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LETTER TO THE EDITOR

Magnetic ordering and fluctuations in the $S = 1/2$ square Heisenberg antiferromagnet $Cu(DCO_2)_2 \cdot 4D_2O$

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Abstract. Elastic and quasielastic neutron scattering measurements have been performed on the $S = \frac{1}{2}$ square Heisenberg antiferromagnet copper (II) deuteroformate tetradeuterate, $Cu(DCO_2)_2 \cdot 4D_2O$. The sublattice magnetization was measured below $T_N = 16.54(5)$ K, and the critical exponent β was found to cross over from 0.23(1) to 0.32(2) at a reduced temperature $\varepsilon = (T_N - T)/T_N$ of 0.06 as T_N was approached from below. The temperature dependence of the inverse correlation length of the two-dimensional antiferromagnetic correlations and of the sublattice susceptibility above T_N was consistent with the predictions of the quantum non-linear sigma model of Chakravarty and co-workers for a spin-wave stiffness of 13.4(4) K.

The discovery of superconductivity in ceramics containing CuO_2 layers has led to intense theoretical and experimental research into the properties of $S = \frac{1}{2}$ square Heisenberg antiferromagnets with the Hamiltonian

$$\mathcal{H} = \sum_{\langle ij \rangle} J \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{1}$$

where J is the nearest-neighbour in-plane superexchange interaction [1,2]. Experimental activity in this field has been hindered by difficulties in preparing large, high-quality single crystals of suitable model materials. In addition, the large magnitude of J in these compounds makes it difficult to measure spin-wave energies by neutron scattering at small q where q equals $\tau - Q$, τ being an antiferromagnetic reciprocal lattice vector and Q the scattering vector. The large value of J also gives rise to critical fluctuations near T_N that span an unusually broad range of energies. This in turn creates experimental difficulties in studying the elastic and quasielastic magnetic properties [3–6]. There is clearly a need to find other examples of $S = \frac{1}{2}$ square Heisenberg antiferromagnets which may not only be prepared in the form of large single crystals but also possess a range of values of J.

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The traditional source of two-dimensional (2D) antiferromagnets is provided by ternary halides of general formula A_2BX_4 (where A is a univalent cation, B a first-row transition metal cation and X a halide ion), typified by K_2NiF_4 [7,8]. Of the B cations that can be represented magnetically by $S = \frac{1}{2}$, Co^{2+} has strong Ising character and materials containing Cu^{2+} are 2D *ferro*magnets. Consideration of a wider range of ternary halides [9] also failed to produce a material of proven suitability. However, the layered hydrate $Cu(HCO_2)_2 \cdot 4H_2O$ (CFTH) *does* appear to possess square arrays of $S = \frac{1}{2}$ Heisenberg moments coupled antiferromagnetically [10,11].

CFTH has a transition from a paraelectric to an antiferroelectric phase at 236.1 K [12]. The lower-temperature structure has a monoclinic unit cell (space group $P2_1/n$) with $a = 8.113$ Å, $b = 8.119$ Å, $c = 12.45$ Å and $\beta = 101.28°$ [13]. The application of a high-temperature series expansion method to static magnetic susceptibility measurements provides an estimate for J of 71.5 K [14–16]. At 16.5(1) K magnetic long-range order sets in, driven by a weak interlayer interaction J', where $|J'/J|$ is of the order of 10^{-5} [17]. The ground state magnetic structure is believed to be a simple four-sublattice array: polarized neutron scattering measurements detected no canting away from this configuration in zero external magnetic field [18]. Proton magnetic resonance measurements show that the critical exponent for sublattice magnetization, β, crosses over from 0.22(2) to 0.30(1) at a reduced temperature, $\epsilon = (T_N - T)/T_N$, of 0.05 [19].

In this letter we present a neutron scattering study of the sublattice magnetization and two-dimensional fluctuations above T_N for a single crystal of the totally deuterated material $Cu(DCO_2)_2 \cdot 4D_2O$.

A solution of $Cu(DCO_2)_2$ was prepared by dissolving the deuterated carbonate, $Cu_2CO_3 \cdot (OD)_2 \cdot D_2O$, in a solution of d_2-formic acid in D_2O, both supplied by MSD Isotopes [11]. The carbonate had been synthesized by the addition of Na_2CO_3 to a solution of Cu^{2+} in D_2O. Single crystals of $Cu(DCO_2)_2 \cdot 4D_2O$ were grown by slowly evaporating the solution in a vacuum desiccator at approximately 25 °C. The crystals were stored under argon saturated with D_2O to prevent dehydration.

A crystal of dimensions $5 \times 3 \times 2.5$ mm^3 was wrapped in aluminium foil, placed in a helium flow cryostat and mounted on the Eulerian cradle of the four-circle neutron spectrometer D10 at the Institut Laue–Langevin. This instrument is situated on a neutron guide having an angular divergence of 15′ and may be used either as a two-axis diffractometer or as a three-axis machine using a vertically focussing pyrolytic graphite (PG) (002) analyser. Both modes use a PG(002) monochromator and a PG filter producing a wavelength of 2.36 Å and a flux of $\geqslant 5 \times 10^6$ cm^{-2} s^{-1} at the sample position. The rocking curve of the crystal indicated two crystallites separated by about 0.45° and due correction had to be made in calculating the instrumental resolution function.

The sublattice magnetization was measured at the magnetic reflection $(0\,-1\,1)$ on warming the sample from 2.0 K to 29.0 K (figure 1). Scans were made with the instrument operating in the three-axis mode and the reflections $(0\,-1\,0)$ and (001) were constrained to be in the scattering plane. The critical scattering near T_N was found to be negligible compared to the elastic contribution. The data were corrected for background scattering and least-squares fitted to a power-law expression of the form

$$I_T - I_B = A[(T_N - T)/T_N]^{2\beta} \tag{2}$$

where I_B is the background intensity and I_T is the intensity at temperature T. The

results of our two best fits are shown in figure 2, and yield an estimate for T_N of 16.54(5) K and a cross-over in β from 0.23(1) to 0.32(2) at $\varepsilon = 0.06$. These values are close to those of Koyama *et al* [17] who interpreted the smaller value as evidence for the new chiral universality class proposed by Kawamura [19] to exist in canted Heisenberg ferro- or antiferromagnets. However, it is not clear [18] that there is any canting in the magnetic ground state of CFTD with no external magnetic field applied. Those who believe that the magnetic ground state is canted propose that its origin lies in the inequivalence of the g-tensor at the two sublattice sites in the planes: in such a case the critical properties are *not* expected to belong to a new universality class [20]. Thus the origin of the anomalous value of β remains uncertain. Similar behaviour has also been seen in the square Heisenberg antiferromagnets $Mn(HCO_2)_2 \cdot 2H_2O$ [21] and $Cu(HCO_2)_2 \cdot 2CO(ND_2)_2 \cdot 2D_2O$ [17], in the square Heisenberg *ferro*magnet K_2CuF_4 [22] and in the 2D Heisenberg honeycomb-lattice antiferromagnet with planar anisotropy $BaNi_2(PO_4)_2$ [23]. Clearly, the behaviour we observe is not confined to $S = \frac{1}{2}$ Heisenberg antiferromagnets.

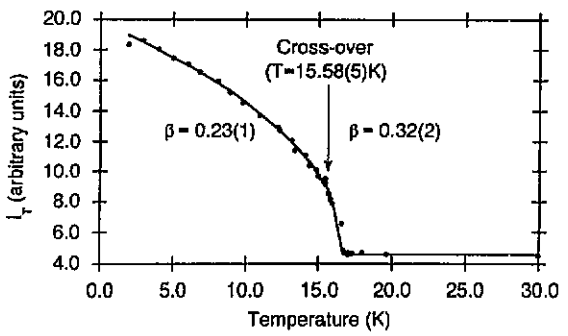

Figure 1. Magnetic Bragg peak intensity (proportional to the square of the sublattice magnetization) for $Cu(DCO_2)_2 \cdot 4D_2O$ measured at the magnetic reflection (0 −1 1). The line through the points is the best fit to the power-law expression (2) with the appropriate values of β above and below the cross-over.

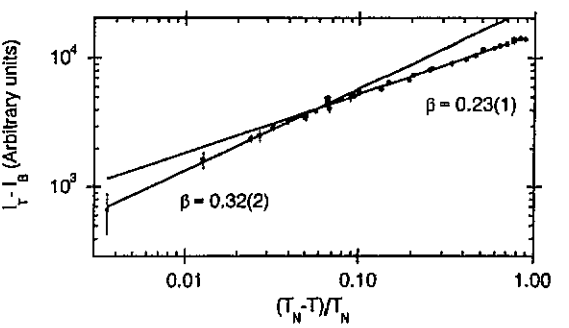

Figure 2. Log–log plot of the background-corrected magnetic Bragg peak intensity, $I_T - I_B$, against reduced temperature, $\varepsilon = (T_N - T)/T_N$, with $T_N = 16.54$ K. The lines are the results of least squares fits to a power law in ε with the critical exponent crossing over from 0.23(1) for ε above 0.06 to 0.32(2) for ε below 0.06.

The analyser crystal was removed and the spectrometer was used in two-axis mode to measure the frequency-integrated paramagnetic critical scattering between

16.8 K and 37.0 K. To ensure that the low-frequency fluctuations were integrated, the scattered vector, k_f, was set parallel to c^* [3,24] and the rods of critical scattering at $(0\,-1\,l)$ were scanned at $l = 0.223$. The vectors (010) and (001) were constrained to lie in the scattering plane. The inverse correlation length, κ, and a measure of the sublattice static susceptibility, $S(q = 0)$, were derived from the data by least-squares fitting to Lorentzian curves convoluted with the instrumental resolution function. The dimensions of the two ellipses making up the resolution function (one for each crystallite) were measured on the nearby $(0\,-1\,0)$ Bragg reflection. Examples of these scans and the results of least-squares fits are given in figure 3. The form of the fluctuations clearly demonstrates the 2D character of CFTD; further proof has been provided recently by inelastic neutron scattering measurements on a single crystal of CFTD [25]. These show a magnetic mode at 0.60(5) meV at the antiferromagnetic zone centre which disperses strongly along b^* with a spin-wave velocity corresponding to a value of J of 9.3(1) meV. Along c^* the mode did not appear to disperse.

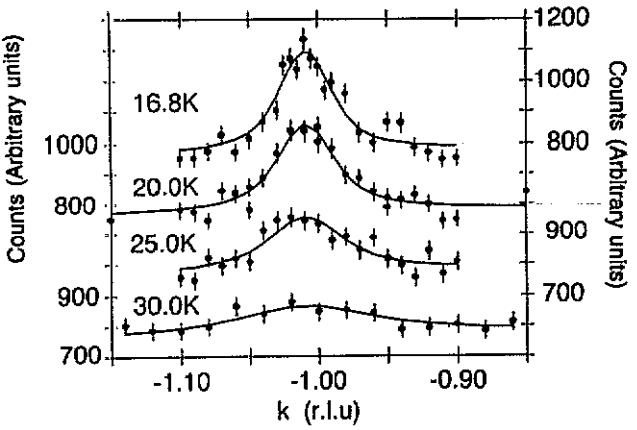

Figure 3. Examples of scans of the frequency-integrated paramagnetic scattering at $(0\,-k\,0.233)$ along k. The solid lines are the results of fits to Lorentzian curves convoluted with the instrumental resolution function.

The dependence on temperature of κ for the 2D Heisenberg quantum antiferromagnet is believed to adopt the form [1,2,26,27]:

$$\kappa = \xi^{-1} = A \exp(-2\pi\rho_s/T). \tag{3}$$

The spin-wave stiffness $\pi\rho_s$ may be related to J using Oguchi's spin-wave method [28] as follows:

$$\pi\rho_s = JS^2B \tag{4}$$

where B describes the correction to order $1/2S$ in the large-S expansion derivation. The value of A in (3) depends on the model used; the easiest to implement is the quantum non-linear sigma model expression of Chakravarty *et al* [26] (CHN). The model also allows one to calculate the dynamic structure factor for the long-wavelength two-dimensional fluctuations in a quantum Heisenberg antiferromagnet with no adjustable parameters provided that there is Néel order at $T = 0$ and that both ρ_s and the uniform susceptibility perpendicular to the direction of the

sublattice magnetization are known. It appears successfully to describe the two-dimensional fluctuations in La_2CuO_4 [4]. Explicitly, the CHN model predicts that for an $S = \frac{1}{2}$ square Heisenberg antiferromagnet, the inverse correlation length depends on temperature thus:

$$\kappa \simeq \frac{1 + (T/2\pi\rho_s)}{C_\xi a} \exp(-2\pi\rho_s/T). \tag{5}$$

This expression is believed to be valid for $\pi\rho_s \geqslant T$. C_ξ is a non-universal constant which is calculated to be approximately 0.5 [26] for this case, and a (5.74 Å) is the nearest-neighbour separation of the Cu ions in the planes. $S(q = 0)$ is given by

$$S(q = 0) \simeq \frac{C_s a^2 (T/2\pi\rho_s)^2}{[1 + (T/2\pi\rho_s)]^4} \exp(4\pi\rho_s/T) \tag{6}$$

where C_s is a constant, calculated to be $\simeq 4.3$ [26,27]. The best least-squares fit of expression (3) to the data is shown in figure 4 and provides an estimate for ρ_s of 13.4(4) K. This may be related to J using Oguchi's spin-wave method [28], which yields $\rho_s \simeq 0.15J$. Quantum corrections to this relationship have been shown to be small, and may be ignored [29]. Thus, $J = 89(3)$ K which compares well with the value $J = 71.5$ K derived from static susceptibility measurements. The same value of ρ_s is used to calculate $S(q = 0)$ using expression (6), and a comparison between calculated and experimental values is also given in figure 4. The only adjustable parameter in the fit is an arbitrary intensity scaling factor.

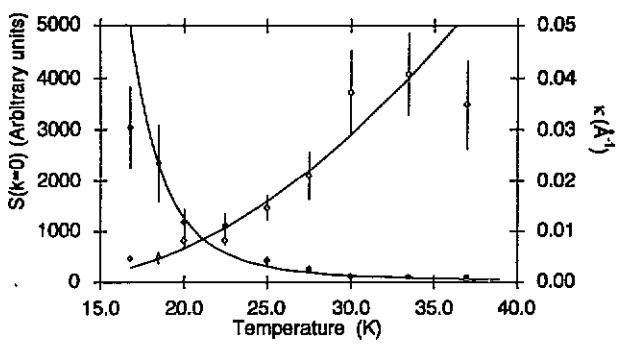

Figure 4. The temperature dependence of the inverse correlation length, κ , and the sublattice susceptibility, $S(q = 0)$. The lines are the results of a least-squares fit to the CHN theory with a spin-wave stiffness of 13.4 K.

We have demonstrated that CFTD provides a suitable model for the study of $S = \frac{1}{2}$ square Heisenberg antiferromagnets. At reduced temperatures below 0.06, β appears to adopt a value that is compatible with a 3D Ising or XY magnet, and not very different from that for a 3D Heisenberg magnet. β crosses over to 0.23(1) at lower temperatures, a value whose origins are difficult to rationalize and which is not unique to $S = \frac{1}{2}$ magnets. The temperature dependence of κ above T_N is like that of La_2CuO_4 once correction has been made for the very different values of J. The CHN model provides an adequate description of the temperature dependence of κ and $S(q = 0)$, though more stringent tests should be made of this model's ability to describe the dynamic properties of such magnets.

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