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Thermopower of zinc-doped Y-Ba-Cu-O

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Absolute thermopower measurements on well oxygen annealed $YBa_2Cu_{3-x}Zn_xO_{7-y}$ ($x=0.025$, 0.05, 0.075, 0.1, 0.15, 0.2, 0.3, and 0.4) were made in the temperature range 250 K to the superconducting transition temperature, T_c (zero). X-ray analysis showed the specimens to be single phase. The T_c decreased drastically with increasing zinc concentration. The thermopower was found to be positive and an enhancement relative to the linear electron-diffusion contribution was observed over a range of temperatures from 125 K down to the onset of the superconducting transition temperature, T_c (onset). The enhancement showed a steep exponential drop as the temperature increases from T_c (onset). There exists unambiguous evidence that phonon drag is not responsible for the peak. The enhancement of thermopower in all these specimens varies more steeply with temperature than what one would expect from electron-phonon interaction. Hence, the cause of the enhancement must be other than the electron-phonon interaction.

Several investigators[1-10] have shown that doping yttrium barium copper oxide with zinc drastically reduces T_c. When the concentration of zinc, x, in $YBa_2Cu_{3-x}Zn_xO_{7-y}$ reaches a value 0.3 or above, Jee *et al.*[5] found a dramatic increase in resistivity, a change over from metallic to semiconducting behavior, and a loss of superconductivity. In praseodymium-doped samples, Goncalves *et al.*[11] found that the decrease in T_c on increasing Pr concentration is accompanied by a rapid increase in the thermopower, and this has been attributed to progressive band filling and a decrease in the number of holes per copper atom. Thus, a study of thermopower in zinc-doped samples is of interest, as it will indicate what happens to the hole concentration on doping.

Sintered pellets of $YBa_2Cu_3O_{7-y}$ and $GdBa_2Cu_3O_{7-y}$, when well annealed in oxygen, show a peak in the thermopower just above T_c.[12-16] Recent measurements of the thermopower of single crystals of $YBa_2Cu_3O_{7-y}$ (Refs. 17 and 18) have shown the following:

(i) the sign of the thermopower both parallel and perpendicular to the *a-b* plane is positive;

(ii) the thermopower along the *a-b* plane shows a peak just above T_c;

(iii) the thermopower perpendicular to the *a-b* plane shows a linear dependence on temperature.

Thus, the thermopower of a well oxygen annealed polycrystalline sample reflects the behavior of the thermopower in the *a-b* plane of the single crystal.

Uher and Kaiser[15] suggested that the peak in the thermopower is probably caused by phonon drag. Srinivasan et al.[16] showed that the peak in the thermopower was not suppressed by replacing yttrium partially with erbium and holmium. If the peak is due to phonon drag, such a substitution would have suppressed the peak. They also showed that in both the undoped and the doped compounds the thermopower in the temperature range T_c to 250 K could be well represented by the equation

$$S=aT[1+b\exp(-T/T_0)] . \qquad (1)$$

The enhancement of thermopower over the linear electron diffusion contribution was shown to be too rapid to be accounted for on the basis of Kaiser's[19] expression for enhancement due to electron phonon interaction. Recently, Kaiser[20] performed a calculation of the enhancement due to electron-phonon interaction in the high-T_c superconductors using the Eliashberg function $\propto^2 F(E)$, calculated by Weber.[21] Kaiser has suggested that if T_c could be lowered by increasing the disorder, it would be possible to separate the the electron-phonon enhancement effect from the phonon drag effect and to verify if the former can be seen at low temperatures. This is the aim of the present work.

Sample of $YBa_2Cu_{3-x}Zn_xO_{7-y}$ were prepared with $x=0.025$, 0.05, 0.075, 0.1, 0.15, 0.2, 0.3, and 0.4. The method of preparation and details of oxygen annealing are described by Krishnan *et al.*[22] The samples were x-ray analyzed. All the peaks in the x-ray diffractograms could be indexed on a single orthorhombic structure. No impurity peaks were detected. Iodimetry gave the oxygen stoichiometry of all the compounds to be 6.85±0.05. The variation of T_c (determined when resistance of the sample dropped to zero)[22] with concentration x agreed well with the data of Jee *et al.*[5] The orthorhombic strain defined as $(b-a)/(b+a)$, where b and a are the lattice parameters at room temperature, again agreed with the data of Jee *et al.*,[5] and did not change with concentration. This indicates that as the concentration x is changed, there is no change in oxygen vacancy ordering.

The thermopower of the samples was determined from 250 K downwards using a setup described by Rao *et al.*[23] Figure 1 shows a plot of the thermopower at 200 K as a function of concentration. In the same figure, the data on the variation of ρ and $d\rho/dT$ with concentration x, reported by Jee *et al.*,[5] is shown as an inset. [Jee *et al.*[5] give the zinc concentration per copper atom, i.e., their formula for the compound is $YBa_2(Cu_{1-z}Zn_z)_3O_{7-y}$ and they have plotted ρ and $d\rho/dT$ versus z. We state the concentration of zinc per formula unit, i.e., our formula for the compound is $YBa_2Cu_{3-x}Zn_xO_{7-y}$. Therefore $x=3z$. Since we have plotted our results versus x, we had to replot the data of Jee *et al.* suitably.] The similarity of the two sets of data is striking at a first glance. The thermopower is nearly independent of concentration up to $x=0.2$. From $x=0.3$ the thermopower increases rapidly. Jee *et al.*[5] explained their resistivity behavior on the assumption that more and more holes get localized above $x=0.3$. The rise in thermopower around the same value of x points to the decrease in the number of mobile holes above $x=0.3$.

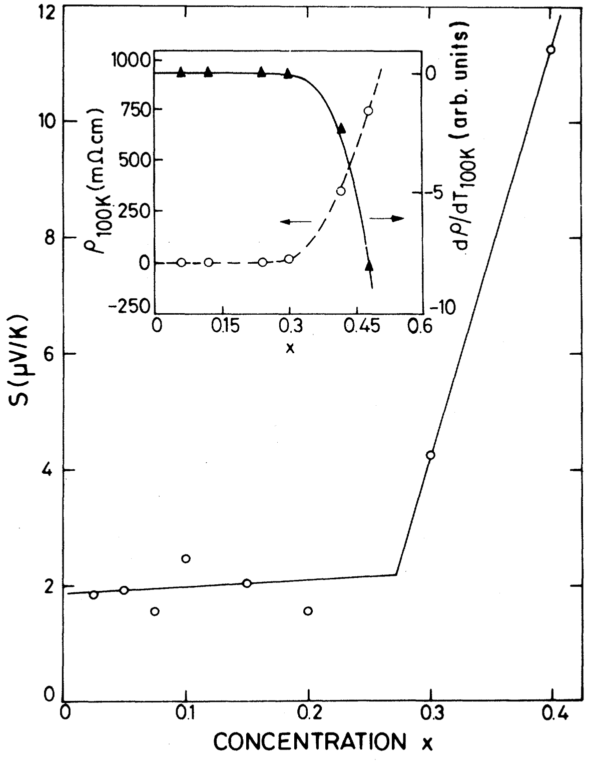

FIG. 1. Variation of thermopower in $YBa_2Cu_{3-x}Zn_xO_{7-y}$ at 200 K as a function of zinc concentration x. [Inset from Jee *et al.* (Ref. 5)].

A decrease in T_c with increasing zinc doping, according to Zhenhui *et al.*,[7] can arise either because

(i) the number of holes per copper atom increases;

(ii) the orthorhombicity of the lattice comes down due to oxygen disorder;

or

(iii) pair breaking effects arise from p or higher wave pairing.

From our results as well as the results of other workers the first two mechanisms do not appear to be operative. Neutron-diffraction studies by Mehbod *et al.*,[10] Xiao *et al.*,[24] and Mazumdar *et al.*[25] indicate that zinc goes predominantly into Cu(2) sites in the plane. The site disorder produced by such a substitution can result in additional scattering of the holes reducing their mean free path. In the case of the Chevrel phase compounds, $Cu_{1.8}Mo_6S_{8-y}Se_y$ and $Cu_{1.8}Mo_6S_{8-y}Te_y$, substitution of Se and Te at the sulphur site leads to a decrease in T_c.[26] Jee *et al.*[5] have observed an increase in resistivity with an increase in zinc concentration, which is clearly evident in Fig. 2 of their paper. The scale in the inset in Fig. 1 of this paper is too rough to show this behavior. The increase in resistivity clearly arises due to additional scattering of the charge carriers caused by the site disorder resulting from the substitution of zinc. This may account for the reduction in T_c of these compounds.

Figure 2 shows the variation of thermopower for all the zinc compounds studied by us. All compounds with $x \leq 0.2$ show a pronounced peak just above T_c. From a measurement of the specific heat of zinc-doped compounds, up to a concentration of $x=0.45$, Jee *et al.*[5] found a Debye temperature almost independent of concentration. This shows that zinc doping does not bring about any major changes in the phonon spectrum. In general, the peak due to phonon drag occurs around $\Theta/10-\Theta/5$, where Θ is the Debye temperature.[27] Under these circumstances one would have expected the peak in the thermopower to occur at about the same temperature in all the zinc-doped compounds if phonon drag were to be the cause of the peak. Also with increasing zinc substitution one would have expected the peak to be suppressed. The observed results are contradictory to both these expectations, providing unambiguous evidence that phonon drag is not responsible for the peak.

In all the samples with $x \leq 0.2$, the thermopower from T_c to 250 K can be well represented by Eq. (1). The continuous lines in Fig. 2 represent the fit to the data given by this equation. Table I lists the parameters a, b, and T_0 for the different zinc-doped samples as well as for the undoped yttrium barium copper oxide.

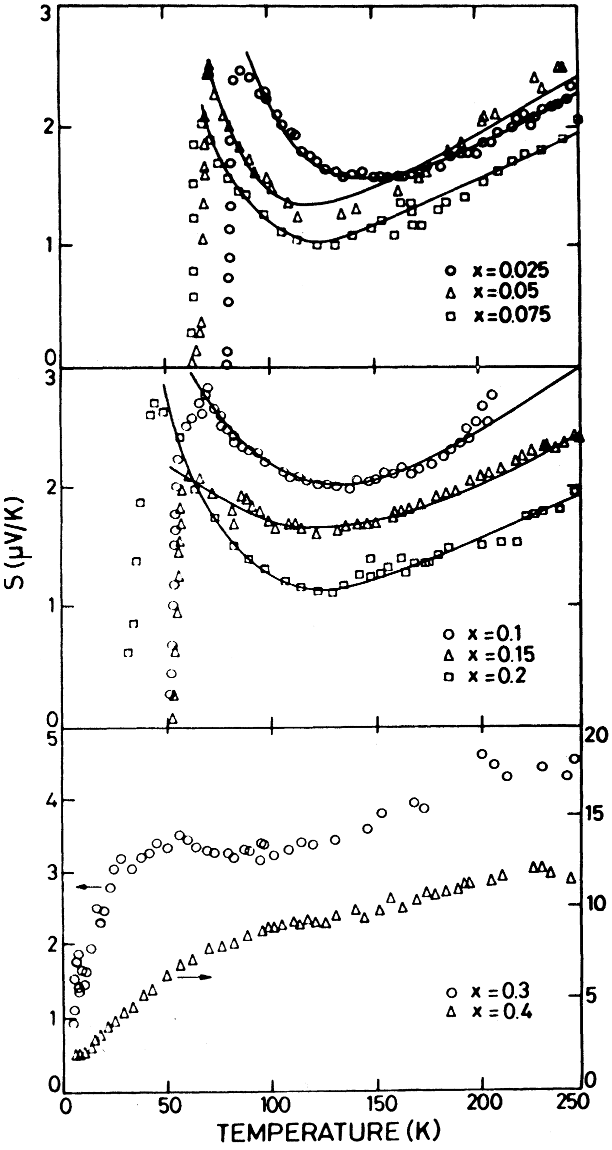

FIG. 2. Variation of thermopower as a function of temperature for $YBa_2Cu_{3-x}Zn_xO_{7-y}$. [The continuous line gives the fit to Eq. (1)].

TABLE I. Parameters *a*, *b*, and T_0 in the fit to thermopower of Eq. (1) for $YBa_2Cu_{3-x}Zn_xO_{7-y}$.

Concentration	*a* (10^{-2} $\mu V/K^2$)	*b*	T_0 (K)	T_c (zero)[a] (K)
0	1.710	189.5	17.7	91.00
0.025	0.904	100.7	23.6	72.85
0.050	0.969	158.9	17.6	66.19
0.075	0.778	154.0	17.6	63.60
0.100	1.207	24.5	29.4	50.08
0.150	0.973	15.8	33.2	47.60
0.200	0.764	23.3	21.5	30.69

[a] Determined resistively.

While the value of *b* changes by one order of magnitude, the value of T_0 changes by a factor of 2. T_0 does not show any correlation with T_c, but seems to be related to oxygen annealing. For small oxygen annealing time, even with oxygen stoichiometry greater than 6.85, one observes a large thermopower nearly independent of temperature. On increasing the annealing time, the thermopower decreases to a few μV per K, and one observes a sharp peak near T_c.

The enhancement of thermopower observed in all the samples varies more steeply with temperature than what one would expect from electron-phonon enhancement as calculated by Kaiser.[20] The mechanism of enhancement must be other than the electron-phonon mechanism.

Tsidilovski and Tsidilovski[28] have proposed the following model to explain the peak in thermopower of $YBa_2Cu_3O_{7-y}$. According to their phenomenological model, the density of states function, $g(E)$, consists of a narrow peak $g_1(E)$ superimposed on a smoothly varying background $g_0(E)$. The peak is located at energy E_1 and has a width *V*. The quantity $\delta=(E_1-E_F)/kT$, where E_F is the Fermi level, is determined by the requirement that the total charge carrier concentration is independent of temperature. Then one can have a characteristic temperature T_1, such that for $T<T_1$, $|\delta|>1$, and for $T>T_1$, $|\delta|<1$. In the former case, $\delta=A/[k_B T g_0(E_1)]$ and in the latter case, $\delta=C(1+DT)^{-1}$, where *A*, *C*, and *D* are constants. The theory then predicts that for $\delta>1$, the thermopower should vary as $1/T$, while for $\delta<1$ it should vary as $1/(1+DT)$, provided $V/k_B T<<1$. While the theory shows that a peak in thermopower is to be expected above T_c, it predicts the thermopower to fall as $1/T$ above T_c. The measured fall is much faster.

Tozer *et al.*[29] have measured the resistivity of a single crystal of $YBa_2Cu_3O_{7-y}$, both parallel and perpendicular to the *c* axis. Their resistivity curve parallel to the *c* axis seems to be flat down to 150 K followed by a sharp rise as the temperature is reduced to T_c. The resistivity can therefore be fitted to the equation

$$\rho_c(T)=\rho_{c0}+\rho_{c1}\exp(-T/T_0)\ , \tag{2}$$

where T_0 turns out to be approximately 25 K. While the increase in resistivity along the *c* axis cannot be directly linked to the peak in thermopower in the *a*-*b* plane, the similarity in the temperature dependence of ρ_c and thermopower in the well oxygenated polycrystalline samples as well as in the *a*-*b* plane of the single crystals of $YBa_2Cu_3O_{7-y}$ suggests a common cause for both.

In conclusion, the present studies on thermopower of zinc-doped yttrium barium copper oxide show the following:

(a) for concentrations up to and including $x=0.2$, the number of mobile holes per copper does not change much, while for $x\geq 0.3$, the number of mobile holes per copper seems to decrease;

(b) the peak in the thermopower near T_c is not due to phonon drag;

(c) the temperature dependence of thermopower of well oxygen annealed samples below 250 K is described by Eq. (1) with the parameter T_0 in the range 17–34 K.

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