Soliton lattice in copper metaborate, CuB_2O_4 , in the presence of an external magnetic field

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Received: 11 July 2001 / Accepted: 13 November 2001 – © Springer-Verlag 2002

Abstract. The spontaneous formation of a magnetic soliton lattice in copper metaborate, CuB_2O_4 , is also stable at a temperature of 4.2 K in the presence of an external magnetic field up to 1.3 T applied along the tetragonal [110] direction similar to the undisturbed case, where it is stable up to a temperature of 10 K. Increasing the external magnetic field induces a phase transition from the incommensurate to the commensurate structure similar to increasing the temperature at zero field as reported earlier. The formation of domain walls (solitons) can therefore be associated with combined effects of Dzyaloshinskii interaction and anisotropy. The T/H phase diagrams show a coexistence region of commensurate and incommensurate phases, in agreement with the theory of a soliton lattice at fields up to 1.3 T.

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

Copper metaborate, CuB_2O_4 , crystallizes in the non-centric tetragonal space group $I4_2d$ [1]. This insulating material shows a complex magnetic behaviour, as first observed by magnetic susceptibility, μSR and heat-capacity measurements [2]. These effects originate from the copper atoms located on two crystallographically different sites, Cu(A) and Cu(B). The Cu(A) atoms in copper metaborate yield an antiferromagnetic arrangement below 20 K. When lowering the temperature below 10 K, an incommensurate magnetic structure is formed, which is due to the formation of a helix by the spins. We refer to [3] for a review of incommensurate structures. Such a behaviour is rather unusual in an insulator, but is predicted by Dzyaloshinskii [4] and experimentally confirmed by our group [5]. We showed in that letter that the Dzyaloshinskii interaction and the anisotropy are the driving forces.

1 Theory

Dzyaloshinskii [4] suggested an antisymmetric spin coupling from symmetry reasons only: whereas the strength of the interaction is proportional to the cross product of the interacting

spins ($\mathbf{S}_1 \times \mathbf{S}_2$), the direction is restricted to a finite number of possibilities by applying group-theoretical considerations governed by the chemical lattice symmetry. Extending the formalism from Anderson theory [6], Moriya [7] included spin-orbit coupling by introducing an anisotropic superexchange interaction. This is in contrast to conventional Heisenberg exchange coupling, which is proportional to the scalar product ($\mathbf{S}_1 \times \mathbf{S}_2$) only. The system can be described in such a case according to [8] by a Hamiltonian of the form

$$H = -2 \sum_{i,j>i} J_{ij} S_i S_j + D \sum_n S_n \times S_{n+1}. \quad (1)$$

As a result, spiral structures are favoured in Dzyaloshinskii–Moriya (DM) interactions due to the presence of a linear term in the gradient of the magnetization (equivalent to Lifshitz invariance in the thermodynamical potential). Such superstructures were simultaneously but independently discussed in publications by Villain [9], Kaplan [10] and Yoshimori [11].

2 Experiments without field

The predicted spontaneous formation of a soliton behavior was observed in CuB_2O_4 [5] using neutron diffraction. At $T = 2$ K the propagation vector of the magnetic structure is $\mathbf{k}_0 \sim (0, 0, 0.15)$ (r.l.u.). For simple cases, theory predicts that this helix gets interrupted by regions yielding phase shifts of $2\pi/n$ in the helix modulation, where n is the order of anisotropy (e.g. $n = 4$ as in CuB_2O_4). These domain walls are the solitons. The incommensurate magnetic structure phase is described as a spin-density wave with constant spin amplitudes and phase modulations. The two magnetic sublattices order differently: whereas the Cu(A) spins are saturated below 10 K, Cu(B) steadily increases and reaches $\sim 0.7 \mu_B$ at $T = 2$ K. The magnetic moments are confined close to the basal ab plane. The presence of higher harmonics of the magnetic satellites and the temperature dependence of the diffuse scattering around the phase transition are consistent with the existence of a magnetic soliton in this three-dimensional lattice, as shown by [4, 12]. It is only allowed in materials with non-centric Cu–O bonds.

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3 Experiments with field

Neutron-diffraction experiments were performed using the spectrometer TASP at SINQ in the elastic mode ($\lambda = 3.8 \text{ \AA}$). A magnetic field has been applied along the $[110]$ crystallographic direction. The propagation vector $\mathbf{k}_0$ ($H = 0$) of the magnetic structure decreases as a function of increasing magnetic field (cf. Fig. 2) with a quadratic law

$$k(H) = k_0(H = 0) - 0.0039H^2 \quad (2)$$

(H in [T], $T = 4.2 \text{ K}$)

The incommensurability of the soliton spirals disappears completely above the critical field $H^* = 1.3 \text{ T}$ at the temperature $T = 4.2 \text{ K}$ as illustrated by the intensity plot in Fig. 1. This suggests that copper metaborate accepts the former commensurate structure as observed by neutron diffraction [5] between 10 K and 20 K at $H = 0$. However, diffraction measurements therefore have to be performed at e.g. 4.2 K and a magnetic field of 1 T along $[110]$. However, for $H > 0$ we observe supplementary higher harmonics proportional to $\mathbf{k} = 2\mathbf{k}_0$, which may be related to a deformation of the helix, yielding additional terms in the Fourier expansion. This behaviour is in agreement with [8], who stated that the magnetic moments tend to align parallel to the field for $\tilde{H} \gg \tilde{J}$, whereas for $\tilde{H} \ll \tilde{J}$ a spin-flop structure is preferred, where the spins align approximately perpendicular to the magnetic field ($\tilde{J} = S^2\sqrt{4J^2 + D^2}$ and $\tilde{H} = Hg\mu_B S$). At a field $H > 1.3 \text{ T}$, this second-order modulation is not observed any more. In contrast to the zero-field case where magnetic satellites of index $3k$ appear close to the temperature of the incommensurate-commensurate phase transition T^* , higher-order harmonics are visible at all temperatures for $H = 1 \text{ T}$. These higher-order peaks appear at positions in reciprocal space which can be indexed as $2\mathbf{k}_0$, where $\mathbf{k}_0$ is the magnetic propagation vector. Measurements performed at $T = 4.2 \text{ K}$ showed that the intensity of the second harmonic increases as a function of increasing magnetic field as $\sim H^2$. Whereas the first satellites

Fig. 1. Dependence of the intensity of the reflections $(0,0,2)$ and $(0,0,2-k)$ in copper metaborate at $T = 4.2 \text{ K}$ as a function of magnetic field H

Fig. 2. Dependence of the propagation vector of the magnetic structure in copper metaborate at $T = 4.2 \text{ K}$ as a function of magnetic field H . The line in the figure is given by (2)

Fig. 3. Intensity of the second-order magnetic satellite $(0,0,2-0.27)$ as a function of increasing magnetic field at $T = 4.2 \text{ K}$

disappear above $H_c \sim 1.3 \text{ T}$, the intensity of the second-order harmonic abruptly increases at H_c (cf. Fig. 3), which indicates the appearance of a phase transition at this critical value of the magnetic field. This new magnetic phase is characterised by a propagation vector $\mathbf{k}_0 = (0,0,0)$, is observable up to $T \sim 6 \text{ K}$ and is characterized by the coexistence of an incommensurate modulation of the magnetic structure together with magnetic intensity at the commensurate position $(0,0,2)$. Due to the I-centering of the chemical cell, Bragg reflections with Miller indices $(00l)$ and $l = 2n$ are forbidden, indicating an antiferromagnetic phase transition at 1.3 T (cf. Fig. 1).

4 Discussion

For magnetic fields lower than $H = 1.3 \text{ T}$, the temperature of a transition from the incommensurate magnetic structure to the commensurate one increases steadily until it reaches

T^* for $H = 0$ T. Close to the phase transition, there is a domain of temperatures where a central peak appears in the incommensurate phase. Interestingly, this central peak was not observed in zero field. It may indicate the coexistence of a commensurate and a presently unknown incommensurate phase in a limited temperature range $4.2 \text{ K} < T < 6 \text{ K}$ at $H = 1.3 \text{ T}$. On the other hand, when the magnetic field is removed the diffraction spectrum is characterized by the superposition of diffuse scattering and magnetic satellites. The application of a magnetic field tends to suppress the diffuse scattering. This seems to be the case at least for fields larger than $H \approx 0.1 \text{ T}$. Measurements at smaller values of magnetic fields will be the subject of a further study. In parallel, the intensity of the satellites goes to zero (cf. Fig. 1). Comparison of the temperature dependence of the neutron intensity taken at the satellites and at the central position for different values of magnetic fields reveal that the transition towards the commensurate phase is ‘smoother’ at low values of magnetic fields. Indeed, the transition is of pure second-order type in the absence of a magnetic field. The intensity of the magnetic satellite remains constant until the field reaches $H \sim 1 \text{ T}$ and then quickly diminishes with increasing magnetic field until it completely disappears at $H_c \sim 1.3 \text{ T}$. Above the critical magnetic field H_c , there is an increase of intensity at the commensurate position $(0, 0, 2)$, as shown in Fig. 1. The theory of Izyumov [13] completely describes the $H - T$ phase diagram for simple incommensurate non-centric structures, but is therefore only valid partially for our case. Our present study in copper metaborate further supports the description of the soliton lattice by [13]. As in the zero-field case [5], this is supported by the observation of higher-order satellites. However, theories are presently limited as the solutions for $n = 4$

are only approximations, but also they are restricted to simple structural cases. Extended theories for both cases, zero field [14] and cases with field [15], are therefore presently being discussed and will be published elsewhere.

Acknowledgements. Neutron beam time provided by ILL (Grenoble) and PSI (Villigen) as well as many discussions with Prof. Dr. I. E. Dzyaloshinskii and Dr. P. Fischer are gratefully acknowledged.

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