Direct observation of competition between superconductivity and charge density wave order in YBa$_2$Cu$_3$O$_{6.67}$

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Superconductivity often emerges in the proximity of, or in competition with, symmetry-breaking ground states such as antiferromagnetism or charge density waves (CDW). A number of materials in the cuprate family, which includes the high transition-temperature (high-$T_c$) superconductors, show spin and charge density wave order$^{6-8}$. Thus a fundamental question is to what extent do these ordered states exist for compositions close to optimal for superconductivity. Here we use high-energy X-ray diffraction to show that a CDW develops at zero field in the normal state of superconducting YBa$_2$Cu$_3$O$_{6.67}$ ($T_c = 67$ K). This sample has a hole doping of 0.12 per copper and a well-ordered oxygen chain superstructure$^9$. Below $T_c$, the application of a magnetic field suppresses superconductivity and enhances the CDW. Hence, the CDW and superconductivity in this typical high-$T_c$ material are competing orders with similar energy scales, and the high-$T_c$ superconductivity forms from a pre-existing CDW environment. Our results provide a mechanism for the formation of small Fermi surface pockets$^9$, which explain the negative Hall and Seebeck effects$^{10,11}$ and the 'T, plateau'$^{12}$ in this material when underdoped.

Charge density waves in solids are periodic modulations of conduction electron density. They are often present in low-dimensional systems such as NbSe$_2$ (ref. 4). Certain cuprate materials such as La$_{2-x}$Nd$_x$Sr$_2$Cu$_3$O$_y$ (Nd-LSCO) and La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) also show charge modulations that suppress superconductivity near $x = 1/8$ (refs 6,7). In some cases, these are believed to be unidirectional in the CuO$_2$ plane, and have been dubbed 'stripes'.$^{2,3}$ There is now a mounting body of indirect evidence that charge and/or spin density waves (static modifications) may be present at high magnetic fields in samples with high $T_c$: quantum oscillation experiments on underdoped YBa$_2$Cu$_3$O$_y$ (YBCO) have revealed the existence of at least one small Fermi surface pocket$^{8,10}$, which may be created by a charge modulation$^{11}$. More recently, nuclear magnetic resonance (NMR) studies have shown a magnetic-field-induced splitting of the Cu2F lines of YBCO (ref. 13). An important issue is the extent to which the tendency towards charge order exists in high-$T_c$ superconductors$^{2,3}$.

Here we report a hard (100 keV) X-ray diffraction study, in magnetic fields up to 17 T, of a detwinned single crystal of YBa$_2$Cu$_3$O$_{6.67}$ (with ortho-VIII oxygen ordering$^{6,12}$, $T_c = 67$ K and $p = 0.12$, where $p$ is the hole concentration per planar Cu). We find that a CDW forms in the normal state below $T_{CDW} \approx 135$ K. The charge modulation has two fundamental wave vectors $q_{CDW} = q_1 = (\delta_1, 0.0.5)$ and $q_2 = (0, \delta_2, 0.5)$, where $\delta_1 \approx 0.3045(2)$ and $\delta_2 \approx 0.3146(7)$, with no significant field- or temperature-dependence of these values. The CDW gives rise to satellites of the parent crystal Bragg peaks at positions such as $Q = (2 \pm \delta_1, 0.0.5)$. Although the satellite intensities have a strong temperature and magnetic field dependence, the CDW is not field-induced and is unaffected by field in the normal state. Below $T_c$, it competes with superconductivity, and a decrease of the CDW amplitude in zero field becomes an increase when superconductivity is suppressed by field. A very recent paper$^{14}$ reports complementary resonant soft X-ray scattering experiments performed on (Y, Nd)Ba$_2$Cu$_3$O$_{6.67}$, as a function of doping and in the absence of a magnetic field. The results are broadly in agreement with our zero field data.

Figure 1a,g shows scans through the $(2 - \delta_1, 0.0.5)$ and $(0, 2 - \delta_2, 0.5)$ positions at $T = 2$ K. Related peaks were observed at $(2 + \delta_1, 0.0.5)$ and $(4 - \delta_1, 0.0.5)$ (see Supplementary Fig. S3). The incommensurate peaks are not detected above 150 K (Fig. 1c). From the peak width we estimate that the modulation has an in-plane correlation length $\xi \approx 95 \pm 5$ Å (at 2 K and 17T—see Methods). The existence of four similar in-plane modulations $(\pm \delta_1, 0)$ and $(0, \pm \delta_2)$ indicates that the modulation is associated with the (nearly square) CuO$_2$ planes rather than the CuO chains. The present experiment cannot distinguish between $\bm{q} - \bm{q}$ and $\bm{q} - \bm{q}$ structures, that is, we cannot tell directly whether modulations along the $a$ and $b$ directions co-exist in space or occur in different domains of the crystal. However, Bragg peaks from the two CDW components have similar intensities and widths (Fig. 1b,g) despite the orthorhombic crystal structure, which breaks the symmetry between them. This suggests that $q_1$ and $q_2$ are coupled, leading to the co-existence of multiple wave vectors, as seen in other CDW systems such as NbSe$_2$ (ref. 4). The scan along the $c^*$ direction in Fig. 1d has broad peaks close to $l = \pm 0.5$ reciprocal lattice units (r.l.u.), indicating that the CDW is weakly correlated along the $c$ direction, with a correlation length $\xi_c$ of approximately 0.6 lattice units.

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In zero field, the intensity of the CDW Bragg peak (Fig. 2) grows on cooling to \( T_c \), below which it is partially suppressed. For \( T > T_c \), a magnetic field applied along the \( c \)-direction has no effect. Below \( T_c \) it causes an increase in the intensity of the CDW signal (Figs 1a and 2b). At \( T = 2 \) K, the intensity grows with applied magnetic field (Fig. 2b) and shows no signs of saturation up to 17 T. The magnetic field also makes the CDW more long-range ordered (Fig. 2c). In zero magnetic field, the \( q \)-width varies little with temperature. However, below \( T_c \) in a field, the CDW order not only becomes stronger, but also becomes more coherent, down to a temperature \( T_{\text{sup}} \) below which the intensity starts to decrease (Figs 2 and 4). All of this is clear evidence for competition between CDW and superconducting orders.

Non-resonant X-ray diffraction is sensitive to modulations of charge density and magnetic moments. In our case, the expected magnetic cross-section increases several orders of magnitude smaller than our observed signal, which must therefore be due to charge scattering. NMR measurements on a sample of the same composition as ours\(^1\) indicate that the CDW is not accompanied by magnetic order, and this is confirmed by soft X-ray measurements, which would also be sensitive to fluctuating order\(^1\). Charge density modulations in solids will always involve both a modulation of the electronic charge and a periodic displacement of the atomic positions\(^1\). We are more sensitive to the atomic displacements than to the charge modulation because ions with large numbers of electrons (as in YBCO) dominate the scattering (see Supplementary Information).

NMR data\(^1\) suggest that CDW order only appears below \( T \approx 67 \) K and \( H > 9 \) T, whereas with X-rays we observe CDW order in zero field up to 135 K. This apparent discrepancy may arise from differing timescales of various probes (see Supplementary Information). X-ray diffraction experiments are usually interpreted as measuring the static order of a given structure, but, if performed with wide energy acceptance, are also sensitive to short-lived structures. Thus, it is possible that the observed CDW is quasi-static and only frozen on the NMR timescale (\( \approx 3 \) ns) at high fields and lower temperatures.
The intensities of the incommensurate Bragg peaks are sensitive to atomic displacements parallel to the total scattering vector \( \mathbf{Q} \). The comparatively small contribution to \( \mathbf{Q} \) along the \( \mathbf{c}^* \) direction from \( l = 0.5 \) r.l.u. means that our signal for a \((h, 0, 0.5)\) peak is dominated by displacements parallel to the \( a \) direction. (There will also be displacements parallel to the \( c \) direction but we are essentially insensitive to them in our present scattering geometry.) Our data indicate that the incommensurate peaks are much stronger if they are satellites of strong Bragg peaks of the form \((\tau = (2n, 0, 0))\) at positions such as \( \tau \pm \mathbf{q} \). This indicates that the satellites are caused by a modulation of the parent crystal structure. The fact that the scattering is peaked at \( l = \pm 0.5 \) r.l.u. means that neighbouring bilayers are modulated in antiphase. The two simplest structures (Fig. 3a,b) compatible with our data (see Supplementary Information) involve the neighbouring \( \mathrm{CuO}_2 \) planes in the bilayer being displaced in the same (bilayer-centred) or opposite (chain-centred) directions, resulting in the maximum amplitude of the modulation being on the \( \mathrm{CuO}_2 \) planes or \( \mathrm{CuO} \) chains respectively. In their \( 2 - \mathbf{q} \) form, these structures would lead to the in-plane ‘checkerboard’ pattern shown in Fig. 3c. Scanning tunnelling microscopy studies of other underdoped cuprates\(^ {16} \) and of field-induced CDW correlations in vortex cores\(^ {17} \) also support the tendency towards checkerboard formation\(^ {18} \), although disorder can cause small stripe domains to mimic checkerboard order\(^ {19} \). Our observation of a CDW may be related to phonon anomalies\(^ {20} \), which suggest that in \( \text{YBCO} \) near \( p \approx 1/8 \) there are anomalies in the underlying charge susceptibility for \( q \approx (0, 0.3) \).

Cuprate superconductors show strong spin correlations, and the interplay between spin and charge correlations may be at the heart of the high-\( T_c \) phenomenon. The spin correlations are largely dynamic, with energies up to several hundred meV. \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) and \( \text{La}_{2-x}\text{(Ba,Sr)}\text{CuO}_4 \) show incommensurate magnetic order, which can be enhanced by suppressing superconductivity in a fraction of magnetic field\(^ {21-24} \); this has some analogies with the CDW order observed here. The magnetic order is static on the \( \approx 1 \) meV frequency scale of neutron diffraction and has been detected in lightly doped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) for \( p < 0.082 \) (ref. 21), and moderately doped \( \text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4 \) for \( p < 0.14 \) (ref. 24). The \( \text{YBa}_2\text{Cu}_3\text{O}_{6+y} \) \((p \approx 1/8)\) sample studied here is expected to have a relatively large spin gap, \( \Delta_0 \approx 20 \) meV (ref. 25), in its magnetic excitations at low temperature, making it unlikely that it orders magnetically. As discussed earlier, this is confirmed by other measurements\(^ {13,14} \); so the CDW does not seem to be accompanied by spin order. Moreover, there is no obvious relationship between \( q_{\text{CDW}} \) and the wave vector of the incipient spin fluctuations \( q_{\text{SF}} \approx (0.1, 0) \) of similarly doped samples\(^ {25} \).

It is interesting to note that \( T_{\text{CDW}} \) corresponds approximately with \( T_{\text{H}} \) (Fig. 4), the temperature at which Hall effect measurements suggest that Fermi surface reconstruction begins\(^ {26} \). A CDW that

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**Figure 2 | Competition between charge–density-wave order and superconductivity.** a, Temperature dependence of the peak intensity at \((1.695, 0, 0.5)\) (circles) and \((0, 3.691, 0.5)\) (squares) for different applied magnetic fields. The square data points have been multiplied by a factor of four. In the normal state, there is a smooth onset of the CDW order. In the absence of an applied magnetic field there is a decrease in the peak intensity below \( T_c \). This trend can be reversed by the application of a magnetic field. b, Magnetic field dependence of the lattice modulation peak intensity at \((1.695, 0, 0.5)\) for different temperatures. At \( T = 2 \) K, the peak intensity grows approximately linearly with magnetic field up to the highest applied field. c,d, Gaussian linewidth of the \((1.695, 0, 0.5)\) CDW modulation plotted versus temperature and field respectively. The raw linewidth, including a contribution from the instrumental resolution, is field-independent in the normal state \((T > T_c)\). In contrast, the CDW order becomes more coherent below \( T_c \), once a magnetic field is applied. This effect ceases once the amplitude starts to be suppressed owing to competition with superconductivity. The vertical dashed lines in a,c illustrate the connection between these two features of the data that define the \( T_{\text{cusp}} \) temperatures. All other lines are guides to the eye. Error bars indicate standard deviations of the fit parameters described in Methods.

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Bilayer centred geometry of the superconducting dome is electron-like. The exact structure of the low-temperature reconstructed Fermi surface is still debated, although recent high-field specific heat experiments place constraints on the possibilities and suggest a small number of pockets. It is interesting to compare the LDA Fermi surface of YBCO (ref. 28) with $\mathbf{q}_{\text{CDW}}$ (Fig. 3d and Supplementary Information). The electronic states most obviously connected by $\mathbf{q}_{\text{CDW}}$ are the bonding bands at $\Gamma$ and near the zone boundary, which lie near the anti-nodal region of the superconducting gap, where the pseudogap is also maximized.

Our results have important implications for the phenomenology and phase diagram of the cuprates (Fig. 4). A simple Landau theory (see Supplementary Information) shows that $T_c$ will be suppressed below the value it would have in the absence of the CDW. We speculate that this is reflected in the shape of the superconducting dome (Fig. 4). One of the defining properties of underdoped cuprates such as ortho-VIII YBCO is the pseudogap. This develops at the ‘crossover’ temperature $T^*$ (for $\text{YBa}_2\text{Cu}_4\text{O}_8$, $T^* \approx 220 \text{ K}$), where there is a suppression of low-energy electronic states, evidence for $Q = 0$ magnetic order9 and rotational anisotropy appears in various physical properties, such as the Nernst effect30. The CDW reported here develops at $T_{\text{CDW}} \approx 135 \text{ K}$, inside the pseudogap state. From Fig. 2a,c we can identify the temperature $T_{\text{cusp}}(H)$ where the suppression of the CDW begins. The level of this competition indicates that the CDW and superconductivity have similar energy scales (10–30 meV), unlike NbSe$_2$, where the CDW order is not significantly suppressed.

We draw attention to the situation in the cuprates that many different kinds of order, such as superconductivity, pseudogap, CDW and antiferromagnetism, occur on comparable temperature scales. When they compete, they do so on an almost equal footing. We may suspect that this is not accidental, and that...
these various orders are ‘intertwined’\textsuperscript{31}. In this context, we can view our present results as indicating that the electron system has a tendency towards two ground states: a charge density wave, which breaks translational symmetry and involves electron-hole correlations, versus superconductivity, which breaks gauge symmetry and involves electron-electron correlations. We note that the \(\mathbf{q}\)-vectors of the CDW lie close to the separation of pieces of Fermi surface that have maximum superconducting gap at optimal doping and have the same sign of the order parameter.

\section*{Methods}

Our experiments used 100 keV hard X-ray synchrotron radiation from the DORIS-III storage ring at DESY, Hamburg, Germany. We installed a recently developed 17 T horizontal cryomagnet designed for beamline use on the triple-axis diffractometer at beamline BW5. The sample was mounted by gluing it over a hole in a temperature-controlled aluminum plate within the cryomagnet vacuum and was thermally shielded by thin Al and aluminized mylar foils glued to this plate. The sample temperature could be controlled over the range ~2–300 K. The incoming and outgoing beams passed through 1 mm thick aluminum cryostat vacuum windows, which gave a maximum of \(\sim 1 \times 10^5\) input and output angles relative to the field direction, which was parallel to the sample \(c\) axis within \(<1^\circ\). Between the beam access windows and the sample plate, there were further aluminum foil thermal radiation shields at liquid nitrogen temperature. A 2 mm square aperture collimated the incoming beam, so that it passed mainly through the part of the sample over the hole in the aluminum plate, greatly reducing background scattering by the plate. Further slits before the analyser and the detector removed scattering by the cryostat windows and nitrogen shields. The scattering plane \((a^*c^*)\) was horizontal. The cryomagnet was mounted on a rotation stage with a goniometer giving \(\chi\) tilt about the field axis. The sample was initially mounted with its \(a\) axis nearly horizontal. The \(\chi\) goniometer allowed the exact alignment of this axis using the (2 0 0) Bragg peak and could also be used for low-resolution scans in the \(b^*\) direction. Magnetic fields were applied with the sample heated above \(T_c\); it was then field-cooled to base temperature. When fields were applied, minor changes in the position and angle of the sample holder were observed; these were corrected by use of horizontal and vertical motion stages under the cryostat rotation stage, and by realigning on the (2 0 0) Bragg peak. During temperature scans, realignment on the (2 0 0) Bragg peak was performed automatically at every temperature point to ensure that all measurements were centred. After results had been obtained with the \(a\) axis horizontal, the sample was remounted with the \(b\) axis horizontal for further measurements. The \(\text{YBa}_2\text{Cu}_3\text{O}_{6.7}\) sample had dimensions \(a \times b \times c = 3.1 \times 1.7 \times 0.6 \text{ mm}^3\) and mass 18 mg. The superconducting transition temperature \(T_c = 67 \text{ K} (\text{width: } 10\%–90\% = 1.1 \text{ K})\) was derived from a zero-field-cooled magnetization curve at 0.1 mT. The single crystal was 99% detwinned and the \(\text{Cu}-\text{O}\) chains were ordered with the ortho-VIII structure by standard procedures\textsuperscript{22}.

The diffracted intensities from the CDW, shown in Fig. 1, are composed of an incommensurate lattice modulation peak on a smoothly varying background. The background along \((h, 0, 0.5)\) mainly originates from the tails of the ortho-VIII peaks (see Supplementary Information). It varies strongly from one Brillouin zone to another; for example, the background around \((2.7, 0, 0.5)\) is of magnitude larger than around \((1.2, 0, 0.5)\). The background has essentially no field dependence (Fig. 1a–c) so subtracting the zero-field from high-field data is a simple way to eliminate the background. This reveals the field-enhanced signal inside the superconducting state (Fig. 1a–d).

As there is a weak temperature dependence in the background (Fig. 1a–c), it is not possible to eliminate it by subtracting a high-temperature curve. Therefore, to obtain the temperature dependences shown in Fig. 2, we fitted the data to a Gaussian function \(G(\mathbf{Q})\) and modelled the background by a second-order polynomial \(B(\mathbf{Q}) = c_0 + c_1 \mathbf{Q} + c_2 \mathbf{Q}^2\). The constants \(c_0\) and \(c_1\) have a small but significant temperature dependence. The low counting statistics resulted in Gaussians fitting equally well as other possible lineshapes such as Lorentzians.

The signal-to-background ratio is best for the \((2 - \delta_1, 0, 0.5)\) peak due to the weaker structural ortho-VIII peak (see Supplementary Fig. S2). From the Gaussian fits to the \((2 - \delta_1, 0, 0.5)\) satellite peak at 2 K and 17 T we can estimate the correlation length \(\xi_1\) along the three crystal axis directions. We define \(\xi_2 = 1/\pi\), where \(\sigma = (\sigma_{\text{axial}} - \sigma^\text{corr})^{1/2}\) is the measured Gaussian standard deviation corrected for the instrument resolution \(\sigma_0\) and expressed in \(\AA^{-1}\). Along the \(a\) axis direction, we find \(\sigma = 6.4 \times 10^{-3} \text{ r.u.} = 1.1 \times 10^{-2} \text{ Å}^{-1}\), and hence \(\xi_2 = 95 \pm 5 \text{ Å}\). Deconvolving the poor instrumental resolution along the \(b\) axis direction for the \((2 - \delta_1, 0, 0.5)\) peak yields a similar correlation length \(\xi_3 = \xi_2\).

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