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Overdoped cuprates with high-temperature superconducting transitions

M. Marezio, O. Chmaissem, C. Bougerol, M. Karppinen, H. Yamauchi, and T. H. Geballe

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Overdoped cuprates with high-temperature superconducting transitions

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Evidence for high- T_c cuprate superconductivity is found in a region of the phase diagram where non-superconducting Fermi liquid metals are expected. Cu valences estimated independently from both x-ray absorption near-edge spectroscopy and bond valence sum measurements are >2.3 , and are in close agreement with each other for structures in the homologous series $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Y,Ce})_s\text{Cu}_2\text{O}_{5+2s+\delta}$ with $s = 1, 2, 3$, and 4. The record short apical oxygen distance, at odds with current theory, suggests the possibility of a new pairing mechanism. The possibility that the charge reservoir layers are able to screen long range coulomb interactions and thus enhance T_c is discussed. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4817895>]

I. INTRODUCTION

In 2010, Chmaissem *et al.*¹ published the structural refinements of the reduced (non superconducting) and oxidized phases (superconducting) for the first four members of the homologous series $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Ce,Y})_s\text{Cu}_2\text{O}_{5+2s+\delta}$ by powder neutron diffraction. The most straightforward interpretation of these data suggested that high temperature superconductivity exists in an unexpected region of overdoped cuprates.

During the past eight years the first six members of the homologous series cited above have been successfully synthesized and investigated.²⁻⁷ The reported results indicate that the Cu valence is anomalously higher than in the well-known high- T_c cuprates such as $\text{YBa}_2\text{Cu}_3\text{O}_7$. The $s = 1$ member, $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2\text{YCu}_2\text{O}_{7+\delta}$, is structurally the same as $\text{YBa}_2\text{Cu}_3\text{O}_7$, but where 25% of the basal Cu cations (i.e., those in the chain layer) are replaced by Mo, and the Ba cations are replaced by Sr. There is a substantial difference between the familiar Hg- $m2(n-1)n$ and Tl- $m2(n-1)n$ homologous series and the present $(\text{Cu}_{0.75}\text{Mo}_{0.25})$ - $12s2$ series. In the Hg- and Tl-series, n represents the number of $(\text{Ca})(\text{CuO}_2)$ blocks in the unit cell, i.e., $n = 1, 2, 3, 4$ means 1, 2, 3, 4 CuO_2 layers per unit cell. In the $(\text{Cu}_{0.75}\text{Mo}_{0.25})$ - $12s2$ series, there are only 2 CuO_2 layers per unit cell; $s = 1$ stands for a single layer of Y, and $s > 1$ stands for $s-1$ additional insulating $(\text{Ce,Y})(\text{O}_2)$ layers that are in the CaF_2 fluorite configuration.

The increase in T_c on going from the $n = 1$ to $n = 3$ members of the Hg- or Tl-based series is believed to be due to interlayer pair tunneling between the CuO_2 layers that suppresses phase fluctuations and possibly, for $n = 3$, because of the interactions between the underdoped inner layer and the overdoped outer layers can enhance T_c .⁸ By contrast, the decrease from 88 to an almost

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constant 56 K observed on going from the $s = 1$ to $s > 1$ for members of the present homologous series is due to the thickening of the insulating fluorite-like layers that prevents interlayer tunneling. The almost constant T_c for $s > 1$ can be understood because the coupling between unit cells is achieved by the same reservoir $(\text{SrO})(\text{Cu}_{0.75}\text{Mo}_{0.25}\text{O}_{1+\delta})(\text{SrO})$ block present in every member of the series. Thus, all the members of this homologous series with $s > 1$ are single layer 214 cuprates but with only one apical oxygen as in a pyramid. If by a first approximation we consider them as single-layer cuprates, the T_c of ~ 56 K is significantly higher than those of the optimally doped single-layer cuprates in which the Cu cations are octahedrally coordinated, with the exception of $\text{Sr}_2\text{CuO}_{4-x}$ and $\text{HgBa}_2\text{CuO}_{4+\delta}$.⁹⁻¹³

II. PREVIOUS RESULTS

Powder x-ray diffraction and high resolution transmission electron microscopy show that the $s = 2$ member contains the following layered sequence: $([\text{Cu}_{0.75}\text{Mo}_{0.25}]\text{O}_{1+\delta})(\text{SrO})(\text{CuO}_2)(\text{Y,Ce})(\text{O}_2)(\text{Y,Ce})(\text{CuO}_2)(\text{SrO})([\text{Cu}_{0.75}\text{Mo}_{0.25}]\text{O}_{1+\delta})$.² The sequence of the higher members is obtained by inserting additional two-layer blocks of $(\text{O}_2)(\text{Y,Ce})$ between the (CuO_2) layers (see Figure 2 of Ref. 1). The as-synthesized (AS) samples were not superconducting. They became so by means of high-pressure oxygenation (HPO) carried out at 5 GPa and 500 °C in the presence of KClO_3 acting as the oxidant. With increasing ratio of KClO_3 to the cuprate phase, the c axis gradually decreased and T_c increased up to 88 K for the $s = 1$, and to ~ 56 K for all the higher members. The thickness of the inserted fluorite block increases from 6.4 Å for $s = 2$ to 11.4 Å for $s = 4$. The lattice parameters of the more recent synthesis of the $s = 5$ and 6 members are in good agreement with those expected from the lower homologues, although the slower reaction rates made further experiments problematic as the samples obtained were not completely single phase.⁷ Nevertheless, the $s = 5$ homologue became superconducting with a T_c of ~ 55 K after a routine HPO treatment that is similar to the $s < 5$ samples. Field-cooled and zero field-cooled susceptibility measurements give evidence for bulk superconductivity (volume fraction $> 30\%$).³ Furthermore, the lack of an appreciable Curie tail above T_c is an evidence that there is little no magnetic second phase present. The Cu valence has been investigated by two independent methods, namely, x-ray absorption near-edge spectroscopy (XANES) and the empirical bond-valence-sum (BVS) method that uses the bond distances determined from the neutron powder diffraction refinements. The BVS determined values for the Cu valence in the CuO_2 layer in the HPO samples are 2.45, 2.31, and 2.34 for the $s = 1, 2,$ and 3, respectively. The XANES measured valence is an average of the Cu cations in the reservoir block and those in the CuO_2 layers. A procedure that relies on the resolved oxygen K-edge peaks in the chains and planes was used to obtain Cu valence in the CuO_2 layers alone.³ The XANES valences for the HPO samples are 2.46, 2.24, 2.28, and 2.26 for $s = 1, 2, 3,$ and 4. The Cu valences of the corresponding non-superconducting AS samples were found to be 2.16, 2.13, 2.14, and 2.14 for the $s = 1, 2, 3,$ and 4, samples, respectively. The BVS valence gains credibility because of earlier work in $\text{YBa}_2\text{Cu}_3\text{O}_7$ where the BVS valence is in reasonable agreement with the values found later by neutron powder diffraction and thermoelectric power measurements.^{14,15} It is plausible to assume that the BVS valence will also be a reliable estimate of the mobile charge density in the present series. The possibility that superconductivity occurs in a region of the phase diagram where it would be expected to be a non-superconducting normal Fermi liquid has been previously postulated to explain the properties of $\text{Sr}_2\text{CuO}_{4-x}$.^{11,12} In 1991, Rukang *et al.* investigated a long list of possible fluorite-inserted cuprates.^{16,17} The formula of their compounds was $\text{MSr}_2(\text{Ln,R})_2\text{Cu}_2\text{O}_y$ with $M = \text{Ti, V, Nb, Ta, Mo, W, Sn, Sb}$ which corresponds to the $s = 2$ members of the respective homologous series. No superconductivity was found in any of these cuprates.^{16,17} The success for the present series seems to be due to the replacement of 25% of Cu in the reservoir layer with Mo and to the extra oxygen that this substitution induces in the same layer.

When the Mo content was varied from 5% to 35% for the $s = 3$ member, it was found that 25% represented the maximum concentration that can be incorporated.⁴ At higher concentrations, the c parameter remained constant and impurities began to appear in the powder pattern. A continuous increase of T_c and the c parameter was observed from 5% to 25%. The same authors tried other cations such as Re, W, and Pb to partially substitute for the Cu of the reservoir layer. Only the

TABLE I. The Cu2 cations bond-valence-sums (BVS) calculated from the structural refinements based on NDP data¹ compared with the valence obtained from XANES data.² The *s* values indicate the four members of the homologous series in the AS and HPO states.

	<i>s</i> = 1		<i>s</i> = 2		<i>s</i> = 3		<i>s</i> = 4	
	AS	HPO	AS	HPO	AS	HPO	AS	HPO
v(Cu2) from BVS	2.21	2.45	2.22	2.31	2.22	2.34	2.20	
v(Cu) from XANES	2.16 ^a	2.46	2.13	2.24	2.14	2.25	2.14	2.26
$\rho(\text{CuO}_2)$		0.53		0.28		0.26		0.27
T_c		88 K		56 K		54.5 K		55.5 K

^aThe oxygen content for this sample was determined by iodometric titration and the same value of 2.16 was obtained. This is an indirect proof that the samples are of high quality.⁵

first two substitutions yielded superconducting samples after high-pressure and high-temperature oxygenation. The (Cu,Re)-1232 compound showed a $T_c \approx 55$ K, while the W counterpart showed a somewhat lower T_c at 53 K. It is possible that W, being larger than Cu or Mo resulted in an ordered layer causing the decrease in T_c . The Pb-substituted 1232 sample did not show any superconductivity after the same oxygenation treatment. All the experimental evidences suggest that a high valence cation is needed in order to induce superconductivity in the oxygenated compounds.

III. RESULTS AND DISCUSSION

Table I summarizes the Cu2 cations BVS calculated from the structural refinements based on neutron diffraction powder data¹ compared with the valence obtained from XANES data.⁶

The density of mobile carriers generally accepted to be given by how much the formal valence of the Cu ions in the CuO_2 layers exceeds 2, usually denoted by δ . Attributing these holes to the Cu ions is just a simple way of keeping track of the charge density. T_c is believed to follow a “universal” curve or “dome” which reaches a maximum at “optimal doping” that occurs for a valence of ~ 2.16 and returns to 0 as the valence approaches 2.28.¹⁵ The present system shows that this behavior is likely not universal. The BVS and XANES analyses find the Cu valence to be ~ 2.45 for the *s* = 1 homologue that has $T_c = 88$ K. The Cu valences of the *s* = 2, 3, and 4 members (with $T_c \approx 56$ K) are in the nominally overdoped region where the universal curve is, or is rapidly, approaching 0.

We interpret the above results to be evidence that the oxygenated charge reservoir blocks play an important role in defining the superconducting properties. The *s* = 1 member, as pointed out in the Introduction, differs significantly from the well known $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure by having 25% of Cu cations in the basal chain layer replaced by octahedrally coordinated Mo^{6+} cations. Consequently, the basal layer of the Mo-substituted compounds contains more oxygen than those of the corresponding layer in $\text{YBa}_2\text{Cu}_3\text{O}_7$ or $\text{YSr}_2\text{Cu}_3\text{O}_7$. Room temperature structural refinements based on powder neutron diffraction data obtained at Argonne National Laboratory show that the δ values for all members of the series vary from 0 for the AS samples to 0.5 for the HPO samples.¹ The total oxygen content for the first member was found to be 7.36 for the non-superconducting sample and 7.56 for the sample with $T_c = 88$ K.

The lack of ordering of the Cu and Mo cations in the basal layer is revealed by the electron diffraction and high resolution electron images for the *s* = 1, 2, and 3 members shown in Figures 1 and 2 for the AS samples. The disorder should also apply to the HPO samples because, while the annealing under pressure increases oxygen content and thus the doping, it is not expected to cause cation diffusion. In Figure 1(a), the electron diffraction pattern along to the [010] axis is shown for the AS *s* = 1 sample. No superstructure spots or diffuse scattering are visible. The same is true for other reciprocal directions. In Figure 1(b), a high-resolution image taken with a JEOL-4000EX microscope operated at 400 kV for the same sample is shown. It can be seen that the experimental image is in good agreement with the simulated structure shown in the inset obtained by using the crystal structure reported in Ref. 1. Figure 2(a) shows an electron diffraction pattern for the AS *s* = 3 sample. Four crystals were investigated and all produced the same results. The electron

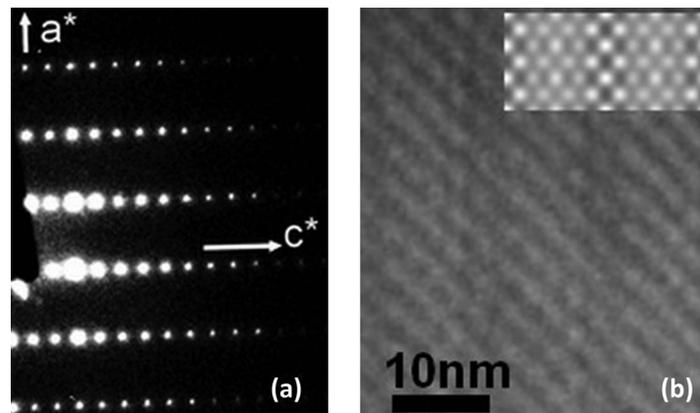


FIG. 1. (a) Electron diffraction pattern corresponding to the basal plane of the AS sample ($\text{Cu}_{0.75}\text{Mo}_{0.25}$)-1212. No extra spots are visible indicating the existence of a superstructure due to the Cu and Mo long-range ordering in the basal plane. (b) A high resolution image showing the $s = 1$ layered structure in agreement with Ref. 1. A simulated structure is shown in the inset.

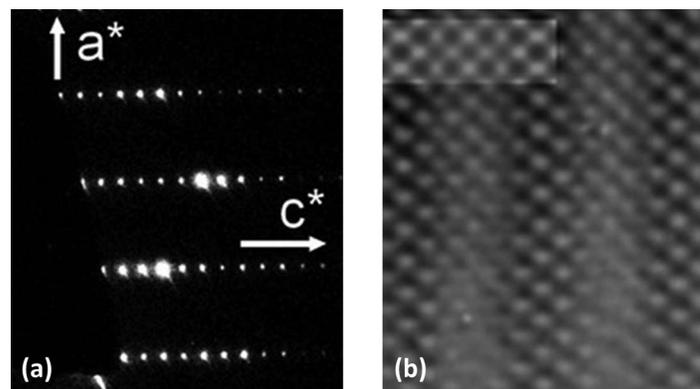


FIG. 2. (a) An electron diffraction pattern corresponding to the basal plane of the AS sample (Cu,Mo)-1232. As in Fig. 1(a) no extra spots are observed. (b) High resolution image showing the $s = 3$ layered structure. A simulated structure is shown in the inset.¹

diffraction pattern is along the [010] zone axis. Neither superstructure spots nor diffuse streaks are visible. In Figure 2(b), a high resolution micrograph is shown with the simulated image displayed in the inset. For the $s = 3$ member, the two types of blocks separated by the CuO_2 layers have about the same thickness, $\sim 8.5 \text{ \AA}$, which is confirmed by the high resolution image.

The failure to observe any long-range order between the Mo and Cu cations in the basal layer by the diffraction experiments is a strong indication that the Mo^{6+} cations are in octahedral coordination. In this environment, Mo^{6+} has an ionic radius of 0.59 \AA which is very close to that of Cu^{2+} in square coordination, 0.57 \AA , while the ionic radius of Mo^{6+} in tetrahedral coordination is estimated to be 0.41 \AA .¹⁸

It remains a challenge to discover the mechanism responsible for superconductivity in the current system. Recently, it has been shown theoretically that the off-site repulsive interactions that reduce T_c in d-wave superconductors can be screened and thus T_c will be enhanced if they are capacitively coupled to either a high polarizable or a metallic charge-reservoir layer.¹⁹ In the present case, the high-frequency susceptibility of the disordered-chain layer may be effective in providing the screening. Experimental investigations such as nuclear magnetic resonance (NMR) are needed to support this model.

Figure 3 shows a possible structural ordered arrangement of the basal plane for all AS samples. The yellow oxygen octahedra surround the Mo cation, which is placed at 000 in the cell or in the

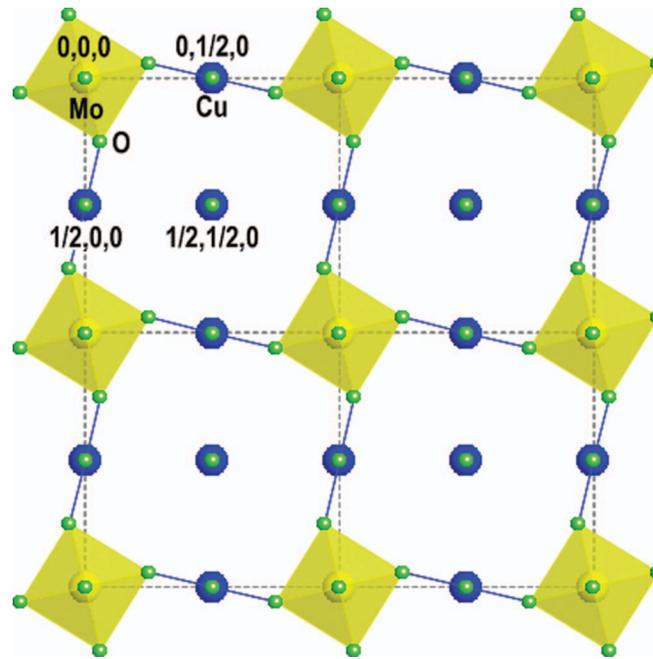


FIG. 3. A possible structural arrangement of the basal plane $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{O}_{1+\delta}$, $\delta = 0$ for all the AS samples. The supercell is indicated. The oxygen atoms are disordered over the $xy0$ and the more symmetrical $\frac{1}{2}y0$ positions. However, for simplicity, only the more symmetrical positions are used and correspond to the small green balls. For only the AS $s = 4$ sample, the oxygen atoms are all in the $xy0$ positions with a 0.125 occupancy factor. The large spheres are: Mo (yellow) and Cu (blue).

hypothetical quadruple-ordered unit supercell. The positions at 100 , 010 , and 110 of the unit cell (or $\frac{1}{2}00$, $0\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}0$ of the quadruple cell) are occupied by Cu cations. To make the drawing less complicated, the oxygen are all placed in the more symmetrical position $\frac{1}{2}y0$. We know from Ref. 1 that this is not true for any of the investigated samples. Actually for the member with $s = 4$, all oxygen in the basal plane are in the less symmetrical positions $xy0$ with $x \approx 1/2$. Therefore, the bonds, especially those between Cu and oxygen, are only a guide for the eyes. The Cu cations at $\frac{1}{2}00$ and $0\frac{1}{2}0$ have a square coordination, while that at $\frac{1}{2}\frac{1}{2}0$ have the dumbbell coordination. Moreover, a complete order between Cu and Mo is assumed in the drawing. The absence of superstructure spots strongly indicates that this is true only on a very short correlation length. Notice that one out of four oxygen $\frac{1}{2}y0$ positions per unit cell is filled, whereas it is one out of eight if the oxygen is in the $xy0$ positions (see Figure 4 of Ref. 1).

The structural arrangement of the basal plane for all HPO samples can be found in Figures 6(c) and 6(d) of Ref. 1. Only for the $s = 1$ member, the oxygen of the basal plane occupy the more symmetrical position O6 ($\frac{1}{2}y0$). For the other members, the oxidation induced an increase of the occupation factor of the more symmetrical site, but the order was not found to be complete. The additional oxygen occupies one empty O5/O6 position of every other cell. Therefore, in the oxidized samples, one cell has one O6/O5 position occupied and the next cell has two. No more oxygen can be incorporated, otherwise the resulting O–O distances would become too short. The Cu at 100 becomes octahedrally coordinated and the one at 110 squarely coordinated, while the one at 010 remains squarely coordinated.

The maximum theoretical value for δ in the HPO samples is 0.5. The occupancy factors of the oxygen sites obtained from the NPD refinements for the insulating AS and superconducting HPO phases as stated above correspond to a total oxygen content of 7.36 and 7.56 for the $s = 1$ member and 9.01–9.41, 11.16–11.72 for the $s = 2, 3$ members, respectively.¹ For the $s = 4$ member, the structural refinement based on neutron powder diffraction data was carried out only for the AS phase. There was not enough left sample to collect data for the HPO phase refinement. The oxygen content of $s = 4$ AS sample was found to be 12.97.

It is important to point out that the apical Cu–O distance in the $s = 1$ AS compound is 2.295(4) Å, very close to that found in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$, 2.301 Å for which $T_c = 90$ K.¹⁴ After the HPO treatment resulting in superconductivity ($T_c = 88$ K), the apical distance in $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{-1212}$ decreases to 2.15(2) Å, contrary to the two-orbital model of Sakakibara *et al.*²⁰ or to any other theory that finds T_c increases with apical O distance.

According to Jorgensen *et al.*²¹ the apical oxygen distance of 2.15 Å together with the O–Cu–O corrugation angle of 166° in the CuO_2 -square layers suggest that the reservoir block of the $s = 1$ member, $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{Sr}_2\text{YCu}_2\text{O}_{7.5}$, has a metallic character. The idea of metallic reservoir blocks is not new. As early as 1996, Tallon and co-workers²² inferred from muon spin relaxation studies that a 50-fold increase in irreversibility field observed when 25% of the Hg cations are substituted by Re and all the Ba cations are replaced by Sr in $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ could be explained by the metallization of the $(\text{Hg}_{0.75}\text{Re}_{0.25})\text{O}_{4+\delta}$ reservoir layer.

IV. CONCLUSIONS AND FUTURE WORK

The high valence value of 2.45 obtained for the $s = 1$ HPO sample indicates, as has already been suggested from earlier experiments in another system, that superconductivity exists in the very overdoped region of the cuprate phase diagram.^{11,12} The increase in T_c found upon annealing which causes a marked decrease in the apical Cu–O distance while the in-plane Cu–O distance remains almost constant cannot be explained by any current theory.²⁰ We suggest that T_c can be enhanced because the longer range repulsive Coulomb interactions in the CuO_2 layers are screened by the highly polarizable charge reservoir layers. However, since no measurements of the superfluid density have been made there, remains the possibility that an undetected inhomogeneity, such as stripe formation, might explain the results without requiring new physics. It is an outstanding challenge for future work to make direct measurements of the superfluid density. Further doping is needed to establish whether or not a second dome exists and whether optimal doping has been achieved. Many other cuprates related to the present series remain to be investigated. The cation substitutions $M = \text{Ti, V, Nb, Ta, Mo, W, Sn, Sb}$ reported by Rukang *et al.* are all $s = 2$ members of the respective $\text{MSr}_2(\text{Ln,R})_2\text{Cu}_2\text{O}_y$ homologous series.^{16,17} The Sr version of these superconducting cuprates is essential because Ba is too big to allow for the extra oxygen that is needed. In order to keep Cu in the reservoir block, these substitutions should be only partial. The preliminary results on Re substitution⁴ seem to suggest that highly oxidized cations are good candidates for producing enhanced superconductivity in the system $\text{YSr}_2\text{Cu}_3\text{O}_y$.

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