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Magnetism in the pseudo-two-leg ladder compound $CaCu_2O_3$

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Abstract

Contrary to $SrCu_2O_3$, the pseudo-ladder two-leg compound $CaCu_2O_3$ does not show a significant spin-gap behavior as expected for typical two-leg ladder systems. Magnetization measurements on single crystals show $CaCu_2O_3$ 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 χ exponentionally vanishing for low temperatures $T \to 0$. On the other hand, for odd-leg ladder compounds $\chi(T \to 0)$ remains finite. This scenario has been confirmed experimentally in the case of $SrCu_2O_3$ (two-leg ladder, TLL) and $Sr_2Cu_3O_5$ (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 $CaCu_2O_3$ (space group: P_{mmn}, #59), i.e. a non-ideal ladder compound with buckled rungs (see Fig. 1) instead of straight rungs as in $SrCu_2O_3$ and $Sr_2Cu_3O_5$.

2. Experimental

$CaCu_2O_3$ single crystals (size about $2 \times 3 \times 1\,mm^3$) 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 $Ca_{1-y}Cu_{2+y}O_{3-\delta}$ ($0.14 \pm \leqslant y \leqslant 0.17$) as described in Refs. [3,4]. The lattice constants determined as

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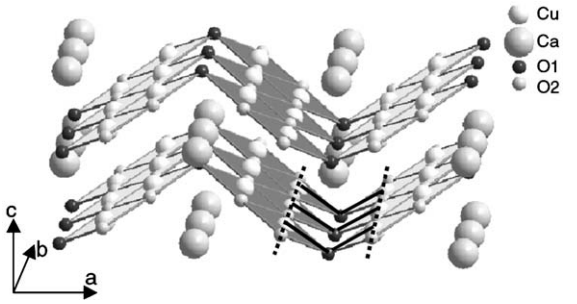

Fig. 1. Crystal structure of $CaCu_2O_3$. The dotted lines mark the two legs of a ladder along the *b*-axis with the buckled rungs (solid lines).

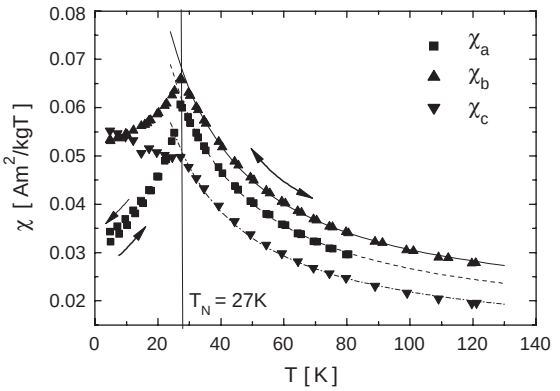

Fig. 2. Magnetic susceptibility χ_a, χ_b, χ_c versus temperature for fields **H** applied parallel to the *a*-, *b*-, and *c*-axis, respectively. The kink at $T_N = 27\,K$ is due to the onset of antiferromagnetic ordering. The curves are fits of a modified Curie law to the measured values for $T > T_N$ (cf. text).

$a = 9.944\,Å$, $b = 4.078\,Å$ and $c = 3.461\,Å$ agree well with published values [5]. Note, that $MgCu_2O_3$, 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 ($\mu_0 H \leqslant 7\,T$) 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 χ_a, χ_b and χ_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, χ_a and χ_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 $CaCu_2O_3$ 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 χ_a *and* χ_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 $LiCu_2O_2$ shows a similar behavior: a ferromagnetic (FM) spiral state is formed below 22 K [8]. The bilayer of frustrated chains in $LiCu_2O_2$ 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 $MgCu_2O_3$ 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, $T > T_N$, χ 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_b along the leg direction. All these terms may be summarized in the "background" χ_0. Thus, above T_N all χ-curves are well described by a modified Curie law: $\chi = C/T + \chi_0$. The Curie constant C as well as χ_0 depend on the direction of **H**. The magnitude of χ_0 is comparable with that estimated for $MgCu_2O_3$ [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 χ_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 $\mathbf{H} \| c$. This confirms the assumption that the ordered moments are perpendicular to the *c*-axis. Then, for changing fields $\mathbf{H} \| c$, the magnetization change is due to a reversible

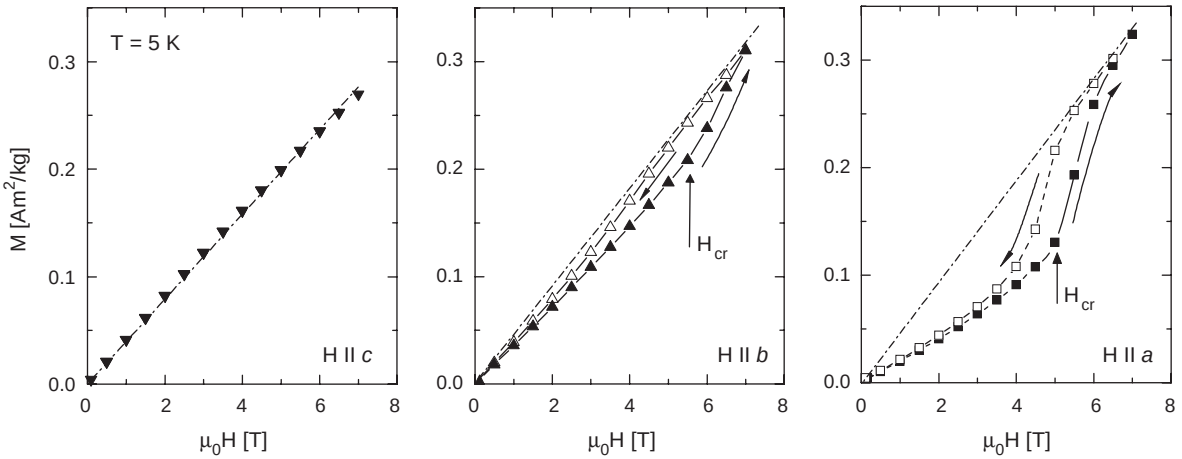

Fig. 3. Magnetization curves at 5 K for magnetic field **H** applied parallel to the *c*-, *b*- and *a*-axis. For **H**$\|b$ and *a* at H_{cr} metamagnetic transitions are found and the $M(H)$ curves show hysteresis. Dash-dot lines: guides for eye to show the linear $M(H)$ dependence above H_{cr}.

rotation of the moments, mainly governed by the balance of Zeeman energy and an exchange energy. For **H**$\|b$ or **H**$\|a$ 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 $CaCu_2O_3$ [7], here the transition is weakened and smeared out. Due to this transition, the magnetization values at 7 T and **H**$\|a$ and **H**$\|b$ exceed that for **H**$\|c$ 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].

4. Discussion

Leading exchange integrals were determined by electronic structure calculations within the local density approximation (LDA), resulting for $CaCu_2O_3$ [10,11] in a hierarchy $J_b \gg |J_c| \gg J_a$, with J_i being the exchange coupling along the axis *i*. Whereas the *topology* of the Cu–O–Cu bonds is the same as that of $SrCu_2O_3$, the bonding angle Cu–O–Cu β within the rungs of the ladders (spanning parallel to *b*) is only about 123°. According to the Goodenough–Kanamori–Anderson rule, for such a bonding angle within the rungs the corresponding AFM exchange J_r is strongly reduced (to about 10 meV) compared to the AFM J_b of a leg.

$MgCu_2O_3$ has the same lattice structure, but $\beta \approx 93°$ 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 $CaCu_2O_3$. 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 0.5*b*. This causes a weak band dispersion along ΓX and a small AFM contribution to J_a. In $CaCu_2O_3$ 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 μ at $T = 0$ is described by the 2D mean-field expression [12]

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

with $\gamma = J_b/|J_c|$ ($g_L = 2.2$), where the square root in (1) results in suppressed value of μ compared to 1 μ_B. With $J_b \approx 130$ meV [10,11] and the observed ordered μ, $J_c \approx 8.6$ meV is estimated from Eq. (1). Note, that for $SrCu_2O_3$ $J_c \approx 1$ meV is much smaller [8], causing the nearly ideal TLL behavior. Adopting the picture of classical spins and a weak AFM exchange $J_{r'} \ll J_r$ 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 $MgCu_2O_3$, due the FM J_r (for AFM J_a and $J_{r'}$) 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 $CaCu_2O_3$ are governed by a considerable AFM exchange interaction

along the *c*-axis, destroying the two-leg ladder behavior. Further studies of the magnetism in $CaCu_2O_3$ especially with respect to the spiral, the magnetic anisotropy and the role of the minority spin subsystem are necessary.

Note added in proof

Our conclusions concerning the theoretical value of J_c has been supported recently by theoretical analysis by P. Sengupta et al., Phys. Rev. B 69 (2004) 064428.

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