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High- $T_c$  Superconducting Cuprates,  $(\text{Ce,Y})_{\text{S}}\text{O}_{2\text{S}-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$ :  $T_c$ -increase with apical Cu-O decrease at constant Cu-O planar distance

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# High- $T_c$ Superconducting Cuprates, $(\text{Ce},\text{Y})_s\text{O}_{2s-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$ : $T_c$ -increase with apical Cu-O decrease at constant Cu-O planar distance

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**Abstract.** 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 XANES measurements and bond valence sum calculations are greater than 2.25 and are in close agreement with each other for structures of the homologous series given in the title with  $s = 1, 2, 3, 4$  and  $5$ . Two questions arise from the present perspective: 1) Is all the action in the  $\text{CuO}_2$  layers? 2) Is there superconductivity beyond the usual dome? The record short apical oxygen distance found in the homologous series especially in the  $s = 1$  member, at odds with the current theory, suggests the possibility of a new pairing mechanism. The apical Cu-O distance in the  $s = 1$  member decreases upon oxygenation from 2.29 to 2.15 Å while the Cu valence increases to 2.45 Å.

Between 2004 and 2010 the researchers at Tokyo Institute of Technology (Japan) and Aalto University in Helsinki (Finland) synthesized the first 5 members of the cuprate homologous series<sup>1-6</sup>:  $(\text{Ce},\text{Y})_s\text{O}_{2s-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$ ,  $s = 1, 2, 3, 4$ , and  $5$ . None of the as-prepared samples (AS) were found to become superconducting, but when the samples were treated under high oxygen pressure (5 GPa, 500° C in the presence of  $\text{KClO}_3$  or  $\text{Ag}_2\text{O}_2$ ) the  $s = 1$  member became superconducting at 88 K, while the  $s = 2, 3, 4$  and  $5$  members exhibited a constant  $T_c$  of about 56 K. The chemical formula and the structural arrangement of the five compounds were determined by conventional x-ray powder diffraction analysis, electron diffraction and high-resolution transmission electron microscopy. The superconducting transition temperatures were determined by FC and ZFC magnetization measurements. Later

Table 1 :Cu valences for the AS and HPO samples estimated from the Cu  $L_{2,3}$  absorption edge and the hole concentration  $p$  on the  $\text{CuO}_2$  layers estimated from the O K absorption edge

	$v(\text{Cu})^*$ AS	$v(\text{Cu})^*$ HPO	$p(\text{CuO}_2)^{**}$	$T_c$
$s = 1$	2.16***	2.46	0.53	88
$s = 2$	2.13	2.24	0.28	56
$s = 3$	2.14	2.25	0.26	56
$s = 4$	2.14	2.26	0.27	56

\*Values estimated from the Cu  $L_{2,3}$  absorption edge. \*\* Values estimated from the O K absorption edge. \*\*\*Value obtained also by iodometric titration.



the same group was able to produce very pure samples for the first 4 members, which allowed them to carry out XANES measurements leading to an estimate of the Cu valence and the holes' concentration for these unusual cuprates. These results are summarized in Table 1.

It is interesting to note that the Cu valence of the cations belonging to the  $\text{CuO}_2$  layers is definitely high when compared to the values of 2.15/2.2+ obtained for the all other superconducting cuprates.

Fig. 1 represents a three-dimensional structural model of the  $s = 2$  member.

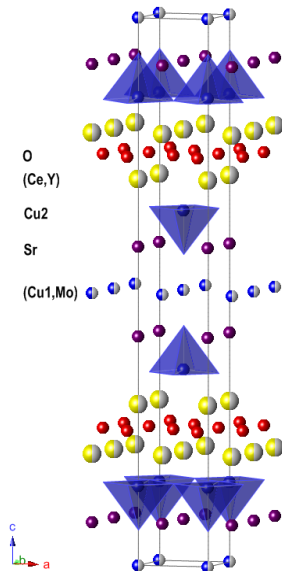


Fig.1: A three-dimensional structural model of the  $s = 2$  member:  $(\text{Ce,Y})_2\text{O}_2\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$ . The oxygen on the basal plane have been omitted. The distance between 2  $\text{CuO}_2$  layers is 5.998 Å. It increases to 8.746 and to 11.441 Å for the members with  $s = 3$  and 4 respectively, while  $T_c$  remains constant at 56 K for both members. The higher-member structures are obtained by inserting additional 2-layer blocks  $(\text{O}_2)(\text{Ce,Y})$  in between  $(\text{Ce,Y})$  and  $(\text{CuO}_2)$ . For example, for the member with  $s = 3$  the sequence between two successive  $\text{CuO}_2$  layers is:  $(\text{CuO}_2)(\text{Ce,Y})(\text{O}_2)(\text{Ce,Y})(\text{O}_2)(\text{Ce,Y})(\text{CuO}_2)$ .

The new samples of the Mo-cuprates allowed reliable structural refinements at room temperature. These refinements were performed at the Argonne National Laboratory<sup>7</sup>. The results confirmed the structural arrangement previously determined by x-ray, and electron diffraction techniques and HRED imaging. Moreover, they revealed important structural features concerning the basal plane occupied by 75% of Cu cations, 25% of Mo cations, and  $\delta$  oxygen atoms. The results are summarized in Table 2.

Table 2: Oxygen stoichiometry of the basal plane  $\delta$  and the total oxygen content for the first four members of the homologous series  $(\text{Ce,Y})_s\text{O}_{2s-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$  from neutron diffraction.

	$s = 1$ AS	$s = 1$ HPO	$s = 2$ AS	$s = 2$ HPO	$s = 3$ AS	$s = 3$ HPO	$s = 4$ AS
$\delta$	1.36	1.56	1.01	1.41	1.16	1.72	0.97
Total oxygen	7.36(16)	7.56(4)	9.01(8)	9.41(17)	11.16(9)	11.72(15)	12.97(7)

The observation that after the HPO treatment the first member shows a  $T_c$  of 88 K while the members with  $s = 2, 3, 4$  and 5 exhibit a constant  $T_c$  of ~56 K is a very strong indication that the charge reservoir layers must play an essential role for the superconducting properties. The first member has actually the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure in which the Ba cations are substituted by Sr and 25% of the planar squarely-coordinated Cu cations are substituted by  $\text{Mo}^{6+}$  cations. These substitutions make a substantial difference in the structure and consequently in the properties because the  $\text{Mo}^{6+}$  cations require an octahedral coordination and therefore the basal  $z = 0$  plane can incorporate a larger amount of oxygen than either  $\text{YSr}_2\text{Cu}_3\text{O}_7$  or  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>8</sup>

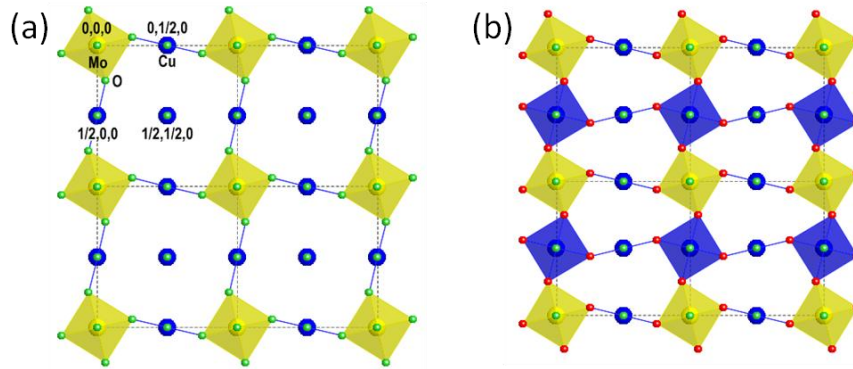
In Table 3 the valence of the Cu cations belonging to the  $\text{CuO}_2$  layers, determined by the bond valence sum (BVS) from the interatomic distances obtained by neutron diffraction data are reported. They are compared to the corresponding values obtained by XANES experiments. The same trend was confirmed. Note that the total oxygen intake is reported in Table 2 whereas in Table 3 only that of the  $\text{CuO}_2$  planes is given. The high-valence value of

2.45 obtained for the  $s = 1$  HPO sample and values greater than 2.25 for the other members indicate that superconductivity can exist in the overdoped region of the generalized cuprate phase diagram.

Table 3: The Cu2 site valence in the  $(\text{Ce,Y})_s\text{O}_{2s-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$  samples calculated from neutron diffraction data and XANES experiments.

	$s = 1$ AS	$s = 1$ HPO	$s = 2$ AS	$s = 2$ HPO	$s = 3$ AS	$s = 3$ HPO	$s = 4$ AS	$s = 4$ HPO
$v(\text{Cu2})$ BVS	2.21	2.45	2.22	2.31	2.22	2.34	2.20	
$v(\text{Cu2})$ XANES	2.16	2.46	2.13	2.24	2.14	2.25	2.14	2.26

Fig. 2 shows possible structural arrangements of all the basal-planes of AS phases (a) and HPO phases (b). The supercells are only a guide for the eyes. The oxygen atoms in the HPO phases with  $z = 0$  are in red.



**Fig. 2:** (a) A possible structural arrangement of the basal plane  $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{O}_\delta$ ,  $\delta = 1$  for all the AS samples. The supercell is indicated. The oxygen atoms are disordered over the  $xy0$  and the more symmetrical  $1/2y0$  positions. However, for simplicity only the more symmetrical positions are used and correspond to the small green balls. The large spheres are: Mo (yellow) and Cu (blue). (b) A possible structural arrangement of the basal plane  $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{O}_\delta$ ,  $\delta = 1.5$  for all the HPO samples. Only for the  $s = 1$  member all the oxygen are in the more symmetrical  $1/2y0$  positions. See reference 7 for details.

The increase in  $T_c$  found upon high-pressure oxygen 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. We suggest that  $T_c$  can be enhanced because the longer range repulsive Coulomb interactions in the  $\text{CuO}_2$  layers are screened by the highly polarizable charge of the reservoir layers. However, since no measurements of the superfluid density (from muon spectroscopy experiments) have been made there still remains the possibility that an undetected inhomogeneity, such as stripe formation, might explain the results without requiring new physics.<sup>8</sup> These experiments are currently underway in Villingen, Switzerland.

It is important to point out that the apical Cu-O distance in the  $s = 1$  AS member is  $2.295(4) \text{ \AA}$ , very close to that found in superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ ,  $2.301 \text{ \AA}$  for which  $T_c \approx 93 \text{ K}$ .<sup>8</sup> After the HPO treatment resulting in the superconducting  $T_c = 88 \text{ K}$ , the apical distance in the first member decreases to  $2.15(2) \text{ \AA}$ , contrary to the two-orbital model of Sakakibara et al<sup>9</sup> or to any other theory that finds  $T_c$  to increase with apical Cu-O distance.

As for the metallization of the reservoir block, according to Jorgensen et al.<sup>10</sup> an apical oxygen distance of  $2.15 \text{ \AA}$  and an O-Cu-O corrugation angle of  $166^\circ$  in the  $\text{CuO}_2$ -square layers suggest that the reservoir block of the  $s = 1$  member, would have a metallic character. The idea of metallic reservoir blocks is not new. As early as 1996 Tallon and coworkers<sup>11</sup> 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  $(\text{Hg}_{0.75}\text{Re}_{0.25})\text{O}_\delta$  reservoir block.

To explain why  $T_c$  decreases on going from the  $s = 1$  to the  $s = 2$  member (88 to 56 K) and then remains practically constant for the  $s = 3$  and 4 we report in Table 4 the thickness of the two blocks existing in the structure of these compounds. They can be viewed as built of two types of blocks: one being the  $\text{CuO}_2$ (fluorite-block of different thickness) $\text{CuO}_2$ , and one of about constant thickness:  $\text{CuO}_2(\text{SrO})(\text{Cu}_{0.75}\text{Mo}_{0.25})(\text{SrO})\text{CuO}_2$ . The fluorite block does not exist in the  $s = 1$  member or in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ . In both cases it consists of only one yttrium layer. Two observations can be made from Table 4: 1) the oxygen insertion increases the thickness of the  $\text{CuO}_2$ (fluorite-block) $\text{CuO}_2$  block even though the extra oxygen is not incorporated into this block. 2) The thickness of the reservoir block, which is the same for all members, decreases when the extra-oxygen is incorporated by the HPO treatment. These observations indicate that these compounds have a strong ionic character because by inserting negative oxygen ions the Coulomb interactions definitely prevail against the size effect. The same observation can be made for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , which is included in Table 4 for comparison. Moreover, the same structure of the “reservoir block” for all members with inserted-fluorite blocks can explain why  $T_c$  remains constant for  $s = 2, 3$ , and 4 members.

Table 4: Thickness (Å) of the 2 blocks separated by the  $\text{CuO}_2$  layer, which make up the structure of the homologous series  $(\text{Ce}, \text{Y})_s\text{O}_{2s-2}\text{Sr}_2(\text{Cu}_{2.75}\text{Mo}_{0.25})\text{O}_{6+\delta}$  or  $(\text{Cu}_{0.75}\text{Mo}_{0.25})-12s2$

Sample	$\text{CuO}_2$ (fluorite-block) $\text{CuO}_2$	$(\text{CuO}_2)(\text{SrO})(\text{Cu}_{0.75}\text{Mo}_{0.25}\text{O}_x)(\text{SrO})(\text{CuO}_2)$
s=1 AS	3.308*	8.242
s=1 HPO	3.434*	8.037
s=2 AS	5.998	8.283
s=2; HPO	6.064	8.161
s=3; AS	8.746	8.237
s=3; HPO	8.801	8.104
s = 4; AS	11.441	8.231
$\text{YBa}_2\text{Cu}_3\text{O}_6$	3.304*	8.513*
$\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$	3.391*	8.269*

\* In  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  and in the  $s = 1$  member the fluorite blocks do not exist, the two  $\text{CuO}_2$  layers are separated by a single Y layer. Furthermore, the basal layers of the first two contain only Cu cations.

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