condensed matter

MDPI

Article

T_c Saturation and Possible Electronic Phase Separation in Strongly Overdoped Cuprates

Amirreza Hemmatzade [1,†], Elena Medina [2], Ludovic Delbes [1], Benoît Baptiste [1], David Hrabovsky [3], Yannick Klein [1], Steven D. Conradson [4], Maarit Karppinen [2] and Andrea Gauzzi [1,*]

[1] IMPMC, Sorbonne Université, CNRS and MNHN, 4, Place Jussieu, 75005 Paris, France
[2] Department of Chemistry and Materials Science, Aalto University, 00076 Espoo, Finland
[3] Sorbonne Université, Mesures Physiques à Basses Températures, 75005 Paris, France
[4] Department of Chemistry, Washington State University, Pullman, WA 90164, USA
* Correspondence: andrea.gauzzi@sorbonne-universite.fr
† Current address: Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland.

Abstract: In order to elucidate the unusual superconducting properties of cuprates in the strongly overdoped region, i.e., at hole-doping levels $p \gtrsim 0.4$/Cu in the CuO_2 plane, we study the structural and superconducting properties of a series of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ powder samples oxygenated under high pressure using different concentrations of $KClO_3$ up to 35 mol %. The analysis of X-ray diffraction data indicates a high purity ~90% of all samples and suggests that the concentration, x, of extra oxygen atoms increases with increasing $KClO_3$ concentration. Surprisingly, the T_c values remain nearly constant within the 80–85 K range independent of $KClO_3$ concentration, which suggests a scenario of T_c saturation. In order to account for this unexpected behaviour, we put forward the hypothesis that overdoping enhances the density of unpaired holes, which is supported by the observation of large values of the Sommerfeld coefficient in all samples. We therefore propose a scenario of electronic phase separation between normal and superconducting holes.

Keywords: superconducting cuprates; overdoping; electronic phase separation

check for updates

Citation: Hemmatzade, A.; Medina, E.; Delbes, L.; Baptiste, B.; Hrabovsky, D.; Klein, Y.; Conradson, S.D.; Karppinen, M.; Gauzzi, A. T_c Saturation and Possible Electronic Phase Separation in Strongly Overdoped Cuprates. *Condens. Matter* **2023**, *8*, 56. https://doi.org/10.3390/condmat8030056

Academic Editors: Antonio Bianconi and Augusto Marcelli

Received: 18 April 2023
Revised: 1 June 2023
Accepted: 29 June 2023
Published: 5 July 2023

Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. The Unexpected Finding of High-T_c Superconductivity in Strongly Overdoped Cuprates

The discovery of high-temperature superconductivity (HTSC) in cuprates by G. Bednorz and K.-A. Müller in 1986 [1] has revolutionised the field of superconductivity and driven research on condensed matter and materials physics towards new and totally unexpected directions. Indeed, in these materials, superconductivity occurs in the presence of sizeable electronic correlations upon electronically doping a pristine charge-transfer antiferromagnetic (AFM) insulating phase associated with Cu^{2+} ions in the CuO_2 plane, as shown in Figure 1a. This situation, which was never envisaged before, differs radically from that of metallic systems described by the conventional BCS theory of electron–phonon pairing. This has led to unprecedented theoretical efforts to develop a suitable microscopic theory of HTSC. A clear indication of unconventional superconducting behaviour is provided by early observations in the most studied systems, such as La_2CuO_4 (La214) and $Bi_2Sr_2CaCuO_{8+x}$ (Bi2212) (see Figure 1b), of a characteristic dome-like dependence of the superconducting critical temperature, T_c, on the excess holes, p, on the planar Cu ions in the Cu2 site in Figure 2. Specifically, superconductivity appears at $p \sim 0.05$ hole/Cu concomitant to the suppression of the AFM state, reaches a maximum at $p \sim 0.15$–0.17 hole/Cu and then decreases until it vanishes at $p \sim 0.26$–0.27 hole/Cu.

Such a dependence has been widely accepted as a universal feature of cuprates [2,3]; the resulting phase diagram shown in Figure 1a has, therefore, served as the phenomenological basis for the development of any microscopic HTSC theory for more than three decades. Although the microscopic theory remains highly controversial—a point that goes beyond

the frame of the present paper—a consensus exists as to a phenomenological scenario where pairing in the CuO_2 plane requires sizeable AFM correlations. As a consequence, research on cuprates has been hitherto focused on the underdoped and optimally doped regions of the electronic phase diagram, where unconventional normal state—or 'strange metal'—properties are found. The overdoped region has remained little studied, possibly because it is widely accepted that, upon approaching the regime of high carrier density in the overdoped region at $p > 0.26$–0.27 hole/Cu where superconductivity disappears, the properties are expected to become conventional, i.e., Fermi liquid (FL)-like.

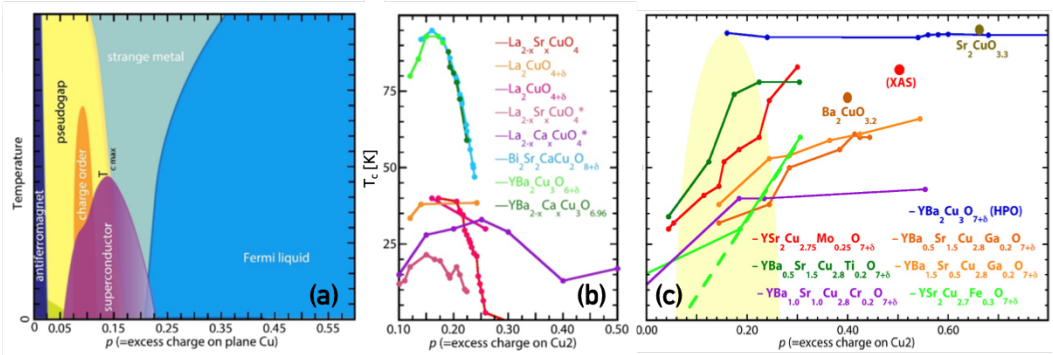

Figure 1. (**a**) Schematic T-p phase diagram of cuprates showing the existence of a characteristic dome-like p dependence of the superconducting critical temperature, T_c, in the $p = 0.05$–0.27 hole/Cu range, where the hole density, p, refers to a unit of CuO_2 plane. (**b**) Experimental diagram showing the above dome-like dependence for a number of cuprate families. Note the recent data on heavily Ca-substituted epitaxial $La_{2-x}Ca_xCuO_4$ thin films showing an extended dome up to $p = 0.4$ and beyond [4]. (**c**) T_c vs. p dependence of high-pressure oxygenated cuprates showing that T_c levels off or continues to slowly increase in the strongly overdoped region up to $p = 0.6$ (from [5] and references therein).

In fact, the above FL scenario for the strongly overdoped region was never verified experimentally in a systematic manner, possibly owing to the difficulty in overdoping the CuO_2 plane, which typically requires high-pressure oxygenation. Available data on a number of high-pressure oxygenated cuprates, initially studied by T. H. Geballe and M. Marezio, rather point to a completely different scenario [5–12]. Figure 1c shows that, in these systems, T_c levels off or continues to slowly increase past the upper limit of the dome of p = 0.26–0.27 hole/Cu, up to the maximum amounts of excess oxygen corresponding to p values ranging from 0.3 to 0.6. These reports have been met with disinterest or disregard until recent studies confirmed that high-T_c superconductivity is a bulk property of such strongly overdoped phases. To the best of our knowledge, a first confirmation of bulk superconductivity has been provided by some of us [13]. Using high-pressure synthesis, we achieved strong overdoping with p = 0.46 hole/Cu, well beyond the superconducting dome of Figure 1a, in high-purity powder samples of the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ system, derived from the $YBa_2Cu_3O_{7-x}$(YBCO) structure (see Figure 2). To facilitate the insertion of extra oxygens x, we replaced the Ba^{2+} ion for the smaller Sr^{2+} one and partially substituted Cu for Mo at the CuO (Cu1) chain site. Previous XANES spectroscopy [8] and bond valence sum analysis of high-resolution neutron diffraction data [13] consistently indicate that the above substitution is effective in increasing the oxygen concentration up to $x = 0.54$. Surprisingly, the resulting $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ phase displays bulk superconductivity at high $T_c \sim 84$ K [13]). This unexpected scenario has been confirmed two years later in the strongly overdoped cuprate Ba_2CuO_{4-y} [14] and, very recently, in heavily Ca-substituted La_2CuO_4 epitaxial thin films [4]. In conclusion, all these data consistently show a much wider superconducting region than previously believed, as apparent from Figure 1b,c.

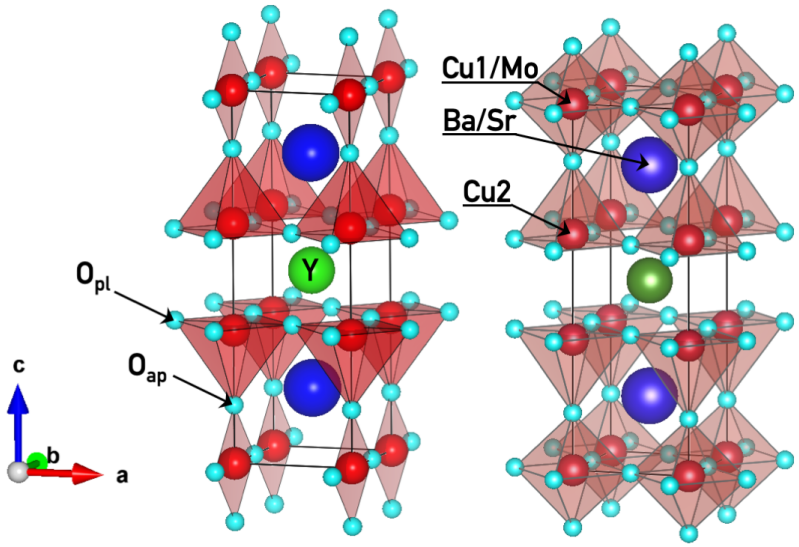

Figure 2. Crystal structures of orthorhombic $YBa_2Cu_3O_7$ (left) and tetragonal $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ (right), where Mo partially substitutes the copper Cu1 chain site. Note the distinct planar (pl) and apical (ap) oxygen sites. In the second structure, Sr substitutes the larger Ba ion, thus leaving more room for extra oxygen atoms.

2. Open Questions about the Strongly Overdoped Region of Cuprates

The observation of high-T_c superconductivity at doping levels $p \gtrsim 0.4$ put into question the current phenomenological description of cuprates and also the validity of the microscopic theories hitherto developed based on the dome-like phase diagram of Figure 1a. This prompts us to investigate further the properties of strongly overdoped cuprates. We single out the following research directions:

The possibility of a novel superconducting branch and of multiband superconductivity. The high T_c value of 84 K in the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ system is much higher than that of the pristine undoped $YSr_2Cu_3O_{7-x}$(YSCO) phase, where $T_c \sim 65$ K [15]. This observation rules out the possibility of secondary superconducting phases in the samples and clearly suggests the existence of a second or much more extended superconducting dome, as pointed out by Scalapino et al. [16]. Indeed, the larger valence $v = 2 + p$ of the Cu atom in the CuO_2 plane corresponds to record short Cu-apical oxygen distances [13]. Hence, both $x^2 - y^2$ and z^2 orbitals of the $Cu^{(2+p)+}$ ion are expected to be active [17], which suggests that one-band theories in two dimensions are unsuitable.

Are strongly overdoped cuprates Fermi liquids? The observation of FL behaviour would lead to the surprising conclusion of high-T_c superconductivity arising from an FL, in full contradiction of the current understanding of superconductivity in cuprates. The opposite finding of non-FL behaviour would also be interesting since this would raise the question whether this unconventional behaviour is similar to that in the optimally doped or underdoped regions. We expect that either case would drive the field toward a new direction.

Electronic phase separation. Our previous results on $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ unveil a significant fraction of normal electrons, as indicated by a sizeable Sommerfeld coefficient $\gamma \sim 10$ mJ Cu mol^{-1} K^{-2} [13]. A similar result has previously been reported on overdoped La214 samples [18], while a vanishing γ is found in optimal Y123 (YBCO) [19]. Considering the high purity of our $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$ sample and that neutron diffraction and muon-spin relaxation results rule out the presence of chemical inhomogeneities within a scale larger than the London penetration depth, $\lambda \sim 1000$ Å, the observation of normal electrons in the superconducting phase suggests a scenario of electronic phase separation between normal and superconducting phases within the intermediate scale ~100 Å between λ and the superconducting coherence length, $\xi \sim 10$ Å [5,13].

Previously, the scenario of nanoscale phase separation has been proposed by several authors not only for cuprate superconductors [20–25] but also for other strongly correlated electron systems, such as manganites and cobaltites [26–28]. Indeed, it has been theoretically argued that electronic phase separation can be stabilised by the competition between long-range Coulomb and short-range magnetic interactions [20], ubiquitous in all the above transition metal oxides. Various experimental techniques, such as nuclear magnetic resonance, Mössbauer spectroscopy, scanning tunneling microscopy and, more recently, by time-resolved or space-resolved synchrotron radiation techniques [29], have been successfully employed to probe dynamical phase separation in a variety of systems.

Beyond the adiabatic approximation. Recently, the local structure and dynamical properties of the strongly overdoped cuprates $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ and $Sr_2CuO_{3.3}$ were studied by means of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy [30,31]. The data analysis unveils huge (∼1 Å) dynamical distortions of the lattice at T_c that involve the apical oxygen, which suggests the existence of a lattice-driven change of the electronic structure in the superconducting state.

In the present paper, we focus on the possibility of an inhomogeneous superconducting phase, as suggested by the large value of γ in superconducting $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7.54}$. In order to elucidate this point, we have prepared and studied a series of powder samples of the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ phase with different concentrations x of extra oxygen atoms in the basal plane of the Cu1 chain site. In the following, we report selected results regarding the structural and superconducting properties of the samples. The new data enable us to draw more precisely the electronic phase diagram in the strongly overdoped region. Our objective is to cover the widest possible range of doping, from the tail of the dome at $p \sim 0.3$ hole/Cu ideally up to the maximum doping, $p \sim 1$ corresponding to Cu^{3+}.

3. Results

For all samples, the analysis of the X-ray diffraction data indicates a phase purity of 90% or better by excluding the inevitable residual KCl phase arising from the decomposition of $KClO_3$ at high temperature during synthesis. In Figure 3, we show a representative X-ray diffraction pattern of the 30% sample and compare it with the calculated pattern using the tetragonal $P4/mmm$ symmetry reported earlier. Although the above good purity level concerns the limited volume fraction probed by X-rays, it is plausible that we would obtain a similar purity level using neutron diffraction. Indeed, in a previous neutron diffraction study [13], we found a phase purity of 94% in a 35% sample prepared under the same conditions. In conclusion, we believe that secondary phases, if any, do not affect significantly the superconducting properties.

In Figure 4, we note that, in the 5–35 % range of $KClO_3$ molar concentration studied, the c-axis parameter decreases monotonically by about 0.02 Å, while the a-axis parameter remains constant within the experimental error. Such a decrease in c-axis parameter is comparable to that obtained on $YBa_2Cu_3O_{7-x}$ [32], where a decrease of 0.04 Å was reported upon increasing the oxygen concentration x from 0.4 to 0.95. This increase in oxygen concentration is identical to that obtained in our $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ system, so the present results suggest that, in first approximation, the amount of extra oxygen atoms incorporated in the structure is proportional to the $KClO_3$ concentration. Future neutron diffraction studies with enhanced resolution may confirm the above conclusion and also enable a direct measurement of the oxygen concentration. Similar to the aforementioned case of $YBa_2Cu_3O_{7-x}$, the increase in oxygen concentration in the basal plane of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ does not seem to change appreciably the a-axis parameter as the latter is mainly determined by the Cu-O distance in the CuO_2 plane.

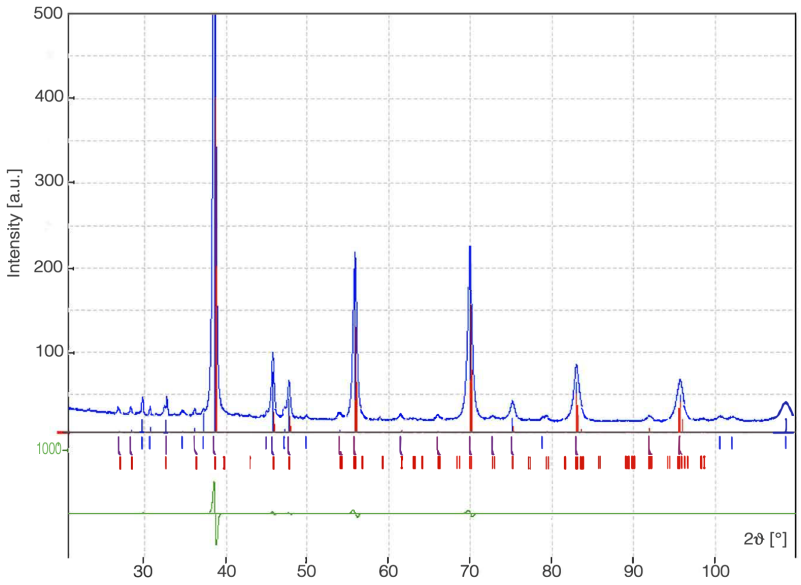

Figure 3. Co K_α X-ray diffraction pattern of the sample prepared with 30 mol % of $KClO_3$. This pattern confirms the purity of the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ phase up to sizeable concentrations of $KClO_3$. The experimental profile is indicated by the solid blue line. Experimental and calculated Bragg peaks are indicated by vertical red and blue ticks, respectively. The extra peaks that do not match the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ peaks are attributed to the residual KCl and $KClO_3$ phases. The green curve represents the difference between experimental and calculated pattern.

In Figure 5, we show the temperature-dependent susceptibility curves for a few representative $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ samples prepared with different concentrations of $KClO_3$ oxidant. The curves were obtained from the zero-field-cooling magnetisation data taken at a 100 Oe field. Note that the onset T_c values vary modestly within the 80–85 K range, as better shown in Figure 4. Taking into account the data scattering, we conclude that T_c does not appreciably change with the concentration of oxidant, with the exception of the 20% sample, which seems to exhibit an anomalous decrease in T_c. The volume fraction falls in the 15–25% range for all samples, except for the above anomalous sample. This indicates that the observed superconductivity is a bulk property of the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ phase and that the T_c seems to saturate independent of the hole-doping level. Figure 4 shows a similar behaviour of the Sommerfeld coefficient, γ, as estimated by extrapolating the C/T vs. T^2 curves down to zero temperature (see Figure 6). Note in all samples a large residual γ in the 10–20 mJ K^{-2} mol Cu range. This confirms previous findings in a $x = 0.54$ sample of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ [13] and in overdoped $La_{2-x}Sr_xCuO_4$ single crystals with vanishing T_c or even beyond in the metallic non-superconducting phase, where γ probes the density of states of normal electrons [18]. Similar values have been reported on optimally doped Bi2212 [33] and overdoped $Tl_2Ba_2CuO_{6+\delta}$ [34] as well. Note that smaller—still not vanishing—values have been reported on the above optimally doped systems [19], which supports a scenario of unpaired carriers in the overdoped region of cuprates. Further evidence of this scenario has recently been provided by optical conductivity measurements on overdoped La214 films, showing a wide Drude-like peak in the zero-temperature limit, well inside the superconducting phase [35].

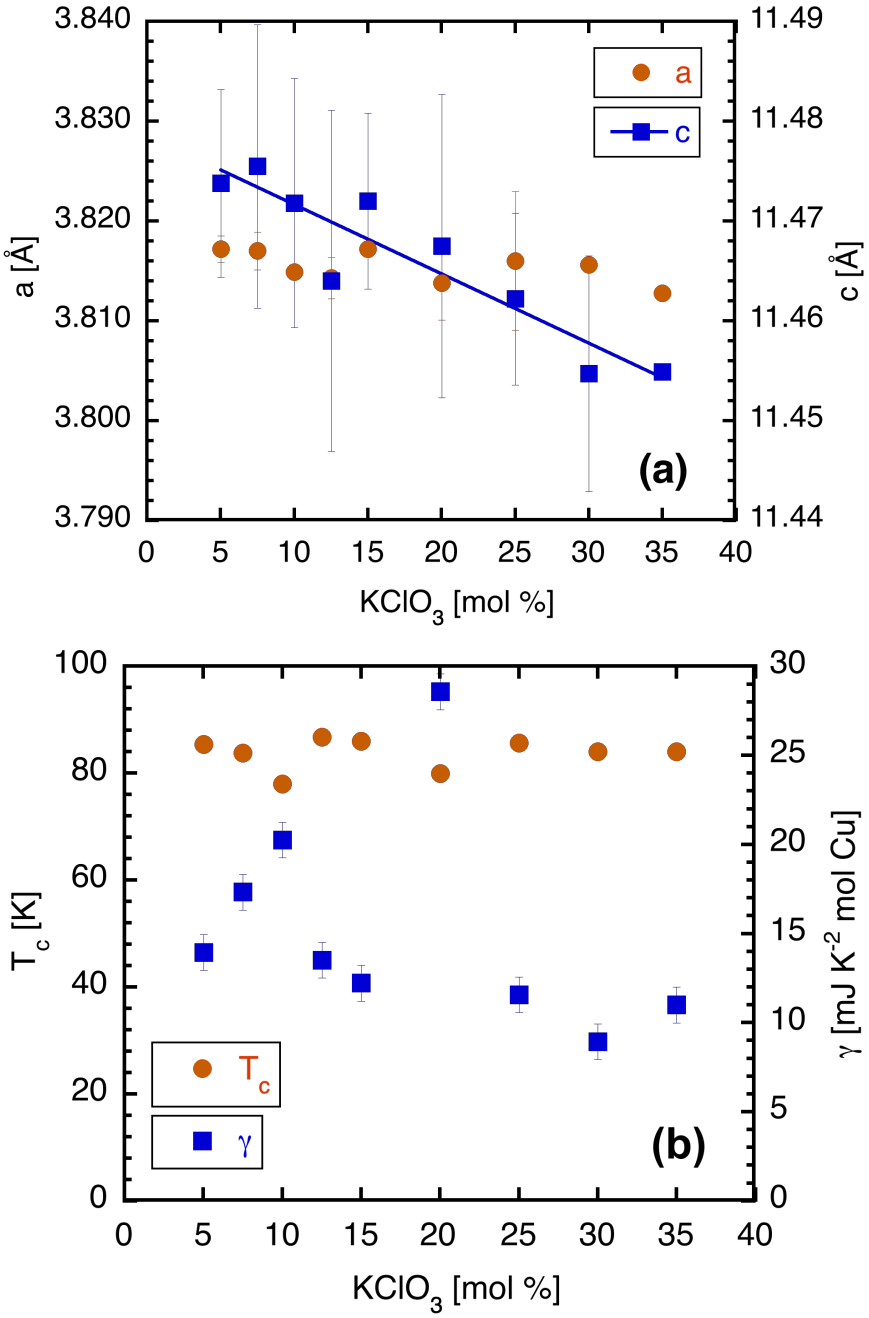

Figure 4. (**a**) Dependence of the $a-$ and $c-$axis parameters on $KClO_3$ oxidant concentration for a series of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ powder samples. Solid lines are linear fits to the experimental points. (**b**) Same as above for the T_c and the Sommerfeld coefficient, γ. The latter is obtained by extrapolating the C/T vs. T^2 curves shown in Figure 6 down to zero temperature. The data of the 35% sample are taken from Ref. [13].

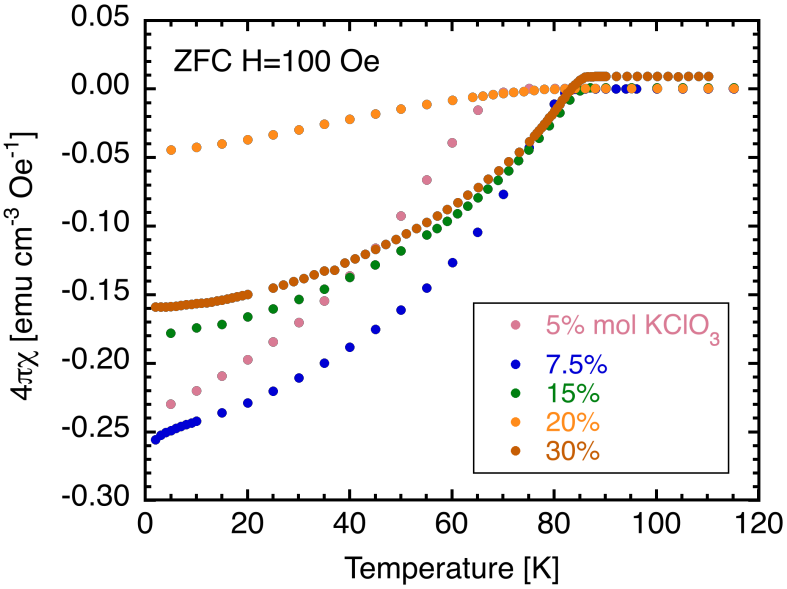

Figure 5. Zero−field−cooling (ZFC) magnetisation curves measured at a field of 100 Oe on a series of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ samples prepared with different molar concentrations of $KClO_3$ oxidant indicated in the legend.

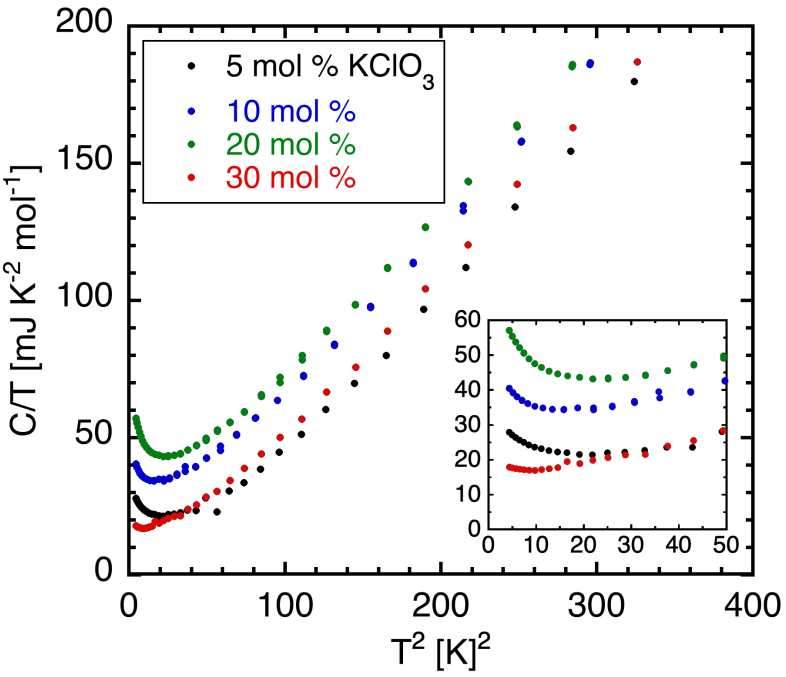

Figure 6. Low−temperature behaviour of the specific heat of four representative $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ samples prepared using different concentrations of $KClO_3$ oxidant indicated in the legend. Inset: detail of the curves in the zero−temperature limit.

4. Discussion

The present systematic study carried out on a series of $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ powder samples prepared under high pressure with different nominal concentrations of extra oxygen atoms, x, confirms the occurrence of bulk superconductivity at 80–85 K in the strongly overdoped region, corresponding to hole concentrations $p \gtrsim 0.4$ in the CuO_2 plane. The above T_c values are significantly higher than those of the pristine unsubstituted $YSr_2Cu_3O_{7-x}$ phase, which rules out the possibility that superconductivity in $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ is associated with a secondary phase. This conclusion is in

agreement with the high purity of the samples, typically 90% or better, as determined by X-ray diffraction, and with the sizeable magnitude of the superconducting fraction in the 15–25% range, estimated by means of susceptibility measurements. The monotonic decrease in the *c*-axis parameter with the nominal molar concentration of $KClO_3$ suggests an increasing amount of extra oxygens, x, in the 5–35 mol % range of $KClO_3$ concentration investigated. A striking result is the nearly constant T_c values, which suggests a quick saturation of superconductivity with oxygen overdoping. This observation is consistent with the large and nearly x-independent values of the Sommerfeld coefficient, γ, which points to a sizeable fraction of unpaired carriers that coexist in the superconducting state. In order to account for this unusual observation, we put forward the hypothesis that overdoping mainly enhances the density of holes with local a_1 symmetry, formed by the hybridisation of the $3d_{z^2}$ orbitals of the Cu ions in the CuO_2 plane. According to a theoretical model proposed by Di Castro, Feiner and Grilli [21], these holes do not contribute to superconductivity and T_c scales with the density of holes with local b_1 symmetry, formed by the hybridisation of the $3d_{x^2-y^2}$ orbitals. We argue that this scenario is suitable for the present case as the record short distance between the apical oxygen and the Cu ion in the CuO_2 plane characteristic of the $Cu_{0.75}Mo_{0.25}Sr_2YCu_2O_{7+x}$ phase [13] is expected to significantly enhance the occupancy of the $3d_{z^2}$ orbital, as pointed out recently [17]. Further experiments on other strongly overdoped cuprate systems would be required to corroborate this scenario and to explore the normal state and superconducting properties in the strongly overdoped region at even higher doping levels, up to $p = 1$.

5. Materials and Methods

The (Cu,Mo)1212 powder samples used in this work were newly synthesised using the citrate sol–gel method and a modified oxidation treatment, as described elsewhere [13]. In brief, appropriate amounts of Y_2O_3, CuO, $SrCO_3$ and MoO_3 were dissolved in 1 M HNO_3 solution. Citric acid and ethylene glycol were added and the solution was heated in oven at 200 °C until a gel was formed. The obtained gel was then dried, powdered and calcined at 600 °C for 12 h. The resulting powder was pressed into a pellet and annealed at 980 °C for 2 × 24 h with intermediate grinding to obtain the as-synthesised product. The oxygenation was carried out by mixing the as-synthesised powder with a variable concentration from 5 to 35 mol % of $KClO_3$. The mixture was then subjected to high-pressure treatment in a cubic-anvil-type high-pressure apparatus at 4 GPa and 500 °C. The powders were studied by means of X-ray diffraction in a conventional Bragg–Brentano $\vartheta - 2\vartheta$ geometry using a commercial X'pert powder diffractometer equipped with a Co K_α anode. The superconducting transition of the powders was studied by means of dc magnetisation measurements as a function of temperature in both zero-field (ZF) and field-cooling (FC) modes at 100 Oe using a commercial SQUID Quantum Design apparatus. A complementary study of the superconducting transition and of the electronic spectrum was carried out by means of specific heat measurements in the 2–300 K range performed using the relaxation rate method implemented in the same PPMS apparatus. This latter study enables us to estimate the Sommerfeld coefficient, γ.

Author Contributions: Conceptualization, A.G., S.D.C. and M.K.; methodology, A.G. and M.K.; writing and editing, A.G.; experiments, A.H., E.M., L.D., B.B., Y.K. and D.H.; supervision, A.G.; funding acquisition, A.G. and M.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been partially funded by the "SUPERSTRONG" project of the French National Agency for Research (ANR) under contract no. ANR-22-CE30-0010.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, [A.G.].

Acknowledgments: The authors acknowledge E. Gilioli for useful discussions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bednorz, G.; Müller, K.-A. Possible high T_c superconductivity in the Ba–La–Cu–O system. *Z. Physik B – Condensed Matter* **1986**, *64*, 189–193. [CrossRef]
2. Zhang, H.; Sato, H. Universal relationship between T_c and the hole content in *p*-type cuprate superconductors. *Phys. Rev. Lett.* **1993**, *70*, 1697–1699. [CrossRef] [PubMed]
3. Tallon, J.L.; Bernhard, C.; Shaked, H.; Hitterman, R.L.; Jorgensen, J.D. Generic superconducting phase behavior in high-T_c cuprates: T_c variation with hole concentration in $YBa_2Cu_3O_{7-\delta}$. *Phys. Rev. B* **1995**, *51*, 12911–12914. [CrossRef]
4. Kim, G.; Rabinovich, K.S.; Boris, A.V.; Yaresko, A.N.; Suyolcu, Y.E.; Wu, Y.M.; van Aken, P.A.; Christiani, G.; Logvenov, G.; Keimer, B. Optical conductivity and superconductivity in highly overdoped $La_{2-x}Ca_xCuO_4$ thin films. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2106170118. [CrossRef]
5. Sederholm, L.; Conradson, S.D.; Geballe, T.H.; Jin, C.Q.; Gauzzi, A.; Gilioli, E.; Karppinen, M.; Baldinozzi, G. Extremely Overdoped Superconducting Cuprates via High Pressure Oxygenation Methods. *Condens. Matter* **2021**, *6*, 50. [CrossRef]
6. Grigoraviciute, I.; Arai, M.; Yamauchi, H.; Karppinen, M. Superconductivity in the 'triple-fluorite-layer' copper oxides (Cu,M)-1232 (M = Mo, W, Re, Pb). *Solid State Commun.* **2006**, *137*, 601–605. [CrossRef]
7. Chmaissem, O.; Grigoraviciute, I.; Yamauchi, H.; Karppinen, M.; Marezio, M. Superconductivity and oxygen ordering correlations in the homologous series of (Cu, Mo)Sr_2(Ce, Y)$_sCu_2O_{5+2s+\delta}$. *Phys. Rev. B* **2010**, *82*, 104507. [CrossRef]
8. Grigoraviciute, I.; Karppinen, M.; Chan, T.S.; Liu, R.S.; Chen, J.M.; Chmaissem, O.; Yamauchi, H. Electronic Structures, Hole-Doping, and Superconductivity of the s = 1, 2, 3, and 4 Members of the (Cu,Mo)-12s2 Homologous Series of Superconductive Copper Oxides. *J. Am. Chem. Soc.* **2010**, *132*, 838–841. [CrossRef]
9. Marezio, M.; Chmaissem, O.; Bougerol, C.; Karppinen, M.; Yamauchi, H.; Geballe, T.H. Overdoped cuprates with high-temperature superconducting transitions. *Appl. Phy. Lett. Mater.* **2013**, *1*, 021103. [CrossRef]
10. Marik, S.; Morán, E.; Labrugère, C.; Toulemonde, O.; Alario-Franco, M.A. $Mo_xCu_{1-x}Sr_2YCu_2O_y$ ($0.3 \leq x \leq 1$) revisited: Superconductivity, magnetism and the molybdenum oxidation state. *J. Solid State Chem.* **2012**, *191*, 40–45. [CrossRef]
11. Marezio, M.; Chmaissem, O.; Bougerol, C.; Karppinen, M.; Yamauchi, H.; Geballe, T.H. High-T_c Superconducting Cuprates, $(Ce,Y)_sO_{2s-2}Sr_2$ $(Cu_{2.75}$ $Mo_{0.25})O_{6+\delta}$: T_c increase with apical Cu-O decrease at constant Cu-O planar distance. *J. Phys. Conf. Ser.* **2014**, *507*, 012031. [CrossRef]
12. Marik, S.; Santos-Garcia, A.J.D.; Labrugere, C.; Morán, E.; Toulemonde, O.; Alario-Franco, M.A. Oxidation induced superconductivity and Mo/Cu charge equilibrium in $Mo_{0.3}Cu_{0.7}Sr_2ErCu_2O_y$. *Supercond. Sci. Technol.* **2015**, *28*, 045007. [CrossRef]
13. Gauzzi, A.; Klein, Y.; Nisula, M.; Karppinen, M.; Biswas, P.K.; Saadaoui, H.; Morenzoni, E.; Manuel, P.; Khalyavin, D.; Marezio, M.; et al. Bulk superconductivity at 84 K in the strongly overdoped regime of cuprates. *Phys. Rev. B* **2016**, *94*, 180509. [CrossRef]
14. Li, W.M.; Zhao, J.F.; Cao, L.P.; Hu, Z.; Huang, Q.Z.; Wang, X.C.; Liu, Y.; Zhao, G.Q.; Zhang, J.; Liu, Q.Q.; et al. Superconductivity in a unique type of copper oxide. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 12156–12160. [CrossRef] [PubMed]
15. Gilioli, E.; Radaelli, P.; Gauzzi, A.; Licci, F.; Marezio, M. Structure and superconductivity of $YSr_2Cu_3O_{7-d}$. *Phys. C Supercond.* **2000**, *341–348*, 605–606. [CrossRef]
16. Scalapino, D.J. A different branch of the high T_c family? *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 12129–12130. [CrossRef]
17. Maier, T.; Berlijn, T.; Scalapino, D.J. Two pairing domes as Cu^{2+} varies to Cu^{3+}. *Phys. Rev. B* **2019**, *99*, 224515. [CrossRef]
18. Wang, Y.; Yan, J.; Shan, L.; Wen, H.H.; Tanabe, Y.; Adachi, T.; Koike, Y. Weak-coupling *d*-wave BCS superconductivity and unpaired electrons in overdoped $La_{2-x}Sr_xCuO_4$ single crystals. *Phys. Rev. B* **2007**, *76*, 064512. [CrossRef]
19. Moler, K.A.; Sisson, D.L.; Urbach, J.S.; Beasley, M.R.; Kapitulnik, A.; Baar, D.J.; Liang, R.; Hardy, W.N. Specific heat of $YBa_2Cu_3O_{7-\delta}$. *Phys. Rev. B* **1997**, *55*, 3954–3965. [CrossRef]
20. Emery, V.J.; Kivelson, S.A.; Lin, H.Q. Phase separation in the t-J model. *Phys. Rev. Lett.* **1990**, *64*, 475–478. [CrossRef]
21. Di Castro, C.; Feiner, L.F.; Grilli, M. Symmetry of Hole States in Superconducting Oxides: Correlation with T_c. *Phys. Rev. Lett.* **1991**, *66*, 3209–3212. [CrossRef] [PubMed]
22. Müller, K.A.; Benedek, G. *Phase Separation in Cuprate Superconductors*; World Scientific: Singapore, 1993 ; pp. 1–394. [CrossRef]
23. Bianconi, A.; Saini, N.L.; Lanzara, A.; Missori, M.; Rossetti, T.; Oyanagi, H.; Yamaguchi, H.; Oka, K.; Ito, T. Determination of the Local Lattice Distortions in the CuO_2 Plane of $La_{1.85}Sr_{0.15}CuO_4$. *Phys. Rev. Lett.* **1996**, *76*, 3412–3415. [CrossRef] [PubMed]
24. Howald, C.; Fournier, P.; Kapitulnik, A. Inherent inhomogeneities in tunneling spectra of $Bi_2Sr_2CaCu_2O_{8-x}$ crystals in the superconducting state. *Phys. Rev. B* **2001**, *64*, 100504. [CrossRef]
25. Pan, S.H.; O'Neal, J.P.; Badzey, R.L.; Chamon, C.; Ding, H.; Engelbrecht, J.R.; Wang, Z.; Eisaki, H.; Uchida, S.; Gupta, A.K.; et al. Microscopic electronic inhomogeneity in the high-Tc superconductor $Bi_2Sr_2CaCu_2O_{8+x}$. *Nature* **2001**, *413*, 282–285. [CrossRef] [PubMed]
26. Uehara, M.; Mori, S.; Chen, C.H.; Cheong, S.W. Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites. *Nature* **1999**, *399*, 560–563. [CrossRef]
27. Kagan, M.Y.; Kugel, K.I.; Khomskii, D.I. Phase separation in systems with charge ordering. *J. Exp. Theor. Phys.* **2001**, *93*, 415–423. [CrossRef]
28. Kagan, M.; Kugel, K.; Rakhmanov, A. Electronic phase separation: Recent progress in the old problem. *Phys. Rep.* **2021**, *916*, 1–105. [CrossRef]

29. Campi, G.; Bianconi, A. Evolution of Complexity in Out-of-Equilibrium Systems by Time-Resolved or Space-Resolved Synchrotron Radiation Techniques. *Condens. Matter* **2019**, *4*, 32. [CrossRef]
30. Conradson, S.D.; Geballe, T.H.; Gauzzi, A.; Karppinen, M.; Jin, C.; Baldinozzi, G.; Li, W.; Cao, L.; Gilioli, E.; Jiang, J.M.; et al. Local lattice distortions and dynamics in extremely overdoped superconducting $YSr_2Cu_{2.75}Mo_{0.25}O_{7.54}$. *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 4559–4564. [CrossRef]
31. Conradson, S.D.; Geballe, T.H.; Jin, C.Q.; Cao, L.P.; Gauzzi, A.; Karppinen, M.; Baldinozzi, G.; Li, W.M.; Gilioli, E.; Jiang, J.M.; et al. Nonadiabatic coupling of the dynamical structure to the superconductivity in $YSr_2Cu_{2.75}Mo_{0.25}O_{7.54}$ and $Sr_2CuO_{3.3}$. *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 33099–33106. [CrossRef]
32. Cava, R.; Hewat, A.; Hewat, E.; Batlogg, B.; Marezio, M.; Rabe, K.; Krajewski, J.; Peck, W.; Rupp, L. Structural anomalies, oxygen ordering and superconductivity in oxygen deficient $Ba_2YCu_3O_x$. *Phys. C Supercond.* **1990**, *165*, 419–433. [CrossRef]
33. Junod, A.; Wang, K.Q.; Tsukamoto, T.; Triscone, G.; Revaz, B.; Walker, E.; Muller, J. Specific heat up to 14 tesla and magnetization of a $Bi_2Sr_2CaCu_2O_8$ single crystal thermodynamics of a 2D superconductor. *Phys. C Supercond.* **1994**, *229*, 209–230. [CrossRef]
34. Loram, J.; Mirza, K.; Wade, J.; Cooper, J.; Liang, W. The electronic specific heat of cuprate superconductors. *Phys. C Supercond.* **1994**, *235–240 Pt 1*, 134–137. [CrossRef]
35. Mahmood, F.; He, X.; Božović, I.; Armitage, N.P. Locating the Missing Superconducting Electrons in the Overdoped Cuprates $La_{2-x}Sr_xCuO_4$. *Phys. Rev. Lett.* **2019**, *122*, 027003. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.