Studies of Multiferroic System LiCu$_2$O$_2$ I
Sample Characterization and Relationship between Magnetic Properties and Multiferroic Nature

Yukio Yasui, Kenji Sato, Yoshiaki Kobayashi, and Masatoshi Sato*

Department of Physics, Division of Material Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602

Single-crystal samples of LiCu$_2$O$_2$ with spin 1/2 Cu$^{2+}$ chains of edge-sharing CuO$_4$ square planes (ribbon chains), have been characterized by X-ray diffraction, thermogravimetric analysis, and magnetic measurements. Neither the atomic deficiency nor the mixing of Cu and Li atoms has been found, indicating that lattice defects conceived as a possible origin of the reported multiferroic behavior can be excluded. Anomalies found in the data of specific heat and neutron magnetic Bragg reflections show clear evidence that the system exhibits successive magnetic transitions at $T_{N1}$~24.5 K and $T_{N2}$~22.8 K. Based on the magnetic structures in the intermediate ($T_{N2}$<T<$T_{N1}$) and low temperature ($T$<$T_{N2}$) phases, determined by the combined studies of neutron scattering and $^7$Li-NMR measurements, we can consistently understand the fact that the multiferroic properties are observed only below $T_{N2}$ by considering existing theories.

Keywords: LiCu$_2$O$_2$, multiferroic, neutron scattering, helical magnetic structure

*corresponding author: e43247a@nucc.cc.nagoya-u.ac.jp

1. Introduction

Quasi one-dimensional Cu$^{2+}$ S=1/2 spins in the so-called ribbon chains of edge-sharing CuO$_4$ square planes attract much attention. For the spins, the exchange interaction between the next-nearest-neighbor spins $J_2$ (NNN) is antiferromagnetic ($J_2$<0) and nearest-neighbor (NN) exchange interaction $J_1$ often becomes ferromagnetic (FM; $J_1$>0) or has a rather small value even when it is antiferromagnetic (AFM; $J_1$>0). This causes the competition of these interactions and induces nontrivial magnetic structures. Theoretically, if $|J_2/J_1|$ is larger than a critical value, the helical magnetic structure is expected.1,2) Actually, LiVCuO$_4$, LiCu$_2$O$_2$, LiZrCuO$_4$ etc. were reported, for examples, to have such helical magnetic structures.3-10)

A renewed interest has been focused on the helimagnet systems11-14) from the point of view of multiferroics, which have the magnetic and ferroelectric simultaneous transitions, and theoretically, it has been pointed out that the helimagnetic structure induces the multiferroic nature.15-18) Recently, the authors’ group have found that LiVCuO$_4$ is a multiferroic, where the relation $P \propto Q \times e_3$ is found,4,6) consistently with the theories.15-18) where $P$, $Q$ and $e_3$ are the ferroelectric polarization, the modulation vector and the helical axis of the ordered spins, respectively. To understand the multiferroic nature, studies of the $S$=1/2 multiferroic systems are very useful, because there are not any complications due to the multi-ordinal effects. Moreover, these $S$=1/2 multiferroic systems are expected to exhibit the interesting phenomena induced by quantum effects.

LiCu$_2$O$_2$ is one of the examples of systems with the CuO$_2$ ribbon chains and its structure is shown schematically in Fig. 1. It is orthorhombic (space group Pnma) and there are four ribbon chains along the b direction in a unit cell.19) The chains are separated by the nonmagnetic Li$^+$ and Cu$^{2+}$ ions. For this system, multiferroic nature was reported by Park et al.20) The data indicate that the occurrence of the ferroelectricity is closely related to the magnetic transition to a nontrivial magnetic structure. However, there are many unsolved problems for the details of the multiferroic behavior. For example, although several groups studied the magnetic structure of LiCu$_2$O$_2$ by means of neutron scattering,21,22) $^7$Li-NMR,7) resonant soft x-ray magnetic scattering,21,22) etc., it has not been completely determined yet. Moreover, it seems to be still unclear if the relation $P \propto Q \times e_3$ holds or not. To clarify these problems, we have carried out systematic studies of the systems, including the preparations of the samples, their characterizations, various kinds of measurements of macroscopic physical quantities, and neutron scattering and NMR studies as the microscopic probes.

In the present paper (paper I), results of the sample characterizations and various macroscopic measurements are mainly presented in relation to the magnetic structure determined by the combined works of the neutron and NMR measurements. (We report the detailed determination of its magnetic structure by the companion paper, paper II.) Powder X-ray diffraction studies, thermogravimetric analysis (TG) and measurements of magnetic properties have been carried out on single-crystal samples of LiCu$_2$O$_2$ to characterize the samples. Much effort has been made to clarify if the lattice imperfections and chemical disorder exist or not in the samples.

Two anomalies have been observed in the $T$-dependence of the specific heat $C_v$ and neutron magnetic scattering intensity, which ensures the existence of two magnetic transitions at $T_{N1}$~24.5 K and $T_{N2}$~22.8 K reported in ref. 8. At these temperatures, we have found that the dielectric susceptibility $\varepsilon$ measured with the electric field $E$ along $c$ has small but clear anomalies. Based on these results and those of the magnetic structure determination described in paper II in detail, the relationship between the magnetic structure and dielectric properties is discussed. Possible effects of the quantum nature of the Cu$^{2+}$ spins are also discussed.

2. Experiments

Single-crystal samples of LiCu$_2$O$_2$ were prepared basically by the method reported in ref. 24. Mixtures of Li$_2$CO$_3$ and CuO powders with the molar ratio 1:4.2 were heated to 1150 °C at a rate of 200 °C/h, kept at the temperature for 10 h, cooled down to
to 900 °C at a rate of 10 °C/h and then quenched to room temperature. The Zn doped single-crystals (LiCu$_2$:Zn$_2$O$_3$) have been grown by a similar method, where the initial mixtures of Li$_2$CO$_3$, CuO and ZnO with a molar ratio 1:2: 4-2x: 2x were used. The obtained crystals were confirmed not to have appreciable amounts of impurity phases by X-ray measurements on the pulverized samples. The crystal axes were determined by observing the X-ray diffraction peaks. The typical size of the crystals was $15 \times 15 \times 1 \, \text{mm}^3$. By a polarized optical microscope, the existence of the twin structure was observed, which is due to the fact that the lattice parameter $a$ is very close to 2$\alpha$.\(^{19}\)

The magnetic susceptibilities $\chi$ and the magnetization $M$ were measured using a SQUID magnetometer in the temperature range from 2 to 300 K in the magnetic field up to 5.5 T. The specific heat $C_s$ was measured by the thermal relaxation method using a Quantum Design PPMS. To study the dielectric susceptibility $\varepsilon$, the capacitance $C$ of the rectangular sample plates with dimensions of 3.0×2.0×0.7 mm$^3$ was measured with the electric field $E//c$, where the electrodes were attached with silver paint to both sides of the plate surface. An ac capacitance bridge (Andeen Hagerling 2500A) with a frequency of 1 kHz was used. If the stray capacitance is negligible, dielectric susceptibility $\varepsilon$ is directly proportional to the observed capacitance $C$.

Neutron measurements on a single crystal were carried out using the triple spectrometer TAS-1 installed at JRR-3 of JAER in Tokai. To avoid the large neutron absorption of Li, we used $^7$Li isotope in the growth of crystals for neutron scattering. The obtained single-crystal samples were ground to powder, and the powder X-ray diffraction pattern was taken at room temperature with the Cu $K\alpha$ radiation to carry out the Rietveld analyses by using the computer program Rietan 2000.\(^{25}\) The thermogravimetric analyses (TG) with use of RIGAKU-TG have been carried out in the flowing O$_2$ and flowing He with 5 % H$_2$ (100 cm$^3$/min.).

### 3. Results and Discussion

The $T$-dependence of the specific heat divided by $T$, $C_s//T$ of LiCu$_2$O$_2$ is shown in Fig. 2(a), where the two anomalies are clearly observed at temperatures $T_{N1}$~24.5 K and $T_{N2}$~22.8 K, confirming the results of ref. 8 obtained by the magnetic and dielectric susceptibility measurements. Figure 2(b) shows the neutron magnetic scattering intensities of 1/2 1-0 0 reflection of LiCu$_2$O$_2$ ($\delta$=0.172). From the figure, we find that the magnetic ordering grows with decreasing $T$ below $T_{N2}$, and that the intensity-$T$ curves exhibits an anomaly at $T_{N2}$, indicating the change of the magnetic structure at this temperature. The behavior of the $^7$Li-NMR spectra (not shown here)\(^{21}\) also supports that the magnetic structure in the intermediate phase is different from that below $T_{N2}$. Figure 2(c) shows the $T$-dependence of the capacitance $C$ measured with the electric field $E//c$ of LiCu$_2$O$_2$, where small but clear peaks of the capacitance can be found at $T_{N1}$ and $T_{N2}$. The relationship between the magnetic structures in the two phases and the dielectric properties will be discussed later.

The $T$-dependences of the magnetic susceptibilities $\chi$ of LiCu$_2$O$_2$ measured under the condition of the zero field cooling (ZFC) are shown in the inset of Fig. 3(a) for the applied field $H//a$ and $H//c$. The broad peaks of $\chi$ at ~35 K can be attributed to the growth of the short-range spin correlation with decreasing $T$. The temperature derivative of $\chi$, $d\chi/dT$ (not shown here) indicates that the susceptibility $\chi$ measured with $H$ parallel to $c$ and $a$ decrease significantly with decreasing $T$ at $T_{N1}$=24.5K and at $T_{N2}$=22.8 K, respectively. With further decreasing $T$, $\chi$ becomes almost constant in the region of $T$ < 10 K, indicating that the Curie component induced by lattice imperfections and/or chemical disorders do not exist for the present single-crystal samples. The $T$-dependences of $\chi$ of the samples of LiCu$_2$:Zn$_2$O$_3$ with $x$=0.05, 0.10 and 0.15 measured under the condition of ZFC for the magnetic field of 0.1 T ($H//ab$-plane) are also shown in Fig. 3(a). The Curie component in the $T$-region of $T$<1.5 K increases with increasing Zn concentration. This result indicate that the free spins are induced by the Zn substitution for Cu. (However, the number of the free spins estimated from the Curie constant is much smaller than that of the doped Zn atoms, which can be understood by the fact that the doped Zn atoms do not always induce free spins and do not cut the spin correlation. It is because the next nearest interaction is large.) These results indicate that the lattice imperfections for the present single-crystal samples of LiCu$_2$O$_2$ is not important for the arguments described below.

Figure 3(b) shows the magnetization curves $M$ of LiCu$_2$O$_2$ measured in two different field directions at 5K. The values of $M$ increase linearly with increasing magnetic fields for both directions of $H//a$ and $H//c$, indicating the nonexistence of a spin flop transition in the magnetic field up to 5.5 T. This should be contrasted with the facts that the spin flop transition is observed at $H= -2$ T and $-4$ T for Li$\text{VCu}_4$\(^{5,10}\) and Li$\text{ZrCuO}_4$\(^{9}\), respectively.

The X-ray powder diffraction pattern taken at room temperature for LiCu$_2$O$_2$ is shown in Fig. 4. We have carried out Rietveld refinement using the space group $Pnm\bar{a}$ with keeping the stoichiometry of LiCu$_2$O$_2$, where the Li$^+$ ionic coordinates are fixed to the reported values.\(^{19}\) The fitting is found to be almost satisfactory ($R_{wp}$=4.45, $S$=1.84), and the obtained structural parameters are consistent with the results reported in Ref. 19. Then, we have tried to carry out additional analyses by using the chemical formula Li$_{1+y}$Cu$_{2-y}$O$_2$, $-1<y<1$, and found the x value of 0.01±0.02 ($R_{wp}$=4.45, $S$=1.84). The analyses adopting the fixed Li$_{1+y}$Cu$_{1.5}$O$_2$ formula reported in ref. 6 have also been carried out, and the values $R_{wp}$=6.63 and $S=2.74$ are obtained. These results also exclude effects of the lattice imperfections of Cu atoms for the single-crystal samples of LiCu$_2$O$_2$ within error bars.

In order to estimate the Li content, thermogravimetric analyses (TG) have also been carried out. The rates of the sample-mass change, $\Delta m$/$m_0$ taken with increasing $T$ in the flowing O$_2$ (thick line) and flowing He with 5 % H$_2$ (thin line) are shown in Fig. 5, where the $m_0$ and $\Delta m$ are the initial sample mass at room temperature and $\Delta m = m(T)-m_0$. For the samples in the plateau region of the $\Delta m$/$m_0$-$T$ curves indicated by the arrows, the thermogravimetric analyses have been carried out, and found followings. In flowing O$_2$ gas, Li$_{1+y}$Cu$_2$O$_2$ decomposes into Li$_2$CuO$_2$ and CuO in the region of 700 °C$\sim$780 °C, as described by the relation,

$$\text{Li}_{1+y}\text{Cu}_2\text{O}_2\rightarrow (1-y)\text{Li}_2\text{CuO}_2+y\text{Li}_2\text{CuO}_3+(3+y)\text{CuO}.$$ (1)
From the weight gain after the sample was completely converted into Li2CuO2 and CuO, we obtained the y value of 0.01±0.05. (The value of Δm/ma=0.0482 for y=0 should be compared with the observed value in the plateau region.) In flowing He with 5 % H2, Li1-eyCu2O decomposes into Li2O, CuO and Cu in the plateau region indicated by the arrow (500 °C<T<600 °C). (At T higher than 600 °C, the de-oxidization reaction of the samples is still progressing, and at 1100 °C, the system finally decomposes to Li2O and Cu.) The chemical formula at the plateau is considered to be described as

\[(Li^+)_{1-2y}(Cu^{2+})\cdot_{1-2y}(Cu^+)\cdot_{2y}(O^2\cdot)\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
samples of LiCu$_2$O$_2$. For the samples of LiCu$_2$O$_2$ prepared in the present studies, the atomic deficiency and the mixing of Cu and Li atoms have not been found within the experimental error bars. Studies by specific heat measurements and neutron magnetic scattering indicate that the system exhibits two magnetic transitions at $T_{N1} \approx 24.5$ K and $T_{N2} \approx 22.8$ K. Based on the obtained magnetic structures determined in the intermediate ($T_{N2} < T < T_{N1}$) and low temperature ($T < T_{N2}$) phases, the relationship between the magnetic structures and dielectric properties has been argued: In the intermediate phase, the system has the collinear magnetic structure with the sinusoidal modulation and the ferroelectricity is not induced, while in the low temperature region, it has the ellipsoidal helical structure and the relation $P \propto Q \times e^3$ has been found to hold, consistently with the theories derived by the phenomenological and microscopic models.

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References
1) R. Bursill, G.A. Gehring, D.J.J. Farnell, J.B. Parkinson, T. Xiang, and C. Zeng: J. Phys.: Condens. Matter 7 (1995) 8605.
2) D.V. Dmitriev, and V.Y. Krivnov: Phys. Rev. B 73 (2006) 024402.
3) B. J. Gibson, R. K. Kremer, A. V. Prokofiev, W. Assmus, and G J. McIntyre: Physica B 350 (2004) e253.
4) Y. Naito, K. Sato, Y. Yasui, Y. Kobayashi, Y. Kobayashi, and M. Sato: J. Phys. Soc. Jpn. 76 (2007) 023708.
5) Y. Yasui, Y. Naito, K. Sato, T. Moyoshi, M. Sato, and K. Kakurai: J. Phys. Soc. Jpn. 77 (2008) 023712.
6) T. Masuda, A. Zheludev, A. Bush, M. Markina, and A. Vasiliev: Phys. Rev. Lett. 92 (2004) 177201.
7) 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 (2004) 020406.
8) S. Seki, Y. Yamasaki, M. Soda, M. Matsuura, K. Hirota, and Y. Tokura: Phys. Rev. Lett. 100 (2008) 127201.
9) Y. Tarui, Y. Kobayashi, and M. Sato: J. Phys. Soc. Jpn. 77 (2008) 043703.
10) M. Sato, Y. Yasui, Y. Kobayashi, K. Sato, Y. Naito, Y. Tarui, and Y. Kawamura: to be published in Solid State Science.
11) T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura: Nature (London) 42 (2003) 55.
12) N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, and S-W. Cheong: Nature 429 (2004) 392.
13) G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez: Phys. Rev. Lett. 95 (2005) 087205.
14) M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S.-W. Cheong, O. P. Vajk, and J. W. Lynn: Phys. Rev. Lett. 95 (2005) 087206.
15) H. Katsura, N. Nagaosa, and A. Balatsky: Phys. Rev. Lett. 95 (2005) 057205.
16) M. Mostovoy: Phys. Rev. Lett. 96 (2006) 257203.
18) H. J. Xiang and M.-H. Whangbo: Phys. Rev. Lett. 99 (2007) 257203.
19) R. Berger, P. Ömerud, and R. Tellgren: J. Alloys Compd. 184 (1992) 315.
20) S. Park, Y. J. Choi, C. L. Zhang, and S-W. Cheong: Phys. Rev. Lett. 98 (2007) 057601.
21) A. A. Rusydin, I. Mahans, S. Müller, M. Rübliausen, S. Park, Y.J. Choi, C.L. Zhang, S.-W. Cheong, S. Smadici, P. Abbamonte, M.v. Zimmermann, and G.A. Savatzky: Appl. Phys. Lett. 92 (2008) 262506.
22) S.W. Huang, D.J. Huang, J. Okamoto, C.Y. Mou, W.B. Wu, K.W. Yeh, C.L. Chen, M.K. Wu, H.C. Hsu, F.C. Chou, and C.T. Chen: Phys. Rev. Lett. 105 (2008) 077205.
23) Y. Kobayashi, K. Sato, Y. Yasui, T. Moyoshi, M. Sato, and K. Kakurai: submitted to J. Phys. Soc. Jpn.
24) S.J. Hibble, J. Köhler, A. Simon, S. Paider: J. Solid State Chem. 88 (1990) 534.
25) F. Izumi and T. Ikeda: Mater. Sci. Forum 321-324 (2000) 198.
26) H. Katsura, S. Onoda, J.H. Han, and N. Nagaosa: Phys. Rev. Lett. 101 (2008) 187207.
27) A.S. Moskvin, Y.D. Panov, and S-L. Drechsler: arXiv:cond-matt/0801.1975.
Fig. 1. The schematic structure of LiCu$_2$O$_2$. The one-dimensional chains of the edge sharing CuO$_4$ squares (CuO$_2$ ribbon chains) run along $b$, which are separated by the nonmagnetic Li$^+$ and Cu$^+$ ions.

Fig. 2. (a) Specific-heat divided by $T$, (b) neutron magnetic scattering intensities of $\frac{1}{2} 1 - \delta 0$ ($\delta \sim 0.172$) reflection and (c) capacitance measured for the electric field $E//c$ are shown against $T$.

Fig. 3. (a) $T$-dependence of the magnetic susceptibilities $\chi$ of LiCu$_{2-x}$Zn$_x$O$_2$ for $x=0.05, 0.10$ and $0.15$ measured under the condition of the zero field cooling for the magnetic field of 0.1 T ($H/ab$-plane). Inset shows the $T$-dependence of $\chi$ of a single crystal sample of LiCu$_2$O$_2$ for two different field directions. (b) Magnetization curves of LiCu$_2$O$_2$ are shown for two different field directions at 5K.
Fig. 4. Powder X-ray diffraction pattern (dots) observed at 300K is shown together with the fitted curve of the Rietveld refinement (solid line) for LiCu2O2.

Fig. 5. The thermogravimetric (TG) curves taken with varying $T$ in the flowing $O_2$ (thick line) and flowing He with 5% $H_2$ (thin line) are shown. In the plateau regions indicated by the arrows, the $\Delta m/m_0-T$ curves are analyzed in order to estimate the Li content of the single crystal samples of LiCu2O2 (see the text for details.)

Fig. 6. (a) and (b) Magnetic ordering patterns which can reproduce the magnetic scattering intensities and $^7$Li-NMR spectra of LiCu2O2 at (a) $T$=23.3K (intermediate phase) and (b) $T$=5K (low temperature phase). In (b) only the rotating planes of the Cu$^{2+}$ spins are shown. Details of analyses of magnetic structures are described in ref. 23. The figures (c) and (d) show the detailed parameters describing the magnetic structures in (a) and (b), respectively. The thick arrows indicate the direction of the Cu$^{2+}$ moments, and $Q$ and $e_3$ are the directions of the modulation vectors and helical axis, respectively. (e) Schematic $\varepsilon$-$T$ curves at around two transition temperatures.