A global inversion-symmetry-broken phase inside the pseudogap region of $\text{YBa}_2\text{Cu}_3\text{O}_y$

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The phase diagram of cuprate high-temperature superconductors features an enigmatic pseudogap region that is characterized by a partial suppression of low-energy electronic excitations¹. Polarized neutron diffraction^{2–4}, Nernst effect⁵, terahertz polarimetry⁶ and ultrasound measurements⁷ on $\text{YBa}_2\text{Cu}_3\text{O}_y$ suggest that the pseudogap onset below a temperature T^* coincides with a bona fide thermodynamic phase transition that breaks time-reversal, four-fold rotation and mirror symmetries respectively. However, the full point group above and below T^* has not been resolved and the fate of this transition as T^* approaches the superconducting critical temperature T_c is poorly understood. Here we reveal the point group of $\text{YBa}_2\text{Cu}_3\text{O}_y$ inside its pseudogap and neighbouring regions using high-sensitivity linear and second-harmonic optical anisotropy measurements. We show that spatial inversion and two-fold rotational symmetries are broken below T^* while mirror symmetries perpendicular to the Cu–O plane are absent at all temperatures. This transition occurs over a wide doping range and persists inside the superconducting dome, with no detectable coupling to either charge ordering or superconductivity. These results suggest that the pseudogap region coincides with an odd-parity order that does not arise from a competing Fermi surface instability and exhibits a quantum phase transition inside the superconducting dome.

The crystal system and point group of a material are encoded in the structure of its second- and higher-rank optical susceptibility tensors⁸, which can be determined from the anisotropy of its linear and nonlinear optical responses. The second-harmonic (SH) response is particularly sensitive to the presence of global inversion symmetry because unlike the linear electric-dipole susceptibility tensor χ_{ij}^{ED} , which is allowed in all crystal systems, the SH electric-dipole susceptibility tensor χ_{ijk}^{ED} vanishes in centrosymmetric point groups, leaving typically the far weaker electric-quadrupole term χ_{ijkl}^{EQ} as the primary bulk radiation source^{9,10}. For these reasons, it has been proposed that optical SH generation may be an effective probe of inversion symmetry breaking in the cuprates¹¹.

To fully resolve the spatial symmetries underlying the pseudogap and its neighbouring regions, we performed both linear and SH optical rotational anisotropy (RA) measurements on de-twinned single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_y$ as a function of oxygen content and temperature. The RA measurements track variations in the intensities of light reflected at the fundamental (I^ω) and SH frequencies ($I^{2\omega}$) of an obliquely incident laser beam, which is resonant with the O $2p$ to Cu $3d$ charge transfer energy ($\hbar\omega = 1.5$ eV), as the scattering plane is rotated about the c axis (Fig. 1a). The use of a recently developed rotating optical grating-based technique¹² made

it possible to perform full 360° sweeps of the scattering plane angle (φ) over large temperature ranges while keeping the incident beam spot ($\sim 100\ \mu\text{m}$) fixed to the same location on the crystal to within a few micrometres.

We first simulate the RA patterns expected from hole-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ ($y > 6$) based on its reported orthorhombic mmm crystallographic point group¹³, which is inversion symmetric and consists of three generators m_{ac} , m_{bc} and m_{ab} that denote mirror symmetries across the a – c , b – c and a – b planes. Unlike its tetragonal parent ($y = 6$) compound¹⁴, the point group of hole-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ endows the crystal only with two-fold (C_2) rather than four-fold (C_4) rotational symmetry about the c axis because the excess oxygen atoms form chains that run along the b axis (Fig. 1a). Figure 1b shows representative linear and SH RA patterns computed in the electric-dipole $I^\omega(\varphi) \propto |\hat{\epsilon}_i^\omega(\varphi)\chi_{ij}^{\text{ED}}\hat{\epsilon}_j^\omega(\varphi)|^2 I_0$ and electric-quadrupole $I^{2\omega}(\varphi) \propto |\hat{\epsilon}_i^{2\omega}(\varphi)\chi_{ijkl}^{\text{EQ}}\hat{\epsilon}_j^\omega(\varphi)\partial_k\hat{\epsilon}_l^\omega(\varphi)|^2 I_0^2$ approximations respectively, where I_0 is the incident beam intensity and both the incident (in) and reflected (out) polarizations $\hat{e}_0$ and $\hat{e}$ are selected to be perpendicular (S_{in} – S_{out}) to the scattering plane (see Supplementary Section 1 for other polarization geometries). The orthorhombic crystal system is identifiable by an ovalar $I^\omega(\varphi)$ pattern with maxima and minima aligned strictly along the a and b axes¹⁵ while the mmm point group is identifiable by a four-lobed $I^{2\omega}(\varphi)$ pattern that is mirror symmetric about the a and b axes.

Figure 2 shows linear and SH RA data from $\text{YBa}_2\text{Cu}_3\text{O}_y$ with hole-doping levels (p) of 0.125 ($y = 6.67$; underdoped; $T_c = 65$ K), 0.135 ($y = 6.75$; underdoped; $T_c = 75$ K), 0.165 ($y = 6.92$; optimal doped; $T_c = 92$ K) and 0.190 ($y = 7.0$; overdoped; $T_c = 86$ K) measured at room temperature ($T > T^*$) in S_{in} – S_{out} geometry (see Supplementary Section 2 for all other geometries). In the linear RA data, we see that the anisotropy ($\chi_{xx}^{\text{ED}} - \chi_{yy}^{\text{ED}}$) becomes more pronounced with hole doping as expected due to the filling of Cu–O chains. However, in contrast to Fig. 1b, the intensity maxima and minima are rotated away from the a and b axes, indicating an absence of m_{ac} and m_{bc} symmetries consistent with a monoclinic distortion. In fact, by using the structure of χ_{ij}^{ED} for a monoclinic crystal system in the expression for $I^\omega(\varphi)$, excellent fits to the data are obtained (Fig. 2). In the SH RA data, we also find clear violations of the mmm point group symmetries at all doping levels. In particular, the alternation in lobe magnitude as a function of φ and the rotation of the lobe bisectors away from the a and b axes indicate an absence of m_{ac} and m_{bc} symmetries consistent with the linear RA data. We find excellent agreement of the data with an electric-quadrupole-induced SH response from the centrosymmetric $2/m$ monoclinic point group (Fig. 2), which consists of two generators 2 and m that denote C_2 and m_{ab} symmetries. On the contrary, fits

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Figure 1 | Layout of optical anisotropy experiment and predicted response of $\text{YBa}_2\text{Cu}_3\text{O}_y$. **a**, The intensity of light reflected at the fundamental (I^ω) and SH ($I^{2\omega}$) frequencies of an obliquely incident beam is measured as a function of the angle (φ) between the scattering plane and the a - c plane of $\text{YBa}_2\text{Cu}_3\text{O}_y$. The Cu-O chains run along the b axis. The incident photon energy (1.5 eV) is resonant with the O $2p$ to Cu $3d$ charge transfer transition (inset). The polarization of the incident (in) and reflected (out) beams can be selected to lie either parallel (P) or perpendicular (S) to the scattering plane. **b**, Rotational anisotropy of the electric-dipole-induced linear response and electric-quadrupole-induced SH response simulated for the orthorhombic crystal system and the mmm point group respectively in $S_{\text{in}}-S_{\text{out}}$ geometry. The crystallographic a and b axes are aligned respectively along the laboratory x and y axes.

Figure 2 | Crystal system and point group of $\text{YBa}_2\text{Cu}_3\text{O}_y$ above T^* . **a-d**, Polar plots of $I^\omega(\varphi)$ and $I^{2\omega}(\varphi)$ measured at $T = 295$ K in $S_{\text{in}}-S_{\text{out}}$ geometry from $\text{YBa}_2\text{Cu}_3\text{O}_y$ with $y = 6.67$ (**a**), 6.75 (**b**), 6.92 (**c**) and 7.0 (**d**). The $I^\omega(\varphi)$ and $I^{2\omega}(\varphi)$ data sets, which have intensity error bars of approximately $\pm 1\%$ and $\pm 10\%$ respectively, are each plotted on the same intensity scale with a scaling ratio of $I^\omega(\varphi) : I^{2\omega}(\varphi) \approx 1 : 3 \times 10^{-11}$. The former are fitted to the electric-dipole-induced linear response of the monoclinic crystal system (red lines) and the latter are fitted to the electric-quadrupole-induced SH response of the $2/m$ point group (blue lines). The angular deviations of the maxima of $I^\omega(\varphi)$ and lobe bisectors of $I^{2\omega}(\varphi)$ away from the a axis are shaded red and blue respectively for clarity.

to electric-dipole-induced SH from the non-centrosymmetric 2 and m monoclinic point groups, as well as to magnetic-dipole-induced¹¹ or surface electric-dipole-induced SH from the $2/m$ point group, do not adequately describe the data (see Supplementary Section 3).

The degree of monoclinicity, which can be qualitatively tracked via the angular deviation of the intensity maximum (lobe bisector) in the linear (SH) RA data away from the a axis, decreases monotonically between $y = 6.67$ and $y = 7$ as shown in Fig. 2. This suggests that the absence of m_{ac} and m_{bc} symmetries at all measured temperatures above T^* (see Supplementary Section 4) originates from vacancy-induced monoclinic distortions of the oxygen sublattice, which are also known to be present in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (ref. 16). This

interpretation is further supported by recent SH RA measurements performed near the charge transfer resonance of layered perovskite iridates^{9,10}, which revealed subtle oxygen sublattice distortions that are difficult to resolve using diffraction-based probes.

Having established the point group of hole-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ above T^* , we proceed to search for changes in symmetry across the strange metal to pseudogap boundary. Previous infrared conductivity experiments¹⁷ have shown that optical transition rates at frequencies well above the pseudogap energy scale ($\hbar\omega \gtrsim 0.3$ eV) do not exhibit any measurable temperature dependence across T^* . As a corollary, any temperature-dependent change in magnitude of χ_{ij}^{ED} or χ_{ijkl}^{EQ} at the frequencies used in this study ($\hbar\omega = 1.5$ eV

Figure 3 | Inversion-symmetry-breaking transition across the phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_y$. **a–d**, Temperature dependence of the linear and SH response of $\text{YBa}_2\text{Cu}_3\text{O}_y$ with $y = 6.67$ (**a**), 6.75 (**b**), 6.92 (**c**) and 7.0 (**d**) normalized to their room-temperature values. Data were taken in $S_{\text{in}}-S_{\text{out}}$ geometry at angles φ corresponding to the smaller SH lobe maxima at $T = 295$ K (see Fig. 2). The error bars represent the standard deviation of the intensity over 60 independent measurements. Blue curves overlaid on the data are guides to the eye. The inversion-symmetry-breaking transition temperatures T_Ω determined from the SH response are marked by the dashed lines. The width of the shaded grey intervals represents the uncertainty in T_Ω . **e**, Temperature versus doping phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_y$. The values of T_Ω (red circles) coincide with the onset of the pseudogap as defined by spin-polarized neutron diffraction^{2–4} (blue squares), Nernst effect⁵ (open blue squares), terahertz polarimetry⁶ (purple diamonds) and resonant ultrasound⁷ (orange circles). The onset of a polar Kerr effect³³ (green diamonds) and short-range charge order as determined by X-ray diffraction^{19,20} (green squares) occur at temperatures below T^* . Error bars denote the uncertainty in the onset temperatures. The superconducting transition temperatures of the samples used in our work are denoted by grey circles.

and $2\hbar\omega = 3$ eV) should be correspondingly weak. Figure 3a–d shows the temperature dependences of both the linear and SH intensities measured at a fixed value of φ in $S_{\text{in}}-S_{\text{out}}$ geometry. For all four doping levels studied in Fig. 2, we observe no change in the linear response as a function of temperature as expected. Surprisingly however, all of the SH responses exhibit a significant order-parameter-like upturn below a doping-dependent critical temperature T_Ω . This dichotomy between the linear and SH responses can naturally be reconciled if bulk inversion symmetry is broken below T_Ω , which would turn on a new and stronger source of electric-dipole-induced SH radiation on top of the already existing electric-quadrupole contribution.

By plotting the doping dependence of T_Ω atop the phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Fig. 3e), we find that the observed onset of inversion symmetry breaking coincides very well with the pseudogap phase boundary T^* defined by spin-polarized neutron diffraction^{2–4}, Nernst anisotropy⁵, terahertz polarimetry⁶ and resonant ultrasound⁷ measurements in the optimal and underdoped regions, suggesting a common underlying mechanism. Moreover, we detect an onset of inversion symmetry breaking even inside the superconducting dome in the overdoped region, which may imply a quantum phase transition slightly beyond $p = 0.20$ near where the pseudogap energy scale has also been extrapolated to vanish¹⁸. Interestingly, the temperature dependence of the SH intensity shows no measurable anomalies after crossing either the superconducting or the charge density wave ordering^{19,20} temperatures (Fig. 3e) and does not rapidly diminish at lower temperatures like the Nernst anisotropy⁵, which may be caused

by charge density wave ordering²¹. This shows that unlike the superconducting and charge-ordered phases, which are competing Fermi surface instabilities²², the observed inversion-symmetry-broken phase is independent of and coexistent with both of them.

To determine which symmetries in addition to inversion are removed from the $2/m$ point group below the pseudogap temperature, we performed a comparative study of the SH RA data measured above and below T_Ω . Figure 4a shows RA patterns measured at 295 K and 30 K in $S_{\text{in}}-S_{\text{out}}$ geometry for the optimal doped sample ($T_\Omega \sim 110$ K), which is representative of all other doping levels studied (see Supplementary Section 5). Below T_Ω we see that the SH intensity is enhanced in a φ -dependent manner that preserves the two-fold rotational symmetry of the pattern, which ostensibly implies that C_2 is preserved in the crystal. However, this interpretation can be ruled out because the inferred above electric-dipole-induced SH radiation is strictly forbidden by symmetry in $S_{\text{in}}-S_{\text{out}}$ geometry for any point group (non-magnetic or magnetic) that contains C_2 (see Supplementary Section 3). The only alternative interpretation is that the order parameter below T_Ω breaks C_2 symmetry, but is obscured in the RA patterns because of spatial averaging over domains of two degenerate orientations of the order parameter that are related by 180° rotation about the c axis. This would imply a characteristic domain length scale that is much smaller than our laser spot size and consistently explains the absence of any signatures of C_2 breaking below T^* in Nernst effect⁵ and terahertz polarimetry⁶ data as well as the need for multiple magnetic domains to refine the polarized neutron diffraction data^{2–4,23}, which are all

Figure 4 | Point group symmetry of $\text{YBa}_2\text{Cu}_3\text{O}_y$ below T^* . **a**, Polar plot of $I^{2\omega}(\varphi)$ measured at $T=30$ K in $S_{\text{in}}-S_{\text{out}}$ geometry from $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ (squares). The intensity error bars are approximately $\pm 10\%$. The blue curve is a best fit to the average of two 180° -rotated domains with $2'/m$ point group symmetry as described in the text. The fit to the $T=295$ K data (pink shaded area) reproduced from Fig. 2c is overlaid for comparison. **b**, Decomposition of the fit to the $T=30$ K data (shaded blue area) into its individual domain contributions (shaded orange and purple areas).

integrated over even larger areas of the crystal compared with our measurements.

The set of all non-centrosymmetric subgroups of $2/m$ that do not contain C_2 consists of the two independent magnetic point groups $2'/m$ and $m1'$ and their associated magnetic and non-magnetic subgroups (see Supplementary Section 6), where the generators $2'$, m and $1'$ denote C_2 combined with time-reversal, m_{ab} and the identity operation combined with time-reversal respectively. Using the two-domain ($\alpha = 1, 2$) averaged expression $I^{2\omega}(\varphi) \propto \sum_{\alpha=1,2} |\hat{e}_i^{2\omega}(\varphi) \chi_{ijkl}^{\text{EQ}} \hat{e}_{j,0}^{\omega}(\varphi) \partial_k \hat{e}_{l,0}^{\omega}(\varphi) + \hat{e}_i^{2\omega}(\varphi) \chi_{ijk,\alpha}^{\text{ED}} \hat{e}_{j,0}^{\omega}(\varphi) \hat{e}_{k,0}^{\omega}(\varphi)|^2 I_0^2$, we were able to reproduce all features of the low-temperature SH RA data, including the small peaks around the b axis (Fig. 4a), by applying the structure of $\chi_{ijk,\alpha}^{\text{ED}}$ for either the $2'/m$ or $m1'$ point group. The decomposition of the fit into its two single-domain components is shown in Fig. 4b to explicitly illustrate the loss of C_2 . An equally good fit to the data can naturally be achieved using any magnetic or non-magnetic subgroup of $2'/m$ or $m1'$ because they necessarily allow the same or more non-zero independent $\chi_{ijk,\alpha}^{\text{ED}}$ tensor elements. Therefore, while further removal of symmetry elements from $2'/m$ or $m1'$ is not necessary to explain the low-temperature data, it cannot be completely ruled out.

In conclusion, our results show that the pseudogap region in $\text{YBa}_2\text{Cu}_3\text{O}_y$ is bounded by a line of phase transitions associated with the loss of global inversion and C_2 symmetries. Although previous terahertz polarimetry measurements on hole-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ thin films reported the onset of a linear dichroic response near T^* that breaks m_{ac} and m_{bc} symmetries⁶, we find that these symmetries are already broken in the crystallographic structure above T^* and are thus necessarily absent in any tensor response that turns on below T^* . The low symmetry of the point group (probably $2'/m$ or $m1'$) underlying the pseudogap region cannot be explained by stripe²⁴ or nematic⁵ type orders alone, which have also been

reported to develop below T^* . Instead it suggests the presence of an odd-parity magnetic order parameter, which is consistent with theoretical proposals involving a ferroic ordering of current loops circulating within the Cu–O octahedra^{11,25–27}, local Cu-site magnetic quadrupoles²⁸, O-site moments²⁹ or magneto-electric multipoles generated dynamically through spin–phonon coupling³⁰. Regardless of microscopic origin, our results suggest that this order undergoes a quantum phase transition inside the superconducting dome slightly beyond optimal doping, which may be responsible for the enhanced T_c and quasiparticle mass³¹ observed in its vicinity. Interestingly, a similar odd-parity magnetic phase has also recently been found in the pseudogap region of a $5d$ transition metal analogue of the cuprates³², which hints at a possibly more robust connection between the pseudogap and this unusual form of broken symmetry.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the [online version of this paper](#).

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Author contributions

L.Z., D.H. and N.P.A. planned the experiment. L.Z. and C.A.B. performed the RA measurements and N.P.A. determined the crystal alignment. L.Z., D.H. and N.P.A. analysed the data. R.L., D.A.B. and W.N.H. prepared and characterized the samples. L.Z. and D.H. wrote the manuscript.

Additional information

Supplementary information is available in the [online version of the paper](https://www.nature.com/reprints). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.H.

Competing financial interests

The authors declare no competing financial interests.

Methods

Material growth. $\text{YBa}_2\text{Cu}_3\text{O}_y$ single crystals were grown in non-reactive BaZrO_3 crucibles using a self-flux technique. The Cu–O-chain oxygen content was set to $y = 6.67, 6.75, 6.92$ and 7.0 by annealing in a flowing O_2/N_2 mixture and homogenized by further annealing in a sealed quartz ampoule, together with ceramic at the same oxygen content. The absolute oxygen content (y) is accurate to ± 0.01 based on iodometric titration. The crystals used in our experiments were de-twinned and aligned to high accuracy by X-ray Laue diffraction.

Optical RA measurements. The RA measurements were performed using a rotating optical grating-based technique¹² with ultrashort (~ 80 fs) optical pulses produced from a regeneratively amplified Ti:sapphire laser operating at a 10 kHz repetition rate. The angle of incidence was $\sim 30^\circ$ and the incident fluence was maintained below 1 mJ cm^{-2} to ensure no laser-induced changes to the samples (see Supplementary Section 7). Alignment of the optical axis to the crystallographic c axis was determined to better than 0.1° accuracy as described in Supplementary Section 8. Reflected fundamental ($\lambda = 800 \text{ nm}$) and SH light ($\lambda = 400 \text{ nm}$) were collected using photodiodes and photomultiplier tubes respectively. Crystals were sealed in a dry environment during transportation and immediately pumped down to pressures $< 5 \times 10^{-6}$ torr for measurements.

Fitting procedure. The high-temperature ($T > T_\Omega$) linear optical anisotropy data were fitted to the expression $I^\omega(\varphi) = A|\hat{e}_i^\omega(\varphi)\chi_{ij}^{\text{ED}}\hat{e}_{j,0}^\omega(\varphi)|^2 I_0$ and the high- ($T > T_\Omega$) and low-temperature ($T < T_\Omega$) SH anisotropy data were fitted to the expressions $I^{2\omega}(\varphi) = A\hat{e}_i^{2\omega}(\varphi)\chi_{ijkl}^{\text{EQ}}\hat{e}_{j,0}^\omega(\varphi)\partial_k\hat{e}_{l,0}^\omega(\varphi)|^2 I_0^2$ and

$I^{2\omega}(\varphi) = (|A|^2/2) \sum_{\alpha=1,2} |\hat{e}_i^{2\omega}(\varphi)\chi_{ijkl}^{\text{EQ}}\hat{e}_{j,0}^\omega(\varphi) + \hat{e}_i^{2\omega}(\varphi)\chi_{ijkl}^{\text{ED}}\hat{e}_{j,0}^\omega(\varphi)\hat{e}_{k,0}^\omega(\varphi)|^2 I_0^2$ respectively. Here A is a constant determined by the experimental geometry, $\hat{e}_0$ and $\hat{e}$ are the polarizations of the incoming and outgoing light in the frame of the crystal, χ_{ij}^{ED} is the linear electric-dipole susceptibility tensor, χ_{ijkl}^{EQ} is the SH electric-quadrupole susceptibility tensor and χ_{ijkl}^{ED} is the SH electric-dipole susceptibility tensor. The $\alpha = 1$ and $\alpha = 2$ versions of χ_{ijkl}^{ED} are related by 180° rotation about the c axis. The non-zero independent elements of these tensors in the frame of the crystal are determined by applying the monoclinic crystal symmetries to χ_{ij}^{ED} and the appropriate point group symmetries ($2/m$ for χ_{ijkl}^{EQ} and either $2/m$ or $m1'$ for χ_{ijkl}^{ED}) and degenerate SH permutation symmetries to χ_{ijkl}^{EQ} and χ_{ijkl}^{ED} . These operations reduce χ_{ij}^{ED} to 5 non-zero independent elements (xx, xz, yy, zx, zz), χ_{ijkl}^{EQ} to 28 non-zero independent elements ($xxxx, yyyy, zzzz, xxyy = xyxx, yyxx = yxyx, xyxy, yxyx, xxzz = xzzx, zzzx = zxxz, xzzx, zxxz, zzzx = yzyz, zzyy = zyzy, yzyz, zyzy, xzyy = xyyz, xyzy, yxzy = yyzx, yxyz = yzyx, yyxz = yzxy, zxyy = zyyx, zyxz, zxxx, xxxz, xxxz = xzxx, xzzz, zzzz, zzzx = zxxz$), and χ_{ijkl}^{ED} to 10 non-zero independent elements ($xxx, xyx = xxy, xyy, xzz, yxx, yyx = yxy, yyy, yzz, zxx = zxz, zzy = yzy$). Values of $R^2 > 0.95$ were achieved for all fits shown. However, the fitted values of the susceptibility tensor elements are not unique. Therefore, the fits serve only to address the qualitative question of whether a certain point group can or cannot reproduce the data. They are not intended to convey any quantitative information about the magnitudes of various tensor elements.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author on request.