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Δ-chains of spin 1/2 in oxygen doped Cu based delafossite

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Abstract

The oxygen doping of delafossite compounds $MCuO_{2+\delta}$ allows the production of various networks of spins 1/2 (Cu^{2+}) by the insertion of additional O atoms in the Cu layers that increase the valence of the Cu atoms. For instance, Δ-chains of spins 1/2 can be stabilized in $YCuO_{2.5}$. In this compound, some glassiness is revealed in magnetostatic measurements while a strongly correlated quasielastic magnetic signal, observed at high temperatures in neutron scattering experiments, decreases in intensity with decreasing T, reflecting a freezing process.

1. Introduction

The discovery of new oxygen doped compounds in the vast family of delafossites has recently raised new interest in the field of magnetism. The structure of delafossites, $M^{3+}A^{+}O_2$, can be described by a stacking of two alternating planes containing, respectively, M^{3+} and A^{+} ions. The M^{3+} are in the centre of the O octahedra, whereas the A^{+}, linked to two O of consecutive planes, form a triangular lattice. In the case of $M^{3+}CuO_2$, with M = Y and La, Cava *et al* [1] have established the possibility of inserting excess O in the Cu planes. Consequently, some Cu atoms become magnetic (Cu^{2+}, spin 1/2) and they are expected to interact by super-exchange via O atoms, assumed to be located in the centre of the Cu triangles. The number of magnetic Cu ions and the topology of the interactions depend on the O content. The physical properties of the first synthesized polycrystalline oxidized samples were investigated [1, 2], in particular their electronic properties showing a semi-conductor behaviour and their magnetic properties through standard magnetization measurements. However, a full determination of their structure was not possible because of the presence of strong disorder in the samples attributed to stacking faults.

High quality samples, $M^{3+}CuO_{2+\delta}$, with M = Y, La and $\delta = 1/2$ or 2/3, were recently synthesized and their structure determined [3, 4]. Especially interesting is the $YCuO_{2.5}$ compound. In this system, the O atoms are located at the centre of corner-sharing magnetic

Cu triangles forming undulating chains [3]. Therefore, this compound could be a physical realization of Heisenberg spins $1/2$ on a Δ-chain (sawtooth lattice). Some theoretical work has been devoted to the properties of this model strongly influenced by topological frustration [5–7]. If the same exchange interaction characterizes all bonds, the system exhibits a twofold degenerate singlet ground state and two different kinds of elementary domain-wall excitations: kink and antikink. The lowest-energy modes are dispersionless and there is an energy gap in the excitation spectrum [5, 6]. The work of Blundell and Núñez-Regueiro [7] is devoted to the case where the triangle base bond J_b and vertex bond J_v are characterized by different exchange interactions. A vanishing of the energy gap was reported for ratios of J_b/J_v larger than 1.53 or smaller than 0.478 74.

In this paper, we report an investigation of the magnetic properties of a well-characterized $YCuO_{2.5}$ sample. Section 3.1 is devoted to magnetostatic measurements and section 3.2 to neutron scattering measurements. We discuss these results in the light of theoretical predictions.

2. Experimental details

Oxygenated $YCuO_{2.5}$ compound with very few stacking faults was obtained through the oxidation of 2H hexagonal $YCuO_2$. The non-oxidized compound was obtained by the solid-state reaction technique [3]. Both $YCuO_{2.5}$ and $YCuO_2$ samples were prepared in large quantities, about 50 g each, required for neutron scattering experiments.

A polarized neutron scattering experiment was performed on the D7 diffuse scattering spectrometer at ILL (Grenoble) with an incident wavelength of 4.8 Å. The XYZ polarization analysis method allowed us to determine separately the nuclear spin incoherent scattering, the nuclear scattering and the electronic magnetic contributions. Standard corrections of the measured signal were performed. The $YCuO_{2.5}$ sample was placed in a cryofurnace allowing measurements at several temperatures between 5 and 500 K.

An inelastic neutron scattering experiment was performed on the IN4 time-of-flight spectrometer at ILL using a wavelength of 2.2 Å (i.e. incident energy of the neutron of 16.9 meV). The energy resolution was 2 meV FWHM. A bank of ^{3}He detectors covered scattering angles from 13° to 118°. Measurements were made at 2, 150 and 300 K in a cryostat on both $YCuO_{2.5}$ and $YCuO_2$ compounds, the latter acted as the 'non-magnetic' reference.

3. Results

3.1. Magnetization measurements

Magnetization measurements were performed by the axial extraction method using a commercial SQUID magnetometer in the range 2–400 K and a magnetometer built at Laboratoire Louis Néel for the high temperature measurements (300–800 K).

The temperature dependence of the magnetic susceptibility χ of $YCuO_{2.5}$ reveals a complex magnetic behaviour. The low temperature part exhibits a Curie-like behaviour that was ascribed to the presence of isolated magnetic moments. When the temperature increases, χ goes through a minimum, then increases with T up to a broad maximum at around 450 K, before a slow decrease with increasing T up to 800 K. Fitting the low T part of the curve by a Curie–Weiss function yields a Curie constant equivalent to a fraction of 1% of the Cu atoms for the best samples. This signal could be due to a weak oxygen disorder. After subtraction of this contribution, the susceptibility can be fitted with an exponential law resulting from the hypothesis of a gap in the excitation [2, 5–7]. The value of the energy gap Δ is around 500 K

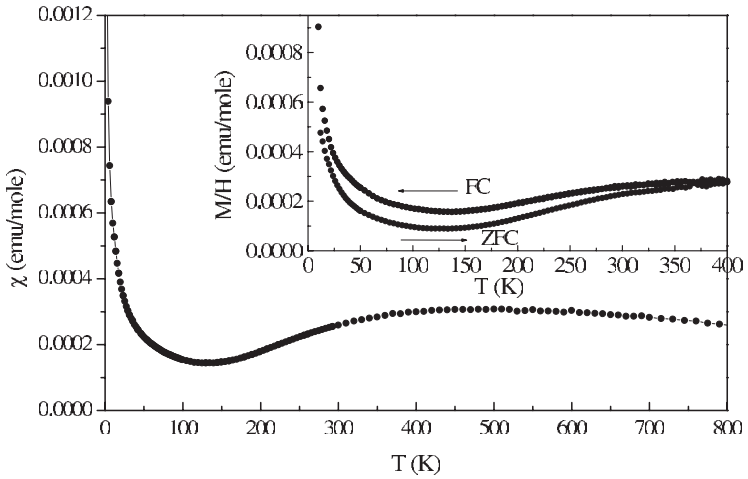

Figure 1. Magnetic susceptibility of $YCuO_{2.5}$ in 10 kOe. Inset: zero-field-cooled and field-cooled M/H curves as a function of temperature in an applied magnetic field of 50 Oe.

which yields a very large value of the exchange interaction $J \approx 2300$ K from the relation $\Delta = 0.2156$ J, valid for the dispersionless gap of the symmetric case [7]. The value of a similar exchange interaction determined in high T_c superconductors, which have comparable Cu–O distances and more favourable exchange paths, is, however, much smaller. This appears to argue against the present interpretation of the energy gap.

An alternative explanation of the magnetic behaviour was looked for through complementary measurements of zero-field-cooled and field-cooled magnetization. A thermomagnetic hysteresis is observed starting from the temperature of maximum in χ (see inset of figure 1). Such an onset of irreversibilities could be an indication of an increased viscosity of the spin correlations due to a freezing of the spin system.

3.2. Neutron scattering results

The paramagnetic neutron-scattering cross section is proportional to the dynamical structure factor:

$$S(Q,\omega) = 2\left\{\frac{\omega}{1-\exp(-\omega/k_B T)}\right\} F^2(Q)\frac{\chi(Q)}{g^2\mu_B^2} f(Q,\omega) \tag{1}$$

where the expression inside the curly brackets is the detailed-balance factor, Q is the momentum transfer, $F(Q)$ (=1 at $Q = 0$) is the magnetic form factor of the localized spins, $\chi(Q)$ is the static susceptibility (Q-independent for non-interacting spins), and $f(Q,\omega)$ is the spectral function representing the dynamics of the spin system. Two different neutron scattering techniques were used to obtain deeper insight into the spatial and dynamical properties of the spin correlations in this system.

3.2.1. Polarized neutron. The first technique, based on polarized neutrons, allows us to separate the nuclear and magnetic parts of the signal, which is integrated in energy over a narrow range [−4, +3.5 meV]. The magnetic contributions at 5, 300 and 500 K are shown in figure 2. A very weak magnetic signal is detected at 5 and 50 K (not shown), except for a peak at around 0.8 Å. This was checked to be due to a few per cent of CuO, magnetically ordered

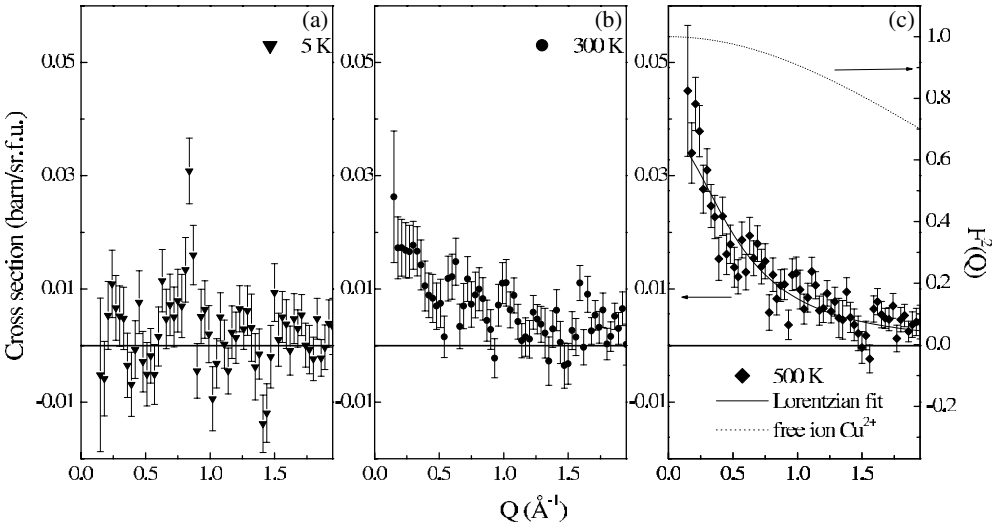

Figure 2. $YCuO_{2.5}$ magnetic contribution at 5, 300 and 500 K, measured on D7. The 500 K spectrum is fitted by a Lorentzian and is compared to the square of the free Cu^{2+} magnetic form factor.

below 230 K. At 300 K, a rise in the paramagnetic signal is observed at low Q values. This magnetic signal gets more intense at 500 K.[5]

The Q dependence of this signal, much narrower than the free Cu^{2+} squared magnetic form factor (see figure 2(c)), indicates short-range spin correlations. Their spatial extent can be roughly estimated from the FWHM of a fitted Lorentzian function (neglecting the Q variation via magnetic form factor). The resulting width of 1.1 $Å^{-1}$ yields a size of correlated magnetic domains of 5–6 Å at 500 K. Quantitatively, the paramagnetic signal from all of Cu with independent spin 1/2 should be 0.15 barns sr^{-1} $f.u.^{-1}$ at zero Q. Instead, we observe a magnetic signal that seems to be much weaker (see figure 2(c)). Part of the missing signal is outside the narrow energy range of this spectrometer, in the tails of the quasielastic signal discussed hereafter, but the loss is too large to be explained by this sole effect.

3.2.2. Inelastic scattering. The time-of-flight measurements give access to $S(Q, \omega)$ but without direct separation of magnetic and nuclear contributions. To achieve this, the non-magnetic compound $YCuO_2$, whose structure is closely related to that of $YCuO_{2.5}$ [3], was used as a reference to determine the phonon spectrum[6].

A magnetic quasielastic signal is observed at 150 and 300 K but none is detected at 2 K. An attempt was made to analyse the Q-dependence of the quasielastic signal observed at the highest temperature although this is very weak. The function $f(Q, \omega)$ in equation (1) can be described by a Lorentzian if the system is characterized by a unique relaxation time, although this is not likely to be the case here. The fitting procedure was performed at different Q values taking into account the convolution of the signal by the instrument resolution function. The result at 300 K shows a decrease of the signal intensity on increasing Q which is in quantitative

[5] This is consistent with the roughly constant χ between 300 and 500 K, since the energy integrated intensity should then increase linearly with T (see equation (1)).

[6] The phonon spectrum of the sample signal (I_S) is calculated at all Q_i values using the Q-dependence of the reference signal (I_R) and the sample spectrum at high Q ($Q_f = 3.6$ $Å^{-1}$) where the magnetic contribution is expected to be rather small. Subtracted from the total signal, this yields the magnetic part: $I_{mag} = I_S(Q_i) - I_S(Q_f)\frac{I_R(Q_i)}{I_R(Q_f)}$.

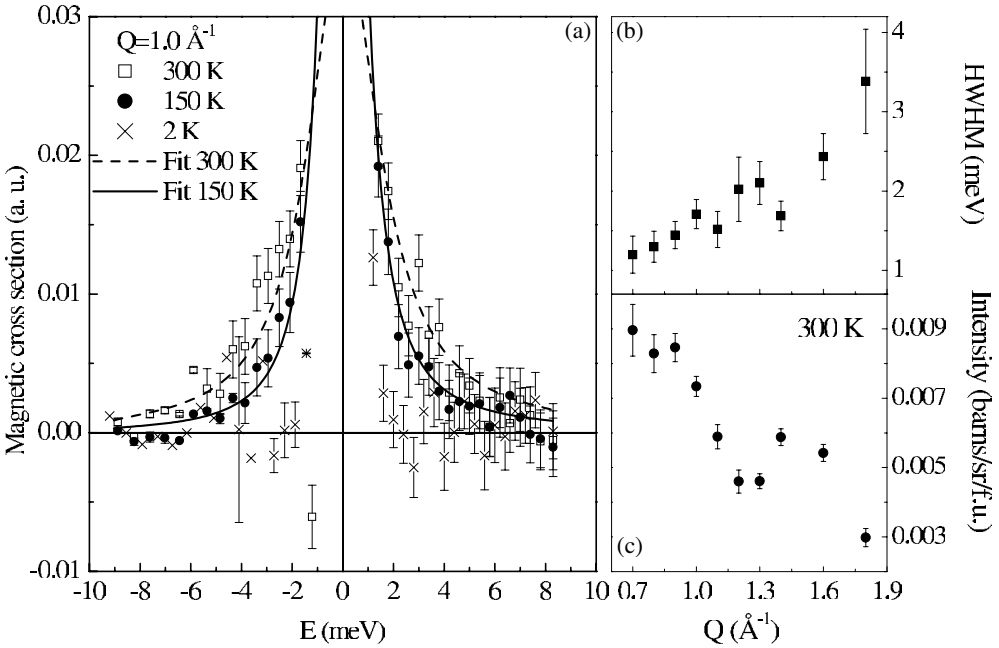

Figure 3. (a): Quasielastic magnetic signal of $YCuO_{2.5}$ for $Q = 1$ Å^{-1} measured on IN4 at different temperatures. Q-dependence of the Lorentzian fit at 300 K: (b) FWHM and (c) intensity.

agreement with the measurements performed on D7. The width of the Lorentzian is increasing with Q from 1 to 4 meV between 0.7 and 1.8 Å^{-1}. This evolution is consistent with the Q^2 increase of the second moment $\langle\omega^2\rangle$ of the spectral function for a Heisenberg paramagnet with exchange interactions [8, 9]. At 150 K, the signal seems even narrower in energy which prevents a reliable analysis of its Q dependence[7].

4. Concluding remarks

At high temperatures, $YCuO_{2.5}$ shows a fluctuating behaviour of interacting magnetic moments. These interactions give rise to spatial and dynamical spin correlations, probed in the neutron scattering experiments. At 150 K, the energy width of the quasielastic signal decreases which indicates a slowing down of the spin dynamics with respect to the characteristic times accessible in the present neutron experiment: $\tau = \hbar/\Delta E \approx 10^{-12}$ s. Part of the signal is also transferred into the elastic peak. At 2 K, no detectable inelastic signal is measured using the IN4 spectrometer. An initial explanation invoking a gap in the excitation spectrum, as predicted for the Δ-chain, was recently revised by μSR measurements on the same sample, indicating antiferromagnetic correlations of frozen magnetic moments below 200 K and down to 2 K [10]. Since the μSR technique is sensitive to much longer fluctuation times, the absence of a low temperature signal in the inelastic neutron experiment could be due to the fact that all the signal is frozen with respect to the characteristic time of this experiment on IN4 but not on the μSR timescale. However, a diffuse magnetic elastic signal should be present within the

[7] The error bars presented in both figures 3(b) and (c) reflect the goodness of the Lorentzian fit and do not take into account the errors introduced during the full data treatment. It is therefore difficult to decide whether the oscillations observed on both intensity and width at 300 K are physical or not.

integrated intensity. The weakness of the magnetic signal detected in the D7 experiment may be due to it being redistributed in Q space reflecting the respective orientation of the frozen magnetic moments.

More studies are necessary to better understand the magnetic properties of this system, in particular the nature of the glassy-like state: is it homogeneous or not, induced by oxygen disorder or related to the topology of the magnetic lattice, still consistent or not with the theoretical predictions of the Δ-chain model?

To go further, inelastic neutron scattering studies with a spectrometer sensitive to smaller energies should allow the clarification of the spin dynamics of the sample. Very recently, the growth of a millimetre-sized single crystal of $YCuO_{2.5}$ was reported [11], which opens the way for anisotropic magnetization measurements and for more sophisticated neutron studies.

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