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 structure (XANES) and bond valence sum (BVS) 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 \( s = 1 \) member, \((\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2\text{YC}_{\text{Cu}}\text{O}_{7+\delta}, 0 \leq \delta \leq 0.5\), is structurally related to \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) in which 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. After oxidation under high pressure the \( s = 1 \) member becomes superconducting with \( T_c = 88\text{K} \). The Cu valence is estimated to be \( \sim 2.5 \), well beyond the \( \sim 2.3 \) value for which other High-\( T_c \) cuprates are considered to be overdoped Fermi liquids. The increase in valence is attributed to the additional 0.5 oxygen ions added per chain upon oxidation. The record short apical oxygen distance, at odds with current theory, suggests the possibility of a new pairing mechanism but further experiments are urgently needed to obtain more direct evidence. From the structural point of view the members with \( s \geq 2 \) are considered to be equivalent to single-layer cuprates because the \( T_c \) is independent of the thickness of the insulating fluorite-like blocks on going from the \( s = 2 \) to the \( s = 5 \). All have \( T_c \sim 56\text{K} \) which is significantly higher than expected because they also have higher than expected Cu valences. The XANES-determined valences normalized to give values in the...
CuO2 layers are 2.24, 2.25, and 2.26 for \( s = 2, 3, \) and 4, while the BVS values determined for the valence in the CuO2 layer alone are 2.31-2.34 for the \( s = 2 \) and 3 members. No evidence for periodic ordering has been detected by electron diffraction and high resolution imaging studies. The possibility that the charge reservoir layers are able to screen long range coulomb interactions and thus enhance \( T_c \) is discussed.

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Introduction:

During the past eight years the first six members of the homologous series (Cu_{0.75}Mo_{0.25})Sr_{2}(Ce,Y)_{s}Cu_{2}O_{5+2s+\delta} have been successfully synthesized and investigated.\textsuperscript{1-6} The reported results indicate that the Cu valence is anomalously higher than in the well-known high-$T_c$ cuprates such as YBa$_2$Cu$_3$O$_7$. The $s = 1$ member, (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$YCu$_2$O$_{7+\delta}$, is structurally the same as YBa$_2$Cu$_3$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. The formulae for the members corresponding to $s = 2, 3, 4, 5, 6$ are: (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_2$Cu$_2$O$_{9+\delta}$, (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_3$Cu$_2$O$_{11+\delta}$, (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_4$Cu$_2$O$_{13+\delta}$, (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_5$Cu$_2$O$_{15+\delta}$, and (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_6$Cu$_2$O$_{17+\delta}$, respectively. There is a substantial difference between the familiar Hg-m$_2$(n-1)n and Tl-m$_2$(n-1)n homologous series and the present (Cu$_{0.75}$Mo$_{0.25}$)-12s$_2$ series. In the Hg- and Tl-series n represents the number of (Ca)(CuO$_2$)$_2$ 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 (Cu$_{0.75}$Mo$_{0.25}$)-12s$_2$ 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 (Ce,Y)(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 $T_c$. In contrast, the decrease from 88 to an almost 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 (SrO)(Cu$_{0.75}$Mo$_{0.25}$O$_{1+\delta}$)(SrO) block present in every member of the series. Thus all the members of this homologous series with $s > 1$ are comparable to single layer 214 cuprates; to a first approximation they can be considered as single-layer cuprates with $T_c$s $\approx 56$ K that are significantly higher than optimally-doped single-layer cuprates with the exception of Sr$_2$CuO$_{4-x}$\textsuperscript{8-11} and HgBa$_2$CuO$_{4+\delta}$\textsuperscript{12}.

Previous Results:

Powder x-ray diffraction and high resolution transmission electron microscopy show that the $s = 2$ member contains the following layered sequence:
The sequence of the higher members is obtained by inserting additional two-layer blocks of (O$_2$)(Y,Ce) between the (CuO$_2$) layers (see Fig. 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 $\sim 56$ 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. Nevertheless, the $s = 5$ homologue became superconducting with a $T_c$ of $\sim 55$ 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 $> 30\%$). Furthermore the lack of an appreciable Curie tail above $T_c$ is 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. 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 YBa$_2$Cu$_3$O$_7$ where the BVS valence is in reasonable agreement with the values found later by neutron powder diffraction and thermoelectric power measurements. 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 Sr$_2$CuO$_{4-x}$.

In 1991 Li Rukang et al. investigated a long list
of possible fluorite-inserted cuprates. The formula of their compounds was $\text{MSr}_2(\text{Ln,R})_2\text{Cu}_2\text{O}_y$ with $\text{M} = \text{Ti, V, Nb, Ta, Mo, W, Sn, Sb}$ which corresponds to the $s = 2$ members of the respective homologous series. No superconductivity was found in any of these cuprates.\textsuperscript{15,16} 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.\textsuperscript{3} 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 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.

### Results and Discussion:

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 $\delta$. 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 $\sim 2.16$ and returns to 0 as the valence approaches 2.28.\textsuperscript{14} The present system shows that this behavior is likely not universal. The BVS and XANES analyses find the Cu valence to be $\sim 2.45$ for the $s = 1$ homologue that has $T_c = 88$ K. The Cu valences of the $s = 2$, 3, and 4 members (with $Tcs \approx 56$ 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 YBa$_2$Cu$_3$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 YBa$_2$Cu$_3$O$_7$ or YSr$_2$Cu$_3$O$_7$. Room temperature structural refinements based on powder neutron diffraction data obtained at Argonne National Laboratory$^{17}$ show that the $\delta$ values for all members of the series vary from 0 for the AS samples to 0.5 for the HPO samples. 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 Fig. 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 Fig. 2a 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 Fig. 2b 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 reference 17. Fig. 3a shows an electron diffraction pattern for the AS $s = 3$ sample. Four crystals were investigated and all produced the same results. The electron diffraction pattern is along the [010] zone axis. Neither superstructure spots nor diffuse streaks are visible. In Fig. 3b a high resolution micrograph is shown with the simulated image displayed in the inset. It can be seen from Table 1 that for the $s = 3$ member the two types of blocks separated by the CuO$_2$ layers have about the same thickness, $\sim 8.5$ Å, which is nicely confirmed by the high resolution image. Our data confirm the results reported in reference 1 for the sample with $s = 3$.

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 Å that is very close to that of Cu$^{2+}$ in square coordination, 0.57 Å, while the ionic radius of Mo$^{6+}$ in tetrahedral coordination is estimated to be 0.41 Å.$^{18}$

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
In the present case the high-frequency susceptibility of the disordered-chain layer may be effective in providing the screening. Experimental investigations such as NMR are needed to support this model.

Fig. 4 shows a possible structural arrangement of the basal plane for all AS samples. The yellow oxygen octahedra surround the Mo cation which is placed at 000 in the subcell or the hypothetical quadruple-ordered unit cell. The positions at 100, 010 and 110 (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. The first two have a square coordination while the one at 110 ($\frac{1}{2}\frac{1}{2}0$) has the dumbbell coordination. The chemical formula of the four reduced samples are: $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2\text{YC}_2\text{O}_7$, $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Y,Ce})_2\text{Cu}_2\text{O}_9$, $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Y,Ce})_3\text{Cu}_2\text{O}_{11}$, and $(\text{Cu}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Y,Ce})_4\text{Cu}_2\text{O}_{13}$.

Fig. 5 represents the basal plane for all HPO samples. The additional oxygen can occupy only one empty position of every other subcell. No more oxygen can be incorporated otherwise the resulting O-O distances would become too short. Consequently the maximum theoretical value for $\delta$ 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.\textsuperscript{17} For the $s=4$ member the structural refinement based on neutron 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. We have not yet made a systematic investigation to determine if there is an optimum doping level at some intermediate value.

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 YBa$_2$Cu$_3$O$_{6.95}$, 2.301 Å for which $T_c=90$ K.\textsuperscript{13} After the HPO treatment resulting in superconductivity ($T_c=88$ K), the apical distance in $(\text{Cu}_{0.75}\text{Mo}_{0.75})$-1212 decreases to 2.15(2) Å, contrary to the two-orbital model of Sakakibara et al\textsuperscript{20} or to any other theory that finds $Tc$ increases with apical O distance.

According to Jorgensen et al.\textsuperscript{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, $(\text{Cu}_{0.75}\text{Mo}_{0.75})\text{Sr}_2\text{YC}_2\text{O}_{7.5}$, has a metallic character. The idea of metallic reservoir blocks is not new. As early as 1996 Tallon and coworkers\textsuperscript{22} 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
HgBa$_2$CaCu$_2$O$_{6+\delta}$ could be explained by the metallization of the (Hg$_{0.75}$Re$_{0.25}$)O$_{4+\delta}$ reservoir layer.

To explain why $T_c$ decreases on going from the $s = 1$ to the $s = 2$ member (87 to 56 K) and then remains practically constant for the $s = 3$ and 4 we report in Table 2 the thickness of the two blocks existing in the structure of these compounds. These structures can be viewed as built of two types of blocks: one being the CuO$_2$(fluorite-block of different thickness)CuO$_2$, and one of about constant thickness: CuO$_2$(SrO)(Cu$_{0.75}$Mo$_{0.25}$)(SrO)CuO$_2$. The fluorite block does not exist in the $s = 1$ member or in YBa$_2$Cu$_3$O$_{6.95}$. In both cases it consists of only one yttrium layer. Two observations can be made from Table 1: 1) the oxygen insertion increases the thickness of the CuO$_2$(fluorite-block)CuO$_2$ block even though the extra oxygen is not incorporated into that 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 YBa$_2$Cu$_3$O$_{6+x}$ which is included in Table 2 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.

**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,\textsuperscript{10,11} that superconductivity exists in the very overdoped region of the cuprate phase diagram. We suggest that $T_c$ can be enhanced because the longer range repulsive Coulomb interactions in the CuO$_2$ layer 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 decisive measurements. Further doping is needed to establish whether or not a second dome exists and whether optimal doping has been achieved. The increase in $T_c$ found upon annealing which causes a marked decrease in the apical O distance while the Cu-O bond length in the plane remains almost constant cannot be explained by any current theory.\textsuperscript{20}

Many other cuprates related to the present series remain to be investigated. The cation substitutions M = Ti, V, Nb, Ta, Mo, W, Sn, Sb
reported by Li Rukang et al.\textsuperscript{15,16} are all $s = 2$ members of the respective MSr\textsubscript{2}(Ln,R)\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} homologous series. 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 substitution\textsuperscript{3} seem to suggest that highly oxidized cations are good candidates for producing enhanced superconductivity in the system YSr\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y}.

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References

1. Morita, Y., Nagai, T., Matsui, Y., Yamauchi, H. & Karppinen, M., High $T_c$ superconductivity in three-fluorite-layer copper oxide. II. (Cu,Mo)Sr$_2$(Ce,Y)$_2$Cu$_2$O$_{11+\delta}$. Phys. Rev. B 70, 174515-174520 (2004)

2. Karppinen, M., Morita, Y., Kobayashi, T., Grigoraviciute, I., Chen, J. M., Liu, R. S. & Yamauchi, H., Hole doping and superconductivity characteristics of the $s = 1, 2$ and 3 members of the (Cu,M)-12s2 homologous series of layered copper oxides. J. Solid State Chem., 178, 3464-3470 (2005)

3. Grigoraviciute, I., Arai, M., Yamauchi, H., & Karppinen, M., Superconductivity in the ‘triple-fluorite-layer’ copper oxides (Cu,Mo)-12s2 (M = Mo, W, Re, Pb). Solid State Comm. 137, 601-605 (2006)

4. Grigoraviciute, I.,Yamauchi, H. & Karppinen, M., Layer-engineering of high-$T_c$ superconductors: (Cu,Mo)Sr$_2$(Ce,Y)$_2$Cu$_2$O$_{13+\delta}$, with a quadruple-fluorite-layer block between CuO$_2$ planes. J. Am. Chem. Soc. 129, 2593-2596 (2007)

5. Grigoraviciute, I., Karppinen, M., Chan, T.-S., Liu, R.-S., Chen, J.-M., Chmaissem, O. & Yamauchi, I., 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. 132, 838-841 (2010)

6. Gao, W., Oishi, K., Suematsu, S., Yamauchi, Y. & Karppinen, M., Homologous series of (Cu,Mo)Sr$_2$(Y,Ce)$_2$Cu$_2$O$_{5+2s+\delta}$ copper-oxide superconductors: Synthesis of members up to $s = 6$. Solid State Comm. 151, 1400-1403 (2011)

7. Chakravarty, S., Kee, H.-Y. & Abrahams, E., Frustated kinetic energy, the optical sum rule, and the mechanism of superconductivity. Phys. Rev. Lett. 82, 2366-2369 (1999); Berg,E., Orgad, D., & Kivelson, S. Phys.Rev. B., 78 094509 (2008)

8. Hiroi, Z., Takano M., Azuma, M. & Takeda, Y., A new family of copper oxide superconductors Sr$_{n+1}$Cu$_n$O$_{2n+1+\delta}$ stabilized at high pressure. Nature 364, 315-317 (1993)

9. Liu, Q.Q., Yang, H., Qin, X.M., Yu, Y., Yang, L.X., Li, Y., Yu, R.C., Jin, C.Q. & Uchida, S., Enhancement of the superconducting critical temperature of Sr$_2$CuO$_{3+\delta}$ up to 95 K by ordering dopant atoms. Phys. Rev. B 74, 100506-100509(R) (2006)

10. Geballe, T.H. & Marezio, M., Enhanced superconductivity in Sr$_2$CuO$_{4-\gamma}$. Physica C 469, 680-684 (2009)
11. Geballe, T.H. & Marezio, M., Comment on “Out-of-plane effect on the superconductivity of Sr$_{2-x}$Ba$_x$CuO$_{3+\delta}$ with $T_c$ up to 98 K”. Phys. Rev. B 82, 216501-216501 (2010)

12. Putilin, S.N., Antipov, E.V., Chmaissem, O. & Marezio, M., Superconductivity at 94 K in HgBa$_2$CuO$_{4+\delta}$. Nature 362, 226 (1993)

13. Cava, R.J., Hewat, A.W., Hewat, E.A., Batlogg, B., Marezio, M., Rabe, K.M., Krajewski, J.J., Peck Jr., W.F. & Rupp Jr., L.W., Structural anomalies, oxygen ordering and superconductivity in oxygen deficient Ba$_2$YCu$_3$O$_x$. Physica C, 165, 419-433 (1990)

14. Tallon, J.F., Bernhard, C., Shaked, R.L. Hitterman, and J.D. Jorgenson Generic superconducting phase behavior in high-$T_c$ cuprates: $T_c$ variation with hole concentration in YBa$_2$Cu$_3$O$_7$. Phys. Rev. B 51, 12911-12914 (1995)

15. Rukang, L., Yingjie, Z., Yitai, Q., Zuyao, C., The preparation and structure of a new layered cuprate: TaSr$_2$(NdCe)$_2$Cu$_2$O$_y$, the Ta analog of the Tl-1222 phase. Physica C 176, 19-23 (1991)

16. Rukang, L., Yingjie, Z., Cheng, X., Zuyao, C., Yitai, Q. & Chengao, F., Formation of a new series of 1222 layered cuprates M$\text{Sr}_2$(LnR)$_2$Cu$_2$O$_y$. J. Solid State Chem. 94, 206-209 (1991)

17. Chmaissem, O., Grigoraviciute, I., Yamauchi, H., Karppinen, M. & Marezio, M. Superconductivity and oxygen ordering correlations in the homologous series (Cu,Mo)Sr$_2$(Y,Ce)$_5$Cu$_2$O$_{5+2s+\delta}$. Phys. Rev. B 82, 104507-104515 (2006)

18. Shannon, R.D., Revised effective radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallog. A 32, 751-767 (1976)

19. S. Raghu, E. Berg, A. V. Chubukov, and S. A. Kivelson, Effects of long-range interactions on unconventional superconductivity, Phys Rev B 85, 024516 (2012); S. Raghu, R. Thomale, and T. H. Geballe, Optimal $T_c$ of cuprates: role of screening and reservoir layers, to be published.

20. Sakakibara, H., Usui, H., Kuroki, K., Arita, R. & Aoki, H., Two-orbital model explains the higher transition temperature of the single layer Hg cuprate superconductor compared to that of the La-cuprate superconductor. Phys. Rev. Lett. 105, 057003-057006 (2010)

21. Jorgensen, J.D., Hinks, D.G., Chmaissem, O., Argyriou, D.N., Mitchel, J.F. & Dabrowski, B., Structural Features that Optimize High Temperature Superconductivity. Proceedings of the first Polish-US Conference on High Temperature Superconductivity. "Lecture Notes in Physics" (1996). Published by Springer-Verlag
22. Tallon, JL, Bernhard, C., Niedermayer, Ch., Shimoyama, J., Hahakura, S., Yamaura, K., Hiroi, Z., Takano, M. & Kishio, K., A new approach to the design of high-T-c superconductors: Metallised interlayers. Journal of Low Temperature Physics 103, 1379-1384 (1996)

**Figure Captions**

Fig. 1: Structure of (Cu,Mo)-1222. For clarity, only the oxygen atoms within the fluorite-like CeO$_2$ blocks are plotted.

Fig. 2: (a) Electron diffraction pattern corresponding to the basal plane of the AS sample (Cu$_{0.75}$Mo$_{0.25}$)-1212. No extra spots are visible which would indicate 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 reference (14). A simulated structure is shown in the inset.

Fig. 3: (a) a [010] electron diffraction projection for the AS sample (Cu,Mo)-1232. No long range ordering observed between the Mo and Cu cations. (b) A high resolution image showing the s = 3 layered structure in agreement with reference (14). A simulated structure is shown in the inset.

Fig. 4: A possible structural arrangement of the basal plane (Cu$_{0.75}$Mo$_{0.75}$)O$_{1+\delta}$, $\delta$ = 0 for all the AS samples. The subcell is indicated. The extra oxygen atoms are disordered over the xy0 and the more symmetrical $\frac{1}{2}$y0 positions. For only the AS s = 4 sample, the oxygen atoms are in the xy0 positions with a 0.125 occupancy factor. Spheres are: Mo (yellow), Cu (blue), and O at (red at $\frac{1}{2}$y0 and green at xy0). Additional oxygen atoms (green) are shown at the corners of the Mo octahedral and on top of the Cu spheres.

Fig. 5: A possible structural arrangement of the basal plane (Cu$_{0.75}$Mo$_{0.75}$) O$_{1+\delta}$, $\delta$ = 0.5 for all the HPO samples. The subcell is indicated. The oxygen atoms are all in the $\frac{1}{2}$y0 positions with a 0.375 occupancy factor. This occurs only in the HPO s = 1 sample. In all others members the oxygen is disordered over the $\frac{1}{2}$y0 and the less symmetrical xy0 positions. Same color scheme as in Fig. 4.
Table 1
Thickness in Å of the 2 blocks separated by the CuO$_2$ layers, which make up the structure of the homologous series ($\text{Cu}_{0.75}\text{Mo}_{0.25}$)-12s2

| Sample   | CuO$_2$(fluorite-block)CuO$_2$ | (CuO$_2$)(SrO)(Cu$_{0.75}$Mo$_{0.25}$O$_x$)(SrO)(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                                                    |
| YBa$_2$Cu$_3$O$_6$ | 3.304*                        | 8.513*                                                   |
| YBa$_2$Cu$_3$O$_{6.95}$ | 3.391*                        | 8.269*                                                   |

* In YBa$_2$Cu$_3$O$_6$ and YBa$_2$Cu$_3$O$_{6.95}$ the fluorite blocks do not exist, the two CuO$_2$ layers are separated by a single Y layer. Furthermore, the basal layer contains only Cu cations.
Table 2
The Cu2 cations bond-valence-sums (BVS) calculated from the structural refinements based on neutron diffraction powder data\textsuperscript{17} compared with the valence obtained from XANES data.\textsuperscript{2} The s values (1, 2, 3, 4) indicate the four members of the homologous series in the as-prepared (AS) and HPO state.

|        | s = 1 |        | s = 2 |        | s = 3 |        | s = 4 |
|--------|-------|--------|-------|--------|-------|--------|-------|
|        | AS    | HPO    | AS    | HPO    | AS    | HPO    | AS    | HPO    |
| $v$(Cu\textsubscript{2}) from BVS | 2.21  | 2.45   | 2.22  | 2.31   | 2.22  | 2.34   | 2.20  |
| $v$(Cu) from XANES     | 2.16* | 2.46   | 2.13  | 2.24   | 2.14  | 2.25   | 2.14  | 2.26   |
| $\rho$(CuO\textsubscript{2}) | 0.53  | 0.28   | 0.26  |        | 0.26  |        | 0.27  |
| $T_C$     | 87 K  | 56 K   | 54.5 K| 55.5 K |       |        |       |        |

*As stated in reference 5 the oxygen content for this sample was determined by iodometric titration and exactly the same value of 2.16 was obtained. This is an indirect proof that the samples are of high quality.
Figure 3a

Figure 3b
Figure 4
Figure 5