CORRIGENDUM

Corrigendum: Oxygen vacancy-induced magnetic moment in edge-sharing CuO2 chains of Li2CuO2–δ (2017 New J. Phys. 19 023026)

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In this corrigendum, we present corrections to the paper ‘Oxygen vacancy-induced magnetic moment in edge-sharing CuO2 chains of Li2CuO2–δ’ (2017 New J. Phys. 19 023026) by Shu et al. Equation (7) shown in the paper is wrong due to copying error, which has been corrected following the referenced source with modifications. The J1 values for Li2CuO2–δ (δ ~ 0 and 0.16) shown in table 6 should be doubled for a consistent comparison based on the definition of used Hamiltonian.

(1) Correction to equation (7): Equation (7) shown in the paper by Shu et al is wrong [1], the correct one with proper units must follow the original form of equation (3) in [2] by Takeda et al with an added z"J" term as

\[ \chi = \chi_{1D}/[1 - 2(2\delta' + z"J"')\chi_{1D}/Ng^2g^2]. \]

(2) Correction to table 6: Because the J'–J'–J" model used in the paper by Shu et al followed the Hamiltonian defined by Takeda et al as \( \mathcal{H} = -2\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1} \), the conventional coupling constants \( J_i \) based on the Hamiltonian \( \mathcal{H} = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \) must have the \( J_i = 2 J'' \) relationship for a consistent comparison. The \( J_i \) values shown in the 4th and 5th rows of table 6 in the paper by Shu et al should be doubled, i.e., \( J_i \) for \( \delta \sim 0 \) and 0.16 are \( \sim 130 \) K and 122 K, respectively, which is also consistent to the \( J_1 \) estimation as shown in the figure 2 of reply to the comment raised by Kuzian et al [3]. In addition, strictly speaking, it is not appropriate to position J'/J" in the J3/J5 columns, because the former is for the dipole–dipole inter-chain coupling for each FM chain as a unit, and the latter is for inter-chain individual spin exchange coupling.

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Oxygen vacancy-induced magnetic moment in edge-sharing CuO$_2$ chains of Li$_2$CuO$_2$–$\delta$

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Keywords: edge-sharing chain, magnetic moment, vacancy defect, magnetic susceptibility, molecular orbital, exchange coupling

Abstract

Li$_2$CuO$_2$ is a typical charge transfer insulator with CuO$_2$ chains that are composed of edge-shared CuO$_4$ plaquettes. The existence of oxygen vacancies for single crystals prepared under various oxygen partial pressures has been confirmed by the chemical and thermogravimetric analyses. The puzzling discovery of extra magnetic moment near the oxygen site by earlier neutron scattering studies has been verified by a thorough Curie–Weiss law analysis of spin susceptibilities, and resolved quantitatively with a molecular orbital model of edge-sharing CuO$_2$ chains containing oxygen vacancies.

1. Introduction

Li$_2$CuO$_2$ is a charge-transfer insulator composed of weakly coupled CuO$_2$ chains with Li atoms in the interstitial sites, where each chain is formed with edge-shared CuO$_4$ plaquettes, as shown in figure 1. While the CuO$_4$ plaquette is the building block of the Cu–O plane as the common signature of high $T_c$ cuprate superconductors [1], Li$_2$CuO$_2$ has been explored intensively in parallel, including its orthorhombic crystal structure [2], antiferromagnetic spin ordering of $T_N \sim 9$ K [2], field-induced ferromagnetic transition below $\sim 2.8$ K [3], charge and orbital excitation [4], and Zhang–Rice type excitations [5]. In particular, neutron scattering studies suggest that oxygen has a magnetic moment of $\sim 0.11 \mu_B$ in Li$_2$CuO$_2$ [6], which is puzzling and has been examined theoretically to suggest a strong moment transfer to the oxygen ions due to orbital hybridization [7].

While most of the studies of Li$_2$CuO$_2$ assumed that the studied samples were stoichiometric without considering the Li or O defects, it was also found that the effective moments fitted from the paramagnetic regime of the spin susceptibility data varied from $\sim 1.8$ to $2.07 \mu_B$ for samples prepared using different preparation conditions [3,8–10]. Clearly, strong sample-dependent studies have been made without careful chemical composition analysis, especially on lithium and oxygen non-stoichiometry, which could invalidate the theoretical calculations and experimental interpretations made for the perfectly stoichiometric compound. In addition, the effective magnetic moments per Cu$^{2+}$ estimated from the Curie–Weiss law fitting were found to be consistently larger than the spin-only value for $S = 1/2$ of 1.732 $\mu_B$ (assuming $g = 2$), which has often been attributed to the unquenched orbital contribution due to strong d–p hybridization, but a reasonable molecular orbital model remains to be established to illustrate the proposed hybridization. We believe that the role and stoichiometry of lithium and oxygen in Li$_2$CuO$_2$ should be re-examined in detail, especially from a molecular orbital model approach, which allows a clear picture of localized spins that correspond to the unpaired electrons in hybridized orbitals of copper and oxygen.

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2. Experimental details

Li$_2$CuO$_2$ - $\delta$ single crystals were grown using the optical floating-zone method under various pressure and oxygen partial pressures. The initial feed rod was prepared using a stoichiometric 2:1 ratio of dehydrated LiOH and CuO through mixing and grinding. The initial heating was performed at 470 °C for 12 h, and the final annealing was performed at 550 °C under oxygen flow. In the final annealing period, feed rods of $\sim$3–5 mm in diameter and $\sim$8–10 cm long were prepared with a hydraulic press for the optical floating-zone crystal growth. Li$_2$CuO$_2$ melts congruently and the crystal can be pulled from the stoichiometric feed rod through stages from polycrystalline to single crystalline after the first $\sim$10 mm of pulling. Although lithium loss was expected for its high vapor pressure [11], to control the lithium and oxygen loss, mixed O$_2$/(O$_2$+N$_2$) gas (from 20% to 100%) of pressure up to 7 bar has been applied and reported.

Three chemical composition analysis methods have been applied to all crystal samples, including the inductively coupled plasma (ICP) mass spectrum, which focused on the Li and Cu content, the electron probe microanalysis (EPMA), which focused on the Cu and O ratio, and finally an independent oxygen content check, which was performed using the oxygen/nitrogen combustion analyzer (EMGA-920, Horiba). The O$_2$/N$_2$ combustion technique provides an independent and direct method for oxygen content determination. We found that a high pressure atmosphere does help to reduce Li loss during growth, although Li loss can also be compensated effectively with approximately 10% Li excess in the feed rod for growth at ambient pressure. A series of crystal samples that grew under 7 bar gas pressure and have been confirmed to be without Li vacancy were investigated in this work. However, it was found that even if a high pressure (7 bar) of 100% pure oxygen was maintained in the floating-zone furnace growth chamber, oxygen vacancy was unavoidable to show $\delta$ as high as $\sim$0.16 ± 0.01. Oxygen content can be tuned accurately using low-temperature post annealing with the thermogravimetric analysis method under oxygen flow. For example, Li$_2$CuO$_2$ $\pm$0.01 powder can be prepared through post-annealing at 400 °C for two days using the as-prepared sample of Li$_2$CuO$_1$ $\pm$0.02. Homogeneous oxygen vacancy-free single crystal sample was prepared with an additional ultrahigh oxygen pressure annealing, using a cubic anvil apparatus with mixed oxidizer of KClO$_4$ at 6 GPa and 800 °C for 30 min.

The transmission electron microscope (TEM) samples were prepared by crushing Li$_2$CuO$_2$ - $\delta$ single crystal samples into small pieces, dropping them onto a carbon-coated Cu grid, and rapidly loading them into the TEM.
Electron energy loss spectroscopy (EELS) spectra of Li$_2$CuO$_{2-\delta}$ were acquired at 200 kV with a JEOL-2100 field emission TEM equipped with a Gatan Tridiem 863 system.

3. Results and discussions

3.1. Phase purity and structure analysis

The phase purity for the growth of Li$_2$CuO$_{2-\delta}$ under various oxygen partial pressure ($p_{O_2}$) has been examined using synchrotron x-ray, as shown in figure 2(a). Minor impurity phase of LiCu$_2$O$_2$ can only be identified in the crystals grown under 100% Argon atmosphere at 7 bar pressure, which is consistent to that reported by Wizent et al on the optical floating-zone growth of Li$_2$CuO$_2$ under 40 bar gas pressure [11]. The lattice parameters for Li$_2$CuO$_2$ samples prepared under various oxygen partial pressures at 7 bar are summarized in table 1, where no significant oxygen partial pressure dependence is found and these refined values are in good agreement with those reported in the literature [12]. On the other hand, the structural refinement results indicate that a significant oxygen partial pressure dependence is observed on the average Cu–O bond length and O–Cu–O bond angle, as summarized in figure 2(b). The combined observations of insensitive lattice size change with significant change on the average bond length/angle strongly suggest the existence of randomly distributed oxygen vacancies, without breaking the bulk crystal symmetry for the emergence of an impurity phase. In order to examine this hypothesis, independent chemical analyses are required.

The bond angles shown in figure 2(b) revealed one more interesting phenomenon on bond angle also. For an ideal edge-sharing CuO$_2$ chain, it is expected that the O–Cu–O bond angle should be close to 90° considering the $d$–$p$ hybridization. However, it is found that the O–Cu–O bond angle for sample with nearly zero oxygen vacancy still shows a bond angle approaching ~91°. We believe such rectangular distortion is related to the Coulomb attraction between O$^{2-}$ and Li$^+$ arrays along the $c$-direction (see figure 1). In fact, similar rectangular
distortion has also been found consistently in compounds containing edge-sharing CuO₂ chains, including Ca₂Y₂Cu₅O₁₀ and La₆Ca₈Cu₂₄O₄₁ [13].

3.2. Lithium and oxygen stoichiometry
Both lithium and oxygen contents of Li₂CuO₂₋ₓ have been cross examined using three different techniques, including ICP which focused on the ratio of Li:Cu, EPMA for the Cu:O ratio when Li is too light for an accurate determination, and the oxygen content which is determined directly and independently with an oxygen combustion analyzer, as summarized in table 2.

The Li content has been found to be constant near 2 per formula unit consistently within error, especially for crystals grown under 7 bar atmosphere or with feed rod containing 10% Li excess at the ambient pressure. The oxygen contents are significantly lower than 2 per unit when the EPMA is normalized relative to Cu, which is also verified by the oxygen combustion analysis independently with the expected 29.24% by weight for oxygen in the vacancy-free sample. Moreover, starting from a sample with a determined oxygen vacancy level, the oxygen content can also be tuned in situ and the final content could reach as high as 2.00(1) after as-grown crystal is annealed in O₂ atmosphere at 400 °C for two days, as demonstrated in figure 3. It is clear that the existence of oxygen vacancy defects is common and severe in Li₂CuO₂₋ₓ at the level of δ ~ 0.15–0.3, even for crystals grown under the high-pressure pure oxygen atmosphere up to 7 bar.

3.3. Magnetic susceptibilities
The magnetic susceptibilities for single crystal samples grown under various oxygen partial pressures at 7 bar atmosphere are confirmed to be paramagnetic (PM) at high temperature and with an antiferromagnetic (AF) ground state of T₉ ~ 9 K, similar to those reported in the literature [2, 14]. Since the powder data could average out the orbital anisotropy, and the Curie–Weiss law fitting is valid for T > J/kₐ in the true PM state only, we have examined the susceptibility data using anisotropic single crystal measurement results first. The representative anisotropic measurement results of single crystal Li₂CuO₂₋ₓ (δ ~ 0.16) are displayed in figure 4. A complete Curie–Weiss law fitting of χ = χ₀ + C/(T - Θ) has been performed for magnetic field applied along the three major crystallographic orientations using data above ~250 K, as summarized in table 3.

The powder-averaged homogeneous susceptibility (χ = M/H) of an orthorhombic system can be calculated from the anisotropic single crystal measurement results as

\[
\chi = \frac{1}{3}(\chi_0 + \chi_a + \chi_c).
\]

For a perfect powder sample preparation, it is expected that Curie constant C = Nιₑff² /3kₐ and g value obtained directly from the powder measurement should be close to the powder-average of the anisotropic measurement results following

Table 1. The lattice parameters for Li₂CuO₂₋ₓ crystals grown under different oxygen partial pressures at 7 bar. Homogeneous oxygen vacancy-free crystal has been prepared with additional ultrahigh oxygen pressure (+HP) annealing.

| ρ₂₃ (%) | a (Å) | b (Å) | c (Å) |
|---------|-------|-------|-------|
| 20      | 3.66097(8) | 2.86381(7) | 9.3934(3) |
| 50      | 3.66030(1)  | 2.86360(1)  | 9.3921(4)  |
| 80      | 3.66090(1)  | 2.86370(1)  | 9.3940(4)  |
| 100     | 3.66144(6)  | 2.86529(9)  | 9.3962(4)  |
| + HP    | 3.66144(8)  | 2.86476(8)  | 9.3909(3)  |

Table 2. For Li₂CuO₂₋ₓ crystals grown under different oxygen partial pressures at 7 bar and the vacancy-free crystal prepared with additional ultrahigh oxygen pressure (+HP) annealing, chemical composition analysis results from three methods are shown, including ICP (normalized to Cu), EPMA (normalized to Cu), and Oxygen Combustion Analysis.

| ρ₂₃ (%) | Li:Cu (ICP) | Cu:O (EPMA) | δ       | O (wt%) |
|---------|-------------|-------------|---------|---------|
| 20      | 1.998(1):1  | 1:1.71(1)   | 0.29(3) | 26.05(5) |
| 50      | 2.001(1):1  | 1:1.77(1)   | 0.23(1) | 26.77(5) |
| 80      | 1.997(1):1  | 1:1.82(1)   | 0.18(1) | 27.32(5) |
| 100     | 2.002(1):1  | 1:1.84(1)   | 0.16(2) | 27.56(5) |
| + HP    | 2.001(1):1  | 1:2.00(2)   | 0.00(1) | 29.24(8) |
respectively. The powder-averaged Curie constant \( C \) and the \( g \)-factor can be derived from equations (2) and (3) using the single crystal anisotropic measurement results, as shown in table 3. Alternatively, a direct Curie–Weiss law fitting can be applied to the powder averaged data of \( \chi(T) \) which are derived from the single crystal measurement results with equation (1), as summarized in table 4. Comparing the \( C \) and \( g \) values derived from the single crystal anisotropic measurement results (table 3) and those obtained from the direct fitting using the powder averaged data of \( \chi(T) \) (table 4), the satisfactory agreement suggests that the magnitude of the extracted Curie constant is accurate and reliable without potential contamination from the anisotropic orbital contribution due to preferred orientation and the temperature-independent terms.

The temperature-independent term \( \chi_0 \) of \( \chi(T) \) for Li\(_2\)CuO\(_2\) includes the core diamagnetic \( \chi_{\text{core}} \), Van Vleck paramagnetic \( \chi_{\text{VV}} \), and Pauli paramagnetic \( \chi_{\text{Pauli}} \) contributions. Since \( \chi_{\text{Pauli}} = 0 \) for the insulator,
Table 3. Curie–Weiss law fitting of $\chi(T) = \chi_c + C/(T - \Theta)$ for the anisotropic measurement of single crystals Li$_2$CuO$_2$, of $\delta \sim 0.16$ and 0. Powder averaged values of $C$ and $g$ are derived using equations (2) and (3), and under the assumption of the existence of single type of copper spin ($S = 1/2$) in the fitted temperature range.

| Single crystal | Fitting range 250–550 K |
|----------------|-------------------------|
| $\delta \sim 0.16$ | $\chi_c$ (cm$^3$ mol$^{-1}$) | $C$ (cm$^3$ K mol$^{-1}$) | $\Theta$ (K) | $g$ |
|----------------|-------------------------|
| $\chi_a$ | $-0.00003(3)$ | $0.607(5)$ | $-34.55$ | $2.546$ |
| $\chi_b$ | $-0.00002(9)$ | $0.459(3)$ | $-29.41$ | $2.213$ |
| $\chi_c$ | $-0.00002(4)$ | $0.414(5)$ | $-32.83$ | $2.106$ |
| Powder average | $-0.00003(3)$ | $0.493(8)$ | | | $2.296$ |

| $\delta \sim 0$ | $\chi_c$ (cm$^3$ mol$^{-1}$) | $C$ (cm$^3$ K mol$^{-1}$) | $\Theta$ (K) | $g$ |
|----------------|-------------------------|
| $\chi_a$ | $-0.00003(3)$ | $0.408(2)$ | $-36.22$ | $2.087$ |
| $\chi_b$ | $-0.00002(8)$ | $0.380(1)$ | $-30.61$ | $2.013$ |
| $\chi_c$ | $-0.00002(5)$ | $0.342(7)$ | $-33.92$ | $1.910$ |
| Powder average | $-0.00002(8)$ | $0.377(1)$ | | | $2.004$ |

Table 4. Curie–Weiss law analysis using powder averaged data of the anisotropic single crystal measurement results, i.e. fitting directly using the $\chi(T)$ data derived from the anisotropic measurement results with equation (1) between 250 and 550 K. $g$ values are evaluated under the assumption of the existence of single type of copper spin ($S = 1/2$) in the fitted temperature range.

| $pO_2$ (%) | $\delta$ | $\chi_c$ (cm$^3$ mol$^{-1}$) | $C$ (cm$^3$ K mol$^{-1}$) | $\Theta$ (K) | $\mu_{eff}$ ($\mu_B$) | $g$ |
|-------------|-----------|-------------------------|-------------------------|-----------|------------------|---|
| 20          | 0.29(3)   | $-0.00004(3)$ | $0.594(4)$ | $-27.42$ | $2.184(5)$ | $2.522(5)$ |
| 50          | 0.23(1)   | $-0.00003(5)$ | $0.544(3)$ | $-28.3(3)$ | $2.090(4)$ | $2.413(4)$ |
| 80          | 0.18(1)   | $-0.00003(7)$ | $0.510(3)$ | $-30.8(2)$ | $2.024(6)$ | $2.337(3)$ |
| 100         | 0.16(2)   | $-0.00003(3)$ | $0.493(2)$ | $-32.5(2)$ | $1.988(7)$ | $2.296(2)$ |
| +HP         | 0.00(1)   | $-0.00003(4)$ | $0.377(1)$ | $-32.9(5)$ | $1.736(5)$ | $2.004(5)$ |

$\chi_s = \chi^\text{core} + \chi^\text{VV}$.

(4)

Based on the total core diamagnetic contribution calculated from the sum of the close shells of 2$\chi_L$,$^\text{core} + 2\chi_{Cu}$,$^\text{core} + 2\chi_O$,$^\text{core} = -3.62 \times 10^{-5}$ cm$^3$ mol$^{-1}$ [15], the $\chi^\text{VV}$ is deduced to be in the order of 10$^{-6}$ cm$^3$ mol$^{-1}$ experimentally, which is found about one order smaller than those reported for some representative cuprate compounds, including CuBr$_2$, LiCuVO$_4$, and YBa$_2$Cu$_3$O$_7$ [16–18]. On the other hand, for the theoretical $\chi^\text{VV}$ derived via the second order perturbation of energy as $\chi = \frac{\partial E}{\partial H}$ [19], such effective orbital Zeeman effect would contribute significantly only when the orbital splitting is small. Since the 3d-orbital degeneracy of Cu$^{2+}$ in a square planar CEF is lifted into a four-fold splitting of $t_{2g}$, $e_g$, and $a_{1g}$, $e_g$ [20], the sizable CEF gap is not expected to produce significant contribution to $\chi^\text{VV}$. In fact, no matter how these nine electrons in 3d$^9$ are distributed within the four-fold split energy levels, no significant Zeeman energy gain is expected under the field.

For an ideal PM behavior which is best described by the Curie–Weiss law for isolated spins under the competing influence of temperature and field, it is expected that the thermal energy must overcome the nearest neighbor spin exchange coupling $J$. The exchange coupling constant reported in the literature for Li$_2$CuO$_2$ has been shown in the range of $J/k_B \sim 100–228$ K [10]. The temperature range of 250–550 K used in the Curie–Weiss law fitting must safely satisfy the condition of $T > J/k_B$, as well as the Curie’s law approximation condition of $\frac{g^4\mu_B^2SH}{k_B^2T} \ll 1$ in the Brillouin function [21]. The data of $1/\chi$ are shown to deviate from the high temperature linear fitting below $\sim 135$ K (figure 4), which suggests that the thermal energy becomes weaker than the spin coupling strength, and the onset of $1/\chi$ linear deviation could be used as a rough estimate to the nearest neighbor spin exchange coupling. Following the mean field approximation of Weiss temperature $\Theta \propto \sum z_i J_i$ [22], it is implied that the strongest spin exchange coupling $J/k_B$ for Li$_2$CuO$_2$ must be near $\sim 135$ K, which is in good agreement with those estimated by the $J_1-J_2-J_3$ model and the molecular quantum chemical calculations by treating La$_2$CuO$_2$ as an edge-sharing spin chain system [14, 23].

3.4. Copper and oxygen valence

Based on the ionic model description, the existence of oxygen vacancy in Li$_2$CuO$_2$ implies the emergence of Cu$^{2+}$ following the requirement of neutrality as Li$^+$($Cu_2^{2+}$O$^{2-}$)$_2$. It is curious to examine this assumption by checking the actual copper valence change as a function of $\delta$. The EELS spectra of the oxygen K-edge and copper
$L$-edge have been widely used as a typical technique for valence determination in transition metal oxides [24]. The EELS spectra of O-$K$ and Cu-$L$-$2,3$ edges for both stoichiometric Li$_2$CuO$_2$ and oxygen-deficient Li$_2$CuO$_{1.84}$ samples are shown in figure 5(a), respectively, with the background subtracted.

The Cu-$L$-$2,3$-edge (figure 5(a)) displays two sharp spectral peaks at $\sim$935 and 955 eV corresponding to the $L_3$ and $L_2$ ionization edge, respectively [25]. The spectral feature of the Cu-$L$-$2,3$-edge is nearly identical for Li$_2$CuO$_2$ and Li$_2$CuO$_{1.84}$, which implies that the copper valence does not change due to oxygen vacancy creation. The intensity ratio of $L_2,3$ peaks ($L_2/L_3$) has also been used to analyze the valence change qualitatively; for example, Co$^{4+}/3+$ valence change has been supported by the Co $L_3/L_2$ ratio [26]. The $L_3/L_2$ ratios of CuO, a typical compound of Cu$^{2+}$ with $3d^9$ configuration, and Cu$_2$O, a typical compound of Cu$^+$ with $3d^{10}$ configuration, have been shown to be close to $\sim$3.3 and $\sim$2.3, respectively [25, 27]. Our results indicate that the $L_3/L_2$ intensity ratios for both Li$_2$CuO$_2$ and Li$_2$CuO$_{1.84}$ are nearly identical ($\sim$3.3 $\pm$ 0.1) and very similar to that of CuO, which suggests that all Li$_2$CuO$_{2-x}$ samples have an identical copper valence close to Cu$^{2+}$, and that the copper valence does not change with the level of oxygen vacancy within the range of $\delta$ studied in this work.

In addition to the observation of copper $L$-$2,3$-edge, two spectral peaks near $\sim$532 and 540 eV are assigned to the oxygen $K$-edge. Compared the O-$K$ edge peaks, no significant peak shift is found to indicate an oxygen valence change, although the intensity of 532 eV peak is shown reduced significantly for Li$_2$CuO$_{1.84}$. Similar 532 eV peak reduction has also been observed in several other transition metal oxides [26, 28, 29], which could be closely related to the oxygen non-stoichiometry.

3.5. Magnetic moment near the oxygen vacancy site
For the stoichiometric Li$_2$CuO$_2$ as a charge-transfer insulator [4], it is expected that the localized spin of Cu $3d^9$ following the Curie–Weiss law should have a Curie constant equal to 0.374 cm$^3$ K mol$^{-1}$, i.e., with a spin-only effective moment $\mu_{\text{eff}} = 1.732 \ \mu_B$ for $S = 1/2$ with $g = 2$. However, the Curie constants are found to increase

![Figure 5](image-url)
with oxygen vacancy level, so that the derived $\mu_{\text{eff}}$ values are larger than the expected spin-only value of 1.732 $\mu_B$ for $\delta = 0$, as shown in figure 6 and tables 3, 4. Although it is convenient to assign the excess contribution of $\mu_{\text{eff}}$ to the unquenched orbital contribution, or to the possible large moment transfer between Cu-$d$ and O-$p$ orbitals qualitatively [7], a quantitative magnetic moment analysis is expected. Moreover, if we consider that all detected spins are coming only from copper, then an oxygen vacancy is expected to create the effect of an n-type electron on the unquenched orbital contribution, or to the possible large moment transfer between Cu-$d$ and O-$p$ orbitals. Since the Seebeck coefficients measured between 300 and 650 K (figure 5(b)) indicate that the doped carrier for Li$_2$CuO$_{2-\delta}$ ($\delta \approx 0.16$ and 0.29) is p-type, the localized and unpaired electrons may generate two localized spins of $\mu$ at higher $\delta$, as predicted by the equation of

$$C_{\text{Cu}} = \frac{N_c (1.732 \mu_B)^2}{3k_B} (1 - 2\delta) = 0.374(1 - 2\delta),$$  

as shown in figure 6, where $N_c$ is the Avogadro number and $k_B$ is the Boltzmann constant. Unexpectedly, the ionic model prediction for $C(\delta)$ has been shown failed to describe the experimental results correctly, as illustrated in figure 6.

Since a molecular model using hybridized Cu-$d$ and O-$p$ orbitals is required to describe the physical properties of Li$_2$CuO$_{2-\delta}$ correctly, as hinted by the spin-polarized local density approximation studies [7], we propose that based on a molecular orbital model of Li$_2$CuO$_{2-\delta}$ with oxygen vacancy existence, each O- vacancy may donate at most two electrons (holes) to the system being either itinerant as free charge carriers or localized showing detectable spins. Since the Seebeck coefficients measured between 300 and 650 K (figure 5(b)) indicate that the doped carrier for Li$_2$CuO$_{2-\delta}$ ($\delta \approx 0.16$ and 0.29) is p-type, the localized and unpaired electrons (holes in the valence band) must have energy below the Fermi level and act as localized spins to follow the Curie–Weiss law.

Starting from the inspiring observation that $\mu_{\text{eff}}$ shows the spin-only value of 1.732 $\mu_B$ (i.e., $C = 0.374$ cm$^3$ K mol$^{-1}$ for $S = 1/2$ with $g = 2$) for $\delta \approx 0$ only (figure 6 and table 4), a modified Curie–Weiss law is proposed to correlate that every oxygen vacancy (0) may generate two localized spins of $S' = 1/2$, in addition to the existing Cu$^{+2}$ of $S = 1/2$. As a result, the Curie constant should include both contributions proportional to the localized spins corresponding to Cu and oxygen vacancy, i.e., $C_{\text{total}} = C_{\text{Cu}} + C_{\text{O}}$. The complete formula for the Curie constant can thus be expressed as

$$C_{\text{total}} = \frac{N_c (1.732 \mu_B)^2}{3k_B} (1 + 2\delta) = 0.374(1 + 2\delta),$$

i.e., the $C_{\text{total}}$ versus $\delta$ plot is expected to have a linear relationship with an intercept of 0.374 cm$^3$ K mol$^{-1}$ and a slope of 0.374 $\times$ 2. For the five experimental data points of $C_{\text{total}}$ versus $\delta$ plotted in figure 6, a linear regression returns a slope close to 0.374 $\times$ 2, as predicted by equation (6) within experimental error. In particular, only sample of zero oxygen vacancy shows the Curie constant being close to 0.374 cm$^3$ K mol$^{-1}$ as the spin-only value for $S = 1/2$ with $g = 2$. In addition, based on the successful verification of the re-interpreted Curie–Weiss law analysis expressed by equation (6), earlier qualitative assumption of single type copper spin of $S = 1/2$ with $g > 2$ (see tables 3 and 4) has been reinterpreted satisfactorily by both the copper spins of $S = 1/2$ with $g = 2$ and the localized spins of $S' = 1/2$ with $g = 2$ generated by oxygen vacancies quantitatively.

Figure 6. The Curie constant versus $\delta$ of Li$_2$CuO$_{2-\delta}$ obtained from the Curie–Weiss law fitting of spin susceptibilities. The two straight lines correspond to the two models of $C(\delta)$ described by equations (5) and (6), which clearly shows the validity of the proposed model described by equation (6).
Current results strongly support the fact that an additional magnetic moment can be generated from oxygen vacancies. These results are consistent with the proposals supported by the $\mu$SR and neutron scattering experiments\cite{6, 30}, although early studies ignored the possible existence of oxygen vacancies completely. Based on the current study, the sample studied by Chung et al showing an oxygen moment of $\sim0.11$ ($\mu_B$) may correspond to an oxygen vacancy level of at least $\delta\sim0.1$ \cite{6}, which is consistent to the growth atmosphere studies reported in this work also.

### 3.6. Molecular orbital model of localized spins

The proposed molecular orbital model of Li$_2$CuO$_2$ has also been examined using density functional theory (DFT) calculations, as shown in figure 7(a). DFT calculations, with the B3LYP functional and the 6–31G(d) basis set implanted in the Gaussian 09 package \cite{31}, have been performed to visualize the corresponding molecular orbitals and bonding characters of a single CuO$_4$ plaquette. The natural bond orbital analysis shows that Cu donates 4$s$, 4$p_x$, 4$p_y$, and 4$d_{z^2}$ atomic orbitals to form four hybridized Cu–O bonds, and the $s$, $p$, and $d$ orbitals have contributions of $\sim23\%$, $50\%$, and $27\%$ to each bond, respectively, in reasonable agreement with the requirement of an $sp^2d$ orbital hybridization, as illustrated in figure 7(a). The $\sigma$ bond formed with hybridized Cu–4$p^2d$ orbitals and O–2$p_{xy}$ orbitals in a CuO$_4$ square planar shape shows the HOMO state of a binding energy $\sim5.5$ eV. We find that the binding energy of the $\sigma$ bond between Cu–O is consistent with the excitation of $\sim5.4$ eV obtained from the resonant inelastic x-ray scattering study conducted previously \cite{4, 5}.

Based on the proposed molecular orbital model of an edge-sharing CuO$_2$ chain, we can examine the interesting consequence when one of the oxygen atom is removed from the chain, as illustrated in figure 7(b). Each oxygen vacancy is expected to create two dangling bonds (unpaired electrons) near the outer valence shell of Cu in proximity to the oxygen vacancy site. The oxygen vacancies can generate unpaired electrons at the excited state, but they are also trapped near the oxygen vacancy site, as reflected by the conducting property of a charge transfer insulator with detectable extra localized spins.

According to the proposed molecular orbital model of Li$_2$CuO$_{2-\delta}$ with oxygen vacancy existence, it is also interesting to note that to avoid the destruction of an edge-sharing CuO$_2$ chain, at most one in six oxygen atoms can be missing from every two adjacent edge-shared CuO$_4$ plaquettes (see figure 7(b)), i.e., $\delta = 0.33$, which has been supported by the fact that the largest $\delta$ is found near $\sim0.30$ before decomposition. Moreover, no Li$_2$CuO$_{2-\delta}$...
3.7. Emergent FM moment at low temperature

Although both $T_N$ and $\Theta$ of Li$_2$CuO$_2$ decrease, no significant $\delta$-dependence (table 4), it is noted that emerging FM moment is observed for samples with $\delta = 0$ below $\sim 3$ K, as shown in figure 8. In contrast, no FM moment is detectable for sample with $\delta \sim 0$, as verified by the non-hysteretic $M(T)$ behavior and the zero spontaneous moment below $\sim 3$ K (inset of figure 8). Similar FM moment has also been identified and confirmed with neutron scattering on the nominal Li$_2$CuO$_2$ sample without oxygen content verification, where the observed FM moment was proposed due to spin canting [3, 6].

Based on the confirmed 3D AF spin structure of antiferromagnetically coupled FM chains for Li$_2$CuO$_2$ [2, 6], as illustrated in figure 9(a), the magnetic moments near the randomly distributed oxygen vacancy sites must be sitting in the 1D (along the $b$-direction) and 2D (within $ab$-plane) FM environment constructed by the Cu$^{2+}$ spins. At high temperatures well above $T_N$, both the Cu and oxygen moments show PM behavior, as described satisfactorily by the revised Curie–Weiss law data analysis shown above. On the other hand, for temperatures well below $T_N$, the localized spins due to oxygen vacancies are distributed randomly and at the excited state, which are expected to order at a temperature much lower than $T_N$. In particular, the isolated spins near the oxygen vacancy sites are expected to be aligned by the local FM environment of the Cu$^{2+}$ spins in 1D and 2D (see figure 9), so that the total FM moment per $ab$-layer does not cancel out along the $c$-direction completely, similar to the ferrimagnetic ordering for the intermediate spins of Co$^{3+}$ which are built on the matrix of the A-type AF ordered Co$^{4+}$ spins below $T_N$ in Na$_{0.82}$CoO$_2$ [32]. We have estimated that the spontaneous FM magnetization at 2 K for $\delta \sim 0$ of $\sim 20$ emu mol$^{-1}$ (inset of figure 8) corresponds to about $0.1 \mu_B$ per oxygen, which agrees very well with the 0.11 $\mu_B$ estimated from neutron diffraction study [6]. The observation that sample of $\delta \sim 0$ does not show FM moment below $T_N$ is consistent with the proposed interpretation.

3.8. Exchange couplings estimated from $\chi(T)$

The 3D AF spin structure of Li$_2$CuO$_2$ has been solved by the neutron diffraction as antiferromagnetically coupled FM chains [2, 6], as illustrated in figure 9(a) with the on-site spin anisotropy along the $a$-direction, which has also been confirmed by the anisotropic magnetic susceptibilities shown in figure 4. The spin structure can also be categorized as an A-type 3D AF spin ordering of antiferromagnetically coupled planes with FM intra-plane ($ab$-plane) coupling. In the first order approximation for the magnet couplings among Cu$^{2+}$ spins, we may consider that the spin system is composed of antiferromagnetically coupled FM chains with three magnetic couplings, including the nearest neighbor intra-chain coupling $J$, the nearest-neighbor inter-chain coupling $J'$ along the $a$-direction, and the next nearest-neighbor inter-chain coupling $J''$ along the $a/2$-direction, as illustrated in figure 9(b). Following the derived spin susceptibility $\chi(T)$ expression of an 1D isotropic Heisenberg ferromagnet in the mean field approximation [33, 34],

$$\chi = \chi_{1D} [1 - 2 (z'' J'' + z' J')]$$  \( (7) \)
and

\[
\chi_{1D} = \frac{N g^2 \mu_B^2}{4 k_B T \left( 1 + \frac{J}{k_B T} \right)}. \tag{8}
\]

where \(z' = 2\) and \(z'' = 4\) correspond to the coordination numbers for \(J'\) and \(J''\), respectively, as shown in figure 9(b). With the defined \(A = \left[ \frac{z''}{z'} \right]\) ratio, the best fitting parameters of \(\chi(T)\) for \(\delta \sim 0.16\) and 0 are summarized in table 5. The signs of \(J'' - J' - J''\) indicate that the intra-chain coupling \((J)\) is FM, inter-chain coupling within the \(ab\)-plane \((J')\) is FM, and the inter-chain coupling along the diagonal direction \((J'')\) is AF, which is consistent to the neutron diffraction results as illustrated in figure 9(a) [2, 6]. These fitted intra-chain and inter-chain coupling constants are comparable to those obtained using the \(J_1-J_2-J_3\) model and molecular quantum chemistry calculation also [14, 23].

![Figure 9](image_url)

**Figure 9.** (a) The magnetic couplings \(J_i (i = 1–6)\) for the antiferromagnetically FM chains in \(\text{Li}_2\text{CuO}_2\). The spin structure is plotted based on the neutron diffraction results proposed by Sapina et al. [2] and Chung et al. [6]. (b) A simplified inter-chain coupling model of FM chains projected in the \(ac\)-plane is shown, where \(J'\) and \(J''\) roughly correspond to the averages of \(J_{34}\) and \(J_{56}\) shown in (a), respectively.

**Table 5.** The intra-chain \((J)\) and inter-chain \((J', J'')\) couplings for \(\text{Li}_2\text{CuO}_{2-\delta}\) single crystal samples of \(\delta \sim 0.16\) and 0 are extracted from the fitting of temperature-dependent spin susceptibility data with equation (7). The nearest-neighbor \(J'\) and the next-nearest-neighbor \(J''\) are depicted in figure 9(b) with defined ratio of \(A = \left[ \frac{z''}{z'} \right]\).
It is interesting to find that the fitted value of $A = \frac{J^F}{J^R}$ (table 5) is nearly equal to the ratio of $\frac{d_P}{d_i}$ as\footnote{Note that the actual inter-chain distance for $f^F$ is close to 5.24 Å for $f$ with a small angle cosine correction.}:

$$A = \left| \frac{J^F}{J^R} \right| \sim \frac{d_P}{d_i} \approx \frac{5.240 \text{ Å}}{3.662 \text{ Å}} = 1.431,$$

which implies that the inter-chain coupling strength is inversely proportional to the corresponding inter-chain distance. The implication that a coupling strength is inversely proportional to the distance is consistent to a magnetic dipole–dipole interaction type\footnote{For a spin system of weakly AF coupled spins with a 3D AF ordering below $T_N$, the emerging field-induced spins of FM coupling at high field could lead to a positive $\Theta$ upon Curie–Weiss law fitting, however, this 'pseudo $\Theta$' is ill-defined due to the violation of the conservation of spin size and number within the fitting temperature range.}.

Although the spin structure does not distinguish the origin of the magnetic interaction type, it should be noted that the intra-chain coupling must be of electronic exchange type due to the Cu–O orbital hybridization via Cu–O–Cu superexchange route, but the inter-chain coupling lacks such route in Li$_2$CuO$_2$. The bonding structure of Li$_2$CuO$_2$ are edge-sharing CuO$_2$ chains separated by the highly ionic interstitial arrays of Li (see figure 1), which supports the scenario of dipole–dipole type magnetic interaction among FM chains positively. In addition, based on the first-principles DFT electronic structure calculations by Xiang et al\footnote{It should be noted that in the evaluation of $J_i$ using the Heisenberg spin Hamiltonian, the ground state of a FM spin ordering corresponds to $J_i$ with a negative sign to indicate its lowered total energy. However, for an AF spin ordering, a minus sign is added before the Hamiltonian to counter the negative sign introduced by the term of $s_i \cdot s_m$, so that $|J|$ is negative for the AF coupling' is often claimed beforehand for the AF ground state.} [36], it is suggested that the next-nearest-neighbor interchain interactions could be responsible for the absence of spiral magnetic order.

### 3.9. Exchange coupling constants $J_i$ and $\Theta$

The magnetism of edge-sharing CuO$_2$ spin chain system is the foundation to the understanding of high $T_c$ cuprate superconductors of edge-sharing Cu–O plane\footnote{For the edge-sharing CuO$_2$ chain with nearest neighbor intra-chain $J_i$ of FM coupling, weaker but not negligible next nearest neighbor intra-chain $J_2$ of AF coupling has been identified from the spin chain Heisenberg model fitting experimentally, e.g., $\alpha = |J_2/J_1|$ ratio for the nominal Li$_2$CuO$_2$ was found in the range of 0.23–0.60 [10]. Such frustration phenomenon has been shown common in many edge-sharing spin chain}. Comparing the representative samples having edge-sharing CuO$_2$ chains, from $\text{Ca}_4\text{Cu}_5\text{O}_{10}$ (i.e., Ca$_4$Cu$_5$O$_{10}$ or Ca$_2$Y$_2$Cu$_5$O$_{10}$) with interstitial Ca/Y atomic arrays, to (La,Ca,Sr)$_2$Cu$_3$O$_7$ with sandwiched two-leg spin ladder layers\footnote{(La,Ca,Sr)$_2$Cu$_3$O$_7$ is tabulated in table 6, the reported $\chi(T)$ diverges at the positive $T_f$}, which is clearly inconsistent to the experimental results from $\chi(T)$ measurement (figure 4, i.e., no divergent behavior of $\chi(T)$ is observed near +50 K).

In general, the Weiss temperature $\Theta$ fitted from the Curie–Weiss law $\chi = \chi_0 + C/(T - \Theta)$ reflects the FM (positive) or AF (negative) tendency in the molecular field approximation\footnote{$\Theta$ value calculated by the molecular field treatment, as first introduced by Weiss successfully on the ferromagnet [45]. Smart extended it to the antiferromagnet as [22]}. For a ferromagnet with Curie temperature $T_c$, $\Theta = T_c$ and $\chi(T)$ diverges at $T_c$, i.e., $\frac{\chi}{T_c} = 0$. On the other hand, for an antiferromagnet with Néel temperature $T_N$, the $\Theta$ is negative and often $|\Theta| \approx T_N$. Unless there exists frustration condition like that found in the triangular or Kagome lattice, the positive and negative values of $\Theta$ must imply the ground states of FM and AF spin orderings at low temperature, respectively\footnote{Since the Néel temperature $T_N$ is not necessarily equal to $|\Theta|$ but depends strongly on the degree of frustration and spin anisotropy, the accuracy of $\Theta$ value estimated from an incomplete selection of $J_i$ is questionable in the molecular field approximation, otherwise the calculated values of $J_i$ and $\Theta$ become misleading. For example, by comparing the reported $J_i$ in the literature with those assigned in figure 9(a) and tabulated in table 6, the reported $\Theta$ estimated from an incomplete selection of fitting parameters of $J_i$ has led to a positive $\Theta$ as large as +50 K [10], which is clearly inconsistent to the experimental results from $\chi(T)$ measurement (figure 4), i.e., no divergent behavior of $\chi(T)$ is observed near +50 K.}. The degree of frustration has often been defined by the ratio of $|\Theta|/T_N$ [44].

$\Theta$ value can be evaluated by the molecular field treatment, as first introduced by Weiss successfully on the ferromagnet [45]. Smart extended it to the antiferromagnet as [22]

$$\Theta = \frac{S(S + 1)}{2k_B} \sum_i z_i J_i,$$

where $z_i$ is the number of the neighboring exchange coupling constant $J_i$. Since $\Theta$ represents the effective energy estimated from the sum of all neighboring exchange couplings $J_i$, it is expected that the sign of $\Theta$ must be negative for the antiferromagnet, otherwise, the $\chi(T)$ must diverge at a positive $\Theta$, similar to the ferromagnet that diverges at the positive $T_c = \Theta$. Since the Néel temperature $T_N$ is not necessarily equal to $|\Theta|$ but depends strongly on the degree of frustration and spin anisotropy, the accuracy of $\Theta$ value calculated with equation (10) relies sensitively on the $J_i$ assignment. It is required that all sizable $J_i$'s of correct corresponding $z_i$'s must be assigned correctly in the molecular field approximation, otherwise the calculated values of $J_i$ and $\Theta$ become misleading. For example, by comparing the reported $J_i$ in the literature with those assigned in figure 9(a) and tabulated in table 6, the reported $\Theta$ estimated from an incomplete selection of fitting parameters of $J_i$ has led to a positive $\Theta$ as large as +50 K [10], which is clearly inconsistent to the experimental results from $\chi(T)$ measurement (figure 4), i.e., no divergent behavior of $\chi(T)$ is observed near +50 K.
system, including Ca$_2$Y$_2$Cu$_4$O$_{10}$ which was claimed to be the first quasi-1D FM chain with $\alpha \sim 0.19$ and being closest to the criticality of $\alpha_c = 0.25$ [39]. On the other hand, Xiang et al have explored why is spiral spin ordering absent in Li$_2$CuO$_2$ based on the electronic structure calculations using first-principles DFT [36]. We propose that the inconsistent $\alpha$ values could be due to the different oxygen vacancy levels. In particular, considering a perfect FM spin chain, the occurrence of AF coupling among the next nearest neighboring copper spins is totally unexpected for coupling via electron exchange only. We propose that the frustrating nature of $J_2$ could be due to the randomly distributed localized spins created near the oxygen vacancy sites. A separate neutron scattering experiment to map the $\alpha = |J_2/J_1|$ as a function of $\delta$ for Li$_2$CuO$_{2-\delta}$ is required to examine this proposal.

4. Conclusions

In summary, we have examined the paramagnetic state of the magnetic susceptibilities of Li$_2$CuO$_2$ showing contribution from the magnetic moment near the oxygen vacancy site. The Curie–Weiss law fitting to the magnetic susceptibilities have been re-visited with a two-component Curie constant model quantitatively to suggest that the localized moment generated by the oxygen vacancies should add to the existing copper spins. The intra- and inter-chain coupling constants for Li$_2$CuO$_{2-\delta}$ have been evaluated with the modified model of an 1D Heisenberg ferromagnetic chain. In contrast to the intra-chain coupling of electronic exchange coupling, the inter-chain coupling has been deduced to be dipole–dipole interaction type.

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Table 6. The exchange coupling constants $J_i$ and $\Theta$ for Li$_2$CuO$_2$ obtained in this study are compared with those estimated by other methods. Due to the different $J_i$ labelings used (‘$-$’ sign represents FM coupling for the lowered energy state in the defined Heisenberg model Hamiltonian), we have converted all $J_i$ labelings into the labeling system shown in figure 9(a) in unit of Kelvin. For example, the $J_a$, $J_{ab}$, $J_b$, $J_c$, and $J_f$ defined in [3] correspond to $J_1$, $J_2$, $J_3$, $J_4$, and $J_5$ shown in figure 9(b), respectively.

| $J_i$(K) | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $\Theta$(K) | Remark |
|----------|-------|-------|-------|-------|-------|-------------|--------|
| $dJ_i$(Å) | 2.86  | 5.73  | 3.66  | 4.25  | 5.24  | 6.62        |        |
| $\alpha_i$ | 2     | 2     | 2     | 4     | 8     | 8           |        |
| $\delta \sim 0$ | −65  | −103  | 71    | $*$   | $J_i-J_i^*$ defined in equation (7) and figure 9 |
| $\delta \sim 0.16$ | −61  | −90   | 62    | $*$   | $\Theta_{a,b} \sim -32$ K from Curie–Weiss law fitting (table 3) |

| [36] | −163  | 85   | 0.58  | $*$  | −0.12 | $*$ Missed $J_a$, $\alpha$ assumed $J_a$ negligible |
| [23] | −135* | 94*  | NA    | NA   | NA    | $*$ Used Cu$_2$O$_2$ clusters molecular calculations |
| [14] | −100  | 40†  | †     | †    | †     | † $J_l \sim 16$ K is equivalent to the average of $J_{l=0}$ |
| [2]  | NA    | NA   | *     | *    | NA    | $*$ $J_a = 2J_l$ was argued from orbital overlap |
| [6]  | 2.88  | −1.92* | 2.16  | 0.96 | 4.86  | † $*$ All AF except $J_a$, $\Theta_{b,c} = -15$ K. |
| [10] | −218  | 76   | *     | 1*   | 9*    | +50 $*$ Defined $J_l(-J_l)$ and $J_l(-4J_l)$ but missed both $J_3$ and $J_4$ |
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