

Superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$

H. A. Blackstead

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

J. D. Dow

Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504, U.S.A.

(Submitted 18 January 1994)

Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 4, 262–267 (25 February 1994)

Neutral oxygen, or the pairing of holes via O^{-2} , is identified as the essential ingredient of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$. “Fabrication” of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ from semiconducting $\text{PrBa}_2\text{Cu}_3\text{O}_7$ in a thought experiment or *Gedankenexperiment* leads to (i) prediction of the range of superconducting compositions $6.5 < x < 7$, (ii) an understanding of the two-stepped character of the critical temperature $T_c(x)$, (iii) a natural explanation of photoinduced superconductivity, (iv) elucidation of the major doping studies, (v) a derivation of Tokura’s empirical rule relating the critical oxygen composition x_c of the alloy $\text{Y}(\text{La}_{2y}\text{Ba}_{2-2y})\text{Cu}_3\text{O}_x$ to the critical La content y_c : $x_c = 6.5 + 2y_c$, and (vi) identification of the charge-reservoir layers (the layers containing the Cu–O chains) as the root of superconductivity.

Efforts to understand the superconductivity observed in $\text{YBa}_2\text{Cu}_3\text{O}_x$ for $6.4 < x < 7$ have overlooked the implications of the fact that $\text{PrBa}_2\text{Cu}_3\text{O}_7$ has the same crystal structure as superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ and yet is a semiconductor (or insulator).^{1,2} This means that the superconductivity must be related to the *differences* in the two materials.

The two main differences are that (i) Y^{+3} replaces Pr^{+4} (Ref. 3), and (ii) oxygen atoms may be missing from the Cu–O chains in the charge-reservoir planes of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Ref. 4). (Figure 1 illustrates the nomenclature.^{5,6}) These differences can be understood if one performs a *Gedankenexperiment* or thought experiment that “fabricates” $\text{YBa}_2\text{Cu}_3\text{O}_x$ from $\text{PrBa}_2\text{Cu}_3\text{O}_7$ by replacing each Pr^{+4} ion³ with Y^{+3} plus a hole, h^{+1} . Each hole will then migrate to a region containing O^{-2} , the only negative ions in the system. For every two unit cells, there will be two such holes, and they can (on the average) *pair with one another* at an O^{-2} site to form *neutral oxygen*. Such neutral oxygen will be only loosely bound in the crystal structure, and hence some may diffuse away, producing oxygen vacancies. Thus, the natural location for the neutral oxygen, which is both (i) created by hole–hole pairing and (ii) a progenitor of vacancies, lies in the charge-reservoir layers of $\text{YBa}_2\text{Cu}_3\text{O}_x$, specifically, in the Cu–O chains: the part of the unit cell associated with missing oxygen.⁴ There is only one oxygen site per unit cell in the charge-reservoir (chain) layers of $\text{YBa}_2\text{Cu}_3\text{O}_x$, and we propose that half of these sites are occupied by O^{-2} ions and the rest are occupied by either neutral O^0 or by neutral vacancies.

The movement of holes among the neutral oxygen and the O^{-2} ions of the charge-reservoir (chain) layers leads to hole-pairing and to superconductivity. For

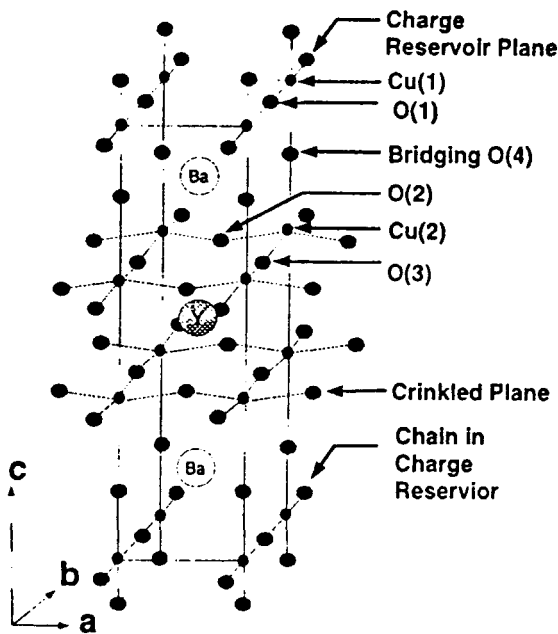


FIG. 1. Crystal structure of ideal $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ref. 5). The crystal structure of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is the same, except that Pr replaces Y. The notation is not unique. (The notation is discussed in Ref. 6.) The charge-reservoir Cu-O chain layers are at the top and the bottom of the unit cell.

$x \rightarrow 7$, half of the oxygen atoms are charged O^{-2} and half are neutral, on the average; and the carriers in the resulting partially filled bands are holes. The superconductivity is BCS-like⁷ and rooted in the charge-reservoir (chain) layers, with the hole-pairing reaction being $2h^{+1} + \text{O}^{-2} \rightarrow \text{O}^0$, mediated by the field of O^{-2} ions, in addition to the acoustic phonon field of conventional superconductivity.

This picture has the materials $\text{PrBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_x$, each in a locally charge-neutral state, with all cations essentially in their normal valence states: Pr, Y, Ba, and Cu are in the +4, +3, +2, and +2 charge-states, respectively. All seven oxygen atoms are in the -2 charge state for $\text{PrBa}_2\text{Cu}_3\text{O}_7$, so that the net charge is zero (i) in the charge-reservoir (chain) layers, (ii) in the Ba-O planes, and (iii) in the sandwich of Pr^{+4} plus the two adjacent crinkled cuprate planes: $[\text{CuO}_2]^{-2}$ (see Fig. 1). In $\text{YBa}_2\text{Cu}_3\text{O}_x$, charge neutrality requires that 6.5 out of 7 oxygen sites in the unit cell be occupied by oxygen in the O^{-2} state, and so we should think in terms of a "supercell" that is twice the size of the conventional unit cell and contains two oxygen sites in the Cu-O chains of the charge-reservoir layers: one of these supercell oxygen sites is occupied by an O^{-2} ion and the other is occupied by either a neutral oxygen atom or a neutral vacancy.

The data (Fig. 2) for the critical temperature^{8,9} $T_c(x)$ are clear evidence that neutral oxygen atoms, rather than vacancies, provide the essential element for super-

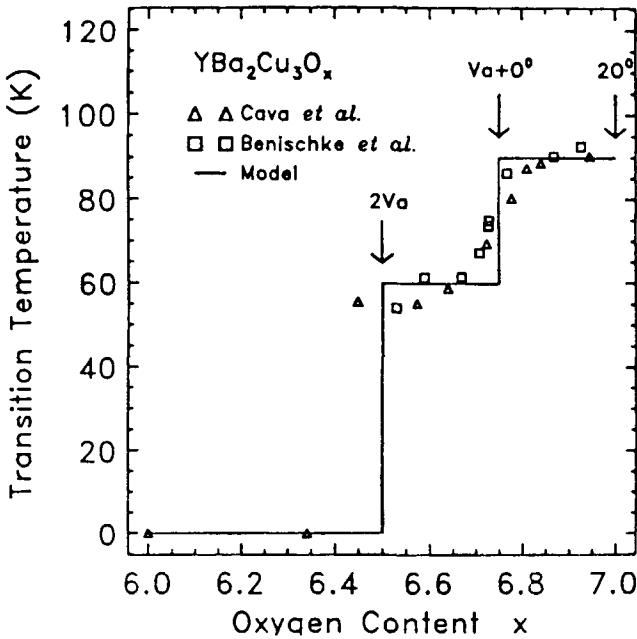


FIG. 2. Superconducting critical temperature (in K) versus oxygen content x of $\text{YBa}_2\text{Cu}_3\text{O}_x$. The data of Cava *et al.* (triangles; Ref. 8) and of Benischke *et al.* (squares; Ref. 9) are also displayed in the figure. The solid line is what is expected on the basis of the prediction of two reference materials, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (no neutral oxygen; two vacancies per four unit cells) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ (one vacancy and one neutral oxygen per four unit cells), with values of T_c chosen to fit the data. The arrows indicate the occupancies of charge-reservoir (chain) layer oxygen sites in four unit cells of typical material: (two vacancies, denoted $2V_a$) for $x=6.5$, (one vacancy and one neutral oxygen) for $x=6.75$, and (two neutral oxygen) for $x=7$.

conductivity. In the limit of material maximally loaded with oxygen, $x \rightarrow 7$, there are no vacancies, and so Fig. 2 is the experimental proof that vacancies are not responsible for the high-temperature superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_x$. In this limit, the $\text{YBa}_2\text{Cu}_3\text{O}_x$, in contrast with $\text{PrBa}_2\text{Cu}_3\text{O}_7$, must have (on the average) 0.5 neutral oxygen atoms per unit cell (or one per supercell) in order to be electrostatically neutral, and so the superconductivity for $x \rightarrow 7$ must be associated with the neutral oxygen.

This simple picture of superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$ readily explains why the critical temperature $T_c(x)$ has the two-stepped form of Fig. 2. At $x=6.5$, there is no "superconductivity-related" neutral oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_x$, only "structural" O^{-2} ions, and the material is locally charged neutral. Hence, at $x=6.5$ the superconductivity should disappear. It does at $x=6.4$. [This minor discrepancy between the simple theoretical picture ($x=6.5$) and experiment ($x=6.4$) is attributed to the fact that Cu can assume the Cu^{+1} charge state (and does in small concentrations¹⁰⁻¹³), facilitating deviations from the normal oxygen content at the $\Delta x=0.1$ level.] For $6.5 < x < 6.75$ the typical supercell has one vacancy, and so the superconductivity of these materials

is adversely affected by holes that scatter from the vacancies, and T_c is low (“60-K material”). However, for $6.75 < x < 7$, the typical supercell does not have such a vacancy, and T_c is higher (“90-K material”).^{14,15}

Note that no significant change of Cu occurs at $x=6.75$, and so Cu (in whatever valence state) cannot be the essential ingredient of the superconductivity described in Fig. 2.

Photo-induced superconductivity^{16,17} can be understood as photo-removal of electrons from O^{-2} ions to traps (very likely oxygen vacancies). In effect, the light increases the neutral oxygen content of the material, causing it to superconduct transiently for $x < 6.4$. Thus intense photon bleaching of $YBa_2Cu_3O_x$ with $x \approx 6.7$ should lead to an increase in T_c , similar to that observed in Fig. 2 for $x=6.75$.

This picture leads to natural explanations of the many doping studies: (i) adding a positive charge to a unit cell locally quenches the superconductivity (and quenches it globally once enough cells are poisoned); (ii) adding a negative charge does not; and (iii) adding a magnetic moment breaks pairs and quenches superconductivity only if the moment is within or adjacent to the charge-reservoir Cu–O chain layers, where the superconductivity is rooted. Thus the replacements ($Y^{+3} \rightarrow Pr^{+4}$) and ($Cu^{+2} \rightarrow Fe^{+3}$, Co^{+3} , Al^{+3} , or Ga^{+3}) effectively remove a unit cell from the superconducting region of $YBa_2Cu_3O_x$ and ultimately lead to a reduction^{15,18} of T_c , while ($Y^{+3} \rightarrow Ca^{+2}$ or Na^{+1}) does not significantly degrade the superconductivity.¹⁹ Isovalent substitutions ($Ba^{+2} \rightarrow Sr^{+2}$) and ($Y^{+3} \rightarrow [rare-earth]^{+3}$ or Sc^{+3}) have little effect on the superconductivity.^{20,21} Even the replacement ($Y^{+3} \rightarrow Dy^{+3}$), with Dy^{+3} having a very large magnetic moment (angular momentum $J=15/2$), has almost no effect,^{6,20} although such a large magnetic moment is expected to break Cooper pairs—it does not, because the superconductivity is rooted in the charge-reservoir Cu–O chain layers that are remote from both the crinkled cuprate planes and the Dy site (see Fig. 1). The isovalent substitution ($Cu^{+2} \rightarrow Zn^{+2}$) destroys the superconductivity,¹⁸ because Zn, which preferentially occupies chain sites, is so electropositive²² and attracts holes away from oxygen.²³ The replacement ($Cu^{+2} \rightarrow Ni^{+2}$) occurs only in the crinkled cuprate planes, and has a less adverse effect than Zn^{+2} on the superconductivity, because (i) Ni is less electropositive (causing it to scatter holes less efficiently than Zn) and (ii) although magnetic, Ni is remote from the chain layers and from the root of superconductivity.²⁴

In $Y(La_{2y}Ba_{2-2y})Cu_3O_x$, charge neutrality requires that the concentration of oxygen be $x=6.5+y+x_0$. Here we have assumed the valences of Y, La, Ba, Cu, and ionic oxygen to be +3, +3, +2, +2, and –2, respectively. The concentration of charged oxygen is $x-x_0$, and we have allowed for x_0 neutral oxygen—which is certainly necessary in La-free material ($y=0$) whenever we have $x > 6.5$. Concentrating on the facts that (i) a neutral interstitial oxygen atom added to a unit cell of La_2CuO_4 is thought to be a progenitor of superconductivity (yielding a cell with one neutral oxygen and two La,²⁵ (ii) the chemical environment of a La atom in the $YBa_2Cu_3O_x$ crystal structure is not too different from that in La_2CuO_4 , and (iii) the minimum observed transition temperature for the $Y(La_{2y}Ba_{2-2y})Cu_3O_x$ system is ≈ 40 K, the same as for $La_2CuO_{4-\delta}$, we identify the onset of superconductivity in $Y(La_{2y}Ba_{2-2y})Cu_3O_x$ (i.e., the insulator-superconductor boundary) with the condi-

tion $x_0=y$, namely, the incorporation of one neutral oxygen for every two La. It follows that $x_c=6.5+2y_c$, which is Tokura's empirical rule²⁶ relating the critical oxygen composition x_c to the critical La doping parameter y_c .

In models that (unlike ours) assign the root of superconductivity to the crinkled cuprate planes, some theoretical gymnastics are required to explain how the superconductivity is insensitive to the strong magnetism of Dy^{+3} at the Y site:²⁷ Theoretical claims that magnetic ions at that site do not couple effectively to the Fermi liquid are difficult to accept, given the experimental fact that the observed relaxation of Y nuclear spins is Korringa-like,²⁸ which proves that the coupling is efficient. Moreover, most models that assign the root of superconductivity to the crinkled planes often claim that the chain-Cu is in the Cu^{+3} state, contrary to the experimental evidence.²⁹ Since the crinkled cuprate planes are the same in both superconducting $YBa_2Cu_3O_x$ and nonsuperconducting $PrBa_2Cu_3O_7$, these planes cannot be the essential ingredient of oxide superconductivity. Indeed, $Y_{1-y}Pr_yBa_2Cu_3O_x$ does not superconduct for $y>0.6$ (Refs. 1 and 30), indicating that crinkled cuprate planes plus modest concentrations of holes are not the essential elements of oxide superconductivity either. Finally, there exist high-critical-temperature oxide superconductors that contain no Cu, such as $(Ba,K)(Pb,Bi)O_x$ with $x\approx 3$, suggesting that neither cuprate planes nor Cu (in any valence state) is *essential* to high-temperature superconductivity.

The idea that pairing of holes at an oxygen site might convert O^{-2} to O^0 and lead to high-temperature superconductivity has been suggested before by Khomskii and Zvezdin,³¹ but in the context of the conversion involving two Cu^{+3} ions being simultaneously converted to Cu^{+2} in $YBa_2Cu_3O_x$. Our model is similar, but does not require the active role of Cu in any valence state (especially not two Cu^{+3} ions), obtains its holes from the rare-earth atoms being under-charged (Y^{+3} replacing Pr^{+4}) rather than from the Cu-O chains of the charge-reservoir layers, uses a Khomskii-Zvezdin mechanism to account for conversion of Cu^{+2} to Cu^{+1} ,¹³ and is compatible with oxide superconductivity in materials without Cu, such as $(Ba,K)(Pb,Bi)O_x$ with $x\approx 3$.

In summary, we propose that the pairing of holes via O^{-2} ions is the essential ingredient of oxide superconductivity. Hence we have a BCS-like model with holes as carriers, and with hole-hole pairing similar in some aspects to that proposed by Khomskii and Zvezdin. While the Cu facilitates the superconductivity in this material (especially when there is an O^{-2} deficiency¹³), its role is not essential to the general phenomenon of high-temperature superconductivity.

More evidence supporting this picture, application of these ideas to all major high-temperature oxide superconductors, and a mathematical description of our model, will be presented in a long paper soon.³² Nevertheless, much of the essential physics of high-temperature superconductivity in $YBa_2Cu_3O_x$ can be deduced from the differences between $YBa_2Cu_3O_x$ and $PrBa_2Cu_3O_7$ and from interpreting what $T_c(x)$ (Fig. 2) implies about the role of vacancies and neutral oxygen in the superconductivity.

We are grateful to the U.S. Air Force Office of Scientific Research, the U.S. Army Research Office, the U.S. Office of Naval Research, and the U.S. Department of

Energy for their financial support of this work (Contract Nos. AFOSR-91-0418, DAAL03-91-G-0054, N00014-92-J-1425, and DE-FG02-90ER45427), to R. W. Hanson for his moral support, to D. Pulling for technical support, and to R. E. Allen, R. Bhatt, M. Chandrasekhar, D. Finnemore, D. Ginsberg, D. Johnston, R. V. Kasowski, T. Lemberger, M. McElfresh, F. Mueller, and S. Y. Ren for enlightening discussions.

- ¹J. L. Peng, P. Klavins, R. N. Shelton *et al.* Phys. Rev. B **40**, 4517 (1989).
- ²J. J. Neumeier, T. Bjornholm, M. B. Maple *et al.* Physica C **166**, 191 (1990).
- ³Note that $\text{PrBa}_2\text{Cu}_3\text{O}_7$ fully loaded with oxygen is expected to have Pr in the Pr^{+4} state (ionic radius of 0.92 Å, compared with 0.92 Å for Y^{+3}), while less fully loaded samples may have Pr^{+3} (ionic radius 1.06 Å) instead. Variations in the oxygen loading are doubtless responsible for some of the different claims in the literature about the charge state of Pr being +3. The steric constraints and charge-conservation almost certainly prohibit $\text{PrBa}_2\text{Cu}_3\text{O}_x$ with $x > 7$ from having Pr primarily in the +3 state when the material is fully loaded with oxygen, because the Pr^{+3} ion is so large and because the +4 charge state is necessary for the unit cell to be electrostatically neutral. Ionic radii are tabulated in F. S. Galasso, Structure, Properties, and Preparation of Perovskite-Type Compounds (Pergamon Press, Oxford, 1969), p. 52.
- ⁴A. W. Hewat, Neutron News **1**, 28 (1990), and references therein.
- ⁵H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).
- ⁶Copper Oxide Superconductors, ed. by C. P. Poole, Jr., T. Datta, and H. A. Farach (John Wiley & Sons, New York, 1988), p. 125 *et seq.*
- ⁷J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).
- ⁸R. J. Cava, A. W. Hewat *et al.* Physica C **165**, 419 (1990).
- ⁹R. Benischke, T. Weber, and W. H. Fietz, Physica C **203**, 293 (1992).
- ¹⁰Ref. 11, p. 292.
- ¹¹C. H. Pennington and C. P. Slichter, in Ref. 12, Vol. II, p. 269 *et seq.* (1990).
- ¹²Physical Properties of High-Temperature Superconductors, edited by D. M. Ginsberg (World Scientific, Singapore), and references cited there.
- ¹³Ref. 11, p. 317 discusses evidence that, as x decreases from 7, more Cu is found in the Cu^{+1} state. This is to be expected from charge-balance considerations when there is a deficiency of O^{-2} ions, and indicates that a Cu^{+2} ion accepts an electron from an O^{-2} , converting it to O^{-1} and facilitating its later transition to O^0 . An oxygen content of $x = 6.4$, instead of $x = 6.5$, could occur in superconducting material with only 7% of the Cu in the Cu^{+1} charge state.
- ¹⁴Superconducting materials of this class have been prepared with oxygen content $x > 7$, but have required replacement of the Y^{+3} by a combination such as $(\text{La}^{+3})_{1-y}(\text{Ca}^{+2})_y$. This combination does not increase T_c (see Ref. 15, p. 314).
- ¹⁵J. T. Markert, Y. Dalichaouch, and M. B. Maple, in Ref. 12, I, 265 (1989).
- ¹⁶V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk *et al.* Phys. Rev. B **47**, 9017 (1993); V. I. Kudinov, A. I. Kirilyuk, N. M. Krienes *et al.* Phys. Lett. A **151**, 358 (1990); V. I. Kudinov, I. L. Chaplygin, A. I. Kirilyuk *et al.* Phys. Lett. A **157**, 290 (1991).
- ¹⁷G. Yu, A. J. Heeger, G. Stucky *et al.* Solid State Commun. **72**, 345 (1989); G. Yu, C. H. Lee, A. J. Heeger *et al.* Phys. Rev. Lett. **67**, 2581 (1991).
- ¹⁸Ref. 15, pp. 307–312.
- ¹⁹Ref. 15, pp. 313–315.
- ²⁰Ref. 15, p. 273.
- ²¹Ref. 15, p. 306.
- ²²The electronegativities of O, Pb, Bi, Hg, Ni, Cu, Ga, Zn, Al, Y, Pr, Ca, Sr, and Ba are 3.44, 2.33, 2.02, 2.00, 1.91, 1.90, 1.81, 1.65, and 1.61, 1.22, 1.13, 1.00, 0.85, and 0.89 respectively. [After Table of Periodic Properties of the Elements (Sargent-Welch Scientific Company, Skokie, Illinois, 1980).]
- ²³M. A. Castro, S. M. Durbin, and M. McElfresh, "Pair breaking from magnetic Ni and Fe in $\text{YBa}_2\text{Cu}_3\text{O}_7$," to be published.
- ²⁴Ref. 15, p. 313.
- ²⁵J. D. Jorgensen, Physics Today, p. 34 (June, 1991).
- ²⁶Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzari, Phys. Rev. B **38**, 7156 (1988), Fig. 1.
- ²⁷A. J. Freeman, J. Yu, S. Massidda, and D. D. Koelling, Physica **148B**, 212 (1987).
- ²⁸Ref. 11, p. 285.
- ²⁹Ref. 11, p. 273.

³⁰Ref. 15, p. 301.

³¹D. I. Khomskii and A. Z. Zvezdin, *Solid State Commun.* **66**, 651 (1988).

³²H. A. Blackstead and J. D. Dow, "Oxide superconductivity," to be published.

Published in English in the original Russian journal. Reproduced here with the stylistic changes by the Translations Editor.