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Transport studies of bulk $Pb_{0.2}Hg_{0.8}Ba_2Ca_{1.75}Cu_3O_x$

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Measurements of the resistance versus temperature $R(T)$ were made on samples of $Pb_{0.2}Hg_{0.8}Ba_2Ca_{1.75}Cu_3O_x$ above their superconductive transition temperatures. Current-voltage (I-V) characteristics were also studied at 77, 27, and 4.2 K in applied magnetic fields varying from 0 to 4.5 T. The $R(T)$ data confirmed the visual observation that the samples were granular. The I-V curves were generally fit best by a modified Ambegaokar-Halperin model from which were obtained the resistance of the samples, the critical current density, and the pinning potential. The first two properties were dominated by the granular nature of the samples, whereas the pinning potential represented an intrinsic property of the material.

Recently Soulen *et al.*[1] adapted the theory of Ambegaokar-Halperin (AH) (Ref. 2) to account for dissipation in superconductors. They successfully fitted the I-V curves of several Pb-Bi-Sr-Ca-Cu-O (Pb-BSCCO) tapes and coils which they measured as a function of temperature and magnetic field. In this article the study is extended to include examples of the superconducting material Pb-Hg-Ba-Ca-Cu-O.

Two Pb-Hg-Ba-Ca-Cu-O samples were made and studied. The first, sample 1, was prepared by heating nitrates of Ba, Ca, and Cu at 600 °C for 20 h, grinding the mixture to a powder and then reacting once again at 600 °C for 24 h.[3] The powder was then mixed with HgO and PbO, placed in a sealed quartz tube, and reacted in an oven at 855 °C for 6 h to produce a boule of $Pb_{0.2}Hg_{0.8}Ba_2Ca_{1.75}Cu_3O_x$. Visual inspection of the material in an optical microscope showed that it was very granular. X-ray diffraction indicated that the boule was composed primarily of 1223 phase (95%) with a small amount of $BaCuO_2$ and $CaHgO_2$ (<1%) present. The 1223 phase had a tetragonal unit cell with dimensions $a=3.8498(2)$ Å and $c=15.847(2)$ Å. Grains of the 1223 phase were studied by energy dispersive spectroscopy (EDX) which showed the metal ions for Hg:Pb:Ba:Ca:Cu in the proportions 1.16:0.14:2.0:1.38:2.56 (normalized to 2.0 Ba ions per unit formula). Sample 1 was cut from the boule in the form of a rectangular parallelepiped (length: 1 cm; width: 0.165 cm; height: 0.075 cm) with a cross-sectional area of 1.2×10^{-2} cm^2. The electrodes used for the voltage measurements were spaced 0.3 cm apart.

Preparation of the second sample, numbered 2, differed only in the last step where the reacted Ba, Ca, and Cu powders were mixed with HgO and PbO and placed in a gold tube which was sealed inside a stainless steel pouch. This assembly was inserted into a hot isostatic press where the mixture was reacted at 900 °C and at a pressure of 30 000 Psi in order to form a boule. Inspection of this material in an optical microscope showed that it was less granular and denser (almost 97% of theoretical density) than the material prepared by the simple reaction described above. X-ray diffraction indicated that the material was composed of 1223 phase (66%), 1212 phase (33%), and a small amount of $BaCuO_2$ (1%). The 1223 phase had a tetragonal unit cell with dimensions $a=3.8530(2)$ Å and $c=15.851(2)$ Å. EDX studies of grains of the 1223 phase showed the metal ions for Hg:Pb:Ba:Ca:Cu in the proportions 1:22:0.17:2.0:1.44:2.79. Sample 2 was cut from the boule in the form of a rectangular parallelepiped (length: 1 cm; width: 0.11 cm; height: 0.066 cm). The cross-sectional area was 7.26×10^{-3} cm^2. The electrodes used for the voltage measurements for this sample were spaced 0.254 cm apart.

The samples were mounted into a Bakelite holder and electrical contacts were made by soldering copper wires directly to the sample using indium solder. A four-contact I-V configuration was used. In order to prevent overheating, the samples were immersed directly into the liquid nitrogen, neon, or helium in a dewar. The dewar fit inside a Helmholtz coil which could be rotated and which provided fields up to 6 T with an imprecision of about 1 mT. For the data reported here, the Helmholtz coil was oriented such that the sample current was always normal to the applied magnetic field. I-V curves were measured under computer control. The current supply provided a minimum current increment of 5 mA.

Above T_c the temperature dependence of the normal-state resistivity $\rho_N(T)$ (Fig. 1) and its derivative $d\rho_N(T)/dT$ (see inset) were measured for sample 2. From this figure it is clear that the midpoint of the superconductive transition (T_c) and its width were 133.6 and 2.5 K, respectively. In order to fit the temperature dependence of the resistivity we used a model for granular materials developed by Halbritter.[4] The model presumes that the material consists of grains of average diameter a which are connected by grain boundaries which have a grain-boundary resistance per unit area, R_{gb}. In a granular system the conduction path followed by the current is lengthened and its cross-sectional area is reduced. To

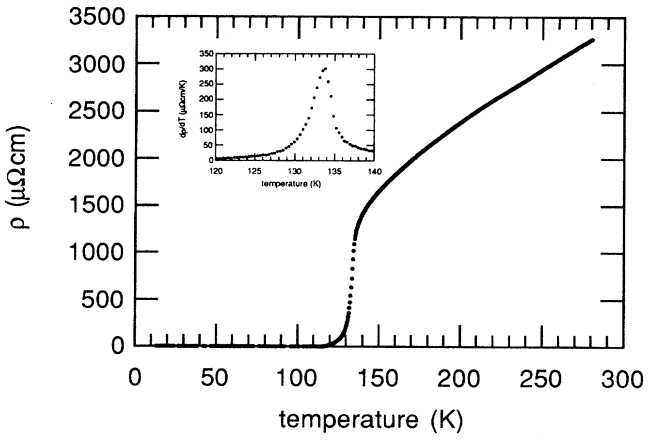

FIG. 1. The temperature dependence of the normal-state resistivity $\rho_N(T)$ and its derivative $d\rho_N(T)/dT$ (inset) for sample 2.

account for both of these effects, the intrinsic resistivity of the material is scaled by a percolation parameter p. Thus the total resistivity in Halbritter's model is written as

$$\rho_N(T)=(R_{gb}/a)+p(\alpha^i T+\rho_{0L}^i), \tag{1}$$

where α^i and ρ_{0L}^i represent the properties of the pure material. These quantities are not yet available for pure Pb-Hg-Ba-Ca-Cu-O as synthesis of this material is still evolving. The best estimates we make are based on the latest $\rho(T)$ curves from the University of Houston. From these curves we conclude that $\alpha^i=4.7$ $\mu\Omega$ cm/K and $\rho_{0L}^i=-250$ $\mu\Omega$ cm. Using Eq. (1) with these parameters, we found values for p and (R_{gb}/a) of 2.4 and 728 $\mu\Omega$ cm^2, respectively. They indicate that the sample is rather granular. From the same fit of $\rho_N(T)$ we obtained the following extrapolated values: $\rho_N(77)=1034$ $\mu\Omega$ cm, $\rho_N(27)=399$ $\mu\Omega$ cm, and $\rho_N(4.2)=184$ $\mu\Omega$ cm. We were unable to measure the resistance of sample 1 because its resistance became very large while being stored at room temperature after the I-V curves were taken but before $R(T)$ was to be measured. Nevertheless, on the basis of other evidence to be presented below, we infer that this sample is even more granular than sample 2.

Examples of the I-V curves obtained at temperatures of 77, 27, and 4.2 K for samples 1 and 2 are shown in Fig. 2, where the magnetic field was set equal to 0.01 T in all cases. The voltage is plotted on a logarithmic scale to display the behavior of the I-V curves at low voltage. The voltage was measured both as the current was increased and as the current was decreased; the lack of hysteresis indicated that heating of the immersed sample was not significant. Note that the current scale is roughly 10 times smaller for sample 1, providing the first clue that this sample was more granular than sample 2. Several sets of I-V curves were obtained for magnetic fields between 0 and 6 T at the same three temperatures for these samples.

The I-V curves for both samples were fitted by a modification of the AH model[1] which yielded three parameters: R which is related to the normal resistance R_N of the material, I_c which is the critical current, and γ which is defined as $\gamma=U(H,T)/k_BT$. Here k_B is Boltzmann's constant and

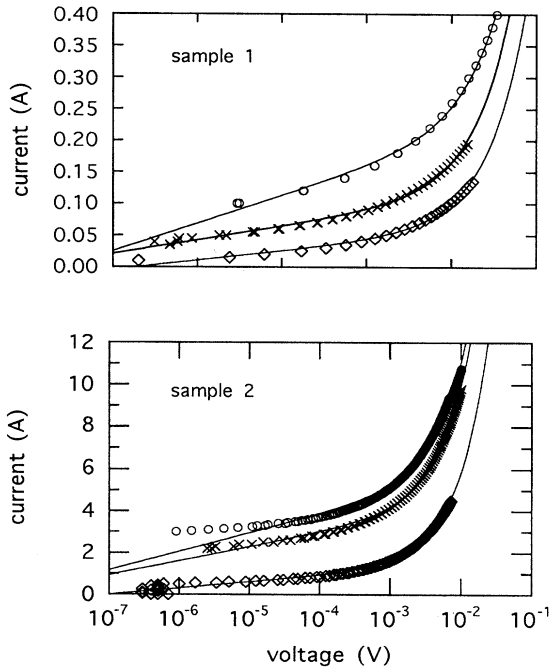

FIG. 2. I-V curves for samples 1 and 2 at temperatures of 77 K ($\diamond$), 27 K ($\times$), and 4.2 K ($\circ$) in a magnetic field of 0.01 T.

$U(H,T)$ is the pinning potential. The following equation, which previous work (Ref. 1) showed was an adequate substitute for the full solution to the AH solution, was used for the fitting:

$$I(V)=m_1+m_2\ln(V)+m_3V, \tag{2}$$

where $m_1=(2/\pi)I_c[1-(1/\gamma)\ln(I_cR)]$, $m_2=(2/\pi)(I_c/\gamma)$, and $m_3=(1/R)$. The fits of Eq. (2) to the data are represented in Fig. 2 as the solid lines. The quality of the AH fits to the data is apparent. For sample 1 at $T=77$ K and $H=0.01$ T, the fitted parameters were $I_c=0.092\pm0.003$ A, $\gamma=9.3\pm0.3$, and $R=0.0218\pm0.0005$ Ω. At $T=27$ K and $H=0.01$ T, the fitted parameters were $I_c=0.185\pm0.003$ A, $\gamma=12.6\pm0.2$, and $R=0.0172\pm0.0005$ Ω. At $T=4.2$ K and $H=0.01$ T, the fitted parameters were $I_c=0.370\pm0.008$ A, $\gamma=12.5\pm0.3$, and $R=0.0184\pm0.0005$ Ω. The temperature dependence of R is consistent with Eq. (1): it enters the residual resistance region somewhere above 27 K (the values of R at $T=27$ and 4 K are equivalent to within their fitted uncertainties). γ increases monotonically as the temperature is lowered and also saturates below 27 K.

To compare the values for I_c obtained in this manner with those obtained by a more traditional definition, we also calculated I_c from the conventional definition using a 1 μV/cm criterion.[5] For $T=77$, 27, and 4.2 K, we obtained $I_c=0.0085$, 0.043, and 0.071 A, respectively. As expected from their respective definitions, I_c defined by the AH fits is larger than that defined by the voltage criterion.[1] A similar conclusion is reached by conducting a similar analysis of the data for sample 2.

The resistivity $\rho(T,H)=R(T,H)(A/l)$ was calculated from the AH fits and is presented in Fig. 3 for samples 1 and

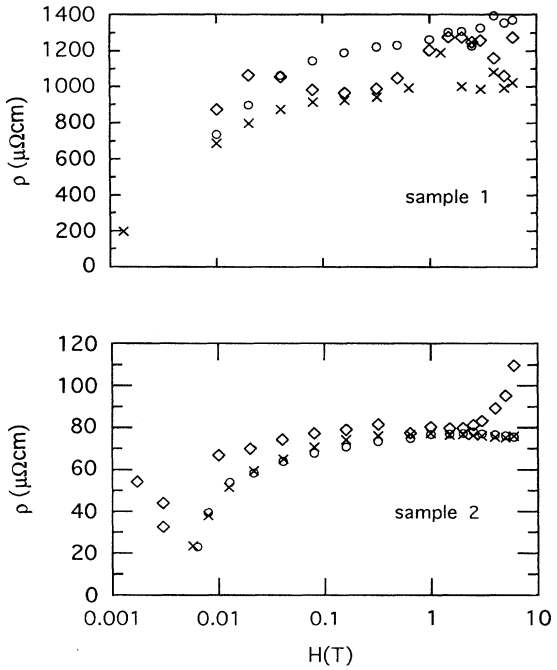

FIG. 3. The resistivity $\rho(T,H)$ calculated from the AH fits and is presented for samples 1 and 2 at temperatures of 77 K (◇), 27 K (×), and 4.2 K (○).

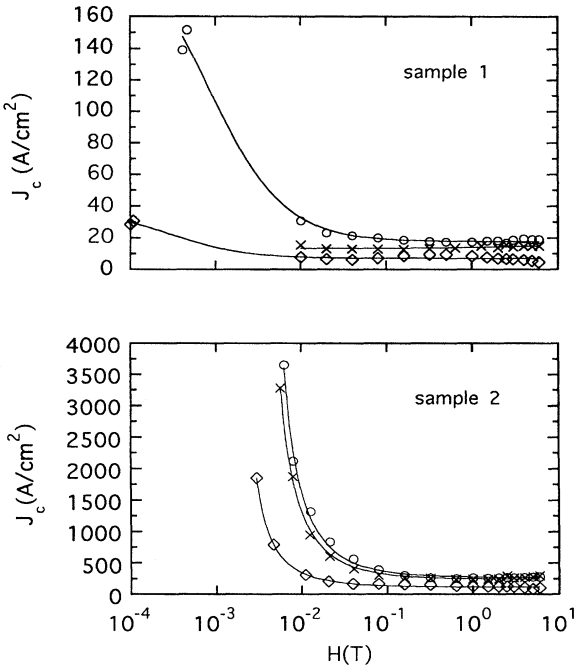

FIG. 4. The dependence $J_c(H,T)$ obtained from the AH fits for samples 1 and 2 at temperatures of 77 K (◇), 28 K (×), and 4.2 K (○).

2 at temperatures of 77, 27, and 4.2 K. The resistivity of sample 1 is roughly 10 times larger than that for sample 2, attesting to the greater granularity of the former. We observe that $\rho(T,H)$ for sample 2 lies below the extrapolated value of $\rho_N(T)$ which implies that $\rho(T,H)$ is a measure of the flux-flow resistivity rather than a direct measure of the normal-state resistivity. This interpretation has already been given to data similarly analyzed for thin films of granular Y-Ba-Cu-O.[6]

The magnetic-field dependence of the critical current density $J_c(H,T)$ obtained from the AH fits is shown for both samples in Fig. 4 where the magnetic field has been corrected for the field generated by the current. Small magnetic fields are seen to have a profound effect on J_c which is yet another manifestation of granularity.[7] Furthermore, the critical current density of sample 1 is a factor of 10 smaller than that for sample 2 in accordance with its greater granularity.[5] The data were fitted to an equation of the form

$$J_c(H,T)=\frac{A(1-t)^m}{(H+H_0)}+B, \tag{3}$$

where $t=T/T_c$, H_0 is the vector combination of the residual magnetic field in the superconducting solenoid (typically 0.005 T) and the magnetic field generated by the current, while A and B are fitted parameters. Equation (3) represents the function derived by Peterson and Ekin[7] to describe the effect of magnetic field on the critical current of an array of weakly-coupled, circular grains which behave as Josephson junctions. At low magnetic fields, where the current is carried by the Josephson junctions, J_c is very sensitive to magnetic field and thus varies inversely with H [the first term in Eq. (3)]. At higher magnetic fields, where the current follows a path through material with essentially bulk properties, the critical current is relatively insensitive to magnetic field [the second term in Eq. (3)]. Curves fitted through the data points

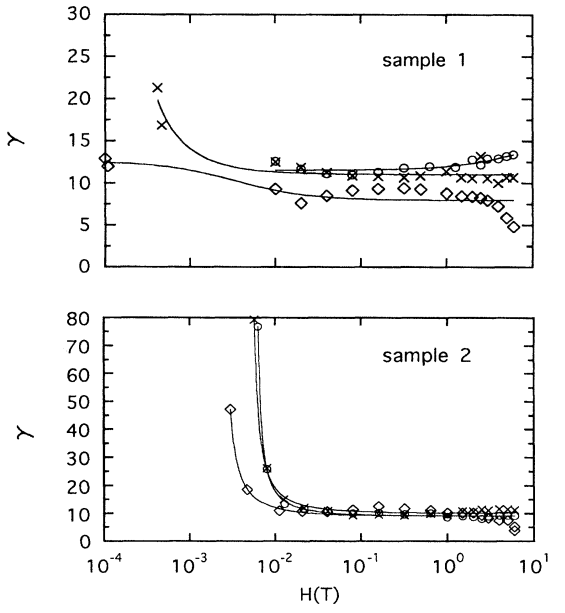

FIG. 5. The dependence $\gamma(H,T)$ obtained from the AH fits for samples 1 and 2 at temperatures of 77 K (◇), 27 K (×), and 4.2 K (○).

using Eq. (3) are shown in Fig. 4. Curves of $J_c(H,T)/(1-t)^{1.5}$ for each sample collapse to a common curve (not shown). This value for m is reasonable and in accordance with what is generally found for other superconductors. The uncertainty in m (± 0.5) is large, however, due to the fact that $J_c(H)$ was measured at only three temperatures. Values for B for sample 1 were 17.7, 14.1, and 7.0 A/cm^2 at $T=4.2$, 27, and 77 K, respectively. Values for B for sample 2 were 272, 244, and 118 A/cm^2 at $T=4.2$, 27, and 77 K, respectively. These values for B are so small compared to those obtained for other, less granular ceramic superconductors that we conclude that, even at comparatively high magnetic fields, the critical current density is limited by granularity. Thus in neither case then do these values for B represent the intrinsic properties of the material.

Also obtained from the AH fits is the parameter $\gamma=U(H,T)/k_BT$ which is plotted in Fig. 5 for both samples. The most notable features is that, above a relatively small magnetic field of 10^{-2} T, γ converges to a value between 9 and 12 which is independent of the sample and temperature. Analysis of granular Y-Ba-Cu-O films[6] and Bi-Sr-Ca-Cu-O (Ref. 1) by the same procedure yields similar behavior where γ attains values of 30 and 15, respectively. We interpret this behavior observed for Pb-Hg-Bi-Sr-Ca-Cu-O as an indication of an intrinsic property of the material.

In conclusion, we have fabricated samples of $Pb_{0.2}Hg_{0.8}Ba_2Ca_{1.75}Cu_3O_x$ and found that their measured transport properties were dominated by their granular nature which masked eduction of most of the intrinsic characteristics of the material. The exception is the pinning potential which we believe reflects an intrinsic property. These samples, being dominated by grain-boundary effects, provide an excellent opportunity to test the applicability of the AH model in a regime where it is especially well suited. Determination of the intrinsic critical current density must await, however, the time when such materials can be made with considerably fewer grain boundaries.

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[5] That is, a slope is drawn tangent to the I-V curve at $V=1$ μV. The intercept on the current axis defines the value of I_c.

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