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Thermopower of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ single crystals under uniaxial stress

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We have studied the effect of uniaxial stress σ_{11} along the a direction, up to 150 MPa, on the thermoelectric power $S(\sigma_{11},T)$ and electrical resistance $R(\sigma_{11},T)$ of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ single crystals from the transition temperature to room temperature. Both S and R increase monotonically with increasing σ_{11}. Above T_c, $S(\sigma_{11},T)$ is positive and linear with T, and $\Delta S(\sigma_{11},T)/\Delta T=-41$ nV/K^2 for all σ_{11}. The extrapolated $S(\sigma_{11},T=0)$ increases with σ_{11}, with $\Delta S(\sigma_{11},0)/\Delta\sigma_{11}=(1.5\pm0.4)\mu\text{V K}^{-1}\text{GPa}^{-1}$. The effect of σ_{11} on $S(\sigma_{11},0)$ is similar to the effect of a reduction in the hole density due to annealing under different oxygen atmospheres. $S(\sigma_{11},T)$ drops sharply at the superconducting transition temperature $T_c(\sigma_{11})$. We discuss our results in terms of several recently proposed models.

Since the discovery of high-temperature superconductors by Bednorz and Muller,[1] much experimental and theoretical work has been done to explain their properties. Many of these are still not well understood, e.g., the normal-state transport properties, such as the T dependence of the Hall constant[2,3] and the strongly sample-dependent Seebeck coefficient.[4,5] Measurements of transport properties, especially the thermoelectric power S, are an important step towards understanding the mechanisms of the new oxide superconductors. They give fruitful information about the carrier balance, the electron energy band structure, and the electron-excitation interactions. Studies of the T dependence of S in some high-T_c compounds under high magnetic fields,[6,7] as a function of cation doping,[8–13] the anisotropy of S,[2,5,14,15] the effect of annealing[16,17] and of pressure[18,19] have been reported recently. Only a few experiments related to S have been performed using single crystals.[2,5,14,16]. In this paper we present measurements of the temperature and stress dependence of the thermoelectric power and resistance of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ single-crystalline samples.

The $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ crystals were grown by annealing the quenched glass at 835 K as first specified by Matsubara *et al.*[20] Detailed sample growth and characterization reported elsewhere shows that the whiskerlike samples are single crystalline[21] with the a axis along the length of the whisker. It is possible that some $(Bi,Pb)_2Sr_2CaCu_2O_x$ is present in these crystals. It is important to note that these crystals were annealed in one atmosphere of O_2. Further studies of crystals annealed at other pressures of O_2 are ongoing. To study the effect of σ_{11} on S and R, $(Bi,Pb)Sr_2Ca_2Cu_3O_x$ samples with typical dimensions (2–4 mm)×(10–100 μm)×(1–10 μm) were mounted on a quartz puller as described by Overcash, Skove, and Stillwell.[22] The strain ϵ_{11} along the a axis was obtained from the measurement of the change in sample length. The uniaxial stress $\sigma_{11}=Y_{1111}\epsilon_{11}$ was calculated using the Young's modulus ($Y=25$ GPa) reported earlier.[23] Note that this value of Y is lower than that expected from other experiments[24,25] by about a factor of 3.

For the thermopower measurements, a temperature gradient $\Delta T=2$ K was applied across the sample. The gradient was measured using a AuFe (0.07 at. %)-Cu thermocouple. The average temperature of the sample was measured using a platinum resistance thermometer placed near the sample.

Two methods were used to get the thermoelectric power data. In the first method, the linearity of the thermal voltage ΔV vs the thermal gradient ΔT was checked by slowly increasing ΔT and monitoring ΔV. This process was repeated for selected values of σ_{11} and at regular intervals of T(1 K near T_c, and 10 K at high temperatures). The ΔV vs ΔT plots were linear for all values of σ_{11} and T explored. $S(\sigma_{11},T)$ was then estimated from the slope of the ΔV vs ΔT plots. In the second method, σ_{11} was set and a computer changed T by small increments. At each temperature the gradient heater was turned off and ΔV_0 was measured. This step corrected for any unintentional thermal gradient across the sample. ΔT was then set to 2 K and the thermal voltage ΔV measured. In both steps the system was allowed to reach equilibrium by waiting for about 20 s before measuring the thermal voltage. $S(\sigma_{11},T)$ for a specific σ_{11} and T was then estimated for each set of data. The second method has the advantage of providing high-density computer controlled data acquisition. Its drawback is the difficulty of maintaining σ_{11} constant while T is changing. The difference in the thermopower data obtained by the two methods is about 5%. At each temperature, we subtracted the Seebeck coefficient of copper to obtain the absolute $S(T)$ for the sample. Thus we report the results of method 2, but checked these with method 1.

Figure 1 shows typical a-direction R vs T and S vs T curves at $\sigma_{11}=0$. The R and S measurements were performed from room temperature to 77 K. The $R(T)$ behavior is similar to the $YBa_2Cu_3O_7$ system,[26] while $S(T)$ is quite different.[27–29]. $S(T)$ is positive and has a maximum near 100 K. dS/dT is constant at -41 nV/K^2 from 300 K to about 105 K. S reaches its maximum at 100 K before dropping to zero near 86 K. For some samples, there was a residual nonzero thermopower below the transition temperature of about 1 μV/K. $S(\sigma_{11},T)$

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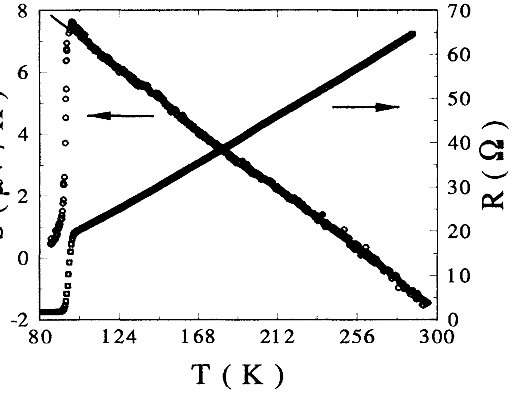

FIG. 1. A typical measurement of the thermopower S and resistance R as a function of temperature T.

crosses zero above room temperature. Similar linear S vs T results were obtained using vacuum annealed BiSCCO samples. Annealing in vacuum lowers T_c and the zero crossing temperature with almost no effect on the slope. Stress-effect measurements on samples annealed in different O_2 atmospheres are in progress. All the above linear results are in qualitative agreement with published results at zero strain.

The σ_{11} dependences of the S vs T and R vs T curves around T_c are shown in Fig. 2. The R vs T results were taken during a cooling run. We verified that the results were reversible during the subsequent warming run, showing that the sample was in good thermal contact with the temperature sensor. Figure 2(b) shows the S vs T plot acquired during a heating run. Both Figs. 2(a) and 2(b) show that T_c is suppressed by σ_{11} without any broadening of the transition and the results are reversible when stress is released. The value of $\Delta T_c/\Delta\sigma_{11} = -(6.8\pm1.5)$ K/GPa estimated from the thermopower data agrees with that estimated from the piezoresistivity measurements.[30]

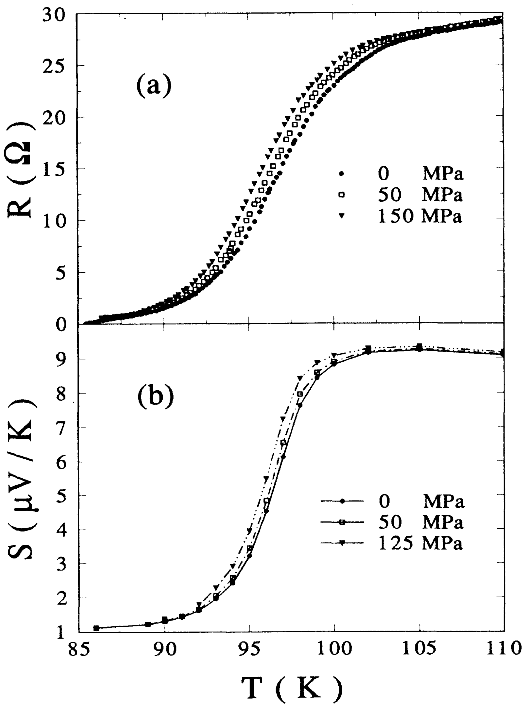

FIG. 2. Resistance and thermopower as a function of T with stress as a parameter.

Figure 3 shows the ratio $[S(\sigma_{11},T)/S(0,T)]$ vs σ_{11} at different temperatures near T_c. S increases with σ_{11}. The effect is more pronounced for T within the transition. This is attributed to the σ_{11} induced decrease in T_c shown in Fig. 2(b). In order to more closely display the influence of σ_{11} on S, we present in Fig. 4 a plot of $\Delta S(\sigma_{11},T)$ vs T. $\Delta S(\sigma_{11},T)$ is defined as

$$\Delta S(\sigma_{11},T) = S(\sigma_{11},T) - S(0,T) \ . \tag{1}$$

For a given σ_{11}, and $T > T_c$, $\Delta S(\sigma_{11},T)$ is independent of T except near T_c. $\Delta S(\sigma_{11},T)$ increases with σ_{11} with a rate

$$\Delta S(\sigma_{11},T)/\Delta\sigma_{11} = (1.5\pm0.4)\ \mu\text{V}\,\text{K}^{-1}\,\text{GPa}^{-1} \ .$$

The peak near T_c is due to the σ_{11}-induced suppression of T_c. In summary, above T_c $S(\sigma_{11},T)$ is linear with T for all σ_{11} $[S(\sigma,T) = A(\sigma) + B(\sigma)T]$. The zero intercept $A = S(\sigma_{11},0)$ and the slope B change with the stress by $\Delta A/\Delta\sigma = 0.66$ μV/(K GPa) and $\Delta B/\Delta\sigma = 89$ nV/(K^2 GPa).

The observed effect of uniaxial stress on S is similar to the effect of reducing the hole concentration in the Cu-O planes by chemical doping.[8,10,12,13] The effect of hydrostatic pressure on T_c has been related to pressure-induced changes in the number of mobile holes. Murayama *et al.*[31] have shown that the Hall constant decreases with pressure suggesting that pressure increases the number of holes n_h. They have thus attributed the pressure-induced enhancement of T_c to the pressure-induced increase in n_h. The intuitive argument is that under hydrostatic pressure the apical oxygen comes closer to the Cu-O

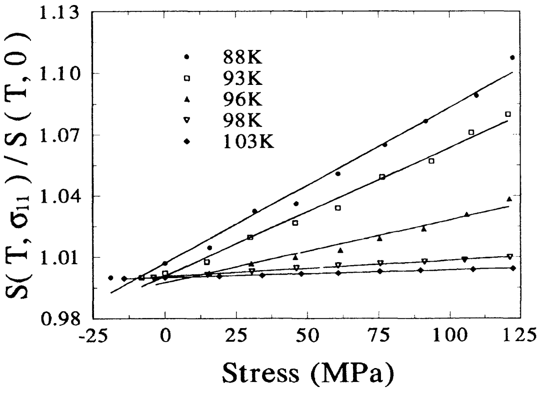

FIG. 3. The relative change in the thermopower as a function of stress with temperature as a parameter.

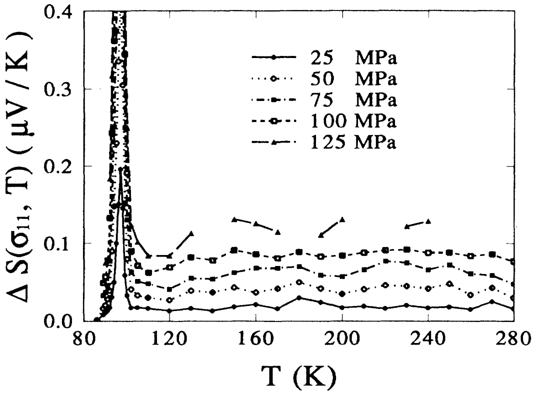

FIG. 4. The difference between the zero stress thermopower and the thermopower at various stresses as a function of temperature.

planes leading to an increase in n_h. In a similarly simplified picture, one would predict that uniaxial stress along the a axis would bring the apical oxygen closer to the plane as a result of Poisson contraction along the b and c axes and that pressure and a-axis uniaxial stress would change n_h and T_c in the same direction. This is contrary to our experimental results, which show that T_c decreases with stress. However, there is potentially another mechanism involved when uniaxial stress is applied. Stress along the a axis could result in a lowering of n_h because of weaker Cu-O bonding. As a result of the competition between these effects, n_h (and therefore T_c) would decrease, thus also explaining the increase in resistivity. Assuming that all the σ-induced change in T_c is due to changes in n_h, we have estimated

$$\Delta n_h/\Delta\sigma_{11}=0.29\times10^{27}\ (\mathrm{m})^{-3}(\mathrm{GPa})^{-1}$$

from the value $dn_h/dT_c=4.3\times10^{25}\ \mathrm{K}^{-1}(\mathrm{m})^{-3}$ (Ref. 31); this corresponds to $\Delta n_h/n_h=1.6\%$ at a strain of 0.5%, assuming $n_h=2.2\times10^{27}\ (\mathrm{m})^{-3}$, or $\Delta n_h/n_h\Delta\epsilon=3.2$. Assuming a single band model ($\rho^{-1}=ne\mu$) and that only n_h is affected by σ_{11} this implies $\Delta\rho/\rho\Delta\epsilon\approx3.2$ which is consistent with the previous piezoresistance measurements which give $\Delta\rho/\rho\Delta\epsilon\approx3$ near T_c and ≈1.6 at room temperature.[30] The measurements near T_c may be affected by changes in the fluctuation conductivity.

As mentioned above, the thermoelectric power increases with decreasing temperature. One explanation has been given by Zhang *et al.*[32] (model one). They suggested that there are two kinds of carriers: localized carriers, giving the constant part of the thermopower, and mobile carriers, contributing to the diffusion part of the thermopower which is proportional to the temperature. Thus

$$S=S_1+S_2=A+BT\ . \tag{2}$$

This is based on the assumption that the contribution of phonon drag should be rather small above T_c. The solid line in Fig. 1 is the least-squares fit to Eq. (2), where $A=13.48\mu\mathrm{V/K}$, and $B=-41\ \mathrm{nV/K^2}$. Based on this model we estimate separately the effect of σ_{11} on the mobile holes and the localized carriers. From the changes in B and using the approximation $S_2\propto1/n_h(\partial n_h/\partial E)$ (Ref. 36) we estimate a change in the mobile carriers $\Delta n_h/n_h\Delta\epsilon=0.6$ which is of the same order of the magnitude as the values estimated from $T_c(\sigma_{11})$ and $\rho(\sigma_{11})$ measurements.

Several other models have been suggested to explain the linear thermopower and the effect of chemical doping on S. Below we give an estimate of the effect of σ_{11} on the pertinent parameters of two such models. Forro, Lukatela, and Keszei[16] (model two) suggested a two-band model: a broadband and a localized band with a peak at E_0 and a bandwidth Γ. Such a peak in the density of states could be due to a van Hove singularity. According to this model, S would have two components as follows:

$$S=AT/(B^2+T^2)+\alpha T\ , \tag{3}$$

where the linear term αT is attributed to the normal carrier contribution. A and B are related to E_0 and Γ through the relations[33]

$$A=2(E_0-E_F)/|e|\ ,\quad B^2=-(E_0-E_F)+\Gamma^2/(\pi k_B)^2$$

where E_F is the Fermi energy, e the charge of the electron, and k_B is Boltzmann's constant. The effect of Stress on the three parameters of this model from a nonlinear squares fit to our data is given by

$$\frac{d\alpha}{d\sigma}=91\mathrm{nV}/(\mathrm{K^2GPa})\ ,\quad \frac{d|E_0-E_F|}{d\sigma}=1.5\mathrm{K/GPa}\ ,$$

and $d\Gamma/d\sigma=13$ K/GPa. Here the units of E and Γ have been divided by the Boltzmann constant. The relative changes of $\Delta E/(E_0\Delta\epsilon)$ and $\Delta\Gamma/(\Gamma_0\Delta\epsilon)$ are nearly the same: 0.14 and 0.11, respectively. The change $d\alpha/d\sigma$ is comparable to $\partial B/\partial\sigma$ estimated from model one, 89 nV/(K^{2}GPa), as expected.

Another model (model three) is based on the assumption that high-T_c superconductors have strongly correlated electrons. According to Chaikin and Beni,[34]

$$S_1=-(k_B/e)\ln[2(1-\eta)/\eta] \tag{4}$$

for the constant part of the thermopower [A in Eq. (2)], which represents the contributions of relatively localized carriers. Here η is the hole density per Cu site. Fitting our data to Eq. (4),[35] we find 0.30 holes per site at zero strain. The stress-induced change in hole density can be estimated from successive fits of $S_1(\sigma_{11},T)$ and give: $\Delta\eta/\Delta\sigma_{11}\approx1.6\times10^{-3}$ (1/GPa), or $\Delta n_h/\Delta\sigma_{11}=0.7\times10^{25}\ (\mathrm{m})^{-3}(\mathrm{GPa})^{-1}$.

The values of $\Delta n_h/(n_h\Delta\epsilon)$ obtained using measurements of $T_c(\sigma)$ and $\rho(\sigma)$ and models for $S(\sigma)$ are consistent. From $\Delta T_c/\Delta\epsilon$, we get $\Delta n_h/(n_h\Delta\epsilon)=3$. The room-temperature piezoresistance measurement $\Delta R/(R\Delta\epsilon)$, leads to $\Delta n_h/(n_h\Delta\epsilon)\approx1.6$.[37] The linear fit of the thermopower data ($S=A+BT$) implies

$$\frac{\Delta B}{(B\Delta\epsilon)}=-0.6\approx-\frac{\Delta n_h}{(n_h\Delta\epsilon)}\ .$$

Using Forro's model yields $\Delta n_h/(n_h \Delta\epsilon) \approx 1.7$. The fact that three different experimental determinations, $T_c(\sigma)$, $\rho(\sigma)$, and $S(\sigma)$, give roughly the same value for $\Delta n_h/(n_h \Delta\epsilon)$ suggests that uniaxial stress, just as hydrostatic pressure, may change the concentration of mobile holes via a change in Cu-O bond length, and direction. Our measurements, however, fail to distinguish between the various models for the thermopower.

In summary, we have measured the temperature and stress dependence of the thermoelectric power and resistance. Both the thermoelectric power and the electrical resistivity increase monotonically with increasing stress. $\Delta T_c/\Delta\sigma_{11}$ determined from either the resistivity or the thermopower is negative. The effect of stress on the thermopower in the normal state is similar to the defect of oxygen depletion due to annealing or to cation substitution.

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