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The effect of Sr substitution on superconductivity in $\text{Hg}_2(\text{Ba}_{1-y}\text{Sr}_y)_2\text{YCu}_2\text{O}_{8-\delta}$: II. A bond valence sum approach to the hole distribution

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Abstract

The effects of Sr substitution on superconductivity, and more particularly the changes induced in the hole doping mechanism, were investigated in $\text{Hg}_2(\text{Ba}_{1-y}\text{Sr}_y)_2\text{YCu}_2\text{O}_{8-\delta}$ by a ‘bond valence sum’ analysis, with Sr content going from $y = 0.0$ to 1.0 . A comparison with $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ and $\text{Cu}_2\text{Ba}_2\text{YCu}_2\text{O}_8$ systems suggests a possible explanation of the T_c enhancement from 0 K for $y = 0.0$ to 42 K for $y = 1.0$. The charge distribution among atoms of the unit cell was determined from the refined structure, for $y = 0.0\text{--}1.0$. It shows a charge transfer to the superconducting CuO_2 plane via two doping channels $\pi(1)$ and $\pi(2)$, i.e. through $\text{O}_{2\text{apical}}\text{--Cu}$ and $\text{Ba/Sr}\text{--O}_1$ bonds respectively.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

This study is devoted to understanding the effects of Sr substitution in the mercury bilayer cuprate $\text{Hg}_2\text{Ba}_2\text{YCu}_2\text{O}_{8-\delta}$ (Hg-2212) structure. It is also often associated with a chemical pressure effect accounting for the smaller size of Sr substituted for Ba. In part I, we extracted precise structural data on bond lengths by neutron powder diffraction (NPD) analysis [1]. We studied the effect of Sr substitution on the barium site in the $\text{Hg}_2(\text{Ba}_{1-y}\text{Sr}_y)_2\text{YCu}_2\text{O}_{8-\delta}$ series and compared to the effect of mechanical pressure. This was motivated by the previous observation that, as in $(\text{La}, \text{Sr})_2\text{CuO}_4$ (LSCO) [2–4], Sr substitution in Hg-2212 enhances T_c

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from 0 K for the unsubstituted compound to 42 K in the fully substituted $\text{Hg}_2\text{Sr}_2\text{YCu}_2\text{O}_{8-\delta}$ compound. This enhancement can also be obtained by mechanical pressure which increases T_c for pure Ba based Hg-2212 by 50 K under 20 GPa [5]. Moreover, $T_{c\max}$ can be pushed to 60 K by Ca doping in $\text{Hg}_2\text{Sr}_2(\text{Y}_{0.80}\text{Ca}_{0.20})\text{Cu}_2\text{O}_{8-\delta}$ [6, 7].

In the previous paper [1], we showed that Sr induces an overall shrinkage of the structure due to its ionic radius being smaller than that of Ba. The detailed analysis of the position shifts of each atom is summarized as follows. Both Cu and O1 (in-plane) move up (see figure 5 in [1] for the structure description and atom labels), i.e. towards the Ba/Sr site, and also become closer in their plane. This does not affect the buckling angle of the superconducting planes (i.e. the Cu–O1–Cu angle). The Cu–O1 bond length reduction is probably one of the most important effect contributing to enhancement of T_c . Note that the rate dT_c/da (where ‘ a ’ is the unit cell length in ångströms) induced by Sr substitution ($\approx 850 \text{ K } \text{\AA}^{-1}$) is consistent with that observed in compressed epitaxial films of LSCO ($\approx 1000 \text{ K } \text{\AA}^{-1}$) [8]. The vertical movements of O2, Ba/Sr, Hg/Y are modest in comparison to that of O3 which shifts significantly towards the Hg/Y plane, making it flat. Hence the ‘ BaO_9 ’ polyhedron becomes smaller and better connected to the superconducting block (SB, composed of the two CuO_2 superconducting planes separated by the Y plane). The ‘ CuO_5 ’ pyramid flattens due to the enormous reduction of the Cu–O2_{apical} distance that becomes very small, i.e. 2.27 Å, as compared to the case for unsubstituted Hg-12 ($n - 1$) n compounds where Cu–O2 is close to 2.75–2.80 Å [9–12]. Even in the fully Sr substituted (Hg, Re)-1212 or (Hg, Re)-1223 [13] or in the 91% Sr substituted (Hg, Pb)-1223 [14], Cu–O2 remains larger, being close to 2.40–2.47 Å in all cases. It is instructive to compare the Sr substitution effect, i.e. the chemical pressure effect, to the mechanical pressure effect, but this is a complex matter because chemical pressure does not simply mimic mechanical pressure. In both cases, the charge reservoir (CR, composed by the double (Hg/Y)O3 layer, linked to its two neighbouring Ba/SrO2 planes) is compressed. But, the difference concerns the following: in Hg-2212, the SB thickness decreases with mechanical pressure (Hg-2212 data from [15, 16]) while it increases with the chemical pressure [1]. The same difference for the SB is also observed, between mechanical pressure in Hg-1223 [17] and chemical pressure in Sr substituted $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ (Cu-1212) [18], $\text{Cu}_2\text{Ba}_2\text{YCu}_2\text{O}_8$ (Cu-2212) [19] and Hg-12 ($n - 1$) n layered cuprates [13, 20]. It cannot be directly linked with the variation of T_c , since in Hg-2212 Sr enhances T_c , while in Cu-1212, Cu-2212 and Hg-12 ($n - 1$) n it decreases T_c [21–24].

It is well known that in layered cuprates, the T_c is governed by the hole concentration in the CuO_2 planes [25]. However, being a mixed valence (in ‘chemical terms’) compound, the holes are distributed over the Cu (3d) and oxygen sites (2p) of the CuO_5 polyhedron and in the 3d Cu orbitals ($3d_{z^2}$, $3d_{x^2-y^2}$). Many efforts have been made experimentally to find strategies for enhancing T_c over the last few decades and, a few years ago, Brown [26], Tallon [25] and Karppinen *et al* [27] introduced and used the concept of the ‘bond valence sum’ (BVS) to quantify the relationship between the atomic structure and electronic properties; the aim is to describe how charges are distributed among the different parts of the structure to provide a better insight into the efficient parameters promoting T_c . With this aim, they took advantage of the very detailed and precise data on bonds lengths extracted from NPD analysis.

In this paper, we will use the refined structure determined from NPD analysis for three compositions of the $\text{Hg}_2(\text{Ba}_{1-y}\text{Sr}_y)_2\text{YCu}_2\text{O}_{8-\delta}$ series: $y = 0.0, 0.5$ and 1.0 (for more details, see tables 1 and 2 in part I of this work [1]). The data for the unsubstituted compound $y = 0$ are based on the original Hg-2212 structure determined by Radaelli *et al* [28, 29].

The calculation of the formal valence of copper from the refined compositions (O3 and Y/Hg occupancies) gives 2.13 (assuming 13% of Y on the Hg site and $n(\text{O}3) = 0.88$), 2.21 and 2.06 for $y = 0.0, 0.5$ and 1.0 respectively. Then, no coherent correlation between this Cu

Table 1. Bond valence sums (BVS) of cation and oxygen sites in Sr substituted Hg-2212 calculated from the Rietveld refined structure. The R_{ij}^0 constants are based on arithmetic mean values weighted by the refined composition. For the Cu–O bond, tabulated $R_{ij}^0(\text{Cu}^{3+}\text{–O})$ and $R_{ij}^0(\text{Cu}^{2+}\text{–O})$ values were considered, weighted to fit the copper valence determined from the refined composition.

Sr content		Hg/Y	Ba/Sr	Y	Cu	O1	O2	O3
0.0	R_{ij}^0	1.977	2.285	2.014	1.686	—	—	—
	BVS	2.04(4)	2.12(2)	2.80(1)	2.13(2)	−2.07(1)	−2.01(3)	−1.75(3)
0.5	R_{ij}^0	1.979	2.202	2.014	1.690	—	—	—
	BVS	2.21(4)	1.92(4)	2.85(1)	2.27(2)	−2.07(1)	−1.95(2)	−1.86(3)
1.0	R_{ij}^0	1.982	2.118	2.014	1.682	—	—	—
	BVS	2.11(4)	1.72(2)	2.83(1)	2.32(2)	−2.06(1)	−1.84(2)	−1.79(3)

valence (or the oxygen content) and the continuous increase of T_c can be found. However, as shown by Alonso *et al* [30], a simple formal valence analysis is not appropriate in the case of Hg-2212. The doping level of the CuO_2 planes should be lower than expected from ionic considerations. As shown in the following discussion, the BVS approach allows one to better estimate the charge distribution in the 2212 lattice and to identify the different doping channels involved in the charge transfer induced by Sr substitution.

2. The ‘bond valence sum’ method

2.1. Background

The BVS method [26] expresses the charge distribution and the crystalline stress on the different sites of a crystal structure.

The BVS are calculated according to equation (1):

$$V_i = \pm \sum S_{ij} = \pm \sum \exp[(R_{ij}^0 - r_{ij})/B] \quad (1)$$

where V_i is the valence of the ion i , R_{ij}^0 (in Å) is an empirical distance, specific to each i – j pair of ions (tabulated values can be found in the literature [26, 31]), r_{ij} is the experimental bond length (in Å) of the i – j pair considering only the first-nearest neighbours and B is an empirical constant equal to 0.37. The R_{ij}^0 values are listed in table 1.

For each site, the calculations give a value which is the sum of the valence of the site and its stress state (compression or extension of the coordination polyhedron around the site) with respect to compounds where the structure is undistorted. The more stressed the site, the greater the deviation from the valence of the undistorted structure. The differences between the calculated V_i and the formal valences are then due to the stress induced by the neighbouring sites for atoms having a fixed valence (for example Ba^{2+} , Sr^{2+} or Y^{3+}) and/or by a charge transfer from the neighbouring sites for atoms able to have an intermediate valence state, for instance copper in the pyramidal coordination ($\text{Cu}^{2+\delta}$). This concept initially developed for ionic compounds has been applied successfully to strongly correlated systems where electrons are rather localized. It was used for many compounds, including high T_c superconductors where correlation of the in-plane hole density with T_c has been discussed [25]. The enhancement of T_c observed in our Hg-2212 series could be correlated with a modification of the charge transfer which occurs between the CR and the SB. In such a case, a BVS analysis could quantify this modification. The values of the Cu – O_2 apical bond length (around 2.27 Å for $y = 1.0$) and the buckling angle of the CuO_2 superconducting planes (around 14°) are close to those measured in Cu-1212 (one Cu–O chain in the CR) and Cu-2212 (a double Cu–O

chain in the CR) compounds; thus changes of the charge distribution similar to those in the Sr substituted Hg-2212, Cu-1212 and Cu-2212 systems can be expected. Thus, our BVS analysis will compare Sr substituted Cu-1212 [18], Cu-2212 [19] and also (Hg, Pb)-1223 (Ca instead of Y between the CuO₂ planes) [14] with our Sr substituted Hg-2212.

2.2. BVS analysis of $Hg_2(Ba_{1-y}Sr_y)_2YCu_2O_{8-\delta}$

In our BVS calculations a modified 2212 structure of the $y = 0$ composition (initially proposed by Radaelli *et al* [28, 29]) was used for consistency with our refinements, i.e. Hg is partly replaced by Y, as shown by Loureiro [15] and confirmed by our previous work [6]. We kept the atomic positions determined by Radaelli *et al* and replaced the Y/Hg and O3 occupancies with the values refined by Loureiro: 0.13/0.87 and 0.88 (instead of 0.78) respectively. This choice will affect only the BVS of the atoms bonded to O3 or Hg/Y, i.e. Hg/Y and O3 themselves, and not significantly Ba whose BVS is more affected by the four Ba–O1 and four Ba–O2 contributing bonds.

One can take two different approaches to calculate the contribution of sites which are occupied by two kinds of cations: Hg²⁺/Y³⁺, Ba²⁺/Sr²⁺ or Cu^{2+δ}. The first one is to consider each atom individually with its specific R_{ij}^0 with the BVS of the site calculated from the weighted sum of the two individual BVS. In this calculation we consider in a first approximation a unique coordination number for both cations. For Ba/Sr sites and $y = 0.5$ for example, one adds a contribution calculated considering a site with 0.5 Ba (characterized by $R_{ij}^0(Ba^{2+}-O) = 2.285 \text{ \AA}$) to a second one with 0.5 Sr ($R_{ij}^0(Sr^{2+}-O) = 2.118 \text{ \AA}$). That was the point of view adopted by Karpinski *et al* in the calculation of the copper BVS at the two Cu sites of Cu-2212 [19]. The second approach considers that the cation–oxygen distances calculated from the refinement of NPD data represent a spatial average of the sites which already takes into account the substitution effects. In this case, for each bond, one uses an average R_{ij}^0 value and the corresponding refined r_{ij} distance, which is in fact already averaged. For instance, to calculate the BVS of a Ba/Sr site, a fully occupied site with an average R_{ij}^0 of Ba–O and Sr–O pairs is considered. This was the method used by Licci *et al* for the compound Cu-1212 [18]. Here, we used both approaches, and because the differences between the R_{ij}^0 are not large, they give BVS values which are very close to each other (within a 2%). Consequently, the two approaches give the same tendencies versus the Sr content. We present here only the BVS values calculated by the second method.

To summarize (see table 1), the value R_{ij}^0 (Cu–O) of the Cu site was calculated by assuming a linear dependence of R_{ij}^0 between the limiting values, i.e. 1.679 Å for R_{ij}^0 (Cu²⁺–O) and 1.73 Å for R_{ij}^0 (Cu³⁺–O), on the basis of the formal valence calculated from the NPD refined composition. This gives R_{ij}^0 (Cu–O) = 1.686, 1.690 and 1.682 Å for $y = 0.0$, 0.5 and 1.0 respectively. We note here that R_{ij}^0 (Cu–O) does not change among the series. Thus, the variation of the BVS of Cu is essentially caused by the shrinkage of the Cu–O1 (i.e. the a axis) and Cu–O2 distances, and not by the insignificant change of its R_{ij}^0 . The O3 occupation factor was taken into account for the BVS calculations for Ba/Sr and Hg/Y sites. For the Ba/Sr site, the weighted (nominal Sr content) average of $R_{ij}^0(Ba^{2+}-O) = 2.285 \text{ \AA}$ and $R_{ij}^0(Sr^{2+}-O) = 2.118 \text{ \AA}$ was taken into account. For the Hg/Y site, we took the weighted (i.e. the refined Y contents 13, 17 and 24% for $y = 0.0$, 0.5 and 1.0 respectively) average of $R_{ij}^0(Hg^{2+}-O) = 1.972 \text{ \AA}$ and $R_{ij}^0(Y^{3+}-O) = 2.014 \text{ \AA}$. In the BVS calculation for the Hg/Y site, Hg/Y–O2, Hg/Y–O3 (vertical) and the four different planar Hg/Y–O3 bond distances were considered. The whole BVS calculations for each site were done considering the first neighbours. All the values are summed up in table 1. In most published calculations, the BVS

error bar is often not indicated, or calculated, or is underestimated. In our case, the errors were estimated by taking into account not only the uncertainty of the refined distances but also the error bars of the refined occupancy factors (of O3 for example) and the R_{ij}^0 error bars resulting from the precision of the refined composition. In all cases, the different changes observed are larger than the error bars. Although our BVS values are rather close to the formal ionic valence values, some differences remain, expressing a charge transfer that is now discussed.

2.3. Charges transfer in cuprates

The carrier concentration in cuprates directly controls their superconducting properties. Its determination and distribution over the sites of the unit cell are thus very important, but not trivial. It may be modified by oxygen doping or charge compensation upon heterovalent substitution. One must distinguish compounds in which oxygen dopes the Cu–O chains (in Cu-1212 for example) from those where the doping oxygen is located in the centre of the Hg/Tl squares (Hg-12 ($n-1$) n , Tl-12($n-1$) n or Tl-22($n-1$) n families). In addition to different experimental methods (thermogravimetric, wet-chemical redox analysis, XANES or XPS spectroscopies), the BVS method based on a bond valence length correlation is very convenient for identifying the charges of the different sites. As shown by Karppinen *et al* [27], one must distinguish three different channels for hole doping of the superconducting planes: $\pi(1)$ through a shortening of the Cu–O2 (i.e. apical oxygen) bond, $\pi(2)$ through a lengthening of the O1–(Ba/Sr) bond (i.e. in-plane oxygen) or $\pi(3)$ through a lengthening of the O1–(Y/Ca) bond.

When oxygen dopes the charge reservoir, channels $\pi(1)$ and $\pi(2)$ are activated in the case of Cu-1212, while only the channel $\pi(1)$ is activated in the case of Hg-1201 or Hg-1212 (and Tl-12 ($n-1$) n or Tl-22($n-1$) n families also) [32]. Generally, channel $\pi(3)$ is activated when the doping affects the site located in between the CuO₂ planes, Ca²⁺/Y²⁺ for example. For Sr substitution in Hg-2212, one expects the charge transfer to occur principally through channel $\pi(1)$, i.e. by a charge transfer along the Cu–O_{2^{apical}} bond, and secondly through channel $\pi(2)$, i.e. along the Ba/Sr–O1 bond, because the Cu–O2 bond length decreases by -8.0% , O1–(Ba/Sr) decreases by -2.8% and O1–Y remains unchanged (-0.3%), as illustrated in figure 10 of part I [1].

An other interesting feature, observed in $(Y_{1-x}Ca_x)Ba_2Cu_3O_{7-\delta}$ (i.e. Cu-1212) by Merz *et al* [33] using x-ray absorption spectroscopy, concerns $T_{c\max}$ which is not only controlled by the hole concentration in the CuO₂ planes, but also by the presence of holes in the apical oxygen site. Even though the CuO₂ planes do contain a sufficiently large hole concentration to superconduct, occurrence of superconductivity requires the presence of holes in the apical site. Moreover, raising the oxygen content in the charge reservoir (i.e. in the Cu–O chains) increases the hole concentration for both in-plane and apical oxygen sites. In contrast, holes introduced by replacing Y³⁺ by Ca²⁺ appear solely in the CuO₂ planes and enable (or enhance) superconductivity only if a minimum number of holes were already present on the apical oxygen sites.

3. Discussion

After having presented the different channels in charge transfer, we use BVS data and this scheme to discuss the Sr substitution effect.

Figure 1 shows the changes of BVS versus the Sr content for the CR and SB (already defined in introduction) and their constitutive layers. The BVS of CR and SB was calculated by summing the corresponding BVS values for each site belonging to the CR and SB blocks.

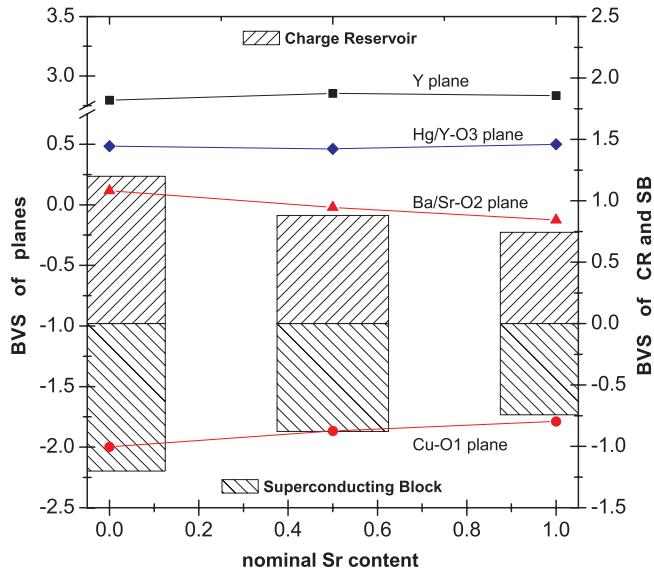


Figure 1. Left scale: BVS variations of the Y, CuO₁, BaO₂ and (Hg, Y)O₃ planes of Hg-2212 versus Sr content (points), calculated considering the refined composition. Right scale: the resulting BVS of the CR and SB (bars) are also plotted. The error bars are not indicated for clarity.

The same was done for the atomic planes and plotted in the same figure. The very clear trend is an increase of the BVS for the SB and a symmetrical decrease for the CR. Both variations show a charge redistribution of their constituting planes (one Y and two CuO₁ planes for SB, and two Hg/YO₃ and two Ba/SrO₂ planes for CR). While no change of BVS is observed for Y and Hg/Y-O₃ planes, only the BVS of Ba/Sr-O₂ and Cu-O₁ layers are affected by the Sr substitution.

Let us now discuss the effects atom by atom. These are illustrated in figure 2 showing the BVS variations for each atom. The four graphs are stacked in the same order as in the 2212 structure and drawn at the same scale to help with direct comparison. The BVS of Y (≈ 2.8) and O₁ (≈ -2.06) sites remain nearly constant, as in Cu-1212 [18] or Cu-2212 [19] (not drawn in figure 2). The main effect of Sr substitution is a strong decrease of the BVS of the Ba/Sr site, accompanied by an important increase of the BVS of its neighbouring O₂ oxygen and of Cu. This is the signature of a significant charge transfer from the CR to the SB essentially affecting the superconducting CuO₂ plane.

The modest variation of the BVS of the Hg/Y site (in the CR) is related to the increasing substitution of the Y³⁺ (table 1 in part I [1]) compensated by the increasing O₃ oxygen content. The BVS of Hg/Y and O₃ sites do not change monotonically with Sr content; they cannot therefore be directly correlated with the T_c increase.

In figure 2 we also plot the BVS variation of the Ba/Sr site in Cu-1212 [18] compared to that in Hg-2212. The comparison to the formal value of the Ba/Sr valence (+2) quantifies the stress of the site. In both cases, for $x < 0.5$, the large cationic Ba site in the $y = 0.0$ composition is compressed ($BVS - 2 > 0$). This stress, which plays an important role in the charge transfer from the CR to the SB [18, 34–36], is reduced by Sr substitution. The decreases of this stress with Sr substitution are quite similar in Hg-2212 and Cu-1212; however, T_c increases in Hg-2212 while it decreases in Cu-1212. Then, at first sight, this parameter does not seem to be of first order in the enhancement mechanism of T_c in Sr substituted Hg-2212. However,

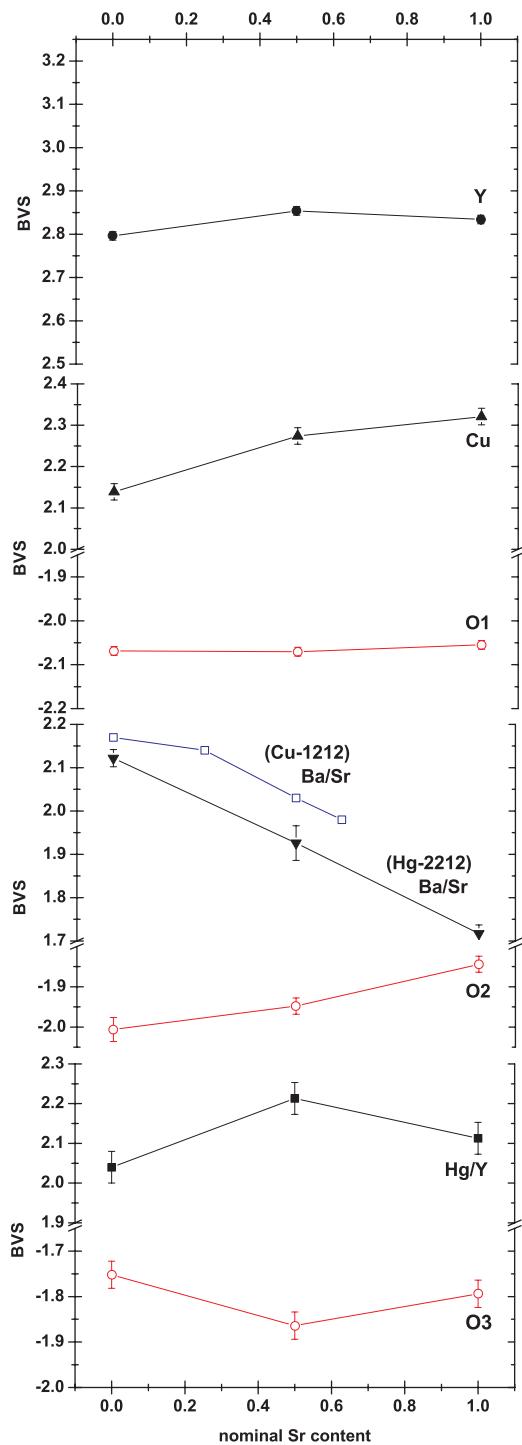


Figure 2. BVS variations of the atoms in Hg-2212 versus Sr content. The BVS variation for the equivalent Ba/Sr site in Cu-1212 [18] is also plotted for comparison.

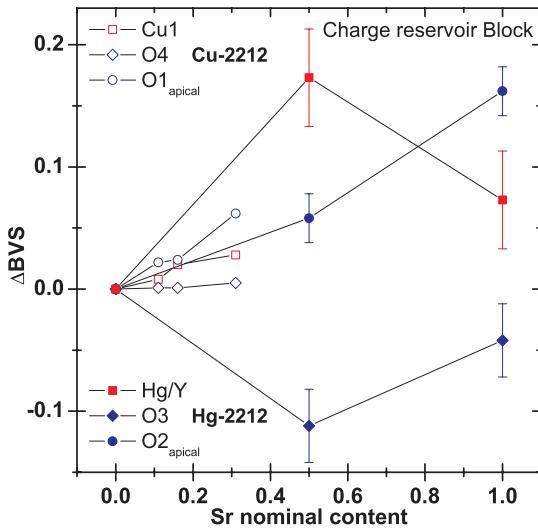


Figure 3. Relative BVS variations of the cationic site of the CR (i.e. Cu1 for Cu-2212 [19], Hg/Y for Hg-2212), oxygen of the CR (O4 for Cu-2212, O3 for Hg-2212) and apical oxygen (O1 for Cu-2212 and O2 for Hg-2212) versus Sr content.

the redistribution of the charges associated with this stress relaxation is the important point to consider. One notices also that this release is correlated with the increase of the thermal Debye–Waller factor from 0.5 \AA^2 to a value higher than 1.5 \AA^2 for $y = 1.0$ (see table 1 in [1]), the Sr–O bond being stretched for this Sr content.

The comparison of the behaviour of the Hg/Y site with that of the equivalent site in the Cu-2212 compound [19], i.e. the copper atom of the Cu1(O1, O4) planar square in the CR, is interesting and shows a contrasting behaviour—figure 3 (Δ BVS—i.e. the variation of the BVS with respect to the composition $y = 0.0$). The data plotted in this figure are not corrected for stress. When this is done (as explained in [19]), no variation of the BVS of O4 (in the chains of Cu1 in Cu-2212) is observed, while a charge transfer occurs from the apical O1 oxygen (whose BVS decreases) to the Cu1 site (whose BVS increases). For Hg-2212, such charge transfer from apical O2 oxygen to the equivalent Hg/Y site does not occur.

Figure 4 compares Δ BVS for Cu and O atoms of the superconducting CuO₂ planes for Cu-1212 [18], Cu-2212 [19] and Hg-2212 (this work). When Sr is introduced, the BVS of Cu increases for these three compounds. In Cu-1212 and Cu-2212 the BVS of oxygen atoms (i.e. O2 and O3 in Cu-1212 and Cu-2212) decreases symmetrically, as expected for in-plane charge transfers [18, 19]. Surprisingly, the BVS for the in-plane O1 oxygen in Hg-2212 behaves differently, staying nearly constant whatever Sr is. This indicates a different mode of charge transfer between Hg-2212 and Cu-1212 or Cu-2212 cuprates. We assume that the stress relaxation of the Ba/Sr site, i.e. its movement towards O3, occurs differently and opens different channels of charge transfer (corresponding to different effects on Cu–O2, Ba/Sr–O1 and Y–O1 bonds).

Figure 5 shows for Hg-2212 the net hole concentration of the equivalent CuO₂ planes ‘ $p(\text{CuO}_2)$ ’ [25, 27] versus the nominal Sr content. It is defined as $p(\text{CuO}_2) = V(\text{Cu}) + 2V(\text{O1}) + 2$, i.e. equal in fact to the sum $\pi(1) + \pi(2) + \pi(3)$, $\pi(1)$, $\pi(2)$ and $\pi(3)$ being respectively the three different contributions associated with the three channels: $\pi(1) = S_{\text{Cu–O2}}$, $\pi(2) = 4S_{\text{Ba/Sr–O1}}$ and $\pi(3) = 4S_{\text{YO1}}$ (see section 2.3 and equation (1)). These three partial hole concentrations contributing to the total value $p(\text{CuO}_2)$ are also shown on

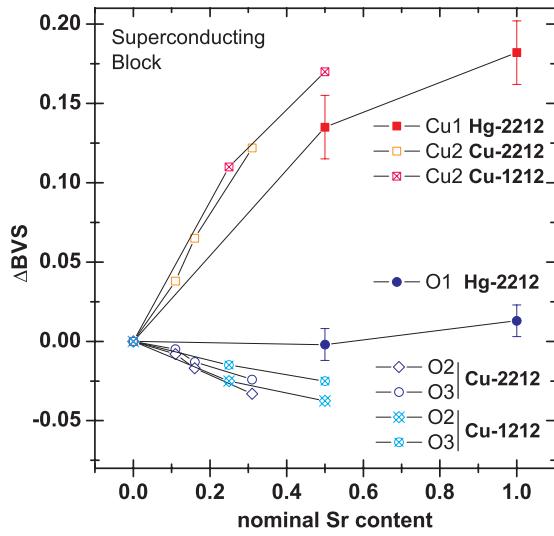


Figure 4. Relative BVS variations of copper and oxygen of the SB versus Sr content in Cu-1212 [18], Cu-2212 [19] and Hg-2212.

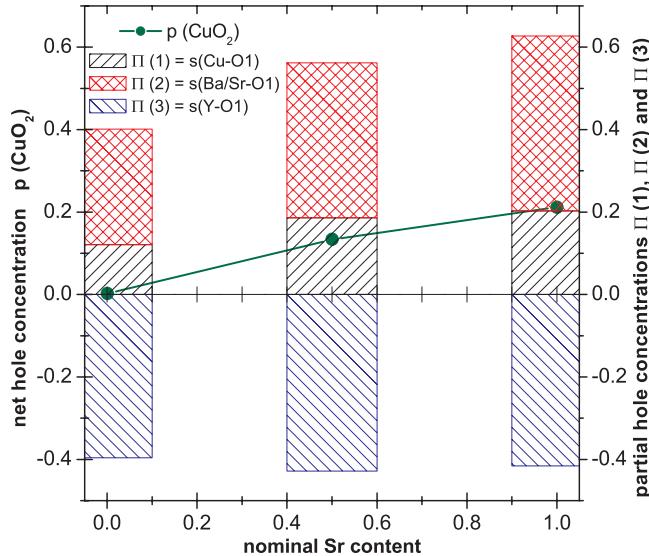


Figure 5. The effect of Sr content on the net hole concentration $p(CuO_2)$ in the CuO_2 planes of the Hg-2212 series (points, left scale). The three different contributions $\pi(1)$, $\pi(2)$ and $\pi(3)$ to $p(CuO_2)$ are also plotted (bars, right scale). The error bars are not indicated for clarity.

the right scale of figure 5. The contributions of channels $\pi(1)$ and $\pi(2)$ increase with the Sr content, while the contribution of channel $\pi(3)$ remains negative and constant. In other words, the relaxation of the stress on the Ba site by Sr substitution activates the channels $\pi(1)$ and $\pi(2)$, i.e. the charge transfer from the CR to the SB via $O_{2\text{apical}}\text{--Cu}$ and Ba/Sr--O_1 bonds. A similar evolution is also observed in the monolayer (Hg, Pb)-1223 replaced with Sr [14]. Moreover, in this 1223 compound the $\pi(3)$ contribution increases with Sr content, while in

Hg-2212 it remains constant and negative (≈ -0.4). Indeed, for Hg-2212 no significant change of the Y–O1 bond occurs when Sr is substituted for Ba, in comparison to the case for (Hg, Pb)-1223 where the equivalent Ca–O1 bond increases by 0.02 Å [14]. This is probably a major difference that could explain why T_c decreases when Sr is substituted for Ba in (Hg, Pb)-1223 while it increases in Hg-2212.

In conclusion, the BVS calculations show how Sr substitution affects the charge distribution in the Hg-2212 layered structure. Two layers play a major role in this charge redistribution: Ba/SrO₂ and CuO₁ sheets, while Hg/YO₃ and Y sheets are not important in this respect. The release of stress on the Ba/Sr site caused by Sr substitution induces a charge transfer from the Ba/SrO₂ layer (and not from the Y plane) to the CuO₂ plane. This model may be the key to explaining the increase of T_c with Sr content. In addition, it would be interesting to compare the charge distribution of Hg-2212 compressed by Sr substitution with that obtained for mechanical compression, but this kind of study requires one to know very precisely the Hg-2212 structure under high pressure (up to 7–10 GPa), and particularly the oxygen positions. Unfortunately, such data (for neutron powder diffraction) are rare [15, 16] and not available in the literature for Hg-2212. Determination of the electronic structure of different Sr-substituted Hg-2212 compounds would also be very useful; however, such calculations only became possible recently and they have only been carried out for the Hg₂Ba₂YC₂O₈ composition [30].

4. Conclusion

Following the first part of this work, devoted to the study of structural effects induced by Sr substitution in Hg₂(Ba_{1-y}Sr_y)₂YC₂O_{8-δ} (using neutron powder diffraction) and its effects on T_c (enhancement from 0 K for $y = 0.0$ to 42 K for $y = 1.0$), this second part is focused on an analysis of the charge distribution in the 2212 lattice, using the refined structures obtained previously and BVS calculations.

The bond valence sum approach gives a relevant idea of the doping mechanism related to the Sr substitution. From the BVS analysis, we demonstrate that the shrinkage of the Cu–O1 bond of the superconducting plane is accompanied by a reduction of the stress on the Ba/Sr site which favours a charge transfer from the Ba/Sr–O2 plane to the CuO₂ superconducting plane by activating the two doping channels $\pi(1)$ and $\pi(2)$, i.e. through O₂_{apical}–Cu and Ba/Sr–O1 bonds respectively, and not via $\pi(3)$, i.e. through Y–O1 bonds. This could explain the observed T_c increase with the Sr content.

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