Correlation between weak ferromagnetism and crystal symmetry in Gd$_2$CuO$_4$-type cuprates

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Correlation between copper weak ferromagnetism (WF) and crystal structural symmetry of the Gd$_{2-x}$M$_x$CuO$_4$ (M = Bi or Tb; 0 ≤ x ≤ 0.5) systems is reported. Detailed powder x-ray Rietveld refinement analysis on Gd$_{2-x}$M$_x$CuO$_4$ shows a systematic variation of oxygen distortion angle α(Cu-O-Cu) with ionic size where the lattice layer mismatch lowers the crystal symmetry to an orthorhombic O' phase with pseudo-tetragonal lattice parameter a$_0$~b$_0$~5.508 Å. Weak ferromagnetic or canted antiferromagnetic order is the direct result of this oxygen distortion which causes a α-transfer Cu(3d$_{x^2}$-y^2)-O(2p$_x$)-Cu(3d$_{x^2}$-y^2) superexchange interaction in the CuO$_2$ plane with a non-180° coupling angle. The small WF saturation moment $m_s$ of ~2–6 × 10$^{-2}$ μ$_B$/Cu$^{2+}$ can be deduced from the copper moment $μ_s$(Cu$^{2+}$) canting angle $θ$= (π – α)/2 ~2–7°. Magnetic data and internal exchange field $B_{ex}$ estimation indicate that Cu$^{2+}$ WF saturation moment $m_s$(Cu$^{2+}$) decreases with larger Bi$^{3+}$ doping and increases with smaller Tb$^{3+}$ doping.

I. INTRODUCTION

For the high-$T_c$ cuprate systems, superconductivity always occurs near the metal-insulator transition boundary due to strong electron correlation. In the insulator side, copper magnetic moment $μ_s$(Cu$^{2+}$) ($d^9$, $s$ = 1/2) forms a three-dimensional (3D) long-range magnetic ordering through the quasi-2D σ-transfer Cu(3d$_{x^2}$-y^2)-O(2p$_x$)-Cu(3d$_{x^2}$-y^2) indirect superexchange interaction in the CuO$_2$ layers. It is observed that Cu spins in most cuprate insulators form an antiparallel antiferromagnetic (AF) arrangement below Néel temperature $T_N$(Cu) with zero saturation moment $m_s$(Cu$^{2+}$). However, a peculiar Cu weak ferromagnetic (WF) or canted antiferromagnetic (CAF) order with nonzero $m_s$ is observed below $T_N$(Cu)~260–285 K for the tetragonal $T'$ phase Gd$_2$CuO$_4$1-15 and a true AF order is recovered only at a much lower temperature of $T_N$(Cu)~20 K through spin reorientation. At temperature around 7–8 K, a possible 3D quasi to 2D crossover for Cu AF ordering is reported from neutron study before the Gd$^{3+}$ sublattice AF ordering of $T_N$(Gd)~6.5–7 K.15 At even lower temperature, a heat capacity broad shoulder followed with a peak near 2 K is observed,8 indicating complex magnetic phase diagram at low temperature due to Gd-Cu interaction.

Extensive magnetic and structural studies on Gd$_2$CuO$_4$(Refs. 1–15) and related compounds (Gd,M)$_2$CuO$_4$ (M = R$^{3+}$ rare earths, Ce$^{4+}$, Sr$^{2+}$, or Bi$^{3+}$)1,3,5,7,10,14 and metastable systems R$_2$CuO$_4$ (R = Y, Tb; Tm) and related compounds16-21 are reported. Since the occurrence of weak ferromagnetism requires an additional antisymmetric Dzyaloshinsky-Moriya-type exchange interaction term in otherwise symmetric Cu-O-Cu superexchange interaction, it is speculated that a slight oxygen distortion in the CuO$_2$ layer is necessary for Cu WF/CAF order in the Gd$_2$CuO$_4$-type cuprates.2,5,14 Although single-crystal x-ray diffraction on Gd$_2$CuO$_4$ gives a good fitting using the tetragonal $T'$-phase space group 14/mmm with Cu(0,0,0) and oxygen O(1)(0,1,0) in CuO$_2$ layer formed a perfect square-planar arrangement,1 large plane oxygen mean-square displacement $U_{eq}$ of 2.5 Å$^2$ at room temperature indicates that stable oxygen position may not be in the ideal (0,1/2,0) sites. Single-crystal neutron diffraction of $^{158}$Gd$_2$CuO$_4$ based on $T'$-phase structure shows that Cu moments order below $T_N$(Cu) to a basically AF structure with the propagation vector $k$ = ($1/2$, 0, 0). The Cu moments are oriented parallel to the [110] direction of the tetragonal basal plane.8,9 The inconsistency between weak ferromagnetism and x-ray/neutron-diffraction data indicates that a distorted $T'$ structure is necessary to account for the WF/CAF order. Recently, a neutron structural study at room temperature reports a long-range superstructure of the $T'$ phase in Gd$_2$CuO$_4$. The oxygen squares surrounding the Cu sites are found to rotate around the c axis by a small angle (~5°) which leads to a reduced orthorhombic symmetry (space group Agam).12 This structural deformation from $T'$ phase to O' phase is believed to be crucial for the occurrence of weak ferromagnetism.

In order to study the correlation between Cu weak ferromagnetism and crystal symmetry, we report here a detailed magnetic and powder x-ray Rietveld structural studies on Gd$_2$CuO$_4$ and related systems (Gd,M)$_2$CuO$_4$ (M = Bi or Tb).

II. EXPERIMENTS

The Gd$_{2-x}$Bi$_x$CuO$_{4+δ}$ (0 ≤ x ≤ 0.1) and Gd$_{2-x}$Tb$_x$CuO$_{4+δ}$ (0 ≤ x ≤ 0.5) samples with nominal composition were synthesized by solid-state reaction using high-purity Gd$_2$O$_3$ (99.99%), Bi$_2$O$_3$ (99.999%), Tb$_2$O$_3$ (99.9%) and CuO (99.9%) powders. Samples were thoroughly mixed and carefully calcined between 900–950 °C in air for 1 day with several intermediate regrindings. The calcined powders were then pressed into pellets and sintered in air at 1000 °C for 2 days and air quenched to room temperature. Oxygen content parameter $δ$ was determined from the standard iodometric titration method to be <0.003.

Powder x-ray Rietveld analysis data were obtained with a Rigaku Rotaflx 18-kW rotating anode diffractometer using
graphite monochromatized Cu-K\(_\alpha\) radiation with a scanning step of 0.02° (10-second counting time per step) in the 2\(\theta\) range of 20–100°. A RIQAS refinement program\(^{22}\) was used with inorganic crystal structure database (ICSD) and diffraction database (ICDD). The magnetization and magnetic susceptibility measurements were carried out with a Quantum Design MPMS or a \(\mu\)-metal shielded MPMS\(_2\) superconducting quantum interference device (SQUID) magnetometer down to 2 K in applied magnetic fields from 1 G–5 T.

### III. RESULTS AND DISCUSSION

In the \(R_2\text{CuO}_4\) insulating system (\(R=\text{Pr, Nd, Sm, Eu, Gd}\)), \(\text{Gd}_2\text{CuO}_4\) compound with the smallest Gd\(^{3+}\) ionic radius\(^{23}\) of 0.938 Å is the only member which shows weak ferromagnetism. If the oxygen distortion in the CuO\(_2\) layer is crucial for the formation of this peculiar WF/CAF order, then the cause of oxygen distortion must be closely related with the lattice layer mismatch between smaller (Gd-O)\(_2\) layers and CuO\(_2\) layer. Since all other \(R_2\text{CuO}_4\) compounds with larger rare earth \(R^{3+}\) ions show no sign of WF order, a doping in the Gd sites with larger non-rare-earth Bi\(^{3+}\) ions (0.96 Å) should also reduce the degree of oxygen distortion in the CuO\(_2\) layer.

In order to study the correlation between weak ferromagnetism and oxygen distortion, powder x-ray Rietveld structural refinement analysis was performed on the Bi\(^{3+}\)-doped compounds \(\text{Gd}_{2-x}\text{Bi}_x\text{CuO}_{4+\delta}\) (\(x=0, 0.05, \text{and } 0.07\)) at room temperature. Very small oxygen content parameter \(\delta\) of <0.003 determined from iodometric titration can be neglected. Based on the previous reported orthorhombic space group \(\text{Acam (Cmca, No. 64)}\) from neutron study with fully occupied atomic positions,\(^{12}\) the scale factor, lattice parameters, atom coordinates, and isotropic temperature factors were refined. For the undoped \(\text{Gd}_2\text{CuO}_4\) sample, the final step-pattern \(R\) factor \(R_p=6.99\%\), \(R_{wp}=7.07\%\), \(R_B=7.00\%\) (209 reflections) were obtained with goodness-of-fit parameter \(s\) of 2.82 for 4001 steps. The Bragg reflection \(R\) factor \(R_B\) was 7.00% for 209 reflections. The structural parameters for the orthorhombic \(O'\)-phase \(\text{Gd}_2\text{CuO}_4\) are listed in Table I and the refinement patterns are shown in Fig. 1. Good fitting between the calcu-

### FIG. 1

Experimental (dotted), calculated (curve) and difference of the powder x-ray-diffraction patterns of orthorhombic \(O'\) phase \(\text{Gd}_2\text{CuO}_4\) at room temperature.

### TABLE I. Structural parameters of orthorhombic \(O'\) phase \(\text{Gd}_2\text{CuO}_4\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Occupancy</th>
<th>(B_{iso}) (Å(^2))</th>
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</thead>
<tbody>
<tr>
<td>Gd</td>
<td>8d</td>
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<td>0</td>
<td>0.3495</td>
<td>1</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.54</td>
</tr>
<tr>
<td>O(1)</td>
<td>8f</td>
<td>0.2719</td>
<td>0.2240</td>
<td>0</td>
<td>1</td>
<td>0.77</td>
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<tr>
<td>O(2)</td>
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<td>1/4</td>
<td>0.2513</td>
<td>1/4</td>
<td>1</td>
<td>0.71</td>
</tr>
</tbody>
</table>

\(R\) factors: \(R_p=6.99\%\), \(R_{wp}=7.07\%\), \(R_B=7.00\%\) (209 reflections)

Selected interatomic distances (Å) and angle (degree)

- Cu-Cu: 3.895 Å
- Cu-O(1): 1.941 Å
- Cu-O(2): 3.550 Å
- Gd-Gd: 3.578 Å
- Gd-O(1): 2.510 Å
- Gd-O(2): 2.274 Å

Cu-O(1)-Cu distance: 169.1°
TABLE II. Structural parameters of undistorted tetragonal $T'-$phase model for Gd$_2$CuO$_4$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$B_{iso}$ (Å$^2$)</th>
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<tbody>
<tr>
<td>Gd</td>
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<td>0</td>
<td>0</td>
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<td>1</td>
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<tr>
<td>Cu</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.54</td>
</tr>
<tr>
<td>O(1)</td>
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<td>1/2</td>
<td>0</td>
<td>1</td>
<td>1.70</td>
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<tr>
<td>O(2)</td>
<td>4d</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>1</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Selected interatomic distances (Å) and angle (degree)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu</td>
<td>3.895</td>
<td>180°</td>
</tr>
<tr>
<td>Cu-O(1)-Cu</td>
<td>1.948</td>
<td></td>
</tr>
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</table>

The proposed correlation between weak ferromagnetic/ canted antiferromagnetic (WF/CAF) order and structural symmetry in the CuO$_2$ plane for temperature range $T_{N}(Cu)<T\leq T_{N}(Cu)<300$ K is shown in Fig. 3. The CuO$_2$ plane of the HT$O'$ phase is no longer a perfect square plane. The rotation/displacement of the O(1) 8(f)(x,y,0) squares around the Cu sites leads to two unequal Cu-O(1) bond lengths of $d_1=1.941$ Å and $d_2=1.972$ Å for Gd$_2$CuO$_4$ and a Cu-O(1)-Cu bond angle $\alpha$ of 169.1° instead of 180°. Since the Cu-3$d_{z^2-\gamma^2}$ orbital is anisotropic, in order to achieve maximum wave-function overlap with nonorthogonal AF coupling between Cu-3$d_{z^2-\gamma^2}$ and O-2$p_{\sigma}$ orbitals, the Cu orbital and thus its magnetic moment $\mu$(Cu$^{2+}$) must cant a small angle $\theta=(\pi-\alpha)/2$ of 5.4° away from the orthorhombic [100]/[010] direction or the pseudotetragonal [110] direction.
tion observed from preliminary low-temperature neutron data.\(^6\) This creates an additional antisymmetric Dzyaloshinsky-Moriya-type exchange interaction term and the effective interaction between Cu spins in the CuO\(_2\) plane is still the 2D \(\sigma\)-transfer type but with an angle \(\alpha\text{(Cu-O(1)-Cu)}\neq 180^\circ\). Below 3D ordering temperature \(T_{N}(\text{Cu})\) of 282 K, the canted antiferromagnetic (CAF) alignment will create a net WF saturation moment \(m_s\text{(Cu}^2^+)\) = \(\mu\text{(Cu}^2^+)/\sin \theta\). If the usual neutron-derived copper moment of \(\mu\text{(Cu}^2^+)\sim 0.3–0.5\mu_B\) is used,\(^24\) then the saturation moment \(m_s\) of \(\sim 3–5 \times 10^{-2}\mu_B/\text{Cu}^2^+\) is derived using room temperature canting angle \(\theta\) of 5.45\(^\circ\).

If the WF saturation moment \(m_s\) is closely related to the Cu-O(1)-Cu bonding angle \(\alpha\), a systematic variation of WF order can then be deduced for the Bi-doped system through the Rietveld refinement studies. The temperature dependence of low-field magnetization with estimated magnetic canting angle \(\theta\) for the Bi-doped Gd\(_{2-x}\)Bi\(_x\)CuO\(_4\) (\(x = 0, 0.05, 0.07,\) and 0.1) polycrystalline bulk samples in a low applied field \(B_{a}\) of 1 G. The temperature dependence of magnetized magnetic moment with estimated magnetic canting angle \(\theta\) of the Gd\(_{2-x}\)Bi\(_x\)CuO\(_4\) system (\(x = 0, 0.05,\) and 0.07) from high-field \((B_a>B_{sat})\) magnetic data.

Doping can be clearly seen. The low field of 1 G is used in order to minimize the interference from large Gd\(_{3}^+\) moment \(\mu\text{(Gd}^{3+})\sim 7\mu_B\). With room-temperature paramagnetic magnetization \(m\) (300 K) of only \(\sim 2 \times 10^{-5}\mu_B\) per formula unit in 1 G large magnetized moment of \(\sim 1–2 \times 10^{-3}\mu_B/\text{f.u.}\) below \(T_{N}(\text{Cu})\) is mostly from the magnetized WF domain with nonzero copper saturation moment \(m_s\text{(Cu}^2^+)\) in each domain. \(T_N\text{(Cu)}\) decreases from 282 K for \(x = 0\) to 270 K for \(x = 0.05,\) 258 K for \(x = 0.07,\) and 256 K for \(x = 0.1,\) The sharp decrease of magnetized moment below \(T_N\text{(Cu)}\) around 22–24 K in 1 G indicates a Cu moment spin reorientation to the true AF ground state with zero saturation moment \(m_s\). The Gd\(_{3}^+\) moments eventually order antiferromagnetically at \(T_{N}\) of 7 K for \(x = 0,\) and 6.4 K for \(x = 0.1.\)\(^14\)

The copper WF/CAF saturation moment \(m_s\text{(Cu}^2^+)\) is difficult to be determined directly from high-field magnetization measurements even with a well oriented single crystal due to the interference of large Gd\(_{3}^+\) moment \(\mu\text{(Gd}^{3+})\) and the nature of copper weak ferromagnetism, where the WF saturation moment \(m_s\) is always smaller than the copper moment \(\mu\text{(Cu}^2^+)\) of \(\sim 0.3–0.5\mu_B.\)\(^24\) However, one can estimate the WF internal exchange field \(B_{int}\) created by the saturation moment \(m_s\). For this purpose, inverse molar magnetic suscept-

![FIG. 4. Temperature dependence of magnetized magnetic moment per formula unit \(m(T)\) with estimated magnetic canting angle \(\theta\) for larger Bi\(_{3}^+\)−doped Gd\(_{2-x}\)Bi\(_x\)CuO\(_4\) (\(x = 0, 0.05, 0.07,\) and 0.1) polycrystalline bulk samples in a low applied field \(B_{a}\) of 1 G.](Image)

![FIG. 5. Inverse molar magnetic susceptibility \(\chi_{m}^{-1}(T)\) for Gd\(_{0.95}\)Bi\(_{0.05}\)CuO\(_4\) in various applied fields of 1 G, 100 G, 1 kG, 2 kG, 1 T, and 5 T. The solid line is a Curie-Weiss fit with negative intercept \(\theta_p\).](Image)

![FIG. 6. Estimated WF internal exchange field \(B_{int}(T)\) with estimated magnetic canting angle \(\theta\) of the Gd\(_{2-x}\)Bi\(_x\)CuO\(_4\) system (\(x = 0, 0.05,\) and 0.07) from high-field \((B_a>B_{sat})\) magnetic data.](Image)

![FIG. 7. Temperature dependence of magnetized magnetic moment \(m(T)\) with estimated magnetic canting angle \(\theta\) for smaller Tb\(_{3}^+\)−doped Gd\(_{2-x}\)Tb\(_x\)CuO\(_4\) system (\(x = 0, 0.1,\) and 0.5) in 1 G.](Image)
tivities $\chi_m^{-1}(T)$ for a typical Bi-doped Gd$_{1.95}$Bi$_{0.05}$CuO$_4$ compound in various applied fields $B_a$ from 1 G–5 T are shown collectively in Fig. 5. $T_N$(Cu) of 270 K and $T_N$(Gd) of 6.5 K are nearly field independent. $T_N$(Cu) decreases from 24 K in 1 G to 20 K in 100 G, 12 K in 1 kG, 8.5 K in 2 kG, ~7 K in 1 T, and merges with $T_N$(Gd) in 5 T. Since the weak internal field is only in the order of $10^2$–$10^3$ G, the paramagnetic Gd$^{3+}$ moment contribution increases its domination such that the magnetic susceptibility, in higher field can be approximately fitted with in a Curie-Weiss form of $\chi_m = C/(T + \theta_p)$. For $B_a = 5$ T, the Curie constant of 15.9 cm$^3$/mol gives an effective Gd$^{3+}$ moment $\mu_{\text{eff}}$ of 7.99 $\mu_B$, which is close to the free ion $\mu_{\text{eff}}$(Gd$^{3+}$) of 7.94 $\mu_B$ if the small Cu$^{2+}$ ordered moment is neglected. The negative Curie-Weiss intercept $\theta_p$ of 17.8 K is larger than $T_N$(Gd) or $T_N$(Cu) of ~6.6 K. The temperature dependence of the internal exchange field $B_{\text{int}}(T)$ for $T > T_N$(Cu) can then be estimated using the formula

$$B_{\text{int}}(T) \sim [M(T,B_a)/\chi_m(T)] - B_a,$$

where magnetization $M(T,B_a)$ is measured in an applied field $B_a$~1–2 kG$>$B$_{\text{int}}$ and the Curie-Weiss susceptibility $\chi_m = C/(T + \theta_p)$ from higher field (~1–5 T) fitting is used. The estimated WF internal field $B_{\text{int}}$ for the Gd$_{1-x}$Bi$_x$CuO$_4$ system ($x = 0$, 0.05, 0.07) with estimated magnetic moment canting angle $\theta$ is shown in Fig. 6. The internal field is temperature dependent where maximum $B_{\text{int}}$ observed decreases from around 720 G for $x = 0$, to 500 G for $x = 0.05$ and 150 G for $x = 0.07$. For $T \sim T_N$(Cu)$\sim 10$ K at $B_a$ of ~2 kG, $B_{\text{int}}$ decreases sharply to zero due to the disappearance of copper saturation moment in the true AF state. Residual $B_{\text{int}}$ observed above $T_N$(Cu) may be due to the simplified formula used or from the intrinsic 2D short-range quantum spin fluctuation. The small internal field of 720 G observed for Gd$_3$CuO$_5$ is consistent with this small saturation moment $m_s$. Since the structural-related canting angle $\theta(T)$ is temperature dependent, the saturation moment $m_s(T)$ in each WF domain wall and the internal exchange field $B_{\text{int}}(T)$ will also be temperature dependent. For temperature below $T_N$(Cu), a WF/CAF to AF magnetic transition should be accompanied with an orthorhombic to tetragonal (or high-temperature HTO$'$ phase to low-temperature LTT$'$ phase) structural transition with $\theta = 0$ in the true AF state. A detailed low-temperature magnetic and structural study is necessary to confirm this speculation. Table III shows the correlation between the magnetic and structural variation for the Gd$_{2-x}$Bi$_x$CuO$_4$ system. With slightly larger Bi doping ($r_{\text{Bi}}^{3+} = 0.96$ Å$> r_{\text{Gd}}^{3+} = 0.938$ Å), the orthorhombic lattice parameter $a_0$ and $b_0$ increase monotonically with progressive Bi doping as expected. The unit-cell volume $V = a_0b_0c_0$ increases from 360.7 Å$^3$ for $x = 0$ to 361.2 Å$^3$ for $x = 0.07$. The longer Cu-O(1) bond lengths $d_1$ and $d_2$ during Bi doping decrease wave-function overlap and $T_N$(Cu) from 282 K for $x = 0$ to 258 K for $x = 0.07$. However, with large Bi doping, the lattice layer mismatch between the smaller [(Gd, Bi)$_2$O$_3$] layers and CuO$_2$ plane is reduced, which results in a less oxygen distortion in the CuO$_2$ plane. Smaller oxygen distortion restores the Cu-O(1)-Cu bond angle $\alpha$ from 169.1° for $x = 0$ to 175.2° for $x = 0.07$. The resulting smaller canting angle $\theta = (\pi - \alpha)/2$ of 2.4° for $x = 0.07$ as compared with 5.5° for $x = 0$ reduces the estimated copper WF saturation moment $m_s$ from 4.8×$10^{-2}$ $\mu_B$ to 2.1×$10^{-2}$ $\mu_B$ using $\mu_{\text{eff}}$(Cu$^{2+}$)$-0.5 \mu_B$, and the maximum internal field $B_{\text{int}}(\text{max})$ from 720–150 G.

Since Gd$_3$CuO$_5$ is the smallest stable compound in the $R_2$CuO$_4$ system under ambient pressure sample preparation condition, based on the similar ionic size consideration, a doping in the Gd sites with smaller rare-earth $R^{3+}$ ions should increase the oxygen distortion in the CuO$_2$ layer. The temperature dependence of magnetization for smaller Tb$^{3+}$-doped system Gd$_{2-x}$Tb$_x$CuO$_4$ ($x = 0$, 0.1, and 0.5) is shown in Fig. 7. A monotonical increase of magnetized magnetic moment per formula unit $m(T)$ as well as canting angle $\theta$ with progressive smaller Tb$^{3+}$ ion (0.923 $\mu_B$) doping confirms our speculation on the correlation between weak ferromagnetism and oxygen distortion. A low field of 1 G is again used to minimize the Gd$^{3+}$/Tb$^{3+}$ contribution. Large WF contribution of magnetized moment of $1-7 \times 10^{-2} \mu_B$/Cu$^{2+}$ is observed below $T_N$(Cu) 282 K for $x = 0$ and 276 K for $x = 0.1$ and 0.5. Spin-reorientation temperature $T_m$(Cu) remains around 22 K for all compounds. The rare earth (Gd/Tb) sublattice orders antiferromagnetically at $T_N(R)$ of 6.2 K for $x = 0.1$ and 0.5.

In conclusion, detailed Rietveld refinement gives a direct correlation between the oxygen distortion angle $\alpha$(Cu-O-Cu) and the ionic size in the (Gd,M)$_2$CuO$_4$ cuprates. For smaller (Gd, M) ions, tetragonal $I'\prime$ phase is no longer stable at room temperature and lattice layer mismatch lowers the symmetry to an orthorhombic O$'$ phase. Weak ferromagnetic or canted antiferromagnetic (WF/CAF) ordering below $T_N$(Cu) is the direct result of this oxygen distortion angle that causes a non-180° Cu-O-Cu coupling. True antiferromagnetic ordering was restored only at temperature below $T_N$(Cu).

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