Strong magnetoelastic coupling and unconventional electric polarization in multiferroic $\text{Li}_{0.99}\text{Cu}_{0.01}\text{CrO}_2$: A case of 2D triangular lattice antiferromagnet

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This work reports an experimental study on the temperature dependence of the structural parameters of LiCrO_2 (LCO) and $\text{Li}_{0.99}\text{Cu}_{0.01}\text{CrO}_2$ (LCCO) by using synchrotron x-ray diffraction technique. A significant magnetoelastic coupling is revealed by the anomalies observed in lattice parameters at the magnetic and electric phase transitions, apparent as step-like features in both Cr–O, Li–O bond lengths as well as O–Cr–O bond angles. Magnetic, dielectric, and electric polarization measurements reveal the antiferromagnetic and antiferroelectric (AFE) ordering at 119 and 61 K, respectively for LCCO. Interestingly, a fairly large uncompensated spontaneous electric polarization appears for LCCO in contrast to nearly compensated polarization value for LCO below the AFE ordering. This is correlated to the structurally driven enhancement (~ 4 times) of the interlayer Cr–O–Li/Cu–O–Cr superexchange interaction for LCCO. We argue that strong magnetoelastic coupling holds the key for the observed uncompensated spontaneous electric polarization in LCCO.

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Coupling between structural and magnetic functionalities in strongly correlated systems, the so called magnetoelastic coupling, is one of the foremost topics in the physics of materials that are fundamentally and technologically promising.¹ This phenomenon, a subset of the recent terminology of multiferroicity,^{2–5} attracts renewed attention after the discovery of colossal magnetoresistance.⁶ This coupling usually appears as a structural change at the magnetic transition or change in magnetic functionalities at the structural transition. In such a backdrop of versatile abundance of scientific studies,^{2–5} the evidence of magnetoelasticity with isostructural transition is quite rare, while those inheriting large atomic displacement are even rarer.^{7,8} In the following study we observe a fairly large oxygen displacement at an isostructural transition, giving rise to ~ 0.02 Å step-like increase in Cr–O bond length as obtained from the x-ray diffraction studies using high-flux synchrotron source in a two-dimensional (2D) triangular lattice antiferromagnet (AFM), $\text{Li}_{0.99}\text{Cu}_{0.01}\text{CrO}_2$ (LCCO). Most interestingly, this displacement enhances remarkably (~ 10 times) due to minimal Cu doping in LiCrO_2 (LCO).

The ordered rock salt structure with $R\bar{3}m$ space group of LCO attracts significant attention for the unique 2D triangular lattice structure. As evident in Fig. 1(a) the layers consisting of Cr–O–Li–O–Cr atoms are stacked along c -axis. Notably, the intralayer Cr ions form typical 2D triangular lattice as displayed in Fig. 1(b). The intralayer exchange interaction (J) dominates over weak interlayer interaction (J') mediated through the long Cr–O–Li–O–Cr superexchange path.⁹ The dominant 2D intralayer interaction effectively leads to the AFM transition at $T_N \approx 62$ K.^{10–14} The Cr atoms surrounded by oxygen octahedra displayed in Fig. 1(d) exist in Cr^{3+} state with $S = 3/2$. The AFM ordering below T_N , however, produces a ground state characterized by strong spin frustration and a proper screw type [Fig. 1(c)] 120° spin structure in the (110) plane.^{15,16} The double- Q 120°

FIG. 1: (Color online) (a) Ordered rock salt structure. The broken paths at the bottom indicates the superexchange paths between interlayer Cr atoms. (b) 2D triangular lattice formed by Cr atoms. (c) Proper screw spin structure in (110) plane. (d) CrO_6 octahedron displaying O–Cr–O bond angles.

structure with nonequivalent wave numbers, $q = (\frac{1}{3}\frac{1}{3}0)$ and $(-\frac{2}{3}\frac{1}{3}\frac{1}{3})$ were characterized by alternate stacking of Cr^{3+} layers with opposite vector spin chirality along the c -axis. Although spontaneous electric polarization was not significantly observed below T_N , the strong signature of a peak was evident in the dielectric constant at T_N .¹⁷ This feature was attributed to the possible antiferroelectric (AFE) transition directed by the alternate stacking of the Cr^{3+} layers with opposite vector spin chirality.¹⁷

According to spin-current model or inverse Dzyaloshinskii-Moriya (D-M) model,¹⁸ a proper-

screw magnetic structure cannot cause ferroelectricity, although ferroelectricity has been occasionally found in few compounds such as ZnCr_2Se_4 ,^{19–21} CuCrO_2 ,¹⁷ and $\text{CuFe}_{1-x}\text{Al}_x\text{O}_2$ having such a magnetic structure.^{22–24} These interesting issues have been reviewed recently in considerable detail.^{25,26} However, the possible origin of AFE state in LCO has not been addressed adequately. It was although anticipated that the intricate AFE state might be ascribed to the interlayer electrostatic and/or spin-lattice interaction and a possible lattice distortion was proposed to be the factor behind this electric ordering at T_N .¹⁷

In the present investigation, we demonstrate that the interlayer structural distortion at T_N is imperative for the observed AFE state and multiferroicity in LCO. Interestingly, an unconventional AFE ordering with a fairly large spontaneous electric polarization is revealed due to minor doping of Cu in LCCO in contrast to nearly compensated electric polarization in LCO below the AFE ordering.¹⁷ We note that magnitude of spontaneous electric polarization in LCCO is comparable to the value reported for ferroelectric AgCrO_2 having delafossite structure.¹⁷ Recently, a similar evidence of uncompensated spontaneous electric polarization was reported in RMn_2O_5 series where Jahn-Teller distortion led to the displacement of Mn^{3+} ions giving rise to the uncommon canted AFE state.^{27–29} Here, we display another unique case of uncompensated spontaneous electric polarization in a dissimilar system apart from the involvement of Jahn-Teller effect. Rather, a strong magnetoelastic coupling without orbital degeneracy in LCCO holds the key for the observed unconventional electric ordering.

Polycrystalline specimens, LiCrO_2 and $\text{Li}_{0.99}\text{Cu}_{0.01}\text{CrO}_2$ are prepared by solid state reaction.⁹ Stoichiometric proportion of Li_2O_3 (Aldrich, 99.99%), Cr_2O_3 (Aldrich, 99.9%), and CuO (Aldrich, 99.9%) powders are mixed thoroughly, pressed into a pellet, and sintered at 800°C for 48 hours in air with an intermediate grinding. Single phase chemical composition is confirmed by x-ray diffraction studies at room temperature recorded in a SEIFERT x-ray diffractometer (Model: XRAY3000P) using $\text{Cu K}\alpha$ radiation. This is further confirmed by the synchrotron x-ray powder diffraction studies measured in the range 10–300 K at P07 beam line of Petra III, Hamburg, Germany at a wavelength of $0.1347\text{ \AA}$ (92 keV). The synchrotron powder diffraction data are analyzed with the Rietveld technique using a commercially available software MAUD (materials analysis using diffraction). Electron diffraction (ED) and element mapping analysis were done using Transmission Electron Microscopy (TEM) of JEOL JEM, 2100F field emission microscope equipped with an energy dispersive x-ray spectrometer. Heat capacity (C) is measured using a home built set up in the range 8–200 K.³⁰ Dielectric constant are measured on the compressed ($\sim 6.0 \times 10^9\text{ Kg/m}^2$) powder specimens in the range 10–300 K using an E4980A LCR meter (Agilent Technologies, USA) equipped with a cryocooler

FIG. 2: The ZFC-FC magnetization for LCO (a) and LCCO (d). Left and right insets of (d) show the dM/dT and ZFC magnetization with T . Thermal variation of heat capacity (C) for LCO (b) and LCCO (e), highlighting the region around the peaks. The corresponding insets show the thermal variation in a wide temperature range. The real part of dielectric constant (ϵ') for LCO (c) and LCCO (f) measured at 5 kHz. (g) Thermal variation of electric polarization (P) for LCO and LCCO. Inset shows thermal variation pyroelectric current (I_p) for LCCO. The dashed straight line indicate position of T_{AFE} .

(JANIS, USA). The pyroelectric current (I_p) is recorded in an electrometer (Keithley, model 6517B) at a constant temperature sweep rate (4.0 K/min) and integrated with time for obtaining temperature variation of electric polarization (P). For measuring polarization a poling electric field (500 kV/m) is applied during cooling process and removed just before the measurement of I_p in the warming mode. Electrical contacts are fabricated using an air drying silver paint. The dc magnetization is measured by a commercial magnetometer of Quantum Design (MPMS, evercool).

Thermal variation of zero-field cooled (ZFC) and field-cooled (FC) magnetization for LCO and LCCO are displayed in Figs. 2(a) and 2(d), respectively. In accordance with the previous reports^{9,31,32} a broadened maximum is evident for LCO in both the ZFC and FC magnetization close to 61 K (T_N), below which the AFM ordering starts. Temperature variation of C displays a kink at T_N in Fig. 2(b) as it was reported for LCO.^{9,17} The nature of ZFC and FC curve in the thermal variation are no-

FIG. 3: (a) Magnetic hysteresis loops at 6 K for LCO and LCCO. (b) Temperature variation of coercivity (H_C).

ticeably modified due to minimal doping of Cu in LCCO compared to LCO as displayed in Fig. 2(d). An extraordinary large FC effect is noticed for the measurement at 100 Oe. The maximum in the ZFC magnetization shifts towards a much higher temperature (~ 119 K) as evident in the right inset of Fig. 2(d) and is associated with a very weak and broadened signature around 61 K, as more clearly depicted in the dM/dT vs T plot of the left inset. We note that the peak around 119 K in LCCO is close to the magnetic ordering temperature at 130 K for CuCr_2O_4 .^{33,34} Although transition temperatures in both cases are near, signature of transitions in the ZFC magnetization are markedly different. CuCr_2O_4 displayed a step-like increase in ZFC magnetization below 130 K, in contrast to the peak observed in LCCO. To rule out the possible impurity phase of CuCr_2O_4 , we examine extensive x-ray powder diffraction studies using high flux synchrotron radiation, electron diffraction, and element mapping analysis using TEM as described below. However, in all the characterizations any impurity phase of CuCr_2O_4 could not be figured out. Thermal variation of C does not reveal any convincing signature around 119 K, although a prominent kink is observed at 61 K as shown in Fig. 2(e) for LCCO. This transition at 61 K is evident in the thermal variation of real component of dielectric constant (ϵ') for LCO and LCCO as shown in Figs. 2(c) and 2(f), respectively. Additionally, a weak and broadened signature is noted in $\epsilon'(T)$ close to 119 K for LCCO as depicted by an arrow in Fig. 2(f). The results indicate possible magnetoelectric coupling at both the transition temperatures in LCCO.

Unlike magnetization results, $\epsilon'(T)$ exhibits almost similar peaks at 61 K for both the compounds. Quite a sharp peak in $\epsilon'(T)$ typically indicates fluctuation of P at T_N , which was suggested due to AFE ordering (T_{AFE}) in LCO.¹⁷ To conclude the origin of similar strong fluctuation of electric polarization, the pyroelectric current (I_p) is recorded with T in the warming mode for LCCO. A sharp deep in $I_p(T)$ is observed in the thermal variation, at which the peak is noticed in $\epsilon'(T)$ as evident in the inset of Fig. 2(g). Time integrated I_p provides the electric polarization (P) which is depicted with T for LCCO and compared with LCO in Fig. 2(g). Interestingly, non-zero P is noticed at low temperature for LCCO, unlike very low P observed for antiferroelectric LCO.¹⁷ With

decreasing T , P displays a broadened maximum followed by a decreasing trend instead of monotonous increase or stable P -value typically found for ferroelectric ordering. It may, however, be noted that the magnitude of P is quite large compared to that of LCO and comparable to the saturated P -value for ferroelectric AgCrO_2 .¹⁷ The similar uncompensated P involving AFE ordering has been rarely reported in very few systems.^{27–29} A kind of intricate canted AFE state has been proposed in RMn_2O_5 .^{27–29} Our observation also indicates a kind of AFE ordering below T_{AFE} close to 61 K with a fairly large uncompensated electric polarization. However, probable origin of such unconventional AFE ordering, as discussed elsewhere in the text, is totally different from that proposed in RMn_2O_5 series.^{27–29}

In accordance with the previous reports^{9,31,32} magnetization curve ($M-H$) for LCO exhibits typical linearity passing through origin in the AFM ground state as shown in Fig. 3(a) by the continuous curve. Notably, a coercivity (H_C) appears in LCCO as displayed at 6 K in Fig. 3(a) by the broken curve. The H_C still survives at ~ 135 K, higher than T_N , as depicted in Fig. 3(b), and it increases with decreasing temperature. The slope of increase of H_C changes close to T_{AFE} followed by another change around 20 K. If we consider that Cu ion in LCCO does not contribute to the moment value as realized in CuCrO_2 ,¹⁷ the increase of high field magnetization along with the appearance of H_C indicates emergence of uncompensated moment ascribed to the Cr moment. It may be presumed that appearance of coercivity ascribes to any impurity phase as a result of minor Cu doping, although x-ray synchrotron results, ED pattern, and element mapping analysis do not reveal trace amount of impurity phase in LCCO. However, such a large value of $H_C \approx 3.7$ kOe at 6 K compared to $H_C (\approx 0.5$ kOe at 2 K) of FM CuCr_2O_4 ,³³ the most likely impurity phase if exists in LCCO, rules out the possible existence of impurity phase in LCCO. This issue has to be confirmed using thorough neutron studies at low temperature which is beyond the scope of this work.

The structural properties are meticulously investigated by x-ray powder diffraction studies using high flux synchrotron source over a wide temperature range from 10–300 K for both the compounds. The microstructural parameters as a function of temperature are obtained from careful analysis of the diffraction patterns using Rietveld refinement. The refinement is done using $R\bar{3}m$ space group with atomic positions, Li/Cu ($0\ 0\ \frac{1}{2}$), Cr ($0\ 0\ 0$), and O ($0, 0, z$) for both the compounds in the whole temperature range. Representative examples of the fits (continuous curves) with the experimental data (symbols) at 30 (insets) and 300 K are displayed in Figs. 4(a) and 4(b) for LCO and LCCO, respectively. The difference plot is shown at the bottom of each plot, indicating single phase of the compound. As evident in the difference plot of LCCO any convincing signature of minor component of CuCr_2O_4 could not be detected. Moreover, reasonably small values of the reliability pa-

FIG. 4: (Color online) Rietveld refinement of x-ray powder diffraction patterns (black symbols) at 30 (insets) and 300 K for (a) LCO and (b) LCCO. Solid curve demonstrates the fit. The plot at the bottom is the residual. (c) The ED pattern for LCCO displaying (110) plane. Element mapping analysis of Cr (e) and Cu (f) on the selected area of LCCO as highlighted in (d). (g)-(j) show T variations of a , c , V , and normalized integrated intensities of (003) peak for both. Insets of (h)-(j) highlight the data close to the transitions.

rameters R_w (~ 3.54), R_{exp} (~ 3.43), and χ^2 (~ 1.03) assure the authenticity of the refinement. To characterize further, the ED pattern and element mapping analyses are performed. One of the representative examples of ED pattern is depicted in Fig. 4(c). As evident in this ED pattern, the other ED patterns also display planes corresponding to $R\bar{3}m$ space group of LCCO. The results of the element mapping of Cr and Cu for the selected area of two particles as depicted in Fig. 4(d) are displayed in Figs. 4(e) and 4(f), respectively. The homogeneous distribution of Cr and Cu further confirms homogeneity of the structural phase with a single phase crystalline structure. Thus, we rule out the possibility of minor impurity phase of CuCr_2O_4 in LCCO. Thermal variation of the lattice constants a and c are shown in Figs. 4(g) and 4(h), respectively, for LCO and LCCO. Error bars are given in the plot. Since error bars are smaller in size than the size of the symbols, it is not visible in the plot. Temperature variations of a nearly overlaps close to T_N and T_{AFE} . Conversely, thermal variation of c differs signifi-

FIG. 5: (Color online) (a)–(c) and (d)–(f) show T variation of Cr–O, Li–O bond lengths, and O–Cr–O bond angles for LCO and LCCO, respectively.

cantly through out the temperature range. Interestingly, the negative thermal expansion is observed below T_N at 61 K and 119 K for LCO and LCCO, respectively. Additionally, a small anomaly is observed at T_{AFE} in $c(T)$ for LCCO. In the inset of the figure the regime of negative thermal expansion is mainly highlighted. The T variation of unit cell volume (V) is displayed in Fig. 4(i) for both the compounds, showing a monotonous decrease with decreasing T , while the inset shows the signatures of T_N and T_{AFE} . Integrated intensity of (003) peak normalized by the intensity at 300 K is depicted in Fig. 4(j) for both the compounds, showing a minimum with T for both the compounds. Importantly, the anomalies are evident in the curves as evident in the inset. The results are consistent with the observed anomaly or sharp change in T variation of the integrated intensity at the ferroelectric transition in the literature.^{35–37}

We note that Cr^{3+} ions form equilateral octahedra which is depicted as a representative example in Fig. 1(d). Two kinds of O–Cr–O bond angles (α_1 and α_2) are noticed, such that, $\alpha_1 + \alpha_2 = 180^\circ$. Thermal variation of Cr–O ($d_{\text{Cr-O}}$), Li–O ($d_{\text{Li-O}}$) bond lengths, and O–Cr–O bond angle (α_1) are shown in Figs. 5(a)–5(f) for LCO and LCCO. More convincing signatures of T_N and T_{AFE} are evident in the thermal variation of the microscopic structural parameters for both these compounds. We note that the signatures at T_N for LCCO and T_N (or T_{AFE}) for LCO are identical except for the degree of change in the structural parameters. This change is magnified for LCCO. We further note that the nature of changes at T_{AFE} are opposite in both the compounds. A step like rise in $d_{\text{Cr-O}}$ associated with the step like falls in $d_{\text{Li-O}}$ and α_1 is evident with decreasing T for LCCO. These are in contrast to the decrease of $d_{\text{Cr-O}}$ along with the increase of $d_{\text{Li-O}}$ and α_1 at T_{AFE} for LCO. Inter-

FIG. 6: (Color online) The C_{mag} with T around T_{AFE} for (a) LCO and (b) LCCO. Continuous curves display the low- T fit using Eq. (1).

estingly, this change is remarkably amplified (~ 10) for LCCO. As depicted by the broken curves in Fig. 1(a) the interlayer superexchange linkages are mediated through several Cr–O–Li–O–Cr paths. Therefore, the changes of $d_{\text{Cr–O}}$ and $d_{\text{Li–O}}$ are crucial which manipulate the distance between interlayer Cr atoms. The value of interlayer Cr–Cr distance ($d_{\text{Cr–Cr}}$) is found to decrease significantly for LCCO compared to the value of LCO as evident in the thermal variation of the lattice constant, c in Fig. 4(h). The value of intralayer Cr–Cr distance is exactly same as lattice constant, a which remains nearly similar close to T_N and T_{AFE} for both the compounds. Thus, the results reveal that the intralayer Cr–Cr exchange interaction remains the same. Rather, interlayer Cr–Cr superexchange interaction enhances for LCCO. As depicted in Figs. 5(c) and 5(f) for LCO and LCCO, respectively, α_1 are close to 90° below T_N . Thus, one would expect ferromagnetic (FM) superexchange interaction. The interplay between intralayer Cr–Cr AFM and interlayer FM superexchange interactions eventually leads to the overall magnetism where intralayer interaction dominates for LiCrO_2 .¹¹ In fact, stronger $J/J' \sim 10^3$ was reported for LCO.⁹ Here, reasonably weaker J/J' or stronger J'/J is anticipated for LCCO because of shorter $d_{\text{Cr–Cr}}$ as discussed below.

In Figs. 6(a) and 6(b) the magnetic contribution to C (C_{mag}) are shown for LCO and LCCO, respectively. The C_{mag} is estimated by subtracting the calculated non-magnetic contribution using Debye model with Debye temperature (Θ) about 800 K. Here, we have followed the work of Alexander *et al.*, in which they fitted heat capacity of nonmagnetic LiCoO_2 for extracting C_{mag} of LiCrO_2 .⁹ Recently, $C_{\text{mag}}(T)$ has been calculated by Du *et al.* at low- T ($T \ll T_N$) based on spin-wave theory for a 2D triangular lattice AFM.³⁸ Neglecting J'/J ($\sim 10^{-3}$) the $C_{\text{mag}}(T)$ for $J/k_B = 80$ K and $S = 3/2$ is⁹

$$C_{\text{mag}}(T) = \left(\frac{1.6125 \times 10^{-5}}{\sqrt{J'/k_B}} \right) T^3. \quad (1)$$

Using Eq. (1) the experimentally obtained $C_{\text{mag}}(T)$ are fitted for $T \ll T_N$. The continuous curves in Figs. 6(a) and 6(b) display quite satisfactory fits, which provide $J'/k_B = 0.1208$ and 0.5109 K for LCO and LCCO, respectively. The value obtained for LCO is close to that

reported by Alexander *et al.*⁹ Importantly, the value of J'/k_B increases up to more than ~ 4 times for LCCO. The interlayer superexchange interaction, J' is ferromagnetic and the increase in its value is consistent with the reduced interlayer Cr–Cr distance. Thus dominant J' in LCCO may lead to the appearance of H_C and huge increase of T_N .

This investigation points to the fact that the isostructural transitions are the key for observed electric ordering in LCO and LCCO. For LCO Seki *et al.* proposed that the opposite spin chirality of a proper screw structure in the alternate Cr-layer produces AFE ordering.¹⁷ Here, we additionally demonstrate that the magnetic and electric ordering are associated with the isostructural transition for LCO. We note that the minor doping of Cu releases the magnetic frustration as T_N increases significantly for LCCO. Interestingly, the T_{AFE} remains unchanged while T_N is nearly doubled for LCCO. The T_N and T_{AFE} are associated with the two significant isostructural transitions. The step-like changes in $d_{\text{Cr–O}}$, $d_{\text{Li–O}}$, and α_1 for LCCO are enormously enhanced at T_N and T_{AFE} compared to LCO. The changes at T_N are nearly doubled for LCCO. On the other hand, the isostructural transition at T_{AFE} for LCCO are opposite in character and changes nearly ~ 10 times compared to LCO. Appealingly, uncompensated spontaneous electric polarization is observed in LCCO, which is almost canceled out for LCO, below T_{AFE} . The structurally driven boost up of the interlayer FM superexchange interaction holds the key for reorganization of the magnetic structure below T_{AFE} . This further leads to the uncompensated spontaneous electric polarization as the magnetic structure is intimately correlated with the electric polarization.¹⁷ Analogous to the AFE ordering in LCO, a probable AFE ordering with uncompensated electric polarization is thus anticipated for LCCO. This unusual AFE state has been rarely found in the literature,^{27–29} which needs to be elucidated thoroughly on various systems revealing new paradigms.

In conclusion, an unconventional AFE ordering is revealed in LCCO compared to nearly compensated AFE ordering in LCO. We argue that strong microstructural change at the isostructural transition is the key to this unconventional electric ordering in LCCO. The structurally driven enhancement of the interlayer superexchange interaction leads to the emergence of uncompensated electric and magnetic polarization in LCCO.

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