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High magnetic field behaviour of the triangular lattice antiferromagnet, $CuFeO_2$

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Abstract

The magnetic phase diagram of the triangular lattice antiferromagnet $CuFeO_2$ has been studied using single-crystal neutron diffraction measurements in a magnetic field of up to 14.5 T and also by magnetisation measurements up to 12 T. At low temperature, two well-defined first-order magnetic phase transitions were found in this range of applied magnetic field: at $H_{C1} = 7.6\,T$ and $H_{C2} = 13.2\,T$, with the later one corresponding to a transition from a four to five sublattice structure. Cooling the sample in a high magnetic field resulted in the locking of the magnetic structure into the intermediate temperature incommensurate structure. © 2001 Elsevier Science B.V. All rights reserved.

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$CuFeO_2$ belongs to a family of the ABO_2-type compounds with the delafossite structure (space group R3 m). The crystal structure consists of hexagonal layers of Cu, O and Fe with a stacking sequence of O^{2-}–Fe^{3+}–O^{2-}–Cu^{+}–O^{2-}–Fe^{3+}–O^{2-} along the *C*-axis, where the triangular lattice of magnetic Fe^{3+} ions are separated by non-magnetic layers of Cu^{+} and O^{2-}. Therefore in this compound, the magnetic interactions are highly frustrated between neighbouring triangular layers as well as within a layer. $CuFeO_2$ also has a pronounced quasi two-dimensional character.

In zero field, the antiferromagnetic ordering of $CuFeO_2$ occurs in two steps: $T_{N1} = 14.2\,K$ separates a high-temperature paramagnetic and an intermediate incommensurate structure, while $T_{N2} = 11.1\,K$ divides an incommensurate phase from the low-temperature 4-sublattice ground state. Five spin-flop like magnetisation anomalies have been observed previously for a powder sample of $CuFeO_2$ with a magnetic field of up to 70 T [1].

Here we report on single-crystal heat capacity, magnetisation and neutron diffraction measurements. Single crystals of $CuFeO_2$ were grown by the floating zone method using an image furnace [2]. The specific heat measurements in zero field were made using a standard heat pulse-relaxation method. The magnetisation data were collected using a vibrating sample magnetometer in an applied magnetic field of up to 12 T. The neutron scattering measurements were carried out using the E1 spectrometer at the BENSC, HMI, Germany. The single-crystal sample was aligned within a vertical field cryomagnet in two different orientations in order to access the two types of reflections, *(h k 0)* and *(h h l)*.

The low-temperature specific heat measurements of the $CuFeO_2$ single crystal (Fig. 1) show a remarkable difference for the two magnetic phase transitions. The first transition into the IT phase is marked by a broad peak in the specific heat at a temperature of around 14 K. The second transition into the LT phase is accompanied by a much sharper, more intense peak at $T \approx 11\,K$. The presence of short range magnetic correlations dominates the heat capacity at all temperatures up to 40 K, well above the 3d magnetic ordering temperature. Only about three quarters of the magnetic entropy is recovered at $T < T_{N1}$, as shown on the inset to Fig. 1, while the remaining quarter of the entropy is spread over $T > T_{N1}$.

The first-order nature of the lower temperature phase transition is clear from the temperature dependence of

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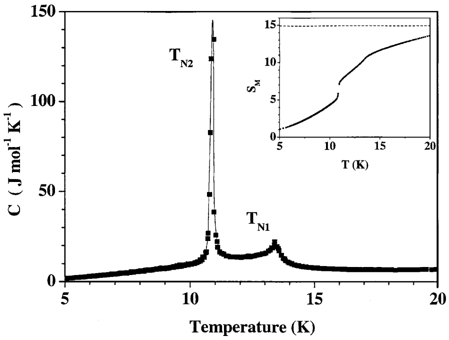

Fig. 1. Low-temperature heat capacity of a $CuFeO_2$ single crystal. The inset shows the temperature dependence of the magnetic entropy. The dashed line indicates the maximum possible magnetic entropy $R\ln(2S+1) = 14.90\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for $S = \frac{5}{2}$.

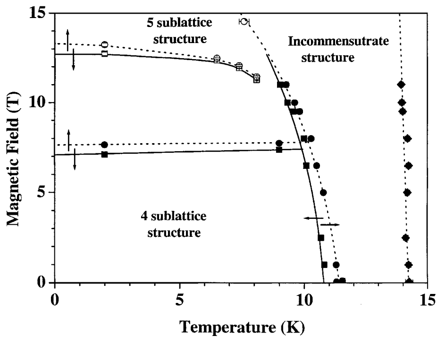

Fig. 2. Magnetic phase diagram of $CuFeO_2$, $H//C$, as obtained from magnetisation (solid symbols) and neutron diffraction (open symbols) data. Solid and dashed lines correspond to decreasing and increasing temperature or magnetic field, respectively.

the magnetisation data. $M_{H//C}$ exhibits a dramatic jump at T_{N2}, while a small kink at T_{N1} became obvious only after differentiation of the data. When the sample was warmed and then cooled in a low applied magnetic field, hysteresis in the magnetisation is evident only around T_{N2}, while in a high applied field the magnetisation curves $M(T)$ for increasing and decreasing temperature are significantly different for all temperatures below T_{N2}. In a low applied field $CuFeO_2$ is magnetically highly anisotropic. The anisotropy decreases abruptly in a field above the spin-flop phase transition at $H_{C1} = 7.6/7.1\,\mathrm{T}$, however, it does not disappear completely as expected for a simple 3d collinear antiferromagnet. Even at $H = 10\,\mathrm{T}$ $M_{H//C}$ is still only 73% of $M_{H\perp C}$.

In zero magnetic field the low-temperature magnetic structure is characterised by the appearance of magnetic Bragg reflections at the positions $((2n+1)/4, (2n+1)/4, (6m+3)/2)$, in agreement with observations by Mitsuda et al. [3]. At intermediate temperatures, $T_{N2} < T < T_{N1}$, the 4-sublattice magnetic structure is replaced by an incommensurate phase, in which the magnetic Bragg reflections occur at positions $(q, q, (6m+3)/2)$, where m is an integer and the value of q is temperature dependent and ranges from 0.19 to 0.225. In the vicinity of T_{N2} and T_{N1}, the width of the magnetic peaks is not resolution limited, which suggests the absence of true long-range magnetic ordering. However, at all temperatures away from the phase boundaries the width of the magnetic peaks is resolution limited. At $T = 10.5\,\mathrm{K}$, both commensurate and incommensurate peaks are present in the diffraction pattern. For both low- and intermediate-temperature phases, the application of a magnetic field of up to 14.5 T, does not change the position, intensity or width of the magnetic peaks — the structure remains unchanged by a field applied perpendicular to the C-axis.

In zero magnetic field no purely magnetic reflections have been found in the $(h\,k\,0)$ scattering plane. On the application of a magnetic field above 13 T along the C-axis at low temperature, scans in the $(h\,k\,0)$ plane of the reciprocal lattice revealed new magnetic Bragg peaks at position $(n/5, m/5, 0)$, where $n, m \neq 0, n+m$ is even. This observation suggests that the magnetic field induces a transition from a purely antiferromagnetic structure in zero field to an ordering with a ferromagnetic component along the C-axis. The transition to the high-field phase is accompanied by significant hysteresis, of about 0.5 T. The widths of the new magnetic peaks are resolution limited.

The temperature dependence of the intensity, width and positions of the $(n/5, n/5, 0)$ peaks show remarkable variations in behaviour for different values of n. Warming the sample above T_{N2} in the magnetic field results in a shift of the peak positions from $(\frac{1}{5}, \frac{1}{5}, 0)$ to (0.225, 0.225, 0) and from $(\frac{2}{5}, \frac{2}{5}, 0)$ to (0.385, 0.385, 0). When the sample was cooled back down to 2 K in an applied magnetic field, the peak with $n \approx 1$ regained only approximately half its integrated intensity and remained at its incommensurate position (0.203, 0.203, 0). For the reflection with $n \approx 2$, the loss of integrated intensity was significantly smaller, and the change of its position from commensurate to incommensurate was still evident.

The overall phase diagram of $CuFeO_2$ for magnetic fields applied along the hexagonal axis is shown in Fig. 2. It contains an intermediate temperature incommensurate magnetic phase as well as three different commensurate magnetic phases at low temperatures in fields of up to 14.5 T.

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