Magnetism in the pseudo-two-leg ladder compound CaCu$_2$O$_3$

M. Wolf$^{a,*}$, K.-H. Müller$^a$, D. Eckert$^a$, S.-L. Drechsler$^a$, H. Rosner$^b$, C. Sekar$^a$, G. Krabbes$^a$

$^a$Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden, P.O. Box 270116, 01171 Dresden, Germany
$^b$Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Nöthnizer Str. 40, Germany

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Abstract

Contrary to SrCu$_2$O$_3$, the pseudo-ladder two-leg compound CaCu$_2$O$_3$ does not show a significant spin-gap behavior as expected for typical two-leg ladder systems. Magnetization measurements on single crystals show CaCu$_2$O$_3$ to be a three-dimensional (3D) antiferromagnet ($T_N = 27$ K), showing relatively strong magnetic anisotropy and metamagnetic transitions. The 3D behavior is due to exchange between the ladders as deduced from electronic structure calculations within the local density approximation.

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1. Introduction

Cuprates, containing Cu–O ladders, are of high interest because of their possible relation to high-$T_c$ superconductors. Moreover, they show fascinating and fundamental effects of low-dimensional magnetism. In the ideal case for isolated ladders with antiferromagnetic (AFM) exchange within the rungs and legs, even-number-of-legs compounds (briefly “even-leg ladder compounds”) reveal spin-gap behavior and thus a magnetic susceptibility $\chi$ exponentially vanishing for low temperatures $T \rightarrow 0$. On the other hand, for odd-leg ladder compounds $\chi(T \rightarrow 0)$ remains finite. This scenario has been confirmed experimentally in the case of SrCu$_2$O$_3$ (two-leg ladder, TLL) and Sr$_2$Cu$_3$O$_5$ (three-leg ladder) [1,2]. However, this “even–odd rule” is violated when the Cu–O sublattice does not form ideal ladder structures. Here we study the magnetic properties of the pseudo TLL (PTLL) compound CaCu$_2$O$_3$ (space group: $P_{mmm}$, #59), i.e. a non-ideal ladder compound with buckled rungs (see Fig. 1) instead of straight rungs as in SrCu$_2$O$_3$ and Sr$_2$Cu$_3$O$_5$.

2. Experimental

CaCu$_2$O$_3$ single crystals (size about 2 x 3 x 1 mm$^3$) were cut from a boule, grown in an IR furnace by the traveling solvent floating zone method. The crystals were found to be phase pure as confirmed by X-ray diffraction, energy dispersive X-ray (EDX) and thermogravimetric analysis [3]. However, the EDX results indicate a deficiency of Ca, with a balancing excess in Cu, corresponding to a nonstoichiometric composition Ca$_{1-y}$Cu$_{2+y}$O$_{3-\delta}$ ($0.14 \pm \delta \leq y \leq 0.17$) as described in Refs. [3,4]. The lattice constants determined as
Fig. 1. Crystal structure of CaCu$_2$O$_3$. The dotted lines mark the two legs of a ladder along the $b$-axis with the buckled rungs (solid lines).

$a = 9.944\, \text{Å}, \, b = 4.078\, \text{Å}$ and $c = 3.461\, \text{Å}$ agree well with published values [5]. Note, that MgCu$_2$O$_3$, to be referred to below, has the same lattice structure [6]. Magnetic measurements on single crystals have been performed in a SQUID magnetometer for temperatures from 5 K up to 120 K in magnetic fields ($\mu_0 H \leq 7$ T) applied along the different crystallographic axes. The magnetic susceptibility has been determined from magnetization measurements at 1 T.

3. Results

The temperature ($T$) dependencies of the magnetic susceptibilities $\chi_a$, $\chi_b$ and $\chi_c$, measured in magnetic fields $H$ along the crystallographic axes $a$, $b$ and $c$, respectively, display a sharp kink at $T_N = 27$ K (see Fig. 2). Below $T_N$, $\chi_a$ and $\chi_b$ decrease with decreasing $T$. These features are typical for a 3D AFM ordering with a Néel temperature at $T_N$ and correspond to our previous results on powder samples [4]. The long-range AFM ordering has been confirmed by neutron scattering studies in Ref. [7]. Comparing our $\chi(T)$ curves, we conclude that at $T < T_N$ the moments should be mainly perpendicular to the $c$-axis. Furthermore, these $\chi(T)$-curves show that in CaCu$_2$O$_3$, the moments below $T_N$ are not parallel to one of the crystallographic axes. In that case, below $T_N$ only one of the $\chi(T)$-curves should decrease with decreasing $T$, whereas in our case $\chi_a$ and $\chi_b$ decrease. This suggests the moments to have non-zero $a$- and $b$-components, whereas in Ref. [7] an AFM spiral magnetic structure with spins rotating in the $a$–$c$-plane (perpendicular to the ladder direction) was reported. In this context we remind that LiCu$_2$O$_2$ shows a similar behavior: a ferromagnetic (FM) spiral state is formed below 22 K [8]. The bilayer of frustrated chains in LiCu$_2$O$_2$ corresponds to a bilayer of frustrated PTLLs in the present case. Concerning the difference in magnetic structure we suppose that it may be due to a high sensitivity of the AFM structure to details of the sample as e.g. composition, which in our case deviates from ideal stoichiometry. Such a sensitivity has also been observed for MgCu$_2$O$_3$ when doping with Li [6]. Another possibility is, that the response of two coupled subsystems is observed, which consists of the majority spins in the ordinary PTLLs and of minority spins of unknown origin.

In the investigated temperature range, $T > T_N$, $\chi$ contains contributions from Van Vleck and diamagnetic terms as well as contributions from the PTTLs, which are small, as the maximum of the susceptibility, revealed by all 1D $S = 1/2$ systems, for the PTTLs is at about 1200 K due to the huge exchange integral $J_0$ along the leg direction. All these terms may be summarized in the “background” $\chi_0$. Thus, above $T_N$ all $\chi$-curves are well described by a modified Curie law: $\chi = C/T + \chi_0$. The Curie constant $C$ as well as $\chi_0$ depend on the direction of $H$. The magnitude of $\chi_0$ is comparable with that estimated for MgCu$_2$O$_3$ [6], as expected due to the similarity of the structure and properties of the constituting ions. Adopting a Landé factor $g_L \approx 2$, from the averaged Curie constant $C$ the concentration of the minority spins can be estimated as about 4%, similarly to the value of about 3% reported in Ref. [7]. May be, that these minority spins are related to the detailed composition of the compound.

Below $T_N$ the magnetization has been measured for $\mu_0 H$ up to 7 T and corrected for $\chi_0$, which is not related to the AFM sublattices. For $T = 5$ K and $H$ parallel to the $a$-, $b$- and $c$-axis of the single crystal the resulting magnetization curves $M(H)$ are shown in Fig. 3. $M(H)$ shows no hysteresis and depends linearly on $H$ for $H || c$. This confirms the assumption that the ordered moments are perpendicular to the $c$-axis. Then, for changing fields $H || c$, the magnetization change is due to a reversible

Fig. 2. Magnetic susceptibility $\chi_a$, $\chi_b$, $\chi_c$ versus temperature for fields $H$ applied parallel to the $a$-, $b$- and $c$-axis, respectively. The kink at $T_N = 27$ K is due to the onset of antiferromagnetic ordering. The curves are fits of a modified Curie law to the measured values for $T > T_N$ (cf. text).
rotation of the moments, mainly governed by the balance of Zeeman energy and an exchange energy. For $H \parallel b$ or $H \parallel a$ the $M(H)$ curves reveal hysteresis. At a critical field $H_{cr} \approx 5-6$ T the slope of $M(H)$ increases, resulting in metamagnetic transitions which are suggested to be of spin-flop type as displayed by ideal antiferromagnets for $H$ applied parallel to the ordered moments. Because of the complex magnetic structure of CaCu$_2$O$_3$ [7], here the transition is weakened and smeared out. Due to this transition, the magnetization values at 7 T and $H \parallel a$ and $H \parallel b$ exceed that for $H \parallel c$ for the same field strength. A phenomenological description of the $M(H)$ curves for $H > H_{cr}$ by a two-sublattice model with AFM exchange, uniaxial anisotropy and Zeeman energy results in an exchange energy of about 9 meV and an anisotropy constant of 0.14 meV per Cu moment. Such an anisotropy for the $S = 1/2$ Cu$^{2+}$ ions may be due to an anisotropic exchange [9].

MgCu$_2$O$_3$ has the same lattice structure, but $\beta \approx 93^\circ$ and $J_r$ and $J_c$ change even the sign as evidenced by observed magnetic structure [6]. The reduction of $J_r$ itself does not explain the lacking spin gap in CaCu$_2$O$_3$. It is the changed lattice structure with different interladder distances of Cu and O which enhance critically $|J_c|$ [11] and destroy the ideal TLL scenario. In both PTLL-compounds, neighboring rungs in $a$-direction, are shifted to each other by 0.5b. This causes a weak band dispersion along $IX$ and a small AFM contribution to $J_a$. In CaCu$_2$O$_3$ a large FM contribution is excluded by the observed AFM pitch angle of the spiral state [7]. Hence, $J_a$ is the smallest coupling. Ignoring $J_r$ [7,10], to first approximation, the problem is reduced to chains coupled in the $b$-$c$ plane. The ordered magnetic moment $\mu$ at $T = 0$ is described by the 2D mean-field expression [12]

$$\mu/\mu_B = 0.273 g_L \sqrt{1/\gamma(1 + 0.095/\gamma) \ln^{1/3}(1.3\gamma)}$$

(1)

with $\gamma = J_b/|J_c|$ ($g_L = 2.2$), where the square root in (1) results in suppressed value of $\mu$ compared to 1 $\mu_B$. With $J_b \approx 130$ meV [10,11] and the observed ordered $\mu$, $J_c \approx 8.6$ meV is estimated from Eq. (1). Note, that for SrCu$_2$O$_3$ $J_c \approx 1$ meV is much smaller [8], causing the nearly ideal TLL behavior. Adopting the picture of classical spins and a weak AFM exchange $J_c \ll J_r$ between nearest neighbors on adjacent ladders along $a$, $J_a \approx 1$ meV can be estimated from the measured pitch angle, confirming our LDA result of an exchange hierarchy mentioned above. In MgCu$_2$O$_3$, due the FM $J_r$ (for AFM $J_a$ and $J_c$) there is no frustration along $a$ within each ladder layer. Hence, no spiral is formed in accordance with Ref. [6].

To conclude, the magnetic properties of CaCu$_2$O$_3$ are governed by a considerable AFM exchange interaction.
along the c-axis, destroying the two-leg ladder behavior. Further studies of the magnetism in CaCu₂O₃ especially with respect to the spiral, the magnetic anisotropy and the role of the minority spin subsystem are necessary.

Note added in proof

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