Magnetic Ground State and Transition of a Quantum Multiferroic $LiCu_2O_2$

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Based on resonant soft x-ray magnetic scattering, we report that $LiCu_2O_2$ exhibits a large interchain coupling which suppresses quantum fluctuations along spin chains, and a quasi-2D short-range magnetic order prevails at temperatures above the magnetic transition. These observations unravel the fact that the ground state of $LiCu_2O_2$ possesses long-range 2D-like incommensurate magnetic order rather than being a gapped spin liquid as expected from the nature of quantum spin-$\frac{1}{2}$ chains. In addition, the spin coupling along the c axis is found to be essential for inducing electric polarization.

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Multiferroicity of frustrated magnets, in which magnetism and ferroelectricity coexist with gigantic magnetoelectric coupling, has attracted a revival of interest because electric polarization can be induced by magnetic order [1–3]. Most of these multiferroics are manganites, in which the magnitude of the spin of Mn ions is large and hence spins are semiclassical. The recent discovery of multiferroic behavior in cuprates, such as $LiCu_2O_2$ [4–6], $LiCuVO_4$ [7], and CuO [8], implies that multiferroic manganites might be part of a wider class of materials possibly with a similar mechanism for all of the observed multiferroicity. However, in contrast to manganites, $LiCu_2O_2$ and $LiCuVO_4$ are generally believed to be spin-chain materials with a quantum spin. Because of the low dimensionality and the spin-$\frac{1}{2}$ nature, strong quantum fluctuations must have profound effects on multiferroicity [9,10]. Therefore, in addition to addressing the mechanism for generating the electric polarization, it raises an important issue on how the induced electric polarization by magnetism can survive out of quantum fluctuations.

Neutron results indicated that the spin-chain structure of $LiCu_2O_2$ is spiral [11]. At first sight, arising of the induced polarization $\mathbf{P}$ in $LiCu_2O_2$ seems to be best understood in terms of the spin-current model [12] or the inverse Dzyaloshinskii-Moriya interaction [13], where $\mathbf{P}$ is induced by two neighboring spins $\mathbf{S}_i$ and $\mathbf{S}_j$ on the chain and is determined by $\mathbf{S}_i \times \mathbf{S}_j$. Calculations using the Berry phase method support that the spiral spins with spin-orbit coupling can induce $\mathbf{P}$ [5]. In contrast, Moskvin *et al.* argued that, in the scenario of spin current, the induced polarization due to two consecutive CuO_4 plaquettes along the chain gets canceled exactly [14]. Based on the parity-breaking exchange interaction, they further proposed the c-axis coupling of spins is essential for the observed multiferrocity [15].

Experimentally, conflicting results were reported regarding the magnetic structure and its relation to the observed $\mathbf{P}$ in $LiCu_2O_2$ [4,6,11]. For instance, whether the spiral spins lie in the ab [11] or bc [6] plane remains controversial, while the spin-current model requires spiral spins lying in the bc plane to generate the observed ferroelectricity along the c axis. $LiCu_2O_2$ also exhibits a strong competition between classical and quantum spin-exchange interactions. Measurements of Li nuclear magnetic resonance revealed a signature of an incommensurate static modulation of magnetic order below 24 K [16]. In contrast to these signatures of classical spin correlations, measurements of electron spin resonance indicated that $LiCu_2O_2$ possesses the characteristics of a spin liquid with an energy gap in the magnetic excitation spectrum [17,18]. In addition, there are evidences of double magnetic transitions and two anomalies in dielectric response occurring near 22 and 24 K [4,6,11], but $\mathbf{P}$ is only observed below 22 K [6]. These results clearly indicate that magnetic phases involved and their relation to the electric polarization are more complicated than those adopted in the theoretical modeling.

Characterization of the magnetic ground state of $LiCu_2O_2$ is crucial for revealing the effect of quantum fluctuations on the induced ferroelectricity. Since any real experiment probing magnetic order is performed at a finite temperature, to reveal the zero-temperature phase, one can measure an extension of the spin-spin correlation beyond the Néel temperature (T_N). For example, the zero-temperature order of a 2D spin-$\frac{1}{2}$ quantum Heisenberg antiferromagnet extends to a finite-temperature regime known as the renormalized classical regime [19,20] and is accessible at finite temperatures. In such a case, the spin-correlation length ξ is inversely proportional to the probability of rotating spins in neighbors; ξ decays exponentially with the increase of temperature.

In this Letter, we present measurements of resonant soft x-ray scattering on $LiCu_2O_2$ to characterize its magnetic ground state and transition. Implications of the spin-correlation lengths along and perpendicular to the spin chain are addressed. In particular, by investigating the temperature dependence of its short-range spin order above T_N, we unravel the spin order of the ground state. Our results, when combined with dielectric measurements, imply that the spin coupling along the c axis is essential for inducing electric polarization.

Complementary to neutron scattering, resonant soft x-ray magnetic scattering constitutes an effective experimental method to probe the magnetic order of transition metals with a good momentum resolution [21,22]. With the incident photon energy tuned about the L-edge ($2p \rightarrow 3d$) absorption, the resonance effect enhances the scattering cross section markedly and produces a direct probe of the ordering of $3d$ states in transition metals. Like x-ray magnetic circular dichroism in absorption, the imbalance between the scattering amplitudes associated with the change of magnetic quantum number Δm being ± 1 yields the spin sensitivity in x-ray scattering [21].

$LiCu_2O_2$ has a layered orthorhombic crystal structure with the space group $Pnma$, and lattice parameters $a = 5.73$, $b = 2.86$, and $c = 12.4$ Å at room temperature. Chains of edge-sharing CuO_4 plaquettes run along the b axis, and double layers of Cu^{2+} stack along the c direction with intervening layers of Cu^{+} ions, as illustrated in Fig. 1(a). To understand its magnetic order, we measured resonant soft-x-ray magnetic scattering on $LiCu_2O_2$ with the elliptically polarized undulator beam line of National Synchrotron Radiation Research Center (NSRRC), Taiwan. The photon energy was set to be 930 eV, corresponding to the $2p_{3/2} \rightarrow 3d$ transition of Cu^{2+}. For this photon energy, the instrumental q resolution of the half width at half maximum (HWHM) is estimated to be of 0.0003 $Å^{-1}$. Single crystals of $LiCu_2O_2$ were grown with the floating-zone method, and characterized with x-ray diffraction (XRD). Although our crystals were found to be twinned with mixing of the a- and b-axis domains as reported in the literature [4,6,11], x-ray scattering measurements select domains of a well-defined crystallographic orientation.

Our previous measurements on $LiCu_2O_2$ with a naturally grown (100) surface show that the scattering intensity maximizes at $\vec{q} = (0.5, 0.174, 0)$ in reciprocal lattice units [23], as summarized in Figs. 1(c)–1(e). The analysis of photon-energy dependence indicates that the scattering peak results from magnetic Cu^{2+} rather than nonmagnetic Cu^{+}. The spin-correlation length ξ_b along the b axis, defined as the 1/HWHM of the momentum scan, i.e., q_b scan, is 2100 Å. In addition, the observed in-plane correlation length ξ_a along the a axis is notably large, ~690 Å. Because the interchain interactions of 1D spin-chain materials tend to suppress quantum spin fluctuations and restore semiclassical behavior, our observation of substantial interchain coupling explains why $LiCu_2O_2$ exhibits a classical-like magnetic feature of long-range incommensurate order, although it is a system of a quantum spin chain. Hence $LiCu_2O_2$ has a 2D-like magnetic order; one can examine the magnetic properties at zero temperature through measuring the spin correlation above T_N.

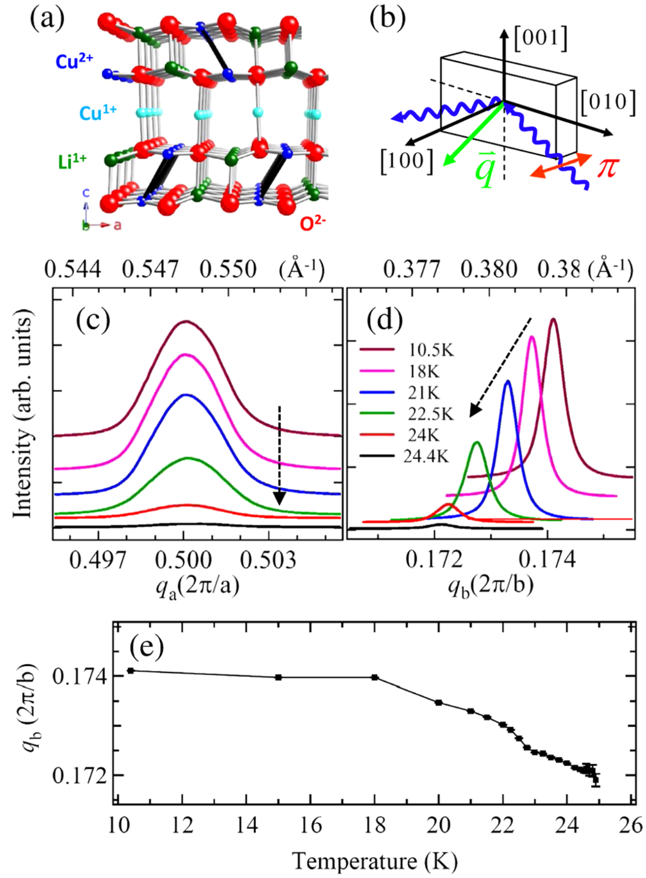

FIG. 1 (color online). (a) Illustration of the crystal structure of $LiCu_2O_2$. (b) Scattering geometry with the **E** vector of x ray in the ab plane, i.e., the π polarization. (c),(d) q_a and q_b scans at selected temperatures below 25 K. (e) Temperature dependence of q_b. The incident photon energy was set at 930 eV. All q_a scans were recorded with q_b fixed at the maximum of scattering intensity, and vice versa.

To achieve a measurement of the short-range spin correlation, we used a cleaved $LiCu_2O_2(001)$ crystal, of which the surface quality is superior to that of a crystal with a twinned (100)/(010) surface, although XRD results indicate both crystals have comparable qualities of bulk structure. Because our scattering setup is a two-circle diffractometer, the (001) crystal surface limits our scattering measurements to modulation vectors expressed in terms of ($\vec{q}_{ab}$, q_c), in which $\vec{q}_{ab}$ and q_c are projections of $\vec{q}$ onto the ab plane and the c axis, respectively. Figure 2

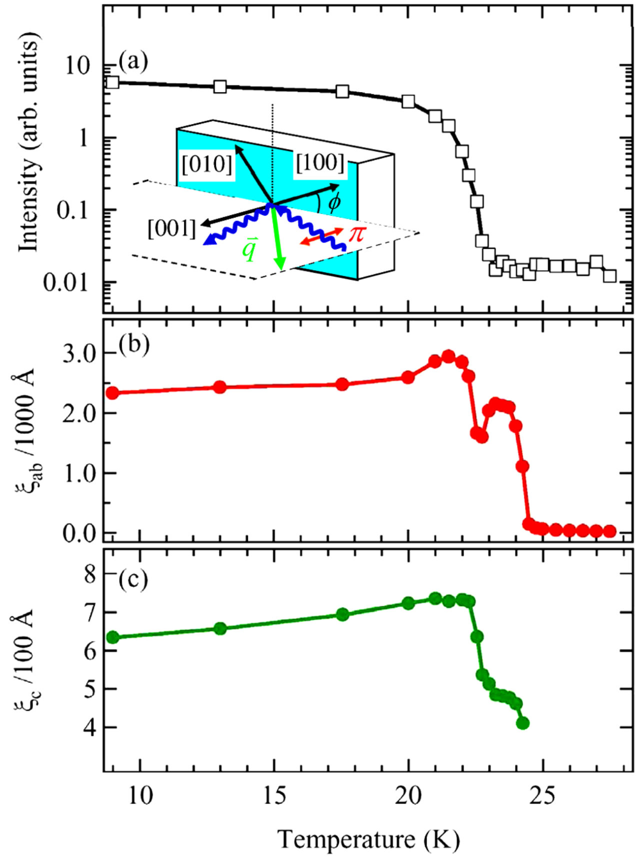

FIG. 2 (color online). Temperature dependence of resonant scattering intensity, correlation lengths ξ_{ab} and ξ_c from a cleaved $LiCu_2O_2(001)$ with $\vec{q} \sim (0.5, 0.17, 1)$, shown in (a), (b), and (c), respectively. The inset of (a) illustrates the scattering geometry described in the text.

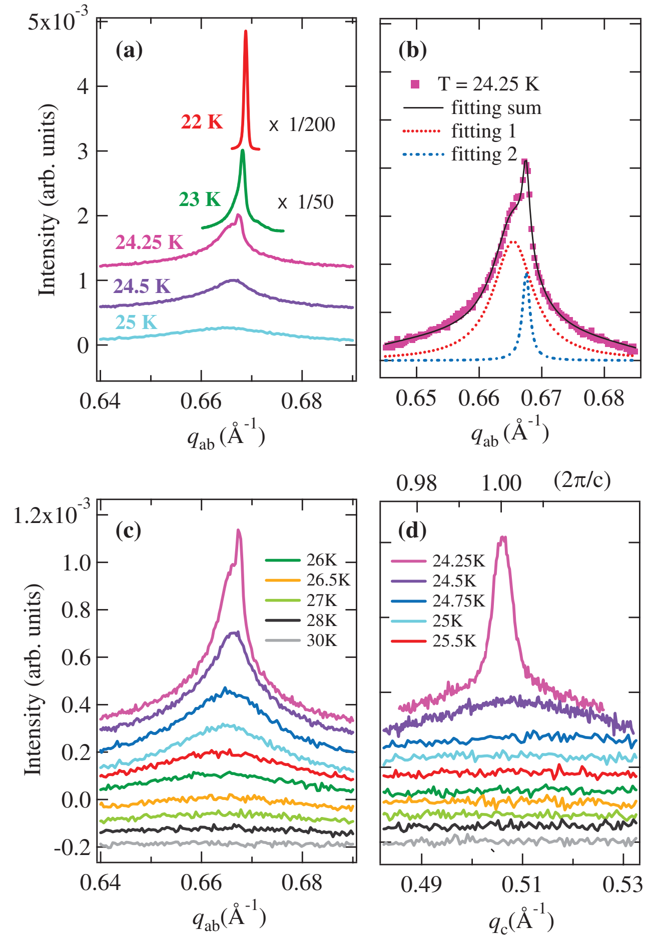

FIG. 3 (color). q_{ab} and q_c scans of soft x-ray scattering on cleaved $LiCu_2O_2(001)$ with $\vec{q} = (0.5, q_b, 1)$ at various temperatures above T_{N1}. q_{ab} is defined in the text. Curves 1 and 2 in (b) are Lorentzian components obtained from a nonlinear least square fitting. All curves are offset vertically for clarity.

plots the temperature dependence of scattering intensity and spin-correlation lengths of $\vec{q} = (0.5, q_b, 1)$ with $q_b \sim 0.17$ at various temperatures below 28 K. The inset of Fig. 2(a) illustrates the scattering geometry in which the scattering plane is defined by the c axis and an in-plane vector $\vec{q}_{ab}$ directed at an angle ϕ off the a axis by $\sim 34.8°$, depending upon temperature. The spin correlations along $\vec{q}_{ab}$ and the c axis are, respectively, denoted as ξ_{ab} and ξ_c. Our data show that ξ_{ab} exhibits two maxima at 21.5 K (T_{N1}) and 23.5 K (T_{N2}). These two transitions are consistent with two anomalies in specific heat and the temperature derivative of magnetic susceptibility [6]. As the temperature decreases across T_{N2}, the interlayer coupling starts to overcome thermal fluctuations; a short-range 3D spiral order begins to develop and forms a precursor phase. With further cooling below T_{N1} where an electric polarization is induced by spin order, a long-range order is established. That is, T_{N1} is the onset temperature of induced polarization, and T_{N2} is the transition temperature of the precursor of spin order.

Furthermore, we remarkably found that there exists a short-range order above T_{N2}. Figure 3 shows q_{ab} scans and q_c scans of $\vec{q} = (0.5, q_b, 1)$ at selected temperatures above T_{N1}. The derived temperature dependence of q_b from data in Fig. 3 is consistent with q_b shown in Fig. 1(e). In addition to the modulation vector with $q_b = 0.174$ which corresponds to the correlation length showing two transitions as in Fig. 2(b), another broad component with $q_b \sim 0.172$ appears in the vicinity of T_{N2}, i.e., the fitting curve 1 in Fig. 3(b). Fitting the q_{ab} scan with two Lorentizan components for temperatures above 22.5 K, we found that the broader one does not vanish even at temperatures beyond T_{N2}. Momentum scans along the c direction reveal further that the scattering intensity does not depend on q_c for temperatures above 24.5 K, whereas it shows a well-defined maximum in the q_{ab} scan, as plotted in Figs. 3(c) and 3(d). These results unravel a short-range in-plane spin order above T_{N2}. Since **P** is only observed below T_{N1} [6] where the spin correlation is built in along the c axis, our measurements imply that the spin coupling along the c axis is essential for inducing electric polarization in $LiCu_2O_2$, corroborating the proposal of Moskvin *et al.* [15].

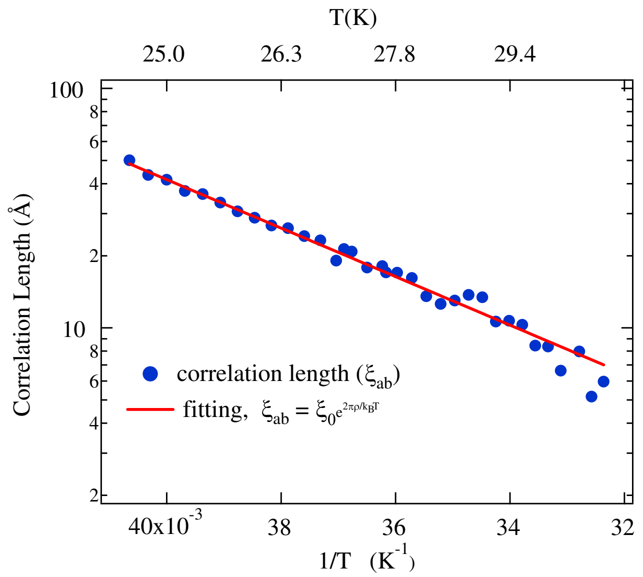

FIG. 4 (color online). Temperature dependence of correlation length ξ_{ab} above T_{N2}. The circles depict ξ_{ab} plotted on a logarithmic scale versus reciprocal temperature. The data are fitted with an expression $\xi_0 e^{2\pi\rho/k_BT}$ explained in the text.

We measured the detailed temperature dependence of spin correlation length ξ_{ab}, as depicted in Fig. 4, to characterize the spin order in the ground state of $LiCu_2O_2$. A plot of ξ_{ab} on a logarithmic scale versus reciprocal temperature is nearly a straight line, indicating that ξ_{ab} decreases exponentially with increasing temperature when T is above T_{N2}. We found that the in-plane correlation length conforms to an expression $\xi_{ab} = \xi_0 e^{2\pi\rho/k_BT}$, in which ρ and k_B are the spin stiffness and the Boltzmann constant, respectively. For an average in-plane spin coupling J and ρ being $JS(S+1)$, the data of ξ_{ab} are satisfactorily fitted with this expression if J is 4.2 meV, which has the same order of magnitude as that of the nearest-neighbor coupling concluded from neutron scattering [11] and first-principles calculations [16,24]. This observed exponential decay unravels the renormalized classical nature of 2D-like spin interaction and implies that $LiCu_2O_2$ exhibits a long-range 2D-like spin order in its ground state rather than being a gapped spin liquid.

In summary, measurements of soft x-ray scattering indicate that $LiCu_2O_2$ exhibits a long-range 2D-like incommensurate magnetic order. The spin order in the ground state of $LiCu_2O_2$ shows a semiclassical character although the system has the quantum nature of spin $\frac{1}{2}$. In addition, the spin coupling along the c axis is found to be essential for inducing electric polarization.

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[1] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).
[2] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) **429**, 392 (2004).
[3] S.-W. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007).
[4] S. Park, Y. J. Choi, C. L. Zhang, and S.-W. Cheong, Phys. Rev. Lett. **98**, 057601 (2007).
[5] H. J. Xiang and M.-H. Whangbo, Phys. Rev. Lett. **99**, 257203 (2007).
[6] S. Seki, Y. Yamasaki, M. Soda, M. Matsuura, K. Hirota, and Y. Tokura, Phys. Rev. Lett. **100**, 127201 (2008).
[7] Y. Naito, K. Sato, Y. Yasui, Yusuke Kobayashi, Yoshiaki Kobayashi, and M. Sato, J. Phys. Soc. Jpn. **76**, 023708 (2007).
[8] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, Nature Mater. **7**, 291 (2008).
[9] S. Furukawa, M. Sato, Y. Saiga, and Onoda, arXiv:0802.3256v2.
[10] H. Katsura, S. Onoda, J. H. Han, and N. Nagaosa, arXiv:0804.0669v1.
[11] T. Masuda, A. Zheludev, A. Bush, M. Markina, and A. Vasiliev, Phys. Rev. Lett. **92**, 177201 (2004); **94**, 039706 (2005).
[12] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).
[13] I. A. Sergienko and E. Dagotto, Phys. Rev. B **73**, 094434 (2006).
[14] A. S. Moskvin and S.-L. Drechsler, Phys. Rev. B **78**, 024102 (2008).
[15] A. S. Moskvin, Yu. D. Panov, and S.-L. Drechsler, arXiv:0801.1975v1.
[16] A. A. Gippius, E. N. Morozova, A. S. Moskvin, A. V. Zalessky, A. A. Bush, M. Baenitz, H. Rosner, and S.-L. Drechsler, Phys. Rev. B **70**, 020406(R) (2004).
[17] L. Mihaly, B. Dora, A. Vanyolos, H. Berger, and L. Forro, Phys. Rev. Lett. **97**, 067206 (2006).
[18] S. Zvyagin, G. Cao, Y. Xin, S. McCall, T. Caldwell, W. Moulton, L.-C. Brunel, A. Angerhofer, and J. E. Crow, Phys. Rev. B **66**, 064424 (2002).
[19] S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988); Phys. Rev. B **39**, 2344 (1989).
[20] M. Greven, R. J. Birgeneau, Y. Endoh, M. A. Kastner, B. Keimer, M. Matsuda, G. Shirane, and T. R. Thurston, Phys. Rev. Lett. **72**, 1096 (1994).
[21] J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988).
[22] See, e.g., J. Okamoto, D. J. Huang, C.-Y. Mou, K. S. Chao, H.-J. Lin, S. Park, S.-W. Cheong, and C. T. Chen, Phys. Rev. Lett. **98**, 157202 (2007), and references therein.
[23] S. W. Huang, D. J. Huang, J. Okamoto, W. B. Wu, C. T. Chen, K. W. Yeh, C. L. Chen, M. K. Wu, H. C. Hsu, and F. C. Chou, Solid State Commun., doi:10.1016/j.ssc.2008.04.040.
[24] V. V. Mazurenko, S. L. Skornyakov, A. V. Kozhevnikov, F. Mila, and V. I. Anisimov, Phys. Rev. B **75**, 224408 (2007).