High-temperature superconducting $YSr_2Cu_3O_{7.5}$ under pressure

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The transition temperature (T_c) of the high-temperature superconductor $YSr_2Cu_3O_{7.5}$ under hydrostatic pressures up to 1.7 GPa has been measured. The T_c was observed to increase from 62.6 to 67.8 K. Such a large positive dT_c/dP of ~3 K/GPa is in strong contrast to that expected from the heavily doped nature of the sample, as suggested by the thermogravimetric and thermopower measurements. [S0163-1829(98)05841-X]

I. INTRODUCTION

The physical properties of cuprate high-temperature superconductors (HTSr's) have been shown to depend critically on their carrier concentration (p), induced by cation and/or anion doping.[1] A compound is known as optically doped when $p=p_o$ where its T_c is maximum, underdoped when $p<p_o$, or overdoped when $p>p_o$. The underdoped HTSr's are suggested to be a ''strange'' metal that defies description of the Fermi-liquid picture, and the overdoped ones to be a ''normal'' metal.[2] While extensive studies[2] in the underdoped HTSr's reveal various anomalies in both the normal and superconducting states of the compounds, data on overdoped HTSr's are sparse. Therefore, it would be interesting to find and study high quality samples of overdoped HTSr's.

It was demonstrated a few years ago that $YSr_2Cu_3O_x$ (YSCO), isostructural to $YBa_2Cu_3O_x$ (YBCO), forms only under high oxygen pressure,[3] or at ambient pressure in air by the partial substitution of Cu in the CuO chain in YSCO by elements of valence greater than $+2$.[4] In view of the similar chemical and structural characteristics of YSCO and YBCO, the presence of a high oxygen partial pressure during the formation of YSCO suggests that the YSCO sample so prepared may be heavily overdoped.

We have therefore synthesized $YSr_2Cu_3O_{7.5}$ under a high pressure of 3 GPa at ~1050 °C and studied the pressure effect on its T_c up to 1.6 GPa. We found that the T_c of $YSr_2Cu_3O_{7.5}$ increases with pressure at a large rate, dT_c/dP, of ~$+3$ K/GPa, similar to an underdoped HTSr but in contrast to the heavily overdoped nature of the sample based on the thermogravimetric and thermoelectric power (TEP) measurements. The implications of this observation will be discussed.

II. EXPERIMENT

The samples were prepared by thoroughly mixing powders of Y_2O_3 (99.5%), SrO (99.5%), and CuO (99.95%) with the cation ratio Y:Sr:Cu$=1:2:3$. The powder mixture was heated in an alumina crucible at ~980 °C for 60 h in a flowing O_2 with several intermittent grindings to form the precursor. Such a high-temperature heat treatment was shown[5] to minimize the C contamination from the air. The precursor was then mixed with the oxidizing agent $KClO_3$ in a molar ratio of $KClO_3$:$YSr_2Cu_3O_{6.5}=x$ for $0<x<2$, and pressed into cylinders of 4 mm $\oslash \times 7$ mm. The pellets were wrapped with gold foil and loaded into the sample chamber of a Rockland Research piston-cylinder high-pressure rig, using MgO as a pressure medium, and a graphite furnace. The pellets were pressurized to ~3 GPa and heated to 1000–1050 °C for 2–8 h before being quenched to room temperature.

The structure of the sample was characterized by powder x-ray diffraction (XRD) using a Rigaku D-MAX/BIII diffractometer with the Cu(K_α) line and the composition by Japan Electron Optics Laboratory energy dispersive x-ray analysis (EDAX). The oxygen content y in $YSr_2Cu_3O_y$ is determined by using thermogravimetric analysis (TGA) employing a TA Instruments Thermal Analyst Model 2100. The thermopower measurement was made using a high-precision technique previously developed.[6] The superconducting transition at ambient was determined resistively by the standard four-lead method using a Linear Research LR-400 bridge and magnetically using a Quantum Design superconducting quantum interference device magnetometer. Under pressure, the transition was determined resistively. The high-pressure environment was generated by the modified clamp technique inside a Teflon cell housed in a Be-Cu cylinder,[7] using the 3M fluorinert as the pressure medium. The temperature was determined by an alumel-chromel thermocouple and the pressure by a superconducting Pb manometer; both were situated next to the sample inside the high-pressure cell.

III. RESULTS AND DISCUSSION

The XRD results show that all YSCO samples, with an oxidant $KClO_3$ to $YSr_2Cu_3O_{6.5}$ molar ratio $0<x<2$ made under 3 GPa at 1000–1050 °C, contain mainly the $YSr_2Cu_3O_y$ phase with varying small amounts of oxide impurities, as exemplified in Fig. 1 for $x=0.45$. The cation composition of Y:Sr:Cu from EDAX measurements is 1:2:(2.9–3) across the YSCO grains. It is interesting to note that the YSCO sample prepared with low x displayed a certain degree of orthorhombicity which decreases to zero with increasing x, as evident in inset of Fig. 1 where the orthorhombic (200) and (020) lines merge into the tetragonal (200) line with increasing x. A similar orthorhombic to tetragonal transition with x was also observed in YBCO previously.[8] The purest samples were obtained for $x\sim0.45$. The lattice parameters for these samples were $a=3.795$ Å and $c=11.38$ Å, in agreement with the previous reports.[3]
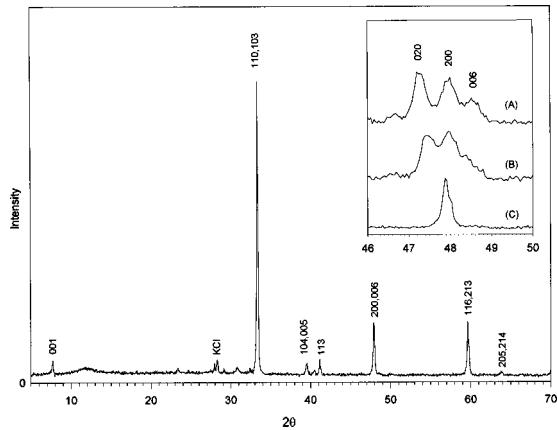
FIG. 1. XRD using the $Cu(K_\alpha)$ line for $YSr_2Cu_3O_y$ with molar ratio of $KClO_3:YSr_2Cu_3O_{6.5}=x=0.45$. Inset: the (200) and (020) lines for various x's. A: 0; B: 0.03; and C: 0.45.

Therefore only samples synthesized with $x=0.45$ were examined in this investigation.

TGA data give an oxygen content $y=7.5\pm0.2$ in our samples as prepared with $x=0.45$. This suggests that the YSCO sample is heavily overdoped, since the optimal doping of y_o is ~6.95 for YBCO. The TEP measurements provide a value of -2.6 mV/K at 290 K, showing again that the sample is overdoped,[9] although not so heavily doped as compared with the $y=7.5$ suggests.

The YSCO samples prepared by the high-pressure synthesis technique usually display a small Meissner volume fraction of only a few percent in an external field of 1 mT.[3,4] This has been attributed to the possibly low carrier concentration of the compound.[4] By minimizing the C contamination through high-temperature heating the starting materials and adjusting the synthesis conditions, a Meissner volume fraction of $\geq15\%$ with an onset transition at 63.5 K was achieved in our samples at 0.5 mT (Fig. 2). A volume fraction $>50\%$ was detected by reducing the measuring field to below 0.1 mT. This suggests that the previously observed low volume fraction can be attributed to the pinning in the samples.

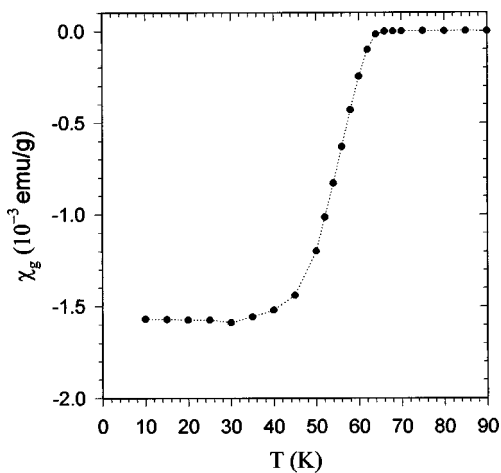The YSCO samples as synthesized behave as a metal re-
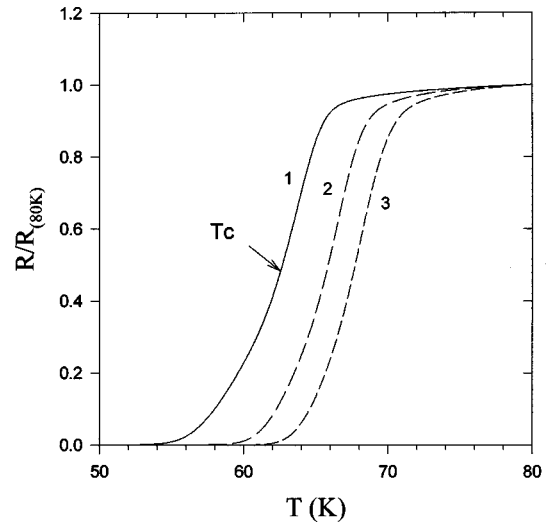

FIG. 3. Normalized resistance vs temperature at different pressures for $YSr_2Cu_3O_{7.5}$. 1: 0 GPa; 2: 0.93 GPa; and 3: 1.68 GPa. The midpoint transition temperature (T_c) is defined at the temperature at 50% of the normal state resistance.

sistively above the superconducting transition which is between 64 and 59 K with a tail to 54 K. Under pressure the superconducting transition is shifted upward in parallel as shown in Fig. 3. The midpoint transition temperature (T_c) is plotted as a function of pressure in Fig. 4, showing a linear P dependence of T_c at a rate of $+3$ K/GPa.

A universal quadratic p dependence of T_c has been proposed for HTSr's,[1] i.e., $T_c=T_c^{max}[1-a(p-p_o)^2]$, where T_c^{max} is the highest T_c when the HTSr is optimally doped at $p=p_o$ and a is a constant which determines the doping range where superconductivity occurs. Based on this $T_c(p)$ relation, various phenomenological models[10] were advanced to account for the pressure effect on T_c of HTSr's. By assuming that P affects only p via P-induced charge transfer,[11] dT_c/dP is expected to be positive when $p<p_o$, zero when $p=p_o$ and negative when $p>p_o$. This seems to agree qualitatively with earlier studies. However, later investigations showed that, even for optimally doped HTSr's, dT_c/dP is nonzero and positive. By allowing P to influence T_c^{max} at a rate of $dT_c^{max}/dP=0.96$ K/GPa via a channel other than P-
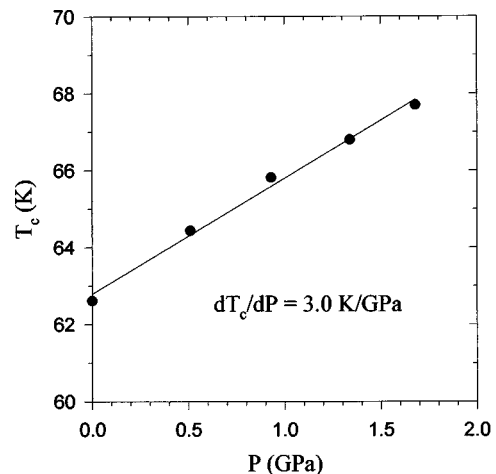

FIG. 2. Field-cooled magnetic susceptibility in 5 Oe vs temperature for $YSr_2Cu_3O_{7.5}$.

FIG. 4. The midpoint T_c vs pressure for $YSr_2Cu_3O_{7.5}$.

induced charge transfer,[12] the $T_c(P)$ behavior of $YBa_{2-x}La_xCu_3O_7$ and $(Y_{1-x}Ca_x)Ba_2Cu_3O_7$ over a fairly wide doping range was understood. $YSr_2Cu_3O_y$ is isostructurally and chemically similar to YBCO; one would therefore expect the similar model applicable to YSCO, i.e., dT_c/dP is negative or if positive should be small ($<dT_c^{max}/dP$) when YSCO is heavily doped, as indicated by the TGA and TEP data. Unfortunately, the observed dT_c/dP of $YSr_2Cu_3O_{7.5}$ is +3 K/GPa which is three times the value of dT_c^{max}/dP proposed for the YBCO system.[12] Three possibilities arise for the observation: (1) the YSCO samples examined are not overdoped, (2) the dT_c^{max}/dP of YSCO is much larger than that of YBCO, and (3) the pressure-induced charge-transfer model is inappropriate in this case.

Previous studies revealed that C can enter the YSCO (YBCO) lattice by replacing all Cu in the CuO chain for every n CuO chains to form at ambient pressure the oxycarbonate $Y_nSr_{2n}Cu_{3n-1}(CO_3)O_{7n-3}$ [$Y_nBa_{2n}Cu_{3n-1}(CO_3)O_{7n-3}$] (Ref. 13) or by replacing part of the Cu in the CuO chain to form also at ambient pressure $YSr_2Cu_{3-z}(CO_3)_zO_{7-z}$ [$YBa_2Cu_{3-z}(CO_3)_zO_{7-z}$] (Ref. 14) which is actually the disordered $n=1/z$ member of the previous homologous series. The incorporation of C into YSCO (YBCO) results in a substantial reduction in the c axis of the basic orthorhombic cell, the formation of superlattices and a great suppression of T_c. It also leads to a reduction of hole concentration for a fixed oxygen content and the reduction increases rapidly with the C content. This may be responsible for the absence of superconductivity in the YSCO oxycarbonates even after annealing in a 5 MPa O_2 atmosphere, previously reported.[14] Although the XRD data showed that the structure of $YSr_2Cu_3O_{7.5}$ was tetragonal, with $a=3.795$ Å and $c=11.38$ Å, and the EDAX results gave a cation ratio of Y:Sr:Cu=1:2:(2.9–3.0) within our resolution of a few percent, a small amount of C contamination cannot be excluded in our samples which may be expressed as $YSr_2Cu_{3-z}C_zO_{7.5}$. It should be noted that neither K nor Cl was detected in the YSCO grains. Assuming that the maximum possible Cu deficiency is due to C contamination, i.e., $z=0.1$, and that the C distributes itself uniformly in the sample, it gives a C/Cu=1/29, in agreement with our gas-effusion cell measurements, corresponding to the $n=10$ member of the YSCO oxycarbonate. The average Cu valence in the sample remains to be an overdoped value of +2.6 ±0.1, in comparison with the optimal value of +2.33 for YBCO. For the Cu valence in the oxycarbonate $YSr_2Cu_{3-z}C_zO_{7.5}$ to be less than +2.33 and therefore to be underdoped, z has to be greater than 0.6. It has been shown[14] that oxycarbonate YSCO is not superconducting, even with a smaller $z=0.4$ which results in a lattice parameter c as small as 11.185 Å. Increasing the oxygen content of such a $z>0.5$ compound is expected to further reduce c. On the other hand, our $YSr_2Cu_3O_{7.5}$ is superconducting and has a $c=11.38$ Å. Therefore, $YSr_2Cu_3O_{7.5}$ must contain $z\ll0.4$ and cannot be changed from its overdoped state to an underdoped state by C incorporation, provided that the ionic model is still valid for each O atom to provide two holes for $y>7$.

It was shown previously that the pressure induced charge transfer depends on the filling of the O sites in the CuO chain layer in YBCO.[15] For $YSr_2Cu_3O_{7.5}$, the O-site filling can be very different from the underdoped YBCO and therefore the pressure induced charge transfer may not play an important role. The large positive dT_c/dP observed must be associated with factors other than carrier density.[16] Whether this is characteristic of an overdoped HTSr or specific to overdoped YSCO remains unresolved. A heavily overdoped $YBa_2Cu_3O_{7.5}$ is being prepared and investigated.

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