CONDENSED MATTER PHYSICS

Orbital symmetries of charge density wave order in $YBa_2Cu_3O_{6+x}$

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Charge density wave (CDW) order has been shown to compete and coexist with superconductivity in underdoped cuprates. Theoretical proposals for the CDW order include an unconventional *d*-symmetry form factor CDW, evidence for which has emerged from measurements, including resonant soft x-ray scattering (RSXS) in $YBa_2Cu_3O_{6+x}$ (YBCO). Here, we revisit RSXS measurements of the CDW symmetry in YBCO, using a variation in the measurement geometry to provide enhanced sensitivity to orbital symmetry. We show that the (0 0.31 *L*) CDW peak measured at the Cu *L* edge is dominated by an *s* form factor rather than a *d* form factor as was reported previously. In addition, by measuring both (0.31 0 *L*) and (0 0.31 *L*) peaks, we identify a pronounced difference in the orbital symmetry of the CDW order along the *a* and *b* axes, with the CDW along the *a* axis exhibiting orbital order in addition to charge order.

INTRODUCTION

While the presence of charge density wave (CDW) order in the cuprates appears to be ubiquitous (*1*–*11*), open questions remain about the microscopic character of the CDW order and whether it is also generic. In particular, theoretical studies (*12*–*21*) have predicted the CDW charge modulation to have a *d* form factor in contrast to a more conventional *s* (*s*′) form factor. Whereas a *s* (*s*′) CDW involves a simple, monopolar sinusoidal modulation of the charge density on the Cu (O) sites, a *d* form factor CDW involves a quadrupolar modulation on the bonds between Cu atoms, namely, the O sites, that are out of phase for bonds oriented along *x* and *y*, giving a form factor with $d_{x^2-y^2}$ symmetry (see Fig. 1A). Such a *d* form factor CDW has been observed in $Bi_2Sr_2CaCu_2O_8$+*x* (BI2212) and $Na_xCa2\text{-}_xCuO_2Cl_2$ (NCCOC) using scanning tunneling microscopy (STM) (*22*). Further evidence of a dominant *d* form factor CDW order was provided by nonresonant hard x-ray scattering in $YBa_2Cu_3O_{6+x}$ (YBCO) (*23*) and by resonant soft x-ray scattering (RSXS) measurements at the Cu *L* edge of the (0 0.31 1.48) CDW Bragg peak in YBCO (*24*). However, the ability of the RSXS measurements to distinguish between dominant *d* and dominant *s* or *s*′ factor CDW orders was close to the experimental accuracy, providing some ambiguity to the conclusion of a dominant *d* form factor CDW order in YBCO. In contrast to these observations, RSXS measurements at the Cu *L* and O *K* edges in the spin-charge stripe ordered cuprate $La_{1.875}Ba_{0.125}CuO_4$ (LBCO) find the CDW order to have predominantly *s*/*s*′ form factor (*25*), indicating that the symmetry of the CDW form factor may not be generic to the different cuprate materials. Moreover, Achkar *et al.* (*25*) also showed that the orbital symmetry of CDW order is not generic even within YBCO, differing for CDW order propagating along the *a* and *b* axes.

In this study, we present new RSXS measurements of the orbital symmetry of CDW in YBCO. We follow an experimental approach similar to (*24*) and (*25*) but with two key advances: (i) We use a different experimental geometry that provides much greater contrast to the *d* versus *s*′ or *s* form factor than past work and (ii) use this technique to study both the CDW order propagating along the *a* and *b* axes by investigating the (0.31 0 *L*) and (0 0.31 *L*) Bragg peaks, respectively. With the enhanced sensitivity to *d* versus *s*′ or *s* form factors, we find no clear evidence for a *d* form factor CDW in YBCO, contrary to the conclusions of Comin *et al.* (*24*). Rather, measurements of the (0 0.31 *L*) peak at the Cu *L* appear to be dominated by an *s* form factor component of the CDW order, similar to LBCO (*25*). In addition, by studying both the (0.31 0 *L*) and (0 0.31 *L*) Bragg peaks, we detail how the density wave order in YBCO exhibits a profound difference in orbital symmetry in addition to the previously established unidirectional character in the CDW Bragg peak intensity and correlation length (*6*, *26*–*28*) or nuclear magnetic resonance (NMR) line broadening (*29*). Specifically, we show that the density wave order involves orbital order in addition to the established charge order but only for CDW order propagating along the *a* axis and not along the *b* axis. Two orbital order scenarios are discussed involving modulations of states beyond the expected $3d_{x^2-y^2}$ orbitals or orbital rotations that break *bc* and *ab* plane symmetries, such as an oscillation of the orbitals about the *b* axis.

The experimental technique involves measuring the resonant x-ray scattering at the Cu *L* absorption edge ($\hbar\omega$ = 931.4 eV) and the CDW wave vector. At this photon energy, the scattering intensity is sensitive to modulations in the Cu 3d or core 2p states and has proven to be an effective probe of CDW order in the cuprates. By varying the photon polarization relative the crystallographic axes, resonant x-ray scattering can also provide insight into the orbital symmetry of the density wave order. This can be understood by considering the CDW scattering intensity, *I*, on resonance in terms of tensor quantities, akin to the index of refraction in an anisotropic medium

$$I(\vec{\mathbf{Q}}, \hbar\omega, \vec{\boldsymbol{\epsilon}}, \vec{\boldsymbol{\epsilon}}') \propto \left| \vec{\boldsymbol{\epsilon}}' \cdot \hat{F}(\vec{\mathbf{Q}}, \hbar\omega) \cdot \vec{\boldsymbol{\epsilon}} \right|^2 \quad (1)$$

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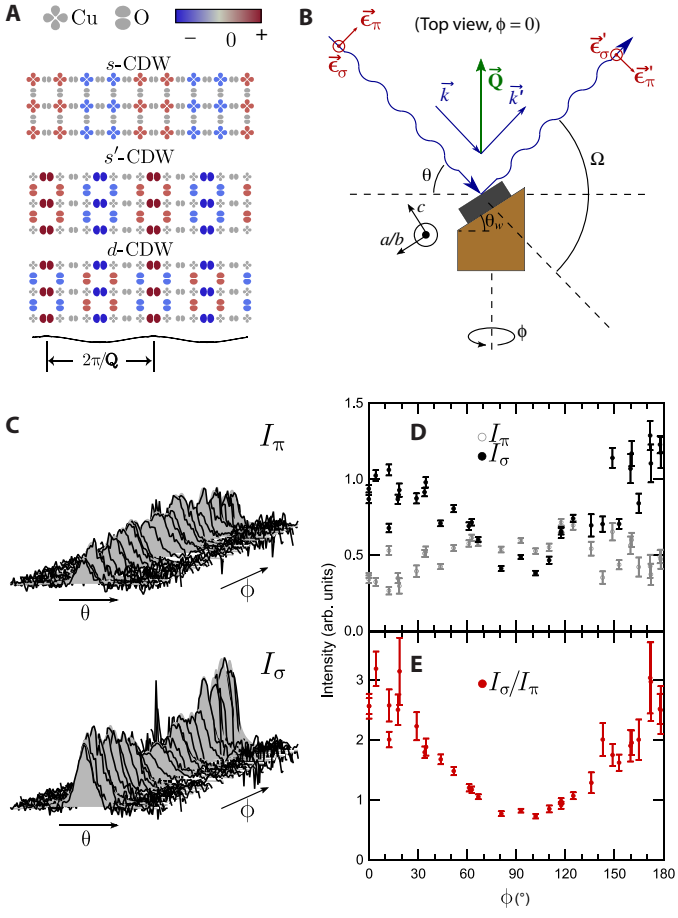

Fig. 1. Representations of CDW form factors and the experimental technique, resonant soft-x ray scattering, used to probe the CDW orbital symmetry. (**A**) Representation of the CuO_2 planes depicting *s*, *s*′, and *d* form factor CDW orders. (**B**) Schematic of the experimental geometry as seen from above, showing the orientation when $\phi = 0°$. As ϕ is rotated, the scattering vector $\vec{\mathbf{Q}}$ remains unchanged, but the incident ($\vec{\epsilon}$) and scattered ($\vec{\epsilon}'$) photon polarizations vary relative to the crystallographic axes. (**C**) Intensity measurements of the CDW peaks for YBCO-6.75 at (0 0.31 1.32). The peak profiles with fluorescent backgrounds removed as a function of θ and ϕ for π and σ polarizations. Lorentzian fits to each peak are shown as gray shading. The amplitudes I_σ and I_π (**D**) and ratio I_σ/I_π (**E**) versus azimuthal angle. arb. units, arbitrary units.

where $\vec{\epsilon}$ and $\vec{\epsilon}'$ are the incident and scattered polarization vectors, respectively, and

$$\hat{F}(\vec{\mathbf{Q}},\hbar\omega) = \sum_j \hat{f}_j(\hbar\omega)\, e^{i\vec{\mathbf{Q}}\cdot\vec{r}_j} = \begin{bmatrix} F_{aa} & F_{ab} & F_{ac} \\ F_{ba} & F_{bb} & F_{bc} \\ F_{ca} & F_{cb} & F_{cc} \end{bmatrix} \quad (2)$$

is a tensoral expression of the x-ray scattering structure factor. $\hat{f}_j$ is the atomic scattering form factor tensor for an atom at site, *j*, and the symmetry of $\hat{f}_j$ follows from the local point group symmetry of that site (*30*). Accordingly, the symmetry of $\hat{F}(\vec{\mathbf{Q}},\hbar\omega)$ relates to (but is distinct from) the point group symmetry of individual sites and how that symmetry is modulated by the density wave order.

For instance, a simple *s* or *s*′ form factor CDW order, corresponding to a sinusoidal modulation of charge density (and properties proportional to charge density), would have a scattering tensor that has the same symmetry as the average ($\vec{\mathbf{Q}} = 0$) electronic structure. For the CuO_2 planes of YBCO, where holes in Cu $d_{x^2-y^2}$ orbitals dominate the electronic structure that is probed at 931.4 eV, this is approximately D_{4h} symmetry, and $\hat{F}(\vec{\mathbf{Q}},\hbar\omega)$ would be a diagonal tensor with $F_{aa} \simeq F_{bb} >> |F_{cc}|$. In contrast, CDW order with a dominant *d* form factor may feature a symmetry with negative F_{aa}/F_{bb}, indicative of a density modulation on *x*- and *y*-oriented "bonds" that are out of phase (*24*, *25*). This could be seen at the Cu *L* edge due to shifting in the energy of the Cu $2p_x$ and $2p_y$ core states (*14*, *24*, *25*) or more directly in the occupation of the O 2p state by probing the CDW peak at the O *K* edge (*25*). Other symmetries to $\hat{F}(\vec{\mathbf{Q}},\hbar\omega)$ may be signatures of a density wave order that involves orbital order or magnetic order.

Experimentally, the symmetry of $\hat{F}(\vec{\mathbf{Q}},\hbar\omega)$ can be determined by measuring the CDW Bragg peak intensity at a fixed $\vec{\mathbf{Q}}_{CDW}$ and rotating the sample azimuthally such that the orientation of $\vec{\epsilon}$ and $\vec{\epsilon}'$ vary relative the crystallographic axes, as shown in Fig. 1 (*24*, *25*). This approach has been used in analysis of the (0 0.31 1.48) peak in YBCO (*24*) to provide evidence that the CDW has a dominant *d* form factor. However, the measurements by Comin *et al.* (*24*) use a probing geometry with $\Omega \simeq 170°$ ($L \simeq 1.5$), where the CDW peak intensity is maximal. These measurements, while statistically favoring a *d* form factor, did not provide strong contrast between *s*, *d*, and *s*′ form factor models. Here, we revisit this analysis by measuring the azimuthal dependence of the CDW order at $\Omega \simeq 134°$ ($L \simeq 1.3$) in addition to $\Omega \simeq 170°$ ($L = 1.48$). Notably, the measurements with $\Omega \simeq 134°$ ($L \simeq 1.3$) probe the same CDW peak as $\Omega \simeq 170°$ ($L \simeq 1.48$), owing to the fact that the quasi two-dimensional CDW peak in YBCO is very broad in *L*. However, the variation in measurement geometry affects how $\vec{\epsilon}$ and $\vec{\epsilon}'$ span the crystallographic axes as ϕ is rotated, yielding greater sensitivity to the sign of F_{aa}/F_{bb}, and thus the form factor of the CDW order, for lower Ω. In addition, we also explore the orbital symmetry of the CDW order measured for both the (0.31 0 *L*) and (0 0.31 *L*) peaks, representing CDW order propagating along the *a* and *b* axes, respectively.

RESULTS AND DISCUSSION

The results of the measurements and subsequent fits for the (0 0.31 *L*) and (0.31 0 *L*) peaks using geometries with $L \simeq 1.48$ and $L \simeq 1.33$ are shown in Fig. 2. In addition, data from Comin *et al.* (*24*) of the (0 0.31 *L*) peak in YBCO-6.75 with $L \simeq 1.48$ are reproduced in Fig. 2A and are shown to be in good agreement with our measurements. The first observation to make about the data in Fig. 2 is a notable difference between measurements of the (0.31 0 *L*) and (0 0.31 *L*) peaks, with the (0 0.31 *L*) peaks exhibiting substantially larger dependence on ϕ. We take this as compelling evidence to support the existence of two different orbital symmetries for the CDW order propagating along *a* and *b*.

The data in Fig. 2 can be fit to determine the components of the scattering and the underlying symmetry of the CDW order. Applying this first to the (0 0.31 *L*) peak, we note that the fit parameters from Comin *et al.* (*24*) used to argue a *d* form factor CDW, shown as the dashed black line in Fig. 2A, agree reasonably well with our measurements for $\Omega = 170°$. However, this model does not agree with our measurements at $\Omega = 134°$ (Fig. 2C), where a minimum in I_σ/I_π at $\phi \simeq 60°$ would be expected instead of the observed minimum at $\phi \simeq 100°$. In contrast, a model with $F_{aa} \simeq F_{bb} >> |F_{cc}|$ fits well to both $\Omega = 170°$ and 134° measurements (a least squares fit gives $F_{bb}/F_{aa} =$

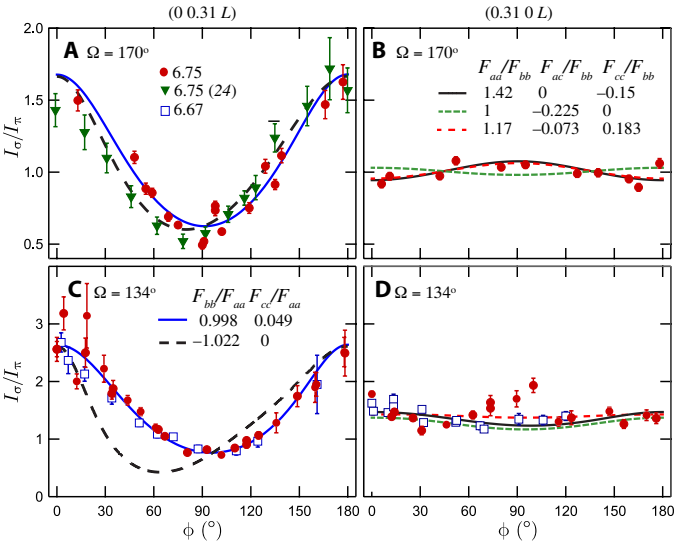

Fig. 2. The ratio of measured scattering intensities with σ and π incident polarization versus ϕ for the density wave order peaks at (0 0.31 *L*) and (0.31 0 *L*) for samples with O content 6.67 and 6.75. I_σ/I_π for (0 0.31 *L*) is shown in (**A**) and (**C**) with data from (*24*) reproduced in (A). I_σ/I_π for (0.31 0 *L*) is shown in (**B**) and (**D**). The top row (A and B) shows data taken at Ω ≃ 170° (*L* = 1.48), while the bottom row (C and D) shows Ω ≃ 134° (*L* = 1.33). The lines are fits to model calculations. For the (0 0.31 *L*) peak, a scattering tensor with $F_{aa} \simeq F_{bb} >> F_{cc}$ agrees well with the data, whereas the dominant *d* form factor model in (*24*) (dashed black) does not reproduce the Ω = 134° data. For the (0.31 0 *L*) peak, a range of parameters corresponding to qualitatively different symmetries provide comparable quality fits.

0.998 ± 0.020 and $F_{cc}/F_{aa} = 0.049 \pm 0.041$). This symmetry for $\hat{F}(\vec{\mathbf{Q}}, \hbar\omega)$ is consistent with the Cu *L* edge measurements of the CDW order being dominated by an *s* form factor component of the CDW order, which would entail a modulation in the orbital occupation (or property proportional to the orbital occupation) of Cu $3d_{x^2-y^2}$ states. That is, for the (0 0.31 *L*) peak, the symmetry of the Cu orbitals that are spatially modulated in the CDW is the same as the average symmetry of the in-plane Cu. This symmetry ($F_{aa} \simeq F_{bb} >> |F_{cc}|$) is similar to that found in Cu *L* edge measurements of the CDW order in LBCO, where a predominant *s*′ symmetry to the CDW order was also deduced from measurements at the O *K* edge (*25*).

This result introduces the possibility that, similar to LBCO, the CDW order in YBCO also has predominantly *s*/*s*′ orbital symmetry, differing from the *d* form factor CDW order observed in Bi2212 and NCCOC by STM (*22*). However, we note that the absence of evidence for a *d* form factor CDW order in the present measurements does not fully rule out its relevance to YBCO. A *d* form factor density wave order is suggested by the pattern of oxygen displacements deduced from nonresonant x-ray scattering measurements (*23*). Reconciling that result with our present observations may require understanding details of how different experimental techniques couple to form factor of the density wave order. For instance, STM measurements in Bi2212 indicate that a *d* form factor coexists with *s* and *s*′ form factors and that the degree of *s*, *s*′, and *d* contributions to the form factor depends on the sample bias, with a *d* form factor dominant at the pseudo-gap energy scale, but a substantial *s*′ contribution at lower and higher bias (*31*, *32*). That is, the *s*, *s*′, and *d* contributions to the form factors depend on the energy and momentum of electronic states. Similarly, it is anticipated that the coupling of resonant x-ray scattering measurements to the symmetry of the density wave order have dependence on the incident photon energy (*25*). While the I_σ/I_π ratio in resonant x-ray measurements at ϕ = 0 does not appear to exhibit an energy dependence at the Cu *L* edge (*5*), indicating the symmetry probed is approximately energy independent at the Cu *L* edge, the electronic states and subsequent sensitivity to the CDW form factor can vary between the Cu *L* and O *K* edges or within the O *K* edge (*25*). Moreover, we anticipate that measurements at the Cu *L* edge are more sensitive to *s* than *d* or *s*′ contributions to the form factor CDW (*24*, *25*). Future theoretical work on the microscopic character CDW order may enable these measurements place quantitative constraints on the degree of *d* form factor density wave order in YBCO.

We now turn our attention to fitting the symmetry of $\hat{F}(\vec{\mathbf{Q}}, \hbar\omega)$ for the (0.31 0 *L*) peak. In contrast to the (0 0.31 *L*) peak, fits of the symmetry of $\hat{F}(\vec{\mathbf{Q}}, \hbar\omega)$ show a substantial departure from the average point group symmetry of the CuO_2 planes for the (0.31 0 *L*) peak. This indicates significant orbital ordering in addition to charge order for the density wave orders propagating along the *a* axis that is not observed (i.e., not present or too small to distinguish) along the *b* axis. Unfortunately, the present measurements are unable to uniquely determine the symmetry of $\hat{F}(\vec{\mathbf{Q}}, \hbar\omega)$. Rather, as shown for selected fits in Fig. 2 (B and D), a range of parameters/symmetries with different physical interpretations provide adequate fits to the data (the regions of fit parameters with comparable reduced χ^2 are shown in the Supplementary Materials). This analysis reveals two symmetry distinct scenarios that are found to fit well to the data: models having substantial in-plane orbital asymmetry $F_{aa} > F_{bb}$ and/or models having off-diagonal $F_{ac} = F_{ca} \neq 0$ elements.

The first scenario, involving a substantial in-plane asymmetry, $F_{aa} > F_{bb}$, may result from a modulation of the in-plane Cu electronic structure that involves Cu 3d orbitals beyond simply the $3d_{x^2-y^2}$ states that are known to dominate the low-energy electronic structure of the CuO_2 planes. Alternately, $F_{aa} > F_{bb}$ may be indicative of a chain layer contribution to the scattering. However, analysis of the energy dependence of the CDW resonant x-ray scattering did not reveal a contribution to the CDW peak from Cu in the chain layer, which resonates at different photon energies from the Cu in the CuO_2 planes (*5*, *33*). Moreover, the azimuthal dependence of the (0.31 0 *L*) peak does not vary as a function of temperature (Fig. 3) or doping (Fig. 2), ruling out contributions from ortho chain ordering to the (0.31 0 *L*) peak.

In the second scenario, the sizeable off-diagonal $F_{ac} = F_{ca}$ terms indicate a density wave order with substantial breaking of *bc* and *ab* plane mirror symmetries. This could occur if the orientation of the unoccupied Cu d orbitals oscillates about the *b* axis such that the *bc* and *ab* plane mirror symmetry of an individual Cu site is broken and modulated with period of the CDW. Such a state may be consistent with the previously reported pattern of lattice displacements refined from nonresonant hard x-ray scattering (*23*). As depicted in Fig. 4, these lattice displacements may result in both a modulation of the orbital occupation and orbital orientation, which would be consistent with the presence of finite $F_{ac,ca}$ terms in the scattering tensor. However, since similar patterns of lattice displacements for CDW order along the *a* and *b* axes are deduced from nonresonant x-ray scattering (*23*), we may have expected to observe off-diagonal terms in the (0 0.31 *L*) as well.

The key question that arises from these results is why the (0.31 0 *L*) and (0 0.31 *L*) peaks exhibit different orbital symmetries.

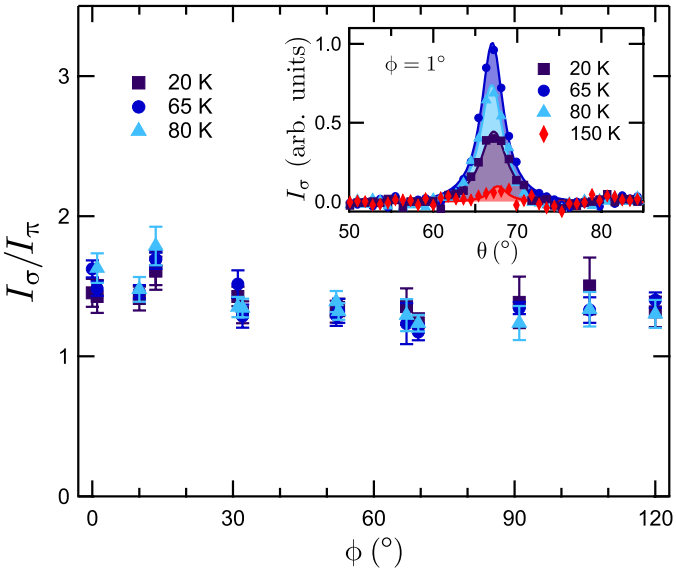

Fig. 3. Measurement of the (0.31 0 1.32) peak in YBCO-6.67 for a series of temperatures and azimuthal rotations, ϕ. I_σ/I_π versus ϕ at different temperatures overlap within uncertainty and show no sign of a temperature dependence in the form factor. Inset: Scans of the intensity of the (0.31 0 1.33) peak with σ polarization at ϕ = 1° at various temperatures.

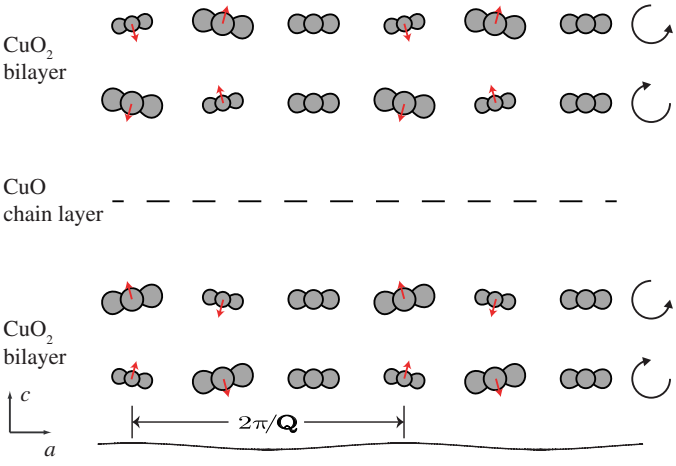

Fig. 4. A simplified pattern of modulated charge (depicted by the size of the Cu 3d orbitals) and orbital symmetry that would give rise to off-diagonal, F_{ac}, elements in $\hat{F}(\vec{Q},\hbar\omega)$. The pattern of lattice displacements of the Cu atoms deduced from nonresonant x-ray diffraction is shown as red arrows (*23*). These displacements trace out ellipses in the *ac* plane as position advances along the *a* axis. These displacements (as well as the displacements of the neighboring O, Y, and Ba atoms) break and modulate the local *bc* and *ab* plane mirror symmetries. This modulation can lead to an alternation in the orbital occupation (charge) of the Cu (roughly associated with the proximity of the in-plane Cu to the chain layer), and the direction of atomic displacements can lead to an alternation in the orientation of the unoccupied orbitals. A more realistic model must incorporate the impact of O displacements on Cu 3d orbital occupation.

In many respects, the density wave orders along *a* and *b* appear similar, having comparable correlation lengths, temperature dependencies, energy dependence, intensities at 1/8 doping, and patterns of lattice displacements (*5*, *6*, *23*, *26*). However, they also have key differences, such as different doping dependence to their intensities (*6*, *26*) and response to applied magnetic field (*28*). Moreover, NMR has shown differences in line broadening for O(2) and O(3) sites (*2*), as well as differences between Cu sitting below full and empty chains (*29*), that may relate the to the asymmetry observed here. An explanation of these differences may lie in identifying the origin of the different orbital symmetries of the density wave orders along *a* and *b*.

MATERIALS AND METHODS

Measurements were performed at the Resonant Elastic and Inelastic X-ray Scattering (REIXS) beamline of the Canadian Light Source synchrotron (*34*). Samples were mounted on a copper plug angled at $\theta_w = 32.5°$ and 35.5° to achieve $L = 1.48$ and $L = 1.33$, respectively, as depicted in Fig. 1A. The photon energy was set to 931.3 eV, the peak of the Cu L_3 absorption edge where the CDW ordering peak is maximal (*3*, *5*). The incident photon polarization was set to either σ and π. However, the scattered photon polarization or energy is not resolved. *H* and *K* scans at various ϕ values were performed by rocking θ at fixed Ω such that the peak is centered at a fixed $\mathbf{Q}_{CDW}$ that does not vary with ϕ. ϕ = 0 is defined in Fig. 1 and relates to α from (*24*) by $\alpha = 180° - \phi$.

Two single-crystal samples of $YBa_2Cu_3O_{6+x}$ with oxygen stoichiometry of $x = 0.75$ and 0.67, respectively, were measured using the same samples from previous experiments in (*25*, *35*). The CDW peak amplitudes were determined by first subtracting a fluorescent background using a fifth-order polynomial and then fitting the CDW peaks to a Lorentzian function, similar to (*25*). Variations in the details of the fitting procedure were explored and showed little effect on the ϕ dependence of I_σ/I_π. Analysis of the symmetry of $\hat{F}(\vec{\mathbf{Q}},\hbar\omega)$ included the impact of the polarization dependence of the absorption coefficient on the scattering intensity, as detailed in (*25*). Figure 1 (A and B) shows the (0 0.31 *L*) peak intensities versus ϕ of the YBCO-6.75 sample on the 35.5° plug with backgrounds removed.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/45/eaay0345/DC1

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