To what degree is Hg-1201 able to act as an archetype of HTSC cuprate phenomena? From Seebeck results to stripe phase behaviour

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Abstract.   Upon closely examining the Seebeck behaviour of Hg-1201 we have discovered that the system, whether stoichiometric or mercury deficient, appears to behave in similar fashion to the LBCO and YBCO-123 systems in that a dip appears in $T_c(p)$ at $p \sim 1/8$. We have earlier indicated that this concentration of holes marks the point at which stripe phase formation in the organization of charge and spin in the two-subsystem, mixed-valent, HTSC materials passes from one charge wall loading scheme to another.

We observe a strong difference in doping characteristics between the mercury-deficient and mercury-stoichiometric systems, and assemble here a plausible scenario of what is involved. While $HgBa_2CuO_{4+\delta}$ indeed does offer very considerable potential advantages as an archetype to the cuprate HTSC phenomenon, excess anion systems like this clearly introduce materials complexities. These will always demand careful attention and perhaps not endear the system to many accustomed to the relative simplicities of a cation-doped system.

1. Potential archetypal position of Hg-1201 in HTSC hierachy

At first sight Hg-1201 has all the desired characteristics of the perfect archetype for the HTSC cuprate problem: (i) it is 'only' a quaternary, and the crystal chemistry of its three quite different cations does not support anti-site defects; (ii) its mode of hole doping via oxygen excess looks straightforward and not too crystallographically or electronically disruptive; (iii) the system can be changed from under- to over-doped fairly easily and very extensively; (iv) the single CuO_2 plane per cell makes its band structure relatively simple, multiple signals (as in nmr) are held to a minimum, and the c-axis anisotropy is clearly expressed; (v) the CuO_2 planes are almost flat, not buckled as in other HTSC materials; (vi) the system is tetragonal and therefore theoretical questions concerning the precise symmetry of the superconducting order parameter (e.g. pure d versus d + s) are much better posed; (vii) T_c is at 97 K the highest for any simple single-layer system, and claims to electronically driven superconductivity should accordingly be more readily demonstrable.

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2. Problems in Hg-1201 from excess oxygen crystal chemistry and mercury non-stoichiometry

As time has passed it has become apparent from a chemistry/materials point of view that the system is appreciably more awkward and complex to deal with than its HTSC forerunners, such as LSCO, YBCO-123 or even BSCCO. There is more than one expression of this, but the underlying cause is that the Hg in 1201-HBCCO is of lower valence and/or lower ionization potential than for most other counter-ions commonly appearing in HTSC systems. This has the effect of mixing the mercury levels more covalently throughout the valence band. More significantly there is the potential for actual band overlap between the bottom of the first CB state with the top of the VB, leading to 'self-doping'. The latter would produce complications in the circumstances at E_F, notably in simple carrier counting routines [1]. Even with rather electropositive counter-ions such as La^{3+} and Ba^{2+} it is well established that it is only just possible to achieve formal trivalence for copper in these oxides. Indeed Cu_{III} is inaccessible in halides other than fluorides, while with most sulphides not even Cu_{II} is reached. This situation arises because of the rapid approach towards shell closure encountered at the end of the 3d transition metal series (see [2]). If band overlap is a potential problem for the parent undoped compound, then it certainly will be so in the presence of more loosely bound excess-oxygen-derived valence states in $HgBa_2CuO_{4+\delta}$. Complication with respect to carrier count will come whenever the $pd\sigma^*$ state of $d_{x^2-y^2}$ symmetry within the CuO_2 chessboard planes is not sufficiently antibonding for E_F to be raised completely clear of the top of the entire complement of non-bonding p states—besides, of course, the d_{z^2}-derived $pd\sigma^*$ state. When that is not the case the above states will start to become depopulated as the Fermi sea is oxidized, i.e. its overall electron content is reduced via appropriate chemical modification to the 'charge reservoir'. In $YBCO_y$ this circumstance seems to onset beyond $y \sim 6.94$.

As regards the mercury content, the low heat of formation of HgO and likewise of its required inclusion into $HgBa_2CuO_{3+\delta}$ (i.e. $HgBa_2CuO_{4+\delta}$) imply that Hg–O is rather easily lost from the system [3–7]. Indeed to obtain fully Hg-loaded Hg-1201 it is necessary to encapsulate the reactants HgO and $Ba_2CuO_{3+\delta}$, not only to prevent evaporation and decomposition of HgO at relatively low temperatures $\sim 400\,°C$, but also to secure full attachment of the HgO content at the final reaction temperature of around $800\,°C$. Unfortunately at the latter temperature, customarily used in forcing the reaction, the 1201 compound appears to be only metastable, and given the chance it will decompose again on cooling. Short reaction times and product quenching have been employed as means towards obtaining stoichiometric material. However a multiple phase content then invariably results [2, 7]. The highest single-*phase* content for the product appears to be obtained when in fact the HgO content in the sample is considerably less than stoichiometric. Accordingly we and others, knowingly or otherwise, have studied this sub-stoichiometric single-phase product in lieu of $HgBa_2CuO_{4+\delta}$ itself, prior to becoming fully aware of the significant complications thereby introduced. Nonetheless it proves possible to extract much from the results that is of interest and which illuminates the HTSC problem. From the outset however it has to be realized that results from this material—defective in HgO to the extent of up to 30%—relate to a system differing appreciably from $HgBa_2CuO_{4+\delta}$ itself.

The problem once more lies, as foreseen from the early band structural work [1], in the considerable disturbance to the carrier counting routines, so important to HTSC phenomenology. It is well established that $T_c(p)$ in the square-planar cuprate HTSC systems looks quite generally to maximize at a carrier count of $p = 0.16$, a figure remarkably independent of either structural or chemical detail. As was shown in [2] this concentration
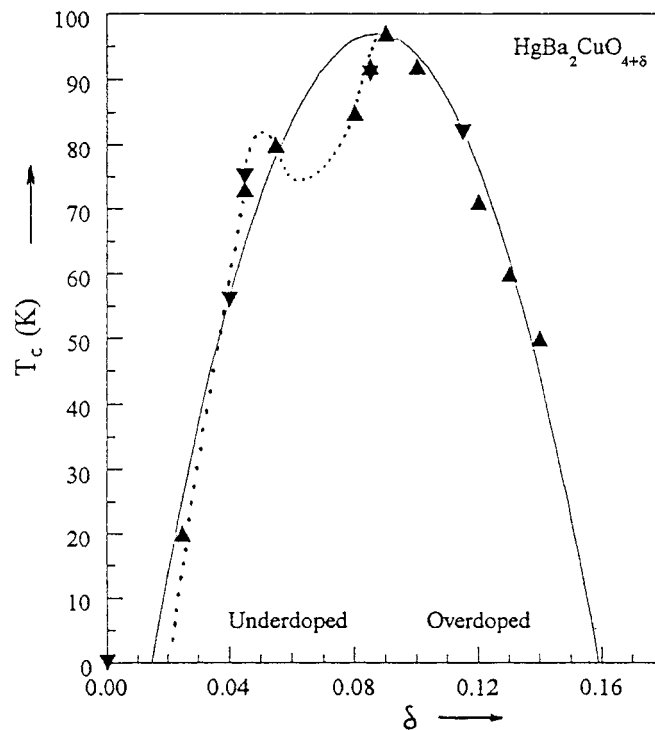
Figure 1. Composite figure for data up to 1996 from Edwards *et al* [11] of $T_c(\delta)$ for near-Hg-stoichiometric $HgBa_2CuO_{4+\delta}$. The figure displays a maximum in T_c at $\delta = 0.08$ (i.e. implies $p = 2\delta$). We have added the dotted line, bringing to light the strong dip in T_c around $p = 1/8$.

marks a special point in the development of metallicity in these systems—essentially mixtures of the two integral-valence Mott insulators $d^9(Cu_{II})$ La_2CuO_4 and $d^8(Cu_{III})$ $LaCuO_3$. At $p = 0.16$ the interface between the two subsystems becomes optimized as regards intersubsystem charge transfer. (By that point the level of metallicity gained is sufficient for magnons no longer to provide a source of significant spin-flip scattering, while, conversely, it still is limited enough for the system to remain sufficiently locally constituted and support the negative-U process introduced in [2] (and discussed further in [8] and references therein). To the latter process we have attributed the introduction of HTSC into these systems.)

In circumstances where the Fermi level is not carried by the $d_{x^2-y^2}$ band alone, but is driven in part into the upper reaches of the non-bonding p band, then—with growth in formal Cu_{III} content in this way restricted—further oxidation (i.e. removal of electrons) results in the generation of an effective O^{1-} content. (This is a more likely eventuality than passage of E_F into $pd_{z^2}\sigma^*$, given the very large c-axis Jahn–Teller distortion present in Hg-1201.) Even for allegedly near-mercury-stoichiometric material some recent papers would indicate that the entirely O^{2-} count there being assumed in fact cannot be correct. Thus Antipov, Aksenov and coworkers [9, 10], while claiming from neutron powder diffraction work a mercury content n(Hg) of greater than 0.9, find it a problem to reconcile their iodometry with their neutron results (see [9]; figure 8). Also in [9], when comparison is made between the effects upon T_c of insertions of excess oxygen and of excess fluorine, the forms of the $T_c(\delta)$ curves that emerge from the neutron powder diffraction cannot be taken to represent a standard closed valence band situation. This observation stands despite the fact that the work finds twice the

Cu valence
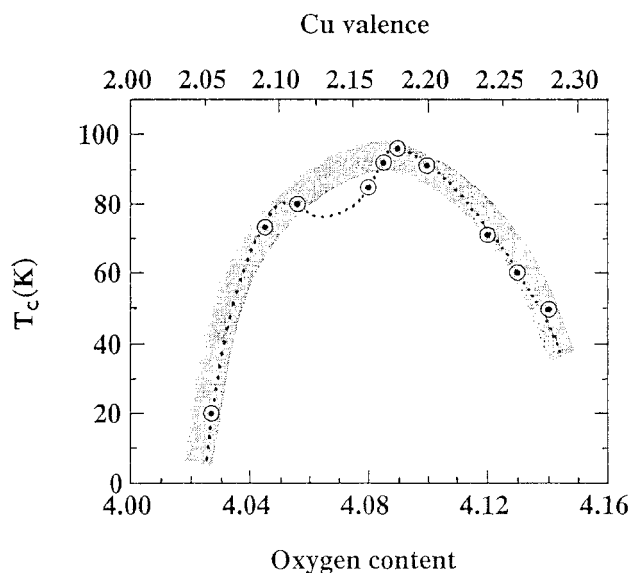
Figure 2. Comparable result from Fukuoka *et al* ([13] figure 4) to that shown in figure 1, exposing a dip in $T_c(p)$ at $1/8$ (when we take $p = 2\delta$). We have linked together the data points by the dotted line to reveal this feature: originally the broadly hatched parabola was used.

δ value for the fluorine case as for the oxygen case (as under simple state counting for F^{1-} and O^{2-} respectively). The problem is that in the oxygen excess case $T_c(\delta)$ is found to peak nearer to $\delta = 0.16$ than to 0.08. This observation has to be contrasted with the iodometry data, where there continues to be extracted a customary optimization of T_c with regard to p—and *not* δ—at 0.16 (see figure 8 in [9]). The latter peaking was presented within a curve suggesting near-parabolic form to the $T_c(p)$ dependency. While such a round-topped form to the $T_c(p)$ curve, imputed here from the data of [9], may seem in evidence too in several other publications, invariably the data points gathered are actually rather sparse. Figure 1 shows an attempt by Edwards *et al* [11]—see also [12]—at a composite representation of the $T_c(p)$ data existing in 1996 for 'stoichiometric' material. The closest individual approach pointing to a classic $p = 2\delta$ variance for T_c is that from Fukuoka *et al* ([13], figure 4) who it should be noted use a very small encapsulation tube to prepare their samples. Their data are reshown, again with indicated modification, as figure 2. It ought to be noted that the latter plot is in strong contrast to the non-standard, flat-topped $T_c(p)$ plot obtained somewhat earlier by Xiong *et al* [14]. The latter results, presented again with some modification, appear in figure 3. Within figure 3 one must observe that p is now only $\sim\delta$, *not* 2δ. Moreover a plateau exists at 97 K ($= T_c^{max}$) extending to $p \sim 0.2$, while p values run out beyond 0.25. Behaviour very like the latter now we have closely reproduced and amplified using comparably prepared samples [15], as will be presented below. When using the precursor pellet sealed tube technique of Xiong *et al* [14] the mercury content of the sample pellet is determined by the relative initial and final weights of the two pellets. Transition widths for these ceramic samples measured resistively and magnetically are typically $\sim$5 K. T_c is normally assessed in the present work as the maximum gradient point of the Seebeck coefficient itself [15]. The Seebeck runs were made using a temperature differential of 0.4 K. A high pressure oxygen bomb was used to secure highly overdoped samples and Zr gettering to secure highly underdoped ones.
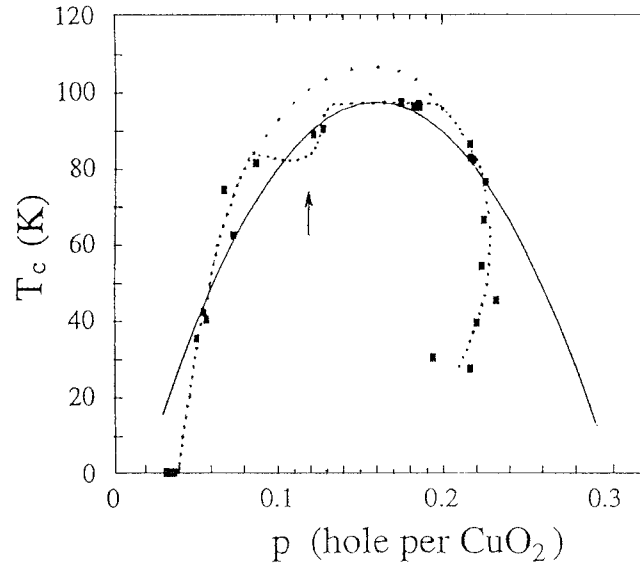
Figure 3. Thermoelectric Seebeck data from mercury-deficient Hg-1201 obtained by Xiong *et al* ([14], figure 3) and plotted against a *non*-standard parabola for $T_c(p)$, for which the prefactor 50 replaces the standard value of 82.6 within the empiric expression of Presland *et al* [25]—see text. The dotted curve that we have added brings out further features of note: (i) the dip at $p \sim 0.11$, (ii) the plateau running from 0.13 to 0.19 and (iii) the fall-back in effective p-value at very high levels of oxygen loading. For this system it is found that $p = 0.72\delta$—i.e. much less than the regular $p = 2\delta$ of figures 1 and 2 for near-Hg-stoichiometric material.

3. Novel $T_c(p)$ plot reached from Seebeck data. Discovery of $p = 1/8$ dip and implication of stripe phase formation

The modifications we have made above to figures 2 and 3 reveal the reason why we are particularly interested in these results. We have been much involved with what of late has become referred to as 'stripe phase' formation—namely the periodic micro-segration, dynamic and static, of charge and spin within the two-subsystem environment at the several nanometre level. Such a tendency was directly picked up first from neutron spin diffraction results, but subsequently has been recorded in its more fundamental charge aspect by using electron and x-ray diffraction (see section 6 and appendix B in [8], and [16]). This micro-organization is of a sufficient time-scale to couple to the lattice, primarily communicated via the Jahn–Teller effect. The wavevector periodicity of the incipient incommensurate order is governed not by the Fermiology, as with a CDW/PSD [17], but directly by the carrier count. Accordingly it may readily show lock-in effects as the periodicity impressed by the stoichiometry becomes commensurate with the basic lattice.

In LBCO and related systems it is well documented that a very specific carrier-lattice coupling response exists around $p = 1/8$. Indeed T_c there becomes very significantly depressed, and takes on a more normal isotope exponent ($\alpha \sim 1/2$) in sharp contrast to a near-zero value around T_c^{max}. Correspondingly, as expanded upon in [16], the so-called 'plateau' in T_c for $YBa_2Cu_3O_{6+x}$ near $x = 6.65$ ought properly to be viewed as a dip in T_c around $x = 6.75$: the feature demonstrably involves charge rather than chain oxygen ordering. For LSCO it has been observed that at $x = 1/8$ there occurs a distinct break in the rate of variation with p of the ordering wavevector q. This crossover was suggested in
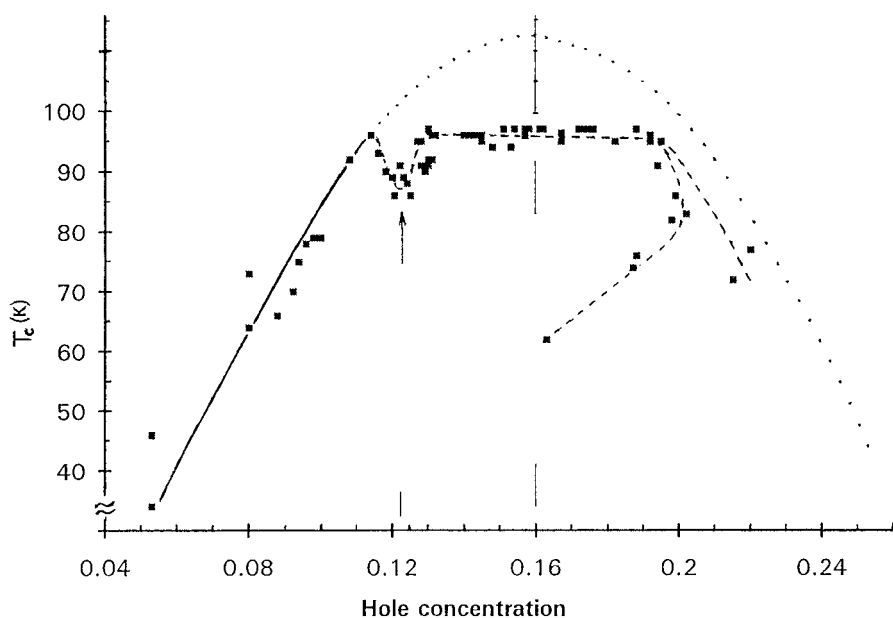
Figure 4. Our results obtained from Seebeck measurements [15], comparable to those shown in figure 3 from Xiong *et al* [14] on similarly produced material but now obtained at a much higher data point density, clearly establish the previously mentioned features.

[16] to mark passage from one type of specified 'stripe phase' charge wall loading scheme to another. In the case of LBCO the ordering near $p = 1/8$ becomes quasi-static, and the structured carrier-freed domains of Cu_{II} revert to a more antiferromagnetic as distinct from randomized RVB condition. The outcome in LBCO is that near $p = 1/8$ a very strong depression of T_c is witnessed. This becomes total in the case of $(La/Nd/Sr)_2CuO_4$, where the presence of the Nd spins encourages magnetism and charge localization. With LSCO itself events are much slighter than in LBCO, due probably to its somewhat smaller polarizibility (cf $SrTiO_3$ versus $BaTiO_3$). What is more in LSCO the maximum impairment of superconductivity seems to develop around the higher-order commensurate value of $3/26$ or 0.1154—see [16].

Whether or not all the above phenomena constitute a side-show to the main concern, the origin of HTSC—and in essence we believe they do—they clearly provide sufficient interest in their own right for us to examine the degree to which they are restricted to the LBCO and YBCO-123 families, or might prove common to all cuprate HTSC systems. In particular are they to be found in Hg-1201?

That a dip in $T_c(p)$ for the HgO-defective 1201-based material which we ourselves have been closely examining does actually exist became evident as more and more samples were tested [15]. In figure 4 we present the high degree to which our Seebeck results support and amplify the $T_c(p)$ plot obtained by Xiong *et al* [14] from similarly produced samples (figure 3). In their case δ was determined by TGA and neutron powder diffraction. Their and our p-values are deduced from application of the universal relationship established by Obertelli *et al* [18] between p and the room temperature Seebeck coefficient for HTSC cuprates. Our δ value changes by contrast have been monitored by weighing a pellet of known cationic composition. All the 'odd' features duplicate between the two sets of data, namely (i) the dip in $T_c(p)$ near $p = 0.12$; (ii) the $T_c(p)$ plateau running from $p = 0.14$ to 0.19; (iii) a fall-back in the

effective *p*-value in the very highly oxygen-loaded regime not reported for Hg-rich samples and (iv) values of 2δ which are throughout far in excess of the effective *p*-values. Experimental matters are included in more detail in two theses [15].

The work of Xiong *et al* [14] was presented originally as though the material being used were near Hg stoichiometric. However, an associated paper [19] published shortly afterwards, involving a closer Rietveld fitting to neutron powder diffraction data from the same samples, entertained the option that the material might be significantly Hg defective (see their table IV). This we find to be the inevitable result whenever their 'precursor technique' (used to control the single-*phase* character of the product) is employed to prepare one's samples [15].

4. What can be salvaged of an archetypal status for Hg-1201?

A further neutron powder study of Hg-1201 recently has appeared from Jorgensen *et al* [20]. This pursues the matter of multiple-site oxygen insertion, surfacing now as a generic problem in those HTSC systems manipulated by excess oxygen content. It long has been recognized that $La_2CuO_{4+\delta}$ is a considerably more complex system structurally than its cation-substituted counterpart $(La/Sr)_2CuO_4$. (This discounts stripe phase formation, which, as the present paper would indicate, appears to extend to most if not all HTSC cuprate systems.) The complexities in point here include (i) macro-phase separation [21] and martensitic microstructure [22], (ii) multiple site oxygen defects and (iii) carrier counts not in compliance with the simple prescription $p = 2\delta$ [23]. Already for $La_2CuO_{4+\delta}$ neutron work [24] has cast light upon the latter two matters (which clearly are interlinked), and would suggest the presence of oxygen polyions like O_2^{2-}, O_3^{5-} etc.

It is apparent that the new neutron paper from Jorgensen *et al* [20] must refer to Hg-deficient material as its figure 5 displays a $T_c(\delta)$ plot which presents all the special characteristics enumerated above for such material. Again one is able to make out the dip at $p \sim 1/8$, implying the presence of the stripe phase. Note too the plateau in T_c running from $\delta = 0.135$ to 0.19. If the under- and over-doped wings of this T_c plot were to be treated as from a $T_c(p)$ variation structured in accord with the empiric parabolic form of the generalized expression of Presland *et al* [25] $T_c(p) = T_c^{max}[1 - 88.6(p - 0.16)^2]$, this would in fact yield a T_c^{max} about 15 K higher than the present recorded plateau value of 96 K (see the present figure 4). The small lattice parameter differences measured between the two types of material mean that such a ΔT_c cannot simply represent a chemical pressure effect [26]. The new neutron results for this distinctive system indicate that not only does p fall in magnitude below 2δ, but indeed below δ as well over a significant range of low oxygen substitution—conclusions we had surmised from our own Seebeck and magnetic work (see [15]). The plateau of Jorgensen *et al* in $T_c(\delta)$ is matched by a plateau in cell volume at 143.6 Å^3 (see figure 6 in [20]). This could be taken to imply two-phase behaviour. However our Seebeck data indicate a *p*-value which continues to increase smoothly across this δ-range (over which p runs from 0.135 to 0.19). Oxygen 'staging' as in $La_2CuO_{4+\delta}$ could well introduce or contribute to these complications.

The above neutron work [20] claims that, in addition to the customary cell face-centred O(3) site at (1/2, 1/2, 0), there exists in 'Hg-1201' a second excess oxygen site, O(4). The latter is assessed to be displaced from the central O(3) site to $(x, x, 0)$, i.e. towards an Hg site. It is likely that this oxygen shift actually is away from an Hg vacancy and towards the opposite Hg atom, itself displaced towards the O(4) atom to create an Hg–O(4) bond ~ 2 Å. This bond is thus not dissimilar in length to the Hg–O bond of the *c*-axis interconnects (1.97 Å) or to the 45°-rotated Cu–O bond of the CuO_2 planes (1.94 Å). It is well known that the Hg ion normally

is rather loosely constrained within the (a, b) plane: note its B_{11} is $\gg B_{33}$ in the Debye–Waller vibration ellipsoid [19]. Because of the displaced O(4) position and of the very low p-count with which at low δ it is determined to be associated, a plausible species for this excess oxygen below $\delta = 0.08$ would be the diatomic superoxide ion O_2^{1-}. At higher oxygen excess contents between $\delta = 0.08$ and 0.20 this O(4) species looks to oxidize progressively to the peroxy-ion O_2^{2-}. It is across this latter range that the ultimately dominant $n(O3)$ dopant population becomes established. From our Seebeck work we would like to associate the principal $n(O3)$ population with O^{1-}. Suddenly at $x = 0.20$ the O_2^{2-} population appears to dissociate into two O^{1-} and transfer into the O(3) sites. Hence at no time for the strongly mercury-deficient material does O^{2-} figure within the *dopant* oxygen population.

All such modifications in charge balance in proximity to a 'dopant' centre will automatically induce the near-neighbour Ba ion position to respond locally to define differentiated populations in the symmetry-unrestricted Ba z-parameter [11, 19]. It is just such local differentiation of conditions around dopants in HTSC materials that, as we have maintained throughout, serve to establish a two-subsystem environment and so facilitate the negative-U route to HTSC. Within cation-doped systems it has long been evident [27], though not always acknowledged [28], that such inhomogeneous conditions exist. More recently comparable local probe studies have been undertaken as well on $La_2CuO_{4+\delta}$, and once again these make manifest the strong distinction between those Cu sites away from and those in direct proximity to dopant sites [29]. The two-signal nmr responses of LCO+ and of LSCO emerge as being virtually identical under comparable doping levels. This observation demonstrates that the main difference between the site categories is indeed primarily dictated by the dopant effective charge, rather than the precise changes in crystallographic site environment. NMR, NQR, EXAFS and other similar local probe studies should now be undertaken on the Hg-1201-based systems in order to discover whether comparable site distinctions again can be revealed. This particularly is the case for the Hg-stoichiometric system, if the latter still is to lay any claim to use as HTSC archetype. As was emphasized above, such study will require careful production of the samples, employing an encapsulated environment from which all HgO loss is prevented [9]. Despite HgO being itself charge neutral, plainly its loss results in a virtually distinct system, displaying a markedly different oxygen-excess behaviour and associated p/δ relationship.

5. Generality of present results re stripe phase behaviour

If the dip in $T_c(p)$ that we have uncovered at $p \sim 1/8$ present both for $HgBa_2CuO_{4+\delta}$ and for its mercury-deficient counterpart does indeed betoken a crossover in stripe phase formation, then it is of immediate concern to extend the study further to systems such as BSCCO-2212. The EXAFS results obtained by Bianconi and coworkers from BSCCO already reveal a multi-site population varying as a function of temperature [16, 30]. More pointedly now we again find hidden within the literature clear indication that dips in $T_c(p)$ of the above discussed type indeed arise both for oxygenated BSCCO and for its RE^{3+}-substituted counterpart [31].

Postscript

Since this manuscript was completed it has been demonstrated by neutron diffraction that incommensurate spin (and by implication charge) organization does indeed arise in LaCuO$_{4+\delta}$ [32]. No such direct diffraction evidence is as yet forthcoming from BSCCO-1212 [33], nor indeed HBCO-1201 for which suitable crystals are not available.

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