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Electron-phonon contribution to thermopower in Si-doped superconducting Bi compounds

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Resistivity ρ and thermoelectric power S as a function of temperature on samples of nominal composition $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_3(Cu_{1-x}Si_x)_4O_{12-\delta}$, for different x values at small concentrations, have been carried out. We find a correlation between ρ and an enhancement in S observed above T_c. We analyze the results in terms of conventional theoretical models that include vertex and other electron-phonon $(e\text{-}p)$ corrections to the scattering due to impurities. It is argued that in the copper oxides the $e\text{-}p$ effects, usually negligible in normal metals at temperatures small compared to the Debye temperature, might be significant near and above T_c. A small contribution due to the phonon drag effect is also discussed. It is suggested that the trends of our results adjust to the predictions of those conventional models. [S0163-1829(97)06830-6]

After a decade of intense activity, it has been clearly established that many properties of high-T_c superconductors (HTS's), in the normal (N) metallic state as well as in the superconducting (S) state, are anomalous compared to those of simple or conventional metals (SM's). Although thermoelectric power (TEP) is usually taken as representative of those anomalous properties, it has to be realized that TEP behavior is not simple even in SM's.[1–3] A subject which has been under focus for a long time is the contribution of the electron-phonon (e-p) interaction to the transport coefficients of SM's and alloys.[4,5] Much of the discussion has been centered on whether the e-p mass enhancement affects TEP.[6] Contrary to an early conclusion in the sense that this effect is unobservable,[5] later work has established that at low and intermediate T ($T \sim \Theta_D/2$, where Θ_D is the Debye temperature), there is a renormalization in the TEP.[1,6] Thereafter, the current opinion, supported by experiments,[6–9] has been that the renormalization factors do not affect any of the other electron transport coefficients but TEP. The effect of the e-p interaction on electron transport coefficients in SM's is still an open question; this is emphasized in a recent work on the renormalization of TEP (Ref. 3) and on the Drude conductivity.[10] Here we concentrate on TEP in Si-doped BSCCO bulk samples.

There are no reasons to expect that TEP behavior in more complex materials, like copper oxides, is simpler than in SM's and alloys. Nevertheless, there is a universal trend [11] present in most of the HTS materials that can be exploited to interpret the scattering mechanisms. In the N state, the T dependence of the Seebeck coefficient S shows a broad maximum above T_c. At higher temperature it is more often linear in T but the $T=0$ extrapolated value is nonzero. These features, not found in SM's, are rather common in alloys and transition metals.[12] It is usually assumed that in the S state S is zero. As has been pointed out by Ginzburg,[13] in the S state the TEP does not vanish and its value, although small, can be used to discern between s and d waves. This small effect has not been reported in current TEP measurements, however, and will not be considered here. Instead, we examine in this work any possible contribution from electron scattering by phonons and impurities in the intermediate T regime ($T_c < T < \Theta_D$).

Our previous works on TEP have been restricted to single-composition Bi2223 and Y123 thin films in the range $1.5T_c \leq T \leq 300$ K,[14] where the usual diffusion contribution fits the results well. Here we study the effect of substituting copper atoms by silicon to obtain the nominal composition $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_3(Cu_{1-x}Si_x)_4O_{12-\delta}$ with $0<x<0.15$. The samples were prepared by the solid-state reaction method using high-purity powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, and metallic Si. The materials were ground thoroughly, preheated at 800 °C for 20 h, and then ground and pressed in the form of pellets at a pressure of ~ 7 torr/cm ^{2}. Thereafter the pellets were sintered at 850 °C ±5 °C for 140 h in air and cooled down with the furnace turned off. X-ray-diffraction patterns (obtained with a Philips powder diffractometer model PW 1700) for samples doped up to $x \leq 0.03$ do not show appreciable differences with undoped samples ($x=0$), where the high-T_c phase (2223) is predominant. Larger Si concentrations ($x>0.03$), however, yield multiphase samples (2212, 2223) and SiO_2 impurities. No evidence was observed of the formation of the 2234 phase ($T_c \sim 95$ K) neither by XRD nor resistivity and magnetic susceptibility measurements.

Resistivity and magnetic susceptibility measurements showed, mainly, the presence of the high-T_c phase (2223) with a $T_c \sim 110$ K for Si concentration up to $x \sim 0.03$. Larger Si concentrations decreased the diamagnetic signal, indicating a reduction of the high-T_c superconducting volume; by $x>0.10$, the zero-resistance phenomenon disappeared above the boiling point of liquid N_2. An enhancement of j_c (140 A/cm^2) for about twice the j_c value of undoped samples was observed for samples with $x \sim 0.03$, which could be a consequence of pinning of magnetic flux lines or could be due to an increase of the homogeneity of the samples. Larger Si doping levels ($x>0.03$) inhibit the formation of the high-T_c phase and decrease j_c.[15]

Rectangular specimens of ~10 mm×2 mm×1 mm size were cut out from the prepared pellets for electrical resistance and TEP measurements. The four-probe technique and differential method were used for electrical resistance and TEP measurements, respectively. A temperature gradient $\triangle T \sim$ 0.1–0.2 K was produced and the temperature differ-

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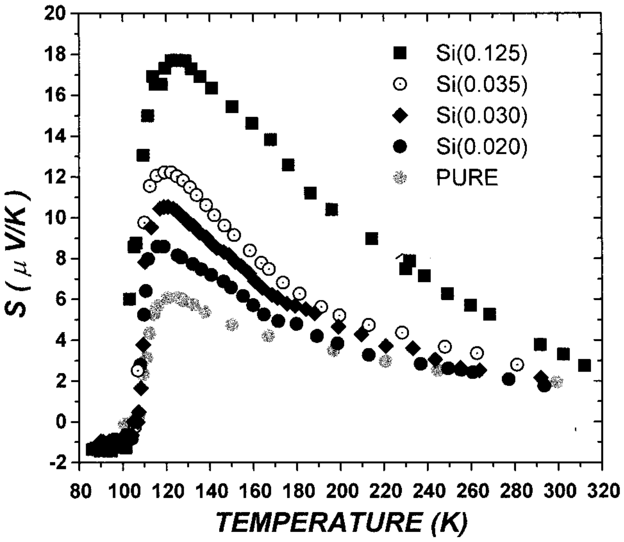

FIG. 1. Thermoelectric power data as a function of temperature for several Si concentrations.

ence ($\triangle T$) across the samples was monitored with calibrated copper-Constantan thermocouples. Pt-100 sensors were used to know and control the bare temperature for each measured point. All voltages were measured using a Keithley nanovoltmeter model 182 with a resolution of 0.05 μV. The estimated absolute accuracy of the TEP data is $\sim 5\%$.

The observed trends and the order of magnitude of the TEP reported in this work (cf. Figs. 1 and 2) are similar to the results of other authors for related compounds.[11,16–19] There are, however, some peculiarities that we discuss at the end of the paper. In what follows, we briefly examine our results and compare them with previous work on TEP.

The TEP is positive and decreases with T, except just below T_c for doped samples. As in all previous reports on the TEP of different copper oxides, there is a hump near and above T_c. Besides the hump above T_c and the nonzero extrapolated value of the Seebeck coefficient as $T \rightarrow 0$, there is a shift of the peak toward higher T and an increase of S with x (Fig. 1) in agreement with previous works on Bi-based bulk samples.[11,18,19] The latter fact has been interpreted as an increase of the band filling with electrons (remember that Si replaces Cu atoms).[19] The former feature will be discussed below. Resistivity measurements by varying x show a correlation between ρ and the S peak (cf. Table I). Contrary to earlier observations, we do not find a linear behavior in the region from T_c to about 250 K. Our results in this region are more similar to those recently reported by Gasumyants *et al.*[19] If a large value of the e-p coupling parameter λ is accepted, one can explain the hump and the nonlinear behavior in the intermediate-T regime [17,18] using the e-p mass enhancement proposed by Opsal *et al.*[6] An alternative explanation has been elaborated by Trodahl in terms of the phonon-drag contribution S_p.[20] He argues that this contribution, usually negligible, provides a significant correction to S in the range $T_c < T <$ 200 K. Interestingly enough, the TEP in infinite-layer-structure thin films with $T_c < 25$ K well above Θ_D follows the same pattern of the HTS.[21] The main conclusion in the latter work is that there is a correlation between T_c and the *phonon-drag voltage* S_pT consistent with strong-coupling theory.

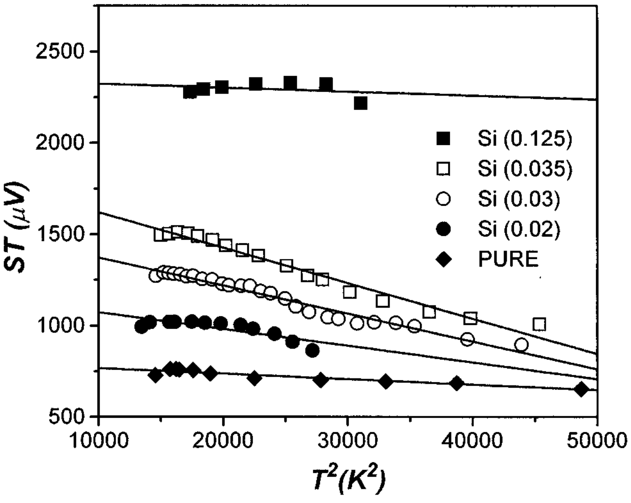

FIG. 2. Plot of ST vs T^2 as a function of the Si concentration x.

Next we examine a possible conventional explanation to the hump above T_c using e-p calculations to lowest order. By no means does our interpretation discard other alternative proposals.

It has been claimed by some authors[22] that, in a Fermi liquid (FL) model, even for a fully interacting e-p system,[3] the Mott formula is valid at any T except by a very small correction term that is negligible:

$$S = S_M + \delta S. \tag{1}$$

This fact, already anticipated by previous workers,[23] has been used as an argument against a conventional behavior in the cuprates.[22] Next we argue that, if a bad metal is approximated by the FL model, the e-p mass enhancement yields a significant correction to the Mott formula.

It is assumed that a generalization of the Mott expression, in the sense of Vilenkin and Taylor[23] and of Jonson and Mahan,[24] is valid in a metal with resistivities as high as those in the cuprates in the N state. We write

$$S_M = \alpha T. \tag{2}$$

For simplicity, any dependence in T of the coefficient in Eq. (2) is included in δS.[23–25]

In a FL model to lowest order, for $T < \Theta_D$, the contribution to δS arising from the full e-p term is quadratic in T and linear in ρ.[3] We call it $\delta S'$:

$$\delta S' / S_M = b \rho T, \tag{3}$$

where $b \sim 10^4/(\Omega\ \text{cm K})$. Notice that ρ in the cuprates is three or more orders of magnitude greater than in SM's. We speculate that the above expression (or its equivalent in a less restricted model) should be valid for HTS materials near and below T_c in the absence of the electron condensation, and that the ρ linear dependence holds above T_c. As a result, it is plausible to expect $\delta S'/S_M \sim 1$ in a certain range of T. For $T > \Theta_D$, the leading term decreases as $1/T^2$:[3]

$$\delta S'/S_M \propto (\Theta_D/T)^2; \tag{4}$$

i.e., there must be a maximum in $\delta S'$ for a certain $T_{\max}$. Notice that in HTS's, Θ_D is several hundreds kelvin, 3 or more times as much as Θ_D in SM's (aluminum is an exception, but S in Al has a large peak around 80 K). Due to the high value of ρ and Θ_D in the cuprates, it is reasonable to expect that there is an intermediate range of T below the Debye temperature ($\sim \Theta_D/2$) and above T_c where $\delta S'$ is significant. We emphasize that the whole δS in Eq. (1) does not include only the e-p mass enhancement, as will be discussed below.

Figure 2 is a plot of ST vs T^2 in a restricted range of T ($150 < T < 250$ K). After several polynomial fittings to our experimental results, we have concluded that, in this range, TEP decomposes essentially into two terms, $S = \alpha T + \beta/T$; i.e., higher order terms are negligible. This relationship has been noticed in previous works.[14,20,21] Notice that TEP here does not follow the simple form above in an ample region of T. The first term αT is the usual diffusion term given in Eq. (2). The second one has sometimes been identified with the phonon drag,[20,21] but obviously it should include more than one contribution. Although there is no consensus regarding the interpretation of the main contribution to δS, from Fig. 2 we conclude that, in the range under consideration, the two terms above provide an accurate description of the physics involved. The above analysis favors e-p as an important contribution without discarding other possible terms.

We focus now on our experimental results. They are summarized in Table I for the different samples, i.e., for different Si doping levels x. The second and third columns contain the value of the resistivity just at the onset of superconductivity, ρ_o, and at 200 K, ρ_{200}. At a low concentration level it increases more or less linearly as a function of x. Going back to Eq. (3) and assuming that the linear dependence in ρ of the e-p contribution remains above T_c, one finds out that the universally observed increase of S with ρ is to be expected.

TABLE I. Resistivity just above T_c, ρ_o, and at 200 K, ρ_{200}, intercept β, and slope α in Fig. 2, for different x values.

Sample	ρ_o (mΩ cm)	ρ_{200} (mΩ cm)	β (μV)	α (μV K^{-2})
Pure	1.40	2.35	965.4	-0.00286
0.02	1.43	2.46	1006.1	-0.00571
0.03	1.68	2.59	1265.4	-0.00822
0.035	2.22	3.12	1314.6	-0.00649
0.120	6.96	8.30	2828.8	0.02000

The fourth column contains the value of the intercept β in Fig. 2. The slope α is presented in the fifth column. The evolution of these values with x is very meaningful: (1) Since by increasing x the size of the S peak (proportional to β) increases, one has reasons to believe that the weight of the e-p contribution is increasing as well.[26] (2) A greater slope is interpreted as a more important contribution from diffusion as impurities are added to the sample, which seems reasonable.

In conclusion, we report TEP measurements on nominal Si-doped $(\mathrm{Bi}_{0.8}\mathrm{Pb}_{0.2})_2\mathrm{Sr}_2\mathrm{Ca}_3\mathrm{Cu}_4\mathrm{O}_{12-\delta}$. The universal trends reported in the literature, i.e., a large peak that increases with doping and a decrease of S with T in a set of lines S vs T, are also found in this work. Contrary to previous reports,[11,18,20] the lines are not parallel or straight lines, a feature that has already been noticed.[19] We observe as well a small shift of the peak to higher T when adding Si. We provide an explanation of our results in terms of previous FL models that include high-order correction terms in the e-p interaction.

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[25] The simple expression, Eq. (2), for S_M is valid only in restricted regions of T. A lot of work has been devoted to analyze many contributions different to the e-p term discussed here. See, e.g., Ref. 2 and references therein.

[26] As stated at the beginning of the paper, the critical current increases with x when adding Si up to $x \sim 0.03$; it happens as well when doping with Ag. These features will be analyzed in a forthcoming paper.