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A Determination of the Oxidation States and Internal Stresses in $Ba_2YCu_3O_x$, $x = 6–7$ Using Bond Valences

I. D. BROWN

Institute for Material Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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A bond valence analysis of the title compound indicates that Cu^{1+} is found only on the Cu1 site but Cu^{3+} is found on both sites with a 25% occupancy on Cu2 and a 50% occupancy on Cu1 for $x = 7$. The analysis also predicts how the electron holes would be distributed over the four crystallographically distinct O atoms if they reside on the O rather than the Cu atoms. Modeling the two end members using Kirchoff-like network equations and a distance-least-squares refinement shows that the bonds most sensitive to Cu oxidation are those formed by Ba and that the structure is subject to internal stresses that are close to a ferroelastic instability at $x = 6$ and a ferroelectric instability at $x = 7$. © 1989 Academic Press, Inc.

1. Introduction

From the stoichiometry of $Ba_2YCu_3O_x$ (YBCO) one would expect, in addition to Cu^{2+}, to find Cu^{1+} present when $6.0 < x < 6.5$ and Cu^{3+} when $6.5 < x < 7.0$.

Is it possible to determine how the different oxidation states distribute themselves over the two Cu sites? This paper describes how the observed bonding geometry can be used to infer the distribution of the charges and to reveal the presence of internal stresses and potential instabilities in the two end members.

Information about the oxidation state of Cu comes from the length of the Cu–O bonds since higher oxidation states result in shorter bonds. Bond valences (s) are calculated from the bond lengths (R) using the equation

$$s = \exp((R_0 - R)/B), \quad (1)$$

where R_0 and B are constants whose values have been tabulated for many bond types (*1*). It has been shown (*2*) that for most inorganic compounds the sum of the bond valences around any atom lies within 0.1 of its formal oxidation state, a result that can be used to determine the oxidation states in mixed oxidation compounds such as YBCO (*3, 4*). This rule, known as the Valence Sum Rule, is obeyed in most compounds in which bonds are found only between atoms of opposite formal charge, regardless of whether the bonds are ionic or covalent in character. For convenience the terminology of the ionic model is retained in this paper without implying that the bonding is necessarily ionic.

Bond valence sums at Cu have been calculated for YBCO by Capponi *et al.* (*5*), Hewat *et al.* (*6*), and David *et al.* (*7*) for the structures whose determinations they report and by O'Keeffe and Hansen (*8*) for

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the two end members whose structures they also model. In YBCO with $x = 6.8$ to 7.0 Capponi *et al.*, Hewat *et al.*, and O'Keeffe and Hansen conclude that the Cu^{3+} is distributed (almost equally) between the two sites while David *et al.* conclude that it occurs only on the Cu1 site. The latter group appear to have made an addition error in calculating the valence sums around Cu2 but the results reported by the Grenoble group (*5*, *6*) and O'Keeffe and Hansen (*8*) are in general agreement with the present analysis though only the latter confirm their analysis by reporting the valence sums around all atoms.

While the results obtained in these earlier studies give an essentially correct picture of what happens in the end members, the analyses did not consider other compositions nor the difficulties inherent in applying the bond valence approach to YBCO. First, the structure of YBCO is highly constrained, having only as many free crystallographic parameters as it has crystallographically distinct atoms. Under these conditions the Valence Sum Rule is often not well obeyed and cannot be relied on. Second, the value of R_0 in Eq. (1) varies with the oxidation states of the two atoms that define the bond. Thus the calculated bond valence sum depends in part on an already assumed oxidation state. Third, there are not many well characterized oxides containing Cu^{3+} that can be used to determine R_0 for Cu^{3+}–O^{2-} bonds and there is some question as to whether the electron hole resides on the Cu or the adjacent O atoms. Against these difficulties the bond valence model provides a number of checks of internal consistency. The average Cu oxidation state determined from the bond valence sums (i.e., from the observed bond lengths) should lead to charge neutrality and the valence sums around the non-Cu atoms should be equal to their formal oxidation states.

In Section 2 of this paper the problem of determining the correct R_0 parameters is discussed. Section 3 describes the bond valence calculations and points out some consequences which are checked in Section 4 by modeling the end members of the series under various assumptions of charge distribution. The internal stresses which are revealed by these analyses are described and their consequences explored in Section 5 and Section 6 describes the charge distribution that is found. Section 7 summarizes the important conclusions of this study.

2. Determination of the Bond Valence Parameters R_0

Crucial to this analysis is the choice of the parameters R_0 and B in Eq. (1). Brown and Altermatt (*1*) have shown that B can be set to 0.37 for most, if not all, bonds and have determined values of R_0 for many cation–anion combinations including Cu^{2+}–O^{2-} (R_0 = 1.679 Å) by solving Eq. (2) for R_0,

$$V = \Sigma\, s_i = \Sigma\, \ln((R_0 - R_i)/0.37), \quad (2)$$

where the sum is taken over all the bonds, i, in a cation coordination sphere and V is set equal to the oxidation state of the cation. Values of R_0 for each of the known oxygen coordination spheres around a particular cation (e.g., Cu^{2+}) were averaged to give the reported values. A similar analysis of Cu^{1+} compounds gives R_0 = 1.60 Å. The determination of R_0 for Cu^{3+} is more difficult, partly because of the paucity of good structure determinations and partly because of uncertainty in the correct formulation of the atomic charges. Photoemission and Auger spectra of YBCO and similar compounds containing Cu^{3+} have been interpreted (*9*) as indicating that the copper is not in the d^8 configuration (corresponding to Cu^{3+}) but d^9 and that the electron holes are to be found in $2sp$ levels of the O atom. If the compound $NaCuO_2$ is formulated as $Na^+Cu^{2+}O^{1.5-}$ rather than $Na^+Cu^{3+}O^{2-}$ a different value of R_0 will be obtained.

Although values of R_0 can be calculated for both formulations of the oxidation state, the formulation with Cu^{2+} presents both conceptual and practical difficulties. One of the virtues of the bond valence approach is that the sum of the bond valences around any atom, whether cation or anion, is equal to the atom's formal oxidation state. In most compounds oxidation states are integers and are well defined by the usual rules of chemistry. Formulation of Cu in $NaCuO_2$ as Cu^{2+} requires a fractional (-1.5) oxidation state for O. In more complex structures where the O atoms are not all equivalent, the fractional oxidation states cannot be assigned *a priori* and one looses the ability to use the valence sums around the O atoms as a check on the consistency of the bond valence analysis. In addition, for bonds formulated as Cu^{2+}–O^{x-}, either a different value of R_0 must be found for each value of x or an appropriately weighted mean of R_0 for the (hypothetical) Cu^{2+}–O^{-} bond and R_0 for the Cu^{2+}–O^{2-} bond must be used. Given the small number of suitable structures for determining R_0, there are good computational reasons for staying with the simpler Cu^{3+} formulation. Fortunately there is an easy transformation between the two. Equation (1) can be rewritten to show that changing R_0 to R_1 scales the bond valences by $\exp((R_1 - R_0)/B)$ which, in this case, means multiplying the bond valences calculated for Cu^{3+} by $\frac{2}{3}$ (to give the correct valence sum at Cu).[1] It then follows that the valence sums at an O atom will be reduced in direct proportion to the total strength of the Cu–O bonds it receives and this in turn gives a prediction for the way in which the electron holes are distributed among the O atoms. Without loss of generality, therefore, the bond valences can be calculated by assuming the holes are on the Cu. The bond valences can then be transformed to the case where the holes are on O and the implications of this assignment can be explored.

A practical problem in determining R_0 arises from the lack of accurate structure determinations of compounds containing Cu^{3+}. Only compounds in which all the Cu is assigned as $+3$ and all the ligands are O can be used. Of the following compounds that satisfy these criteria, namely,

1. Li_3CuO_3 *(10)*
2. $LaCuO_3$ *(11)*
3. $SrLaCuO_4$ *(12)*
4. MCuO$_2$, M = Na, K, Rb, Cs *(13, 14)*
5. $KCu(IO_6H)_2O_2H_2(H_2O)_6$ *(15)*,

compounds 2 and 3 must be excluded as they are highly constrained (few free crystallographic parameters) and under these conditions the Valence Sum Rule cannot be relied on as discussed below. Compound 1 has a poorly refined structure (R = 0.11) with a Li–O distance that is clearly too short. It too should be excluded. This leaves five compounds, four of which are essentially isostructural, from which to derive the value of R_0. The isostructural series 4 gives R_0 = 1.739 Å and compound 5 gives 1.711 Å. The value of 1.73 Å is used in the following calculations.

3. Calculation of the Bond Valence Sums

Thirteen determinations of the structure of YBCO with differing values of x were examined. Because different authors use different labeling schemes for the O atoms, I have adopted a rational labeling scheme in which O*b* is the atom lying along the *b* direction, and O*c* is the atom lying along the *c* direction, from Cu1 (the origin). The atoms lying in the plane of Cu2 are labeled Op or Op*a* and Op*b* where Cu2–Op*a* lies along the *a* direction and Cu2–Op*b* lies along the *b* direction.

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[1] Strictly the ratio will be slightly different for each bond since R_1 will depend on the actual oxidation state of the terminal O atom. This difference will hardly be significant given the other uncertainties of the analysis.

Whenever possible room temperature studies were used but those for the compounds with $x = 0.42$ and 0.65 were available only at high temperature where the unit cell is thermally expanded. In these cases the bond distances were multiplied by 0.985 and 0.990, respectively, to simulate room temperature values.

Bond valences were determined from the bond lengths using Eq. (1). B was taken as 0.37, values of R_0 used for Cu^+ and Cu^{3+} are those given above. Values of R_0 for other atoms were taken from (*1*). As a check bond valence sums were calculated around all atoms (Table I). Valences around Cu were initially calculated on the assumption that all Cu atoms were Cu^{2+}. Deviations of the valence sums from 2.0 at the Cu sites were taken to be *prima facie* evidence of partial occupation by Cu^{1+} or

TABLE I

VALENCE SUMS CALCULATED WITH THE Cu^+, Cu^{2+}, AND Cu^{3+} OCCUPANCIES GIVEN IN TABLE IV (EXPECTED VALUES IN PARENTHESES)

x	Cu1	Cu2	Y	Ba	Ob	Oc	Opa	Opb
	*	*	(3.00)	(2.00)	(2.00)	(2.00)	(2.00)	(2.00)
6.0	1.17	2.06	2.78	1.75	—	1.74	2.02[a]	
6.0	1.18	2.09	2.86	1.81	—	1.77	2.07[b]	
6.0	1.19	2.10	2.90	1.82	—	1.79	2.09[c]	
6.20	1.53	2.08	2.88	1.86	*1.52*	1.85	2.05[d]	
6.42	1.86	2.04	2.80	1.93	*1.59*	1.90	1.99[e]	
6.65	2.00	2.10	2.90	2.07	*1.63*	1.92	2.05	2.10[e]
6.77	2.11	2.16	2.88	2.06	*1.74*	1.97	2.04	2.03[a]
6.79	2.08	2.20	2.89	2.18	*1.75*	1.98	2.07	2.05[f]
6.81[g]	2.24	2.12	2.82	2.14	*1.82*	2.00	*2.03*	2.01[h]
[i]	2.09	2.20	2.82	2.14	*1.80*	1.99	2.05	2.03
6.85[g]	2.40	2.09	2.90	2.14	1.85	2.03	*2.04*	2.02[j]
[i]	2.17	2.21	2.90	2.14	*1.81*	2.02	2.06	2.04
6.91	2.19	2.23	2.90	2.19	*1.83*	2.01	2.07	2.05[k]
6.93	2.30	2.19	2.88	2.17	*1.83*	2.03	2.04	2.02[a]
7.00	2.38	2.20	2.88	2.20	1.85	2.04	2.04	2.03[f]

Note. The italicized valences correspond to sites that are partially vacant.

* See Table IV for expected values of Cu valence sums.

[a] Ref. (*6*).

[b] A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, *Mater. Res. Bull.* **22,** 1007 (1987).

[c] C. C. Torardi, E. M. McCarron, P. E. Bierstedt, A. W. Sleight, and D. E. Cox, *Solid State Commun.* **64,** 497 (1987).

[d] K. Kamaras, C. D. Porter, M. G. Doss, S. L. Herr, D. B. Tanner, D. A. Bonn, J. E. Greedan, A. H. O'Reilly, C. V. Stager, and T. Timusk, *Phys. Rev. Lett.* **59,** 919 (1987).

[e] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36,** 3608 (1987).

[f] F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, *Phys. Rev. B* **35,** 8778 (1987).

[g] Using authors' occupation numbers for O.

[h] M. A. Beno, L. Soderholm, D. W. Capone II, D. C. Hinks, J. D. Jorgensen, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, *Appl. Phys. Lett.* **51,** 57 (1987).

[i] All O vacancies assumed to be on the Ob site.

[j] Ref. (*7*).

[k] M. Francois, E. Walker, J.-L. Jordan, K. Yvon, and P. Fischer, *Solid State Commun.* **63,** 1149 (1987).

Cu^{3+}. Bond valences were then calculated with Cu as Cu^+ or Cu^{3+} as appropriate and new valence sums around Cu determined. The proportion of Cu^{3+} (y) on the site was determined using the equation

$$y = (V_2 - 2)/(V_2 + 1.0 - V_3), \quad (3)$$

where V_2 is the valence sum at Cu calculated with $R_0 = 1.679$ and V_3 is the valence sum with $R_0 = 1.730$. A similar expression was used to determine the fraction of Cu^+ in the cases where it was present.

The valence sums around all atoms are listed in Table I. Those around Y, Op*a* and Op*b* remain close to 3.0 and 2.0, respectively, at all values of x. The valence sum around O*b*, the site that is assumed to contain the vacancies, falls as the O atoms are removed, indicating a tendency for the atoms to relax away from the vacant sites. The valence sums around O*c* and Ba also drop as x decreases, but the valence sums around the Cu atom, while dropping in absolute terms, increase relative to their expected value as shown in Fig. 1. The discrepancy around the Cu atoms could be removed (for $x > 6.5$) by using $R_0 = 1.753$ Å for the Cu^{3+}–O^{2-} bond (a value that is unacceptably large), but the behavior shown in Fig. 1 is typical of crystals with internal stress and suggests that the discrepancy arises, not from an incorrect choice of R_0, but from the inability of the highly constrained structure to relax sufficiently to satisfy the Valence Sum Rule. In order to test this hypothesis the two end member structures were modeled to see if these deviant valence sums were reproduced.

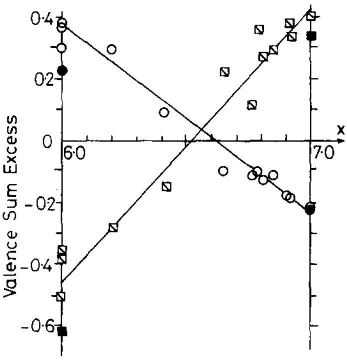

FIG. 1. Differences between the observed valence sums and the oxidation states for Ba (squares) and Cu (circles) per formula unit (Ba_2Cu_3). Open figures are from experiment, the solid figures are from the models (Tables II and III).

4. Modeling the Structures

In order to examine the effects of the geometric constraints the two end member YBCO structures were modeled with the program STRUMO (*16*) using the Kirchhoff network equations (which predict bond distances that satisfy the Valence Sum Rule) and Distance Least-Squares (DLS, which finds the atomic coordinates that minimize the difference between the predicted and observed bond lengths weighted according to the bond valence). The Kirchhoff equations predict the bond valences by distributing the atomic valences as uniformly as possible between the bonds consistent with the Valence Sum Rule. Bond lengths predicted by this procedure usually agree to within 0.05 Å with those observed provided that the atoms show no special electronic effects such as the Jahn-Teller distortion which is observed around Cu2.[2] In order to allow for this effect the valence of the Cu2–O*c* bond was held at its observed value. In the DLS refinement the bond distances predicted by the Kirchhoff analysis provide sufficient constraints (6 and 11 respectively for $x = 6$ and 7) to determine all the variable atomic coordinates (4 and 6 resp.). The lattice parameters were fixed at their observed

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[2] The presence of a Jahn-Teller distortion is usually indicated by an atom having a lower site symmetry than might have been expected. In the case of YBCO its presence is indicated by the fact that, without using the constraint described in the text, the Kirchhoff equations predict that Cu–O*c* will be *shorter* than Cu–Op, as originally noted by O'Keeffe and Hansen (*8*).

values and no nonbonding distances were used as targets. The results are summarized in Tables II ($x = 6.0$) and III ($x = 7.0$). In the latter table three models are developed *a*) with Cu^{3+} only on the Cu2 site, *b*) with Cu valence distributed as shown in Table IV and *c*) with Cu^{3+} only on the Cu1 site. The values calculated from the Kirchhoff analysis are given on the left and those from the DLS refinement in the center. The observed values are given on the right. Although for the Kirchhoff predictions, the valence sums are required to be equal to their ideal values, there is no guarantee that the predicted distances can actually be realized within the constraints of the observed unit cell. The DLS calculation gives the best fit that is possible in the real crystal and reflects the constraints that apply to the observed structure. In all cases the DLS calculation yields both bond lengths and valence sums that are much closer to the observed values than are those of the Kirchhoff analysis, supporting the idea that the discrepancies arise from the constrained nature of the crystal structure. The DLS model for $x = 6$ (Table II) shows, as observed, a valence deficit on Ba and O*c* and a valence surplus on Cu2. For $x = 7$ (Table III) model *a* gives the poorest fit with experiment and, although models *b* and *c* appear to be similar, model *b* best reproduces the sensitive Ba–O bonds. The true valence distribution thus lies close to the values given in Table IV (corresponding to model *b*) but the possibility of a higher Cu^{3+} content on the Cu1 site cannot be ruled out. One unexpected result of developing the above three models is the discovery that, because of the change of R_0 with oxidation number, the Cu–O bond lengths are not as good indicators of the Cu oxidation states as the Ba–O bonds. The filled points in Fig. 1 represent the results of the model calculations (model *b* in the case of $x = 7$). They show the success of the models in reproducing the deviations of the observed valence sums from their expected values and confirm that it is the internal stresses arising from the constrained structure that are responsible.

TABLE II

MODELING OF THE STRUCTURE OF $Ba_2YCu_3O_6$

	Kirchhoff model	DLS model	Observed
	Distances (Å)		
Ba–O*c*	2.68	2.74	2.78
Ba–O*p*	2.98	3.03	2.91
Y–O*p*	2.38	2.39	2.40
Cu1–O*c*	1.86	1.86	1.79
Cu2–O*c*	*2.47*	2.44	2.47
Cu2–O*p*	1.96	1.94	1.94
rms(obs − calc)	0.06	0.06	
	Bond valence sums		
Ba	*2.00*	1.69	1.81
Y	*3.00*	2.96	2.86
Cu1	*1.00*	1.00	1.18
Cu2	*2.00*	2.11	2.09
O*c*	*−2.00*	−1.78	−1.77
O*p*	*−2.00*	−2.00	−2.07
rms(obs − calc)	0.17	0.10	

Note. Values in italics were assumed in the calculation.

5. Internal Stress in YBCO

The ideal pervoskite structure (ABO_3) can be used as a model for the internal stresses in YBCO. Perovskites consists of two components, a large atom (A) that occupies the middle of a cubic cage (BO_3). If the A atom is too large for the cage (indicated by valence sums at A that are larger, and at B that are smaller, than expected), the cage is in tension and the A atom in compression. If A is too small, the situation is reversed. If the valence sum at each cation differs by more than 0.2 from its ideal value (see Figs. 5 and 6 of (*3*)) the cubic structure is distorted either by the B atom moving off center in its octahedron (when A

TABLE III

MODELING $Ba_2YCu_3O_7$

	Kirchhoff model			DLS model			Observed		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
				Distances (Å)					
Ba–O*c*	2.71	2.75	2.79	2.72	2.74	2.76		2.74	
Ba–O*b*	2.78	2.87	2.99	2.76	2.84	2.95		2.87	
Ba–Op*b*	3.36	3.09	2.94	3.09	3.00	2.90		2.96	
Ba–Op*a*	3.36	3.09	2.94	3.16	3.06	2.95		2.98	
Y–Op*b*	2.38	2.38	2.38	2.38	2.38	2.37		2.41	
Y–Op*a*	2.38	2.38	2.38	2.37	2.38	2.38		2.38	
Cu1–O*b*	1.96	1.90	1.86	1.94	1.94	1.94		1.94	
Cu1–O*c*	1.92	1.86	1.81	1.91	1.86	1.81		1.85	
Cu2–O*c*	*2.30*	*2.30*	*2.30*	2.29	2.30	2.27		2.30	
Cu2–Op*b*	1.94	1.94	1.97	1.95	1.96	1.97		1.96	
Cu2–Op*a*	1.94	1.94	1.97	1.93	1.94	1.95		1.93	
rms (obs − calc)	0.18	0.06	0.05	0.07	0.03	0.03			
				Bond valence sums					
Ba	*2.00*	*2.00*	*2.00*	2.19	2.17	2.17		2.20	
Y	*3.00*	*3.00*	*3.00*	3.04	3.01	3.01		2.88	
Cu1	*2.00*	*2.50*	*3.00*	2.04	2.38	2.56	2.06	2.38	2.59
Cu2	*2.50*	*2.25*	*2.00*	2.48	2.20	2.12	2.29	2.20	2.14
O*c*	*2.00*	*−2.00*	*−2.00*	−1.97	−2.05	−2.09	−2.01	−2.04	−2.09
O*b*	*2.00*	*−2.00*	*−2.00*	−2.10	−1.95	−2.03	−1.80	−1.85	−1.94
Op*b*	*2.00*	*−2.00*	*−2.00*	−2.07	−2.01	−2.00	−2.06	−2.03	−1.99
Op*a*	*2.00*	*−2.00*	*−2.00*	−2.13	−2.04	−1.97	−2.09	−2.04	−2.01
rms (obs − calc)	0.16	0.11	0.18	0.14	0.06	0.06			

Note. Values in italics were assumed in the calculations.

is too large) giving rise to a ferroelectric phase (e.g., $BaTiO_3$) or by the cage collapsing by a rotation of the octahedra (when *A* is too small) giving rise to a ferroelastic phase. In both cases the environment of the cation that is in tension is distorted, a procedure that can increase its valence sum without changing its average bond length (*2*). Undistorted cubic perovskites are quite rare and are only found when the valence sums of the cations in the cubic phase lie close to their ideal values.

The structure of YBCO is composed of oxygen deficient slabs of perovskite-like material having a thickness of two cubes (in the *c* direction) but extending indefinitely in the *a* and *b* directions. The Ba atoms lie in the cavities of the Cu_3O_x cages. At $x = 6$ the cavity is larger than the Ba ion as indicated by the low valence sums illustrated in Fig. 1, but for $x = 7$ the cavity is smaller than the Ba ion, the fit being perfect somewhere around $x = 6.55$. The change in size arises from the decrease in the Cu ionic radius with increase in oxidation state and the increase in the Ba ionic radius with coordination number. The magnitude of the discrepancies between the observed and expected valence sums shown in Fig. 1 suggests that the structures of both end members are close to instability. At $x = 6$ the Ba atom is in a cavity that is too large. The resulting stress would be relieved by a collapse of the cages (e.g., by a ferroelastic rotation of the

TABLE IV

Percentage of Cu^+, Cu^{2+}, and Cu^{3+} Found on the Cu1 and Cu2 Sites for Different Oxygen Contents Derived from the Valence Sums at Cu Corrected for the Expected Under- and Over-bonding Shown in Fig. 1

		Cu1				Cu2			
x	x'	Cu^+	Cu^{2+}	Cu^{3+}	Expected valence	Cu^+	Cu^{2+}	Cu^{3+}	Expected valence
6.00	5.97	95	5	0	1.05	5	95	0	1.95
6.20	6.22	57	43	0	1.43	0	100	0	2.00
6.42	6.41	18	82	0	1.82	0	100	0	2.00
6.65	6.63	0	99	1	2.01	0	88	12	2.12
6.77	6.77	0	84	14	2.14	0	80	20	2.20
6.79	6.80	0	90	10	2.10	0	75	25	2.25
6.81	6.81	0	89	11	2.11	0	75	25	2.25
6.85	6.88	0	79	21	2.21	0	73	27	2.27
6.91	6.91	0	76	24	2.24	0	71	29	2.29
6.93	6.93	0	62	38	2.38	0	76	24	2.24
7.00	7.00	0	51	49	2.49	0	75	25	2.25

Note. x is the oxygen content determined from the diffraction stoichiometry and x' is the oxygen content required to neutralize the Cu distribution shown. The expected valences are those implied by the oxidation state distribution given. They should be compared with the valence sums given in Table I.

CuO_4 planes) to lower the symmetry around Ba as pointed out by O'Keeffe and Hansen (*8*). At $x = 7$ the Ba atom is in a cavity that is too small. The resulting tension in the Cu_3O_x cages is already partially relieved by the orthorhombic distortion which both lengthens the Cu1–Ob bond and increases the average Cu2–O bond length through the distortion it produces in the environment of Cu2. The distribution of the Cu^{3+} over both sites probably also helps to relieve the stress. None the less, the Cu atoms are still in cavities that are too large. Relief could be accomplished by a transformation that increases the range of Cu–O distances such as a ferroelectric displacement of the Cu atoms from the centers of their coordination spheres.

6. Valence Distribution in YBCO

Table IV gives the best estimates of the valence distribution in the structures examined though, as noted above, there may be more Cu^{3+} on the Cu1 site. The same results, expressed in terms of the apparent oxidation states of the two Cu atoms, are shown in Fig. 2. The distributions in Table IV were calculated using Eq. (3) with valence sums corrected (using the straight lines in Fig. 1) for the effects of internal stress. They give a satisfactory prediction of the stoichiometry as shown by a comparison of x and x' in Table IV.

In agreement with the previous studies (*8*, *17*) Cu^{1+} occupies the Cu1 site exclusively but is gradually replaced by Cu^{2+} as x increases from 6.0 to 6.5. Because of the relatively small differences in the geometry at different values of x, the changes that occur in the valence sums at Cu result almost entirely from changes in the occupation numbers of the O atoms. Reducing the occupation number of an O atom by 0.1 reduces the apparent valence of each adjacent Cu atom by the same amount. Since there is some disagreement between authors about which O site contains the va-

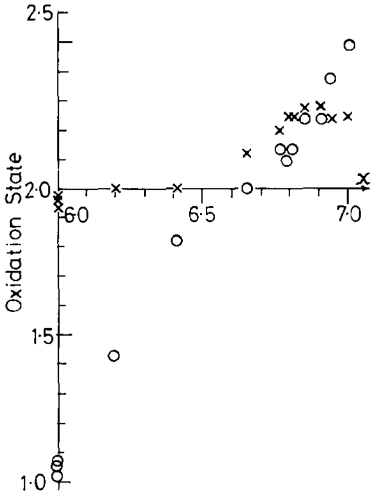

FIG. 2. Apparent oxidation state (vertical axis) of Cu1 and Cu2 as a function of x, the oxygen content (horizontal axis). The circles refer to the Cu1 site, the crosses to Cu2. Oxygen vacancies are all assumed to occur at the Ob site.

cancies, there are problems in calculating accurate valences for the Cu sites. In this analysis I have assumed that the vacancies all occur on the Ob site though Table I also includes the valence sums calculated assuming the authors' assignments of occupation numbers where these are different. If the vacancies were to occur only on Ob and if the bond lengths were not to change with x, then the valence of the Cu1 site would change linearly from 1.0 at $x = 6.0$ to 3.0 at $x = 7.0$. Over most of this range the bond lengths indeed do not change, but between $x = 6.5$ and 6.75 the Cu1–Oc bond becomes 0.05 Å longer and the Cu2–Oc bond becomes 0.15 Å shorter with the result that for $6.50 < x < 6.75$ the valence of Cu1 lies about 0.1 valence units below that of Cu2. For $6.75 < x < 7.0$ the geometry again remains fixed and the additional electron holes move onto Cu1. At $x = 7.0$ the formal charge of Cu1 has increased to 2.50 while that of Cu2 remains at 2.25 as shown in Fig. 2. If the O vacancies occur on the Opa sites, as has been suggested by some of the authors, the charge on Cu1 would tend to remain higher than that on Cu2 but, in any case, both sites would be partially occupied by Cu^{3+} and both models predict the same charge distribution at $x = 7.0$. The modeling of the structure with $x = 7$ under the assumption of three different valence distributions confirms the distribution and indicates its accuracy.

According to Auger and photoemission spectroscopy (*9*), the electron holes do not, in fact, reside on the Cu atoms as assumed in this analysis but, as pointed out above, this does not invalidate the analysis. On the contrary, the analysis, suitably modified, provides the opportunity of determining the distribution of holes over the different oxygen atoms in the unit cell. By reducing the bond valences by a factor of $\frac{2}{3}$ and calculating the change produced in the valence sums at the O atoms it is found that at $x = 7.0$, and about 0.2 electron holes are expected on Ob, 0.15 on Oc, 0.12 on Opa, and 0.10 on Opb.

7. Conclusions

The present analysis shows that bond geometry can be used as a tool for determining the distribution of electron holes even in a constrained crystal such as YBCO. It cannot determine whether the holes are on the Cu or the O atoms, but it can determine which bonds they are associated with. In the case of crystals like YBCO that are crystallographically constrained, the bond valence sums may not correspond well to the actual oxidation states of the ions and a careful analysis of all the valence sums and a modeling of the structure under various assumptions is needed to obtain a full understanding of the charge distributions. Such an analysis also reveals the nature of the internal stresses in the crystal and its incipient instabilities.

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