

# Unexpected effects of gold on the structure, superconductivity, and normal state of $\text{YBa}_2\text{Cu}_3\text{O}_7$

Marta Z. Cieplak

*Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218,  
and Institute of Physics, Polish Academy of Sciences, Warsaw, Poland*

Gang Xiao

*Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218,  
and Department of Physics, Brown University, Providence, Rhode Island 02912*

C. L. Chien

*Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218*

J. K. Stalick and J. J. Rhyne

*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

(Received 14 May 1990, accepted for publication 18 June 1990)

Using high-resolution x-ray and neutron diffraction measurements, we have shown that gold can be doped into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (1:2:3) up to 10% per formula unit, exclusively at the Cu(1) sites. Au doping causes a larger uniaxial expansion along the  $c$  axis, accompanying an increase in the Cu(1)—O(1) bond length and a decrease in the Cu(2)—O(1) bond length. The superconducting transition temperature ( $T_c$ ) is enhanced upon Au doping and the normal-state transport properties are altered even for small levels of Au doping. The widely held belief in the inert nature of Au with regard to high  $T_c$  superconductors is therefore invalid. These findings also raise questions concerning results using single crystals grown from gold crucibles.

Chemical doping has proven to be a powerful method in unraveling the crucial aspects of high  $T_c$  superconductors.<sup>1-5</sup> The carrier concentration, crystal structure, normal state, and superconducting properties can all be altered in a systematic way by suitable doping. On the other hand, noble metals, particularly Au, have been widely considered to be inert as far as high  $T_c$  superconductors are concerned. In part, this is because the only known gold oxide ( $\text{Au}_2\text{O}_3$ ) decomposes at a low temperature of 160 °C.<sup>6</sup> Thus the incorporation of Au into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (1:2:3) after processing at 950 °C seems unlikely. Certainly, the successful utilizations of gold as buffer layers for high  $T_c$  films, gold-superconductor composites, gold contacts, gold tunneling barriers, etc. further reinforce this belief.<sup>7-10</sup> Equally significant, gold crucibles have now enjoyed the status of producing some of the best high  $T_c$  single crystals to date. Such single crystals have been subjected to intense research in order to capture the fundamental properties intrinsic to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

We show in this work that the confidence in gold as an inert participant is premature. Results from a variety of measurements provide compelling evidence that gold can be incorporated into 1:2:3 up to 10 at. % per formula unit, and occupies the Cu(1) chain site. Our perception of the inability of gold to enter a complex oxide structure has to be altered. Equally important, gold is actually found to enhance  $T_c$ , the only dopant element that has accomplished this feat. In addition, the normal-state properties have also been affected in a significant way. Since small amounts of gold can alter substantially the properties of 1:2:3, the precise content of gold must be ascertained in single crystals grown from gold crucibles. Those containing appreciable amounts of gold are unlikely to reflect the

intrinsic properties of pure 1:2:3.

We have prepared the samples with solid-state reaction methods using several routes. Of those, the two methods with the best results, which are consistent with each other, are the following. In the first method, we first made 1:2:3 powder from high-purity  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  processed at 950 °C in oxygen for 100 h with two intermediate grindings and pressings. The 1:2:3 powders were then mixed with Au powders according to  $(\text{YBa}_2\text{Cu}_3\text{O}_7)_{1-x}\text{Au}_x$  before annealing at 950 °C in  $\text{O}_2$  for 50 h. In the second method, we used  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$ , and Au as starting materials with the proportions of  $(\text{YBa}_2\text{Cu}_3\text{O}_7)_{1-x}\text{Au}_x$ , before going through the same processing conditions as above. There are no discernible differences between these two sets of samples in crystal structure, lattice parameter, superconducting, and normal-state properties. Curiously and unexpectedly, attempts to directly substitute Au for Cu, i.e.,  $\text{YBa}_2(\text{Cu}_{1-x}\text{Au}_x)_3\text{O}_7$  under the same fabrication conditions have resulted in larger amounts of impurity phases. It is possible that achieving single-phase specimens may require different processing conditions which we have not mastered, or an excess of Cu facilitates Au doping. In the following, we discuss results taken from samples made by the first two routes.

The phase purity of every sample has been determined by powder x-ray diffraction. All samples with  $x$  up to 0.1 contain predominantly 1:2:3 single phase, except a very small amount of  $\text{CuO}$ , but with no evidence of separate Au phase, whereas those with  $x > 0.1$  all contain two phases: 1:2:3 and Au. The lattice parameters were determined by fitting the diffraction peaks using modified Gaussian functions and subsequently fitting the positions of at least 20 peaks. Figure 1 shows the lattice parameters  $a$ ,  $b$ , and  $c$  of the orthorhombic structure. The  $a$  and  $b$

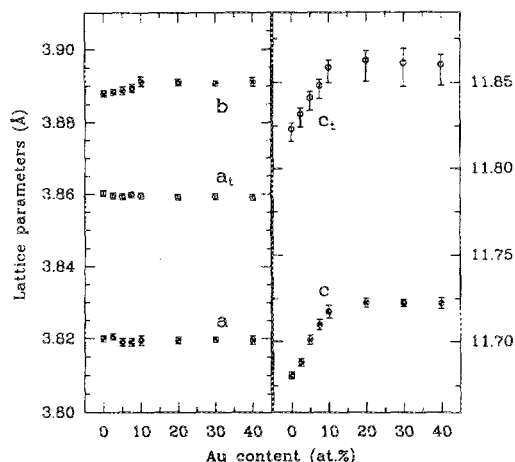


FIG. 1. Dependence of lattice parameters  $a$ ,  $b$ , and  $c$  of the orthorhombic structure and  $a_t$  and  $c_t$  of the tetragonal structure on gold content. The latter values were obtained from samples annealed in Ar for 1 h at 800 °C.

parameters remain essentially constant, but most remarkably, the  $c$  parameter increases by a large amount upon doping with Au up to  $x = 0.1$ , beyond which it levels off. We have also annealed the samples in Ar for 1 h at 800 °C to obtain the tetragonal structure whose lattice parameters  $a_t$  and  $c_t$  are also shown in Fig. 1. As expected, the value of  $c_t$  is much larger than  $c$  due to the loss of oxygen. However, the value of  $c_t$  again increases with Au content up to  $x = 0.1$  and then levels off. These results indicate clearly that Au has entered into the structure and caused an expansion of the  $c$  axis. Gravimetric weight loss measurements also indicate incorporation of Au up to  $x = 0.1$ , beyond that, the excess Au exists as a separate Au phase.

We then used neutron diffraction and Rietveld total profile analysis<sup>11</sup> to measure a sample with Au content of  $x = 0.08$  and an undoped sample. The results are shown in Table I, using the site notation of Ref. 12. The lattice parameters determined by neutrons are in excellent agreement with those from x-ray diffraction. As listed in Table I, the Cu-O plane assembly is essentially not affected by Au doping. The Cu—O bond lengths [Cu(2)—O(2) along the  $a$  axis, and Cu(2)—O(3) along  $b$  axis] in the plane assembly change by less than 0.04%. In the Cu-O chain assembly, the Cu(1)—O(4) length along the chain direction ( $b$  axis) also changes little (0.06%). However, along the  $c$  axis, the bond length between the Cu(1) chain site and the bridging oxygen O(1) increases by a huge amount of 1.36% whereas the Cu(2)—O(1) bond length reduces by 0.3%. The expansion of the  $c$  axis, upon Au doping, is therefore not simply a uniform displacement of all atoms in the cell. Instead, the bridging oxygen O(1) has been displaced toward the Cu(2) sites. The uniaxial expansion due to Au doping causes predominantly a change in the Cu(1)—Cu(2) distance (+0.4%) and a minor change in the Cu(2)—Cu(2) distance (−0.1%). Another important result from the neutron diffraction (see Table I) is that the oxygen content in the Au-doped sample is 7.04 as opposed to 6.98 in 1:2:3. Upon Au doping, excess amounts of oxygen have been drawn into the structure occupying the O(5) sites. Unfortunately because of the near coincidence

TABLE I. Structure parameters of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  doped with 8 at. % of gold and selected bond lengths determined by neutron diffraction at 295 K. The site notation is that given in Ref. 12.  $B$  is the thermal parameter and  $n$  is the occupancy number. Numbers in parentheses represent statistical errors in the last decimal place,  $f$  denotes that the parameter was fixed.  $R_N$ ,  $R_{wp}$ , and  $R_e$  are the nuclear, weighted profile, and expected  $R$  factor of fit, respectively.

YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7.04</sub> with Au ( $x=0.08$ ) $Pmmm$ space group					
Atom	$x$	$y$	$z$	$B$	$n$
Y	0.5	0.5	0.5	0.54(3)	1.0( $f$ )
Ba	0.5	0.5	0.1848(2)	0.67(4)	2.0( $f$ )
Cu(1)	0.0	0.0	0.0	0.47(3)	1.0( $f$ )
Cu(2)	0.0	0.0	0.3557(1)	0.53(3)	2.0( $f$ )
O(1)	0.0	0.0	0.1596(1)	0.90(4)	2.0( $f$ )
O(2)	0.5	0.0	0.3790(2)	0.55(3)	2.0( $f$ )
O(3)	0.0	0.5	0.3779(2)	0.59(4)	2.0( $f$ )
O(4)	0.0	0.5	0.0	0.051(3) [ $\beta_{11}$ ] 0.014(2) [ $\beta_{22}$ ] 0.0039(3) [ $\beta_{33}$ ]	1.0( $f$ )
O(5)	0.5	0.0	0.0	2.0( $f$ )	0.04(1)

$$\begin{aligned}
 a &= 3.8197(1) \text{ \AA} & R_N &= 3.41 \\
 b &= 3.8888(1) \text{ \AA} & R_{wp} &= 5.75 \\
 c &= 11.7121(4) \text{ \AA} & R_e &= 3.91 \\
 & & \chi &= 1.47
 \end{aligned}$$

Selected bond distances (Å)

	1:2:3	1:2:3 with 8% Au	Changes
Cu(1)—O(1)	1.844(3)	1.869(2)	+ 1.36%
Cu(1)—O(4)	1.9432(1)	1.9444(1)	+ 0.06%
Cu(2)—O(1)	2.305(3)	2.297(2)	− 0.34%
Cu(2)—O(2)	1.9299(5)	1.9291(3)	− 0.04%
Cu(2)—O(3)	1.9614(5)	1.9617(3)	+ 0.01%
Cu(1)—Cu(2)	4.149(1)	4.166(1)	+ 0.41%
Cu(2)—Cu(2)	3.383(3)	3.379(2)	− 0.11%

in neutron scattering factors of Cu and Au, neutron diffraction could not definitively place the location of Au, although the bond distances indicate that substitution on the Cu(1) site is probable.

On the other hand, the x-ray scattering factors of Cu and Au, dictated by the atomic number, are very different. The same sample with  $x = 0.08$  has been analyzed using a Scintag high-resolution x-ray diffractometer with a scattered beam monochromator. A total profile refinement procedure<sup>13</sup> was used to locate the positions of Au. The essential x-ray result of the refinement ( $R_{wp} = 8.83$ ,  $\chi = 2.57$ ) is that Au occupies exclusively the Cu(1) sites. The refined occupancies are Au(1) = 0.084(4) and Au(2) = −0.005(3), consistent with the 8% as-prepared concentration. Combining neutron and x-ray diffraction results, we have shown conclusively that Au enters the structure of 1:2:3, and occupies the Cu(1) sites.

It has been established<sup>4,5</sup> in 1:2:3 that all the divalent dopants ( $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ) substitute the Cu(2) plane sites, whereas all the trivalent dopants ( $\text{Al}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ga}^{3+}$ ) occupy the Cu(1) sites. Whenever the Cu(1) site has been doped by a trivalent dopant, there is always an increase in the oxygen content. By way of analogy, Au most probably is in the trivalent state, which indeed is a common valence state for Au.<sup>6</sup> One can also use the ionic size argument. The effective ionic radius of  $\text{Au}^{3+}$  is 0.85 Å, a value close

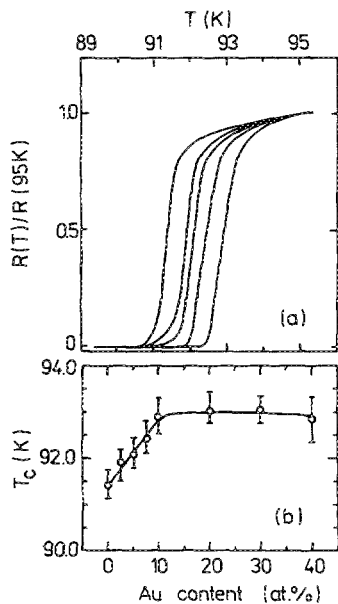


FIG. 2. (a) Normalized resistivity vs  $T$  in the vicinity of  $T_c$  for the Au-doped samples, from left to right, with  $x = 0, 0.025, 0.05, 0.075$ , and  $0.1$ . (b) Dependence of  $T_c$  on gold content. The bars denote a 90–10% resistivity drop.

to that of  $\text{Cu}^{2+}$  ( $0.73 \text{ \AA}$ ), but the radius of  $\text{Au}^{1+}$  is  $1.37 \text{ \AA}$ , much too large for the Cu(1) site.

The incorporation of Au into 1:2:3 has surprising effects on the superconducting and normal-state properties. The detailed behaviors near  $T_c$  are shown in Fig. 2(a). All the samples are superconducting, having sharp transitions, which have also been observed in magnetometry measurements. Most interestingly, Au systematically enhances the value of  $T_c$ . As shown in Fig. 2(b),  $T_c$  increases by about  $1.5 \text{ K}$  at  $x = 0.1$ , beyond which  $T_c$  remains unchanged. This is the first instance where a dopant on the Cu sites does not deteriorate but enhances  $T_c$ .

Most significantly,  $T_c$  is enhanced even when there is a dramatic change in the normal-state properties. Figure 3 shows the temperature dependence of the resistivity of the Au-doped samples. A linear temperature dependence is evident, but the slope (shown in the inset) is increased by a factor of 2 in the solubility range. The reduction in slope above  $x = 0.1$  is due to the precipitation of metallic Au

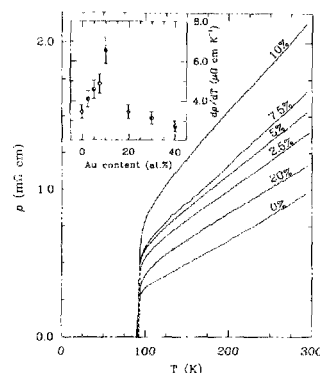


FIG. 3. Temperature dependence of resistivity  $\rho$  of the Au-doped samples. In the inset, the values of  $d\rho/dT$  at room temperature are shown.

grains. Also noted is the residual resistivity  $\rho(0 \text{ K})$ , which remains at a low value (i.e., small impurity scattering). The dramatic increase in the resistivity slope, a feature prominent in many theories of high  $T_c$  superconductivity, is an important result, which shows that superconductivity remains intact for a wide range of different resistivity slopes. These findings also raise disturbing questions concerning single crystals grown from Au crucibles, without ascertaining the impurity level of Au in the crystals.

It is certainly a surprising and intriguing result that when some of the Cu(1) sites are replaced by the much heavier Au ions,  $T_c$  not only can be retained, but actually increased. The increase in carrier concentration is one possible explanation for the  $T_c$  enhancement. Neutron results show an increase of oxygen content of about  $0.06$  for the sample with  $x = 0.08$ . Assuming  $\text{Au}^{3+}$  replaces  $\text{Cu}^{2+}$ , there would be a net increase in hole carriers by about  $0.04/\text{unit cell}$ . However, the bridging oxygen O(1), believed to be crucial to charge transfer among the ions, may well play a key role here. As mentioned earlier, doping of Au causes the Cu(1)—O(1) bond length to increase by  $1.36\%$  and the Cu(2)—O(1) bond length to shrink by  $0.3\%$ . These are the largest changes occurring in the structure upon Au doping. The enhancement of  $T_c$  may be the result of a reduction in the Cu(2)—O(1) bond length.

In summary, we have conclusively demonstrated that Au can be doped into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  occupying only the Cu(1) chain sites, causing a large uniaxial expansion in the  $c$  axis and drawing additional oxygen into the structure. The bridging oxygen O(1) is displaced, resulting in a large increase in the Cu(1)—O(1) distance and a decrease in the Cu(2)—O(1) distance. Doping with Au enhances  $T_c$  and alters the normal-state properties significantly.

We thank Dr. T. Egami and Dr. A. Wold for useful discussions. This work has been supported by NSF grant No. DMR88-22559.

- <sup>1</sup>G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, *Phys. Rev. B* **35**, 8782 (1987).
- <sup>2</sup>Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, *Nature* **328**, 512 (1987).
- <sup>3</sup>J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Jr., *Phys. Rev. B* **36**, 8393 (1987).
- <sup>4</sup>G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne, and J. A. Gotaas, *Nature* **332**, 238 (1988).
- <sup>5</sup>C. L. Chien, G. Xiao, M. Z. Cieplak, D. Musser, J. J. Rhyne, and J. Gotaas, in *Superconductivity and its Applications*, edited by H. S. Kwok and D. T. Shaw (Elsevier Science, Singapore, 1988), pp. 110–117.
- <sup>6</sup>N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, Oxford, 1984), p. 1373.
- <sup>7</sup>F. H. Streitz, M. Z. Cieplak, G. Xiao, A. Gavrin, A. Bakhshai, and C. L. Chien, *Appl. Phys. Lett.* **52**, 927 (1988).
- <sup>8</sup>C. L. Chien, G. Xiao, F. H. Streitz, A. Gavrin, and M. Z. Cieplak, *Appl. Phys. Lett.* **51**, 2155 (1987).
- <sup>9</sup>J. W. Ekin, T. M. Larson, N. F. Bergren, A. J. Nelson, A. B. Swartzlander, L. L. Kazmerski, A. J. Parson, and B. A. Blankenship, *Appl. Phys. Lett.* **52**, 1819 (1988).
- <sup>10</sup>H. Akoh, F. Shinoki, M. Takehashi, and S. Takada, *Jpn. J. Appl. Phys.* **27**, L519 (1988).
- <sup>11</sup>H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
- <sup>12</sup>F. Becc, S. Miraglia, A. Santoro, and R. S. Roth, *Phys. Rev. B* **35**, 8778 (1987).
- <sup>13</sup>A. C. Larson and R. B. Von Dreele, GSAS-Generalized Structure Analysis System, Los Alamos National Laboratory Rept. (LA-UR-86-748), 1987.