailed analysis of the magnetic structure of CuB_2O_4 in the incommensurate phase is in progress and will be published elsewhere. We note that a microscopic description of the magnetic soliton lattice in copper metaborate shall be able to describe in full the experimental data presented here. To the best of our knowledge, such a theory is not available yet.

Acknowledgements

Helpful discussions with A. Wills (ILL) are gratefully acknowledged.

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