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Magnetic order of $LiCu_2O_2$ studied by resonant soft x-ray magnetic scattering☆

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ABSTRACT

We present results of resonant soft x-ray magnetic scattering measurements on single crystals of $LiCu_2O_2$ to address the magnetic order. $LiCu_2O_2$ exhibits a long-range magnetic order incommensurate with the lattice, and the modulation vector is $(0.5, \zeta, 0)$ in reciprocal lattice units with $\zeta \sim 0.174$, depending upon the temperature. The spin–spin correlation length along the spin chain deduced from the width of momentum scan is larger than 2100 Å. The inter-chain correlation length that lies within the *ab* plane was discovered to be substantial, ~690 Å.

Magnetic properties of low-dimensional frustrated spin systems have attracted much interest for many years. A quasi-one-dimensional system of spin 1/2 chain with intensive interplay of geometric frustration and quantum fluctuation is interesting and important because of the competition between the nearest- and next-nearest-neighbor interactions, i.e., J_1 and J_2, respectively. In the classical regime, such a competition results in magnetic ground states of long-range incommensurate spiral spins with a propagation vector $\cos^{-1}(J_1/4J_2)$, if $|J_2/J_1| > 1/4$ [1]. For quantum systems, quantum fluctuations can destroy the long-range order and give rise to gapped spin-liquid phases with commensurate spin correlations [2–6], and other exotic states depending upon $|J_2/J_1|$ [7]. In addition, 3D interactions in real quasi-1D materials tend to suppress quantum spin fluctuations and restore semiclassical behavior.

$LiCu_2O_2$ is a mixed-valent magnet which is highly frustrated and with an equal number of Cu^{2+} and Cu^{+} oxidation states. The magnetic Cu^{2+} is located at the center of the square base of a fivefold-oxygen pyramid and form edge-shared chains running along the *b* axis with the Cu–O–Cu bond angle of 94°; adjacent CuO_2 chains are connected by Li^{+}, forming 2D layers of Cu^{2+} in the *ab* plane. Double layers of Cu^{2+} stack along the *c* direction with intervened layers of non-magnetic Cu^{+} ions, as illustrated in Fig. 1.

Several experiments evidenced that $LiCu_2O_2$ exhibits a strong competition between classical and quantum spin correlations. Measurements of electron spin resonance (ESR) suggested that $LiCu_2O_2$ possesses characteristics of a spin-liquid state with an energy gap of 6 meV in the magnetic excitation spectrum [7]. In contrast, measurements of Li nuclear magnetic resonance (NMR) revealed a clear signature of incommensurate static modulation of magnetic order below 24 K [8]. Neutron results also found that the spin structure of $LiCu_2O_2$ is spiral with an incommensurate propagation vector $\vec{q} = (1/2, \zeta, 0)$, $\zeta \sim 0.174$, and the magnetic

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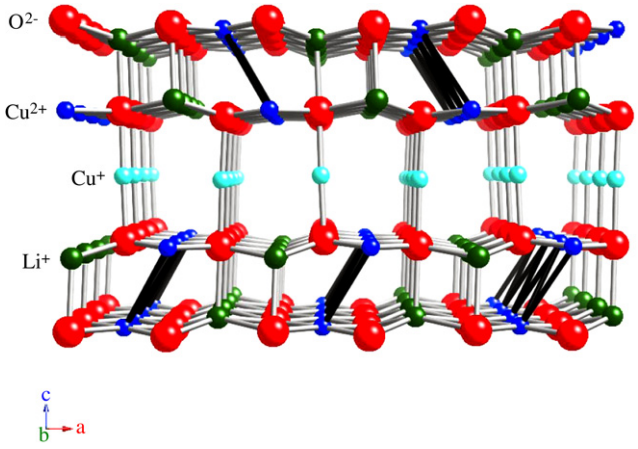

Fig. 1. Illustration of the crystal structure of $LiCu_2O_2$. The green, blue, cyan, and red spheres denote Li, Cu^{2+}, Cu^{+}, and O ions,respectively. The black chemical bonds highlight the zigzag spin chains.

moments of Cu^{2+} were found to lie in the *ab* plane [9]. Recent ESR results [10] also concluded that the spin wave spectrum of $LiCu_2O_2$ with spiral order has a gap of 1.4 meV and supported spin moments being in the *ab* plane.

In addition to its novel magnetic properties, $LiCu_2O_2$ was discovered to be one member of multiferroics in which magnetism and ferroelectricity coexist and ferroelectric polarization can be reversibly flipped by applied magnetic fields [11,12]. However, the direction of electric polarization deduced from the antisymmetric exchange interaction such as the spin-current model [13] suggests the spin spirals to be in the *bc* plane, rather than the *ab* plane [11]. Very recent measurements of polarized neutron scattering confirmed the existence of transverse spiral spin components in the *bc* plane and also implied the existence of large quantum fluctuation [12].

In this work, complementary to neutron scattering, we present results of resonant soft x-ray scattering to study the magnetic order of $LiCu_2O_2$. With photon energy tuned around the *L*-edge ($2p \rightarrow 3d$) absorption of transition metal, resonant soft x-ray scattering takes place through a dipole allowed transition, and a core-level electron Ψ_{2p} is virtually promoted to an intermediate state Ψ_{3d} above the Fermi level. The resonance effect enhances the scattering cross section dramatically and gives rise to a direct probe of the ordering of 3d states in transition metals. For the polarization vectors of incident and scattered x-rays being $\vec{e}_i$ and $\vec{e}_s$, the resonant scattering amplitude of x-ray with wavelength λ is

$$f_{\mathrm{mag}}^{\mathrm{res}} = -\mathrm{i}\frac{3\lambda}{8\pi}(\vec{e}_s^{\,*} \times \vec{e}_i)\cdot\hat{z}(F_{1,1} - F_{1,-1}), \qquad (1)$$

where $F_{1,\pm1}$ are scattering amplitudes associated with the change of magnetic quantum number Δm being ±1; $\hat{z}$ is the quantization axis of magnetization [14]. Resonant soft x-ray magnetic scattering thus provides us an effective experimental method to probe magnetic order with a good momentum resolution [15–19].

We measured resonant soft-x-ray magnetic scattering on $LiCu_2O_2$ with the elliptically-polarized-undulator beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Single crystals of $LiCu_2O_2$ were grown with the floating zone method, and characterized with x-ray diffraction at room temperature. $LiCu_2O_2$ has a layered orthorhombic crystal structure with the space group *Pnma*, and the lattice constants $a = 5.73$ Å, $b = 2.86$ Å, and $c = 12.417$ Å. Our crystals were found to be twined with mixing of the *a*- and *b*-axis domains as observed previously in the literature [9,11,12]. $LiCu_2O_2$ crystals were cut to have a twined (100)/(010) surface for scattering measurements. The scattering

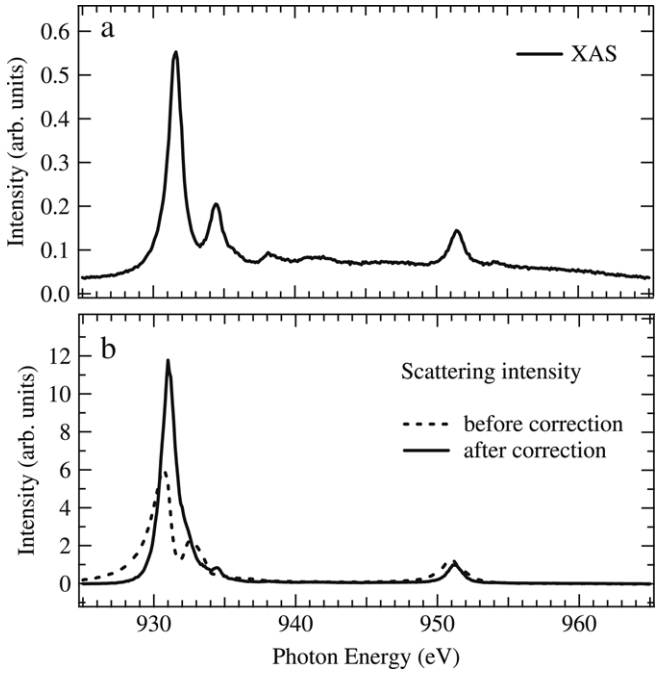

Fig. 2. Photon-energy-dependent spectra of (a) x-ray absorption and (b) scattering of $LiCu_2O_2$ around the Cu $L_{2,3}$ edges. The absorption spectrum was obtained from the fluorescence-yield method; the scattering spectra were recorded by fixing the momentum transfer to be (1/2, 0.174,0). Dashed and solid lines in (b) are scattering spectra before and after correction for self-absorption, respectively. The correction method is described in the text. All spectra were measured at 10 K.

plane defined by the directions of the incident and scattered x-rays is in the *ab* plane of the lattice.

Fig. 2 shows the x-ray absorption spectrum (XAS) of $LiCu_2O_2$ around the Cu $L_{2,3}$ edges obtained from the fluorescence-yield method in which the fluorescence was collected by a detector composed of an electron multiplier and a CsI thin film for converting photons into electrons. In our fluorescence-yield measurement, the angle between the incident beam and the surface normal was 30°. As plotted in Fig. 2, the L_3 manifold of XAS which originates from the $2p_{3/2} \rightarrow 3d$ transition consists of one main peak and one small peak, corresponding to the divalent and monovalent copper ions in the ground state, respectively. In other words, the XAS peak centered at 931.4 eV corresponds to the transition from the electronic configuration $3d^9$ in the ground state of Cu^{2+} to $\underline{2p}_{3/2}3d^{10}$ in the final state of the absorption process, where $\underline{2p}_{3/2}$ denotes the core hole created in the $2p_{3/2}$ level. Like the XAS of Cu_2O, the small XAS peak of 934.4 eV originates from the absorption of Cu^{+} in which the electronic configuration for the ground state and the XAS final state are, respectively, $3d^{10}$ and $\underline{2p}_{3/2}3d^{10}4s^1$ [20–22].

To understand the magnetic order of $LiCu_2O_2$, we first set the photon energy $\hbar\omega$ corresponding to the $2p_{3/2} \rightarrow 3d$ transition of Cu^{2+} and measured the scattering intensity through momentum scans, i.e., the q scans, along the [100] and [010] directions. The data were recorded at the sample temperature of 10 K with the polarization vector $\vec{e}$ in the scattering plane. The scattering intensity maximizes at $\vec{q} = (1/2, 0.174, 0)$ in reciprocal lattice units. Note that only domains with the *a* axis normal to the crystal surface contribute to the x-ray magnetic scattering of such $\vec{q}$; our scattering measurements thus probe $LiCu_2O_2$ of a well defined crystallographic orientation, although the crystal is twined. The data indicate that the magnetic order of $LiCu_2O_2$ is incommensurate with its lattice and the modulation vector is (1/2, 0.174, 0) at 10 K. In addition to XAS, Fig. 2 plots the measured photon-energy dependence of scattering intensity $I(q, \hbar\omega)$ with

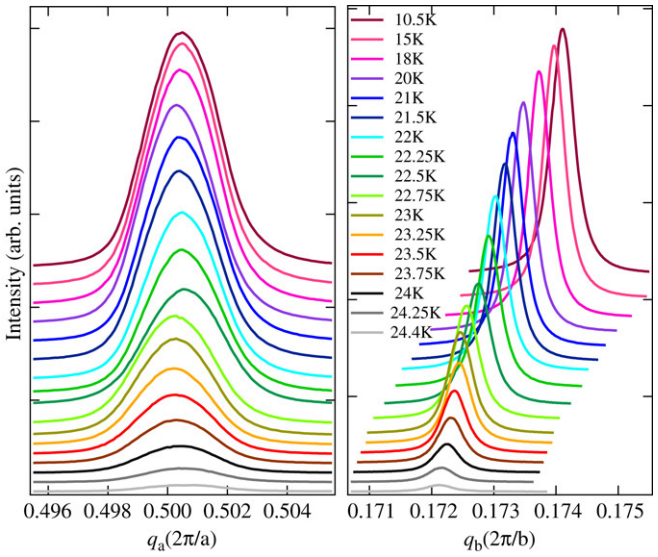

Fig. 3. Momentum scans of resonant soft x-ray scattering of $LiCu_2O_2$ along the [100] and [010] directions at various temperatures below 25 K. The incident photon energy was set at 930 eV. q_a and q_b are the components of momentum transfer in the ab plane, i.e., $\vec{q} = (q_a, q_b, 0)$. All q_a scans were recorded with q_b fixed at the maximum of scattering intensity, and vice versa.

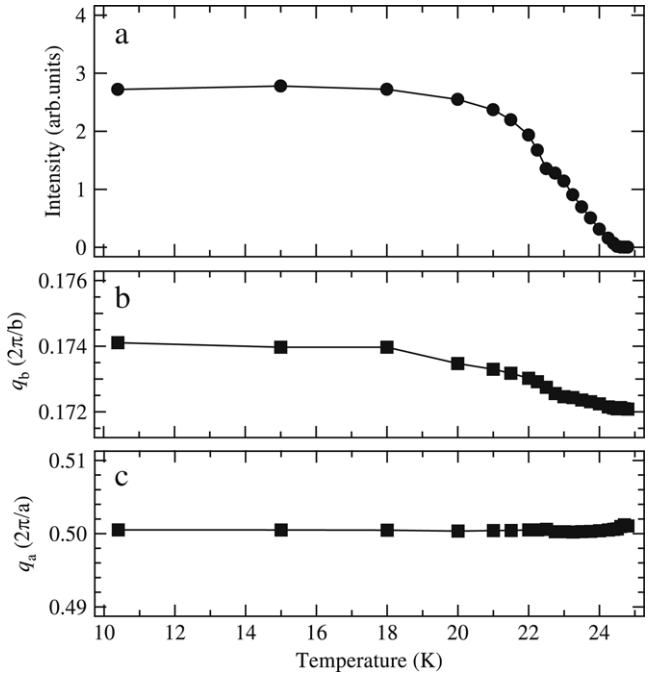

Fig. 4. Temperature-dependent scattering intensity and components of momentum transfer deduced of data shown in Fig. 3. The scattering intensity plotted in (a) is the peak area momentum scans; the components of momentum transfer q_a and q_b plotted in (b) and (c) are obtained from fitting momentum scans to a Lorentzian function with a linear background.

the momentum transfer fixed at $\vec{q} = (1/2, 0.174, 0)$. Peaks of $I(q, \hbar\omega)$ appear to be shifted from those of XAS by an energy between 0.5 and 1.9 eV. In fact, there exists a self-absorption effect. One needs to correct the measured scattering intensity $I(q, \hbar\omega)$ for self absorption; the scattering intensity is proportional to the scattering cross section multiplied by an x-ray absorption correction $A(q, \hbar\omega)$, i.e., $I(q, \hbar\omega) \propto |f^{res}_{mag}|^2 A(q, \hbar\omega)$. For a single crystal, $A(q, \hbar\omega)$ is proportional to the inverse of absorption coefficient μ [23]. The energy scan of magnetic scattering after such correction is also depicted in Fig. 2. Clearly, the scattering intensity of the energy corresponding to XAS peaks of Cu^+ is much weaker than that corresponding to those of Cu^{2+}, consistent with the expectation that the magnetic moment of Cu^+ is negligible because of the $3d^{10}$ configuration.

NMR and neutron measurements indicate that the Néel temperature T_N of the spiral magnetic order in $LiCu_2O_2$ is between 22 and 24 K. Fig. 3 shows q scans along the [100] and [010] directions at various temperatures below 25 K. To reduce the self-absorption effect, the incident photon energy was set at 930 eV. The q scans were fitted to a Lorentzian function with a linear background to determine the peak position and the half-width at half maxima (HWHM). We define the spin–spin correlation length as the inverse of HWHM, i.e., $\xi \equiv 1/\text{HWHM}$. The correlation lengths along the [100] and [010] directions were found to be 690 Å and 2110 Å, respectively, at 10 K. The observed correlation length along the spin chain is substantially larger than the inverse of HWHM in neutron measurements, because the width of q scan in neutron scattering is often limited by instrumental resolution. This result indicates the existence of long-range incommensurate magnetic order in $LiCu_2O_2$, although the spin-1/2 chains have a strong quantum character. In addition, measurements of soft x-ray magnetic scattering surprisingly reveal that there exists substantial in-plane interaction perpendicular to the spin chain.

We plot the temperature-dependent scattering intensity and the components of the modulation vector along [100] and [010], i.e., q_a and q_b, in Fig. 4. The decrease of scattering intensity with the increase of temperature suggests that the onset temperature of magnetic order is about 24.5 K. Above this temperature, the long-range magnetic order collapses because thermal fluctuation overcomes the interlayer coupling. In addition, as the temperature increases, the peak position in the q scan along the [100] direction remains unchanged, while that along [010] moves toward a smaller value. That is, the modulation vector is $(1/2, \zeta, 0)$ with ζ being 0.174 at 10 K, and ζ starts to decrease and depart away from 0.174 when the temperature goes above 17 K. These results are consistent with that observed by neutron scattering [9]. In the classical regime, if $|J_2/J_1|$ is greater than $\frac{1}{4}$, the propagation vector is $\cos^{-1}(J_1/4J_2)$ in units of the reciprocal lattice constant and the pitch angle of spin spirals is $2\pi\zeta$. The measurement of $\zeta = 0.174$ indicates that the pitch angle is 62.6° and $J_1/J_2 = 0.184$ at 10 K. The measured ratio J_1/J_2 is consistent with the results of inelastic neutron scattering [24] and LSDA + U calculations [25]. The temperature dependence of ζ suggests that there is a competition between the nearest- and next-nearest-neighbor exchange interactions J_1 and J_2. The change in modulation vector implies that such competition leads to an increase of J_1/J_2 as the temperature approaches to the transition temperature, resulting in a decrease in the pitch angle of spin spirals.

In summary, measurements of soft x-ray magnetic scattering indicate that $LiCu_2O_2$ exhibits a long-range magnetic order incommensurate with the lattice, and the modulation vector is $(0.5, \zeta, 0)$, $\zeta \sim 0.174$. Such a magnetic structure is derived from the ordering of divalent Cu^{2+} ions rather than monovalent Cu^+. In addition, there is a temperature-dependent competition between the nearest- and next-nearest-neighbor exchange interactions, and the ground state is of a renormalized classical character although the system has the quantum nature of spin 1/2.

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