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Possible existence of a Van Hove singularity near the Fermi surface of $HgBa_2CaCu_2O_{6+\delta}$

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The superconducting transition temperatures (T_c's) of $HgBa_2CaCu_2O_{6+\delta}$ with different dopings and different ambient T_c's were examined magnetically under hydrostatic pressures. We observed that T_c increases with pressure linearly at a rate of 0.22±0.02 K/kbar up to 18 kbar for as-synthesized samples with an ambient $T_c \sim 111$ K, but at a similar initial rate only below ~4 kbar, and at a reduced rate of 0.11±0.02 K/kbar above, for the oxygenated samples with an ambient $T_c \sim 117$ K. The observation suggests the possible existence of a Van Hove singularity in the electronic energy spectrum of $HgBa_2CaCu_2O_{6+\delta}$ and a possible pressure-induced Fermi-surface-topology change in the oxygenated compound.

I. INTRODUCTION

Recently, Putilin *et al.*[1] observed superconductivity up to 94 K in $HgBa_2CuO_{6+\delta}$ with one CuO_2 layer per unit cell, which is the first member of the homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$[Hg 1:2:$(n-1)$:$n$] with $n=1,2,3,\ldots$. Later, Schilling *et al.*[2] detected superconductivity up to 133.5 K and zero resistance at 95 K in multiphased Hg-Ba-Ca-Cu-O (HBCCO) samples with 15% of the sample volume containing Hg 1:2:1:2, Hg 1:2:2:3, and an ordered superstructure with a period ~84 Å composed of a defined stacking sequence of the unit cells of Hg 1:2:1:2 and Hg 1:2:2:3. Subsequently, we[3] obtained similar multiphased HBCCO samples displaying superconductivity up to ~140 K, a main resistive transition at ~135 K, and a zero resistance at ~107 K. Again, the samples contained the (Hg 1:2:1:2)/(Hg 1:2:2:3) superstructure with a period of 42 Å, and nonsuperconducting impurities. In an attempt to determine the phase responsible for the high-superconducting transition temperature (T_c), we succeeded[4] in preparing samples with Hg 1:2:1:2 as the major phase and found that Hg 1:2:1:2 exhibits a main transition at ~112 K prior to oxygenation and at ~117 K after prolonged oxygenation.

Novikov and Freeman[5] have calculated the electronic structure and the Fermi surface of Hg 1:2:0:1. They found that the Fermi surface has a shape of a rounded square and that a major Von Hove saddle-point singularity exists near the Fermi surface E_F, due to the two-dimensional characteristics of Hg 1:2:0:1. A strong influence of doping on the electron density of states and thus on the superconducting properties of the compound was, therefore, predicted. Hg 1:2:1:2 has[4] a layered structure with two CuO_2 layers per unit cell. Its electronic structure may display similar singularities near E_F. As E_F crosses these singular points with change of E_F, a drastic change in T_c or dT_c/dE_F may occur. It has been shown that both doping and pressure can shift the E_F of layered cuprate high-temperature superconductors.[6] We have, therefore, decided to use the combined influence of oxygenation and pressure to search for the possible existence of singular points in the electron energy spectrum of Hg 1:2:1:2.

We have measured the T_c of four Hg 1:2:1:2 samples under hydrostatic pressures up to 18 kbar; two as-prepared samples with midpoint T_c varying from ~111.6 to 112.4 K and a transition width of <2 K, and three oxygenated with a midpoint T_c at ~118.2 to 119.8 K and a transition width of ≤3 K. We found that T_c is enhanced by pressures for all samples. For the as-prepared samples, T_c increases linearly with pressures at a rate $dT_c/dP = 0.22 \pm 0.02$ K/kbar throughout our pressure range of 18 kbar. However, for the oxygenated samples, T_c initially increases with pressure at a similar rate of ~4 kbar but at a reduced rate of 0.11±0.02 K/kbar above. The observation suggests the possible existence of a singular point in the electron energy spectrum of Hg 1:2:1:2 and an electron transition may have been induced by the combined effect of doping and pressure as in the present investigation.

II. EXPERIMENT

During the course of our study on HBCCO, we found that the formation of the superconducting phases of HBCCO is extremely sensitive to the precursor and synthesis conditions, such as the reaction atmosphere and the reaction temperature. The samples investigated were synthesized using our modified solid-state reaction technique with proper control of the reaction atmosphere, which has enabled us to achieve samples containing more than 90% Hg 1:2:1:2, or more than 70% Hg 1:2:2:3 by sample volume with 100% yield. Details of our technique will be published[7] elsewhere. Here, we would like to describe briefly only the main steps used for preparing Hg 1:2:1:2. A precursor material with a nominal composition of $Ba_2CaCu_2O_5$ (not a compound) was prepared by calcinating at 800° C a thoroughly mixed powder of appropriate amounts of $BaCuO_2$ and CaO in an oxygen atmosphere for 16 h. The calcinated powder was then transferred to a glove bag to reduce its exposure to air to a minimum, where it was mixed with HgO in the propor-

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tion of 1:1. The well-mixed powder was compacted into pellets which were than sealed in evacuated quartz tubes. The quartz tubes were subsequently sealed in stainless-steel tubes for safety. The sealed mixed powders were then placed inside a furnace and slowly heated at a rate of ~160° C/h to 800° C, and kept at this temperature for 9 h before being cooled to room temperature. The slow heating was successfully used to avoid any rupture of the quartz tube which might have resulted from the unreacted Hg vapor. When the $Ba_2CaCu_2O_5$ precursor which had been exposed to air overnight was used, the quartz tube ruptured for reasons yet to be determined. Oxygenation was carried out at 300° C in flowing oxygen. Characterization was carried out by x-ray diffraction using a Rigaku DMAX/BIII powder diffractometer, and the composition was determined qualitatively by an energy dispersive spectrometer for x-ray analysis using a Link EXL analyzer. The standard inductance bridge, operated at 16 Hz in an ac field of ~5 Oe peak to peak, was employed to determine the ac magnetic susceptibility under pressures from ambient to 18 kbar, and a Quantum Design superconducting quantum interference device (SQUID) magnetometer for dc magnetization at ambient pressure. The high-pressure environment was generated inside a Teflon cup housed in a Be-Cu high-pressure clamp,[8] using the 3M Fluorinert as a pressure medium. The pressure was measured with a superconducting Pb manometer which was located next to the sample inside the Teflon cup, and the temperature by an Chromel-Alumel thermocouple above 10 K or a Ge thermometer below 20 K.

III. RESULTS AND DISCUSSION

Four Hg 1:2:1:2 samples A, B, C, and D were investigated in the present study: A and C as synthesized, and B and D after oxygenation for 30 h at 300° C. Samples A and B were the same specimen previously examined.[4] The x-ray results of these samples showed that Hg 1:2:1:2 with lattice parameters $a = 3.862(1)$ Å and $c = 12.707(5)$ Å accounts for >50% of the volume of samples A, B, and C and >90% of that of sample D. The minor impurity phases are $CaHgO_2$, Hg 1:2:0:1, $Ba_2Cu_3O_{5.9}$, and $BaCuO_2$ in samples A, B, and C; and $Ba_2Cu_3O_{5.9}$ and $CaHgO_2$ in sample D. The x-ray-diffraction pattern of sample D is shown in Fig. 1. Annealing does not generate any detectable change in the lattice parameters. The dc magnetic-susceptibility (χ_{dc}) results are displayed in Fig. 2(a) for samples (A) (which is the same as C), and B, and, in Fig. 2(b), for sample D. It is clear that all samples examined are of high quality, as is evidenced by the sharp magnetic transition and large superconducting volume fraction (particularly for sample D); and that annealing at 300° C in flowing oxygen for > 10 h enhanced T_c by ~5 K; and further annealing under the same condition has no more effect on T_c. It should be noted that oxygenation at 300° C for a time period of $<5h$ broadens the superconducting transition with an onset at higher temperature. This implies that Hg 1:2:1:2 with a $T_c \sim 117$ K may be the equilibrium phase oxygenated at 300° C. Equilibrium phases of Hg 1:2:1:2 at other oxy-

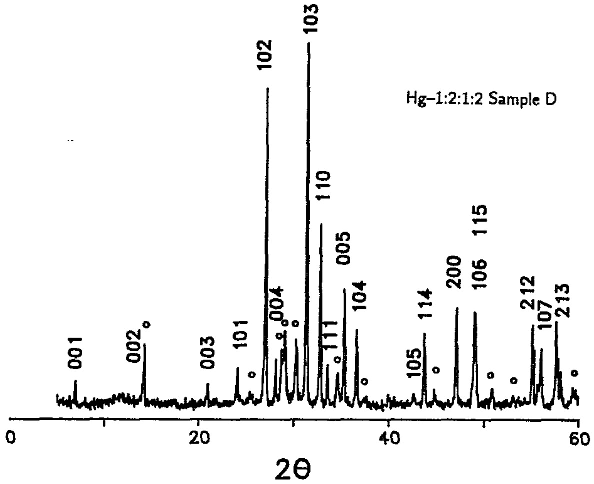

FIG. 1. X-ray-diffraction pattern of Hg-1:2:1:2 sample D (○ impurities: $CaHgO_2$ and $Ba_2Cu_3O_{5.9}$).

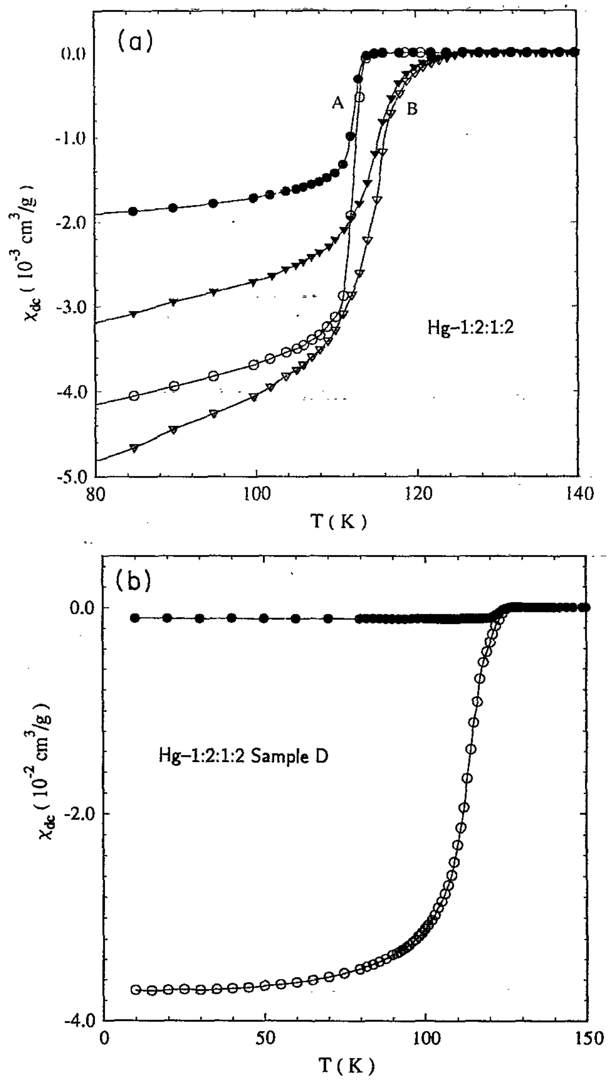

FIG. 2. χ_{dc} vs T; (a) for samples A and B; and (b) for sample D (solid symbols for field cooled; open symbols for zero-field cooled).

genation temperatures and other oxygen pressures are being explored in our laboratory.

Because of their sharp transitions, only the as-synthesized and long-annealed samples with ambient T_c's at ~111 and ~117 K were studied under pressure. The ac magnetic-susceptibility (χ_{ac}) results for the as-synthesized and oxygenated samples under various pressures are represented by those for sample A in Fig. 3(a) and sample B in Fig. 3(b), respectively. The numbers in Figs. 3(a) and 3(b) denote the sequential order of the experimental run. The superconducting transitions of all samples are shifted toward higher temperature with increased pressure, reversibly. Since the χ_{ac}'s determined in the present experiment are relative measurements, no attention has been given to the changes in the magnitude of χ_{ac} under pressures as shown in Figs. 3(a) and 3(b), which may have resulted from the change in the sample position during pressurization. The onset T_{c0} and midpoint T_{cm} are defined in the insets of Figs. 3(a) and 3(b). We found that the pressure effects on T_{c0} and T_{cm} are the same. Therefore, in Fig. 4 we have summarized the pressure dependence of the T_{cm}'s for samples A, B, and C and T_{c0} for sample D. The T_{c0} is shown for sample D because of its broad χ_{ac} transition, in contrast to the narrow χ_{dc} transition shown in Fig. 1. This may be attributed to the unusual microconnectivity of the sample grains. It should be noted that the pressure dependence of the T_{c0} of sample D is almost the same as the T_{c0} for sample C. T_c (either T_{c0} or T_{cm}) increases linearly with pressure for samples A and C prior to oxygenation at a rate of 0.22±0.02 K/kbar. However, for the post-oxygenated samples B and D which have a higher T_c, the T_c increases at an initial rate ~0.23±0.02 K/kbar up to ~4 kbar but at a reduced rate of 0.11±0.03 K/kbar above. Such a break in the slope is clearly evident in Fig. 4.

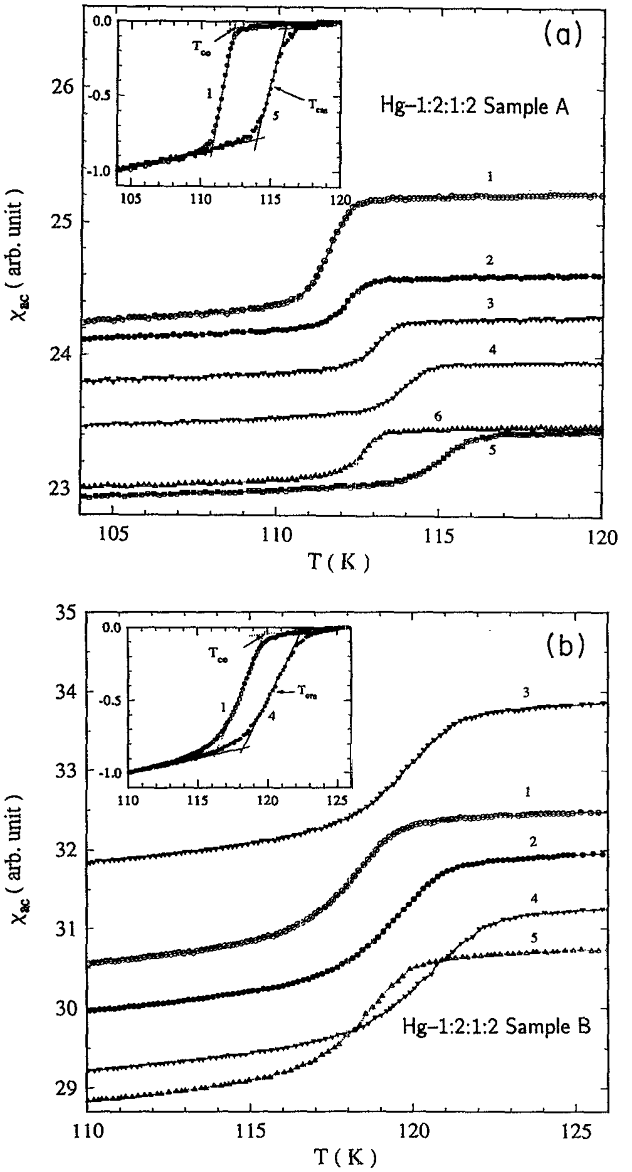

FIG. 3. χ_{ac} vs T for (a) sample A; 1: ambient pressure, 2: 1.50 kbar, 3: 4.72 kbar, 4: 10.76 kbar, 5: 15.91 kbar, and 6: 3.23 kbar; and (b) sample B; 1: ambient pressure, 2: 6.09 kbar, 3: 9.41 kbar, 4: 17.95 kbar, and 5: 1.60 kbar. Insets: defines the onset T_{co} and the midpoint T_{cm} of samples A and B.

It is known[9] that critical or singular points $E_c \equiv E(\bar{k}_c)$ exist in the electron energy spectrum $E(\bar{k})$ of a solid, where $\nabla E(\bar{k}_c)=0$. As the Fermi energy E_F crosses these critical points $E(\bar{k}_c)$, the topology of the Fermi surface changes, leading to a change of electron density of states at E_F, i.e., $\Delta N(E_F)$. The exact value of $\Delta N(E_F)$ depends on the details of $E(\bar{k})$. In general, there are four types of singularities which need not be major. The influence of $\Delta N(E_F)$ induced by a Fermi-surface-topology change on T_c has been examined previously.[10] A distinct change in T_c and/or dT_c/dP will follow when a change occurs in the Fermi-surface topology. Such a Fermi-surface-topology-change can be induced by shifting the E_F to cross E_c through chemical doping and/or pressure doping. The latter is due to pressure generated charge transfer. The pressure effect on T_c of Hg 1:2:1:2, shown in Fig. 4, can now be understood in terms of the possible

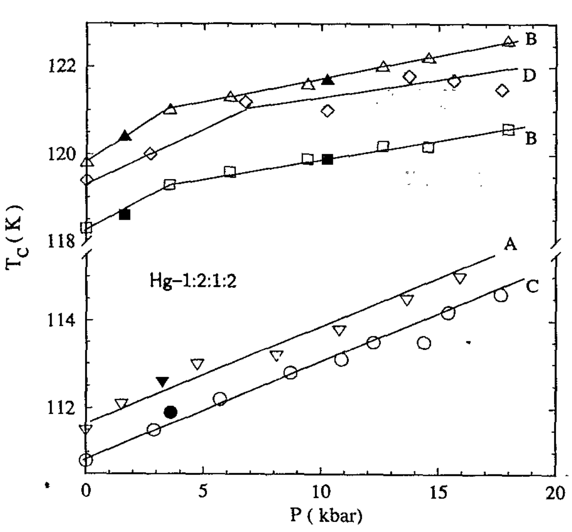

FIG. 4. T_c vs P. (○, ▽, and □ for T_{cm}; and ◇ and △ for T_{c0}. Solid symbols obtained on pressure decreasing.)

existence of a singular point E_c near E_F in its electron energy spectrum. Assume that the E_F of the as-prepared Hg 1:2:1:2 lies below E_c and that pressure enhances E_F. A pressure of 18 kbar brings E_F closer to E_c but not enough to cross E_c. Consequently, only a linear effect on T_c is observed in the as-synthesized samples A and C. By increasing the hole concentration through oxygenation, E_F is brought closer to E_c at ambient pressure, and a smaller pressure of ~4 kbar is thus sufficient to push E_F over E_c. As E_F passes E_c, a distinct change of dT_c/dP results, as shown by the oxygenated samples B and D. This is consistent with the recent band-structure calculations on Hg 1:2:0:1 (Ref. 5) and Hg 1:2:1:2 (Ref. 11), where major Von Hove singularities exist at the X and R points in the Brillouin zone below E_F (in the electron sense). According to these calculations, the singular point is a major one and a drastic T_c increase will result as E_F moves close to E_c. However, what we have observed is a continuous T_c increase, although with a large change in dT_c/dP. The singular point near E_F, implied in our experiment, may be a minor one.

In conclusion, we have measured, under pressure, magnetically the T_c of the as-synthesized and oxygenated Hg 1:2:1:2 samples which display narrow transitions with midpoint T_c's at ~111 and ~117 K, respectively. We found that T_c increases linearly at a rate of 0.22±0.02 K/kbar up to 18 kbar for the as-synthesized samples, whereas T_c increases at a rate of 0.23±0.02 K/kbar up to ~4 kbar but at a reduced rate of 0.11±0.03 K/kbar above for samples annealed at 300° C in flowing oxygen. The results suggest the possible existence of a singularity in the Hg 1:2:1:2 electron structure, consistent with recent band calculations,[5,11] although such a suggested singular point may be a minor one.

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