Nonstoichiometry of $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ single crystal and its relation to magnetic ordering

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(Received 21 May 2010; accepted 27 July 2010; published online 29 October 2010)

We report the first systematic study on the nonstoichiometry of Li/Cu ionic ratios x and oxygen defect concentrations δ in $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ solid solution. Nonstoichiometric crystals with intentional Li-deficient ($x=0.97$) or Li-excessive ($x=1.06$) concentrations were prepared by slow-cooling and floating-zone methods. By applying different oxygen pressures during growth, different magnitudes of oxygen defects were obtained, revealing varied magnetic and electrical properties. Our results strongly suggest that Li/Cu and oxygen nonstoichiometry in these crystals are responsible for the varied temperatures of helimagnetic ordering. © 2010 American Institute of Physics.

[doi:10.1063/1.3483244]

I. INTRODUCTION

LiCu_2O_2 has garnered extensive interest in recent years because of its unusual magnetic order at low temperature.^{1–3} Chains of Cu^{2+}O_5 pyramids extend along the crystallographic b axis and are separated by chains of Li^+O_5 pyramids along crystallographic a axis and layers of nonmagnetic Cu^+ ions along the c axis. In this low-dimensional spin system, the nature of the magnetic interactions is known to be driven by quasi-one-dimensional chains of spin 1/2 Cu^{2+} ions with nearest and next-nearest interactions which are determined by the angle of the Cu–O–Cu bond in the CuO_4 squares. Upon a decrease in temperature, a spiral magnetic order sets in typically at around 24.2 K (T_{N1}) and 22.5 K (T_{N2}), presenting a complex rearrangement of the spin structure which is associated with competition of ferromagnetic and antiferromagnetic exchange interactions between neighboring Cu^{2+} ions.^{1,4} Ideally in exact stoichiometry, this compound contains magnetic Cu^{2+} and nonmagnetic Cu^+ copper ions in the ratio of 1:1. Nonetheless, due to the similar ionic size between Li^+ and Cu^+ , nonstoichiometry of this material has been suggested to be responsible for the structural deviations from the $Pnma$ symmetry.^{4,5} The chemical formula was further proposed by Bush *et al.* as $(\text{Li}_{1-u}^+\text{Cu}_u^{2+})(\text{Cu}_{1-v}^+\text{Cu}_v^{2+}) \times (\text{Cu}_{1-t}^{2+}\text{Li}_t^+)\text{O}_{2+\delta}$ in which u , v , and t represent mutual substitutions of cations, and δ which represents additional defects of oxygen.⁶ However, no information is given so far about the existing range of solid solubility; therefore, an open question concerning the magnitude and its influence of these nonstoichiometric factors on long-range ordering remained to be fully clarified.

Previous experiments and theoretical models are based on severely twinned crystals which are normally quenched from high temperature.^{1–6} The crystal composition reported by Hsu *et al.* was determined as $\text{Li}_{0.83}\text{Cu}_2\text{O}_2$ (Li-deficient) by iodometric titration and thermogravimetric methods,⁷ largely different from the previous information of Li-rich

$\text{Li}_{1.15}\text{Cu}_{1.85}\text{O}_{2+\delta}$ through measuring the crystal density.^{1,6} Yasui *et al.* following the same recipe reported their crystals to be near-stoichiometric without Li deficiency.⁸ The inconsistency complicated by unknown chemical and defect information requires clear elucidation. Here we report the slow-cooling experiments which strategically control the nonstoichiometry of crystals. By varying nominal compositions of the melt, $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ crystals either with stoichiometry or different magnitude of Li/Cu nonstoichiometry are successfully obtained. The magnetic measurements clearly indicate that the helimagnetic ordering is related to the Li/Cu nonstoichiometry in these crystals.

The floating-zone (FZ) technique provided a possibility to grow crystals in near equilibrium conditions with a well-controlled solid-liquid interface. Recently, there are good indications that it can actually apply in growing excellent crystals in this material system. Hsu *et al.* reported a successful FZ growth of near-stoichiometric LiCu_2O_2 crystal.⁷ Huang *et al.* reported measurements of resonant soft x-ray magnetic scattering using near-stoichiometric FZ samples.^{9,10} Chen *et al.* measured the band structure by performing polarization-dependent soft x-ray absorption using similar samples and reported a good correlation with theoretical calculation.¹¹ In this study, magnetic properties of the $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ phase are further modified by appropriately controlling the nominal compositions of the melt and the atmospheres during FZ growth. The influence of the magnitude of Li/Cu substitutions and oxygen defect concentrations on magnetic order temperatures are qualitatively discussed.

II. EXPERIMENTAL METHODS

Li_2CO_3 and CuO powders of 3N purity in selected ratios (x in $\text{Li}_x\text{Cu}_2\text{O}_2$ ranging from 0.5 to 8) were weighted, mixed in a ball mill for 4 h, and put in a round-shape aludum crucible (aspect ratio height/diameter=1.2–2.1). The crucible was heated up to 1100 °C in air and maintained at this temperature for 2 h. The melt was subsequently cooled from 1100 °C to around 930–950 °C at a rate of 3–5 °C/h, and

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afterward the crucible with the crystallized melt was quenched. As-grown crystals were carefully taken from a crystallized chunk after crushing the crucible.

Nominal compositions of stoichiometric and several off-stoichiometric ratios ($0.9 \leq x \leq 1.4$) were intentionally selected for FZ growth. Powder materials of Li_2CO_3 and CuO were mixed and then the mixture was calcined at 800°C for 12 h. The reacted bulk sample was reground into fine powders, pressed into a rubber tube under a hydrostatic pressure of 400 kg/cm^2 , and subsequently sintered at 820°C for 12 h. The apparatus of crystal growth was an infrared radiation furnace with two 1.5 kW halogen lamps (model 15HD, NEC Nichiden Machinery). While heating the solid rod, the melt was formed and was suspended by surface tension between the upper feed rod and lower rod with identical compositions. After lowering both rods, crystallization occurred at the growth front between the lower rod and the melt. Experiments were carried out in an enclosed quartz tube applying different gas types and pressures during growth. The growth was controlled at a translation rate of 5–10 mm/h and at an optimal rotation rate of 10 rpm.

Powder XRD measurements were carried out with an x-ray diffractometer (Phillips PW3040/60) using $\text{Cu } K_\alpha$ radiation, a scanning rate of $0.01^\circ/\text{s}$, and θ - 2θ scans from 10° to 80° . The crystal structure and symmetry were confirmed by single crystal diffraction using a synchrotron source in the National Synchrotron Radiation Research Center (NSRRC). Chemical compositions were determined by the inductively coupled plasma atomic emission spectrometer analyzer, model Perkin Elmer 300DV. Three standard samples, containing Li_2CO_3 and CuO powders in the Li:Cu ratio of 1:1.8, 1:2.0, and 1:2.2, were weighted and directly dissolved in nitric acid without heat treatment in order to avoid Li evaporation loss. The concentrations of Li and Cu were close to nominal values within 2% experimental errors. The thermogravimetric analysis was carried out to further confirm the Li/Cu nonstoichiometry with the use of MAC DTA/TG (model 2000) in flowing O_2 .^{7,8} The in-plane resistivity of a single crystal was measured by the conventional ac four-probe method (“Quantum Design,” model PPMS) over a temperature range of 2.9–300 K. The electrical contacts were established by baking silver epoxy onto the sample, which was annealed in an oxygen environment for 2 h at 200°C . The magnetization as a function of temperature was measured in a superconducting quantum interference device magnetometer (SQUID-VSM). The sample was cooled down to 2 K in zero magnetic field strength. A magnetic field was then applied perpendicular to the a - b plane of the crystal and the magnetization was measured on warming up to 300 K.

III. RESULTS AND DISCUSSION

A. Li/Cu nonstoichiometry in slow-cooled crystals

The intended $\text{Li}_x\text{Cu}_2\text{O}_2$ phases with a range of Li concentrations were grown via the slow-cooling (SC) method, see Table I. When growing with Cu-rich melt in SC_1 ($x=0.5$) and SC_2 ($x=0.7$), unwanted LiCu_3O_3 crystals dominated and contained very few $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals with poorer

TABLE I. Results of $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals in slow-cooling experiments.

Sample	Melt x value	Compound(s)	Crystal x value
SC_1	0.5	LiCu_3O_3	...
SC_2	0.7	$\text{Li}_x\text{Cu}_2\text{O}_2 + \text{LiCu}_3\text{O}_3$	...
SC_3	0.9	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.97
SC_4, 5, 6	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.00
SC_7	2	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.05
SC_8	4	few $\text{Li}_x\text{Cu}_2\text{O}_2$	1.03
SC_9	8	None	...

quality. Good-quality Li-deficient $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ crystals were obtained using the melt of $x=0.9$ (SC_3). Large crystals with dimensions typically $5\text{ mm} \times 5\text{ mm}$ can be easily cleaved from the crystallized chunk of the stoichiometric melt (SC_4). Furthermore, for SC_4, 5, and 6, the size and quality of as-grown crystals was not sensitive to experimental changes, such as the crucible aspect ratio ($H/D=1.2$ – 2.1), the temperature of growth end (930 – 950°C), and the rate of cooling (3 – 5°C/h). Figure 1(a) displays sharp (001) diffraction lines of the LiCu_2O_2 phase, indicating the (a , b) habit of the sample without impurities, such as Li_2CuO_2 , LiCu_3O_3 , and CuO . As shown in the right inset of Fig. 1(a), owing to the ease of severe twin formation in slow-cooled crystals, typical fourfold symmetry of (101) phi scan was

FIG. 1. (Color online) (a) θ - 2θ scan and (101) phi scan (right inset) on $\text{Li}_{1.00}\text{Cu}_2\text{O}_2$ crystal (SC_4) using synchrotron beam. The crystal platelets with (001) face of several square millimeter areas are shown in left inset: from right to left $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ (SC_3), $\text{Li}_{1.00}\text{Cu}_2\text{O}_2$ (SC_4), and $\text{Li}_{1.05}\text{Cu}_2\text{O}_2$ (SC_7) crystal, respectively. (b) Dependence of crystal c parameter with nominal melt compositions. Solid symbols represent slow-cooled crystals and hollow symbols indicate crystals grown by FZ. The inset reveals compositional dependence of the melt and as-grown crystals.

FIG. 2. (Color online) Temperature dependence of $d\chi(T)/dT$ and in-plane resistance (the inset) with varied Li-nonstoichiometry for SC-grown $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals (■ $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ of SC_3, ● $\text{Li}_{1.00}\text{Cu}_2\text{O}_2$ of SC_4, and ▲ $\text{Li}_{1.05}\text{Cu}_2\text{O}_2$ of SC_7). The magnetic field was applied perpendicular to crystal a - b plane.

observed (combining equally the diffraction lines of two domains A+B perpendicular to each other). X-ray rocking curves of (101) Bragg-reflections reveal in-plane and out-of-plane mosaic structure at room temperature. The full-width at half-maximum (FWHM) values of near-stoichiometric crystals (SC_4) have a range of 0.108° – 0.155° , showing that these crystals normally contain undefined magnitude of structural disorder due to nonequilibrium growth and quenching. On the Li-rich side, Li-excess crystals in composition of $\text{Li}_{1.05}\text{Cu}_2\text{O}_2$ were successfully obtained from the Li-rich melt of $x=2$ (SC_7). The FWHM value of SC_7 crystal is 1.421° indicating a degraded crystallinity as there is a larger magnitude of disorder within the nonstoichiometric crystal. Intentionally increasing Li concentrations in the melt resulted in small crystals with poorer crystallinity at the crucible bottom in SC_8 ($x=4$). The highly Li-rich melt became more viscous while nearly the whole solid appeared amorphous for SC_9 ($x=8$).

The crystallographic c parameters of crystals shown in the main panel of Fig. 1(b) decrease with larger melt x values, allowing us to conclude that the $\text{Li}_x\text{Cu}_2\text{O}_2$ phase can be preferably crystallized from the melt in a compositional range of $x=0.9$ – 2 . As shown in the inset of Fig. 1(b), cation compositions of as-grown crystals experience deviations from stoichiometry, indicating linear relation with the nominal composition of melt. The solubility range of the $\text{Li}_x\text{Cu}_2\text{O}_2$ phase was nearly 7.5%, ranging from $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ (Li-deficient) to $\text{Li}_{1.05}\text{Cu}_2\text{O}_2$ (Li-excess). It also implies that Li-excess crystals with smaller lattice c parameters can be obtained from the Li-rich melt, and vice versa. The near-stoichiometric crystals can be attained from the growth of the stoichiometric melt, suggesting that the solidus-liquidus phase transition should be congruent.

Figure 2 compares $d\chi(T)/dT$ of varied Li/Cu nonstoichiometric crystals. As seen in this plot, it has a characteristic flattop that peaks at temperatures $T_{N1}=24$ K and $T_{N2}=22.6$ K of stoichiometric $\text{Li}_{1.00}\text{Cu}_2\text{O}_2$ crystal (SC_4), in agreement with previous reports.^{1,6} Two anomalies positioned at temperatures $T_{N1}=24.4$ K and $T_{N2}=23.4$ K are clearly observed, suggesting an increase of the magnetic ordering temperature for Li-deficient $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ crystal

(SC_3). On the other hand, for Li-excess $\text{Li}_{1.05}\text{Cu}_2\text{O}_2$ crystal (SC_7), the round-shape flattop extends between 18 and 23 K without a clear maximum. It is interesting to note that the disappearance of magnetic peculiarity is very similar to the Zn-doped $\text{LiCu}_{2-y}\text{Zn}_y\text{O}_2$ ($y=0.08$) sample in which the next-nearest interaction was blocked due to nonmagnetic Zn^{2+} ions substituting on Cu^{2+} atomic sites.¹² This strongly suggests that excess Li^+ ions could occupy Cu^{2+} sites and influence or cut the spin correlations within the b -axis spin ladder chain.¹ As shown in the inset of Fig. 2, the effects resulting from $\text{Li}^+ \rightarrow \text{Cu}^{2+}$ substitutions of Li-excess crystal (SC_7) are anticipated to be accompanied by the insertion of holes into $-\text{LiCuO}_2-$ layers and subsequently lowering its resistance at low temperature comparing with stoichiometric (SC_4) and Li-deficient (SC_3) crystals. Moreover, the transitions shift to higher temperatures while Li concentrations decrease in crystal, further indicating that the temperature when magnetic ordering sets in is determined by Li/Cu mutual substitutions.

B. Li/Cu and oxygen nonstoichiometry in floating-zone crystals

Powders of varied x values, including 0.9, 1.0, 1.2, and 1.4, were utilized to grow crystals in chambers flowing with oxygen and/or argon as shown in Table II. The effect of the atmosphere on the growth stability is crucial. While growing crystals in air (FZ_1) and in oxygen of 1 atm (FZ_3), a large quantity of good crystals was obtained. Growth at an oxygen pressure of 2 atm (FZ_4) resulted in the appearance of undesirable LiCu_3O_3 due to violent evaporations. For FZ_5 ($x=1.0$) and FZ_7 ($x=1.2$), only LiCu_3O_3 crystals were obtained at an oxygen pressure up to 5 atm. $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals without the formation of LiCu_3O_3 can be obtained when extra Li_2CO_3 was added to compensate the evaporation losses ($x=1.2$ of FZ_6 at 2 atm and $x=1.4$ of FZ_9 at 3 atm). To compare the influence of atmosphere, powder of nominal ratios at 0.9 (FZ_2 in O_2 and FZ_10 in Ar) and 1.4 (FZ_8 in O_2 and FZ_13 in Ar) were prepared to grow crystals. Largest crystals of approximately 5 mm $\times$ 2 mm with excellent crystallinity were produced in Ar atmosphere from a slightly Li-rich melt (FZ_11 and 12). We conclude that the $\text{Li}_x\text{Cu}_2\text{O}_2$ phase can be crystallized from the melt with nominal x values in the range of 1.0 and 1.4 in FZ [open symbols in Fig. 1(b)]. The stability region of the $\text{Li}_x\text{Cu}_2\text{O}_2$ phase is summarized from SC and FZ results to be within the range of $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ and $\text{Li}_{1.06}\text{Cu}_2\text{O}_2$. The crystals can be obtained at such a high growth rate (5–10 mm/h) also implies the solidification of LiCu_2O_2 from melt is congruent.

The main panel of Fig. 3 shows (101) ϕ scan close to twofold symmetry revealing that near-stoichiometric FZ crystal was nearly untwined. The right inset of Fig. 3 demonstrates the x-ray rocking curve of (101) Bragg-reflections on FZ_3 crystal (left inset of Fig. 3). Typical values of FWHM for FZ samples range from 0.038° to 0.097° (0.055° of FZ_3; 0.097° of FZ_6; 0.089° of FZ_11 and 0.038° of FZ_12). It appears that these values are smaller than those of slow-cooled near-stoichiometric samples typically in the range between 0.108° and 0.155° , not to mention much

TABLE II. Growth parameters and results of $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals in floating-zone experiments.

Sample	Melt x value	Atmosphere	Pressure (atm)	Compound(s)	Crystal x value
FZ_1	1.0	air	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.97
FZ_2	0.9	O_2	1	LiCu_3O_3	...
FZ_3	1.0	O_2	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.99
FZ_4	1.0	O_2	2	$\text{Li}_x\text{Cu}_2\text{O}_2 + \text{LiCu}_3\text{O}_3$	...
FZ_5	1.0	O_2	5	LiCu_3O_3	...
FZ_6	1.2	O_2	2	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.02
FZ_7	1.2	O_2	5	LiCu_3O_3	...
FZ_8	1.4	O_2	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.01
FZ_9	1.4	O_2	3	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.06
FZ_10	0.9	Ar	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.97
FZ_11	1.0	Ar	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.97
FZ_12	1.2	Ar	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	0.99
FZ_13	1.4	Ar	1	$\text{Li}_x\text{Cu}_2\text{O}_2$	1.02

smaller than Li-excess crystal (SC_7) of 1.421° . Because of a well controlled S/L interface and slow cooling process to terminate the growth, the mosaic structure was effectively eliminated suggesting that crystal growth by FZ was significantly successful. It is worth mentioning that near-stoichiometric ($\text{Li}_{0.99}\text{Cu}_2\text{O}_2$) crystal (FZ_12) had the highest quality with the smallest FWHM of 0.038° .

The influence of the atmosphere on oxygen concentrations of as-grown crystals and thereby on the magnetism is our next concern. Figure 4(a) compares $d\chi(T)/dT$ measurements of crystals grown in different atmospheres. As seen in this plot, it is expected that the crystal grown in air (FZ_1) has a flattop that extends between $T_{N1}=24$ K and $T_{N2}=22.5$ K, similar to stoichiometric SC-crystal (SC_4). Higher temperatures of anomalies were observed for crystals grown in Ar (FZ_11, $T_{N1}=24.5$ K and $T_{N2}=22.9$ K). On the other hand, T_{N2} shifted to a lower temperature and the precursor transition T_{N1} which is supposed to be dominating for $H\parallel c$ was unclear for crystals grown in oxygen (FZ_3, $T_{N2}=21.8$ K).¹³ As shown in the left inset of Fig. 4(a), temperature dependence of specific heat divided by T, C/T , shows well-defined transition peaks for crystals of FZ_11 (T_{N1}

$=24.5$ K and $T_{N2}=22.9$ K) and FZ_1 ($T_{N1}=24.6$ K and $T_{N2}=22.8$ K). A clearer T_{N1} for FZ_3 crystal ($T_{N1}=23.5$ K and $T_{N2}\sim 22.1$ K) is observed in the specific heat measurement. These ordering temperatures are correlated well with magnetization measurements. Clearly, increasing oxygen concentrations in these three Li-deficient crystals by increasing the oxygen pressure during growth shift the magnetic anomalies to lower temperatures. Although we cannot clearly

FIG. 3. (Color online) (101) ϕ scan on floating-zone crystal (FZ_3) showing nearly untwined twofold symmetry of domain A. The crystal boule and as-cleaved crystal (FZ_3) are shown in left inset. X-ray rocking curve of (101) Bragg-reflections for the same $\text{Li}_{0.99}\text{Cu}_2\text{O}_2$ crystal is shown in right inset.

FIG. 4. (Color online) (a) Temperature dependence of $d\chi(T)/dT$, C/T (left inset) and in-plane resistance (right inset) for $\text{Li}_x\text{Cu}_2\text{O}_2$ crystals grown in different atmospheres ($\circ$ FZ_1 in air, Δ FZ_3 in O_2 , and $\square$ FZ_11 in Ar). The magnetic field of susceptibility measurement was applied perpendicular to crystal a - b plane. (b) Temperature dependences of $d\chi(T)/dT$ graph for crystals grown in Ar ($\square$ $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$, FZ_11; and ∇ $\text{Li}_{1.02}\text{Cu}_2\text{O}_2$, FZ_13). The inset depicts the compositional dependence of magnetic ordering temperatures. Solid symbols represent slow-cooled crystals and hollow symbols indicate crystals grown by FZ.

identify the type or the quantity of oxygen defects existing in these crystals (in our cases they might be vacancies or interstitials), this trend between magnetic ordering temperatures and oxygen concentrations $2+\delta$ in the $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ phase (δ represents additional defects of oxygen) are quite apparent. The different magnitude of structural disorder which was induced by varied oxygen concentrations gives rise to the onset of exchange coupling at different corresponding temperatures.

The right inset of Fig. 4(a) compares the measurements of in-plane resistance for crystals grown in different atmospheres. The resistance of the crystal grown in Ar atmosphere increased rapidly as the temperature dropped and the crystal became insulating above 250 K. On the other hand, while measuring the crystal grown in oxygen, the resistance increase did not occur until the temperature was lower than 100 K. It is believed that oxygen nonstoichiometry in crystal is accompanied by the modulation of carriers (basically holes) in $-\text{LiCuO}_2-$ layers and it is clear that oxygen concentrations exert a more noticeable influence than previously expected.

Furthermore, the main panel of Fig. 4(b) compares the $d\chi(T)/dT$ graph for $\text{Li}_{0.97}\text{Cu}_2\text{O}_2$ and $\text{Li}_{1.02}\text{Cu}_2\text{O}_2$ crystals which were both grown in Ar. The transition peaks shift to lower temperatures while Li concentration increases in Ar-grown crystals. It is worth mentioning that this temperature deviation arising only from Li/Cu mutual substitutions is similar to that of SC-grown crystals (in Fig. 2). Thus, the temperatures when magnetic ordering sets in are summarized in the inset of Fig. 4(b) and it clearly demonstrates a good correlation with Li concentration x within $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ crystals.

IV. CONCLUSIONS

We demonstrate how to intentionally modify the properties of $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ phase by varying nominal compositions of the melt and atmospheres during growth. $\text{Li}_x\text{Cu}_2\text{O}_{2+\delta}$ crystals, with x ranging from 0.97 (Li-deficient) to 1.06 (Li-excess), were fabricated by slow-cooling and floating-zone methods. The structural defects, owing to Li/Cu mutual substitutions and oxygen defect incorporations, were expected to

correlate with the varied temperatures of antiferromagnetic to helimagnetic transition in different samples. This low-dimensional compound offers a rich chemistry, thereby this contribution is a crucial element in the process of qualitatively understanding the interplay between the magnetism and its structural defects. Detailed measurements on dielectric and ferroelectric properties which are expected to provide precise information about the interactions of Cu–O–Cu exchange coupling are currently investigated.

ACKNOWLEDGMENTS

We thank Y. Y. Chen and W. L. Lee for helpful discussions and the National Synchrotron Radiation Research Center for their support in terms of experimental facilitation. This work was supported under National Science Council (NSC) of the Republic of China Grant No. NSC98-2119-M-001-025.

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