MBE of IL-(Ca,Sr)CuO$_2$ thin films

Infinite-layer cuprate thin films of CaCuO$_2$, Ca$_{0.85}$Sr$_{0.15}$CuO$_2$, and Ca$_{0.96}$Nd$_{0.04}$CuO$_2$ have been epitaxially grown onto (001) (LaAlO$_3$)$_{0.3}$Sr$_2$AlTaO$_6$$_{0.7}$ [(001) LSAT] substrates whereas SrCuO$_2$ was grown on (001) SrTiO$_3$ substrates and superconducting Sr$_{0.96}$La$_{0.10}$CuO$_2$ thin films have been grown onto (110) DyScO$_3$ substrates. Details of the growth have been published earlier (1–3).

Electronic transport measurements

Electronic transport measurements were performed in a Quantum Design DynaCool Physical Property Measurement System in the temperature range between 300 K and 2.0 K. We patterned the IL cuprate thin films into a standard six-pad geometry (200×50 µm) using photolithographic lift-off technique in combination with Ar ion milling for etching of the pattern while each electrode pad was covered with a 100 nm thick silver layer. For superconducting samples, the superconducting transition temperature $T_c$ is defined as $\rho \equiv 0.0000 \mu \Omega \text{cm}$ and we followed this definition to the letter.
Hall measurements were carried out by fixing the sample temperature and monotonically sweeping the magnetic field between -14 T to +14 T. This procedure was common for all IL cuprates grown on (001)SrTiO$_3$ and (001) (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrates. Due to the spontaneous, low-temperature spin reorientation of Dy$^{3+}$ in DyScO$_3$ substrates, the magnetic field sweeps were limited to the -1.5 T to +1.5 T range (4). Note, that magnetic fields larger than ±2.5 T will result in explosion of the DyScO$_3$ substrate. A DC current between 100 nA and 1 µA was applied across the Hall bar and kept constant for all magnetic field sweeps. For measurement of the Hall voltage $V_{xy}$ we used a Stanford Research SRS830 lock-in amplifier. The overall recorded deviation from linear response $V_{xy} \sim B$ was less than 0.10% over the entire field range measured.

From the low-temperature resistivity values at 2.0 K, we determined the mean-free path length $\ell$ of the charge carriers using

$$\sigma_{3D} = \frac{\sigma_{2D}}{d} = \frac{e^2 k_F \ell}{2 \pi \hbar d} \quad (1)$$
where $\sigma_{3D}$ and $\sigma_{2D}$ are the 3D and 2D electronic conductivities, respectively. $d$ is the thickness of the IL cuprates (typically 60 nm), $e$ is the electron charge, and $k_F$ is the Fermi wave vector. For simplicity reasons, we used $k_F = 3.6 \times 10^7 \text{ cm}^{-1}$, a value reported by J. Harter et al. (5) using angle-resolved photoemission spectroscopy.

**X-ray diffraction experiments**

High-resolution reciprocal space maps and $2\theta/\theta$ profiles of infinite-layer CaCuO$_2$, Ca$_{0.85}$Sr$_{0.15}$CuO$_2$, Ca$_{0.96}$Nd$_{0.04}$CuO$_2$, SrCuO$_2$, and Sr$_{0.90}$La$_{0.10}$CuO$_2$ thin films have been measured using a Bruker D8 4-circle diffractometer equipped with a 4-bounce monochromator and a VanTec-1 detector.

**STEM and EELS measurements**

CaCuO$_2$, SrCuO$_2$, Ca$_{0.96}$Nd$_{0.04}$CuO$_2$, and Sr$_{0.90}$La$_{0.10}$CuO$_2$ thin films as well as a Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal were prepared for STEM and EELS measurements by using a Ga$^+$ ion milling process followed by a Ar$^+$ ion milling finish. A double aberration-corrected 200 kV JEOL ARM equipped with a dual energy loss spectrometer was used to characterize the samples. Using HAADF and ABF images we studied the atomic structure of the films. The annular detection angles for HAADF images were 50–133 and 11–23 mrad for ABF images. We traced individual cation displacements across the copper-oxygen planes with a precision of several picometers by the Gaussian fitting method. Optimal STEM conditions for EELS were with a probe diameter of $\sim 0.9 \, \text{Å}$, a convergence semiangle of 20 mrad, and collection semiangle of 88 mrad. The step increments used for line-scanning EELS profiles were 0.12 Å while using a dwell time of 0.05 s per pixel. A dispersion of the 0.25 eV per channel was selected to simultaneously collect the O-$K\prime$ and Cu-$L$ edges with an energy resolution of 0.75 eV. To correct the intrinsic shift of energy of the electron beam, we simultaneously measured the carbon $K$ edge position during the EELS line-scanning process and the absolute energy scale was calibrated carefully. The
Table S 1: Tabulated values of the antiferromagnetic exchange interaction $J$ measured by NMR (nuclear magnetic resonance spectroscopy), RIXS (resonant inelastic x-ray scattering), and neutron diffraction. For bulk materials it is important to recollect the fact that infinite-layer SrCuO$_2$ and infinite-layer CaCuO$_2$ have to be synthesized with oxygen pressures exceeding 5 GPa whereas IL-Ca$_{0.85}$Sr$_{0.15}$CuO$_2$ is stable under 1 atm oxygen pressure. There is an apparent trend that $J$ is reduced for Ca$_{0.85}$Sr$_{0.15}$CuO$_2$ when compared to CaCuO$_2$ or SrCuO$_2$. While the origins of this behavior are unclear and the data points posses large error bars, one might speculate that the thermodynamically driven artifacts, e.g., rabbets or other defects, are driving the antiferromagnetic ground state.

EELS spectra were background-subtracted with a power law function, and multiple scattering was corrected by deconvolution. The EELS elemental profiles were obtained by integrating the Cu-$L_{2,3}$, and O-$K$ edges.

Supplementary Text

0.0.1 Antiferromagnetism in the IL phase

The antiferromagnetic exchange interaction $J$ for the infinite-layer system was reported by several groups and is listed in Table [1] IL-cuprates listed here are antiferromagnetic insulating materials. There is a wide variation of $J$ reported for these materials and none of them has been investigated on a nanoscale. Nonetheless, $J$ appears to be smaller for IL-Ca$_{0.85}$Sr$_{0.15}$CuO$_2$ than it is for IL-CaCuO$_2$. 

\[
\begin{array}{|c|c|c|c|}
\hline
\text{compound} & J \text{ (meV)} & \text{ref.} & \text{comment} \\
\hline
\text{IL-SrCuO}_2 & 42 & (6) & \text{NMR on powder} \\
\text{IL-SrCuO}_2 & 162 & (7) & \text{RIXS on films} \\
\text{IL-CaCuO}_2 & 182 & (8) & \text{RIXS on films} \\
\text{IL-CaCuO}_2 & 157 & (9) & \text{RIXS on films} \\
\text{IL-CaCuO}_2 & 120 & (10) & \text{RIXS on films} \\
\text{IL-Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2 & 86 & (11) & \text{neutron scattering} \\
\text{IL-Ca}_{0.85}\text{Sr}_{0.15}\text{CuO}_2 & 12 & (12) & \text{NMR on powder} \\
\hline
\end{array}
\]
Figure S2: Cross-sectional STEM image of a Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal together with elemental maps.

0.0.2 Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals in comparison to IL-CaCuO$_2$

The superconducting transition temperature of the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal is 92 K. A magnetic field of 10 Oe was applied parallel to the CuO$_2$ planes in a Quantum Design superconducting quantum interference device magnetometer. A crushed Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal was used to determine its lattice constants using $A2aa$ (S.G. 37) symmetry: $a = 5.422$ Å, $b = 5.448$ Å, and $c = 30.783$ Å. In Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, the CuO$_2$ are not sandwiched by a simple cation unlike in the infinite-layer systems CaCuO$_2$ or SrCuO$_2$. Instead, the CuO$_2$ planes are stacked between a SrO-BiO-BiO-SrO sequence. In free-standing and superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals the crystal symmetry is not $I4/mmm$ but $A2aa$. If the crystal symmetry becomes close to $I4/mmm$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, the superconducting transition temperature is reduced ($I3$, $I4$). This can be also seen for epitaxially grown Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ thin films ($I5$), where the flexibility of the CuO$_2$ planes towards distortions is limited and consequently the superconducting transition temperature is lowered. The orthorhombic symmetry as well as the incorporation of SrO-BiO-BiO-SrO stacks is supportive to minimize defects within the CuO$_2$ planes ($I6$). In the infinite-layer CaCuO$_2$ discussed here where the Cu-O bond length
Figure S3: (left) High-resolution scanning transmission electron microscopy image of the CuO$_2$ plane in a Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal. The element selective capability of STEM allows for the extraction of atomic positions stemming exclusively from the CuO$_2$ planes. (right) Photograph of the polished Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal. The CRL of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ are sufficiently polar to maintain infinitely-connected CuO$_2$ planes owing to the high flexibility of BiO$_{1.5+\delta}$. As a consequence, the Jahn-Teller effect is compensated in a way that allows for a cationic-stripe free arrangement of the CuO$_2$ planes, and therefore superconductivity with $T_c = 92$ K. The inset shows the field cooled magnetization measurement under a magnetic field of 100 Oe with the magnetic field aligned parallel to the CuO$_2$ planes of the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal.

is close to the value of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, distortions or symmetry lowering actions are only possible within the CuO$_2$ planes.

0.0.3 Calibration of the energy scale for EELS measurements

In solids, the ionic or covalent character of a bond depends on the bond length, the coordination scheme, and the amount of bonds (17). For the IL-cuprates discussed here, all of those parameters may vary freely and there is no cuprate whose O $K$ edge energy is suitable as an independent reference. We used three different, simple oxides, TiO$_2$, CuO, and TeO$_2$ to establish an independent energy scale for our EELS measurements. TiO$_2$ is an ionic compound with a well-defined O $K$-edge fine structure (18). For the purpose of EELS energy scale calibration
Figure S4: Electron energy loss spectra taken at the O K edge embedded in an ionic TiO$_2$, nearly covalent TeO$_2$, and CuO environment. TiO$_2$ is commercially available from CrysTec, TeO$_2$ single crystals were prepared by a Czochralski growth process (19), and freshly prepared CuO powder was synthesized by reacting finely dispersed Cu sponge (99.9995%) under flowing oxygen for 60 h in a tube furnace. For TeO$_2$, all spectral features of the O K edge appear similar as reported earlier (20) and same is true for TiO$_2$ (21) and CuO (22).

we used a rutile structured TiO$_2$ single crystal (S Fig. S4) from CrysTec GmbH. On the other hand, an entirely covalent oxide would have allowed us to absolutely determine the band width of the O K-edge in solids but this would have required to use solid oxygen crystals. As the usage of solid oxygen crystals (23) is still a technological challenge, we opted for the second best option using TeO$_2$. TeO$_2$ has nearly perfect covalent bonds and is easy to handle under atmospheric conditions. Large $\alpha$ TeO$_2$ single crystals (24) were used to determine the relative shift and associated fine structure of the O K-edge in absence of ionic contributions. Finally we measured the fine structure at the O K edge of freshly prepared CuO, which we prepared from 99.9995% Cu sponge under flowing oxygen.

Energy spectra calibrated by this procedure deviate less than 50 meV from the C-K edge reference.
Figure S5: Determination of the lattice constants of infinite-layer Ca$_{0.94}$Nd$_{0.04}$CuO$_2$ by high-resolution reciprocal scanning transmission electron microscopy imaging (HRRSTEM). This method allows an independent determination of the Cu-O, in-plane Cu-Cu, out-of-plane Cu-Cu, and Cu-Ca lengths. From x-ray diffraction experiments we determined the Cu-O length to 1.931 Å ($a = 3.862 \pm 0.003$ Å) and the out-of-plane Cu-Cu length to 3.168 Å ($c = 3.168 \pm 0.003$ Å). The Cu-O length determined by HRRSTEM is 1.933±0.02 Å whereas the in-plane Cu-Cu distance is 3.849±0.02 Å. The out-of-plane Cu-Cu length determined by HRRSTEM is 3.232±0.02 Å, which is significantly longer than 2× Cu-Ca (3.148±0.02 Å). As a result, the Ca equilibrium position is not at the center but shifted by 0.042±0.02 Å.

0.0.4 Determination of lattice parameters

For the determination of the lattice constants of the IL cuprate materials synthesized and characterized here we used high-resolution x-ray diffraction and applied a Nelson-Riley formalism (25).

Combining the lattice spacing by these independent methods allows for error bars of less than 0.1 pm.
Cross-sectional scanning transmission electron microscopy images were taken of all IL cuprates discussed here and is an important addition to high-resolution reciprocal space mappings as local structural defects and deformations can be highlighted. We are aware that this is standard practice and common amongst research groups growing thin films. However, over a wide range, there are virtually no defects to be found and cross-sectional imagery alone appears to be insufficient to account for the observed electronic response of these materials.
0.0.6 Notes on PrBa$_2$CuO$_7$ and LaBa$_2$CuO$_7$

Samples of high impurity concentrations of LaBa$_2$CuO$_7$ and PrBa$_2$CuO$_7$ materials sometimes show superconductivity. This unclear superconducting behavior further supports the concept of a quantum critical point in cuprate materials.
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