

field parallel to the plane (Fig. 4). A plasma reflectivity edge is seen in the infrared region, and the spectrum fits the Drude formula, as in the case of LSCO and YBCO. The relatively low plasma frequency as well as the large Hall coefficient indicate the low carrier concentration. For comparison, the plasma frequencies of LSCO and YBCO¹² are shown by the arrows in Fig. 4. Note that the plasma energy increases in the sequence LSCO, Bi₂(Sr, Ca)₃Cu₂O_y and YBCO, in order of increasing T_c . As the plasma frequency increases with increasing carrier concentration, the result is suggestive of the correlation between T_c and hole concentration.

The superconducting oxide Bi₂(Sr, Ca)₃Cu₂O_y with $T_c = 80$ K exhibits strikingly similar properties to the previous lanthanide-based cuprates LSCO and YBCO, namely the linear dependence of resistivity on temperature, the anisotropic upper critical field and the positive Hall coefficient. The proposed structure of this material⁵ contains neither lanthanide layers, nor Cu-O chains. We therefore conclude that the normal-state properties, and possibly the superconductivity of Bi₂(Sr, Ca)₃Cu₂O_y, is primarily governed by holes in two-dimensional Cu-O layers, as in the case of the previous high- T_c oxides.

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Significance of plane versus chain sites in high-temperature oxide superconductors

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One of the outstanding questions concerning the high-temperature superconductor YBa₂Cu₃O₇ is the relative importance of the CuO₂ planes (Cu(2) site) and the CuO chains (Cu(1) site). Many theories^{1,2} have stressed the importance of the 3d holes at the Cu sites, which provide an antiferromagnetic correlated background necessary for the coupling of the superconducting electrons. We have substituted Zn(3d¹⁰4s²) and Ga(3d¹⁰4s²4p¹) in the Cu(2) and Cu(1) sites, respectively, while maintaining the oxygen stoichiometry at 7. In the valence states of 2+ and 3+ respectively, the 3d bands of both elements are completely full, without the complication of a magnetic moment. Here we discuss the structural changes that accompany Zn and Ga substitution, as deduced from X-ray and neutron diffraction, and correlate these changes with the superconducting properties. We show that the integrity of the planes is much more important than that of the chains in sustaining high- T_c superconductivity.

Table 1 Structural parameters of YBa₂(Cu_{0.94}Zn_{0.06})₃O₇₋₈ determined by neutron diffraction at 295 K

	$a = 3.8316 (2) \text{ \AA}$	$R_N = 5.58$			
	$b = 3.8899 (2) \text{ \AA}$	$R_{wp} = 12.88$			
	$c = 11.6674 (6) \text{ \AA}$	$R_E = 6.29$			
	$V = 173.90 (2) \text{ \AA}^3$	$\chi = 2.05$			
	$(b-a)/(b+a) = 7.55 (6) \times 10^{-3}$	$\delta = 0.20 (6)$			
Site	x	y	z	B	N
Y	0.5	0.5	0.5	0.55 (9)	1.0 (f)
Ba	0.5	0.5	0.1836 (4)	1.2 (1)	2.0 (f)
Cu(1)	0.0	0.0	0.0	1.1 (1)	1.00 (5)
Zn(1)	0.0	0.0	0.0	1.1 (1)	0.00 (5)
Cu(2)	0.0	0.0	0.3547 (3)	0.47 (8)	1.80 (8)
Zn(2)	0.0	0.0	0.3547 (3)	0.47 (8)	0.20 (8)
O(1)	0.0	0.0	0.1590 (4)	0.9 (1)	2.0 (f)
O(2)	0.5	0.0	0.3771 (4)	0.9 (1)	2.0 (f)
O(3)	0.0	0.5	0.3767 (4)	0.3 (1)	1.90 (3)
O(4)	0.0	0.5	0.0	0.09 (1) [β_a]	0.84 (2)
	—	—	—	0.034 (8) [β_b]	
	—	—	—	0.004 (8) [β_c]	
O(5)	0.5	0.0	0.0	0.6 (f)	0.06 (1)
Comparison of alternate constrained-fit models					
Constrained occupancy				R_N	R_{wp}
Zn(1) = 0.0, Zn(2) = 0.18				5.58	12.88
Zn(1) = 0.18, Zn(2) = 0				5.62	12.94
Zn(1) = 0.66, Zn(2) = 0.12				5.58	12.89

Numbers in parentheses represent the statistical errors in the last decimal place, and 'f' indicates that the parameter was held constant in value. The site notation is that given in ref. 13. The total occupancy (Zn plus Cu) of the Cu(1) and Cu(2) sites was constrained to 1 and 2 atoms, respectively. The thermal parameter B for the orthorhombic O(4) (chain) site and for the O(1) site was refined with an anisotropic thermal ellipsoid of the form $\exp(-h^2\beta_a - k^2\beta_b - l^2\beta_c)$ and illustrates the significantly large mean square amplitude along the a -axis relative to the b and c directions. R_N , R_{wp} , R_E are the nuclear, weighted-profile and expected R -factor of fit respectively. N is the occupancy number.

Copper is a crucial element in the oxide superconductors. A number of groups have substituted the Cu sites by other 3d transition elements (from Ti to Zn)³⁻¹⁰ and metalloid elements (such as Al)^{6,11,12}, to elucidate the role of the Cu site. Although it has been shown that some of the dopants (Co, Ni and Fe) preferentially substitute either the Cu(1) or Cu(2) sites, the large magnetic moments of the dopants severely complicate the interpretation of the superconducting behaviour. Al was found by X-ray diffraction to substitute the Cu(1) site¹¹, but the T_c (superconducting transition temperature) data in the Al-doped samples remain controversial^{6,11,12}. The ideal dopants should be non-magnetic, with electronic configurations similar to that of Cu, and should preferentially substitute either the Cu(1) or Cu(2) sites. Zn and Ga, two elements next to Cu in the periodic table, are excellent candidates.

The samples were made by using a solid-state reaction method, as described in ref. 3. The structures were determined using an automated X-ray powder diffractometer. The diffraction peaks were fitted by modified gaussians, and the lattice parameters were determined by fitting the positions of at least 18 diffraction peaks with an accuracy better than 0.05%. Such procedures are necessary to observe the detailed structural changes. The determined lattice parameters are shown in Fig. 1. All of the YBa₂(Cu_{1-x}Zn_x)₃O₇ samples remain orthorhombic, with a large distortion $((b-a)/(b+a))$, but the structure of the YBa₂(Cu_{1-x}Ga_x)₃O₇ system is very sensitive to the doping and transforms rapidly to the tetragonal structure. Figure 2 shows the diffraction patterns of YBa₂(Cu_{1-x}Ga_x)₃O₇ in the range $46^\circ \leq 2\theta \leq 48^\circ$; the (200), (020) and (006) peaks, relating to the lattice parameters a , b and c respectively, are marked. The values of b and a rapidly approach each other on doping with Ga. At

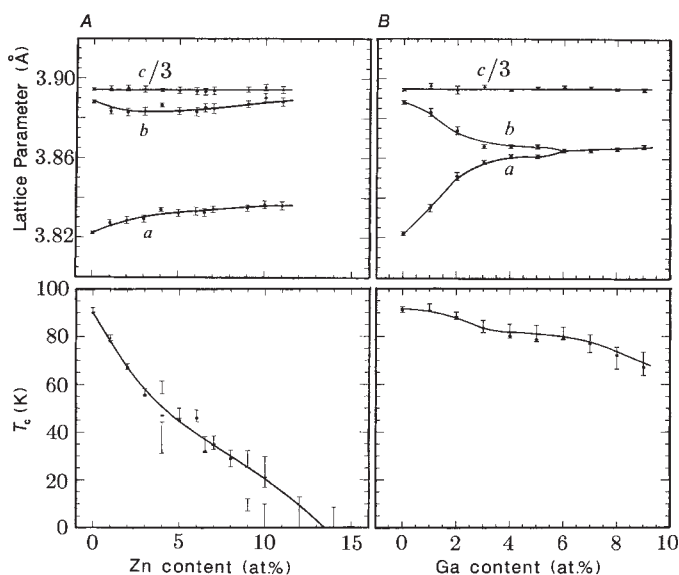


Fig. 1 Lattice parameters (a , b , $c/3$) and superconducting transition temperature (T_c) as functions of dopant content for $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ (A) and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ (B). The filled dots are T_c s obtained from magnetization measurements at an applied field of 30 Oe, and the bars represent the resistive transition (90–10% of the resistivity drop at the onset).

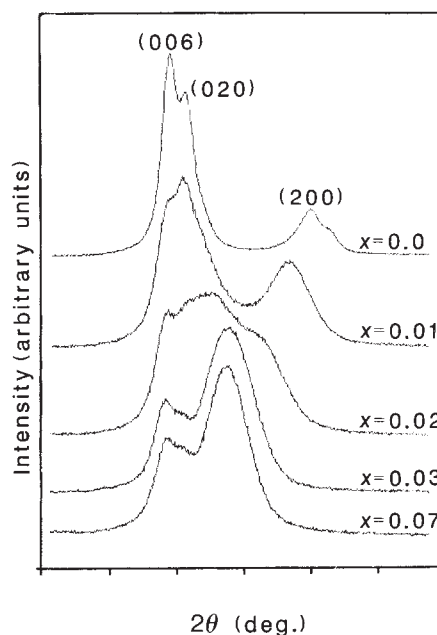


Fig. 2 X-ray diffraction patterns of $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ in the range $46^\circ \leq 2\theta \leq 48^\circ$, for five values of the gallium content, x . The (006), (020) and (200) peaks are related to the lattice parameters c , d and a , respectively.

$x = 0.03$, the (200) and (020) peaks nearly coincide, yielding a single but broadened peak. Careful fitting of at least 18 diffraction peaks indicates that the structure does not become fully tetragonal until $x = 0.06$.

The structures of two representative samples, $\text{YBa}_2(\text{Cu}_{0.94}\text{Zn}_{0.06})_3\text{O}_7$ and $\text{YBa}_2(\text{Cu}_{0.92}\text{Ga}_{0.08})_3\text{O}_7$, have also been measured by using neutron diffraction at the National Bureau of Standards reactor. The scattering intensities were refined using a modified Rietveld analysis procedure, and the essential results are summarized in Table 1 using the site notation of ref. 13. This technique is very sensitive to both oxygen site occupancies and small orthorhombic distortions, the latter sensitivity arising from the combination of high intrinsic spectrometer resolution and the well-defined line shape of the neutron peaks. Both samples exhibited total oxygen contents near seven: $O = 6.80$ (6) and 7.01 (9) for the Zn and Ga samples, respectively. Thus, the sharply reduced orthorhombic distortion of the Ga-doped samples is not driven by oxygen deficiency.

From the neutron refinement, Zn was found to substitute into only the Cu(2) site, which does not lead to a disordering of the b -axis CuO chains. The structure remains orthorhombic, with essentially the same axis distortion as in the undoped $\text{YBa}_2\text{Cu}_3\text{O}_7$ with equivalent O(4) site occupancy. The refined occupancy for the four oxygen sites is given in Table 1. To test the validity of the conclusion that the Zn occupies only the Cu(2) site, three additional refinements were made with constrained Zn (and Cu) occupancies, as shown at the bottom of Table 1. The results were compared to the result of the 'free' refinement (Table 1, centre) using a statistical significance test (equivalent to the Hamilton test). The results show that the Cu(2)-only substitution model is superior to the Cu(1)-only substitution model at the 95% confidence level (slope of the regression line $= 0.857 \pm 0.703$). A $\frac{1}{3} : \frac{2}{3}$ stoichiometric distribution of Zn on Cu(1) and Cu(2) sites does not significantly degrade the R_{wp} factor, nor is it definitively preferred by the significance test. But this distribution is not a stable occupancy when the populations are allowed to refine independently, and thus does not represent the least-squares minimum for the structure function. The replacement of Cu by Zn on the Cu(2) site only is

therefore indicated as the correct configuration.

In the 8% Ga-doped sample, the orthorhombic distortion is quite small, but can be validly determined within the neutron instrument resolution. The ratio $(b-a)/(b+a)$ is $1.02(8) \times 10^{-3}$, which is consistent with the X-ray values of Fig. 1 of lower statistical precision. Using the $Pmmm$ orthorhombic refinement, the total oxygen content was $7.01(9)$ atoms and O(4) and O(5) site occupancies were found to be $0.66(5)$ and $0.35(4)$ atoms respectively, indicating that considerable disorder is induced on the chain-site atoms. In the limit of vanishing orthorhombic distortion, the structure is tetragonal (space group $P4/mmm$), the O(4) and O(5) sites (also O(2) and O(3)) become indistinguishable, and the chain structure is fully disordered. The scattering pattern of the Ga sample was also obtained at 10 K to ascertain if increased orthorhombic distortion was present below T_c . The 10-K value $(b-a)/(b+a) = 0.80(7) \times 10^{-3}$ differs little from that at room temperature. Unfortunately, the neutron scattering amplitudes of Ga ($b = 0.729$) and Cu ($b = 0.772$) are too similar to allow a definitive determination of the site substitution at the 8% Ga level. The remaining refinement parameters (z coordinates and so on) were not significantly different from those quoted in Table 1 for the Zn and are thus not listed. Note, however, that the appreciable O(4)–O(5) oxygen disorder and the very rapid transition towards a tetragonal structure on doping with Ga (see Fig. 1) strongly suggest that Ga substitutes preferentially on the Cu(1) sites, effectively destroying the chain ordering.

The superconducting transition temperatures were determined by both four-probe resistivity and SQUID magnetometry on precision-cut samples. The results are shown in Fig. 1, with good agreement between the two measurements. In the Zn samples, T_c reduces rapidly with Zn content, vanishing at $x_{Zn} \approx 0.13$. In the Ga samples, T_c is reduced only slightly by doping. At $x_{Ga} = 0.06$, where the structure becomes tetragonal, T_c remains as high as 81 K, and thus the high T_c observed is intrinsic to the tetragonal phase. Furthermore, the magnitude of the Meissner effect in the tetragonal phase remains almost the same as that on the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$, indicating bulk superconductivity.

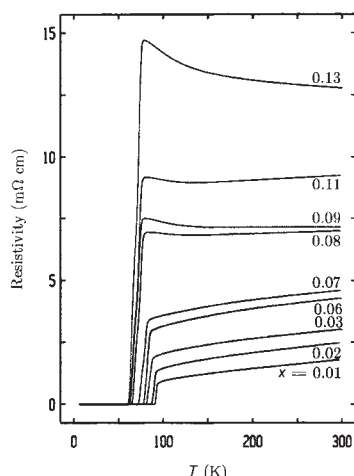


Fig. 3 Temperature dependence of resistivity for $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$.

Our T_c data for Zn-doped samples are in agreement with results from other groups⁵⁻⁸. For example, Takayama-Muromachi *et al.*⁵ have shown that T_c drops to zero at ~13 atm% Zn ($x = 0.4$ in their notation), which is very close to what we have observed.

As Al is similar to Ga in charge and ionic radius, we would expect the Al-doped and Ga-doped systems to be similar. Both show an orthorhombic to tetragonal transition^{6,11}. Siegrist *et al.*¹¹ have shown that Al occupies the Cu(1) site, supporting our claim that Ga substitutes the chain site. The T_c s of the ceramic samples (at 1.7% and 3.3% Al) are similar to those of our Ga-doped samples, but there is a sharp suppression in T_c in the single-crystal samples above 3.3% doping. Such behaviour is not supported by the work of other groups^{6,12}, in which T_c is found to remain high (80 K) up to high (10%) Al doping levels, as for the Ga-doped samples studied here.

Figure 3 shows the temperature dependence of the resistivity of the Ga-doped samples. In the range $0 \leq x \leq 0.07$, the temperature dependence of resistivity in the normal state is very similar, being metallic in nature with a positive temperature coefficient of resistivity (TCR). The resistivity increases nearly in proportion to x . This behaviour is probably due to impurity scattering, which is generally not temperature dependent, but only increases the absolute resistivity. Above $x = 0.07$, the resistivity behaves very differently: in addition to increased normal-state resistivity, the samples no longer have a positive TCR, and there is always an upturn in resistivity before the superconducting transition. Note also the large increase of resistivity between $x = 0.07$ and $x = 0.08$. This change correlates closely with the loss of orthorhombic symmetry.

The charge state of Zn is 2+, the same as that of the Cu(2) site. According to a charge-balance argument the Cu(1) site should be in the 3+ state, which is also the charge state of Ga. The full oxygen stoichiometry is assured by the similarity between the dopant charge states and those of the Cu sites.

Zn and Ga ions both have a $3d^{10}$ configuration. On substituting a Cu site, the local $3d$ holes will be eliminated. As the oxygen contents of both systems remain at 7, the sharply different behaviours of the Zn- and Ga-doped samples must be due to their preferential substitution of the Cu(2) and Cu(1) sites, respectively. The results indicate that the $3d$ holes on the Cu(2) sites are important for high T_c ; the elimination of these holes by the introduction of Zn is deleterious to the superconductivity. On the other hand, the $3d$ holes on the Cu(1) sites play a much less important part; the filling of these holes by Ga ions affects the superconductivity only slightly. We therefore conclude that the CuO_2 planes play a much more decisive role than the CuO chains in sustaining the high- T_c superconductivity.

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Evaluation of the Montsouris series of ozone measurements made in the nineteenth century

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There is growing evidence that ozone levels in the lower troposphere over the continents of the Northern Hemisphere have been increasing during the past decades^{1,2}. Questions regarding pre-industrial or 'background' ozone concentrations have led to the search for data from the early days of ozone monitoring, during the second half of the last century. Unfortunately, most measurements were then made using Schönbein test paper, giving only semi-quantitative information due to poor standardization and the influence of humidity and wind speed on its sensitivity³⁻⁵. We have reinvestigated a set of ozone measurements gathered at the Observatoire de Montsouris, located on the outskirts of Paris, where a quantitative method was established in 1876⁶ and used continuously for 34 years. The evaluation of the technique, together with the analysis of nearly 3,000 of the original daily measurements that previously remained unnoticed in a statistical bulletin of the City of Paris⁷, provides conclusive evidence that ozone levels in central Europe 100 years ago averaged 10 p.p.b. and exhibited a seasonal variation, with a maximum during the spring months. Comparisons with modern data show that ozone levels in rural areas have more than doubled over the past century and that the tropospheric ozone budget is now strongly influenced by photochemical production due to increased levels of NO_x .

The method used at Montsouris was 'iodine catalysed oxidation of arsenite in neutral aqueous solution', see equation (1).

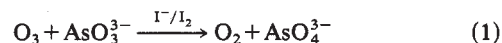
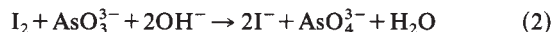


Figure 1 shows the experimental set up, consisting of a bubbler, a precisely calibrated gas meter and a water jet pump⁸. The interior part of the bubbler was made of platinum, with 20 upward facing holes at the bottom. Air entered the Pt tube directly, without the use of an inlet line. Every day the bubbler was prepared, mounted on a balcony of the observatory 5 m above the ground, and ambient air, at a flow rate of 1-2 l per min, was sampled for 24 h. After sampling, the remaining AsO_3^{3-} was titrated with a 5×10^{-4} M I_2 solution after the addition of $(\text{NH}_4)_2\text{CO}_3$ and starch (see equation (2)). An unexposed sample of the arsenite solution served as a reference.



Collection efficiency was shown to be 100% during the first year of operation through the use of two bubblers in series⁶. The AsO_3^{3-} in the second bubbler was never found to be depleted, a result which also demonstrated that the Pt-catalysed oxidation