

# New Type of Orthorhombicity and Cell Volume Expansions near Half Filling of O Intercalation in $\text{ErBa}_2\text{Cu}_3\text{O}_{6.5}$

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Novel orthorhombics are observed on special processing near half filling of the O intercalation in  $\text{ErBa}_2\text{Cu}_3\text{O}_y$ . They are based on local configuration  $(m)n = (1)3$ , where  $m$  is the Cu site and  $n$  its O coordination and designated O(1)3. Specially sequenced getter annealing with slow cooling produces O(1)3 in a region where conventionally prepared materials are based on O(1)4(1)2, corresponding to a mix of four- and twofold O coordination. These O(1)3 can exist as cell volume neutral ( $V^0$ ) materials resembling the volumes of the tetragonal semiconductors. In a narrow region near  $y = 6.46$ , O(1)3 can undergo strong, nearly isotropic cell volume expansions ( $V^+$ ). These materials are larger than their cell volume contracted ( $V^-$ ) O(1)4 counterparts and even larger than the semiconductors at  $y = 6$ . These observations enlarge the phase diagram and pose new questions concerning the general origin of redox processes in superconducting O intercalation cuprates. These questions are discussed based on bond valency calculations. For the cell volume expanded materials a charge rebalancing between Cu and O leading to massive self-doping is suggested. © 1998 Academic Press

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## INTRODUCTION

A general feature in the O intercalation compound  $\text{RBa}_2\text{Cu}_3\text{O}_y$  ( $R =$  selected rare earths and Y) is the transition from semiconducting cell volume neutral (designated  $V^0$ ) to what is conventionally considered hole superconducting. This transition involves a shrinkage of the unit cell volume (designated  $V^-$ ). Due to the rather abrupt onset of orthorhombicity and concomitant development of local environment  $(m)n = (1)4$ , where  $m$  designates the Cu site and  $n$  its O coordination, this shrinkage can occur in an almost steplike manner under equilibrating preparative conditions (1–3). It was considered to mark the transition from charge localization of  $2+$  on one of the Cu sites (Cu(2)) to delocalization with O becoming partly oxidized to  $\text{O}^-$  or, formally speaking, the charge on Cu(2) rapidly increasing to  $>2+$  (Cu is not actually observed with valence  $>2+$ ). In these transitions the other Cu site (Cu(1)) acts as a charge balance (3). Interestingly, no symmetrical behavior at lower  $y$  for

delocalized charge on Cu(2) with  $<2+$  has yet been observed in unsubstituted systems containing apical O, although it was predicted (3) from a local model based on spatial arguments and (1)3 environment. This theoretically possible behavior would correspond to aspects of electron doping and result in  $V$  increases (denoted  $V^+$ ) due to the placing of electrons into antibonding orbitals or the involvement of the larger, reduced Cu ion. Such behavior and the accompanying electron rather than hole superconductivity had so far been reported (4,5) only for systems without apical O, such as  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_y$  and  $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ .

Here we give indications for rather abrupt transitions between  $V^0$ ,  $V^+$ , and  $V^-$  near  $y = 6.5$  in a system with apical O, namely  $\text{ErBa}_2\text{Cu}_3\text{O}_y$ , near  $y = 6.46$ , for which a brief account has been given (6). These results correspond to transitions from hole to what is conventionally considered to correspond to electron doping, with an implicit understanding that holes reside on O and that the actual effective doping as reflected, e.g., in the Hall effect has not been established. The relevant  $V^+$  increases exceed even the  $V$  of the terminal phase with  $y = 6.0$ . These  $V^+$  grow out of newly developed orthorhombics based on (1)3 designated O(1)3. The origins of these transitions are discussed based on bond valence calculations for individual local configurations using existing structural data. It is demonstrated that bond valences on all local configurations involving chain Cu(1) show a rather spontaneous reduction with increasing  $y$  near  $y = 6.5$  in the  $V^0$  to  $V^-$  transition. This Cu(1) reduction oxidizes the plane Cu(2) site, reflecting an expanded charge balance idea not yet noticed in averaging nonlocal calculations. Conversely, the reduction of Cu(2) for lower values of  $y$  involves strong basal plane expansions and a self-doping charge rebalancing.

Previously we designed, through partial Ni substitution, an increased range in  $y$  for new (1)3 orthorhombic  $\text{YBa}_2(\text{Cu}_{0.95}\text{Ni}_{0.05})_3\text{O}_y$  (due to (1)4 chain breaking of random square planar Nid8) in order to search, in these ordered materials, for  $V^+$  effects connected with electron doping or charge localization. Anomalous  $V$  expansions were indeed observed (7–9) for these materials

upon quenching from about 1000 K. Also, when yet more deoxygenated materials were slowly reoxygenated, even more remarkable  $V$  expansion was observed as a temporal effect, and these  $V^+$  orthorhombics were bulk superconductors with  $T_c$  roughly equal to their  $y = 7$  counterparts (9). They lost their  $T_c$  on further oxygenation only to regain it in the final stages of oxygenation. Moreover, memory effects of these  $V$  expansions were encountered. When reduced orthorhombic materials were oxidized at low temperatures, they decreased  $V$  only moderately and remained nonsuperconducting in  $y$  regions, where their conventionally prepared counterparts are superconducting. We became interested, therefore, in whether such behavior is more general and also germane to nonsubstituted materials, in which the origin of these effects could perhaps be more clearly established. We chose  $R = \text{Er}$  because small  $R$  exhibits (2) a larger homogeneous region of orthorhombic phase, which may be implicated in this behavior.

### EXPERIMENTAL

Materials were initially prepared by prolonged calcining at 1150 K and sintering at 1225 K, with subsequent slow cooling in flowing  $\text{O}_2$ . Pieces on the order of 1 g were then getter annealed at 1000 K with measured amounts of Gd in enclosed quartz ampoules and cooled over several days to room temperature (selected variations of this technique also produced  $V$  expansion phenomena, although preparation detail is delicate and will be described elsewhere). Weight monitoring of the  $\text{Gd}_2\text{O}_3$  and the sample established  $y$  in reasonable accord with each other.

### RESULTS

X-ray powder diffraction yields lattice parameters as presented in Fig. 1 together with neutron diffraction data (2) of materials obtained by a vacuum ( $\sim 1000$  K)–reoxygenation (700 K) procedure. Agreement is satisfactory for  $y > 6.5$ . However, in our getter annealed materials, orthorhombic structures with larger  $c$ -axis characteristic of localized tetragonal are observed for  $y < 6.5$ , which we attribute to O(1)3. These materials also show averaged basal plane dimensions slightly larger than those of conventional O(1)4(1)2 materials. As outlined below, our getter annealed materials are also different in that they are nonsuperconductors. To further demonstrate their distinctive nature, we show that they do not liberate  $\text{O}_2$  from acidified  $\text{H}_2\text{O}$ . For this purpose we employ earlier observations (10,11) of  $\text{O}_2$  liberation in dilute acid in the presence of nominal  $\text{Cu}^{3+}$  only. We measure the dissolution of pulverized material in dilute HCl with pH 1.20 and the amount of  $\text{O}_2$  liberated according to  $2\text{Cu}^{3+} + \text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+$ . Oxide dissolution also produces  $\text{OH}^-$ , so the overall rise in pH can also be used as a quantitative measure or corroboration of

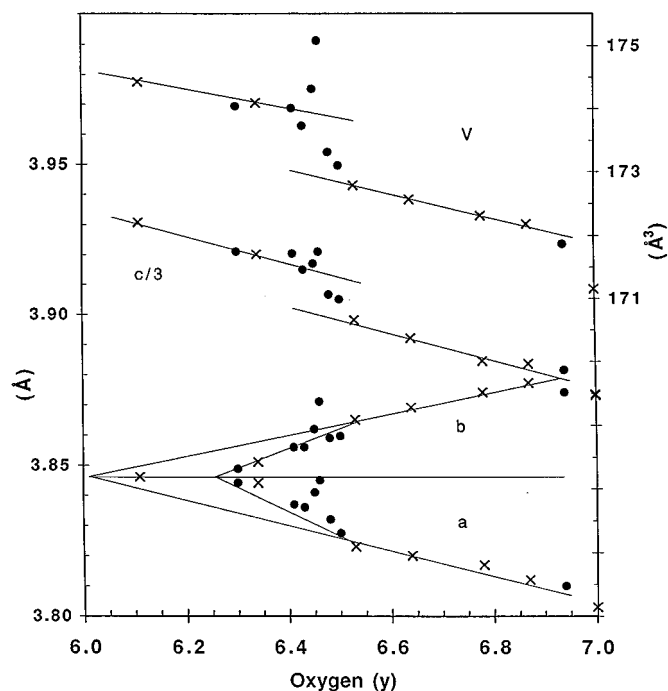


FIG. 1. Lattice parameters as a function of  $y$  in getter annealed (1000 K)  $\text{ErBa}_2\text{Cu}_3\text{O}_y$ . Crossed symbols correspond to neutron diffraction data of Ref. (2). Lattice expansions are observed for  $y = 6.45$  and  $y = 6.46$ , which are attributed to electron doping into antibonding  $x^2-y^2$  orbitals (designated On).

nominal  $\text{Cu}^{3+}$ . For O(1)3 in this study, we do not observe  $\text{O}_2$  within an error of about 5%.

In addition, materials with decreasing  $y$  (from the same initial batch) centered in a narrow range around  $y = 6.46$  show strong  $V$  expansions even beyond those of the tetragonal phase with  $y \sim 6.0$ . The  $V$  expansion is on the same order as the  $V$  shrinkage for  $y = 6.5$  compared to the extrapolated  $V$  of the tetragonal phase. The calibrated (Si) X-ray powder patterns indicate that the well-defined, fully comparable orthorhombic structure develops for the  $V$ -expanded phase. Similar patterns are obtained after additional air exposure at room temperature for about a month, although this exposure has resulted in a further, smaller  $V$  expansion involving predominantly the  $c$  axis, indicating relative stability for the materials. The X-ray patterns allow an unproblematic determination of lattice parameters, such that all reflections are accounted for. A telltale region of the pattern is shown in Fig. 2 in comparison with related structures. The  $V$  expansions derive from both the axis and especially the basal plane and are discussed here as formally representing electron doping on Cu (designated On for negatively doped orthorhombic). At lower  $y$ ,  $V$  shrinks and then increases to values characteristic of the tetragonal range, which indicates localized orthorhombics (Ol). Magnetization measured by a SQUID indicates the rather

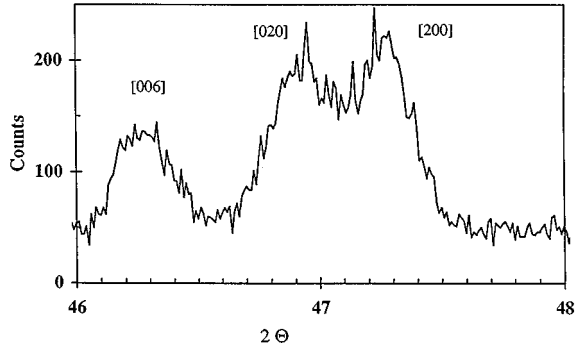


FIG. 2. X-ray powder pattern for the range including [006], [020], and [200] reflections for  $V$ -expanded  $\text{ErBa}_2\text{Cu}_3\text{O}_{6.46}$  (designated On).

abrupt disappearance of bulk superconductivity for  $y < 6.48$  (Fig. 3). Small (0.1%) superconducting volume fractions with  $T_c \sim 10\text{--}15\text{ K}$  appear in the  $V$ -expanded phases, as seen by hysteretic magnetization. They may be connected with  $n$ -type superconductivity. However, these fractions could also represent  $p$ -type superconductivity originating through O-enriched regions. In related studies on  $\text{YBa}_2(\text{CuNi})_3\text{O}_{6.5}$  we find (8) that  $V^+$  varieties can have bulk  $T_c$  slightly higher than the maximum values of their hole-doped,  $V^-$  counterparts. When further oxidized, this  $T_c$  of  $V^+$  is first lost and subsequently regained as  $p$  type. We except that a similar situation will also hold for the present system after suitable optimization, as  $n$ -doped bulk superconductivity can delicately depend on stoichiometry (5). Assuming a calibrating relation  $T_c = 644h/y = 92\text{ K}$  for Op and O hole density  $h = 1$  for both Op and On, we expect  $T_c = 99\text{ K}$  for On.  $T_c$  is larger due to the smaller number of O over which holes are distributed.

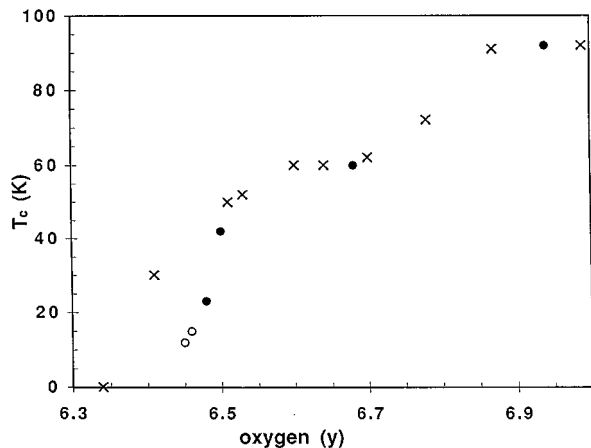


FIG. 3.  $T_c$  (K) vs oxygen content in  $\text{ErBa}_2\text{Cu}_3\text{O}_y$ . Crossed symbols are from Ref. (2). Circles correspond to getter annealed materials. Filled symbols correspond to bulk superconductivity. The line indicates the extrapolative rule of Ref. (3). The  $T_c$  collapse near  $y = 6.5$  reflects the charge disproportionation from  $p$ - to  $n$ -type and localized.

Preliminary measurements of thermoelectric power on not-yet-optimized,  $V$ -expanded materials gave positive Seebeck coefficients (60 mV/K at 290 K), indicating a small net amount of hole carriers. However, because at  $y = 7$  the Seebeck coefficient is negative (12), electron doping is indicated at face value. The situation is complicated by the competing contributions of the two Cu sites and holes on O. It has been suggested that for the  $p$ -doped  $y = 7$  material, the Cu(1) band camouflages the Cu(2) band (12). These complications indicate how questionable even conventional doping assignments really are and that we use them in addition to the  $V$  effects mainly as a convenience.

In independent experiments, we employed a stoichiometric reoxygenation technique. Materials quenched from 1123 K into liquid  $\text{N}_2$  were exposed to a measured volume of air at 650 K for about a week. This also produced O(1)3 for  $y < 6.5$  with a lack of  $\text{O}_2$  evolution in dilute HCl. However, in one batch of samples a small piece of fully oxygenated  $\text{ErBa}_2\text{Cu}_3\text{O}_{y-7}$  was also included. After equilibration, samples which were oxidized in the process showed O(1)3, while the material which was reduced in the process still displayed the characteristics of O(1)4 near  $y = 6.5$ . This could indicate a hysteretic first-order-type transition between O(1)3 and O(1)4. Only through oxidative processes starting from materials without O(1)4 can O(1)3 near  $y = 6.5$  (at these relatively low temperatures) be achieved. Hysteresis effects on reductive processes are expected to extend the stability of O(1)4 to far below  $y = 6.5$ . In this setup, the kinetics of O uptake and desorption can also play a role. In similar experiments at  $T = 823\text{ K}$ , samples are more nearly the same, although the reduced sample being reoxidized shows a larger tetragonal unit cell, again suggesting hysteresis in the structural development.

## DISCUSSION

In the following we will discuss the electronic nature of the new O(1)3 materials with reference to bond valence calculations. The structural properties incurred on hole doping have been studied for, among others,  $\text{RBA}_2\text{Cu}_3\text{O}_y$  with  $R = \text{Y, Er, etc.}$ , e.g., through neutron diffraction (1, 2). The salient feature is the distance  $d_2$  of the apical O to the Cu(2) site. Bond valence calculations (1) show that the Cu(2) site becomes oxidized when  $d_2$  becomes small. Superconducting properties scale with the bond valence on Cu(2) and inelastic scattering (13) corroborates charge transfer. In this accounting no reciprocity was assumed with the overall bond valence on Cu(1). It was stated that a complex redox mechanism appears at play. In the search for this complex redox mechanism an enlarged analysis of the data was attempted considering the individual contribution of local environments ( $m$ ) $n$  (3). This leads to extrapolative laws concerning hole density and  $T_c$  as a result of the competition between (1)2 and (1)4, with discontinuities when one

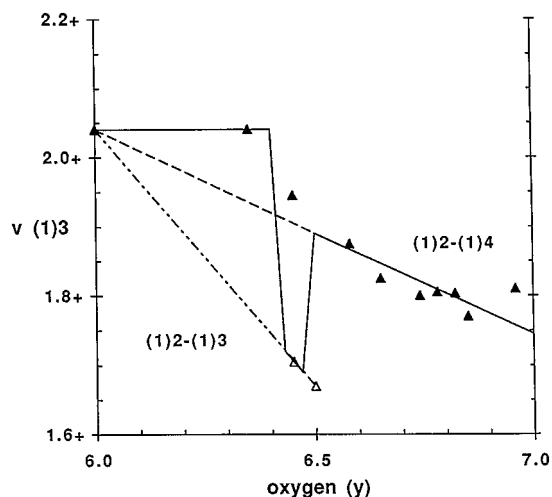


FIG. 4. Bond valence  $v$  for local configurations  $\Delta(1)3$ . The open symbols represent predicted values. The lines correspond to extrapolative rules (Ref. 3) derived from (1)4-(1)2 and (1)3-(1)2 competition.

component becomes a majority and forces its properties on minorities.

Here we demonstrate for the first time the general trends in bond valence of the configuration (1)3 as a function of oxygen content ( $y$ ). Below we show that it is plausible that this configuration and its special redox capabilities are instrumental in bringing about the  $V$ -expanded state. The general trends also extend to (1)2 and (1)4, illuminating the redox behavior of hole-doped materials. It will be understood that all Cu bond valences  $>2+$  actually reflect holes on O. Bond valences,  $v$ , as a function of  $y$  for (1)3 are presented in Fig. 4 using experimental data and the formalism described in (1). Similar trends are observed for (1)2 and (1)4, with  $v$  roughly smaller and larger by 0.5 than  $v(1)3$ . One notices that  $v$  of (1) $n$  for the boundary phases are stable over some range in  $y$ , extrapolate in the intermediate range, and that there exists a pronounced transition near  $y = 6.5$ . This means that in the hole-doped state (Op) the Cu(1) sites are relatively reduced. This range corresponds predominantly to a mix of (1)2 and (1)4. We propose that the  $V^+$ , or formally speaking "electron"-doped, orthorhombics (On) are based predominantly on (1)3. The bond valence calculations indicate that any (1)3 present in Op is relatively reduced ( $v \sim 1.8+$ ). This capability for reduced (1)3 makes it a natural candidate for electron doping near  $y = 6.5$  according to  $\text{YBaCu}_2^{1.67+}\text{Cu}(1)3^{1.67+}\text{O}_{6.5}^{2-}\text{O}^-$ . We have taken  $v(2)5 \sim v(1)3 \sim 1.67+$  such that one O hole and lattice commensurable charge fluctuations ( $k = 3$  or  $2\text{Cu}^{2+}$  alternating with one  $\text{Cu}^+$ ) are generated. One hole on O is comparable to Op with  $y = 7$  and is justified by the potential for similar (slightly higher)  $T_c$  for On [6]. This corresponds to a massive self-doping as reflected in the volume expansion. Similar self-doping may be an answer to the

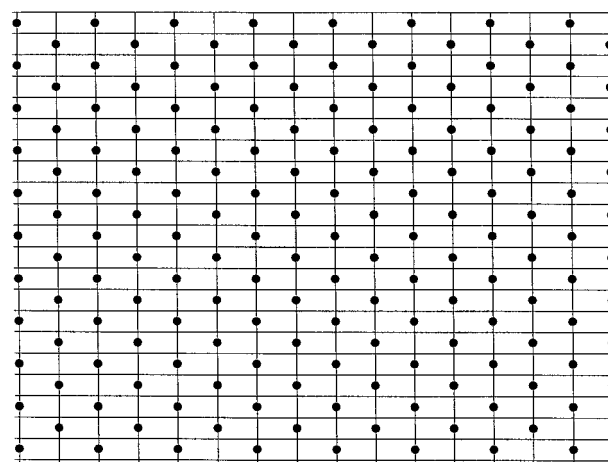


FIG. 5. Schematic representation of O(1)3 orthorhombicity. Circles are O. Alternate  $b$ -axis occupation creates orthorhombicity. This type can occur as semiconductor  $V^0$  and volume expanded  $V^+$ .

question of how record  $T_c$  can be obtained in materials such as  $\text{HgBa}_2\text{CuO}_4$ , which have nominal  $2+$  charge on the metals involved. It is interesting to note that near  $y = 6.5$  materials can also be hole superconducting or semiconducting, depending on the temperature of final annealing. The corresponding formulas are  $\text{YBa}_2\text{Cu}_2\text{Cu}_{0.5}(1)2^+\text{Cu}_{0.5}(1)4^{2+}\text{O}_6^{2-}\text{O}_{0.5}^-$  for the hole superconductor (Op) and  $\text{YBa}_2\text{Cu}_2\text{Cu}(1)3\text{O}_{6.5}^{2-}$  for the semiconductor (Ol). The dramatic transitions l-n-p demonstrated here in  $y$  can accordingly also be predicted within temperature. From the above we propose that all Ol contain a large (1)3 fraction, which is ordered through alternate occupation on the  $b$  axis resulting in orthorhombicity (Fig. 5). Indications for 12% of a related type of order in a tetragonal analog material were found previously (15) through superlattice reflections. For the orthorhombic semiconductors (Ol), the localization of near  $3+$  charge on (1)4 can be avoided. High (1)3 fractions are expected in the range where orthorhombicity of the O(1)4 type breaks down. The resulting competition among (1)3, (1)2, and (1)4 for charge leads to abrupt transitions between Op, On, and Ol when one local configuration becomes dominant with respect to another (3). First-order transitions, as indicated in this study, can be characteristic for the passing from the itinerant to the localized electron regime (16). What is unusual here is the inclusion of abrupt  $V^-$ ,  $V^+$  transitions through internal charge disproportionation and the identification of competing local environments for charge and space as the driving mechanism for this Mott-type transition.

*Note added in proof.* New experiments indicate that O(1)3 observation hinges on pinning of ladder type transformations to O(1)4(1)2 at lower temperatures.

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