Orbital symmetry of charge density wave order in La$_{1.875}$Ba$_{0.125}$CuO$_4$ and YBa$_2$Cu$_3$O$_{6.67}$

A. J. Achkar, F. He, R. Sutarto, Christopher McMahon, M. Zwiebler, M. Hücker, G. D. Gu, Ruixing Liang, D. A. Bonn, W. N. Hardy, J. Geck, and D. G. Hawthorn

1 Department of Physics and Astronomy, University of Waterloo, Waterloo, N2L 3G1, Canada
2 Canadian Light Source, Saskatoon, Saskatchewan, S7N 2V3, Canada
3 Leibniz Institute for Solid State and Materials Research IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany
4 Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA
5 Department of Physics and Astronomy, University of British Columbia, Vancouver, V6T 1Z1, Canada

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Recent theories of charge density wave (CDW) order in high temperature superconductors have predicted a primarily $d$ CDW orbital symmetry. Here, we report on the orbital symmetry of CDW order in the canonical cuprate superconductors La$_{1.875}$Ba$_{0.125}$CuO$_4$ (LBCO) and YBa$_2$Cu$_3$O$_{6.67}$ (YBCO), using resonant soft x-ray scattering and a model mapped to the CDW orbital symmetry. From measurements sensitive to the O sublattice, we conclude that LBCO has predominantly $s'$ CDW orbital symmetry, in contrast to the $d$ orbital symmetry recently reported in other cuprates. Additionally, we find that the $C_4$ orbital symmetry of the Cu sublattice scattering is approximately preserved in LBCO and broken in YBCO. This work highlights orbital symmetry as an additional key property of CDW order that distinguishes the different cuprate families. We discuss how the CDW symmetry may be related to the “1/8-anomaly” and to static spin ordering.

Charge density wave (CDW) order in underdoped cuprates has recently been revealed as an important and generic competitor to superconductivity (SC) [1–5, 7–9]. A significant property of CDW order is that it can exhibit both inter and intra unit cell symmetry breaking. [10, 11] Specifically, CDW order can occur with $d$ rather than $s$ or $s'$ orbital symmetry. [1, 4, 12–15, 17–19] Here, we report resonant soft x-ray scattering measurements of La$_{1.875}$Ba$_{0.125}$CuO$_4$ (LBCO) and YBa$_2$Cu$_3$O$_{6.67}$ (YBCO) that are resolved onto the O 2$p_{z(x)}$ and Cu sublattices and mapped to the CDW symmetry. Our main finding is that LBCO has primarily $s'$ symmetry CDW with a secondary $d$ component, distinguishing it from the predominant $d$ symmetry CDW observed in other cuprates. [4, 20] We propose that the $s'$ symmetry in LBCO may be related to the “1/8-anomaly” and that it favours static spin ordering more than $d$ symmetry. Additionally, we find that $C_4$ orbital symmetry of the Cu sublattice scattering is approximately preserved in LBCO and broken in YBCO. Moreover, in YBCO the symmetry is broken to different degrees along the $a$ and $b$ crystal axes, suggesting either exotic checkerboard order or domains of stripes. Finally, we present implications of energy dependent scattering from the O 2$p_{z(x)}$ sublattices in LBCO.

Stimulated by theory, [1, 17–19] resonant soft x-ray scattering (RSXS) in YBCO and Bi$_2$Sr$_2$–La$_x$CuO$_{6+δ}$ (Bi-2201) [4] and scanning tunnelling microscopy (STM) measurements in Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (Bi-2212) and Ca$_{2−x}$Na$_x$CuO$_2$Cl$_2$ (Na-CCOC) [20] have recently reported that $d$ symmetry characterizes the CDW order in the CuO$_2$ planes. In this $d$-symmetry CDW state, the modulation of charge (or a related microscopic quantity) on O $p_x$ and O $p_y$ sites is out of phase, as depicted in Fig. [1b] for a commensurate, bond-centered CDW. An important question is whether $d$-symmetry CDW order is a generic property of underdoped cuprates and, specifically, if it also occurs in the canonical stripe-ordered La-based cuprates. There are many similarities in the CDW order of the La-based cuprates and other cuprates (e.g. Bi-2212, YBCO) such as an enhancement in CDW intensity at doping levels near $p = 1/8$. [23] Competition with SC and a common spectroscopic signature to the resonant scattering intensity. [2, 3] However, these similarities are at odds with important differences such as the doping dependence of the CDW incommensurability. [7, 8, 23, 25, 26, 28–30] Perhaps most significantly, static spin density wave (SDW) order commensurate with CDW order is only observed in the La-based cuprates. Accordingly, it is not yet clear whether stripe order in the La-based cuprates and CDW order in other cuprates are slightly different manifestations of a common order or truly distinct phases.

Here, we have resolved the orbital symmetry and microscopic character of CDW order in LBCO and YBCO using a RSXS technique where the incident photon polarization is varied relative to the material’s crystallographic axes and the crystal is simultaneously rotated about the CDW ordering wavevector $Q$, as illustrated in Fig. [1a]. With this approach, at the O $K$ edge we are able to determine the relative strength, phase relation and energy dependence of scattering from two O sublattices comprised of O atoms with Cu–O–Cu bonds either parallel ($O_y$) or perpendicular ($O_x$) to $Q$ (see Fig. [1b]). The proportion to $s'$ symmetry was characterized from O $K$ edge measurements in LBCO using a polarization dependent RSXS model developed with parameters directly related to the $d$ and $s'$ symmetry components $Δ_d$.
FIG. 1. Experimental setup and visualization of CDW order. a. Scattering geometry in laboratory frame, $\ell$. b. CDW order with $s$, $s'$ and $d$ orbital symmetries, illustrated for a bond-centered, commensurate, and unidirectional CDW. Green arrows are spins in the lower right panel.

Top view
(\(\phi = 0\))

and $\Delta \omega$. Additionally, RSXS measurements sensitive to the Cu sublattice were used to assess the degree of rotational $C_4$ symmetry on Cu sites in LBCO and YBCO.

Prior to discussing our results, we first describe the polarization dependent RSXS model which is used in this analysis and then parametrize the model in terms of the symmetry components of the CDW order. Within this framework, the CDW orbital symmetries in LBCO and YBCO are elucidated from the experimental data.

**Polarization Dependent Resonant X-Ray Scattering**

On an x-ray absorption edge, the resonant elastic x-ray scattering intensity is given by:

$$I(\epsilon_i, \omega, \mathbf{Q}) \propto |\epsilon_f^* \cdot T(\omega, \mathbf{Q}) \cdot \epsilon_i|^2,$$  \hspace{1cm} (1)

where $\omega$ is the angular frequency, $\mathbf{Q}$ is the momentum transfer, $\epsilon_i$ and $\epsilon_f$ are the incident and scattered polarization, respectively, and

$$T(\omega, \mathbf{Q}) = \sum_n F_n(\omega)e^{-i\mathbf{Q} \cdot \mathbf{r}_n} = \begin{bmatrix} t_{aa} & t_{ab} & t_{ac} \\ t_{ba} & t_{bb} & t_{bc} \\ t_{ca} & t_{cb} & t_{cc} \end{bmatrix}$$  \hspace{1cm} (2)

is a tensor equivalent of the structure factor – a sum over site index $n$ of the atomic scattering form factor, $F_n(\omega)$, with atomic positions $\mathbf{r}_n$. The form factor is given by $F_n(\omega) = F_n^0(\omega) + F_n^R(\omega)$, where $F_n^0(\omega)$ and $F_n^R(\omega)$ are non-resonant and resonant contributions, respectively. The resonant part, $F_n^R(\omega)$, is strongly enhanced on an x-ray absorption edge and has a symmetry that captures the local symmetry of electronic structure. For instance, at the Cu $L$ edge, which probes the Cu $2p \to 3d$ transition, a Cu atom in tetragonal CuO$_2$ planes would have $C_4$ rotational symmetry and

$$F_{C Cu}^R(\omega) = \begin{bmatrix} f_{aa}^R(\omega) & 0 & 0 \\ 0 & f_{bb}^R(\omega) & 0 \\ 0 & 0 & f_{cc}^R(\omega) \end{bmatrix},$$  \hspace{1cm} (3)

where $f_{aa}^R(\omega) = f_{bb}^R(\omega) \gg f_{cc}^R(\omega)$. When summed over $n$, the resulting symmetry of $T(\omega, \mathbf{Q})$ involves both intra and inter unit cell symmetries – symmetry associated with the average form factor, $\overline{F_n^R(\omega)}$ and the orbital symmetry of the CDW modulation.

By scattering at photon energies corresponding to the Cu $L$ (931.4 eV) and O $K$ (528.3 eV) absorption edges, we can resolve the CDW order into the Cu and O sublattices, which occupy the “sites” and “bonds”, respectively, of a single-band CDW model.[1]

At the O $K$ edge, the O sublattice can be further subdivided into two sublattices, O$_x$ and O$_y$, having different symmetries of $\overline{F_n^R(\omega)}$. Since O $2p$ holes are primarily in $\sigma$-bonded $2p_x$ or $2p_y$ orbitals, it follows that one sublattice of O will have $f_{aa}^R \neq 0$ and $f_{bb}^R \approx 0$ and the other will have $f_{aa}^R \approx 0$ and $f_{bb}^R \neq 0$, at least at the O pre-edge photon energies of interest. Referencing to the CDW wavevector, $\mathbf{Q} = (H 0 0)$ or $(0 K 0)$, these two O sublattices can be denoted as $\sigma$-bonded parallel ($O_\parallel$) or perpendicular ($O_\perp$) to $\mathbf{Q}$ (see Fig. [1]). The components of $T(\omega, \mathbf{Q})$ can also be referenced relative to $\mathbf{Q}$. We henceforth refer to the diagonal, in-plane components of $T(\omega, \mathbf{Q})$ as $t_{\perp}$ and $t_{\parallel}$, which sum over $O_\perp$ and $O_\parallel$, respectively [eg., $t_{\perp} = \sum_n f_{aa,n}e^{-i\mathbf{H}n}$ and $t_{\parallel} = \sum_n f_{bb,n}e^{-i\mathbf{H}n}$ for $\mathbf{Q} = (H 0 0)$].

The components of $T(\omega, \mathbf{Q})$ can be determined by varying $\epsilon_f$ and $\epsilon_i$ relative to the crystallographic axes of the sample. As detailed in the Supplementary Information, this is realized experimentally by a combination of rotating the sample azimuthally by an angle, $\phi$, about a fixed $\mathbf{Q}$ and rotating the incident polarization $\epsilon_i$ between $\sigma$ and $\pi$ (see Fig. [1]). Additionally, since the CDW peak in the cuprates is broad in $L$, a wide range of measurement geometries can access the CDW peak and thus probe the components of $T(\omega, \mathbf{Q})$.

**Model Parametrization**

We now turn to investigating the symmetry of CDW order through the symmetry of $T(\omega, \mathbf{Q})$ which provides insight into the microscopic character of the CDW order. To see why this is, we first consider the simple case of CDW order with a sinusoidal modulation of charge density ($s + s'$ symmetry) on a tetragonal CuO$_2$ plane. In this scenario, one would expect to have $|t_{\perp}| \gg |t_{\parallel}|$, at both the Cu $L$ and O $K$ edges, mirroring the $d_{x^2-y^2}$
symmetry of $F^R$. In other words, the scattering tensor, $T$, can to first order remain $C_4$ symmetric even though a unidirectional stripe-like modulation breaks the $C_4$ symmetry of the lattice. If the average electronic structure were instead orthorhombic ($F^R \neq F^R$, $|t_\perp| \neq |t_\parallel|$) might be expected to occur. However, this could also occur if $F^R = F^R$ combined with a CDW state with a different orbital symmetry (e.g., $d + s'$) that modulates the $a$ and $b$ components of $F_n(\omega)$ to different degrees. These differing possibilities highlight how $T(\omega, Q)$ is linked to the underlying symmetry of the CDW order.

To quantify this link, we have parametrized CDW order with mixed orbital symmetries into the single band model from Ref. 11. The charge modulation amplitude $\Delta_{ij}$ (or some other quantity related to CDW order such as an energy shift)23 on bonds connecting nearest neighbour Cu sites $i$ and $j$, is given by:

$$\Delta_{ij} = \sum_{Q^*} \left[ \frac{1}{V} \sum_{k} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \Delta_{Q^*}(\mathbf{k}) \right] e^{iQ^* \cdot (\mathbf{r}_i + \mathbf{r}_j)/2},$$

where $V$ is volume and $Q^*$ are the wavevectors of the CDW order. For 1D stripes, $Q^*$ is given by either $(\pm Q_m 0 0)$ or $(0 \pm Q_m 0)$ whereas checkerboard order has both $(\pm Q_m 0 0)$ and $(0 \pm Q_m 0)$. In this prescription, $i = j$ corresponds to Cu sites and $i \neq j$ corresponds to O sites (bonds between Cu sites). $\Delta_{Q^*}(\mathbf{k})$ captures the symmetry of the CDW state and can contain both site-centred ($\Delta_s$) and bond-centred ($\Delta_d$ and $\Delta_{s'}$) symmetry components. As shown in the Supplementary Information, this model can be mapped onto the O sites and related to the components of $T(\omega, Q)$, giving

$$\frac{\Delta_d}{\Delta_{s'}} = \frac{t_{\parallel}/t_{\perp} - 1}{t_{\parallel}/t_{\perp} + 1},$$

Inspection of Eq. 5 shows that for pure $d$-CDW and $s'$-CDW orders, $t_{\parallel}/t_{\perp}$ has the same magnitude (=1), but with opposite sign. A mixed $d$ and $s'$ state would have $|t_{\parallel}/t_{\perp}| \neq 1$. In regions with $|t_{\parallel}/t_{\perp}| < 1$ (>$1$), the sign of $\Delta_d/\Delta_{s'}$ is negative (positive), giving rise to an anti-phase (in-phase) relation between the $d$ and $s'$ symmetry components. Fig. 2 illustrates the mapping between $t_{\parallel}/t_{\perp}$ and $\Delta_d/\Delta_{s'}$ for O atoms in the CuO$_2$ plane. We note that Eq. 5 applies to both stripe and checkerboard order indicating that, at least in this prescription, $t_{\parallel}/t_{\perp}$ does not clearly distinguish checkerboard order from stripes.

The Cu L edge measurements are more difficult to interpret within this description. Most directly, the scattering intensity at the Cu L edge should be sensitive to the site-centered $s$ symmetry component of the CDW order. However, the O-centered $s'$ and $d$ symmetry components may also influence the symmetry of scattering at the Cu L edge (Cu 2p → 3d transition) by inducing different energy shifts on the Cu core electrons.17

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{The $\phi$ and $L$ dependent RSXS for CDW order in LBCO at the O K and Cu L edges. a. Measured $I_{\sigma}(\bar{3})$ and $I_{\sigma}(\Delta)$ and $I_{\pi}/I_{\sigma} (\bigcirc)$ vs. $\phi$ at the O K edge (528.3 eV). b. $I_{\pi}/I_{\sigma}$ vs. $L$ at the O K edge. Simultaneously fitting the data in b and c (red lines) gives $t_{\parallel}/t_{\perp} = 0.612 \pm 0.035$ and $t_{cc}/t_{\perp} = 0.034 \pm 0.021$; model calculations with these parameters are shown in a as solid lines. d. $I_{\pi}/I_{\sigma}$ vs. $L$ for two samples, S1 and S2, at the Cu L edge (931.3 eV). e. Colour map of $\chi_{\phi}$ with minima (best fit) indicated by black dots. The red rectangles are 95% CI from least squares fitting. The red ellipses are contours of constant $\chi_{\phi}$ reflecting a 95% confidence region. f. Illustration of mapping between $t_{\parallel}/t_{\perp}$ and $\Delta_{d}/\Delta_{s'}$ based on Eq. 5.}
\end{figure}

\section*{RESULTS}

Polarization dependent RSXS in LBCO

In Fig. 2 we investigate the $\phi$ (Figs. 2a and 2b) and $L$ (Figs. 2c and 2d) dependence of RSXS from CDW order in LBCO at the O K and Cu L edges in order to determine the magnitude and sign of $t_{\parallel}/t_{\perp}$. The dependence on $\phi$ of $I_{\pi}/I_{\sigma}$ constrains both the magnitude and sign of $t_{\parallel}/t_{\perp}$ whereas the dependence on $L$ constrains its magnitude (this is illustrated in Supplementary Fig. S2). A simultaneous fit of both the $\phi$ (Fig. 2b) and $L$ (Fig. 2c) dependence of $I_{\pi}/I_{\sigma}$ for LBCO at the O K edge gives $t_{\parallel}/t_{\perp} = 0.612 \pm 0.035$ and $t_{cc}/t_{\perp} = 0.034 \pm 0.021$. In Fig. 2b, we show that calculations (solid lines) of the $\phi$ dependence using these parameters are in excellent agreement with the measured $I_{\pi}$ (green squares) and $I_{\sigma}$ (blue triangles), providing confidence that all relevant factors such as surface geometry and absorption corrections have
been properly taken into account within the model. The reported errors represent 95% confidence intervals (CI) as determined by least squares fitting. In Fig. 2b, maps of the reduced chi-squared statistic, $\chi^2_0$, for the $O K$ (left) and Cu $L$ (right) edges are used to indicate 95% confidence regions of parameter space, defined by contours of constant $\chi^2_0$ (red ellipses), that are more appropriate than the CI (black rectangles). The ratio $|t_\parallel/t_\perp| < 1$ indicates that the O scattering tensor in LBCO breaks $C_4$ symmetry with a smaller modulation for the $O_1$ sublattice than for the $O_2$ sublattice. This result indicates that the Zhang-Rice singlet description of the electronic structure of the cuprates is inadequate for the stripe phase. We cannot rule out that $|t_\parallel/t_\perp| < 1$ results simply from an asymmetry in $F_R$ associated with the low-temperature tetragonal (LTT) phase transition in LBCO, which cant the CuO$_6$ octahedra making each CuO$_2$ plane orthorhombic. However, this would require $t_R/t_\perp = 0.612$, which is difficult to reconcile with the small octahedral tilts of the LTT phase. In contrast, if we interpret our results in terms of orbital symmetry as outlined above, $|t_\parallel/t_\perp| < 1$ is evidence that CDW order in LBCO has mixed, anti-phase $d + s'$ symmetry with a dominant $s'$ symmetry: $\Delta_s/\Delta_{s'} = -0.241 \pm 0.027$. This dominant $s'$ symmetry CDW stands in contrast to the dominant $d$ symmetry CDW reported in YBCO, Bi-2201, Bi-2212, and Na-COC.[4, 20]

Although a clear asymmetry between $t_\parallel$ and $t_\perp$ is observed at the $O K$ edge in LBCO, a similar asymmetry is not observed at the Cu $L$ edge. Rather, the $L$ dependence of $I_{s}/I_s$ is consistent with $|t_\parallel| = |t_\perp| \gg |t_{cc}|$. A fit to the data (Fig. 2a) gives $t_\parallel/t_\perp = \pm 0.982 \pm 0.04$ and $t_{cc}/t_\perp = \mp 0.064 \pm 0.317$, indicating that $t_\parallel/|t_\perp| = \pm 0.42$ on Cu sites and that the scattering tensor asymmetry observed on the O sublattice does not impart a similar asymmetry onto the Cu $2p \rightarrow 3d$ transition. Most simply, this may be understood as resulting from the Cu $L$ edge measurement being most sensitive to the $s$ or $s'$ symmetry components of the CDW order with only a weak sensitivity to the smaller $d$ component identified by the $O K$ edge measurement. This $L$ dependence was measured in two LBCO samples with slightly different incommensurability and mounted differently (sample S1 was on a wedge and S2 was on a flat plug). These two samples exhibit similar $L$ dependence (Fig. 2a) and were both included in the fitting.

**Cu $L$ edge investigation of YBCO**

Turning to YBCO, the $L$ dependence of $I_{s}/I_s$ (Fig. 3a) for $Q = (0 \pm 0.31 \ 0 \ L)$ is consistent with $|t_\parallel/t_\perp| \approx 1$, similar to LBCO. In contrast, the $(0 \pm 0.31 \ 0 \ L)$ peaks exhibit larger values of $I_{s}/I_s$ than the $(0 \pm 0.31 \ L)$ peaks, corresponding to $|t_\parallel/t_\perp| > 1$. Specifically, fitting the data with $t_{cc} = 0$ gives $t_\parallel/t_\perp = 1.091 \pm 0.154$ for $(0 \pm 0.31 \ L)$ and $1.317 \pm 0.087$ for $(0 \pm 0.31 \ 0 \ L)$. If we allow for $t_{cc} \neq 0$, the fit is under-constrained and linear regions in parameter space (Fig. 3b) provide acceptable fits to the data. However, one can reasonably assume that the CDW order is dominated by the CuO$_2$ planes and thus that $t_{cc}$ is small relative to $t_\parallel$. Imposing the constraint that $|t_\parallel/t_\perp| < 0.2$ gives $1.01 \leq |t_\parallel/t_\perp| \leq 1.17$ for $(0 \pm 0.31 \ L)$ and $1.24 \leq |t_\parallel/t_\perp| < 1.39$ for $(0 \pm 0.31 \ 0 \ L)$. These measurements show that the orbital symmetry of CDW order differs along $H$ and $K$ in YBCO, providing further evidence that a simple checkerboard order is not applicable to YBCO.[4, 20] Although an exotic form of checkerboard order may explain this, a simpler view is that there are domains of stripe-like CDW order with different orbital symmetries in YBCO. For the CDW peak along $K$ in YBCO, the observation of $|t_\parallel/t_\perp| \approx 1$ is consistent with the simplest picture of an $s$ symmetry component dominating the scattering from the Cu sublattice. However, since it is not presently evident how $d$ symmetry impacts the Cu $L$ edge measurement, a $d$ symmetry component cannot be ruled out. This conclusion differs from the recent interpretation of the $\phi$ dependence of the $Q = (0 \pm 0.31 \ 1.5 \ L)$ peak (at the Cu $L$ edge) in YBCO as evidence of dominant $d$ symmetry CDW order, based on a plausible microscopic model.[4, 20] In the framework presented here, the clearest evidence for dominant $d$ symmetry would be the observation of $t_\parallel/t_\perp < 0$ at the $O K$ edge. Future work is needed to determine if this indeed occurs in YBCO or other cuprates.

In contrast to the peaks along $K$, those along $H$ do exhibit a more pronounced asymmetry ($|t_\parallel/t_\perp| \neq 1$) that may be evidence for a sizeable $d$ symmetry component to the CDW order in YBCO. However, quantifying the relative components of $\Delta_d$, $\Delta_s$ and $\Delta_{s'}$ requires a more detailed understanding of how these components influence the Cu $L$ edge RSXS.
**O K edge energy dependence of RSXS in LBCO**

The energy dependence of the CDW scattering intensity at the O K edge has been analyzed in the past on either the O_{\parallel} or the O_{\perp} sublattices. Here we present the energy dependence of both sublattices. As shown in Fig. 1 when scaled to equal intensity at 528.3 eV, both $I_{\pi}$ (probing O_{\parallel}) and $I_{\sigma}$ (probing O_{\perp}) exhibit very similar energy dependence. These measurements indicate that although the O K edge exhibits a significant asymmetry in the magnitude of scattering from O_{\parallel} and O_{\perp}, this asymmetry does not manifest as a strong difference in the energy dependence. For $\sigma$-polarization, this energy dependence was previously shown to result from a spatial modulation in the energy of the O 1s $\rightarrow$ 2p transition giving $f_n(\omega) = f(\omega + \Delta\omega_n)$, or more generally $f_n(\omega) = \tilde{f}(\omega + \Delta\omega_n)$. These measurements are also consistent with this phenomenological energy shift model, indicating that the O_{\perp} and O_{\parallel} sublattices are both subject to energy shifts. At present, it is unclear whether an alternate description of the energy dependence based on dynamical nesting would capture the measured polarization and energy dependence.

As previously shown, the measured energy dependence does not correspond directly to modulations in charge density; although it may be a signature of charge density fluctuations, it could also arise due to modulations in other electronic structure parameters such as exchange interactions, the Cu–O hopping or the charge transfer density. These measurements are also consistent with this phenomenological energy shift model, indicating that the O_{\perp} and O_{\parallel} sublattices are both subject to energy shifts. At present, it is unclear whether an alternate description of the energy dependence based on dynamical nesting would capture the measured polarization and energy dependence.

As previously shown, the measured energy dependence does not correspond directly to modulations in charge density; although it may be a signature of charge density fluctuations, it could also arise due to modulations in other electronic structure parameters such as exchange interactions, the Cu–O hopping or the charge transfer energy. Identifying the microscopic origin of the RSXS energy dependence requires further investigation. To this end, we note that despite the good overall agreement between $I_{\pi}$ and $I_{\sigma}$ at the O K edge, the scaled scattering intensity is higher for $I_{\pi}$ than for $I_{\sigma}$ at 529.5 eV. This indicates that a model more sophisticated than the single parameter energy shift model is needed to account for the detailed energy dependence of both $I_{\pi}$ and $I_{\sigma}$ and may provide a clue to the origin of the energy shifts. Specifically, the 529.5 eV peak appears to be more isotropic ($t_\parallel \approx t_\perp$) than the lower energy peak at 528.3 eV. This difference in asymmetry may be related to how states at different energies hybridize with the Cu 3d states. The 529.5 eV peak is closer in energy to the upper Hubbard band (UHB) peak in the X-ray absorption spectrum (XAS) at 530.2 eV, which is present in the O K XAS due to strong mixing between the O 2p and Cu 3d states. In contrast, the lower energy states at 528.3 eV would be present in a doped charge-transfer insulator even in the absence of O 2p–Cu 3d hybridization. Accordingly, the Cu symmetric character of the Cu edge scattering may be reflected more strongly at the UHB than at states closer to $E_F$.

**DISCUSSION**

The observation of dominant $s'$ symmetry CDW order in LBCO should be contrasted with existing evidence for predominantly $d$ symmetry CDW in Bi-2212 and NaCCOC. If we assume both STM and RSXS have similar sensitivity to the CDW symmetry, our measurements highlight CDW orbital symmetry as an additional property of CDW order distinguishing the La-based cuprates from other cuprate families. This difference may be related to the spin ordering properties of these different families - only in the La-based cuprates does static SDW order develop with an incommensurability that is clearly related to the CDW order ($\delta_{\text{charge}} = 2\delta_{\text{spin}}$). The related $\delta_{\text{charge}}$ and $\delta_{\text{spin}}$ in La-based cuprates is generally associated with a correlation between the local charge and the local anti-ferromagnetic (AF) ordering. For example, in a valence bond-solid description of stripes, bond-order (CDW) and SDW order can be related, as shown in Fig. 1, wherein bonds are correlated with the local AF order and sufficiently weak bonds connect ferromagnetically aligned spins.

We now consider how this local charge/AF correlation is influenced by different CDW orbital symmetries. For an $s'$ symmetry CDW, the local charge/AF order for bonds parallel and perpendicular to $Q$ are modulated in phase. This would naturally accommodate static SDW order consistent with observations in La-based cuprates (a commensurate, bond-centered $s'$-CDW+SDW order of this type is depicted in Fig. 1). In contrast, $d$ symmetry bond order would have local charge/AF order for bonds parallel and perpendicular to $Q$ modulated out-of-phase with each other. Accordingly, a $d$ symmetry CDW may prohibit static SDW order that is commensu-
rate with the CDW, or conversely static SDW order may prohibit \(d\) symmetry CDW. This notion of a relation between CDW symmetry and static SDW order is consistent with existing theories. A recent study of CDW order in a three-orbital model that develops both spin and charge stripe order\([33]\) reports a predominantly \(s'\) symmetry CDW with a \(d/s'\) proportion similar in magnitude to our findings in LBCO. In contrast, theories that have reported a \(d\) symmetry CDW order have yet not exhibited both static SDW and CDW orders\([1, 15, 17, 18, 39]\) as found in La-based cuprates.

Finally, we speculate on the role of CDW symmetry in the competition between CDW order and superconductivity, for which various pictures have recently been proposed\([40–44]\). We note that \(T_c\) is more strongly suppressed around \(p = 1/8\) in the LBCO than in other cuprate families. One possibility is that this greater competition may ultimately be rooted in the symmetry of the CDW order, which may have a greater pair-breaking effect for \(s'\) symmetry than for \(d\) symmetry.

**METHODS**

RSXS and x-ray absorption spectroscopy (XAS) measurements at the Cu \(L\) and O \(K\) edges were performed using the in-vacuum four-circle diffractometer\([44]\) at the Canadian Light Source’s REIXS beam line on single-crystal samples of \(\text{YBa}_2\text{Cu}_3\text{O}_{6.67}\) \((T_c = 64.5\ \text{K},\ \rho = 0.116)\) and \(\text{La}_{1.875}\text{Ba}_{0.125}\text{Cu}_4\text{O}_4\) \((T_c \approx 4\ \text{K})\). The LBCO crystals were previously annealed in an \(^{17}\text{O}\) environment\([46]\). Reciprocal lattice units (r.l.u.) were defined using the lattice constants \(a = 3.84\ \text{Å}, b = 3.88\ \text{Å}, c = 11.74\ \text{Å}\) for \(\text{YBCO}\) and \(a = b = 3.787\ \text{Å}, c = 13.24\ \text{Å}\) for LBCO. The YBCO sample was polished and two LBCO samples were cleaved in air prior to measurement. The crystallographic orientation of the samples was verified in the diffractometer using appropriate structural Bragg peaks at \(\sim 2\ \text{keV}\). LBCO samples were mounted separately to flat and wedge-shaped sample plugs. The first sample (S1) exhibited CDW peaks at \(Q = (\pm 0.232\ 0\ 0)\), whereas the second sample (S2) had them at \(Q = (\pm 0.237\ 0\ 0)\), indicating a slight difference in doping (incommensurability). For the \(O\) \(K\) edge azimuthal rotation experiment on LBCO, the wedge angle \(\theta_w\) was 53° (see Fig. 1). Due to a limited motion range on the \(\phi\) motor, manual rotations of \(\phi\) were performed with an in-vacuum screwdriver. Photographs through a levelled telescope were used to measure \(\phi\), yielding a precision of \(\sim 1°\), and referenced to \(\phi = 0°\) as set by the crystallographic orientation. The measurements on LBCO were performed at \(T = 22\ \text{K}\) whereas those on YBCO were at 60 K and 160 K. The vacuum chamber pressure for all measurements was \(P < 1 \times 10^{-9}\ \text{Torr}\). X-ray absorption was measured by total fluorescence yield. Additional details about background subtractions, peak fitting, model calculations and parameter estimation are contained within the Supplementary Information.

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Supplementary Information for:
Orbital symmetry of charge density wave order in La$_{1.875}$Ba$_{0.125}$CuO$_4$ and YBa$_2$Cu$_3$O$_{6.67}$

This supplementary information is divided into four sections. First, we show how the orbital symmetry, $\Delta_{s'}$ and $\Delta_d$, is mapped onto experimentally measurable quantities, $t_\parallel$ and $t_\perp$, for the O sites. Second, we describe the polarization dependent resonant scattering model used to fit the experimental data. Third, we present the dependence of the experimental data on $\phi$, $L$, and $\hbar \omega$. Fourth, we provide calculations that explore the parameter space of the scattering model in order to illustrate the level of confidence in our findings.
ORBITAL SYMMETRY OF CDW ORDER ON OXYGEN SITES

Following Ref. [S1], non-s-wave symmetry CDW order in a single-band model of the CuO₂ planes can be parameterized by $\Delta_{ij}$, which characterizes the charge modulation (or some other quantity related to charge order such as an energy shift) [S2 S3] on bonds connecting nearest neighbor Cu sites $i$ and $j$:

$$\Delta_{ij} = \sum_{Q^*} \left[ \frac{1}{V} \sum_k e^{iQ^*(r_i-r_j)} \Delta_{Q^*}(k) \right] e^{iQ^*(r_i+r_j)/2}, \quad (S1)$$

where $V$ is volume and $Q^*$ are the wave vectors of the CDW order: $Q^* = (\pm Q_m, 0, 0)$ or $(0, \pm Q_m, 0)$ for 1D stripes and $Q^* = (\pm Q_m, 0, 0)$ and $(0, \pm Q_m, 0)$ for checkerboard order. In this prescription, $r_i$ indexes the Cu sites so that $\Delta_{ii}$ corresponds to Cu sites and $\Delta_{ij}$ with $i \neq j$ corresponds to bonds between Cu sites (i.e. O sites). Including the $s$, $s'$ and $d$ symmetry terms,

$$\Delta_{Q^*}(k) = \begin{cases} \Delta_s + \Delta_{s'}(\cos k_x a + \cos k_y b) + \Delta_d(\cos k_x a - \cos k_y b) & Q^* = (\pm Q_m, 0, 0) \\
\Delta_s + \Delta_{s'}(\cos k_x a + \cos k_y b) - \Delta_d(\cos k_x a - \cos k_y b) & Q^* = (0, \pm Q_m, 0) \end{cases} \quad (S2)$$

giving rise to spatial modulations of $\Delta_{ij}$ given in Fig. [I].

This model identifies two distinct sublattices for the bonds, $ij$: one set of bonds, $A$, having $r_j - r_i = \pm \hat{a}x$ and the other set, $B$, having $r_j - r_i = \pm \hat{b}y$. For these two sublattices, a stripe state with $Q^* = (\pm Q_m, 0, 0)$ has

$$\Delta_{iA} = (\Delta_{s'} + \Delta_d) \cos[Q_m(r_{ix} + a/2)]$$
$$\Delta_{iB} = (\Delta_{s'} - \Delta_d) \cos[Q_m r_{ix}], \quad (S3)$$

whereas a checkerboard with $Q^* = (\pm Q_m, 0, 0)$ and $Q^* = (0, \pm Q_m, 0)$ has

$$\Delta_{iA} = (\Delta_{s'} + \Delta_d) \cos[Q_m(r_{ix} + a/2)] + (\Delta_{s'} - \Delta_d) \cos[Q_m r_{iy}]$$
$$\Delta_{iB} = (\Delta_{s'} - \Delta_d) \cos[Q_m r_{ix}] + (\Delta_{s'} + \Delta_d) \cos[Q_m(r_{iy} + b/2)]. \quad (S4)$$

Translating this model into bond order on the O atoms, one can associate $\Delta_{iA}$ and $\Delta_{iB}$ with O atoms having holes in $2p_x$ and $2p_y$ orbitals, respectively. Next, we assume that $\Delta_{iA(B)}$ are proportional to modulations in the atomic scattering form factor $DF_{O,iA(B)}(\omega)$ giving

$$\Delta F_{O,iA}(\omega) = C(\omega) \begin{bmatrix} \Delta_{iA} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \text{and} \quad \Delta F_{O,iB}(\omega) = C(\omega) \begin{bmatrix} 0 & 0 & 0 \\ 0 & \Delta_{iB} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (S5)$$

where $C(\omega)$ is a proportionality constant common to $\Delta F_{O,iA}(\omega)$ and $\Delta F_{O,iB}(\omega)$. For scattering at the O K edge in LBCO, the assumption that the energy dependence factorizes from the modulation amplitude and is common to the $A$ and $B$ sublattices seems justified given the approximate proportionality between the $I_x$ and $I_y$ scattering (see Fig. [I]). Then, for a measured $Q = (Q_m 0 L)$,

$$t_{||} = t_{aa} = \frac{C(\omega)}{N} \sum_i (\Delta_{s'} + \Delta_d) \cos[Q_m(r_{ix} + a/2)] e^{iQ_m(r_{ix} + a/2)} \quad (S6)$$
$$t_{\perp} = t_{bb} = \frac{C(\omega)}{N} \sum_i (\Delta_{s'} - \Delta_d) \cos[Q_m r_{ix}] e^{iQ_m r_{ix}}, \quad (S7)$$

where $r_{ix}$ is the position of the Cu sites. Combining Eqs. (S6) and (S7) gives

$$\frac{t_{||}}{t_{\perp}} = \frac{\Delta_{s'} + \Delta_d}{\Delta_{s'} - \Delta_d}, \quad (S8)$$

which is written in terms of $\Delta_d/\Delta_{s'}$ in Eq. [5] parametrizing how the experimental observables, $t_{||}$ and $t_{\perp}$, can be mapped to the symmetry of the CDW order for O sites in the CuO₂ plane.
Polarization dependent scattering

Model derivation and effect of absorption correction

The expression for the polarization dependent scattering intensity (Eq. 1 in main text) references the incident and scattered photon polarization vectors relative to the crystallographic orientation of the sample. To see how variation of the experimental geometry (see Fig. 1a) affects Eq. 1, we express the photon polarization in the laboratory reference frame (denoted by the subscript $\ell$) and Eq. 1 is rewritten as

$$I(\epsilon_i, \omega, Q) \propto |\epsilon_{f,\ell}^* \cdot RT(\omega, Q)R^\top \cdot \epsilon_{i,\ell}|^2,$$

where $R$ is a rotation matrix that rotates the sample ($T(\omega, Q)$ is still referenced to the crystallographic axes) into the geometry necessary to satisfy the Bragg condition for a particular photon energy $\hbar\omega$ and momentum transfer $Q$, and can also rotate the sample azimuthally ($\phi$) about $Q$. For photon detection without polarization sensitivity, both $\epsilon_{f,\sigma}$ and $\epsilon_{f,\pi}$ scattering contribute to the scattering intensity, giving $I(\epsilon_i) = I_{\epsilon_i,\sigma'} + I_{\epsilon_i,\pi'}$.

In calculating the expected scattering intensity for a given symmetry of $T$ using Eq. S9, the rotations that the sample and photon polarization undergo relative to the laboratory reference frame must be specified. We incorporate a laboratory reference frame with $k_i$ along the $(1 0 0)_\ell$ direction and the scattering plane being orthogonal to the $(0 0 1)_\ell$ direction, giving $\epsilon_{i,\sigma} = (0 0 1)_\ell$ and $\epsilon_{i,\pi} = (0 1 0)_\ell$. The sample can be mounted on a wedge, defined by a wedge angle, $\theta_w$, ($\theta_w = 0$ corresponds to a flat surface, i.e. no wedge) that can be rotated azimuthally about $(0 1 0)_\ell$ axis. The azimuthally rotated wedge can then be rotated by an angle $\theta$ about the $(0 0 1)_\ell$ axis. For $\theta_w = \theta = 0$, $\phi = 0$ and $\theta = 0$, the samples are mounted such that the crystalline axes $(0 0 1)_\ell$ and $a [b]$ along $(1 0 0)_\ell$ for investigation of $(H 0 L)$ [(0 K L)] peaks. These rotations can be expressed as a rotation matrix $R$ acting on $T$ given by

$$R = R(\theta)_{001}R(\phi)_{010}R(\theta_w)_{001}R_O,$$

where, for example, $R(\theta)_{001}$ rotates the sample by an angle $\theta$ about the $(0 0 1)_\ell$ axis and $R_O$ provides an initial orientation of the sample to give $c \parallel (0 0 1)_\ell$ and $a [b]$ along $(1 0 0)_\ell$. The scattered photon polarization, $\epsilon_f$, is determined by $\epsilon_i$ and $RTR^\top$ and can be expressed in terms of $\epsilon_{f,\sigma}$ and $\epsilon_{f,\pi}$ as

$$\epsilon_f = \frac{(\epsilon_{f,\sigma}^{\top} \cdot RT R^\top \epsilon_i)\epsilon_{f,\sigma} + (\epsilon_{f,\pi}^{\top} \cdot RT R^\top \epsilon_i)\epsilon_{f,\pi}}{|(\epsilon_{f,\sigma}^{\top} \cdot RT R^\top \epsilon_i)\epsilon_{f,\sigma} + (\epsilon_{f,\pi}^{\top} \cdot RT R^\top \epsilon_i)\epsilon_{f,\pi}|},$$

where $\epsilon_{f,\sigma} = (0 0 1)_\ell$, $\epsilon_{f,\pi} = (-\sin\Omega \cos\theta \cos\phi \cos\theta \sin\phi \sin\theta)$ and $\Omega$ is the detector angle relative to the incident beam. The scattering intensity can be determined without knowledge of $\epsilon_f$ by

$$I(\epsilon_i, \omega, Q) \propto |\epsilon_{f,\sigma}^* \cdot RT(\omega, Q)R^\top \cdot \epsilon_i|^2 + |\epsilon_{f,\pi}^* \cdot RT(\omega, Q)R^\top \cdot \epsilon_i|^2.$$

When comparing experimental results to model calculations, it is also important to account for the polarization dependent x-ray absorption cross-section, $\mu(\omega, \epsilon_i)$, of the incident and scattered photons. This is a minor correction in more electronically isotropic materials, but can have a significant impact in the cuprates, where the absorption coefficient along the $a$, $b$ and $c$ axes varies considerably. To account for geometry dependent attenuation of the incident and scattered x-rays, Eq. S12 must be corrected according to

$$I_{\text{abs}}(\epsilon_i, \omega, Q) \propto \frac{I(\epsilon_i, \omega, Q)}{\mu_i + \mu_f \frac{\sin\alpha}{\sin\beta}},$$

where $\alpha$ and $\beta$ are the angles of the incident and scattered beam relative to the sample surface in the scattering plane and $\mu_i$ and $\mu_f$ are the linear absorption coefficients of the incident and scattered photons respectively. These are given by

$$\mu_i \propto \text{Im}(\epsilon_i^* R \overline{F} R^\top \epsilon_i)$$

and

$$\mu_f \propto \text{Im}(\epsilon_f^* R \overline{F} R^\top \epsilon_f),$$

where $\overline{F}$ is the scattering tensor averaged over all atomic sites (O, Ba, Cu, ...). and includes both resonant and non-resonant contributions. Mirroring the polarization dependent x-ray absorption in the cuprates [S3, S5, S6], we estimate $\text{Im}(f_{aa}) \approx 0.74$ at the O $K$ edge (528.3 eV) in LBCO, 0.45 at the Cu $L$ edge (931.4 eV) in LBCO and 0.66 at the Cu $L$ edge (931.4 eV) in YBCO. [S3, S6] For these estimates in LBCO, we assume that the absorption coefficient is similar to that of LNSCO, where polarization dependent XAS is available.
The effect of the absorption correction on the $\phi$ and $L$ dependence of the model are illustrated in Fig. S1 for LBCO at the O $K$ edge. The calculation without any absorption correction (Eq. S12) is shown as thin solid lines. The effect of including the absorption correction (Eq. S13) is shown with dashed lines. For the usual case where the sample surface is parallel to the wedge surface, the dashed line would be the ideal calculation. However, cleaving the sample LBCO S1 yielded a surface that was not parallel to the sample holder (this can also occur for intentionally miscut surfaces), affecting the angles $\alpha$ and $\beta$ that enter into Eq. S13. The actual surface orientation was estimated with an optical microscope and included in the model calculations, shown as thick lines. The $\phi$ dependence of $I_\sigma$ and $I_\pi$ (Fig. S1a) changes significantly when the absorption correction and the orientation of the surface are incorporated. Examination of Fig. S1a illustrates that modelling the azimuthal dependence of $I_\sigma$ and $I_\pi$ directly (as shown in Fig. 2a in the main text) requires a full characterization of the experimental geometry and the effect of absorption on the incident and scattered photons.

When evaluating the ratio of $I_\sigma$ and $I_\pi$, however, the important differences seen in Fig. S1a are largely factored out, as shown in Figs. S1b and S1c. The effect of the absorption correction is modest, on the order of $\sim 5\%$-$15\%$ near $\phi = 0^\circ, 97^\circ, 180^\circ$, but can be important in accurately determining the parameters $t_{||}/t_{\perp}$ and $t_{cc}/t_{\perp}$. The effect of the angled surface is seen to be less important in calculating the ratios of $I_\sigma$ and $I_\pi$ (Figs. S1b and S1c). This highlights that our estimate of the sample surface orientation (due to the cleave) is not important in the determination of $t_{||}/t_{\perp}$ and $t_{cc}/t_{\perp}$ from fits to the ratio $I_\sigma/I_\pi$.

### Influence of CDW orbital symmetry and c axis scattering contribution on model

The sensitivity of the model to $\phi$ and the scattering geometry is most readily understood through calculations for representative sets of parameters corresponding to different CDW orbital symmetries. In Fig. S2 we show the $\phi$ and $L$ dependence of $I_\sigma/I_\pi$ calculated according to Eq. S13 for values of $t_{||}/t_{\perp} = \pm 1, \pm 0.612, \pm 0.612^{-1}$. We can interpret these cases using Eq. S13 (see Fig. 2) for a mapping between $t_{||}/t_{\perp}$ and $\Delta_d/\Delta_{s'}$. The case $t_{||}/t_{\perp} = +1$ ($-1$) corresponds to pure $s'$ ($d$) CDW symmetry (red lines in Fig. S2). We see that $d$ symmetry (red, dashed) would give rise to a $\sim 3.3\times$ larger maximum in $I_\sigma/I_\pi$ than $s'$ symmetry (red, solid) and the maximum in $\phi$ would be located at $\phi \approx 71^\circ$ rather than $\phi \approx 99^\circ$. The case $t_{||}/t_{\perp} = +0.612$ ($-0.612$) corresponds to $\Delta_d/\Delta_{s'} = -0.241$ ($-0.241^{-1}$). This is an \textit{anti-phase}, mixed $d$ and $s'$ state, with mostly $s'$ ($d$) symmetry, which would appear experimentally as a maximum in $I_\sigma/I_\pi$ near $\phi \approx 79^\circ$ ($\phi \approx 96^\circ$). The mostly $d$ symmetry (black, dashed) would give rise to a $\sim 2\times$ larger maximum in $I_\sigma/I_\pi$ than mostly $s'$ symmetry (black, solid). Similarly, $t_{||}/t_{\perp} = +0.612^{-1}$ ($-0.612^{-1}$) corresponds to $\Delta_d/\Delta_{s'} = 0.241$ ($0.241^{-1}$). This is an \textit{in-phase}, mixed $d$ and $s'$ state, with mostly $s'$ ($d$) symmetry. Again, the different peak positions and maximum values of $I_\sigma/I_\pi$ would distinguish between the mostly $s'$ and $d$ cases.

From this discussion and examination of Fig. S2a, it becomes apparent that the $\phi$ dependence is sensitive to the sign and magnitude of $t_{||}/t_{\perp}$. In contrast, the $L$ dependence is sensitive to the magnitude but not the sign of $t_{||}/t_{\perp}$. Combining both types of measurements enhances the reliability of experimentally determining the sign and magnitude.
FIG. S2. Model calculations for different cases of orbital symmetry in LBCO at the O K edge. a. Calculated $\phi$ (left panels) and $L$ (right panels) dependence of $I_\pi/I_\sigma$ showing sensitivity to the sign and magnitude of $t_\parallel/t_\perp$. b. Calculated $\phi$ and $L$ dependence of $I_\pi/I_\sigma$ demonstrating sensitivity to the $c$ axis contribution $t_{cc}/t_\perp$ of $T$. The blue curve is the best fit to the data.

of $t_\parallel/t_\perp$, ultimately enabling the determination of $\Delta_d/\Delta_s'$. This sensitivity to the magnitude and sign of $\Delta_d/\Delta_s'$ affirms that polarization dependent resonant soft x-ray scattering is a powerful tool in discerning the symmetry of CDW order in the cuprates.

In Fig. S2b, we illustrate how a $c$ axis contribution to the scattering influences the model calculation. The blue curves are the best fit to the experimental data on LBCO at the O K edge. The effect of a non-zero $t_{cc}/t_\perp$ is modest and similar in magnitude to the effect of the absorption correction seen in Figs. S1b and S1c. This highlights the importance of including a full geometry dependent absorption correction in the model, as not doing so could lead to erroneous determinations of $t_\parallel/t_\perp$ and $t_{cc}/t_\perp$. 

\[ Q = (0.232 \ 0 \ 0.611) \]

\[ |t_{cc}/t_\perp| = 0.000 \]

\[ |t_\parallel/t_\perp| + - 
\]

1.000 \[ \text{red dotted} \]

0.612 \[ \text{black dashed} \]

0.612$^{-1}$ \[ \text{green dotted} \]

$\phi = 0.180^\circ$

\[ t_\parallel/t_\perp = 0.612 \]

\[ t_{cc}/t_\perp \
\]

0.000 \[ \text{black} \]

0.034 \[ \text{blue} \]
EXPERIMENTAL DATA

Here we provide the experimental data that was used to determine the \( \phi \) and \( L \) dependences of \( I_\sigma \) and \( I_\pi \) shown in the main text. Fig. S3 shows the \( \phi \) dependence of \( I_\sigma \) and \( I_\pi \) in LBCO at the O K edge (\( Q = (0.232 \ 0.611) \), \( \hbar \omega = 528.3 \) eV). For each scan, the detector position (at angle \( \Omega \)) was kept constant and the crystal was rotated about the vertical axis (\( \perp \) to the scattering plane) by \( \pm 15^\circ \). \( I_\sigma \) and \( I_\pi \) were determined by first subtracting the x-ray fluorescence background (\( I_{\text{fluo.}} \)) using a polynomial fit that excluded the peak region and then fitting the resulting data (\( I_{\text{scat.}} \)) with a Lorentzian curve whose amplitude is reported in Fig. 2a in the main text. Figs. S3a and S3b show this analysis procedure for a representative set of measurements. Fig. S3c shows a projected view of the background-subtracted \( I_\sigma \) and \( I_\pi \) data for the full range of \( \phi \) used in fitting to the scattering model.

Here we plot this data against \( \Delta \theta = \theta - \theta_0 \), where \( \theta_0 \) is the center of the peak as identified by peak fitting. Due to a slight misalignment of the \( a \) and \( c \) crystal axes during sample mounting (\( \sim 0.6^\circ \) about wedge normal), the scattering geometry gradually shifted away from the nominal \( Q \)-vector as \( \phi \) was varied. This movement was small enough that minor adjustments to the instrument’s \( \chi \) angle (\( < 1.5^\circ \)) could be used to reposition the CDW peak in the scattering plane, but it did moderately shift the apparent peak position in \( \theta \) as \( \phi \) was adjusted (the maximum deviation was \( \sim 1^\circ \)). By plotting against \( \Delta \theta \), we account for these minor shifts.

**FIG. S3.** Scans through the CDW peak as a function of \( \phi \). a. Normalized intensity of scattering and x-ray fluorescence (open symbols) for incident \( \sigma \) (top panel) and \( \pi \) (bottom panel) photon polarization and polynomial background fit (dashed lines) for select \( \phi \) values. b. Background-subtracted scattering intensity \( I_\sigma \) (open circles) and \( I_\pi \) (open triangles), and corresponding Lorentzian fits (solid lines). In a and b the data is offset vertically for clarity. c. Projected view of background-subtracted \( I_\sigma \) (top) and \( I_\pi \) (bottom) vs. \( \phi \) for full range of measured angles. \( \phi \) values are indicated in legend on right.
The measurement scheme we have employed (Ω remains fixed while θ is rotated) has the advantage of faster data collection speed and reduced noise, but a consequence is that the H, K and L indices all vary to differing degrees that depend on φ. These scans thus correspond to cuts in Q space, as illustrated in Fig. S4a, that depend on φ. Fig. S4b shows a projection onto the H–K plane of these same cuts. As can be seen, a scan at φ = 0° is mostly along H, with no K and some L variation, whereas one at φ = 90° is mostly along K, with some H and L variation.

In Fig. S4, we present the same data as in Fig. S3 but here we have converted θ values into H, K and L indices and plotted the normalized sum of $I_π$ and $I_σ$ scattering in the H–K plane. $H$ and $K$ were shifted by $H_0$ and $K_0$ in order to account for the shifts in θ discussed above (ie. the data is plotted against $ΔH$ and $ΔK$). The normalization is to the sum of the fit amplitudes of the $I_π$ and $I_σ$ data. In this form, the data can be fit to a Lorentzian function $I = A [(ΔH/γ_H)^2 + (ΔK/γ_K)^2 + 1]^{-1}$, where A is the amplitude and $γ_{(H,K)}$ is the HWHM. The H and K correlation lengths are related to $γ_{(H,K)}$ according to $ξ_{(H,K)} = (a,b)/(2πγ_{(H,K)})$. Fitting the normalized $I_π + I_σ$ data with this functional form (see Fig. S4d) gives $ξ_H ≈ 215$ Å and $ξ_K ≈ 184$ Å. These correlation lengths and their ∼17% anisotropy appear consistent with prior hard x-ray scattering data on LBCO [S7].
Fig. S5 shows the photon energy dependence of $I_\sigma$ and $I_\pi$ vs. $H$ of LBCO at the O K edge with $Q = (H \ 0 \ 0.77)$. Similar to the $\phi$ dependent data, the x-ray fluorescence background was first subtracted using a polynomial fit excluding the peak region (the backgrounds shown in Fig. S3 are representative of this procedure). Lorentzian fits were then used to determine the scattering intensities reported in Fig. S5.

Fig. S6 shows the $L$ dependence of $I_\sigma$ and $I_\pi$ vs. $H$ of LBCO at the Cu L edge, $Q = (0.232 \ 0 \ L)$, $\hbar\omega = 931.3$ eV (top panels) and at the O K edge, $Q = (-0.232 \ 0 \ L)$, $\hbar\omega = 528.3$ eV (bottom panels). Similar to the $\phi$ dependent data, the x-ray fluorescence background was subtracted using a polynomial fit excluding the peak region. Lorentzian fits were then used to determine the scattering intensities reported in Figs. 2c and 2d.

Fig. S7 shows the $L$ dependence of $I_\sigma$ and $I_\pi$ of YBCO at the Cu L edge ($\hbar\omega = 931.3$ eV) for the CDW peak along $\pm H$ and $\pm K$. In this case the background subtraction was accomplished by subtracting the measured x-ray fluorescence at 160 K from the measurement at 60 K. Figs. S7a and S7b show a representative set of such backgrounds. Lorentzian fits were then used to determine the scattering intensities reported in Fig. 3.

**FIG. S5.** Energy dependence of CDW scattering peak in LBCO at the O K edge for $\sigma$ (a) and $\pi$ (b) incident photon polarization. Solid lines are Lorentzian fits to the background-subtracted data (filled circles). Photon energy indicated in legend on the right. Data are offset for clarity.
FIG. S6. $L$ dependence of CDW scattering intensity in LBCO at the Cu $L$ (a: $I_\sigma$ and b: $I_\pi$ vs. $H$) and O $K$ (c: $I_\sigma$ and d: $I_\pi$ vs. $H$) edges. Open circles are background-subtracted data and solid lines are Lorentzian fits. Data are offset for clarity.

FIG. S7. $L$ dependence of CDW scattering intensity in YBCO at the O $K$ edge for scans along $H$ (top row) and $K$ (bottom row). a-b. Normalized intensity of scattering and x-ray fluorescence for incident $\sigma$ polarization along $H$ (a) and $K$ (b) at 60 K (solid lines) and 160 K (dashed lines). c-f. Background-subtracted scattering intensity (60-160 K) for $\sigma$ (open triangles) and $\pi$ (open circles) incident photon polarization along $-H$ (c), $-K$ (d), $+H$ (e) and $+K$ (f). Dashed (solid) lines are Lorentzian fits to $I_\sigma$ ($I_\pi$). $L$ values are indicated in legend on right. Data in c-f are offset for clarity.
PARAMETER ESTIMATION AND CONFIDENCE REGIONS

The parameters $t_\parallel/t_\perp$ and $t_{cc}/t_\perp$ were determined by unconstrained, weighted least-squares fitting of the experimental data to $I(\epsilon_{i,\pi}, \omega, Q)/I(\epsilon_{i,\sigma}, \omega, Q)$, as defined by Eq. S13. These were the only free parameters in the fit. For LBCO at the O K edge, both the $\phi$ and $L$ dependent data were fit simultaneously. This simultaneous fit narrowed the confidence regions (CR) as compared to fitting either dataset individually. Since the $\phi$ dependence at the Cu L edge in YBCO and LBCO were not measured here, the fits in those cases are to the $L$ dependence. Fitting to the $L$ dependence alone does not determine the signs of $t_\parallel/t_\perp$ and $t_{cc}/t_\perp$ (see Fig. S2a), but can still constrain their absolute values and their relative sign (ie., $t_\parallel/t_\perp$ and $t_{cc}/t_\perp$ will either have the same or opposite sign).

Although least-squares fitting provides standard errors for the best fit parameters, an examination of $\chi^2_0$, the reduced chi-squared statistic, throughout the parameter space identified that the 95% confidence intervals defined by the standard errors (rectangular regions in Fig. 2e) underestimated the regions of high confidence. The high confidence regions were better described by contours of constant $\chi^2_0$, appearing as ellipses in the $t_\parallel/t_\perp - t_{cc}/t_\perp$ plane for the LBCO O K and Cu L edge data. The contours were selected to represent regions where there was a 95% (or higher) likelihood that the model described the experimental data. To illustrate this point and the level of confidence with which the reported values $t_\parallel/t_\perp$ and $t_{cc}/t_\perp$ are given, we show here how the model calculations vary across the parameter space around the best fit parameters. This analysis is shown in Fig. S8 for LBCO at the O K edge, Fig. S9 for LBCO at the Cu L edge, and Fig. S10 for YBCO at the Cu L edge.

We caution that the absolute values of $\chi^2_0$ reported here should not be over-interpreted as the formal definition of $\chi^2_0$.

![Graphs showing parameter estimation and confidence regions](image-url)
requires that weights be calculated from true variances (ie. $\sigma$ from a normal distribution of repeated measurements). Here, we used statistical errors from fitting the CDW peak to estimate the variance, which can lead to $\chi^2_0 < 1$, indicating that the experimental uncertainty underestimates the variance. Although the magnitudes of $\chi^2_0$ are affected by this detail, one can still use this statistic as a means of identifying regions of parameter space where the model yields good agreement with the data. It is in this sense that we have opted to define the high confidence regions of parameter space where the model agrees with the data.

FIG. S9. $L$ dependence of the model calculations based on Eq. S13, for LBCO at the Cu $L$ edge, at the points indicated in the colour maps of $\chi^2_0$ in the $t_{\|}/t_\perp - t_{cc}/t_\perp$ parameter space. Panel a (b) explores the parameter space of the model along the diagonal (horizontal) direction.

FIG. S10. $L$ dependence of the model calculations based on Eq. S13, for YBCO at the Cu $L$ edge, at the points indicated in the colour maps of $\chi^2_0$ in the $t_{\|}/t_\perp - t_{cc}/t_\perp$ parameter space. The parameter space of the model is explored for the CDW peak along $H$ (a-b) and $K$ (c-d) in the diagonal (left panels) and horizontal (right panels) directions. The maps of $\chi^2_0$ are truncated at values greater than 4 to highlight the region of good agreement.
Lastly, we would like to illustrate the confidence with which the sign of $t_{∥}/t_{⊥}$ is reported for LBCO at the O $K$ edge. An examination of $\chi^2_0$ over a larger region of the parameter space is shown in right panel of Fig. S11. Here $\chi^2_0$ is truncated above $\chi^2_0 = 30$. The value of $\chi^2_0$ outside the plotted region was found to be very large. The same 95% confidence region reported in the main text (Fig. 2e) and shown above (Fig. S8) is shown in light green to provide a sense of scale for the parameter space. In addition to the global minimum at $t_{∥}/t_{⊥} = 0.612$ and $t_{cc}/t_{⊥} = 0.034$, we find a local minimum in $\chi^2_0$ with a small and negative $t_{∥}/t_{⊥}$ and a relatively large and negative $t_{cc}/t_{⊥}$. As shown in Fig. S11, this local minimum has a considerably higher $\chi^2_0$ than the global minimum (right panel) and is a poor fit to the data along $\phi$ (left panel) and $L$ (center panel). We therefore have a high degree of confidence that $t_{∥}/t_{⊥} > 0$, ruling out a dominant $d$ symmetry to the CDW order in LBCO.

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**FIG. S11.** Comparison of global minimum in $\chi^2_0$ with $t_{∥}/t_{⊥} > 0$ with local minimum having $t_{∥}/t_{⊥} < 0$ for LBCO at the O $K$ edge. Model calculations plotted against $\phi$ (left panel) and $L$ (center panel) for the global and local minima indicated by coloured symbols in the right panel. The colour map of $\chi^2_0$ is truncated above $\chi^2_0 = 30$. The 95% confidence region (CR), shown as a light green ellipse, is the same as in Figs. 2e and S8. The global minimum matches the data, whereas the local minimum with $t_{∥}/t_{⊥} < 0$ (corresponding to $|\Delta_d| > |\Delta_{d'}|$) is a poor match.

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