Effect of Fluorination on the Structure and Superconducting Properties of the Hg-1201 Phase

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A fluorination of the reduced $HgBa_2CuO_{4+\delta}$ (Hg-1201) with $T_c = 61$ K resulted first in an increase in T_c up to 97 K and then in a decrease and even a suppression of superconductivity due to overdoping. Neutron powder refinements performed on fluorinated $HgBa_2CuO_4F_\delta$ showed twice the amount of extra fluorine in comparison with those for the oxygenated Hg-1201 phases with close T_c. This supports the ionic model of doping in Hg-1201: two holes per oxygen and one hole per fluorine. The apical distances in Hg-1201 depend on the number of dopant atoms rather than on their charge. The exchange of extra oxygen for a double amount of fluorine shortens the apical Cu-O distances, while the in-plane distances and T_c do not vary. [S0031-9007(97)04992-2]

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$HgBa_2CuO_{4+\delta}$(Hg-1201) is one of the most attractive compounds for investigating the relationship between structure and superconducting properties owing to its simple structure, wide range of superconducting compositions (from underdoped to highly overdoped states), small number of structural parameters, and an absence of stacking faults, cation intermixing, large static atomic displacements, etc. In general, there is good agreement in the published structural parameters of Hg-1201 and their variations caused by changes in the concentration of the extra oxygen located in the Hg-layer. There are severe discrepancies, however, among different papers concerning the occupancies of the Hg and extra oxygen sites, though these parameters are extremely important for understanding the doping mechanism in Hg-based superconductors. The high extra oxygen content (up to $\delta = 0.18$ for the optimally doped Hg-1201 [1]) determined in several studies is in obvious contradiction with the optimal hole number p_{opt} per conduction CuO_2 layer, which is assumed to be $p_{\mathrm{opt}} \approx 0.16$ (see [2] and references therein) and the $\delta_{\mathrm{opt}} = 0.08-0.09$ determined by iodometric titration [3,4]. As a result, the most natural and simplest ionic model of Hg-1201 doping (two holes per inserted extra oxygen atom) is presently under discussion and the reduced doping efficiency of oxygen in Hg-1201 has been assumed [1,5,6].

To verify the different hypotheses, we decided to exchange the extra oxygen in the Hg-1201 structure with extra fluorine atoms. Oxygen and fluorine anions have close crystallochemical behaviors, while their formal charges differ significantly: -2 and -1, respectively. Therefore, assuming a simple charge transfer model, we would expect the extra fluorine concentration to be twice as high for the fluorinated phase for the same doping level. It would also be interesting to determine the dependence of T_c and the structural parameters vs the extra fluorine content.

Single-phase samples of $HgBa_2CuO_{4+\delta}$ were synthesized from a mixture of $Ba_2CuO_{3+\delta}$ and HgO according to the procedure described in [7], then reduced in a dynamic vacuum to the composition $HgBa_2CuO_{4.01}$ determined by iodometric titration. The samples were monophase and exhibited superconductivity with $T_c = 61$ K. The reduced Hg-1201 samples were subsequently fluorinated by XeF_2 under different conditions. All operations were made in a glove box in a dried N_2 atmosphere that excluded the presence of O_2. The syntheses were carried out in Ni crucibles placed in N_2 filled and sealed copper tubes. The times and temperatures of annealing varied from 15 to 50 h and from 150 to 200 °C. The ac susceptibility measurements were performed in the temperature range 12–100 K at an external field amplitude of 1 Oe and a frequency of 27 Hz. The conditions of the treatments, lattice constants (determined using a FR-552 Guinier camera, Ge internal standard) and the superconducting properties of the initial and six fluorinated samples are summarized in Table I.

An increase in the amount of XeF_2 in the reacting mixture or increasing the time of fluorination resulted in a subsequent decrease in both the a and c lattice parameters. Since the decrease in the a parameter (which is equal to double the in-plane Cu-O1 bond distance) occurs due to the increase in the Cu formal valence and, consequently, in the value of δ in the $HgBa_2CuO_4F_\delta$ samples, one can conclude that the fluorine content successively increases from sample #2 to sample #7. All of the fluorinated samples exhibited a bulk superconductivity with relatively high diamagnetic volume fractions, except sample #7. The temperature dependencies of the ac magnetic susceptibility for samples #1–#7 are shown in Fig. 1. One can conclude from this that sample #7 is actually the highly overdoped, nonsuperconducting one. Samples #2 and #3 exhibited the highest $T_c = 97$ K, which is exactly the same as for the optimally oxygenated Hg-1201 samples, and the transitions were sharp and well defined. Samples #4–#6 exhibited broad superconducting transitions, probably due to an inhomogeneous distribution of the fluorine.

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TABLE 1. Fluorination conditions, T_c values, and lattice parameters of $HgBa_2CuO_4F_\delta$. M is the molar ratio of XeF_2 to Hg-1201.

N	Conditions	$T_{c,\text{onset}}/T_c$, K	a, Å	c, Å
1	reduced Hg-1201	61/61	3.8915(5)	9.529(2)
2	$M = 0.1$, 150 °C, 15 h	97/97	3.8828(4)	9.523(1)
3	$M = 0.3$, 200 °C, 15 h	97/97	3.8825(3)	9.510(1)
4	$M = 0.5$, 200 °C, 15 h	96/96	3.8788(5)	9.498(1)
5	$M = 0.4$, 200 °C, 20 h	90/80	3.8742(4)	9.493(2)
6	$M = 0.3$, 200 °C, 30 h	88/80	3.8721(5)	9.482(2)
7	$M = 1.0$, 200 °C, 50 h	78/−	3.8679(7)	9.459(2)

The neutron diffraction measurements of samples #3 and #5 were performed at room temperature with the high-resolution RTOF Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor in Dubna. A cylindrical, 5-mm diam, Ti-Zr can was used to hold the Hg-1201 powder ($m \approx 1$ g). Data processing was carried out by the Rietveld method on the d_{hkl} interval from 0.79 to 2.12 Å. The initial parameters for the neutron data refinement were chosen as those obtained for the oxygenated Hg-1201 samples [3]. To avoid a correlation between occupation and thermal factors, the refinements were carried out with fixed thermal parameters for the Ba, Cu, O, and F atoms. The refinement of the isotropic temperature factor for Hg atoms, assuming full occupancy of this site, resulted in B(Hg) values close to 1 Å^2 for both samples. The refinement of the occupancy of the mercury position with B(Hg) = 1 Å^2 gave the value $n(\text{Hg}) = 0.99(1)$. The high d_{hkl} resolution of the diffraction patterns helped us calculate the difference scattering density map for the basal plane of the unit cell. This map, calculated excluding the F atom, revealed an extra anion only in the middle of the mesh $(\frac{1}{2}, \frac{1}{2}, 0)$ and no anion near the middle of the edge was found. Therefore, we can conclude that the fluorinated Hg-1201 samples have a stoichiometric cation composition with only one site for the oxidizing extra anion.

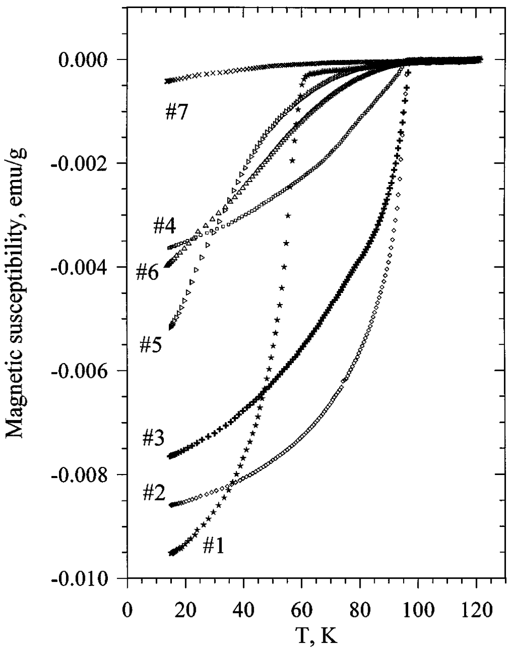

FIG. 1. ac magnetic susceptibility for samples #1–#7 as a function of temperature.

The occupancy of the fluorine position was refined with a fixed thermal parameter of 1 Å^2. The values of $n(\text{F}) = 0.24(2)$ and $n(\text{F}) = 0.32(2)$ were obtained for samples #3 and #5, respectively. The refinement with fixed B(F), which varied between 0.5 and 1.5 Å^2, led to changes in n(F) well inside the standard deviation limit. The variation of B(O2) [other parameters do not correlate well with n(F)] also does not have a strong influence on the fluorine occupancies: It changed from 0.26(2) to 0.23(2) for sample #3 and from 0.35(2) to 0.31(2) for sample #5 if B(O2) is equal to 1.0 or 2.0 Å, respectively. Thus, the n(F) values are significantly larger than the values of 0.124(9) and 0.19(1) obtained for the oxygenated Hg-1201 samples with close T_c values [3]. This comparison is quite correct since oxygenated and fluorinated materials were measured by the same NPD facility and the initial Hg-1201 samples were prepared by the same synthesis technique. The results of the refinement are presented in Table II, together with the relevant bond distances.

Figure 2 shows the dependence of the T_c values vs extra oxygen or fluorine concentration. For the fluorinated series, we also used the initial nonfluorinated sample as the first point. It can obviously be seen that in both cases, there are parabolic-shaped curves which are shifted away from each other along the δ axis. One can conclude that fluorine indeed oxidizes (like oxygen) the (CuO_2) layers in the Hg-1201 structure, followed by a change in T_c, but that the amount of inserted fluorine is approximately twice that of oxygen to achieve the same T_c values and, consequently, the same doping level. Taking into account the different formal valences of these anions (-1 and -2, respectively), we conclude that inserted extra oxygen creates the twice as many holes as fluorine.

The amount of inserted fluorine, however, was found to be significantly larger than could be expected for the optimally doped phase, assuming an optimal hole number $p_{\text{opt}} = 0.16$ (δ_{F} should be equal to 0.16 instead of 0.24 if $V_{\text{Ba}} = V_{\text{Hg}} = +2$, $V_{\text{o}} = -2$ and $V_{\text{F}} = -1$). Therefore,

TABLE II. Structural parameters and relevant interatomic distances for $HgBa_2CuO_4F_\delta$ phases refined from neutron powder data. Parameters without errors were fixed in the final refinement. The commonly used criteria for the quality of the refinement are given: R_I is the R factor for integrated intensities, R_w and R_c are weighted and expected from statistics R factors, respectively.

	Sample #3	Sample #5
a, Å	3.8808(1)	3.8734(1)
c, Å	9.5107(4)	9.4895(5)
V, Å^3	143.24	142.37
Hg, n	1	1
B(Hg), Å^2	1.1 (1)	1.4(1)
Ba, z	0.2979(4)	0.2939(4)
B(Ba), Å^2	0.5	0.5
B(Cu), Å^2	0.5	0.5
B(O1), Å^2	1.0	1.0
O2, z	0.2109(4)	0.2119(4)
B(O2), Å^2	1.5	1.5
F, n	0.24(2)	0.32(2)
B(F), Å^2	1.0	1.0
	$\chi^2 = 0.74$	$\chi^2 = 1.10$
	$R_I = 0.090$	$R_I = 0.10$
	$R_w = 0.042$	$R_w = 0.050$
	$R_e = 0.091$	$R_e = 0.092$
Cu-O2, Å	2.750(4)	2.735(4)
Hg-O2, Å	2.006(4)	2.010(4)
Cu-O1, Å	1.9404(1)	1.9367(1)
Ba-F, Å	2.833(4)	2.789(5)

we can conclude that the doping mechanism in the Hg-1201 superconductor is more complex than a simple oxidation of the (CuO_2) layers by an inserted fluorine or oxygen. They can oxidize not only the (CuO_2) layers, but also, possibly, the HgO_2 "dumbbell" as well. The carrier concentration in the conducting band is a result of the delicate charge balance among these fragments.

Another important conclusion can be made if we plot the dependence of T_c vs the a parameter (equal to double the in-plane Cu-O1 bond length) for the oxygenated and fluorinated samples (Fig. 3). For this graph, the values of the a parameter were taken only from our precise x-ray data that was treated in a similar way to exclude possible systematic errors. All data points can be fitted by one parabolic-like function with a maximum around 97 K at $a = 3.882$ Å. This fact supports the conclusion that this distance and the carrier concentration (V_{Cu}), are crucial parameters determining the magnitude of T_c. Variation of the apical Cu-O2 bond distance caused by the extra anion exchange when $\delta_F \approx 2\delta_0$, however, is well pronounced in contrast to the in-plane bonds. Figure 4 shows a practical linear dependence of the Cu-O2 distance vs δ (oxygen or fluorine). An increase in the amount of the extra anion in the Hg layer results in a compression of the apical Cu-O2 distance. These distances differ significantly between the fluorinated and oxygenated Hg-1201 phases with close T_c and in-plane Cu-O1 bond lengths. For instance, the difference between these distances in the phases with $T_c = 97$ K is about 0.04 Å, which is much larger than the standard deviation and the difference between the c parameters.

The origin of this unusual phenomenon may be explained if we also take into account the variation of the apical Hg-O2 bond distance. This bond length in the fluorinated Hg-1201 phases is significantly larger in comparison with the oxygenated compounds (Fig. 4), where this distance varies from 1.963 Å ($\delta = 0.057$) up to 1.990 Å ($\delta = 0.19$) due to the shift of the O2 atoms towards the more oxidized Cu cations. It is known that the apical Hg-O2 bond is a very strong covalent

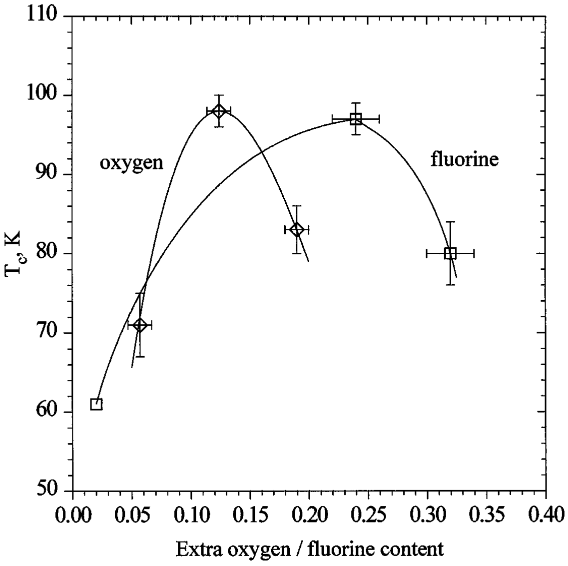

FIG. 2. The behavior of T_c vs extra oxygen or fluorine content. Lines through points are guides to the eye.

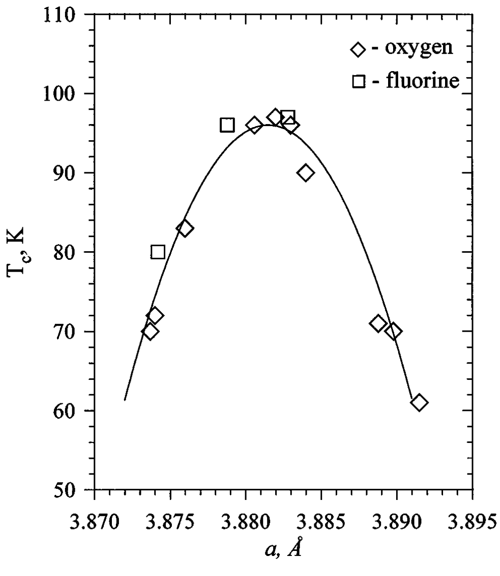

FIG. 3. The behavior of T_c vs the a parameter of the unit cell.

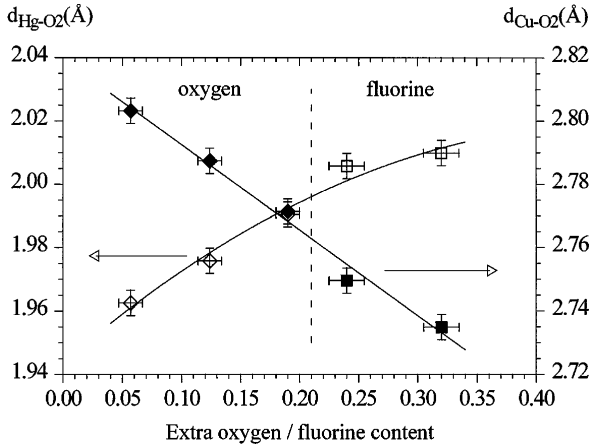

FIG. 4. Bond distances Hg-O2 (left scale, open symbols) and Cu-O2 (right scale, full symbols) as a function of extra oxygen or fluorine content. Data for oxygenated samples ($\delta = 0.057$, 0.124, and 0.19) are taken from Ref. [3]. Lines through points are guides to the eye.

bond and even under high pressure, this distance does not decrease significantly: 1.980(4) and 1.973(19) Å at ambient conditions and under 5.07 GPa, respectively [8]. Therefore, the more probable origin of the elongation of the Hg-O2 distance is not a variation of the formal Cu valence, but an interaction between Hg and the extra anions (even located far from the Hg atom). An increase in the coordination number of Hg by the inserted extra anions is accompanied by a shift of the O2 atoms away from the Hg cations towards the Cu atoms, thus elongating the Hg-O2 distance and shortening the Cu-O2 one. We can conclude that the exchange of extra oxygen for double the amount of fluorine causes a variation of the apical distances, predominantly while the in-plane distance and T_c remain the same. This transformation can be formally considered as an anisotropic compression (along the c axis) of the CuO_6 octahedron.

Our observation that the apical distances in Hg-1201 depend smoothly on the number of anions in the Hg-plane rather than on their charge can provide a new explanation of the well-known fact that the T_c of Hg-bearing superconductors increases under high pressure. Compression of the Cu-O2 bonds in the fluorinated Hg-1201 phases can be considered to be equivalent to an application of approximately 2 GPa of uniaxial pressure along the c axis. However, our study showed no difference in T_c for the fluorinated or oxygenated optimally doped Hg-1201 compounds. The uniaxial pressure experiments performed on a crystal of $YBa_2Cu_3O_7$ also showed no variation of T_c when pressure was applied along the c axis to provide for compression of the apical Cu-O2 bond distances [9]. These results agree with our observations and support the conclusion that the apical Cu-O2 bond compression could not be the only origin of an enhancement of T_c under high pressure in the Hg-based superconducting Cu mixed oxides.

In summary, in the present work, we showed that different amounts of fluorine could be successfully inserted into the reduced Hg-1201 structure. This was followed by a variation of T_c over a wide range, based on whether the sample was in the optimally doped state or in the highly overdoped, nonsuperconducting one. We also determined the dependence of T_c vs fluorine concentration and performed a structural study of the Hg-1201 phases with different fluorine contents. The maximum T_c values for the oxygenated and fluorinated Hg-1201 samples were exactly the same, ~97 K, while the amount of an inserted fluorine was twice that of oxygen, 0.24 and 0.12, respectively (we use the last number according to our recently published data [3]). This supports an ionic model of the hole doping in Hg-1201 by extra anions inserted in the Hg layer: the hole number p is equal to 2δ for oxygen and to 1δ for fluorine if δ is the number of extra anions in the Hg plane. The structural data obtained also showed that the apical distances in Hg-1201 depend strongly on the number of dopant atoms rather than on their charge. The exchange of extra oxygen for a double amount of fluorine further shortens the apical Cu-O bond distances, while the in-plane distances and T_c do not vary.

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