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LETTER TO THE EDITOR

Simulation of the oxygen-atom vacancy in the high temperature superconductor $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2.5}$ ($n = 1$)

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Abstract. These simulation calculations for the oxygen-atom vacancy in the high temperature superconductor $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2.5}$ ($n = 1$) have been performed by means of the tight-binding approximation based on the EMO method. The results indicate that the effect of the oxygen-atom vacancy on the charge distributions at the Tl-, Ba-, Cu- and O-atom sites is appreciably different and that there may exist two kinds of Cu cation with different net charges ($\sim +3.0$ or $\sim +1.0$) due to the oxygen-atom vacancy in the lattice. The electric field gradient at the site of the oxygen-atom vacancy has been calculated. The position of the oxygen-atom vacancy which favours the high temperature superconductivity of $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2.5}$ ($n = 1$) has been discussed.

The content of the oxygen atoms in some high temperature superconductors, like $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, is not precisely stoichiometric. It has been noted that it may be the partial oxygen-atom vacancies in the lattice that allow the occurrence of high temperature superconductivity in these compounds. Therefore, investigation of the effect of the oxygen-atom vacancy on the structural distortion and on the charge distribution at atom sites in the lattice, especially on the valence fluctuation at the Cu-atom site in these high temperature superconductors, should be very helpful to the understanding of the superconducting mechanism and the search for new high temperature superconductors.

The results of some research on the structural distortion and the valence fluctuation at the Cu-atom site caused by the oxygen-atom vacancy in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by means of the empirical atom-atom potentials and the atom cluster model have been published [1–3]. However, it is known that the main advantage of the tight-binding approximation over the atom cluster model is the ability of the former to overcome the difficulty of surface effects of dangling bonds which exist in the atom cluster model. In this letter we shall use the tight-binding approximation to investigate the oxygen-atom vacancy in the high temperature superconductor $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2.5}$ ($n = 1$).

It has been reported that there exist two types of superconducting phase in the Tl–Ba–Ca–Cu–O system [4]. Type I belongs to the primary tetragonal lattice with space group $P4/mmm$, and its ideal chemical formula is $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2.5}$ ($n = 1, 2, 3, 4$). Type II belongs to the body-centred tetragonal lattice with space group $I4/mmm$ and its ideal chemical formula is $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1, 2, 3, 4$). In the compound $\text{TlBa}_2\text{CuO}_{4.5}$ of type I ($n = 1$), there are only 4.5 oxygen atoms in each unit cell; in other words, there is a half oxygen-atom vacancy in each unit cell. Of course, the distribution

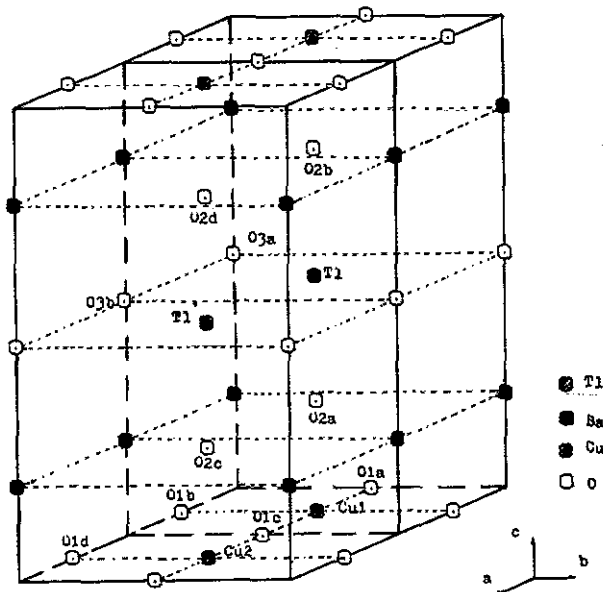


Figure 1. The large unit cell composed of two unit cells in the high temperature superconductor $\text{TlBa}_2\text{CuO}_{4.5}$ with the oxygen-atom vacancy in the lattice.

of point defects in the crystal may be random. However, for simplicity, we can assume that the position of the oxygen-atom vacancy in the lattice is repeated periodically. In this case, there will be an oxygen-atom vacancy in every two unit cells of the $\text{TlBa}_2\text{CuO}_{4.5}$ crystal. Unlike in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, in this kind of high temperature superconductor there are no Cu-O chains along the c -axis direction. [5]. We shall consider only the superlattice structure along the a -axis or the b -axis direction and can therefore treat the two neighbouring unit cells along the a -axis direction in the $\text{TlBa}_2\text{CuO}_{4.5}$ crystal as a single large unit cell (see figure 1). Thus, the new lattice parameters are: $a = 7.694 \text{ \AA}$; $b = 3.847 \text{ \AA}$ and $c = 9.6 \text{ \AA}$. We must point out that this approximation is similar to, but slightly different from, the large-unit-cell approach [6, 7]. According to the large-unit-cell approach we must combine small unit cells to form the large unit cell. However, it would be impossible to perform any tight-binding approximation calculation for such a large cell. To check whether this approximation is reliable, we have carried out some calculations for the perfect $\text{TlBa}_2\text{CuO}_5$ crystal with no oxygen-atom vacancies in the lattice at several K points in the reduced BZ by using the tight-binding approximation. The results show that the variation of the net charge at an atom with K point is not very significant, although the dispersions of some bands are very different. Besides, we focus our attention only on the relative variation of the net charge distribution at atoms with the oxygen-atom vacancy at different positions in the lattice, and not on the dispersion of the bands. We believe that the results obtained by means of this approximation may be reliable, although they may be qualitative.

In this way, we have carried out a series of calculations at a particular K point ($K = 0$) in the new reduced BZ for a large unit cell containing an oxygen-atom vacancy. The coordinates of atoms in the cell used in the calculations were taken from [4]. For simplicity, we have also neglected the possible structural distortion caused by the oxygen-atom vacancy. In the tight-binding approximation based on the EHMO method, we have

Table 1. The orbital parameters used in the calculations.

	VOIP (eV)			Slater exponents		
	s	p	d	s	p	d
Tl	9.827	5.235		2.191	1.656	
Ba	4.287			1.236		
Cu	6.493	3.359	13.367	1.351	0.974	3.531
O	34.024	16.768		2.192	2.018	

used a modified Wolfsberg–Helmholz formula for reducing the counterintuitive orbital mixing in semiempirical and *ab initio* molecular orbital calculations [8]. Thus we can obtain more reliable Mulliken populations. The orbital parameters used in the calculations are listed in table 1. As figure 1 shows, although there are ten different positions that can be occupied by the oxygen atoms in a large unit cell, we need consider only five of them because of their equivalence.

The calculated net charges at atoms in the large unit cell are shown in table 2. It can be shown that the effect of the oxygen-atom vacancy at any position on the net charge at the Ba atom is very small. All the Ba atoms are highly ionic. Because some high unoccupied bands are mainly composed of the orbitals of these Ba atoms, the Ba–Ba layer in the *a*–*b* plane can be considered to be a strongly positively charged insulating layer. The oxygen-atom vacancy at any position can make the net charge at a Tl atom differ from that at another Tl atom, but the discrepancy between them is not very large. From the Mulliken population analysis, it is found that the chemical bond of the Tl atom with the O atom possesses a partial covalent character. Two polyhedra composed of the two Tl atoms and the neighbouring O(3) and O(2) atoms always possess an appreciable negative charge. The Cu–O(1) layer in the *a*–*b* plane possesses an appreciably negative charge and the chemical bond between the Cu atom and the O(1) atom has an apparent covalent character. We have noted that the effect of the oxygen-atom vacancy at any position on the net charge at the Cu atom is very significant. In particular, the oxygen-atom vacancy can cause the valence fluctuation at the Cu atom. It is very interesting that the net charge at a Cu atom is larger than +2, and that the charge at another Cu atom is less than +1. It has been found that both the Cu⁺³ cation and the Cu⁺¹ cation exist in YBa₂Cu₃O_{7-x}. It has also been considered that the valence fluctuation at the Cu atom may play a significant role in the high temperature superconductor. If it does, perhaps, as in YBa₂Cu₃O_{7-x}, then in TlBa₂CuO_{4.5} there may exist valence fluctuations at the Cu-atom site, and this may be caused just by the oxygen-atom vacancy in the lattice.

The calculated results show that the charge distribution in TlBa₂CuO_{4.5} possesses a specially layered character. That is, a highly ionic Ba–Ba insulating layer with strongly positive charge, lying along the *a*–*b* plane, is inserted between the negatively charged Tl–O layer (which is composed of two polyhedra of Tl and O atoms) and the more negatively charged Cu–O layer (where there is an appreciable valence fluctuation at the Cu atom). From the Mulliken population analysis, we have also found that the Tl–O layer and the Cu–O layer can be weakly coupled through the interaction of the O(2) atom with both the Tl atom and the Cu atom.

The electric field gradient at the oxygen-atom vacancy in the lattice is very interesting and helps in the understanding of the movement of both the electron and the hole in the lattice. Therefore, we have also calculated the electric field gradient created by the

Table 2. The net charges at atoms in a large unit cell of $\text{TlBa}_2\text{CuO}_5$ with an oxygen-atom vacancy at different positions in the lattice.

Tl	Ba	Ba	Cu(1)	O(1a)	O(1b)	O(2a)	O(2b)	O(3a)	Tl	Ba	Ba	Cu(2)	O(1c)	O(1d)	O(2c)	O(2d)	O(3b)
2.43	1.98	1.97	1.47	-1.77	-1.79	-1.72	-1.83	-1.81	2.70	1.98	1.97	1.18	-1.58	-1.80	-1.68	*	-1.68
2.55	1.97	1.97	1.80	-1.75	-1.78	-1.70	-1.82	-1.81	2.69	1.99	1.96	0.83	-1.59	-1.80	-1.68	-1.82	*
2.44	1.98	1.97	2.40	-1.70	*	-1.65	-1.83	-1.81	2.54	1.96	1.95	0.62	-1.91	-1.83	-1.60	-1.83	-1.70
2.43	1.98	1.97	2.31	-1.72	-1.72	-1.71	-1.83	-1.81	2.56	1.97	1.95	0.62	*	-1.79	-1.68	-1.83	-1.70
2.56	1.97	1.97	2.14	-1.73	-1.73	*	-1.83	-1.81	2.56	1.98	1.95	0.57	-1.61	-1.81	-1.68	-1.83	-1.69

* The oxygen-atom vacancy.

Table 3. The electric field gradient and the asymmetry parameter at different oxygen-atom vacancy sites in a large unit cell of $\text{TlBa}_2\text{CuO}_{4.5}$.

Site	O(1b)	O(2a)	O(1c)	O(2d)	O(3b)
V_{xx} (10^{21} V m $^{-2}$)	-0.896	-0.184	-0.158	-0.110	-0.486
V_{yy} (10^{21} V m $^{-2}$)	-0.290	-0.078	0.017	-0.032	0.104
V_{zz} (10^{21} V m $^{-2}$)	1.186	0.262	0.141	0.142	0.382
η	0.51	0.40	0.78	0.55	0.572

crystal field at the different sites of the oxygen-atom vacancy by means of the corresponding formula described in detail elsewhere [9]. First we calculated the nine elements (V_{ij}) of the tensor matrix of the electric field gradient from the crystal field; we then diagonalized the tensor matrix to obtain three principal components: V_{xx} , V_{yy} and V_{zz} . Because the calculated electric field gradient is that at the position of the oxygen-atom vacancy, and is not that at the atom, the Sternheimer factor will not be considered in the calculations. The calculated V_{xx} , V_{yy} and V_{zz} , as well as the asymmetry parameter $\eta = (V'_{xx} - V'_{yy})/V'_{zz}$ ($|V'_{xx}| \leq |V'_{yy}| \leq |V'_{zz}|$), are listed in table 3.

Sterne and Wang have pointed out that in the Bi-Sr-Ca-Cu-O system some two-dimensional character in the a - b plane is crucial for the high temperature superconductivity [7]. Since the Tl-Ba-Ca-Cu-O system is very similar to the Bi-Sr-Ca-Cu-O system, it may be reasonable to assume that only when V_{xx} along the a -axis direction and V_{yy} along the b -axis direction possess the same sign may such an electric field gradient be in favour of the movement of both the electron and the hole along the a - b plane. If this is true, the oxygen-atom vacancy at the position of the O(1c) and the O(3b) atoms may be detrimental to the high temperature superconductivity of $\text{TlBa}_2\text{CuO}_{4.5}$. We feel that perhaps the oxygen-atom vacancy at the position of the O(1b) atom may most greatly favour the high temperature superconductivity of $\text{TlBa}_2\text{CuO}_{4.5}$ because it is not only the oxygen-atom vacancy at the site of the O(1b) atom that can cause the largest valence fluctuation at the Cu atom, but also, the absolute values of all principal components, V_{xx} , V_{yy} and V_{zz} , of the electric field gradient are largest at the site of the O(1b) atom.

In summary, in the $\text{TlBa}_2\text{CuO}_{4.5}$ crystal, the charge distribution possesses a certain characteristic arrangement. That is, an insulating Ba-Ba layer with highly ionic charge separates two covalent layers with more negative charge: the Tl-O layer and the Cu-O layer, along the a - b plane. The oxygen-atom vacancy in the lattice can cause the change of the net charge distribution at atom sites and the valence fluctuation at the Cu-atom site. The results show that the oxygen-atom vacancy at some positions may favour the high temperature superconductivity, and that at other positions it may be detrimental to the high temperature superconductivity for the same material. Perhaps this is why the high temperature superconductivity of the material relates to its synthesis process.

References

- [1] Whangbo M-H, Evain M, Beno M A, Geiser U and Williams J M 1988 *Inorg. Chem.* **27** 467
- [2] Evain M, Whangbo M-H, Beno M A, Geiser U and Williams J M 1987 *J. Am. Chem. Soc.* **109** 7917
- [3] Curtiss L A, Brun T O and Gruen D M 1988 *Inorg. Chem.* **27** 1421

- [4] Liang J-K, Zhang Y-L, Hung J-Q, Xie S-S, Che G-C and Cheng X-R 1989 *Sci. China A* **32** 826
- [5] Sterne P A and Wang C S 1989 *J. Phys. C: Solid State Phys.* **21** L949
- [6] Dobrotvorskii A M and Evarestov R A 1974 *Phys. Status Solidi b* **66** 83
- [7] Evarestov R A, Petrashen M I and Ledovskaya E M 1975 *Phys. Status Solildi b* **68** 453
- [8] Ammeter J H, Burgi H-B, Thibeault J C and Hoffmann R 1978 *J. Am. Chem. Soc.* **100** 3686
- [9] Bancroft G M 1981 *Handbook of Spectroscopy* ed J W Robinson (Boca Raton, FL: Chemical Rubber Company)