How pressure enhances the critical temperature for high temperature superconductivity in YBa$_2$Cu$_3$O$_{6+y}$

Michael Jurkutat  
Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany

Carsten Kattinger  
Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany

Stefan Tsankov  
Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany

Richard Reznicek  
Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany

Andreas Erb  
Walther Meissner Institut, Bayerische Akademie der Wissenschaften, 85748 Garching, Germany

Jürgen Haase  
Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany  
Email: j.haase@physik.uni-leipzig.de  
Tel: +49.341.9732601
FIG. 1. **Anvil cell high-pressure exerted on YBa$_2$Cu$_3$O$_{6+y}$ changes the charges in the CuO$_2$ plane.** (a) Schematic of the anvil cell used for NMR; the micro-coil surrounds the single crystal of about 1 nano-L volume, and both are placed in the high pressure chamber with a ruby chip as an optical pressure gauge. (b) Sketch of the crystal structure of YBa$_2$Cu$_3$O$_{6+y}$ with highlighted bonding orbitals in one of the CuO$_2$ planes. The charge content of these bonding orbitals can be measured with Cu and O NMR quadrupole splittings. As indicated in (c) it reflects the corresponding hole contents for Cu ($n_{\text{Cu}}$) and O ($n_O$), from which the NMR doping $\zeta$ follows ($1 + \zeta = n_{\text{Cu}} + 2n_O$).

**ABSTRACT**

High-temperature superconducting cuprates respond to doping with a dome-like dependence of their critical temperature ($T_c$). But the family specific maximum $T_c$ can be surpassed by application of pressure, a compelling observation known for decades. We investigate the phenomenon with high-pressure anvil cell nuclear magnetic resonance (NMR) and measure the charge content at planar Cu and O, and with it the doping of the ubiquitous CuO$_2$ plane with atomic scale resolution. We find that pressure increases the overall doping, as widely assumed, but when it enhances $T_c$ above what can be achieved by doping, it leads to a hole redistribution favoring planar O. This is similar to the observation that the family-specific maximum $T_c$, also increases if the hole content at planar O is raised at the expense of that at planar Cu. Thus, the pressure-induced enhancement of $T_c$ points to the same mechanism.

**I. INTRODUCTION**

High-temperature superconducting cuprates [1] are still central to condensed matter physics, and they carry surprisingly rich electronic properties [2] despite sharing a rather simple CuO$_2$ plane as a common structural unit. By doping the antiferromagnetic parent materials with electrons or holes these properties are induced, in particular superconductivity with its critical temperature ($T_c$) that shows a dome-like dependence on the doping level. However, while the maximum value $T_{c,\text{max}}$ appears at the so-called optimal doping levels (near $\sim 16\%$) for all materials, the family dependent $T_{c,\text{max}}$ differ widely.

Previously, it was shown that nuclear magnetic resonance (NMR) can measure the charges in the CuO$_2$ plane at the atomic level, i.e., in terms of the Cu ($n_{\text{Cu}}$) and O ($n_O$) bonding orbital hole contents, and a simple relation was found [3],

$$1 + \zeta = n_{\text{Cu}} + 2n_O.$$  \hspace{1cm} (1)

This relation is expected if $\zeta$ is similar to the chemical doping that adds to the nominal hole already present in the parent compound (per planar CuO$_2$ unit cell). Interestingly, it was found that the actual sharing of the hole content between Cu and O appears to be a fundamental parameter for $T_c$: $T_{c,\text{max}}$ is nearly proportional to $n_O$ [4], which is largely determined by the parent chemistry. In other words, for increasing $T_c$ electron charge has to be transferred from planar O to planar Cu, an experimental correlation that holds for all known hole-doped cuprates, $T_{c,\text{max}} \approx 200 \text{K} \cdot n_O$ [4], cf. also Fig. 1b-c and Fig. 2a-c.e.

This intriguing relation between $T_{c,\text{max}}$ and the hole sharing in the CuO$_2$ plane may hold information about another mystery of cuprate behavior: the unusual, material-specific pressure dependence of $T_c$ [5, 6]. While the pressure response of $T_c$ is different for the various cuprate families, quite generally, $T_c$ of underdoped cuprates tends to increase with pressure ($p$), while it hardly changes for optimal doping and usually decreases for overdoped materials [7-8]. This suggests that pressure increases planar hole doping (supported by conductivity and Hall measurements [5, 6, 7, 8]). However, some underdoped samples show a significantly higher $T_{c,\text{max}}(p)$ than what can be achieved by chemical doping ($x$). This is of great interest as it may be related to the mechanism of superconductivity.
FIG. 2. Charges in the CuO₂ plane and Tc. (a) The electronic phase diagram is typically used to mark the various cuprate phenomena as a function of doping (x) and temperature (T), however, this may not capture important details, e.g., the maximum value of Tc is not just determined by x. (b) Tc as a function of ζ = nCu + 2nO - 1, i.e., the doping measured with NMR. (c) Tc as a function of 2nO orders the superconducting domes; a near proportionality between Tc,max and nO is revealed [4]. (e) The planar charge distribution in terms of nCu and 2nO [3] reveals significant differences between the various families and relates to the plots (b, c) above. (d) Tc vs. pressure for different doping levels of YBa₂Cu₃O₆+y (YBCO; dark yellow denotes literature data [6]) - Tc slowly decreases for optimally doped YBCO with pressure, while Tc increases for underdoped YBCO, and can even exceed the maximum Tc achievable with chemical doping (gray lines). This raises the question of what happens in terms of nCu and nO as a function of pressure. Results from this work are shown for three different materials, cf. legend.

Clearly, with the NMR results mentioned above, it appears intriguing to explore how pressure affects the charges in the CuO₂ plane at the atomic level. However, since this requires ⁶³Cu and ¹⁷O NMR experiments on oriented single crystals at pressures that can only be achieved with anvil cell devices, such experiments are rather challenging: a micro-crystal surrounded by a radio frequency micro-coil needs to be positioned inside the pressurized region of an anvil cell, as depicted in Fig. 1a. Apart from mechanical issues such as disruptive failures induced by a changing geometry with pressure, for example, the signal-to-noise for the aligning process of the micro-crystal with respect to the magnetic field is a limiting factor. Nevertheless, we were able to meet these requirements to some extent and report on the results obtained for a few micro-crystals of YBa₂Cu₃O₆+y at pressures up to about 44 kbar. We find that pressure indeed has two effects: it increases the overall hole doping in the plane, but it can also change the sharing of the holes between Cu and O and thereby increase Tc as well. These findings underline the importance of the sharing of the planar charges for Tc.

II. PLANAR CHARGE DISTRIBUTION

The common electronic phase diagram of the cuprates, cf. Fig. 2a, assumes that chemical doping (x) is the decisive variable. Since we can measure the NMR doping level ζ given by (1), we prefer to take ζ as the true doping level, if NMR measurements are available, and we use the variable x if chemical doping is known from other sources (e.g. by using the superconducting dome or from stoichiometry) to keep the discussion transparent. Slight differences between the two numbers (ζ and x) become apparent by noting that the superconducting domes do not fall exactly on top of each other in a T-ζ phase diagram, cf. Fig. 2b.

The sharing of charges between Cu and O in the CuO₂ plane (at ambient conditions) is reproduced in Fig. 2e [3], where the black diagonal ‘parent’ line (ζ = 0) separates the hole-doped regime above (ζ > 0) from the electron-doped below it (ζ < 0). The various cuprate families then start at very different points near the parent line, which also determines the ratio (ΔnCu/ΔnO) of how the doped holes enter the plane (slopes indicated by arrows).

To prepare for the later discussion let us focus on YBa₂Cu₃O₆+y (YBCO), full dark yellow squares in Fig. 2e or in more detail in Fig. 3. In the undoped (y = 0) material YBa₂Cu₃O₆, the inherent hole must be shared between...
Cu and O, and we estimate $n_{\text{Cu}} = 0.68$ and $2n_O = 0.32$ from this plot. Upon doping, the holes enter the CuO$_2$ plane as indicated by the dark yellow arrow that points away from the parent line with the slope of $\Delta n_{\text{Cu}} / 2\Delta n_O = 0.52$, cf. Fig. 3. Thus, the question to be answered concerns a possible, pressure-induced redistribution of the charges $n_{\text{Cu}}$ and $n_O$.

In the literature, the change of $T_c$ with pressure ($p$) is typically described by the following equation, where $x$ denotes the chemical doping.

$$
\left( \frac{dT_c}{dp} \right)_{\text{tot}} = \left( \frac{dT_c}{dx} \right) \left( \frac{\partial x}{dp} \right) + \left( \frac{dT_c}{dp} \right)_{\text{intr}}
$$

(2)

The first term on the r.h.s. describes the change of doping due to pressure ($\partial x/\partial p$) with $\partial T_c/\partial x$ given by the slope of the superconducting dome as a function of doping at ambient pressure. The second term $(dT_c/dp)_{\text{intr}}$ describes the (unknown) intrinsic pressure effects on $T_c$, i.e., pressure induced change of the shape of the superconducting dome. It will, therefore, be interesting to compare the NMR data with the scenario given in 2.

### III. HIGH PRESSURE NMR EXPERIMENTS

In order to measure the planar charges under pressure, high-pressure $^{63}$Cu and $^{17}$O anvil cell NMR experiments were performed with home-made anvil cells \[\text{[11]}\] that fit standard NMR magnets (11.7 T and 17.6 T) and home-made probes. Therefore, our anvil cells are rather small compared to what is used by another group \[[12]\] that also engages in single crystal NMR experiments (of other materials) at similar pressures. We used $^{17}$O exchanged small volume (0.3 to 1.5 nano-L) micro-crystals with 3 different stoichiometries: YBa$_2$Cu$_{3-x}$O$_{6.5}$ (Y-6.5), YBa$_2$Cu$_{3}$O$_{6.85}$ (Y-6.85), and YBa$_2$Cu$_{3}$O$_{6.9}$ (Y-6.9). These doping levels were originally determined from $T_c$ measurements (see Supplementary Sec. 3). The crystals were glued on one of the anvil’s culets, and RF micro-coils were placed around them with the leads fed to outside the pressurized region through channels carved in the gasket; paraffin oil ensured hydrostatic conditions. Pressure was applied with a hydraulic press and screws secured the pressure during NMR experiments.

Standard orientation dependent NMR experiments were performed to measure the quadrupole frequencies (splittings of the Zeeman resonance) for $^{63}$Cu and $^{17}$O in the CuO$_2$ plane, from which the hole densities can be determined (see Methods). The NMR doping levels for the samples used here are $\zeta = 0.15, 0.19, 0.23$ for Y-6.5, Y-6.85, and Y-6.9, respectively.

The measured pressure dependence of the NMR quadrupole frequencies ($^{63,17}\nu_Q$) of the aligned single crystals are summarized in Fig. 4. For planar Cu in Fig. 4a we find that $^{63}\nu_Q,$ increases for the underdoped Y-6.5, but it is less sensitive to pressure in the higher doped Y-6.85 and Y-6.9, and even slightly decreases at elevated pressure, consistent with previous reports on underdoped and optimally doped YBCO \[\text{[13]}\].

For planar O in Fig. 4b-c we find that $^{17}\nu_Q,$ (field along the crystal c-direction) and $^{17}\nu_Q, $ (field along the Cu-O $\sigma$-bond) generally increase with pressure for all doping levels, although this is more pronounced for the underdoped

![Fig. 3. Pressure effects on planar charges. (a) Pressure can induce hole doping of the CuO$_2$ plane (I), and the holes arrive predominantly at planar O (II), but pressure can also induce intra-planar hole redistribution from Cu to O (III). (b) The same effects are described in the ‘YBCO-region’ of the $n_{\text{Cu}}$ - 2$n_O$ plane from Fig. 2, with the parent line indicated in black. An underdoped ($x \sim 10\%$) YBCO system would be located near ($n_{\text{Cu}},2n_O$) = (0.72,0.38), indicated by a grey cross. Application of pressure could move the system along any of the grey arrows and end at a certain doping level (dashed line parallel to the optimal doping line). However, it is not clear which path the system will follow: (I) holes enter the plane similar to doping at ambient conditions; (II) holes could predominantly go to planar O; (III) if the charges were just redistributed, the system would follow the black full arrow given the overall doping remained the same.](image)
Y-6.9, Y-6.85 (crossed blue squares) and Y-6.5 (red open squares); α denotes the direction of the external magnetic field $B_0$. (a) $^{63}$Cu along the crystal $c$-axis; (b) $^{17}$O along the $\sigma$-bond direction, and (c) $^{17}$O along the crystal $c$-axis. For Y-6.9 both quadrupole frequencies reflecting the double peak feature of the satellite transitions are displayed (the error, indicated, is typically much less than the symbol size).

Y-6.5. We note that while the literature on $^{17}$O NMR in cuprates under pressure is limited, one study on single crystals of underdoped YBCO up to 18 kbar found increasing $^{17}$O quadrupole splittings as well [14].

Using the pressure-induced changes of $^{63}$Cu and $^{17}$O NMR quadrupole splittings shown in Fig. 4, we determined the planar charges as a function of pressure (see Methods, and for the special behavior of the planar O splittings also [29]).

**IV. PLANAR CHARGES UNDER PRESSURE**

The pressure induced changes ($\Delta_p$) in the average local hole contents ($\Delta_p n_{Cu}$ and $\Delta_p n_{O}$) add up to the total change in hole content ($\Delta_\rho \zeta$) of the CuO$_2$ plane, according to [1], and we find $\Delta_\rho \zeta > 0$ for all samples, i.e., we observe an increase in hole doping with increasing pressure, cf. Fig. 5a. This hole doping is more pronounced for underdoped Y-6.5 with an initial slope of $\approx 5.8 \times 10^{-4}$ holes/kbar, compared to only $\approx 3.5 \times 10^{-4}$ holes/kbar for near optimally doped Y-6.85 as well as Y-6.9.

However, the changes of the site-specific hole contents with pressure differ. This can be seen in Fig. 5b-c. While $\Delta_p n_{Cu} \approx 1.3 \times 10^{-4}$ holes/kbar for underdoped Y-6.5, the materials closer to optimal doping, Y-6.85 and Y-6.9, show a much weaker or no increase at lower pressure and even a decrease in Cu hole content beyond 10 kbar, cf. Fig. 5b. For O we find that pressure causes a similar increase for all three samples, i.e. $2\Delta_p n_{O} \approx 4 \times 10^{-4}$ holes/kbar, cf. Fig. 5c. This clearly indicates a pressure-induced intra-planar charge redistribution, certainly for the higher doped Y-6.85 and Y-6.9, where the O hole content increases stronger than doping, i.e., $2\Delta_p n_{O} > \Delta_\rho \zeta$, and the Cu hole content decreases $\Delta_p n_{Cu} < 0$. The pressure-induced changes of the Cu and O hole contents as a function of pressure-induced doping ($\Delta_\rho \zeta$) are shown in Fig. 5d-e. Again, we observe an excess decrease of $n_{Cu}$ and increase of $n_{O}$, compared to what is expected for changes in doping only.

To summarize, our high-pressure NMR experiments on YBCO have shown that the increase in $T_c$ with pressure is accompanied by changes in the local hole contents, leading to an increase in hole doping, $\Delta_\rho \zeta > 0$, but also favoring an increase in O holes ($n_{O}$) over those at Cu ($n_{Cu}$).
First, we discuss whether our results agree in a more quantitative manner with published data on pressure induced changes of \(T_c\), as shown in Fig. 2. Unfortunately, from our samples with doping levels below and above that of YBa\(_2\)Cu\(_3\)O\(_{6.63}\) we can obtain more quantitative estimates, as we discuss now. The literature data for YBa\(_2\)Cu\(_3\)O\(_{6.63}\) show that \(T_c\) increases from about 64 K at ambient pressure to about 106 K at 160 kbar. This means an increase of \(T_c\text{max}\) of about 11 K compared to that of the optimally doped material. According to our experimental relation, \(T_c\text{max} \approx 200 \text{K} \cdot 2\Delta n_0\), this requires an increase of \(2\Delta n_0\) by 5.5% for an optimally doped YBCO. We can find the position of this material in the \((n_{Cu}, 2n_0)\)-plane (cf. Figs. 2 and 3) near our experimental data (full symbols denote ambient pressure data, and full lines with arrows indicate increasing pressure). Also shown are literature data for YBa\(_2\)Cu\(_3\)O\(_{6.63}\) where the high-pressure point (160 kbar, \(T_c = 106\) K, circled empty diamond) is that of an optimally doped YBCO with appropriate charge redistribution for the enhanced \(T_c\) (\(\Delta T_c\text{max} = 11\) K, \(\Delta n_0 \approx 5.5\%\)). The dash-dotted gray line is a Taylor expansion between the two points, \(\Delta n_{Cu} = 0.52\Delta n_0 + 16[\Delta n_0]^2\), where the first derivative (0.52) is defined by the chemical doping.

V. DISCUSSION

Pressure-induced doping clearly depends on the material and chemical doping, and previous assessments range widely with maximum values up to 0.2%/kbar \([15, 16]\), while we find that \(\partial\zeta/\partial p \approx 0.058(5)\%\)/kbar for the under-

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**FIG. 5.** Planar charge distribution as determined by NMR for samples Y-6.9 (black), Y-6.85 (blue) and Y-6.5 (red). (a) All samples show increasing hole-doping \(\Delta n_{Cu} = \Delta n_{Cu} + 2\Delta n_0 > 0\) with pressure \(p\). The slope \(\Delta n_{Cu}/\Delta p\) appears higher at lower doping levels and decreases at higher pressures. (b) The change in Cu hole content \(\Delta n_{Cu}\) is found to increase for the underdoped sample, and it is weak for higher doping and \(n_{Cu}\), even decreases at elevated pressure. (c) The O hole content \(2n_0\) increases for all samples similarly, with approximately \(4 \times 10^{-4}\) holes/kbar. In order to compare pressure effects to chemical doping (dark yellow lines), we show \(\Delta n_{Cu}\) and \(2\Delta n_0\) as a function of pressure induced doping \(\Delta n_0\) in (d) and (e), respectively. The increase in Cu hole content, \(\Delta n_{Cu}\), is smaller for pressure induced doping compared with that induced by chemical doping for all samples. The O hole content \(2\Delta n_0\) increases much faster with pressure induced doping compared to chemical doping for all samples. For both Cu and O, the underdoped Y-6.5 is closest to chemical doping, where the higher doped Y-6.9 and Y-6.85 also show an intra-planar charge redistribution, i.e. an increase of O holes at the expense of Cu holes. (f) Zoom into the \((n_{Cu}, 2n_0)\)-plane (cf. Figs. 2 and 3) near our experimental data (full symbols denote ambient pressure data, and full lines with arrows indicate increasing pressure). Also shown are literature data for YBa\(_2\)Cu\(_3\)O\(_{6.63}\) where the high-pressure point (160 kbar, \(T_c = 106\) K, circled empty diamond) is that of an optimally doped YBCO with appropriate charge redistribution for the enhanced \(T_c\) (\(\Delta T_c\text{max} = 11\) K, \(\Delta n_0 \approx 5.5\%\)). The dash-dotted gray line is a Taylor expansion between the two points, \(\Delta n_{Cu} = 0.52\Delta n_0 + 16[\Delta n_0]^2\), where the first derivative (0.52) is defined by the chemical doping.
doped Y-6.5, and 0.036(5) %/kbar for the samples near optimal doping. A recent estimate by Alireza et al. [17] of 0.032 %/kbar for fully doped YBCO matches our results quite well. Note that our data imply a pressure induced doping, $\partial \zeta / \partial p$, that is stronger for underdoped YBCO, contrary to modeling assumptions used elsewhere [13] [15].

Pressure favors a higher O hole content $2n_O$ compared to what can be achieved by chemical doping to the extent that, particularly at higher pressure and for higher doping levels, $2n_O$ increases not only through doping but also at the expense of a decreasing Cu hole content ($n_{Cu}$). A similar effect was recently reported with first principle calculations for Bi-based cuprates by Deng et al. [19]. Their results for a pressure induced increase of Cu $3d(x^2-y^2)$ occupation, i.e., a decrease in Cu hole content of $\partial n_{Cu}/\partial p = -0.04\%/\text{kbar}$ is more pronounced than what we find, cf. Fig. 5b. The pressure-induced decrease in $n_{Cu}$, while simultaneously overall doping increases, clearly reveals an intra-planar charge redistribution under pressure.

The sharing of the inherent hole that is nominally on Cu and the distribution of additional (chemically) doped charges, both reveal Cu and O contributions to occupied and unoccupied electronic states. Depending on the context in which cuprates are discussed, this reflects the Cu-O bond covalency, the charge transfer gap, or Cu and O band contributions. An intra-planar redistribution of holes from Cu to O therefore signals an increase in Cu-O bond covalency, i.e., a decrease in the charge transfer gap and an increased contribution of O to unoccupied bands of Cu to occupied bands. The concurrent increase in $T_{c,max}$ under pressure is consistent with not only the proportionality between $T_{c,max}$ and the O hole content seen by NMR. Studies using other methods also suggest an increasing $T_{c,max}$ with a decreasing charge transfer gap [20] [22].

Our results therefore suggest that the sought-after intrinsic effect of pressure on $T_c$, cf. (2), is a decrease of the charge transfer gap. Although our sample set and pressure range were limited, a simple model estimate for the necessary changes of the planar charge contents under pressure in underdoped YBa$_2$Cu$_3$O$_{6.63}$ shows quantitative agreement with what we found in our samples with lower and higher dopings. Additionally, Sadewasser et al. [23] estimated for the intrinsic pressure effect on $T_c$ in YBCO about 0.1 K/kbar. Our data show an increase of $2n_O$ under pressure for all samples of about 0.042(6) %/kbar, cf. Fig. 5. When multiplied with the slope of the $T_{c,max}/(2n_O) \approx 200$ K/hole, this gives 0.084(1) K/kbar in good agreement with [23].

While our results qualitatively and quantitatively account for the intrinsic pressure effect that increases $T_{c,max}$ in YBCO, the pressure phenomenology of $T_c$ differs somewhat for different cuprate families. Clearly, the specific structure and doping level should have an influence on how much pressure affects doping and changes planar bonding.

For La$_{2-x}$Sr$_x$CuO$_4$, for instance, $T_c$ increases for all doping levels, indicating that pressure causes an intra-planar charge redistribution that increases (decreases) planar O (Cu) hole content and has hardly any effect on doping, which is also consistent with the pressure-independent Hall coefficient for all doping levels of this family [9].

For the Bi-, Tl- and Hg-based materials that can be realized in single-layer as well as different multi-layer configurations, the pressure phenomenology is much more complex, e.g., including non-monotonic $T_c$-dependence on pressure for some materials. However, an interesting question concerns triple-layer materials (and beyond), as these exhibit distinct outer and inner CuO$_2$ layers and, under pressure, can exhibit two maxima in $T_c$. Perhaps, this relates to different effects of pressure on the different layers in terms of intra-planar charge distribution as well as doping. The latter effect has already been indicated by first-principle calculations [16].

The weak $T_c$-dependence on pressure in optimally electron-doped materials [24] [26] could be accounted for by similar effects as in YBCO, i.e., compensating effects on $T_c$ with pressure increasing $T_{c,max}$ while also pushing the system to the underdoped regime through hole doping.

Finally, we would like to emphasize that both the previously reported proportionality between $T_{c,max}$ and planar O hole content for different cuprate families [3] [4], and the increase of $T_{c,max}$ under pressure by increasing planar O hole content reported here, do not give any explanation for the peak of $T_c$ at optimal doping and the superconducting dome. Only the height of the latter, $T_{c,max}$, as well as other cuprate properties [27] appear to be fundamentally linked to the role of O in the planar structure. This insight has to be of crucial importance for material chemistry as well as any theoretical attempt at understanding cuprate superconductivity.

VI. METHODS

A. Sample preparation

High-quality single crystals of YBa$_2$Cu$_3$O$_{6.6}$ were grown in non-reactive BaZrO$_3$ crucibles and annealed as described elsewhere [28]. The resulting fully oxygenated single crystals ($y = 1$) were twinned within the a-b plane. For the Y-6.9 sample, a micro-crystal of an approximate size of $150 \times 100 \times 100\mu m^3$ was cut from the slab and subsequently $^{17}$O exchanged, as previously described [29], which results in nearly optimally doped YBCO. In order to produce the $^{17}$O enriched underdoped samples Y-6.5 and Y-6.85, we exchanged larger single crystals with $^{17}$O and subsequently annealed them to obtain the desired chain O content. They were cut into micro-crystals afterwards.
Prior to inserting the crystals into the pressure cell, the crystal axes were determined by polarized light that can easily identify domain boundaries in the twinned $a$-$b$-plane at the surface. The crystals were fixed to one of the culet surfaces with epoxy so that the $c$-axis is nearly parallel to the culet surface [see Supplementary, Fig. 4a]. After closing the pressure cell, the $T_c$ of the enclosed sample was determined using a NMR probe with a cryostat in zero field. The circuit was tuned at about 200 MHz at a temperature slightly above $T_c$. Then, the temperature was lowered throughout the superconducting transition and the concomitant change of the tank circuit frequency was monitored; the process was repeated by starting below $T_c$ and raising the temperature. $T_c$ was defined as the upper temperature where about 10% of the rapid frequency shift had occurred [see Supplementary, Fig. 5].

### B. Pressure cell preparation

Our home-built pressure cells had cylindrical cell bodies with a diameter of about 17 mm and a height of about 20 mm [see Supplementary, Fig. 1a]. The cell body is made from titanium. Optical access to the sample region is possible due to transparent anvils (along the cell axis) and 3 drilled holes in the cell body in radial direction at angles of 120°. The latter allow for an inspection of the anvils and the gasket while the cell is closed to avoid destruction of the single crystal. The ruby luminescence technique was used to measure the pressure through the axial hole [30]. The winding of the RF micro-coil and the preparation of the cell, including the gasket, is described elsewhere [31].

### C. NMR experiments

For the experiments commercial Bruker or Tecmag pulse spectrometers were used with 11.7 T or 17.6 T superconducting magnets. The anvils were mounted on regular home-made probes that fit commercial cryostats for temperature variation. Spin echo ($\pi/2$-$\pi$-$\pi$) pulse sequences were employed, and if possible, whole transitions were excited and recorded, while frequency stepped echoes were employed for broad lines. The $\pi/2$ pulse length for a typical experiment was accordingly 0.5 $\mu$s or 7 $\mu$s. The average pulse power varied between 10 mW and 5 W (note that the small volume of the RF micro-coils requires rather low power levels).

Different RF micro-coil designs were tested, with various filling and Q factors, according to different sizes and shapes of the crystals. The micro-coils were wound from an insulated silver wire (Goodfellow Cambridge Ltd) with diameter of 25 $\mu$m (5 $\mu$m insulation). The DC resistances measured on the closed cells were found to vary between ~0.7 $\Omega$ and ~1.5 $\Omega$ at room temperature (the lead resistances are smaller due to a larger diameter). With a typical coil inductance of 50 nH, this is in agreement with the measured Q factors that ranged between 20 and 40 (the RF skin depth is similar to the radius of the wire). For the first cell (Y-6.5 crystal) we used a nearly elliptical micro-coil to increase the filling factor. The crystal itself was extremely flat and small. It had the dimensions of approximately $90 \times 90 \times 40 \mu$m$^3$. The filling factor was about 0.13 [see Supplementary Fig. 3b]. For the second cell (Y-6.85 crystal), a double-wound micro coil was used with a higher inductance and greater mechanical stability [see Supplementary, Fig. 3a]. The dimension of the crystal was $140 \times 140 \times 90 \mu$m$^3$. The filling factor of this coil was about 0.3. For the third cell (Y-6.9 crystal) a regular cylindrical coil was used. The crystal had the dimensions $150 \times 100 \times 100 \mu$m$^3$. The filling factor of the coil was estimated to be about 0.4.

Since the signal-to-noise ($SNR$) is critical, the noise was always measured and verified that it is of thermal origin, predominantly from the RF micro-coil (an overall noise figure of about 1.25 dB was determined at room temperature).

The highest $SNR$ (per scan) measured (in the time domain) on the central transition of planar $^{63}$Cu for $c \parallel B_0$ at room temperature and a bandwidth of 5 MHz was $SNR = 4.9 \times 10^{-2}$ for the Y-6.9 cell; for the Y-6.85 and Y-6.5 cell the $SNR$ was about $3.2 \times 10^{-2}$ and $0.4 \times 10^{-2}$, respectively. For the planar O central transition, at a bandwidth of 2 MHz, we found $SNRs$ of $2.9 \times 10^{-2}$, $1.8 \times 10^{-2}$, and $0.12 \times 10^{-2}$ for Y-6.9, Y-6.85, and Y-6.5, respectively. With the necessary repetition times, a single spectrum could require 24 hours of signal averaging. Due to the low signal (and $SNR$) for Y-6.5, only a limited set of data was recorded. Nutation experiments were performed to find the pulse lengths that were close (within factor of two) to the estimated RF amplitudes.

For the orientation of a cell with respect to the magnetic field $B_0$ a goniometer that was mounted on the home-built NMR probe was used [see Supplementary, Fig. 1b, Fig. 2]. While the single crystals were glued to one anvil with the $c$-axis parallel to its culet surface, the true crystal orientation was measured with the goniometer that holds the anvil cell [11]. If the satellite linewidths and $SNRs$ permitted, the satellite resonances were followed as a function of angles, cf. [29]. Otherwise, angular dependences for the planar Cu central transition were recorded.

The full angular dependence of the central transition of the Y-6.5 cell is shown in the Supplementary [see Supplementary Fig. 4b].
Determination of charges

The Cu and O splittings along the respective principle axes are related to the planar hole densities as follows [3][32]:

\[ 17\nu_{Q,\sigma} = 2.45\text{MHz} \cdot n_O + 0.39\text{MHz} \] (3)

\[ 63\nu_{Q,c} = 94.3\text{MHz} \cdot n_{Cu} - 5.68\text{MHz} \cdot (8 - 4n_O) \] (4)

In the case of the Y-6.5 sample only splittings in c-direction could be measured, where the changes of the splitting are only half of what is observed along the bond, i.e., \( \Delta p\nu_{Q,c} = 2.45\text{MHz}/2 \cdot \Delta p\nu_{O} \).

In order to determine \( n_O \) from \( 17\nu_{Q,\sigma} \) for the initial chemical doping level for this sample we took literature data summarized in [32] on \( 17\nu_{Q,c}, 17\nu_{Q,\sigma}, T_c \) and O content for various doping levels of YBa\(_2\)Cu\(_3\)O\(_{6+y}\).

VII. AUTHOR CONTRIBUTION

M.J. led NMR experiments and data analysis, supported by C.K., S.T., J.H. Materials were supplied by A.E. who supervised also sample preparation. C.K. led the anvil cell construction with help from R.R. and J.H. All authors contributed to writing of the manuscript, which was led by M.J., C.K. and J.H. The overall project leadership was with J.H.

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M. Jurkutat, current affiliation: Institute for Biological Interfaces 4, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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