Multiferroicity in the spin-1/2 quantum matter of LiCu$_2$O$_2$

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Multiferroicity in LiCu$_2$O$_2$ single crystals is studied using resonant soft x-ray magnetic scattering,
hard x-ray diffraction, heat capacity, magnetic susceptibility, and electrical polarization. Two
magnetic transitions are found at 24.6 K ($T_1$) and 23.2 K ($T_2$). Our data are consistent with a
sinusoidal spin structure at $T_2 < T < T_1$ and with a helicoidal spin structure at $T < T_2$, giving rise to
ferroelectricity. Surprisingly, above $T_2$, the correlation lengths of the spin structures increase as the
temperature increases with dramatic changes of $\sim 42\%$ occurring along the c axis. © 2008
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Low-dimensional spin (S)=1/2 copper-oxides have posed some of the most challenging problems in solid state
physics. The interplay between frustration and quantum spin fluctuations results in a rich phase diagram and unusual mag-
netic properties. In a model with quantum S=1/2 chains and competing nearest-neighbor interactions $J_1$ and next-nearest-
neighbor interactions $J_2$, one expects, depending on $J_1/J_2$, a gapless collinear phase, a gapped disordered dimer liquid
phase, or a quasi long-range ordered helicoidal spin structure.\(^1\)

LiCu$_2$O$_2$ consists of an equal number of Cu$^{2+}$ and Cu$^{2+}$
(Fig. 1(a)). The magnetic Cu$^{2+}$ ions carry $S=1/2$ and are located at the center of edge-sharing CuO$_4$ plaquettes and
form two frustrated quasi-one-dimensional chains along the b axis. These chains are separated by Li$^{1+}$ to form double layers parallel to the ab plane, which are separated by Cu$^{1+}$ sites. The Cu–O–Cu angle is $\sim 94^\circ$. As a result, $J_2$ is weaker than $J_1$. The strength of the interaction between chains ($J_{DC}$) is not clear; however, $J_1$ is ferromagnetic and $J_2$ is antiferromagnetic.\(^2\) This leads to frustration and favors helimagnetism.\(^1\) A similar scenario was recently proposed for an isostructural NaCu$_2$O$_2$.\(^3\)

LiCu$_2$O$_2$ exhibits striking properties such as the presence of a spin-singlet liquid state,\(^3\) incommensurate (IC) magnetic order,\(^3\) as well as ferroelectricity.\(^6\) However, there is no clear understanding connecting all these properties. One problem is the intrinsic chemical disorder. Electron-spin resonance\(^5\) has shown the presence of a spin-singlet state with a spin gap of about 6 meV at 23 K. Specific heat\(^4\) and nuclear magnetic resonance\(^7\) show phase transitions at 24.2, 22.5, and 9 K. Recent neutron diffraction\(^8\) found one transition to IC magnetic superstructure below 22 K with a propagation vector \((2n+1)/2, k, \delta, l\), where $n$, $k$, and $l$ are integers and $\delta$ \sim 0.174. It is concluded that the magnetic superstructure is a helical in the ab plane. This is inconsistent with the obser-
vation of ferroelectricity with an electric polarization along the c direction below $\sim 23$ K.\(^6\) In an attempt to understand the coupling between lattice, charge, and spin degrees we have studied LiCu$_2$O$_2$ single crystal using polarization de-
dependent resonant soft x-ray magnetic scattering (RSXMS), hard x-ray diffraction (HXD), heat capacity, magnetic sus-
ceptibility, and electrical polarization, from the same sample.

The LiCu$_2$O$_2$ single crystal was grown by the self-flux method.\(^4\) The HXD was done at the beamline BW5 of HA-
SYLAB with photon energy of 100.5 keV. The lattice parameters $a=5.6963$, $b=2.8497$, and $c=12.417$ Å of the orthorhombic structure at low temperature were verified. This confirms the high crystalline perfection and the absence of impurity phases. The crystal is found to be microscopi-

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**FIG. 1.** (Color online) (a) The crystal structure of LiCu$_2$O$_2$ and the double chains showing $J_1$, $J_2$, and $J_{DC}$. (b) The scattering geometry with photon polarization $e$. The azimuthal angle $\phi$ is 0° in the geometry shown, where the photon polarization is perpendicular to the c axis. (c) An illustration of Cu 2$p$ → 3$d$ resonant scattering process.
nantly twinned along the \([1,1,0]\) plane with \(a \sim 2b\). Below 23 K \((T_{FE})\), \(LiCu_2O_2\) becomes ferroelectric (FE) and shows a small anomaly in the dielectric constant \(\varepsilon\). Figure 2(b) shows a changing dielectric polarization \(\langle P \rangle\) along the \(c\) direction as a function of temperature. However, the observed polarization \((-4 \mu C/m^2\) is two to three orders of magnitude smaller compared to \(RMnO_3\) and \(RMn_2O_4\).\(^{9,10}\)

Two magnetic transitions are found in the magnetic susceptibility \(\chi\) [Fig. 2(a)]. For an applied magnetic field \(H\) parallel to the \(c\) axis \((H \parallel c)\), \(d\chi/dT\) shows two transitions at 23.2 \((T_1)\) and 24.6 K \((T_2)\), while for \(H \parallel b\), the \(d\chi/dT\) shows only one sharp transition at 23 K. The \(T_2\) coincides with \(T_{FE}\) from heat capacity measurements [Fig. 2(a)]. Our sample does not show any other transition below 23 K.\(^{11}\)

RSXMS was done on a surface which was cleared \textit{in situ} with \((2,1,0)\) orientation at the beamline X1B of the NSLS using a ten-axis, ultrahigh-vacuum-compatible diffractometer.\(^{12,13}\) X-ray absorption spectra (XAS) were measured \textit{in situ} in the fluorescence yield mode. We denote the reciprocal space with Miller indices \((H,K,L)\), which represent a momentum transfer \(Q=(2\pih/a, 2\pik/b, 2\piL/c)\). The angles of incoming photons \((\theta_{in})\) and outgoing photons \((\theta_{out})\) depend on \(Q\) but was approximately \(35^\circ\) and \(55^\circ\), respectively. The azimuthal angle, \(\phi\), is \(\phi=0^\circ\) and \(90^\circ\) [Fig. 1(b)].

Scattering at transition metal \(L\) edges is sensitive to the spin modulation.\(^{14-16}\) Figure 1(c) illustrates \(Cu\) \(2p \rightarrow 3d\) resonant scattering process, which enhances the magnetic scattering from \(Cu^{2+}\). In the cuprate systems, the transition exhibits two main peaks corresponding to final states with \(2p_{1/2}\) and \(2p_{3/2}\) core holes, referred to as the \(Cu\) \(L_1\) and \(Cu\) \(L_2\) absorption edges, respectively. This material is particularly interesting because it has a clear contrast in the scattering of the \(Cu^{2+}\) and \(Cu^{3+}\) sites [Fig. 2(d)]. The peaks at 930 and 933 eV are \(Cu\) \(L_3\) edge of \(Cu^{2+}\) and of \(Cu^{1+}\), respectively.\(^{17}\)

Probing with resonance photon energy \(E=930\) eV, an IC superstructure with \(Q=(0.5, 0.1738, 0)\) at \(T=18\) K is observed [Fig. 2(c)]. This is identical to the magnetic superstructure found by neutron diffraction.\(^5\) Our experiment reveals that the correlation lengths along the \(a\), \(b\), and \(c\) are very large with \(\xi_a=(1662 \pm 20)\), \(\xi_b=(2120 \pm 20)\), and \(\xi_c=(935 \pm 20)\) Å, respectively. X-rays at 930 eV have a penetration depth of 2500 Å.

Figure 2(d) shows the scattering intensity of the superstructure as a function of photon energy \(I_{SS}(E)\), i.e. the resonance profile (RP), at 18 and 24.6 K a. The 24.6 and 18 K measurements represent magnetic scatterings at above and below the FE transition, respectively. The RP is compared to the complex atomic scattering factor of \(Cu\) \(f_{Cu}(\mathbf{q})\) in this case. \(I_{SS}[f_{Cu}]=|Re[f_{Cu}]+Im[f_{Cu}]|^2\). The \(Im[f_{Cu}(\mathbf{q})]\) is determined from the absorptive part of the refractive index \(Im[n]\), which is linearly related to the XAS spectrum, through the relation \(Im[n(\mathbf{q})]=-(r\lambda N/2\piV_{cell})\ Im[\Sigma_d(\mathbf{q})]\), where the \(Re[f_{Cu}](\mathbf{q})\) is calculated from \(Im[f_{Cu}](\mathbf{q})\) by performing a Kramers-Kronig transform. Here, \(r\) is the classical electron radius, \(\lambda\) is the x-ray wavelength, \(N\) is the number of \(Cu\) in the unit cell, and \(f_{j}\) is the complex atomic scattering factor. The XAS measurement was done with an incident x-ray polarization in the \(ab\) plane, at room temperature, corrected for self-absorption, and placed on an absolute scale.\(^{18}\) A gigantic enhancement occurs in the magnetic-CE state. A lattice distortion would result in orders of magnitude smaller scattering intensities.\(^{12}\)

We have performed a HDX study to rule out a lattice modulation.\(^{19}\) Even at 4 K, neither a \((0.5, k \pm \delta, 0)\) nor a \((0.5, k \pm 2\delta, 0)\) reflection was found suggesting that the lattice distortion is extremely small. This is in contrast to ferroelectrics \(TbMnO_3\) in which lattice distortions are observed.\(^{20}\)

Figures 3(a) and 3(b) display the intensity together with the position of the Bragg peak as a function of temperature and polarization of the incoming photon. For \(\phi=90^\circ\), we have found the presence of two magnetic transitions: at \(~23.2\) and \(~24.6\) K, which is consistent with magnetic susceptibility. The intensity increases as temperature decreases, indicating an enhanced magnetic order upon cooling, while \(Q\) also changes with temperature. For \(\phi=90^\circ\), the superstructure vanishes rapidly above \(T_2\). The combination of RSXMS, HDX, magnetic susceptibility, and the electrical polarization measurements provides crucial information regarding the coexistence of FE and magnetic states. At \(T_2<T<T_1\), we find: First, \(d\chi/dT\) shows an anomaly at \(T_1\) for \(H \parallel c\), implying that the \(c\)-direction is an easy axis [Fig. 2(a)]; Second, there is no FE, i.e., \(P=0\) [Fig. 2(b)]; Third, for \(\phi=0^\circ\), RSXMS experiment shows a magnetic Bragg reflection, while for \(\phi=90^\circ\), the superstructures are very weak. For spins which have a component of the magnetic moment along the \(c\) axis, the polarization factor of the magnetic scattering is \(f_{magn}=(e_{m} \times e_{m}) \cdot \mathbf{M} \neq 0\). This implies that the magnetic moment is in the plane of the slab, while the magnitude of the magnetic moment is normal to the slab plane.
Another interesting observation is the smallness of the temperature window between the two transitions. In TbMnO$_3$, the temperature window is $\sim 12$ K. In CoCr$_2$O$_4$, the temperature window is $\sim 65$ K. This supports our picture of an electronically driven phase. Related to this is an increased coherence length with increasing temperature above $T_{FE}$ indicating remaining dynamic FE domain ordering.

In conclusion, we have found two magnetic transitions in LiCu$_2$O$_2$: a sinusoidal spin structure at $T_2 < T < T_1$ and a helicoidal spin structure at $T < T_2$, giving rise to ferroelectricity. The coherence lengths of the superstructure behave in an unusual way, i.e., increasing as the temperature increases. Our results highlight the value of RSXMS for studying the interplay of spin, charge, and lattice degrees of freedom in multiferroics.

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**FIG. 3.** (Color online) (a) Two-dimensional plot of temperature vs (0.5, δ, 0) for $\varphi=90^\circ$. (b) The evolution of the peak position (red dots), $\delta$, and intensity (black and blue dots) of the magnetic scattering for the two polarizations as a function of temperature showing two transitions: $\sim 23.2$ and $\sim 24.6$ K. ([c]--[e]) Correlation lengths of the magnetic ordering as function of temperature.