Effect of pressure on the superconductivity in high-T_c mercury ceramics

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The pressure-dependent magnetic properties of a new class of high-T_c superconducting cuprates with the general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ (Hg-12$(n-1)n$) were investigated. The pressure derivatives of the superconducting transition temperature and the second critical field were measured in the hydrostatic-pressure range (up to 22 kbar). For the Hg-1212 and Hg-1223 phases the derivatives are $dT_c/dP=0.30$–0.35 K/kbar; for the Hg-1201 phase the derivative is much smaller: $dT_c/dP=0.07$ K/kbar. The results obtained are discussed in connection with the impossibility of explaining the effect of pressure on superconductivity only by a change in the carrier density in the Cu–O plane. For the Hg-1201 phase the pressure effect is explained by either the possibility of a pressure-induced rearrangement of the oxygen subsystem or the fact that the system is fundamentally different from a single Cu–O plane. The irreversibility curves were measured for two samples of the Hg-1212 phase is magnetic fields up to 60 kOe. The data obtained are compared to our previous data for the ceramic systems Y-123, Tl-2223, and Bi-2212. The results indicate strong magnetic-flux creep and the existence of regions with different pinning potentials.

1. INTRODUCTION

The recently discovered new class of layered high-T_c cuprates with the general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ (Hg-12$(n-1)n$), where $n=1,2,3,4,...,$[1] is interesting not only as the next representative of metal-oxide high-T_c superconductors but also due to its record high superconducting transition temperatures T_c. Just as in the structurally similar family $TlBa_2Ca_{n-1}Cu_nO_{2n+3-x}$, the value of T_c in the mercury-cuprate series increases substantially with the number of Cu–O planes. The first member of the series already has a transition temperature $T_c=94$ K; synthesis of the second member Hg-1212, whose superconducting transition temperature exceeds 120 K, has been reported in Ref. 2; the preparation of phases with $n=3$ and $n=4$, for which $T_c=132$ K and 131 K, respectively, is reported in Ref. 3.

In the present work we investigated the effect of hydrostatic pressures up to 22 kbar on the critical parameters (T_c,H_{c2}) of samples synthesized at the Institute of High-Pressure Physics of the Russian Academy of Sciences and the Department of Chemistry at Moscow State University. Some magnetic properties of the family $HgB_2Ca_{n-1}Cu_nO_{2n+2+x}$ were also investigated: the irreversibility field $\tilde{H}_c$ and the superconducting transition temperature versus the frequency of the measuring modulation field. The data obtained are compared to the results of our previous investigations of other families of high-T_c metal-oxide superconductors.

2. MEASUREMENT PROCEDURE AND SAMPLES

Two samples of high-T_c mercury ceramics were investigated. The first one was prepared in the form of a tablet. Synthesis was conducted under quasihydrostatic pressure in a toroidal chamber at the Institute of High-Pressure Physics of the Russian Academy of Sciences. The initial charge was a stoichiometric mixture of HgO and a BaCaCuO precursor with the appropriate composition.[3] The second sample was synthesized at the Department of Chemistry of Moscow State University and consisted of a black powder which was annealed in oxygen at 400 °C for 10 h and then pressed into a tablet. X-ray analysis showed that the samples obtained were not single-phase. The x-ray diffraction patterns contained, besides lines from the principal phase (Hg-1212 for the first sample and Hg-1223 for the second sample), lines from phases with lower values of n (Hg-1201 and Hg-1212, respectively). Both samples had dimensions of $1\times1\times0.5$ mm^3, i.e., they were quite massive; this makes it possible to avoid size effects and confidently measure the superconducting transition according to the change in the magnetic susceptibility.

The first sample gave a signal in which two superconducting transitions were observed: a weak transition (according to the magnitude of the Meissner effect) at 92 K and a strong transition at 126 K. Both transitions were quite wide, the widths being 11 K and 8 K, respectively. Both transitions were much wider in a magnetic field, apparently because of the ceramic nature of the samples; only the higher-temperature transition was clearly detected. The second sample, which, as indicated above, was synthesized with annealing in O_2, was of higher quality. In measurements of the superconducting transition performed by different methods (*ac* susceptibility and the torsion method), signals were obtained, just as for the first sample, from two superconducting transitions: a strong transition, according to the bulk Meissner effect, at $T_c=125$ K with a width of 5 K, and a weaker but high-quality transition at $T_c=132$ K with a width of 1.6 K. Similarly, signal degradation occurred in a magnetic field, and the H-dependence of T_c was investigated only for the transition with

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TABLE I. Results of measurements for different phases $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ ($n=1,2,3$).

Sample No.	Phase	T_c, K	Transition width, K	dT_c/dP, K/kbar	$d(\ln T_c)/dP$, $kbar^{-1}$
1	Hg-1201	91.8	11	0.07	$0.08\cdot10^{-2}$
	Hg-1212	126.0	8	0.33	$2.62\cdot10^{-2}$
2	Hg-1212	124.8	5	0.30	$2.40\cdot10^{-2}$
	Hg-1223	132.1	1.6	0.35	$2.65\cdot10^{-2}$

$T_c(H=0)=125$ K. Application of hydrostatic pressure had no effect on the amplitude and shape of the curve of the superconducting transition.

We associate the transition at $T_c=92$ K in the first sample with the Hg-1201 phase. The transition with the highest transition temperature $T_c=132$ K, observed in the second sample, corresponds to the Hg-1223 phase. We associated the transition at $T_c=126$ K in the first sample and at $T_c=125$ K in the second sample with the Hg-1212 phase. The appreciable difference of the superconducting transition temperatures of the two samples in the latter phase is probably associated with the different oxygen content. Unfortunately, we do not know the exact value of the parameter x, but it is known that in similar Tl- and Bi-containing metal oxides even a slight rearrangement of the oxygen sublattice can change T_c substantially.

The measurements were performed in a nonmagnetic autonomous high-pressure chamber. This made it possible to obtain hydrostatic pressures up to 25 kbar. As we have already indicated, the superconducting transition was determined according to the magnetic susceptibility measured by the induction method at modulation frequencies of 60 Hz–55 kHz. We chose as the critical temperature the temperature of the onset of the superconducting transition, which was determined as the point of intersection of the tangent to the susceptibility curve on the section corresponding to the normal state and the tangent at the inflection point of the curve for the transition from the superconducting to the normal state. This is the temperature that is apparently closest to the thermodynamic T_c. A superconducting solenoid was used to generate magnetic fields of up to 6 T. Our experimental technique and method for determining the physical quantities from the experimental data are described in greater detail in Ref. 4.

The analysis performed in Ref. 5 of different methods for measuring the critical parameters of high-T_c superconductors in a magnetic field gives grounds for believing that the critical field obtained in our measurements more likely corresponds to the so-called irreversibility field. Below we employ the notation $\tilde{H}_c$, having in mind the critical field which we measured experimentally by the induction method. The fact that $\tilde{H}_c$ was different from the true second critical field H_{c2} is the main reason why different groups of investigators obtained different results in measurements in high-T_c superconductors disagree. Nonetheless, as we showed in Ref. 6, the relative pressure-induced change in the critical irreversibility field agrees well (with respect to sign and order of magnitude) with the pressure derivative of the true second critical field.

3. RESULTS FOR THE PRESSURE-DEPENDENCE OF T_c AND DISCUSSION

The pressure dependence of T_c which we measured for different phases of the mercury-cuprate series is shown in Table I.

The results are quite unexpected: The phases with higher critical temperatures T_c have a larger pressure derivative. In most work on the effect of pressure on T_c, however, the reverse behavior was observed: In the hydrostatic pressure range high-T_c superconductors with a high critical temperature T_c have small pressure derivatives $d(\ln T_c)/dP$, and high-T_c superconductors with low critical temperature T_c have large pressure derivatives. This trend is easily explained from the standpoint of the effect of pressure on the electronic subsystem. Indeed, the dependence of T_c on the number of carriers in the Cu–O plane is an inverted parabola; low pressures, however, increase the number of carriers x, since charge redistribution occurs even with a small change in the ion positions. For this reason, the point of the curve $T_c(x)$ that corresponds to a composition with a higher value of T_c lies on a section of the parabola whose slope (which determines the value of dT_c/dP) decreases as a function of T_c (see, for example, Ref. 7).

It is necessary to take into account the fact, however, that the pressure dependence of T_c may not only be "internal" (i.e., reflecting the changes occurring in the charge-carrier density, the interplanar and intraplanar distances, the density of states, the average phonon frequencies, etc.) but dT_c/dP can also reflect "external" factors—pressure-induced structural transitions and phenomena such as ordering in an oxygen superlattice, lattice instabilities, and changes in the system of defects. It is the pressure-induced changes in the oxygen sublattice that can influence the behavior of the low-temperature Hg-1201 phase. Here the quantity $d(\ln T_c)/dP$ is more than an order of magnitude smaller than in high-T_c superconductors with close transition temperatures T_c. This is reminiscent of the behavior of the analogous phase of the thallium system with a single Tl–O plane, for which a pressure derivative close to zero or having a large negative value dependent on the oxygen content, was observed. This anomalous behavior was explained in Ref. 8, where it is shown that at low tempera-

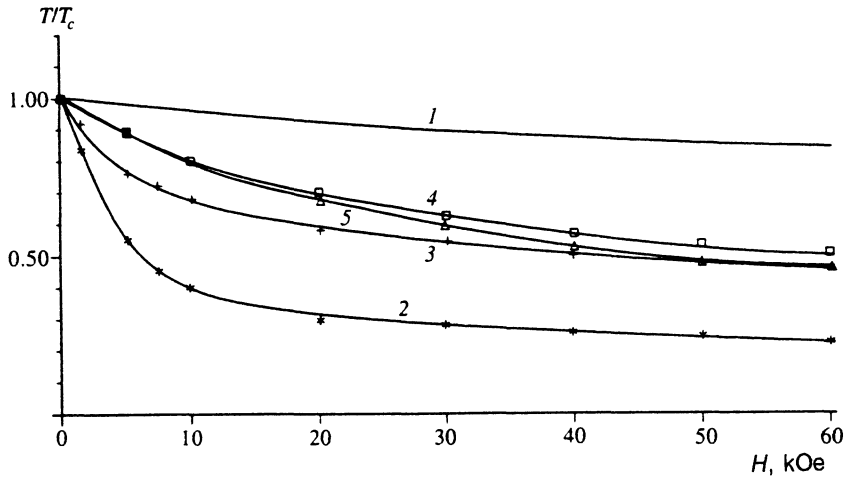

FIG. 1. Irreversibility curves for different high-T_c superconducting ceramics: *1*—$YBa_2Cu_3O_x$(Y-123); *2*—$Bi_2Ba_2CaCu_2O_x$ (Bi-2212) phase; *3*—$Tl_2Ba_2Ca_2Cu_3O_x$; *4,5*—$HgBa_2CaCu_2O_x$ with $T_c=126$ K and $T_c=125$ K, respectively.

tures ($T=50$ K) the superconducting transition temperature is almost pressure-independent. Hence it was concluded (and confirmed by further structural investigations) that the application of pressure at room temperature results in restructuring of the oxygen sublattice, which changes T_c. If the pressure changes at low temperature, however, then there is insufficient thermal energy for such restructuring, and dT_c/dP characterizes "internal" processes.

The small value of dT_c/dP for the Hg-1201 phase could also mean, however, that this phase is different from other phases in the mercury system. First, the Hg-1201 phase has only one Cu–O layer, and for this reason this phase does not contain an interaction between neighboring Cu–O layers, which changes the concentration in the conduction band and therefore the value of T_c. Second, the Fermi surface topology can change (electron-topological transition) at a transition from the 1201 phase into phases with higher values of T_c. According to the data of Ref. 9, the value of dT_c/dP in high-T_c superconductors could be strongly associated with electron-topological transitions. These features are fundamental. Further study of the Hg-1201 phase, including an investigation of the pressure-induced structural changes, is required in order to check these suppositions.

The pressure dependence of T_c for phases in the mercury system with several Cu–O layers apparently reflects mainly the "internal" effects (just as for the thallium system). Here the derivative $d(\ln T_c)/dP$ is comparable to that in Tl and Bi systems with several Cu–O layers at hydrostatic pressures. The large constant pressure derivative could indicate that the maximum of the curve of T_c versus the carrier concentration has still not been reached. Unfortunately, we cannot check this hypothesis, because we are unaware of any work on the dependence of T_c on the oxygen concentration x in the mercury system; moreover, we do not know the exact value of x for our samples. In addition, the pressure-dependent properties of these phases probably indicate more complicated "internal" mechanisms of the effect of pressure on T_c. Indeed, the present model of the change in T_c reflects only the contribution of the electronic subsystem, but a complete theory must also take into account changes in the lattice subsystem, similarly to the theory for classical superconductors. This conclusion was drawn in Ref. 10, where dT_c/dP in the system $Bi_2Sr_2CaCu_2O_{8+x}$ was observed to increase slightly with increasing x, similarly to our result, while T_c first increased with a significant change in the oxygen concentration (left-hand branch of the parabola), reached a maximum, and then once again decreased (right-hand branch of the parabola).

In order to check the effects introduced in the pressure dependence $T_c(P)$ for the second sample, we performed measurements with both increasing and decreasing P. The results were identical. For technical reasons measurements with decreasing pressure could not be performed on the first sample.

4. MEASUREMENTS AND PRESSURE DEPENDENCE OF THE MAGNETIC PROPERTIES

Figure 1 displays atmospheric-pressure irreversibility curves for the transitions at $T_c=126$ K and $T_c=125$ K, i.e., for the Hg-1212 phase. Our data agree well with the linear irreversibility measured in the susceptibility for the Hg-1201 phase. The irreversibility curves which we measured for the ceramics $Tl_2Ba_2Ca_2Cu_3O_x$ ($T_c=105.6$ K), $YBa_2Cu_3O_x$ ($T_c=94$ K)$_g$ and $Bi_2Ba_2CaCu_2O_x$ ($T_c=84.7$ K) are plotted for comparison.[12] The measurements for all samples were performed by the induction method under identical conditions. The modulation frequency was 2 kHz and the modulation field was 0.1 Oe. This enables us to compare the irreversibility curves of all of these systems. It is obvious that in the mercury system the irreversibility curve associated with the second critical field falls above $\tilde{H}_c$ for the Tl and Bi systems. This is as expected, considering that the layers are more closely spaced. The irreversibility curve for the ceramic Y-123 in these normalized coordinates lies much higher.

It is convenient to represent the obtained temperature dependence $\tilde{H}_c(T)$ in the form $1-t=a\cdot H^q$, where $t=T/T_c$; see Fig. 2. The curves contain two regions of

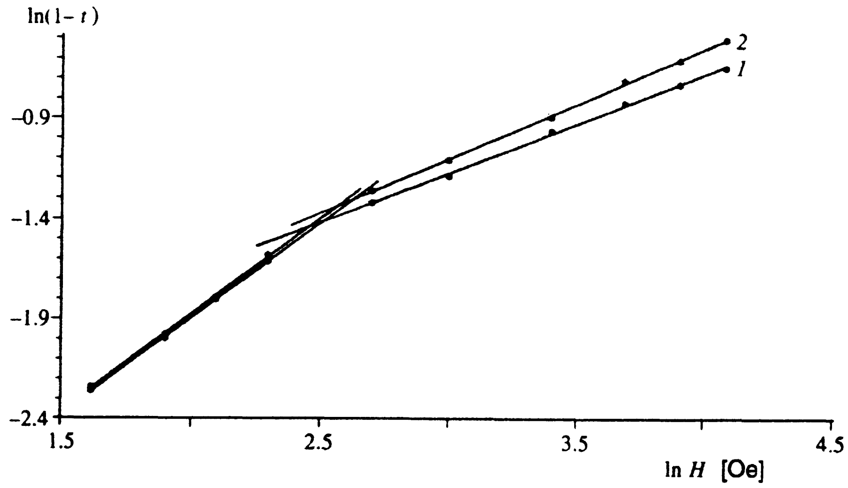

FIG. 2. Irreversibility curves for $HgBa_2CaCu_2O_x$ samples with $T_c=126$ K (curve *1*) and $T_c=125$ K (curve *2*) in logarithmic coordinates; $t=T/T_c$.

magnetic field for which q takes on different values: $q\approx 4/5$ for $H<H^*$ and $q\approx 1/2$ for $H>H^*$, where $H^*=1.5$ kOe. We observed previously the existence of two values of q in $Bi_2Sr_2CaCu_2O_x$ single crystals[13] and $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ ceramic[14] with different values of the magnetic field. The inflection could occur due to the existence of two mechanisms for pinning of the vortex lattice in these superconductors or due to crossover from collective pinning of the vortex lattice in weak fields to a "vortex liquid" state in high fields.

As the pressure increases, the $\tilde{H}_c(T)$ curve shifts along the temperature axis without any appreciable change in shape and slope; the pressure derivative equals 0.15 kOe/K. One can see that the coherence length increases with the pressure.

For the first sample we measured the superconducting transition temperature of the phase with $T_c=126$ K as a function of the frequency of the modulation field for two cases: $H=0$ and $H=20$ kOe. As one can see from Fig. 3, the superconducting transition temperature increases with the frequency f in the entire range; the dependence is nearly logarithmic. At $H=0$ no change was observed in T_c, to within the limits of experimental accuracy. This result agrees numerically with theoretical and experimental investigations of the "irreversibility curve," taking into account magnetic-flux creep, in high-T_c superconductors.[5]

5. CONCLUSIONS

In this work we investigated the effect of hydrostatic pressure on the superconducting transition temperature T_c and the irreversibility field in samples of a new class of high-T_c superconductors: $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ with $n=1,2$, and 3. The pressure derivative for the 1212 and 1223 phases are comparatively large: $d(\ln T_c)/dP=0.30$–0.33 and 0.35, respectively (or $d(\ln T_c)/dP=2.40$–2.62 kbar^{-1} and $2.65\cdot 10^{-2}$ (kbar^{-1}), which could indicate the possibility that T_c could be increased further by synthesizing analogous compounds. The weak dependence of dT_c/dP for samples with different oxygen content with an appreciable change in T_c indicates that either the chosen value of x corresponds to the left-hand branch of the parabola $T_c(x)$ or there exist other mechanisms for the effect of pressure on T_c besides charge transport in the Cu–O planes.

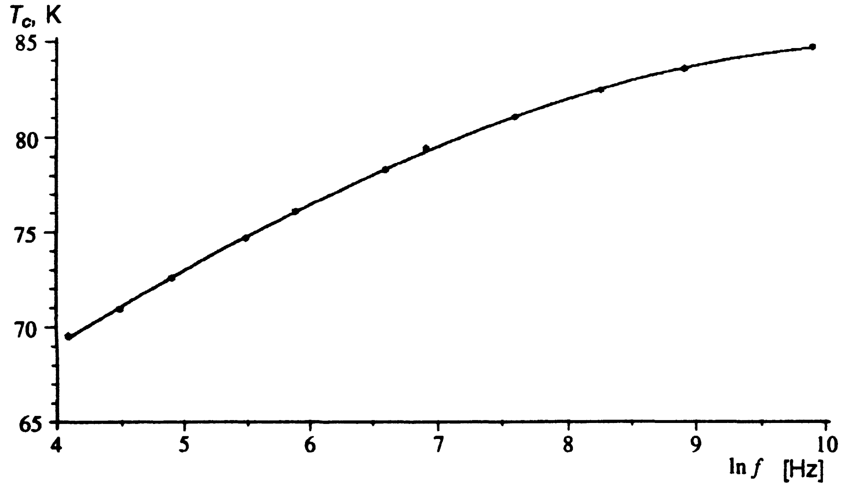

FIG. 3. Superconducting transition temperature in a constant magnetic field ($H=20$ kOe) versus the frequency of the modulation field for the sample $HgBa_2CaCu_2O_x$ with $T_c=126$ K.

For the $HgBa_2CuO_x$ phase the low value of the derivative $dT_c/dP=0.07$ K/kbar ($d(\ln T_c)/dP=8\cdot 10^{-4}$ kbar^{-1}) could indicate that either the oxygen subsystem is rearranged under pressure or that phases with a single Cu–O layer are fundamentally different from phases with several Cu–O layers.

The irreversibility curve characterizing the second critical field and the intensity of magnetic-flux creep is close to the irreversibility curves for the analogous thallium metal ceramic but significantly lower than for the Y-123 system. This indicates that the activation energy of magnetic-flux creep is low. This conclusion is also supported by the strong dependence of the superconducting transition temperature on the frequency of the modulation field. The irreversibility curve contains an inflection point, which characterizes the existence of two regions of the field in which the pinning potentials are different.

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