

Incorporation of gold into $\text{YBa}_2\text{Cu}_3\text{O}_7$: Structure and T_c enhancement

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The structural and superconducting properties of gold-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ compounds have been studied with x-ray and neutron diffraction, optical microscopy, weight-loss analysis, magnetization, and resistivity measurements. The solubility of Au in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is close to 10 at. %, below which all samples are thermally stable up to the processing temperature (950 °C). Metallic Au grains precipitate out when the Au content exceeds 10 at. %. Analysis of the x-ray and neutron-scattering intensities shows that Au substitutes for the Cu(1) chain site exclusively and has a probable valence state of Au^{3+} . The main effect of Au doping is a substantial uniaxial lattice expansion, while the orthorhombic structure is preserved. We present a detailed set of structural data including the Cu-O bond lengths and interplanar distances in a Au-doped sample. Unlike all other known dopants on Cu sites, the Au dopant is not detrimental to the superconducting properties. On the contrary, T_c is slightly enhanced over that of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Such an enhancement, observed for the first time for a Cu site dopant, is intrinsic and reproducible. We discuss the possible causes of the T_c increase and the features of Au dopant useful in the investigation of high- T_c superconductivity.

I. INTRODUCTION

Chemical doping is a crucial investigative tool for the study of high- T_c superconductivity¹⁻³ because the substituents affect the structure and bond lengths and also produce band filling in the parent compound. The determination of crystallographic structure, magnetic, and transport properties of doped cuprate materials provides important information on the correlation between superconductivity and other physical parameters. Cation doping on non-Cu sites (e.g., La, Y), which affects the carrier concentration but with small impact on the Cu-O₂ plane assemblies, generally induces a gradual change in the value of T_c .¹ However, doping the Cu sites with transition-metal elements or *sp* elements affects the high- T_c superconductivity in a much more dramatic fashion.¹⁻³ In every case T_c is suppressed and the normal-state properties are altered. It has been established that dopants at the Cu(2) plane site reduce T_c more drastically than those at the Cu(1) chain site. Furthermore, among the impurities at the Cu(2) site, the degree of T_c suppression depends strongly on the electronic structure of a dopant.¹⁻⁶ For example, Zn^{2+} with a full *d* shell is much more detrimental to T_c than Ni^{2+} with two holes in its *d* shell. Overall, doping at the Cu sites by

impurities has provided us with a wealth of information. The sensitivity of superconducting and normal-state properties to the electronic structure of the dopants will surely serve as an important test for any viable theory of high- T_c superconductivity.

There is another class of dopant, the noble metals (Ag, Au), whose importance as a probe to the cuprate superconductors has been overlooked, although considerable attention has been paid to their technical usage in applications. Shortly after the discovery of $\text{YBa}_2\text{Cu}_3\text{O}_7$, quite naturally, attempts were made to replace Cu by Ag or Au, two elements in the same column as Cu in the Periodic Table. Despite some unconfirmed reports, high- T_c oxides with a large incorporation of Ag or Au could not be formed. Instead, metallic Ag or Au grains coexist with $\text{YBa}_2\text{Cu}_3\text{O}_7$ grains after high-temperature annealing and have little effect on superconductivity.^{7,8} Taking advantage of this observation, many groups have made composite materials^{7,8} of noble metals and $\text{YBa}_2\text{Cu}_3\text{O}_7$, and have fabricated noble-metal buffer layers⁹ and contacts for high- T_c films.¹⁰ The composite materials, while retaining a high- T_c value, are much improved mechanically, have higher critical current densities, and have dramatically reduced normal-state resistivities.^{7,8} Gold contacts on $\text{YBa}_2\text{Cu}_3\text{O}_7$ have achieved the

lowest contact resistance ($< 4 \times 10^{-11} \Omega \text{cm}^2$)¹¹, and gold films have begun to be used in proximity tunneling junctions.^{12,13}

In the growth of single crystals of high- T_c superconductors, Au crucibles are also increasingly used. Many crucible materials (e.g., Pt) have been found to yield poor specimens, whereas Au crucibles seem to produce very good crystals. If such single crystals are to reveal the intrinsic superconducting and normal-state properties, one must ascertain how Au interacts with the superconducting materials.

Despite extensive research on high- T_c composite materials or structures, the important question of the possible doping of noble metals into high- T_c oxides has not been widely investigated. This is influenced in part by the commonly held belief in the inability of noble metals to form stable oxides. The ineffectiveness of noble metals in degrading T_c , and their large ionic sizes, also tend to rule out the possibility of noble-metal incorporation into the structure of the high- T_c oxides. However, there is also evidence to the contrary.⁷ For example, we have found earlier that Au- $\text{YBa}_2\text{Cu}_3\text{O}_7$ composites exhibited a substantial increase in the lattice parameter c , which could be reasonably explained by Au incorporation.

Chemical doping of noble metals into high- T_c oxides is an important question from both chemistry and physics perspectives. According to the chemistry of noble elements,^{14,15} the very low affinity of Ag or Au for oxygen leads to oxides of low thermal stability. Ag_2O and the only known gold oxide Au_2O_3 decompose at a moderate temperature of $T \cong 160^\circ\text{C}$. Therefore, the formation of oxides doped with noble elements which are stable at high temperatures ($T \geq 950^\circ\text{C}$) is a particularly intriguing prospect. The study of the local environment, valence structure, and oxide formation energy will certainly enhance our understanding of the chemistry of noble-metal ions. From a physics point of view, if the noble elements can indeed enter the structure of the oxide superconductors, their extremely weak effect on T_c is rather perplexing. This is particularly so considering their large ionic sizes and atomic weights, the induced lattice expansion, and changes in normal-state properties. A comparative study between noble element dopants may help us to unravel the correlation between superconductivity and other physical properties.

In the present work the structural and superconducting properties of gold-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been investigated in the range from 0 up to 40 at. % Au. We have found that up to 10 at. % Au can be doped into the structure, and above this limit gold precipitates into separate gold grains. We will describe the sample preparation and characterization by x-ray diffraction, neutron diffraction, optical microscopy, and weight-loss analysis. The results demonstrate convincingly that Au is indeed incorporated into the structure, causing an increase in the lattice parameter c . Superconducting properties of the materials have been studied by magnetization and resistivity measurements. A most interesting effect of an increase of superconducting transition temperature has been observed. This is the first observation that a dopant causes a T_c enhancement in $\text{YBa}_2\text{Cu}_3\text{O}_7$. Equally significant, the

enhancement of T_c is accompanied by a large uniaxial lattice expansion, i.e., a *negative* uniaxial pressure. We will discuss, on the basis of the observed structural and superconducting properties, the location of the Au ion in the lattice as well as the cause for the T_c enhancement.

II. SAMPLE PREPARATION AND CHARACTERIZATION

We have prepared three different groups of samples. Group (1) was obtained by a method⁷ used by us previously to produce Au- $\text{YBa}_2\text{Cu}_3\text{O}_7$ composites. A fully oxygenated 1:2:3 compound was first prepared by the usual solid-state reaction method from high-purity starting materials of Y_2O_3 , BaCO_3 , and CuO . The powders were thoroughly mixed, pressed into pellets and sintered at 950°C in oxygen for a total period of about 100 h with two intermediate grindings and pressings. A slow cooling rate was used to assure full oxygenation. Samples of compositions $(\text{YBa}_2\text{Cu}_3\text{O}_7)_{1-x}\text{Au}_x$ with $0 \leq x \leq 0.4$ were then prepared from pure Au and 1:2:3 powders. The Au and stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$ powders were well mixed, pressed into pellets, and annealed at 950°C in an oxygen atmosphere for about 50 h and slowly cooled. Samples in group (2) were prepared with the same chemical formula as in group (1), but instead of using the prereacted 1:2:3, we used Y_2O_3 , BaCO_3 , CuO , and Au as precursors. Group (3) samples were prepared following the procedures as those of group (2), but according to the chemical formula $\text{YBa}_2\text{Cu}_{1-x}\text{Au}_x)_3\text{O}_7$ (i.e., gold was intended to substitute for Cu). The sintering conditions for group (2) and (3) were the same as those used to obtain the pure 1:2:3 compound. In addition, we have also prepared group (1) and (3) samples using silver and platinum.

The phase purity of every sample was checked with a Philips APD 3720 x-ray automated powder diffractometer with $\text{Cu } K\alpha$ radiation. Only samples from groups (1) and (2) containing less than 10 at. % Au were found to form single-phase materials as determined by x-ray diffraction. For the same composition, the diffraction spectra from these two groups are identical despite the difference in the sample preparation; however, the diffraction spectra of group (3) samples are different. Two representative spectra of the samples doped with 10 at. % Au from groups (1) and (3), as well as the spectrum of pure 1:2:3 compound, are presented in Fig. 1. The diffraction peaks of the group (1) sample can be indexed in exactly the same manner as that in the parent orthorhombic 1:2:3 compound, except that the positions of the (00 l) peaks are shifted reflecting a change in the c lattice parameter caused by the incorporation of gold into the bulk materia. There is no impurity peak except only one very weak peak near $2\theta = 36^\circ$, most likely from a trace of CuO . The intensity of this weak peak is less than 1% of the intensity of the (110+103) peaks from the 1:2:3 phase. In contrast to the group (1) and (2) samples, there are significant secondary phases in the group (3) samples as revealed in spectrum (c) in Fig. 1.

We have not been able to obtain single-phase samples

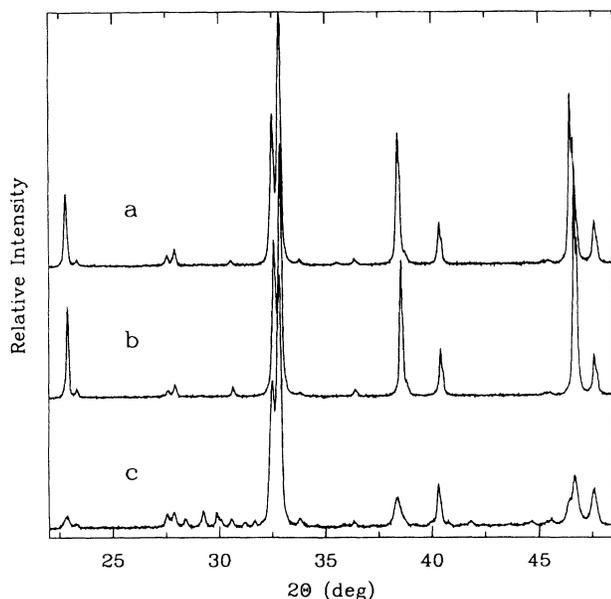


FIG. 1. The θ - 2θ diffraction spectra of pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ curve *b* and the samples doped with 10 at. % of Au, from group (1) (*a*) and group (3) (*c*) (see description of sample preparation in the text).

doped with silver or platinum using either the group (1) or (3) schemes. In the following, we will only discuss the properties of the Au-doped materials from group (1), which are identical to those of group (2).

A. Neutron structure determination

The structure of a group (1) sample doped with 8 at. % Au has also been determined by neutron diffraction at the National Institute of Standards and Technology reactor. Neutrons of wavelength 1.5525 Å derived from a Cu(220) monochromator were used. The angular divergence of the beam was limited by Söller collimators of 10-, 20-, and 10' widths before and after the monochromator and before the sample, respectively. The structure was refined using a modified Rietveld analysis procedure,¹⁶ and the essential results are summarized in Table I using the site notation of Ref. 17. For comparison, the data for a pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample are also included. The neutron diffraction data, which are extremely sensitive to oxide phases, revealed that the only trace of a secondary in the sample is CuO; no other Au-containing phases are present. The amount of CuO present as determined from a neutron refinement of the subsidiary phase is slightly in excess of that which would be formed from the replacement of Cu atoms by Au.

B. Au solubility

The morphology of the samples has been studied by using an optical microscope. Figure 2 displays micrographs of the polished samples with increasing Au content (0, 10, 20, 30, and 40 at. %). The darkest spots are the voids in the ceramic materials. Some were produced by the polishing process, others were intrinsic to the solid-state reaction. The gray grains are the 1:2:3 phase doped with

Au, while the white particles are the precipitated Au metal. The ceramic grains are elongated with an averaged dimension of about $20 \times 50 \mu\text{m}^2$. The Au particles are much smaller with a size averaging about $5 \mu\text{m}$. As is clearly revealed in Fig. 2, the density of metallic Au grains is rather minute in samples containing 10 at. % Au or less. However, it increases dramatically when the Au content exceeds 10 at. %. This is an evidence that the Au content exceeds 10 at. %.

Figure 3 shows a portion of the x-ray diffraction patterns of two samples with 10 and 20 at. % Au [curves (*b*) and (*d*), respectively]. Curves (*a*) and (*c*) are the patterns of the mixture of pure 1:2:3 compound and Au powder (10 and 20 at. %, respectively) before annealing. The arrows mark the diffraction peaks of elemental gold. It is clear that after annealing this peak disappears in the 10 at. % sample, whereas its intensity is simply decreased in the 20 at. % sample. This confirms that Au enters into the 1:2:3 structure and the solubility limit is approximately 10 at. %. It is also noted that the (006) and (020) peaks, which are overlapping in the pure 1:2:3 compound, are split in the doped samples, due to a sizable increase of the *c* lattice parameter.

The lattice parameters of the 1:2:3 compound doped with gold were determined by fitting the x-ray diffraction peaks using modified Gaussian functions and subsequent fitting of the positions of at least 20 diffraction peaks using a standard least-squares reduction method. The dependence of the lattice parameters *a*, *b*, and *c* on the gold content are presented in Fig. 4. All the samples remain orthorhombic throughout the whole range of Au doping. Also shown in Fig. 4 are the lattice parameters (*a_i* and *c_i*) of the samples with tetragonal structure obtained after annealing in argon for 1 h at 800°C. The most prominent feature in the lattice parameters is the large expansion along the *c* axis due to Au doping in the range of 0–10 at. % and the sudden leveling off of the parameter *c* as the Au content is increased above 10 at. %. Both the elongation and the saturation behavior of the *c* axis again strongly support a solubility limit of 10 at. % Au in the 1:2:3 structure. It is noted that while the *c* lattice parameter is expanded by 0.31% at 10 at. % Au, the changes in parameters *a* and *b* are less than 0.08%. Thus, the introduction of Au does not lead to the disordering of the Cu-O chains, since *a* and *b* remain basically unchanged and the orthorhombic structure remains intact.

The lattice parameters (see Table I) determined from neutron diffraction of a 8 at. % Au-doped sample are very consistent with those of the x-ray diffraction data. In addition, the neutron data also show a slight increase in oxygen content of about 1%. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, it is well known that the parameter *c* increases with decreasing oxygen content. Therefore, the uniaxial lattice expansion observed in Au-doped samples is not due to the loss of oxygen content; on the contrary, the oxygen content is slightly higher.

The weight losses of various samples after annealing in argon at 800°C for 1 h are shown in Fig. 5. The error bars are standard deviation from the average of the weight losses of five samples with the same Au content.

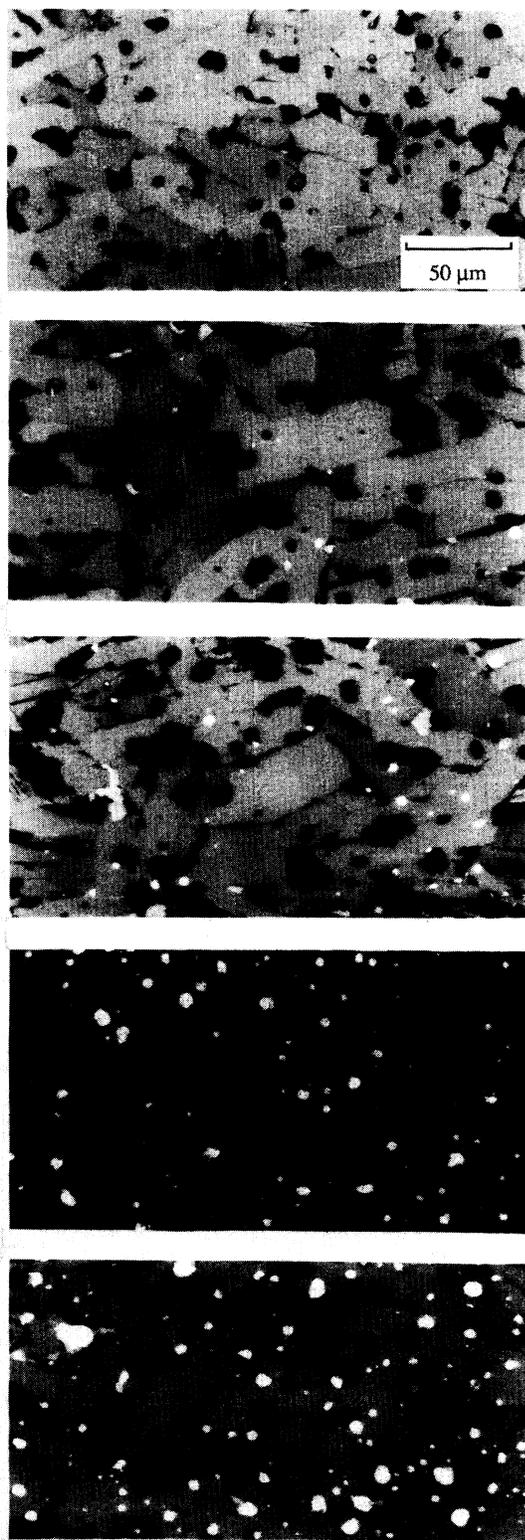


FIG. 2. Optical micrographs of the polished samples with the following Au content (at. %), from top to bottom 0, 10, 20, 30, and 40 at. %. The bright spots are gold grains, the gray grains are 1:2:3 doped with Au, and the darkest spots are voids, either intrinsic or created by polishing.

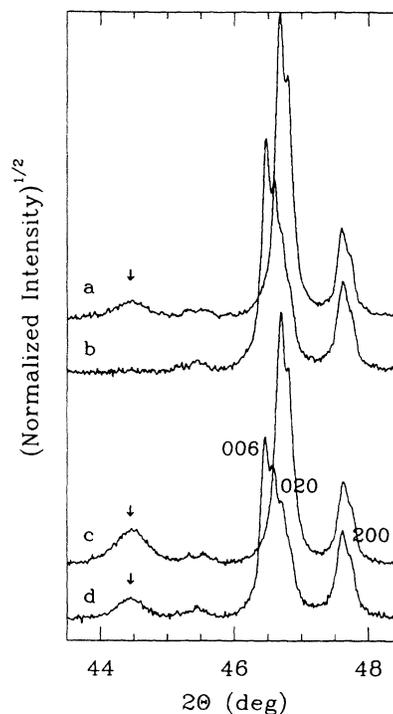


FIG. 3. Part of the diffraction spectra of the samples doped with 10 at. % Au (curve *b*) and 20 at. % Au (*d*) and the powders of 1:2:3 compound mixed with 10 at. % (*a*) and 20 at. % Au (*c*) before annealing. The diffraction peak due to the Au phase is marked by arrows. It disappears after annealing in the sample with 10 at. % Au.

It is observed that the weight loss is not a monotonic function of Au content, rather, it again has a maximum at the 10 at. % Au solubility limit, corresponding to the onset of precipitation of metallic Au.

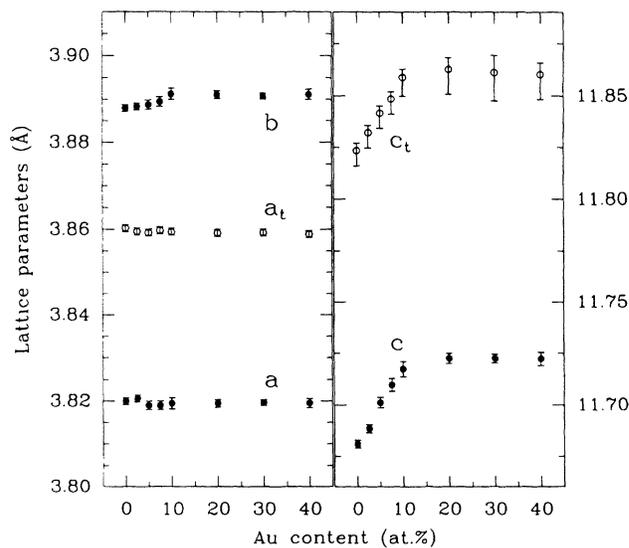


FIG. 4. The dependence of *a*, *b*, and *c* lattice parameters on gold content. The *a_t* and *c_t* are the lattice parameters of the samples annealed in argon for 1 h at 800 °C to reduce the oxygen content.

C. Site location of Au

In light of the above results, determining the exact location of the Au dopant is crucial. Unfortunately, the neutron-scattering amplitude of Au is nearly identical to that of Cu. We could not locate the Au site with certainty with neutron diffraction. However, the analysis of the Cu-O bond lengths provided an important clue. As is

listed in Table I, the Cu-O plane assembly [Cu(2)-O(2) along the *a* axis and Cu(2)-O(3) along the *b* axis] is barely affected by Au doping. The Cu-O bond lengths in the plane change by less than 0.04%. The Cu(1)-O(4) length along the chain direction is increased by about 0.06%, again a minor change. The most significant change occurs in the Cu(1)-O(1) length, the distance between the Cu(1) chain site and the bridging oxygen O(1) site, which is

TABLE I. Results for neutron powder refinement of pure and 8 at. % Au-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$. Numbers in parentheses represent statistical errors in the last decimal place, “*f*” denotes that the parameter was fixed. The site notation is that given in Ref. 17. *B* is the thermal parameter and *n* is the occupancy number. R_N , R_{wp} , and R_e are the nuclear, weighted-profile, and expected *R* factor of fit, respectively.

$\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$ <i>Pmmm</i> space group					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>n</i>
Y	0.5	0.5	0.5	0.63(5)	1.0(<i>f</i>)
Ba	0.5	0.5	0.1845(2)	0.81(6)	2.0(<i>f</i>)
Cu(1)	0.0	0.0	0.0	0.60(5)	1.0(<i>f</i>)
Cu(2)	0.0	0.0	0.3552(2)	0.54(4)	2.0(<i>f</i>)
O(1)	0.0	0.0	0.1579(2)	0.94(6)	2.0(<i>f</i>)
O(2)	0.5	0.0	0.3780(2)	0.71(6)	2.0(<i>f</i>)
O(3)	0.0	0.5	0.3780(2)	0.54(5)	2.0(<i>f</i>)
O(4)	0.0	0.5	0.0	1.97(15)	0.95(1)
O(5)	0.5	0.0	0.0	1.97(<i>f</i>)	0.03(1)

$$a = 3.8229(1) \text{ \AA}$$

$$b = 3.8865(1) \text{ \AA}$$

$$c = 11.6821(4) \text{ \AA}$$

$$V = 173.57(1) \text{ \AA}^3$$

$$(b - a)/(b + a) = 8.25(2) \times 10^{-3}$$

$$R_N = 3.64$$

$$R_{wp} = 9.16$$

$$R_e = 6.43$$

$$\chi = 1.42$$

$\text{YBa}_2\text{Cu}_3\text{O}_{7.04}$ with 8 at. % Au-added <i>Pmmm</i> space group					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>n</i>
Y	0.5	0.5	0.5	0.54(3)	1.0(<i>f</i>)
Ba	0.5	0.5	0.1848(2)	0.67(4)	2.0(<i>f</i>)
Cu(1)	0.0	0.0	0.0	0.47(3)	1.0(<i>f</i>)
Cu(2)	0.0	0.0	0.3557(2)	0.53(3)	2.0(<i>f</i>)
O(1)	0.0	0.0	0.1596(1)	0.90(4)	2.0(<i>f</i>)
O(2)	0.5	0.0	0.3790(2)	0.55(3)	2.0(<i>f</i>)
O(3)	0.0	0.5	0.3779(2)	0.59(4)	2.0(<i>f</i>)
O(4)	0.0	0.5	0.0	0.051(3) [β_{11}] 0.014(2) [β_{22}] 0.0039(3) [β_{33}]	1.0(<i>f</i>)
O(5)	0.5	0.0	0.0	2.0(<i>f</i>)	0.04(1)

$$a = 3.8197(1) \text{ \AA}$$

$$b = 3.8888(1) \text{ \AA}$$

$$c = 11.7121(4) \text{ \AA}$$

$$V = 173.91(1) \text{ \AA}^3$$

$$(b - a)/(b + a) = 8.96(2) \times 10^{-3}$$

$$R_N = 3.41$$

$$R_{wp} = 5.75$$

$$R_e = 3.91$$

$$\chi = 1.47$$

Selected bond distances (\AA)

	1:2:3	1:2:3 with 8 at. % 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%

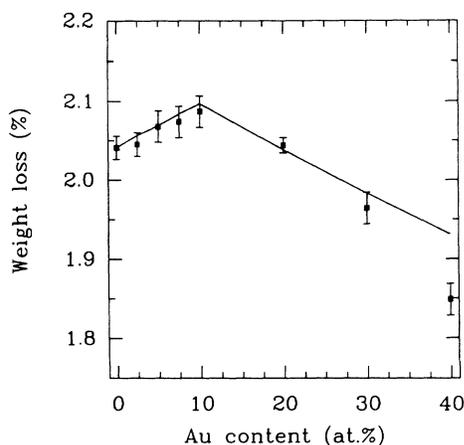


FIG. 5. The weight loss after the argon annealing.

increased by 1.36%. Also significant, the Cu(2)-O(1) length is reduced by 0.3%. Therefore, the most viable explanation is that Au ions substitute the Cu(1) chain site and push the bridging O(1) ions toward the Cu(2) sites. The neutron data also indicate that the uniaxial lattice expansion is predominantly caused by the change in the Cu(1)-Cu(2) distance, but *not* in the Cu(2)-Cu(2) distance.

As stated above, the near coincidence in scattering amplitudes for neutrons of Au (0.763×10^{-12} cm) and of Cu (0.772×10^{-12} cm) precludes the direct determination of the Au-site occupancy by neutron diffraction. However, a strong scattering contrast exists for x rays due to the large difference in atomic number. We have thus taken high-precision x-ray powder data at the National Institute of Standards and Technology (NIST), using a Scintag powder diffractometer with a scattered beam monochromator and Cu $K\alpha$ radiation, on the same nominal 8 at. % Au sample used in the neutron study. A total profile refinement procedure¹⁸ was then used to extract the Cu- and Au-site occupancies. The atomic positional coordinates as determined from the neutron refinement were used as fixed input in the x-ray refinement, due to the relative insensitivity of x-ray diffraction to O atoms. Preferred orientation in even loosely compacted powders is a severe problem affecting the x-ray intensities which can be approximately compensated for in the analysis. The result of the profile refinement ($R_{wp} = 8.83$, $\chi = 2.57$) show that the Au substitutes directly for Cu and only on the Cu(1) chain site. The refined occupancies are $\text{Au}(1) = 0.084(4)$ and $\text{Au}(2) = -0.005(3)$, consistent with the 8% as-grown concentration [note that, as prepared by the group (1) procedure, the composition of the fully substituted material is $\text{YBa}_2\text{Cu}_{2.92}\text{Au}_{0.08}\text{O}_{7+\delta}$]. This provides conclusive direct evidence of the substitution of the Au for Cu(1), and taken together with the neutron second-phase analysis shows that the excess Cu ions formed by adding the Au to the stoichiometric superconductor precipitate from the structure as CuO.

D. Valence of Au

The common valences of Au are Au^+ and Au^{3+} . Although several Au compounds can be formulated as

Au^{2+} , most are mixed-valence species^{14,15} with Au^+ and Au^{3+} . Based on a large number of structural studies of the 1:2:3 superconductor materials,¹⁻⁴ it has been found that the location of a dopant in $\text{YBa}_2\text{Ca}_3\text{O}_7$ is directly related to its valence state. All the divalent dopants (Zn^{2+} , Ni^{2+}) substitute the Cu(2) plane site in $\text{YBa}_2\text{Cu}_3\text{O}_7$, and all the trivalent ones (Al^{3+} , Ga^{3+} , Co^{3+} , Fe^{3+}) go to the Cu(1) chain site, at least in the low-doping limit. One possible cause for the site preference is the nonuniform hole concentration in the Cu(2)-O₂ plane and Cu(1)-O chain assemblies. The Cu(1)-O assembly serves as a charge reservoir. Electrostatically, it is more stable for trivalent ions to go to the Cu(1) site than divalent ions. It is also useful to note from neutron data that, in every case, trivalent ions always draw extra oxygen into the structure. With these facts in mind, we are quite certain that the valence state of Au at the Cu(1) site is Au^{3+} . Another argument that supports this assessment is from the Au ionic sizes. The effective ionic radius¹⁹ of Au^{3+} is 0.85 Å, close to that of Cu^{2+} (0.73 Å), whereas the radius of Au^+ is 1.37 Å, too large to be accommodated at the Cu(1) site. We note also that the only confirmed oxide of gold is Au_2O_3 (i.e., Au^{3+}) and Au^{3+} prefers square planar geometry (coordination number 4)^{14,15} as in Au_2Cl_6 , AuF_4^- , and AuBr_4^- .

III. SUPERCONDUCTING PROPERTIES

The magnetization of the samples was measured with a SQUID magnetometer. Results of the magnetization measurement for pure 1:2:3 compound and one doped with 10 at. % Au are presented in Fig. 6. Superconducting transitions are very sharp in both cases and the doping with Au does not compromise T_c . There is essentially no change in the diamagnetic and Meissner effects

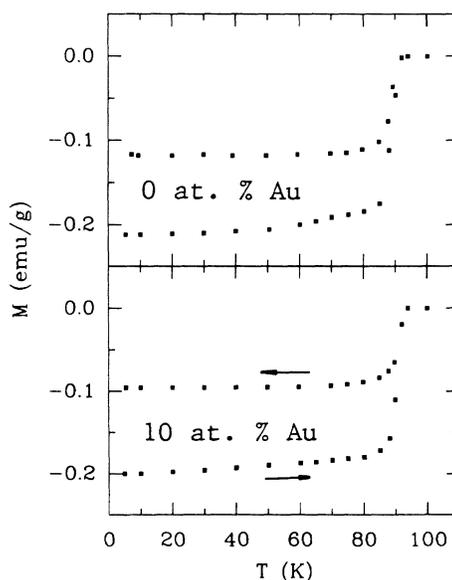


FIG. 6. Zero-field-cooled (increasing temperature) and field-cooled magnetization (decreasing temperature) of the samples with 0 and 10 at. % Au. The magnetic field is 10 Oe.

within the experimental uncertainty. Therefore, Au-doped 1:2:3 materials (≤ 10 at. % Au) remain as bulk superconductors.

Standard four-probe resistivity measurements were performed on samples of regular geometry. All samples exhibit positive temperature coefficients of resistivity, typical of pure superconducting cuprates. Figure 7(a) gives a plot of the normalized resistivity as a function of temperature in the vicinity of the superconducting transitions for a series of samples within the Au solubility limit. The values of T_c determined from resistivity measurements (10, 50, and 90 % resistivity drop) are plotted against Au content in Fig. 7(b). The values of T_c determined from resistivity measurements (10, 50, and 90 % resistivity drop) are plotted against Au content in Fig. 7(b). It is evident that all the transitions remain sharp ($\Delta T_c < 1$ K), and T_c is enhanced by about 1.5 K over that of pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ when Au reaches its solubility limit. The sharpness of transitions and the systematic increase in T_c with Au content are indications of uniform distribution of Au ions within the structure. Above 10 at. % Au, T_c remains unchanged consistent with the fact that Au precipitates out as metallic grains. The data shown in Fig. 7 are reproducible using different batches of samples, indicating that the T_c enhancement is not an artifact. The benign influence of Au ions on superconductivity reflects the fact that Au substitutes for the Cu(1) chain site. Otherwise, T_c would be severely affected if the Cu(2) plane site is invaded, because the Cu(2)-O₂ planes are crucial to high- T_c superconductivity.

It is certainly a surprising and intriguing result that the 1:2:3 structure with 10% of its Cu(1) sites replaced by

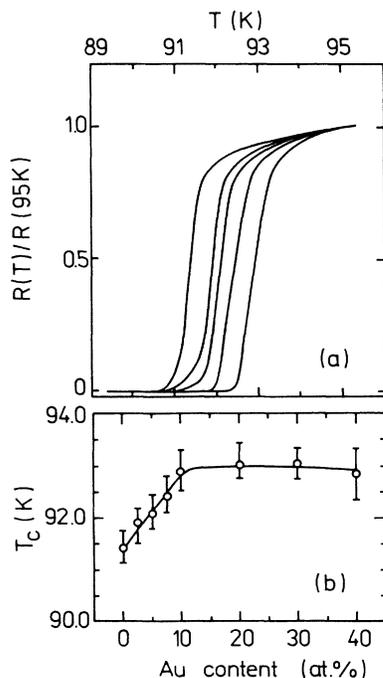


FIG. 7. (a) Normalized resistivity vs temperature in the vicinity of the superconducting transitions for samples with the following Au content (from left to right): 0, 2.5, 5, 7.5, and 10 at. %, (b) the dependence of T_c on gold content. The bars represent 10–90 % resistivity drop.

heavy Au ions (more than three times heavier than Cu) not only could retain its high- T_c value, but also gain a 1.5-K increase in T_c . It is unlikely that the lattice expansion induced by Au doping could cause the T_c enhancement. If anything, experiments with uniaxial pressure along the c axis reveal that T_c increases slightly with decreasing interplanar distances. But in the 8 at. % Au-doped sample, the neutron data in Table I indicate that the Cu(2)-Cu(1) (plane-chain) distance increases by about 0.41%, while the Cu(2)-Cu(2) (plane-plane) distance remains constant within experiment error ($\pm 0.08\%$).

It is well established that the hole concentration has a strong effect on the superconducting properties. For example, an increase in oxygen content raises the carrier concentration (p) and is accompanied by an increase in T_c . Substituent atoms also affect p and lead to changes in the superconducting properties. For the Au substituted materials, the neutron results show that the oxygen content in each unit cell containing 0.08 Au ions has been increased by 0.06 atoms. Assuming that Au^{3+} replaces Cu^{2+} , there is a net increase in hole carriers of about 0.04/unit cell, which may explain the slight increase in T_c .

The role of the bridging oxygen [O(1)] on superconductivity is an unresolved issue. The bond lengths between O(1) and the two Cu sites are believed to be crucial to charge transfer among the ions. Miceli *et al.*²⁰ have studied the correlation between T_c and structural parameters in $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7-\delta}$. They found that when T_c is suppressed to zero by Co doping, the Cu(1)-O(1) bond length is reduced by 1.30% and there seemed to be a linear correlation between T_c and the bond length. They concluded that the suppression of superconductivity is strongly coupled to the chemical bond lengths. However, our results do not support this conclusion. As we have shown, in an 8 at. % Au 1:2:3 sample, the Cu(1)-O(1) distance is expanded by as much as 1.36%, and yet T_c barely changes. Clearly, in this case T_c is insensitive to the Cu(1)-O(1) bond length.

The observation that gold is the only dopant known that is not detrimental to T_c prompts us to ask questions important to superconductivity. For example, Au is a heavy atom which should affect the dynamics of the lattice and, presumably, the electron-phonon coupling. But these changes do not seem to affect the superconducting mechanism. Also, the incorporation of Au may cause changes in various normal-state properties. Studies of these changes could help us to understand which normal-state parameters are relevant to the high- T_c state and which ones are not. In Fig. 8, we present the temperature dependence of resistivity in the Au-doped system. A linear temperature dependence is evident, but the slope is increased as shown in the inset. The reduction in slope above 10 at. % Au is due to the precipitation of metallic Au grains. In the solubility range, the slope of the resistivity can be enhanced by a factor as large as 2 over that of the pure 1:2:3 sample, while the residual resistivity remains at a low value (i.e., small impurity scattering). This result shows that superconductivity is unaffected for a wide range of different slopes of the resistivity.

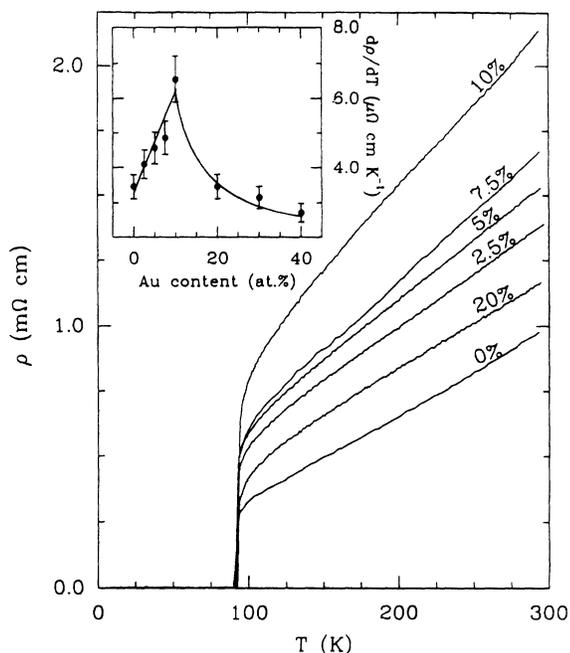


FIG. 8. Temperature dependence of resistivity of samples with different Au content. The inset shows the slope of resistivity vs Au content.

It is instructive to compare Au^{3+} with other Cu(1) site dopants (i.e. Ga^{3+} , Al^{3+} , Co^{3+} , Fe^{3+}).¹⁻⁴ One feature shared by all of these trivalent ions is that they attract more oxygen into the structure. However, while other trivalent dopants induce an orthorhombic to tetragonal structural transition at a low-doping level (3–5%) and reduce T_c to varying degrees, the Au^{3+} has little effect on the orthorhombic structure and T_c increases slightly. Furthermore, other dopants always cause a localization-like resistivity upturn prior to the superconductivity transition. But the resistivity of the Au-doped samples remains linear with temperature in the normal state. These comparisons raise some outstanding questions. Why does Au^{3+} behave differently from other trivalent dopants? Why is the orthorhombic structure maintained with Au^{3+} as opposed to other 3+ dopants? Model calculations²¹ have confirmed that dopants such as Ga^{3+} and Al^{3+} destroy the local chain structure effectively, which causes the orthorhombic to tetragonal transition even at a low-doping level. But why does Au preserve the local chain structure? Is it solely due to the fact that Au^{3+} prefers a square-planar environment (coordination number = 4)? We would like to emphasize here that it is the difference between Au^{3+} and other trivalent ions that makes Au a rather special kind of dopant to probe the oxide superconductors. It would be interesting to study the effect of Au on the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ compound where there is only one Cu site, i.e., the plane site. We have substituted Zn^{2+} , Ga^{3+} , Al^{3+} , Fe^{3+} , Co^{3+} , and Ni^{2+} for Cu in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.²² In every case, T_c is dramatically affected and it is completely suppressed at low-doping levels (1.8–4.2%). This observation clearly reveals the importance of the Cu-O_2 plane as far as superconductivity

is concerned. It remains to be seen whether Au could substitute this Cu site and, if it could, what effect it would have on both the superconducting and normal-state properties.

Our current results on Au-doped 1:2:3 materials provide plausible explanations of some recent findings.^{7,9-13} It has been shown that Au contacts formed on the surface of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have very low contact resistance⁹⁻¹¹ (especially after mild annealing) and a proximity junction with Au as a buffer layer can be made successfully.^{12,13} All these can be attributed to the fact that a small amount of Au can enter the structure without causing oxygen depletion, structural disorder, and T_c degradation. As a result, an intimate contact between the oxide superconductor and Au film can be formed. A mild annealing to promote the interface diffusion would be beneficial to further reduce the contact resistance. Our results also account for the “excellent” single-crystal growth from Au crucibles. It is imperative to determine the extent of Au incorporation in these single crystals, if their properties can be considered intrinsic to high- T_c superconductors.

IV. SUMMARY AND CONCLUSIONS

Contrary to the common belief that noble metals do not react with $\text{YBa}_2\text{Cu}_3\text{O}_7$, we have found that up to 10 at. % of gold ions can be incorporated into the structure. X-ray total profile refinement confirms that the Au dopant substitutes the Cu(1) chain site. The neutron data show that the excess Cu(1) released by the preparation procedure forms CuO. The introduction of Au causes an increase in the lattice parameter c by 0.31% at the solubility limit, but has only a minor effect either on the lattice parameters a and b or the orthorhombicity. Structural analysis on a sample doped with 8 at. % Au indicates that only the Cu(1)-O(1) and Cu(2)-O(1) [O(1) the bridging oxygen] bond lengths suffer significant changes, i.e., +1.36% and -0.3%, respectively, and all the other Cu-O bond lengths are basically unchanged. Also unaffected is the interplanar [Cu(2)-Cu(2)] distance, but the Cu(1)-Cu(2) distance is increased by 0.4%. The oxidation state of gold is Au^{3+} based on ionic size and site location. The oxygen content of the Au-doped 1:2:3 compound increases with doping.

Despite the lattice expansion and the presence of the heavy Au ions, the Au-doped materials remain bulk superconductors, and the superconductivity properties are not compromised at all. Instead, T_c is enhanced by 1.5 K. The benign effect of Au doping on superconductivity is a very useful feature. The presence of Au will change many other properties such as lattice dynamics and some normal-state properties. Studies of the superconducting behavior and the properties affected by Au doping will enable a better understanding of their correlations.

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- ¹J. T. Market, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 265.
- ²C. L. Chien, Gang Xiao, and M. Z. Cieplak, in *Oxygen Disorder Effects in High T_c Superconductors*, edited by J. L. Morán-López and I. K. Schuller (Plenum, New York, 1989).
- ³C. L. Chien, Gang Xiao, M. Z. Cieplak, D. Musser, J. J. Rhyne, and J. A. Gotaas, in *Superconductivity and Its Applications*, edited by H. S. Kwok and D. T. Shaw (Elsevier, New York, 1988), p. 110.
- ⁴Gang Xiao, F. M. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, *Phys. Rev. B* **35**, 8782 (1987); Gang Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhshai, and C. L. Chien, *Phys. Rev. Lett.* **52**, 927 (1988).
- ⁵Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, *Nature (London)* **328**, 512 (1987).
- ⁶J. 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**, 3893 (1987).
- ⁷F. H. Streitz, M. Z. Cieplak, Gang Xiao, A. Gavrin, A. Bakhshai, and C. L. Chien, *Appl. Phys. Lett.* **52**, 927 (1988); Gang Xiao, F. H. Streitz, M. Z. Cieplak, A. Bakhshai, A. Gavrin, and C. L. Chien, *Phys. Rev. B* **38**, 776 (1988).
- ⁸B. R. Weinberger, L. Lynds, D. M. Potrepka, D. B. Snow, C. T. Burila, H. E. Eaton, Jr., R. Cipolli, Z. Tan, and J. J. Budnick, *Physica C* **161**, 91 (1989).
- ⁹C. L. Chien, Gang Xiao, F. H. Streitz, A. Gavrin, and M. Z. Cieplak, *Appl. Phys. Lett.* **51**, 2155 (1987).
- ¹⁰A. D. Wieck, *Appl. Phys. Lett.* **53**, 1017 (1988); K. Mizushima, M. Sagoi, T. Miura, J. Yoshida *ibid.* **52**, 1101 (1988); J. W. Ekin, T. M. Larson, N. F. Bergren, A. J. Nelson, A. B. Swartzlander, L. L. Kazmerski, A. J. Panson, and B. A. Blankenship, *ibid.* **52**, 1819 (1988).
- ¹¹J. W. Jing, Z. Z. Wang, and N. P. Ong, *Physica C* **162-164**, 1061 (1989).
- ¹²H. Akoh, F. Shinoki, M. Takahashi, and S. Takada, *Jpn. J. Appl. Phys.* **27**, L519 (1988).
- ¹³L. H. Green *et al.*, *Physica C* **162-164**, 1069 (1989).
- ¹⁴F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1980), p. 966.
- ¹⁵N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, Oxford, 1984), p. 1364.
- ¹⁶H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969); E. Prince, *U. S. Tech. Note* **117**, 8 (1980); J. K. Stalick and E. Prince (unpublished).
- ¹⁷F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, *Phys. Rev. B* **35**, 8778 (1987).
- ¹⁸A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987 (unpublished).
- ¹⁹R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).
- ²⁰P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, *Phys. Rev. B* **37**, 5932 (1988).
- ²¹Z. X. Cai and S. D. Mahanti, *Phys. Rev. B* **40**, 6558 (1989); G. Baumgärtel and K. H. Bennemann, *ibid.* **40**, 6711 (1989).
- ²²Gang Xiao, A. Bakhshai, M. Z. Cieplak, Z. Tesanovic, and C. L. Chien, *Phys. Rev. B* **39**, 315 (1989); M. Z. Cieplak, Gang Xiao, A. Bakhshai and C. L. Chien, *ibid.* **39**, 4222 (1989); Gang Xiao, J. Q. Xiao, M. Z. Cieplak, and C. L. Chien, *ibid.* **42**, 240 (1990).

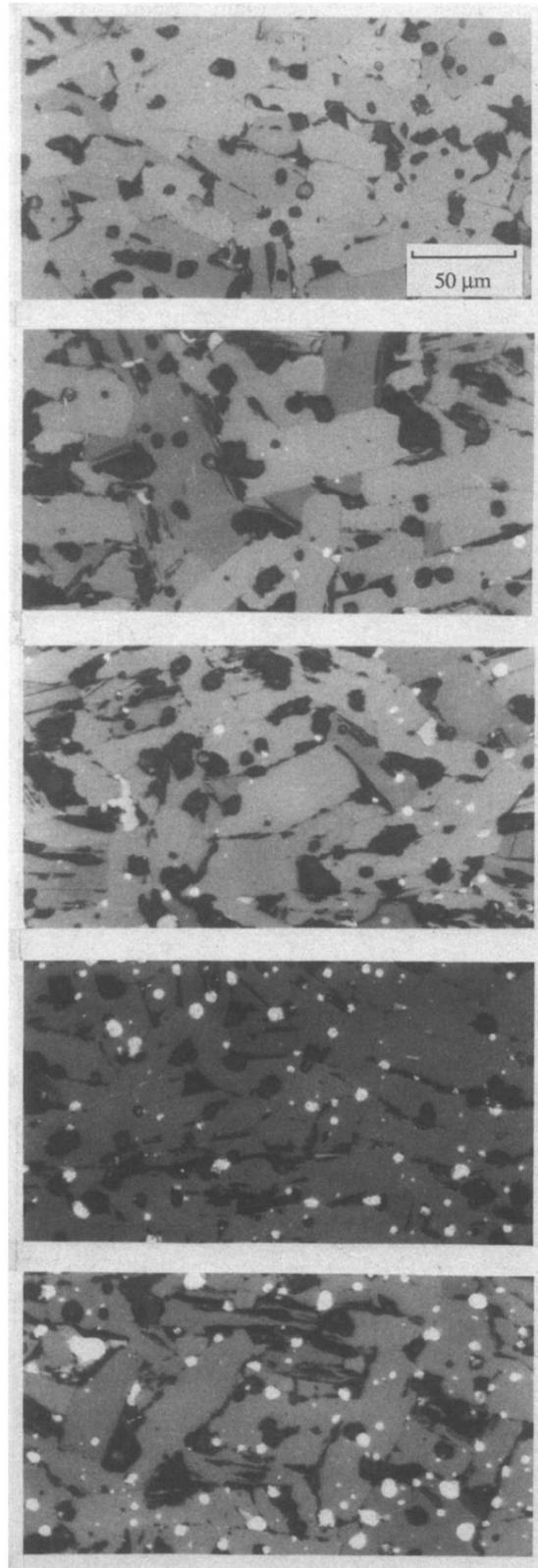


FIG. 2. Optical micrographs of the polished samples with the following Au content (at. %), from top to bottom 0, 10, 20, 30, and 40 at. %. The bright spots are gold grains, the gray grains are 1:2:3 doped with Au, and the darkest spots are voids, either intrinsic or created by polishing.