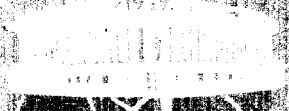


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EFFECT OF FLUORINATION ON THE STRUCTURE
AND SUPERCONDUCTING PROPERTIES
OF THE Hg-1201 PHASE

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1. Introduction

$\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201), the first member of the $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ homologous series, is one of the most attractive compounds for investigating the relationship between structure and superconducting properties among the Cu-based high- T_c materials for several reasons. This phase has the simplest structure among the Hg-based Cu mixed oxides which exhibit superconductivity at high temperatures^{1/}. Its T_c can be easily varied over a wide range – from strongly underdoped to overdoped regions (or even a highly overdoped nonsuperconducting state) – by different heat treatments. The Hg-1201 phase has only one type of (CuO_2) layer and the dependence of T_c vs. extra oxygen content (δ) or the in-plane Cu-O1 bond distance exhibits a parabolic-like behavior. Structural peculiarities that embarrass the precise structural refinement of other Cu-based superconductors, such as stacking faults, cation intermixing, large static atomic displacements etc., are practically absent in the Hg-1201.

Up to now, a large number of x-ray single crystal and neutron powder diffraction experiments have been performed on Hg-1201^{2-8/}. In general, there is a good agreement between the refined structural parameters and their variations caused by changes in the concentration of the extra oxygen located in the Hg-layer. The in-plane Cu-O1 bond distance, as well as the Cu-O2 apical one, decreases if δ increases due to the increase in the carrier concentration in the (CuO_2) layer (or the formal copper valence), while the Hg-O2 bond length increases. The average Ba-O2 interlayer distance and Ba-O3 separation decrease when δ increases.

There are severe discrepancies, however, among different papers concerning the occupancies of the Hg and oxygen sites in the HgO_δ layer, though these parameters are extremely important for understanding the doping mechanism in Hg-based superconductors. For instance, the partial replacement of Hg for Cu, followed by the insertion of an additional extra oxygen O4 located near the middle of the edge, was found in^{2,4,5/}, while other authors did not find this substitution or the O4 atoms^{3,7,8/}. At the same time, different occupancies of the oxygen site in the middle of the Hg-mesh, for optimally doped Hg-1201 samples, were found to range from 0.06^{3/} up to 0.18^{7/}. In our recent neutron diffraction study of pure $\text{HgBa}_2\text{CuO}_{4+\delta}$ samples with stoichiometric cation compositions and different anion contents, the δ -value for the optimally doped phase was found to be 0.12(1)^{8/}.

It should be noted that, in general, the values of the extra oxygen occupancy refined from neutron studies were found to differ from those ones determined by iodometric titration. For instance, the latter technique showed $\delta=0.08-0.09$ for the optimally doped Hg-1201, assuming the formal valences of the atoms to be $V_{\text{Ba}}=V_{\text{Hg}}=+2$ and $V_{\text{O}}=-2^{8-10/}$. The probable explanations of this discrepancy might simply be attributed to the presence of an amorphous Cu-based oxide or metallic Hg in the studied samples, which decreases the concentration of the oxidizer. However, it could also be due to the more complicated doping mechanism for the Hg-1201 structure^{11/} compared to the simple ionic model that assumes a doping of the CuO_2 conducting layer by two holes per one inserted extra oxygen atom.

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 was also considered to be interesting to determine the dependence of T_c and structural parameters vs. extra fluorine content. The optimal superconducting transition temperature in the Hg-based family is very sensitive to variation of the in-plane Cu-O1 bond distances from the first member to the third, as was shown in¹². We assumed that the exchange of the extra oxygen by fluorine in the phases with the same doping level might cause a variation in the Cu-O distances. The larger amount of fluorine in comparison with oxygen could result in an alteration of the neighboring Ba-F and Hg-O2 bond distances and, finally, of the Cu-O ones.

Earlier, we successfully used XeF_2 as a fluorinating agent for the synthesis of the superconducting oxyfluorides $\text{Sr}_2\text{Cu}(\text{O},\text{F})_{4+\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_6\text{F}_2$ ^{13,14}. In the present work, we showed that different amounts of fluorine could be successfully inserted into the reduced Hg-1201 phase. 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.

2. Experimental

Single-phase samples of $\text{HgBa}_2\text{CuO}_{4+\delta}$ were synthesized from a mixture of $\text{Ba}_2\text{CuO}_{3+5}$ and HgO according to the procedure described in¹⁵. The synthesis was carried out at 800°C for 12 hrs. in evacuated sealed silica tubes placed in a three-temperature gradient furnace under controlled mercury and oxygen partial pressures. The fixed oxygen partial pressure of 0.43 bar was created by a mixture of $\text{Co}_3\text{O}_4/\text{CoO}$ and the mercury partial pressure of 4.8 bar was achieved by using a $\text{Ba}_2\text{CuO}_{3+5}/\text{HgBa}_2\text{CuO}_{4+5}$ mixture. After annealing, the sample was slowly cooled to 650°C with a cooling rate of $1.5^\circ\text{C}/\text{min}$ and then quenched in water. The as-prepared samples were heated at 330°C for 18 hrs. in a dynamic vacuum under 10^{-2} torr pressure to reduce the $\text{HgBa}_2\text{CuO}_{4+5}$. Thus prepared, the reduced Hg-1201 sample was monophasic and exhibited superconductivity with $T_c=61$ K. The values of the lattice constants of the Hg-1201 phase were found to be $a=3.8915(5)$, $c=9.529(2)$ Å. The δ -value determined by iodometric titration was equal to 0.01(1).

Fluorination of the reduced Hg-1201 sample was carried out using XeF_2 as the fluorinating agent. All operations were made in a glove box in a dried N_2 atmosphere excluding the presence of O_2 . The 0.4 g of Hg-1201 was mixed with XeF_2 in molar ratios from 1:0.1 to 1:1 and ground together in an agate mortar. 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 hrs. and from 150°C to 200°C .

Phase compositions and lattice parameters of the compounds were determined by x-ray powder diffraction using a FR-552 focusing Guinier-camera ($\text{CuK}_{\alpha 1}$ -radiation, germanium internal standard). Raw x-ray data for the crystal structure determination were

collected using a STADI/P diffractometer (CuK α_1 -radiation, curved Ge monochromator, transmission mode, scintillation counter, step 0.02° (2 θ), time per step 40 s, 6° \leq 2 θ \leq 100°).

The x-ray powder structure refinement was carried out using the RIETAN-97 program. The Rietveld method with a modified pseudo-Voigt profile function was used for the refinement. Since absorption leads to a remarkable distortion of the experimental intensities, the absorption factor was included in the final refinement.

The neutron diffraction experiment was performed with the high-resolution Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor in Dubna. A cylindrical, 5-mm diam, Ti-Zr can without coherent scattering was used to hold the Hg-1201 powder ($m \approx 1$ g). The diffraction patterns were measured at room temperature. The lattice parameter calibration was performed using the Al $_2$ O $_3$ NIST standard SRM-676. Data processing was carried out by the Rietveld method with the MRJA program^{16/} on the d_{hkl} interval from 0.79 to 2.12 Å. For the coherent scattering length, we used 12.69, 5.07, 7.718, 5.803, and 5.654 fm (1 fm=10 $^{-13}$ cm) for Hg, Ba, Cu, O, and F, respectively. The absorption correction was calculated using the tabulated absorption and incoherent scattering cross sections.

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, and the superconducting properties of the initial and six fluorinated samples are summarized in Table 1.

Table 1. Fluorination conditions, T_c values, and lattice parameters for HgBa $_2$ CuO $_4$ F $_\delta$.

N	Synthesis conditions	$T_{c,onset} / T_c$, K	a , Å	c , Å
1	initial reduced Hg-1201	61 / 61	3.8915(5)	9.529(2)
2	0.1XeF $_2$, 150°C, 15 h	97 / 97	3.8828(4)	9.523(1)
3	0.3XeF $_2$, 200°C, 15 h	97 / 97	3.8825(3)	9.510(1)
4	0.5XeF $_2$, 200°C, 15 h	96 / 96	3.8788(5)	9.498(1)
5	0.4XeF $_2$, 200°C, 20 h	90 / 80	3.8742(4)	9.493(2)
6	0.3XeF $_2$, 200°C, 30 h	88 / 80	3.8721(5)	9.482(2)
7	1XeF $_2$, 200°C, 50 h	78 / –	3.8679(7)	9.459(2)

3. Results

The x-ray diffraction patterns of samples #2–4 and #6 contain only the reflections of the Hg-1201 phase. Traces of BaCuO $_2$ (less than 2% of the intensity of the strongest peak in comparison with the main phase) were detected only in sample #5. Despite of the absence of additional reflections in the x-ray diffraction pattern, some amount of yellow-brown amorphous admixture was visually detected in sample #7.

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 the doubled in-plane Cu-O1 bond distance) occurs due to the increase in the Cu formal valence and, consequently, the value of δ in the HgBa $_2$ CuO $_4$ F $_\delta$ samples, one can conclude that the fluorine content successively increases from sample #2 to sample #7.

The probable side reaction during a fluorination may be a partial replacement of the other oxygen atoms (namely, O1 and O2) by fluorine ones. In this case the released oxygen should be adsorbed by an internal surface of copper tubes producing Cu_2O . However, we have never detected any traces of this oxide after heat treatments. Moreover, the variations of Cu-O bond lengths vs. extra anion content (see below) give us an indirect argument that the fluorine is located only in the Hg plane.

All 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. Sample #7 demonstrated a very small superconducting volume fraction that corresponds to a value not higher than 3% of the perfect diamagnetism. Taking this fact into account, we concluded that this sample is actually the highly overdoped, nonsuperconducting one.

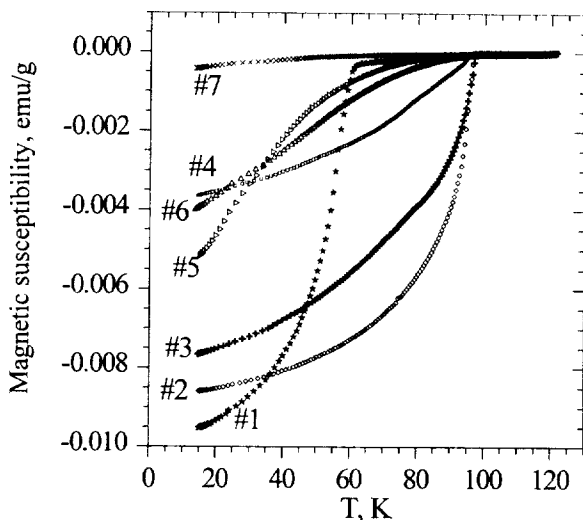


Fig.1. AC magnetic susceptibility for samples #1–7 as a function of temperature.

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 as a result of low fluorination temperatures and short annealing times. This problem made it difficult to determine the exact value of T_c . The $T_{c,onset}$ values can be estimated as 96, 90, and 88 K for samples #4, #5, and #6, respectively. Taking into account these values, we can conclude that for samples #2–7, $T_{c,onset}$ decreases concomitantly with the decrease in the a -parameter and, consequently, the increase in fluorine content due to overdoping.

One can assume that the $T_{c,onset}$ values for samples #5 and #6 (90 and 88 K) cannot be used as the characteristic transition temperatures due to the very weak diamagnetic signals

on their $\chi(T)$ curves down to 80 K. Therefore, we believe that the more realistic transition temperatures for these samples were not higher than 80 K.

The structure refinement was performed for the optimally doped sample #3 and for the overdoped sample #5 using the neutron powder diffraction data. The initial parameters for the refinement carried out in the P4/mmm space group were chosen as those obtained for the oxygenated Hg-1201 samples^{8/}. 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. These values were chosen at a reasonable level according to our previous neutron diffraction study of oxygenated Hg-1201.

The refinement of the isotropic temperature factor for Hg atoms, assuming full occupancy of this site, resulted in B(Hg) values close to 1 Å² for both samples. The refinement of the occupancy of the mercury position with B(Hg)=1 Å² gave the value n(Hg)=0.99(1), which corresponds to the stoichiometric cation composition of the studied samples. The high d_{hkl} resolution of the diffraction patterns helped us calculate the scattering density maps for some planes of the unit cell. The difference scattering density map for the basal plane is shown in Fig.2. This map revealed an extra anion only in the middle of the mesh (1/2,1/2,0). The amplitude of its peak is more than 3 times higher than the most intensive background maxima; 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.

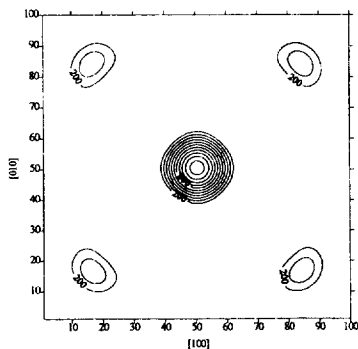


Fig.2. The scattering-density map for the basal plane of sample #3 calculated with the difference of the experimental and calculated structure factors ($F_{\text{expt}} - F_{\text{calc}}$). The fluorine atom was excluded from the calculation of F_{calc} .

The content of the residual extra oxygen in the initial reduced Hg-1201 sample ($T_c=61$ K) was small (about 0.01(1) from iodometric data). It should also be mentioned that a δ -value equal to 0.057(10) was found by our neutron diffraction study of the reduced Hg-1201 phase with a higher $T_c=71$ K^{8/}. Therefore, we can conclude that the extra oxygen content of the initial reduced phase used in the present study was definitely not higher than 0.05. Since this value is close to the standard deviation of the occupancy parameter of the extra anion site, one can conclude that the anion site in the Hg-layer is occupied predominantly by fluorine atoms. Moreover, the neutron coherent scattering lengths of oxygen and fluorine atoms are very close, which is why only fluorine atoms were placed in the (1/2,1/2,0) position.

The occupancy of the fluorine position was refined with a fixed thermal parameter of 1 Å². The values of n(F)=0.24(2) and n(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 \AA^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 changes 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 \AA or 2.0 \AA , 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.

The results of this refinement are presented in Table II, together with the relevant bond distances. The experimental, calculated, and difference neutron diffraction patterns for sample #3 are shown in Fig. 3.

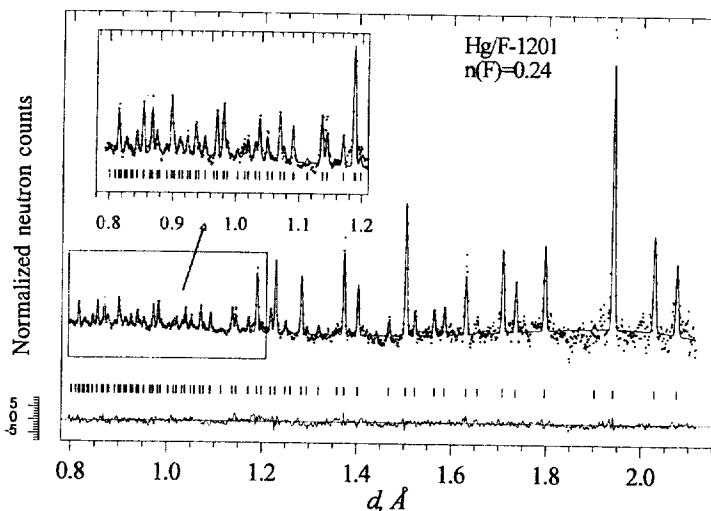


Fig.3. Neutron-diffraction pattern of $\text{HgBa}_2\text{CuO}_4\text{F}_{0.24}$ (sample #3) measured at room temperature. Experimental points, calculated profile, and difference curve are shown. The difference curve is normalized on the mean-square deviation.

The crystal structure of the Hg-1201 phase (sample #4) was refined from the x-ray powder data. The accuracy of the determination of the z coordinate for the apical oxygen atom O2 and the occupancy of the fluorine position from this data is significantly lower in comparison with the neutron diffraction data, but one can obtain reliable parameters for the heavy cations. The refinement of the temperature factors was carried out independently in an isotropic approximation for the Hg, Ba and Cu atoms, while the anions were refined with a common temperature factor. The temperature factor for the Hg atoms was found to be quite large – 1.49(7) \AA^2 . The refinement of the occupancy of this site (with fixed $B(\text{Hg})=1 \text{\AA}^2$) did not reveal any noticeable Hg-deficiency – $n(\text{Hg})=0.990(5)$ – and subsequent refinements were carried out with a fixed unit occupancy of the mercury position. The fluorine content was roughly estimated from the x-ray powder refinement to be 0.3 at fixed $B(F)=1 \text{\AA}^2$. These results are also presented in Table II. A comparison of the

results obtained by x-ray and neutron diffraction for samples #3-5 shows a good agreement between them, including the coordinates, and, consequently, the variation of the relevant bond distances.

Table 2. Structural parameters and relevant interatomic distances for $\text{HgBa}_2\text{CuO}_4\text{F}_x$ phases refined from neutron (samples #3 and #5) and x-ray powder data (sample #4). 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_p , R_w , and R_e are profile, weighted, and expected from statistics R -factors, respectively (the R_p -factor has no sense for HRFD data).

	Sample #3 ($T_c=97$ K)	Sample #4 ($T_c=96$ K)	Sample #5 ($T_c=80$ K)
a , Å	3.8808(1)	3.87628(5)	3.8734(1)
c , Å	9.5107(4)	9.4939(4)	9.4895(5)
V , Å ³	143.24	142.65	142.37
Hg, n	1	1	1
B(Hg), Å ²	1.1 (1)	1.49(7)	1.4(1)
Ba, z	0.2979(4)	0.2955(1)	0.2939(4)
B(Ba), Å ²	0.5	0.66(6)	0.5
B(Cu), Å ²	0.5	0.4(1)	0.5
B(O1), Å ²	1.0	0.9(3)	1.0
O2, z	0.2109(4)	0.210(1)	0.2119(4)
B(O2), Å ²	1.5	0.9(3)	1.5
F, n	0.24(2)	0.3	0.32(2)
B(F), Å ²	1.0	0.9(3)	1.0
	$R_i=0.090$	$R_i=0.026$	$R_i=0.10$
	$\chi^2=0.74$	$R_p=0.050$	$\chi^2=1.10$
	$R_w=0.042$	$R_w=0.064$	$R_w=0.050$
	$R_e=0.091$	$R_e=0.050$	$R_e=0.092$
Cu-O2, Å	2.750(4)	2.75(1)	2.734(4)
Hg-O2, Å	2.006(4)	1.99(1)	2.011(4)
Cu-O1, Å	1.9404(1)	1.9381(1)	1.9367(1)
Ba-F, Å	2.833(4)	2.805(1)	2.789(5)
Ba-O1, Å	2.731(3)	2.7433(7)	2.752(3)
Ba-O2, Å	2.866(2)	2.859(3)	2.847(2)

4. Discussion

Fluorination of the reduced Hg-1201 phase with $T_c=61$ K significantly changes the superconducting transition temperature and structure parameters of this compound. The fluorination results in a successive decrease in the lattice parameters, while the T_c first increases up to 97 K, but, at larger concentrations of the inserted fluorine, decreases and

then even suppresses the superconductivity due to overdoping. This behavior, as well as the optimal T_c values, is very close to that of the oxygenated Hg-1201 superconductor. However, in the latter case, the nonsuperconducting overdoped state was obtained only by high pressure, high temperature synthesis¹⁷⁾, while fluorination allows one to obtain overdoped samples using conventional encapsulation synthesis at low temperature. This difference is due to the distinct oxidizing activities of oxygen and XeF₂. The latter can be successfully used for oxidation of Cu-based materials, especially in overdoped regions.

Our previous investigation of oxygenated Hg-1201 phases and our present research of fluorinated materials were carried out using Hg-1201 samples prepared by the same synthesis technique and characterized by the same NPD facility. A comparison of these results shows their similarity, including the structural arrangement of the HgO₈ layers: a stoichiometric mercury content with only one interstitial anion position in the middle of the mesh. However, the refined values of the occupancy factor of the extra anion position for the samples with similar T_c (97 K for the optimally doped samples and about 80 K for the overdoped ones) were found to be approximately two times larger for the fluorinated samples than for the oxygenated ones: 0.24(2), 0.32(2) and 0.12(1), 0.19(1), respectively. The presence of residual oxygen in the fluorinated samples ($\delta_o < 0.05$), which cannot be distinguished by neutron diffraction from the fluorine atoms, cannot significantly change the refined occupancies.

Figure 4 shows the dependence of the T_c values vs. extra oxygen or fluorine concentration. For the fluorinated series, we also used the initial non-fluorinated sample as the first point. It can obviously be seen that in both cases, there are parabolic-shaped curves that are shifted away from each other along the δ axis. One can conclude that fluorine indeed oxidizes (like oxygen) the (CuO₂) layers in the Hg-1201 structure, followed by a change in T_c , but 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. This fact supports the simple ionic model of Hg-1201 doping: 2 holes per inserted oxygen and 1 hole per inserted fluorine.

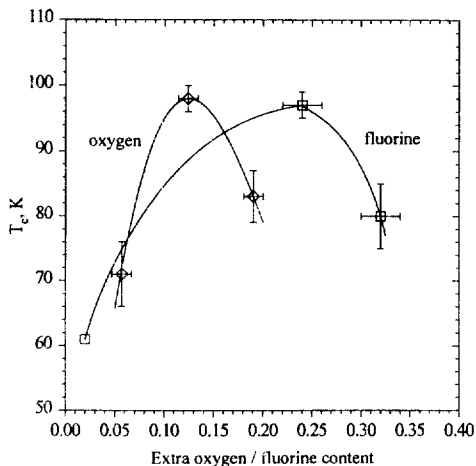


Fig.4. The behavior of T_c vs. extra oxygen or fluorine concentration. The lines are drawn for convenience.

The amount of inserted fluorine, however, was found to be significantly larger than could be expected for the optimally doped phase, assuming an optimal formal copper valence equal to +2.15 - +2.18 (δ_F should be equal to 0.15-0.18 instead of 0.24 if $V_{Ba} = V_{Hg} = +2$, $V_O = -2$ and $V_F = -1$). This discrepancy should be even more

pronounced if we take into consideration the residual oxygen atoms. For a more accurate calculation of the total hole number, p , one can use the relation $p=n+n_o$, where n is the total occupancy of the $(1/2,1/2,0)$ position obtained in the refinement, and n_o is the extra oxygen content in the initially reduced sample ($n_o \approx 0.01-0.02$). Therefore, 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.

Earlier, the existence of an unusual oxidation state +3 was proposed for the Hg-cations in the Hg-1201 structure based on x-ray photoelectron spectroscopy data¹⁸, while another group did not find any evidence of this oxidation state for Hg in the mixed Bi, Hg cuprates¹⁹. These controversial observations, as well as the discrepancies with the iodometric analyses (which determines the total oxidizer concentration in the sample, but not in a single phase), require that this problem be investigated further.

Another important conclusion can be made if we plot the dependence of T_c vs. the a -parameter (the doubled in-plane Cu-O1 bond length) for the oxygenated and fluorinated samples (Fig.5). For this graph, the values of the a -parameter were taken only from the 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 $a = 3.882 \text{ \AA}$.

It is well known that the in-plane Cu-O1 distance depends on the formal Cu valence. An increase in the latter leads to a shortening of this distance. One can speculate that the samples with close values of both T_c and the a -parameter also have close formal copper valences. This is in a good agreement with the different concentrations of extra oxygen and fluorine ($\delta_F \approx 2\delta_O$) found by NPD, taking into account their different formal charges. Therefore, the exchange of an extra oxygen by the twice amount of fluorine in the Hg-1201 structure does not change the in-plane Cu-O1 bond length or, obviously, the formal Cu valence for the optimally doped samples, which exhibit the same T_c values. This fact supports the conclusion that this distance and the carrier concentration (V_{Cu}) are crucial parameters determining the magnitude of T_c .

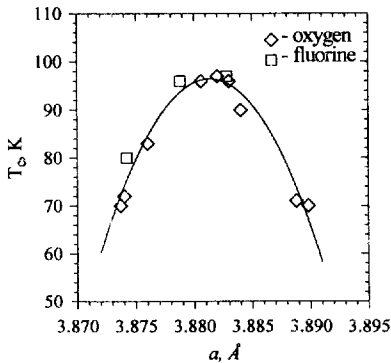


Fig.5. The behavior of T_c vs. the a -parameter of the unit cell for the oxygenated and fluorinated samples.

Variation of the apical Cu-O2 bond distance caused by the extra anion exchange when $\delta_F \approx 2\delta_O$, however, is well-pronounced in contrast to the in-plane ones. The increase in the formal Cu valence by the incorporation of either extra oxygen or fluorine into the Hg-1201 structure causes a compression of all distances in the CuO_6 octahedron. The in-plane Cu-O1 distance depends

on a hole concentration equal 2δ for the extra oxygen and δ for fluorine. The variation of the apical Cu-O2 distance does not appear to depend on the formal valence of the extra anion, but, instead, it is determined by the total concentration of the extra anion in the Hg-layer. Figure 6 (left) shows practically a linear dependence of the apical 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 that in the oxygenated compounds (Fig.6, right), 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.

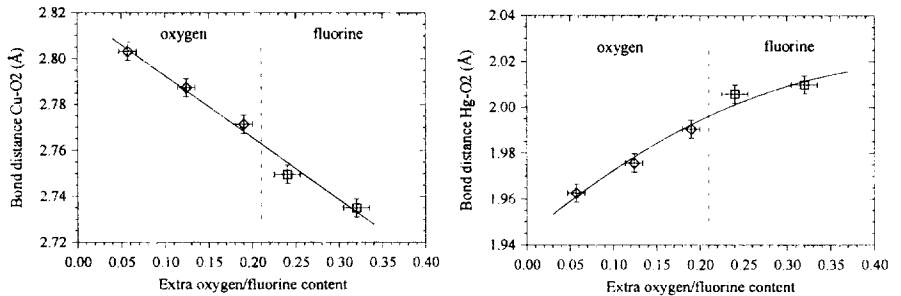


Fig.6. Bond distances Cu-O2 (left) and Hg-O2 (right) as a function of extra oxygen or fluorine content. Lines through points are guides to the eye.

It is known that the apical Hg-O2 bond is a very strong covalent bond and even under high pressure, this distance does not decrease significantly: $1.980(4)$ Å and $1.973(19)$ Å at ambient conditions and under 5.07 GPa, respectively²⁰. Therefore, the more probable origin of the elongation of the Hg-O2 distance is not only a variation of the formal Cu valence, but also the 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 Cu-O2 distances, predominantly, while the in-plane distance and T_c remain the same. This transformation can be formally considered as 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 significantly under high pressure, as it was found in Refs.^{21,22}. A number of studies have found that the Cu-O2

distance is very sensitive to external pressure^{20,23,24/} and its drastic compression may be responsible for the T_c variation. The compressibility of the Cu-O bonds in the oxygenated Hg-1201 structure, studied under high pressure up to 5.07 GPa, was found to be equal to $3.3 \cdot 10^{-3} \text{ GPa}^{-1}$ and $7.6 \cdot 10^{-3} \text{ GPa}^{-1}$ for the in-plane Cu-O1 and apical Cu-O2 bonds, respectively^{20/}. Compression of the apical 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. The T_c of the optimally doped Hg-1201 phase was found to be enhanced under high pressure with $dT_c/dP \approx 2 \text{ K/GPa}^{25/}$. 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$ 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^{26/}. These results agree with our observations and support the conclusion that compression of the in-plane Cu-O1 distances is the most probable origin of an enhancement of T_c under pressure in the Hg-based superconducting Cu mixed oxides.

5. Conclusions

A successful fluorination of the reduced Hg-1201 phase with $T_c=61 \text{ K}$ was carried out with XeF_2 . It led to a wide range of superconducting compositions directly connected with the different fluorine content in the basal plane of the structure. This fact was proved by neutron diffraction data which showed the inserted fluorine atoms only in the middle of the mesh (1/2,1/2,0). The maximum T_c values for oxygenated and fluorinated Hg-1201 samples are exactly the same, $\sim 97 \text{ K}$, while the amount of an inserted fluorine is twice that of oxygen, 0.24 and 0.12, respectively (we use the last number according to our recently published data^{3/}). It supports an ionic model of the hole doping in Hg-1201 by an inserted extra anions 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.

That model is presently under discussion, especially after papers^{27/} and^{27/}, where the relation $p \approx \delta$ was deduced for oxygenated Hg-1201 samples on the basis of TEP and TGA measurements, NPD experiment, and bond valence sum (BVS) calculations. In a recent paper^{28/}, however, it was pointed out that BVS rules are meaningless for a system with considerable numbers of defects and disorder, such as doped superconductors. It seems, also, that the new data reported in Ref.^{29/} can explain the considerable difference between TGA and NPD data on the amount of excess oxygen in Hg-1201 samples, though the authors of that paper also wrote about the reduced doping efficiency of oxygen in Hg-1201. Our data show also that the amount of an inserted extra oxygen ($\delta=0.12$) or fluorine ($\delta=0.24$) for the optimally doped Hg-1201 is larger than those values calculated from the simple ionic model when $V_{\text{Ba}}=V_{\text{Tl}}=+2$, $V_{\text{O}}=-2$ and $V_{\text{F}}=-1$ and assuming an optimal $V_{\text{Cu}} \approx +2.16$. Therefore one can speculate that the created holes in the Hg-1201 structure can be distributed between the conducting (CuO_2) layers and the other structural units like the HgO_2 , “dumbbell”. However, this hypothesis can not explain the discrepancy between NPD and iodometric analysis, and this problem should be investigated further.

Another important conclusion which can be deduced from the presented data is that the apical distance Cu-O2, as well as interlayer Ba-O2 distance, depends strongly on the

number of the dopant atoms rather than on their charge. This is confirmed by the smooth dependence of these distances on δ (oxygen or fluorine).

Finally, we want to stress once more that our results provide new arguments for the importance of the in-plane Cu-O1 distance for the superconducting properties of Hg-1201. It is considered that the apical bond is the parameter responsible for the charge balance between the reservoir and the conducting plane. But our observations, together with high pressure results, show that the structural nature of T_c variation in Hg-1201 can be mainly due to the compression of the in-plane Cu-O bond distances.

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References

1. S.N.Putilin, E.V.Antipov, O.Chmaissem and M.Marezio, *Nature (London)*, **362**, 226 (1993).
2. J.L.Wagner, P.G.Radaelli, D.G.Hinks, J.D.Jorgensen, J.F.Mitchell, B.Dabrowski, G.S.Knapp and M.A.Beno, *Physica C*, **210**, 447 (1993).
3. O.Chmaissem, Q.Huang, S.N.Putilin, M.Marezio and A.Santoro, *Physica C*, **212**, 259 (1993).
4. A.Asab, A.R.Armstrong, I.Gameston and P.P.Edwards, *Physica C*, **255**, 180 (1995).
5. D.Pelloquin, V.Hardy, A.Maignan and B.Raveau, *Physica C*, **273**, 205 (1996).
6. P.Bordet, F.Duc, S.LeFloch, J.J.Capponi, E.Alexandre, M.Rosa-Nunes, S.Putilin and E.V.Antipov, *Physica C*, **271**, 189 (1996).
7. Q.Huang, J.W.Lynn, Q.Xiong and C.W.Chu, *Phys. Rev. B*, **52**, 462 (1995).
8. V.L.Aksenov, A.M.Balagurov, V.V.Sikolenko, V.G.Simkin, V.A.Alyoshin, E.V.Antipov, A.A.Gippius, D.A.Mikhailova, S.N.Putilin and F.Bouree, *Phys. Rev. B*, **55**, 3966 (1997).
9. A.Fukuoka, A.Tokiwa-Yamamoto, M.Itoh, R.Usami, S.Adachi and K.Tanabe, *Phys. Rev. B*, **55**, 6612 (1997).
10. A.Bertinotti, V.Viallet, D.Colson, J.-F.Marucco, J.Hammann, G.Le Bras and A.Forget, *Physica C*, **268**, 257 (1996).
11. D.J.Singh and W.E.Pickett, *Phys. Rev. Lett.*, **73**, 476 (1994).
12. E.V.Antipov, S.N.Putilin, J.J.Capponi, C.Chailout, S.M.Loureiro, M.Marezio and A.Santoro, *Physica C*, **235-240**, 21 (1995).
13. E.I.Ardashnikova, S.V.Lubarsky, D.I.Denisenko, R.V.Shpanchenko, E.V.Antipov and G. Van Tendeloo, *Physica C*, **253**, 259 (1995).

14. R.V.Shpanchenko, M.G.Rozova, A.M.Abakumov, E.I.Ardashnikova, M.L.Kovba, S.N.Putilin, E.V.Antipov, O.I.Lebedev and G. Van Tendeloo, *Physica C*, (in press) (1997).
15. V.A.Alyoshin, D.A.Mikhailova and E.V.Antipov, *Physica C*, **271**, 197 (1996).
16. V.B.Zlokazov and V.V.Chernyshev, *J. Appl. Cryst.*, **25**, 591 (1992).
17. S.M.Loureiro, E.T.Alexandre, E.V.Antipov, J.J.Capponi, S. de Brion, B.Souletie, J.L.Tholence, M.Marezio, Q.Huang and A.Santoro, *Physica C*, **243**, 1 (1995).
18. C.S.Gopinath and S.Subramanian, *Physica C*, **232**, 222 (1994).
19. F.Studer, D.Pelloquin, A.Maignan, C.Michel, M.Hervieu and B.Raveau, *Physica C*, **242**, 1 (1995).
20. V.L.Aksenov, A.M.Balagurov, B.N.Savenko, D.V.Sheptyakov, V.P.Glazkov, V.A.Somenkov, S.Sh.Shilshtein, E.V.Antipov and S.N.Putilin, *Physica C*, **275**, 87 (1997).
21. C.W.Chu, L.Gao, F.Chen, Z.J.Huang, R.L.Meng and Y.Y.Xue, *Nature (London)*, **365**, 323 (1993).
22. M.Nunez-Regueiro, J.-L.Tholence, E.V.Antipov, J.-J.Capponi and M.Marezio, *Science*, **262**, 97 (1993).
23. B.A.Hunter, J.D.Jorgensen, J.L.Wagner, P.G.Radaelli, D.G.Hinks, H.Shaked and R.Hitterman, *Physica C*, **221**, 1 (1994).
24. A.R.Armstrong, W.I.F.David, I.Gameson, P.P.Edwards, J.J.Capponi, P.Bordet and M.Marezio, *Phys. Rev. B*, **52**, 15551 (1995).
25. Y.Cao, Q.Xiong, Y.Y.Xue and C.W.Chu, *Phys. Rev. B*, **52**, 6854 (1994).
26. U.Welp, M.Grimsditch, S.Fleshler, W.Nessler, J.Downey, G.W.Crabtree and J.Guimpel, *Phys. Rev. Lett.*, **69**, 2130 (1992).
27. Q.Xiong, Y.Y.Xue, Y.Cao, F.Chen, Y.Y.Sun, J.Gibson, C.W.Chu, L.M.Liu and A.Jacobson, *Phys. Rev. B*, **50**, 10346 (1994).
28. L.Jansen and R.Block, *Physica A*, **230**, 467 (1996).
29. A.Hamed, R.Ortiz, H.H.Feng, Z.G.Li, P.H.Hor, Y.Y.Xue, Y.Y.Sun, Q.Xiong, Y.Cao and C.W.Chu, *Phys. Rev. B*, **54**, 682 (1996).

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Исследование структуры и сверхпроводящих свойств фторированной Hg-1201 фазы

Исходная Hg-1201 фаза с температурой сверхпроводящего перехода $T_c = 61$ К была успешно фторирована с помощью XeF_2 . Это привело сначала к увеличению T_c до 97 К, а затем к ее уменьшению с последующим подавлением сверхпроводящих свойств, при увеличении содержания фтора в образце. Нейтронографический анализ, выполненный на двух составах $\text{HgBa}_2\text{CuO}_4\text{F}_\delta$, подтвердил внедрение фтора в зарядовый резервуар (Hg-плоскость) и показал удвоенное содержание фтора в структуре ($\delta = 0,24$ и $0,32$) по сравнению с кислородными Hg-1201 фазами, имеющими близкие значения T_c ($\delta = 0,12$ и $0,19$). Этот факт является аргументом в пользу ионной модели образования носителей электрического заряда (дырок) в Hg-1201 при допировании. Замена сверхстехиометрического кислорода на удвоенное количество фтора показала также, что апикальное расстояние Cu-O зависит от числа анионов в базисной плоскости структуры, а не от их заряда. Наоборот, Cu-O расстояния в плоскости CuO_2 , так же как T_c , определяются зарядовым состоянием системы. Это приводит к анизотропному сжатию структуры Hg-1201, что может быть причиной увеличения T_c под воздействием внешнего высокого давления.

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

A fluorination of the reduced Hg-1201 phase with $T_c = 61$ K carried out with XeF_2 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 power refinement performed on fluorinated $\text{HgBa}_2\text{CuO}_4\text{F}_\delta$ samples showed twice the amount of extra fluorine ($\delta \approx 0.24$ and 0.32) in comparison with those for the oxygenated Hg-1201 phases with close T_c ($\delta = 0.12$ and 0.19). This supports the ionic model of the hole doping in the Hg-1201: 2 holes per extra oxygen and 1 hole per extra fluorine. The exchange of extra oxygen for a double amount of fluorine extends the shortening of the apical Cu-O bond distances, while the in-plane distances, as well as T_c , do not vary. These results show that the structural nature of T_c variation in Hg-1201 under high pressure can be mainly due to the compression of the in-plane Cu-O bond distances.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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