

A field induced ferromagnetic-like transition below 2.8 K in Li_2CuO_2 : An experimental and theoretical study

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The low temperature magnetic properties of the Li_2CuO_2 compound have been investigated by means of superconducting quantum interference device magnetometry. We find in addition to an antiferromagnetic phase below 9.5 K a ferromagnetic-like steep rise of the magnetization around 2.8 K. The observed low temperature behavior is discussed by considering second and fourth order magnetocrystalline *effective* anisotropy coefficients, in addition to the exchange couplings reported in the literature. © 1998 American Institute of Physics. [S0021-8979(98)31111-1]

The magnetic properties of ternary copper oxides are currently of considerable interest, in particular with respect to high T_c superconducting compounds. Unlike these perovskite systems the Li_2CuO_2 compound investigated here exhibits an orthorhombic structure consisting of CuO_2 planes stacked along the crystallographic c axis, and separated by Li-rich layers. Within a CuO_2 plane the Cu ions are lined up in chains.^{1,2} Thus this compound was expected to exhibit magnetic properties reminiscent to a one dimensional magnet.³ The magnetic structure of this compound as determined by neutron diffraction² may be described as follows: the magnetic moments within the CuO_2 planes are ferromagnetically ordered, whereas neighboring planes are coupled antiferromagnetically (AF) along the c axis. In addition to an AF ordering transition at $T_N=9.5$ K, we observe at temperatures below 2.8 K the appearance of a ferromagnetic component along the direction of the applied magnetic field. We argue that the observed magnetic behavior corresponds to a noncollinear arrangement of the spin layers due to competing magnetocrystalline anisotropies and interlayer exchange coupling. Experimental evidence supporting this argument is presented.

The procedure for fabricating the polycrystalline Li_2CuO_2 compound has been described elsewhere.² The x-ray diffraction patterns of the sample corresponds to a *single crystallographic phase*. The magnetic properties have been measured by means of superconducting quantum interference device (SQUID) magnetometry with applied magnetic fields up to 10 kOe, and in the temperature range between 2 and 300 K. In all our experiments the temperature dependence of the magnetization is measured during warming

scans. It is important to point out that independent samples fabricated and measured at two different places yield identical structural and magnetic properties.

As has already been reported in the literature,^{1,2} the magnetic properties of the Li_2CuO_2 compound (i) exhibits an AF ground state with a Néel temperature $T_N \approx 9$ K, and (ii) shows a Curie–Weiss behavior of the paramagnetic susceptibility above T_N , with a paramagnetic Curie temperature of about $\Theta \approx -40$ K. In addition we have observed the appearance of a *ferromagnetic* component of the magnetization oriented along the applied magnetic field for temperatures below 2.8 K, cf. Fig. 1. The samples were field cooled (FC) in an applied field of 10 Oe, as well as zero field cooled (ZFC) down to 2.0 K. With increasing temperatures the magnetization for both ZFC and FC conditions were measured by applying a magnetic field of 10 Oe. We notice that both curves overlap above 2.8 K, and show the characteristic kink at the Néel temperature T_N . Note also the change of scale of the magnetization for the data taken above 4 K, cf. Fig. 1(b). In

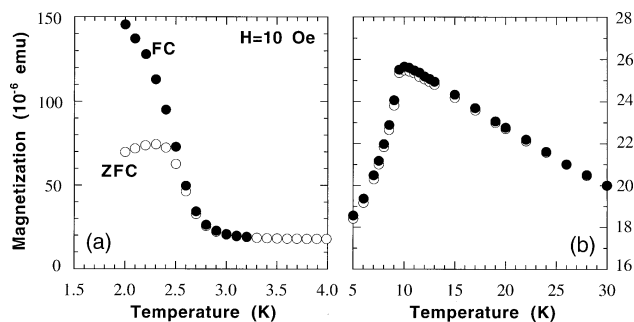


FIG. 1. Temperature dependence of the magnetization of a Li_2CuO_2 sample (67.3 mg). ZFC denotes cooling the sample down to 2.0 K in zero applied field; FC is cooled in a magnetic field of about 10 Oe. (a) Transition from a noncollinear arrangement of the spin layers to a purely AF phase above 2.8 K. (b) Transition from the AF to the paramagnetic phase, with the Néel temperature $T_N \approx 9.5$ K.

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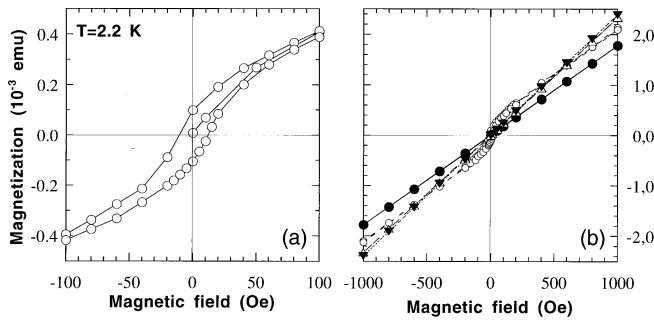


FIG. 2. Magnetic loops of a Li_2CuO_2 sample (67.3 mg) as a function of applied magnetic field. The samples are cooled in zero applied field (ZFC) down to 2.2 K. (a) $T=2.2$ K; first the virgin curve is measured, then the sample is cycled between $H = \pm 10$ kOe. (b) Linear magnetic loops measured at $T=5$ K (\bullet), $T=9$ K (Δ), and $T=14$ K (\blacktriangledown). The hysteresis loop obtained for $T=2.2$ K (\circ) is also shown for comparison.

addition we have monitored the magnetic hysteresis loops $M(H)$ below and above 2.8 K. In the former case we observe a small *remanent magnetization*, cf. Fig. 2(a) for $T=2.2$ K, and a resulting coercive field of about $H_c \approx 12$ Oe. Within these measurements the samples were cooled in ZFC down to 2.2 K. First the virgin magnetization curve $M(H)$ is monitored, then the complete hysteresis loop is measured by cycling the external field through ± 10 kOe. We find that the loops close and the reversible part of the magnetization $M(H)$ is reached for magnetic fields above $|H|=100$ Oe.

No remanence was observed for temperatures above 2.8 K, as shown in Fig. 2(b) for temperatures of about 5, 9, and 14 K. However, for all temperatures investigated the magnetization curves $M(H)$ stay in the linear regime and do not saturate at even the strongest available applied fields, resulting in a high field susceptibility $\chi_{\text{hf}} \approx 2.6 \times 10^{-5}$ emu/gOe at $T=2.2$ K. We note that a complete saturation of the Cu^{2+} ions would render a specific magnetization of about $\sigma_s = 51$ emu/g, assuming $J=1/2$ spins.

In addition we have measured the susceptibility in the paramagnetic phase. A Curie–Weiss behavior was observed, yielding a Curie constant $C_M \approx 0.41$ emu K/mol Oe and the paramagnetic Curie temperature $\Theta \approx -15$ K, which differs from the one reported previously.² From our data we conclude a magnetic moment $\mu \approx 1.05 \mu_B$ per Cu ion, which is consistent with a recent neutron diffraction study yielding a magnetic moment of $\mu \approx 0.96(4) \mu_B$.²

The above results can be explained in terms of a uniaxial magnetocrystalline anisotropy determining the direction of the magnetization with respect to the c axis. Commonly, the uniaxial anisotropy is given as a series in powers of $\cos \theta$, θ being the angle between the magnetization and the c axis. The anisotropic part of the free energy per spin pair may be written as

$$F(T, \theta_1, \theta_2) = -J_c(T) \cos(\theta_1 - \theta_2) - K_2(T) (\cos^2 \theta_1 + \cos^2 \theta_2) - K_4(T) (\cos^4 \theta_1 + \cos^4 \theta_2).$$

$K_2(T)$ and $K_4(T)$ are the second and fourth order *effective*, i.e., temperature dependent, lattice anisotropy coefficients. Expressions of these coefficients as calculated by, e.g., a thermodynamic perturbational expansion of the free energy

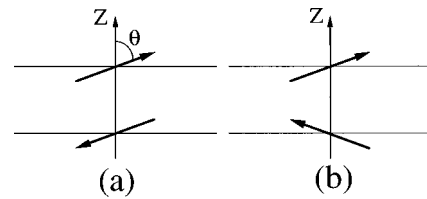


FIG. 3. Sketch of the spin arrangements of two neighboring CuO_2 layers for (a) the purely AF phase, and (b) the noncollinear phase. Note that the latter is metastable since it refers to a local minimum of the free energy. It exhibits a finite remanent magnetization, and may vanish above some temperature T_x . θ is the canting angle between the magnetization and the crystallographic c axis.

are given in Ref. 4. Note that for $K_{2,4} > 0$ a magnetization parallel to the c axis is favored ($\theta=0$), and a perpendicular orientation ($\theta=\pi/2$) for $K_{2,4} < 0$. $J_c(T) < 0$ is the *effective* interlayer exchange coupling connecting q nearest neighbors in adjacent CuO_2 layers, and favoring an AF alignment. Minimization of $F(T, \theta_1, \theta_2)$ with respect to θ_1 and θ_2 reveals the equilibrium canting angles. The most stable state is always the purely AF spin arrangement with $\theta_2 = \theta_1 + \pi$ and a vanishing total magnetization. The case of competing anisotropies $K_2 > 0$ and $K_4 < 0$ may result in a canted magnetization,⁴ i.e., $0 < \theta < \pi/2$, cf. Fig. 3(a).

Most importantly, two additional metastable states may occur corresponding to a noncollinear spin arrangement, cf. Fig. 3(b), which may be in parts thermally populated. The respective canting angles θ_1 and $\theta_2 = -\theta_1$ are determined by $J_c(T)$, $K_2(T)$, and $K_4(T)$ (and also by an applied magnetic field if present), and should be close to $\pi/2$. Quite interestingly, due to the *effective* temperature variation of the involved interactions, the metastable state may *vanish* above some temperature T_x , probably around 2.8 K in the present case. However, below T_x and in the absence of an applied field the two metastable states refer to oppositely oriented magnetizations. Since these two states have the same free energy, they are equally populated, but less populated than the purely AF state. The occupation ratio may be given by $\propto \exp(-\Delta F/k_B T)$, where ΔF is the free energy difference between the stable and the two metastable states. An applied magnetic field may cause a different thermal population of these two metastable states, yielding a small but finite remanent magnetization, cf. the hysteresis loop shown in Fig. 2(a). Also shown in this figure is the virgin curve, i.e., the sample was cooled down to 2.2 K in vanishing magnetic field, resulting in equally populated metastable minima and thus in a vanishing remanence. Furthermore, the ZFC magnetization should vanish at temperatures close to $T=0$, since then the equilibrium thermal population of the metastable states would be vanishingly small. A complete description of the model and the theoretical results will be presented elsewhere.

We do not think that T_x refers to a blocking temperature as present in superparamagnetic systems, since our systems exhibit infinitely extended and strongly coupled ferromagnetic layers. Of course each layer may break up into magnetic domains which will determine essentially the behavior of the hysteresis loops, cf. Fig. 2(a).

In conclusion, the low temperature magnetic properties

of the Li_2CuO_2 compound have been investigated by experimental and theoretical means. At temperatures below 2.8 K the pure AF arrangement of the spin layers is disturbed by the appearance of metastable minima of the free energy, referring to a noncollinear spin arrangement. The origin of such spin configuration is the competition between the AF interlayer exchange coupling, and the magnetocrystalline anisotropy causing a canted magnetization. The thermal population of such minima is observed by the appearance of a finite remanence and coercivity below 2.8 K. Above this temperature the metastable states vanish due to the effective temperature dependence of the involved interactions. At elevated temperatures the compound is an antiferromagnet with Néel temperature $T_N \approx 9.5$ K. The high temperature paramagnetic susceptibility, which closely obeys the Curie–Weiss law, reveals a magnetic moment of about $1 \mu_B$ per Cu ion.

P. J. Jensen wishes to acknowledge the hospitality by the members of the Department of Condensed Matter Physics at

the Royal Institute of Technology. It is a privilege to acknowledge a Gustafsson Stiftelse Visiting Scientist grant, which made this visit possible. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy. Work at the Institut de Ciència dels Materials was supported by the Spanish Comisión Interministerial de Ciencia y Tecnología (Grant No. CICYT MAT 96-1037). Research in Stockholm has been supported by the Swedish funding agencies NFR and NUTEK. It is our pleasure to acknowledge fruitful discussions with Professor V. Madurga and J. Vergara.

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