Disrupted long-range spin-spiral ordering and electric polarization in the Zn-substituted quantum helimagnet LiCu$_{2-x}$Zn$_x$O$_2$

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Long-range spin-spiral ordering in quantum quasi-two-dimensional helimagnet LiCu$_2$O$_2$ is destroyed by ~8% Zn^{2+} substitution and a magnetic anomaly near ~14 K of different character emerges. Zn substitution may have introduced either a magnetic ground state of spin glass in nature, antiferromagnetic ordering with complex easy-plane anisotropy, or a gapped phase which is phase separated and proportional to the Zn substitution level on a short-range ordered background. The magnetic ground state is modified at the same time that the electric polarization disappears.

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Transition-metal oxides with spiral-spin ordering is one interesting class of ferroelectrics beyond the classical ones without spin involvement.[1] The noncollinear spiral-spin structure allows inversion symmetry breaking and manifests a finite-electric polarization.[2] The nature of helimagnetic ordering and its correlation to the existence of electric polarization has been the central topic in multiferroics research. Incommensurate helimagnetic ordering has been found in LiCu$_2$O$_2$ of quasi-one-dimensional (1D) quantum system and accompanies weak electric polarization of multiferroic nature.[3–5] LiCu$_2$O$_2$ has a spin chain structure formed with edge-sharing CuO$_2$ plaquettes in the *ab* plane while these chains are connected through O-Cu-O dumbbells along the *c* direction as shown in Fig. 1.[7] This compound is uniquely composed of nearly equal amount of Cu^{1+} and Cu^{2+} with Cu^{1+} sitting in the O-Cu-O dumbbell (along *c* direction) to connect the nearest-neighboring edge-sharing spin chains. Undoped LiCu$_2$O$_2$ shows a helical spin ordering below ~22 K as indicated by the $d\chi/dT$ peaks and has been verified by magnetic neutron-scattering studies before.[3,4]

Nonmagnetic ion substitution into the low-dimensional quantum-spin system has been proved to be not just a simple
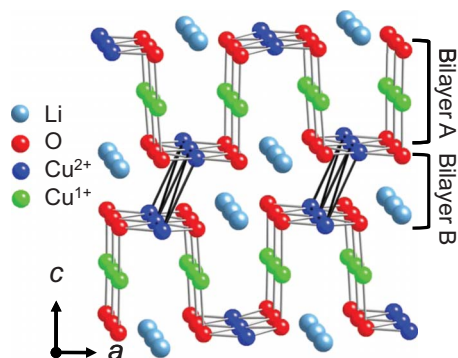
dilution effect. For example, Zn substitution of Cu in the quantum-spin chain CuGeO$_3$ induces an unusual antiferromagnetic (AF) ordering coexisting with the spin-Peierls (SP) state of spin-lattice dimerization.[8,9] The surprising finding of the coexisting AF and SP states (dimerized AF) turns out to be different from the conventional uniform AF state. It is shown that staggered moments can be introduced and with large spatial inhomogeneity in the ordered moment size (correlation length $\xi \sim 10a$) through spin-chain perturbation.[10,11] Clearly nonmagnetic spin zero perturbation is an effective way to probe the mysterious low-dimensional quantum-spin system. In this paper we report another intriguing finding on Zn substituted quasi-1D quantum spin-1/2 system LiCu$_2$O$_2$. A magnetic phase transition below ~14 K is found by ≳8% Zn per CuO$_2$ chain substitution. Magnetic susceptibility measurement results indicate that a phase transition emerges with a character totally different to the original long-range phase transition due to spin-spiral ordering. From combined magnetic susceptibility and specific-heat measurements, we propose that the long-range spiral ordering is destroyed and transformed into a phase of short-range coupling in nature below the original helical ordering temperature. Preliminary x-ray diffraction data do not support a bulk spin-Peierls transition for lack of evidence of lattice doubling along the **b**-axis chain direction, no structure phase transition is found as a result of ~8% Zn substitution either. In addition, spontaneous electric polarization disappears together with the long-range helical spin ordering.

Single crystal LiCu$_{2-z}$Zn$_z$O$_2$ with ~0.08 have been grown using traveling solvent floating-zone method as described previously.[12] Feed rod of nominal Zn levels of 10% is prepared from Li$_2$CO$_3$:CuO:ZnO mixture of molar ratio 1.2:4-z:z, where 20% excess Li is added to the initial to compensate for the Li vapor loss. Li content of the 8% Zn crystal is assumed to be the same as that in undoped one grown from the identical high pressure (0.64 MPa Argon atmosphere) growth conditions, i.e., ~0.87 according to our previously published analysis.[12] The Cu and Zn contents are determined using combined inductive coupled plasma and

FIG. 1. (Color online) Crystal structure of LiCu$_2$O$_2$. The linear chain is defined from the bilayer-A according to Gippius *et al.* (Ref. 6) and the zigzag chain is defined by the bilayer-B according to Masuda *et al.* (Ref. 4).

electron probe microanalysis with an error bar within $\sim 0.1\%$. Magnetic susceptibilities are measured with superconducting quantum interference device magnetometer (Quantum Design MPMS-XL) with a magnetic field of 1 kOe applied along and perpendicular to the ab plane. X-ray diffraction data are taken using synchrotron x-ray facility NSRRC in Taiwan. Dielectric constant is measured from crystals disk with thickness of about $50-100$ μm. The electrical polarization is determined by integration of the pyroelectric current, which is detected at a rate of 0.167 K/s after cooling the samples in a poling field of 1200 kV/m from 50 K.

Nonmagnetic Zn ion substitution to the spin 1/2 Cu^{2+} site within edge-sharing CuO_2 linear chain is expected to disrupt the nearest-neighbor coupling J_1 effectively and cut down the infinite chain into even and odd finite chains, although quantum fluctuation, the next-nearest-neighbor coupling J_2, and interchain coupling $J_\perp$ could still bring up unexpected results. There are two different structural sites of Cu in $LiCu_2O_2$ as shown in Fig. 1, nonmagnetic Zn^{2+} should substitute the Cu^{2+} site only from considerations of both the valence and ionic radius. The ionic radius of Zn^{2+} ion (0.74 Å $CN=4$) is similar to that of Cu^{2+} ion (0.71 Å CN $=4$) for square planar coordination within the CuO_2 chain, which is significantly larger than that of a Cu^{1+} ion (0.60 Å $CN=2$) within the CuO dumbbell.[13] Room-temperature lattice parameters for $z=0.08$ $LiCu_{2-z}Zn_zO_2$ shows identical structure as the undoped $LiCu_2O_2$ at room temperature with $c=12.375(3)$ Å, $a=5.744(3)$ Å, and $b=2.868(2)$ Å. Compared to the undoped sample, a significant reduction on c axis in concomitant with slight increase of a and b axes with not much change on the cell volume. These results suggest the success of Zn substitution to the Cu sites, most probably to the Cu^{2+} site within linear CuO_2 chains instead of the smaller Cu^+ site within the bridging O-Cu-O dumbbell.

Typical magnetic susceptibility measurement results for $LiCu_{2-z}Zn_zO_2$ with $z=0$ and $z=0.08$ per CuO_2 chain are shown in Fig. 2. For 8% Zn sample, there is a clear $\chi(T)$ cusp observed in both orientations with a trend of steplike reduction in a paramagnetic background below ~ 14 K, which is significantly different from the original spiral-spin ordering signature judging from both $\chi(T)$ and $d\chi/dT$ data. For the original $z=0$ sample, the helical spin ordering smoothly crosses two transition temperatures as shown in Fig. 2(a), which correspond to the anisotropic magnetic correlation onset at ~ 24 K for $\|c$ and 22 K for $\|ab$, respectively, and can only be identified from its first derivative of nearly symmetric peak shape.[3,14] On the other hand, z $=0.08$ sample shows a significantly different $\chi(T)$ behavior with a cusp shape reduction near 14 K as shown in Fig. 2(b). The derivative peak shape for $z=0.08$ is asymmetric with an inversion point near the cusp, which is significantly different to that of $z=0$ sample. Judging from the different peak shape of $\chi(T)$ and its derivative, high Zn substitution must have introduced a magnetic transition which is different to the original helical spin ordering.

Weak thermal hysteresis below transition temperature for $z=0.08$ is also found, as indicated in Fig. 3 while no such hysteresis exists for the $z=0$ sample which has a long-range helical spin ordering below ~ 22 K. There are several pos-
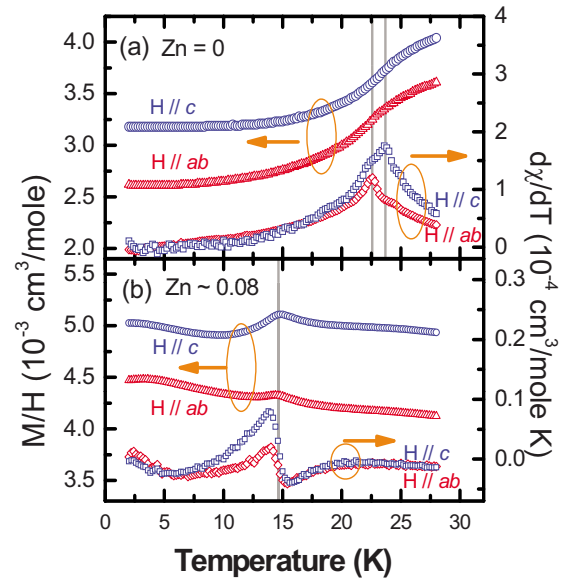

FIG. 2. (Color online) Low-temperature magnetic susceptibility $\chi(T)$ and $d\chi/dT$ of $LiCu_{2-z}Zn_zO_2$ for (a) $z=0$ and (b) $z=0.08$. The magnetic field 1000 Oe is applied in two orientations along ab plane and c axis. The helimagnetic ordering for $z=0$ has a significantly different character of χ and $d\chi/dT$ comparing with the magnetic transformation in $z=0.08$.

sible interpretations on the susceptibility data for $z=0.08$ judging from the cusp shape reduction near 14 K, including AF spin ordering, spin-glass (SG) transition, or a gapped state of different origin, such as spin/charge-density wave (SDW/CDW) and spin dimerization. There are two sections for the hysteresis as shown in Fig. 3, a weak ZFC/FC hysteresis onsets at 14 K and the ZFC broad peak exists near 5 K. The 5 K ZFC/FC hysteresis resembles a typical spin-glass behavior well, although ac susceptibility measurement results are not conclusive on the frequency dependence due to transition width and signal noise. If SG transition does occur near 5 K, the slight hysteresis onsets near 14 K could be due to the extended hysteresis range when domain formation is possible. The possibility of AF ordering cannot be ruled out
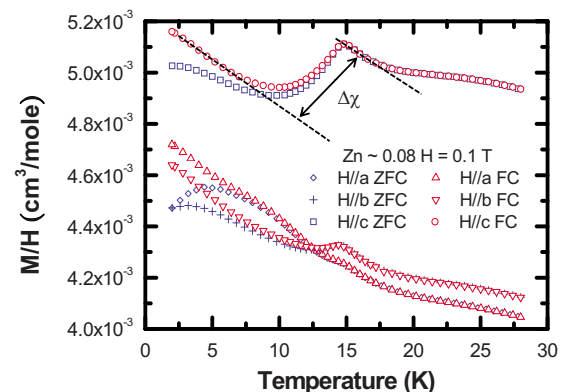

FIG. 3. (Color online) Magnetic susceptibility data of 8% Zn-substituted $LiCu_2O_2$ untwinned single crystal in three axes. A slight hysteresis is found below T_c and a broad hump is observed at lower temperature near 5 K more pronounced for the ZFC data.
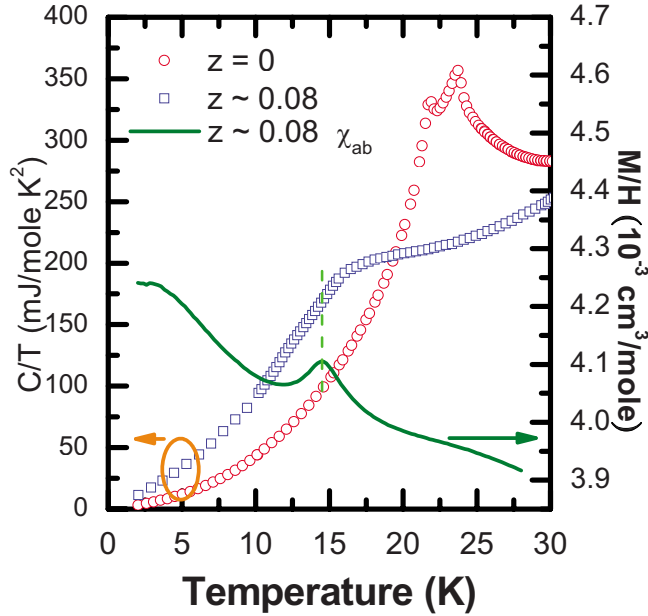
FIG. 4. (Color online) Specific heat of $LiCu_2O_2$ and $LiCu_{2-z}Zn_zO_2$ with $z=0.08$. Magnetic susceptibility for $z=0.08$ under $H\|ab$ is shown for comparison.

FIG. 5. (Color online) Electric polarization and dielectric response along c direction for $LiCu_{2-z}Zn_zO_2$ with $z=0$ and 0.08. An electric field of 1200 kV/m has been applied above the transition temperature before each measurement.

to account for the nearly isotropic susceptibility reduction, especially for a system of complex easy-plane anisotropy exists. In fact, mixed easy-plane anisotropy has been found to be able to interpret the ^7Li asymmetric NMR spectrum for $LiCu_2O_2$ successfully.[6,15] Spin freezing due to Zn perturbation near 5 K is possible while the Zn-introduced randomness is added to the magnetic frustration introduced by FM coupled J_1 and AF coupled J_2.[16] Finally, the obtained susceptibility data could still be interpreted as coming from a gapped system, whether it is due to CDW, SDW, or spin dimerization. We find that the steplike isotropic reduction in spin susceptibility implies a spin-gap opening, although it is not fully open judging from its nonzero susceptibility at the lowest temperature, even after a small Curie contribution with sizable Weiss temperature is corrected. However, we find the fraction of the susceptibility reduction estimated from $\Delta\chi/\chi(T_c)$ to be $\sim7\%$ as shown in Fig. 3, which seems to suggest that only part of the system falls to a gapped state and is close to the Zn substitution level of 8% and isolated spin dimers generated near the Zn centers. The possible existence of dimerized spin remains to be explored using neutron scattering and muon spin-resonance experiments, although conversion of helical spin ordering to spin dimerization has been explicitly depicted from density-matrix renormalization-group calculation for $LiCu_2O_2$ sample with properly assigned easy-plane anisotropy.[15]

The specific heat data for undoped and $\sim8\%$ Zn-substituted samples are shown in Fig. 4. The undoped sample shows typical double peaks which correspond to the two transition temperatures ~22 and 24 K along ab and c directions, respectively, for the spiral-spin ordering. On the other hand, a significantly broader specific-heat anomaly is observed near ~14 K for Zn $\sim8\%$ sample. This broad anomaly indicates that either the phase transition is of short range in nature or significant inhomogeneity exists in this
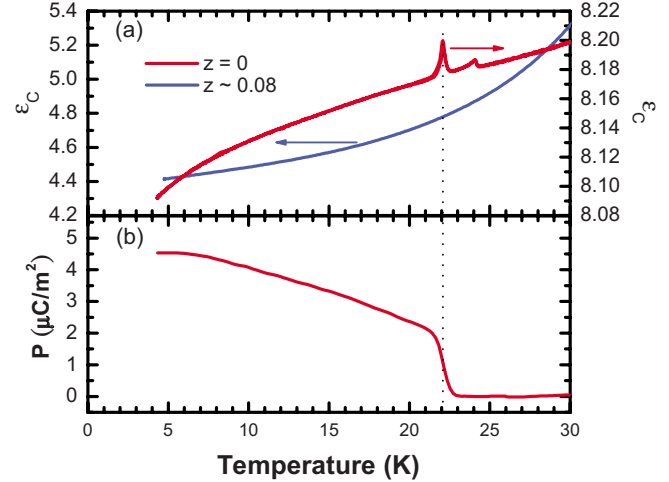
Zn-substituted crystal. The broad C_p peak is inconsistent with the clear $\chi(T)$ cusp observed at T_c assuming a long-range magnetic ordering, unless short-range ordering occurs similar to that of a spin glass. A closer observation of the C_p anomaly near T_c can be viewed as two barely resolved broad peaks sit above and below the transition onset defined by the cusp of magnetic susceptibility, which is consistent to the existence of persistent helical spin ordering on finite spin chains that is cut short by the nonmagnetic Zn, i.e., a short-range ordering as a result cut short helical correlation length. While the magnetic susceptibility data suggests the possibility of spin-gap opening from part of the system and proportional to the Zn-substitution level, current specific-heat data would not be able to support such a view when the minor phase transition at $\sim8\%$ level is buried in a background of persisting helical ordering of short range in nature.

Dielectric constant and electric polarization has been measured for $LiCu_{2-z}Zn_zO_2$ ($z=0,0.08$) single crystals along c direction as shown in Fig. 5. The undoped sample shows the onset of electric polarization below ~22 K and two anomalies near 22 and 24 K in dielectric constant similar to those reported in the literature.[3] However, the 8% Zn-substitution sample shows no trace of electric polarization near its magnetic transition temperature near 14 K as indicated in Fig. 2. Spin-current or inverse Dzyaloshinskii-Moriya mechanism has been applied to interpret the origin of electric polarization through spiral-spin ordering and has been tested by chirality reversal experiment.[3,17] Current dielectric constant measurement results confirm once again that spiral-spin ordering is a prerequisite for the spontaneous electric polarization in the current system and confirm the observed $\chi(T)$ cusp for high Zn substitution to have character other than the spiral-spin ordering.

In conclusion, we have grown 8% Zn-substituted $LiCu_2O_2$ single crystal and characterized it with magnetic susceptibility, specific-heat, and dielectric constant measurements. The magnetic phase transition observed in $\sim8\%$ Zn-substituted sample below ~14 K shows a quite different

character comparing with that of the original sample with a long-range spin-spiral ordering below ~22 K. Preliminary characterization by magnetic susceptibility and specific heat indicates that the original long-range spin-spiral ordering is disrupted and a short-range ordering emerges. While it is hard to distinguish whether the phase transition is due to the existence of a partially gapped phase or spin freezing, a com-plete Zn-substitution study of single crystal $LiCu_{2-z}Zn_zO_2$ should provide a more clear picture on the role of Zn substitution.

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