Pramāṇa – J. Phys., Vol. 29, No. 2, August 1987, pp. L225–L230. © Printed in India.

Enhancement of thermopower in the high T_c superconductor $YBa_2Cu_3O_7$ and related compounds

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MS received 25 June 1987

Abstract. The absolute thermopower of single phase $YBa_2Cu_3O_7$ and $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$ has been measured in the range 250 K to the superconducting transition temperature. It is found that these compounds show a large enhancement of thermopower in the range 150 K down to T_c. This enhancement shows a steep exponential drop as the temperature increases from the transition temperature. The temperature variation of the enhancement is too steep to be accounted for by electron-phonon or electron-local structural excitation mechanisms.

Keywords. High temperature superconductors; enhancement in thermoelectric power.

PACS Nos 74·70; 72·15

The compounds belonging to the family $YBa_2Cu_3O_7$ have been found to become superconducting with T_c around 90 K (Wu *et al* 1987; Subba Rao *et al* 1987a; Ganguly *et al* 1987; Rao *et al* 1987). Several compounds of this family have been synthesised in the single phase with Y either wholly or partially substituted by other rare earth elements and found to be superconducting with a sharp resistive transition and large Meissner effect (Subba Rao *et al* 1987b). The Seebeck coefficient of oxygen treated and air treated samples of $YBa_2Cu_3O_7$ has been reported by Raychaudhri *et al* (1987). They find a negative sign for the Seebeck coefficient of the oxygen treated sample which becomes superconducting and a positive sign for the air treated sample which does not become superconducting down to 90 K.

The absolute thermopower, S, (which is derived from the Seebeck coefficient by correcting for the absolute thermopower of copper) was measured by Vasudeva Rao *et al* (1984) on Chevrel phase solid solutions $Cu_{1.8}Mo_6S_{8-y}Se_y$ and $Cu_{1.8}Mo_6S_{8-y}Te_y$. They found evidence for the enhancement of thermopower for $y=6$ and 7 in the S-Se compounds and for $y=2$, 3 and 4 in the S-Te compounds. Kaiser (1987) explained the enhancement as arising from the renormalization of the energy of the electron due to electron-phonon interaction.

The thermoelectric power, S, of single phase $YBa_2Cu_3O_7$ and $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$ was measured in the range 250 K to the superconducting transition temperature. These samples were prepared by solid state reaction (950°C 24 h air; two repeat grindings and final O_2 treatment for 24 h at 900°C) of high purity oxides of yttrium, and rare earth, barium carbonate and CuO. They were verified to be single phase materials by X ray diffraction. Figure 1 shows the resistivity curves of the two compounds in the

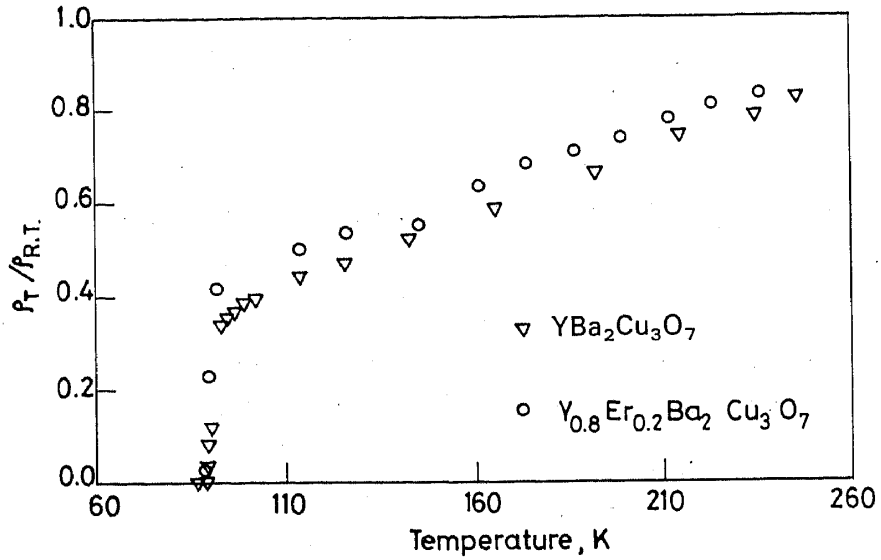

Figure 1. Variation of normalized electrical resistivity with temperature for $YBa_2Cu_3O_7$ (inverted triangles) and $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$ (circles).

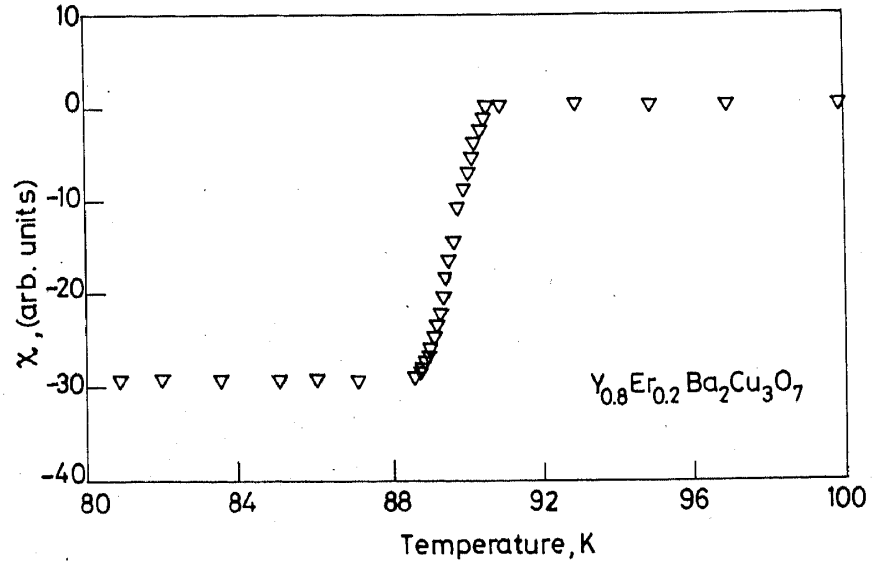

Figure 2. Variation of magnetic susceptibility with temperature for $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$.

temperature region studied here obtained by using a four probe technique. The sharpest transition was observed in $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$, the diamagnetic susceptibility signal of which is shown in figure 2. The transition width was less than 2 K in this sample. Calibration with a sample of lead indicated that more than 70% of the sample volume became superconducting in both cases.

The absolute thermoelectric power of the $YBa_2Cu_3O_7$ compound is shown in figure 3. The thermoelectric power drops to zero at T_c as expected for bulk superconductor. The sign of the absolute thermopower which is obtained from subtracting the measured Seebeck coefficient from the absolute thermoelectric power of copper is positive. Above 150 K the points lie on a straight line which when extrapolated passes through the origin. The slope of the straight line is 0·0171 $\mu V/K^2$, which is about the same order as the slope in the Chevrel phase compounds found by Vasudeva Rao *et al* (1984).

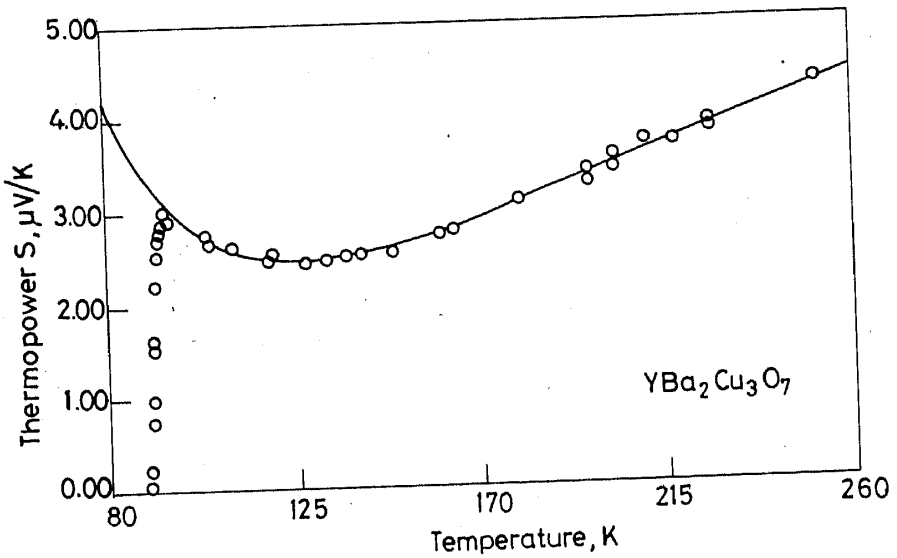

Figure 3. Absolute thermopower vs temperature plot for $YBa_2Cu_3O_7$ (circles) with fit to equation (4) (full line).

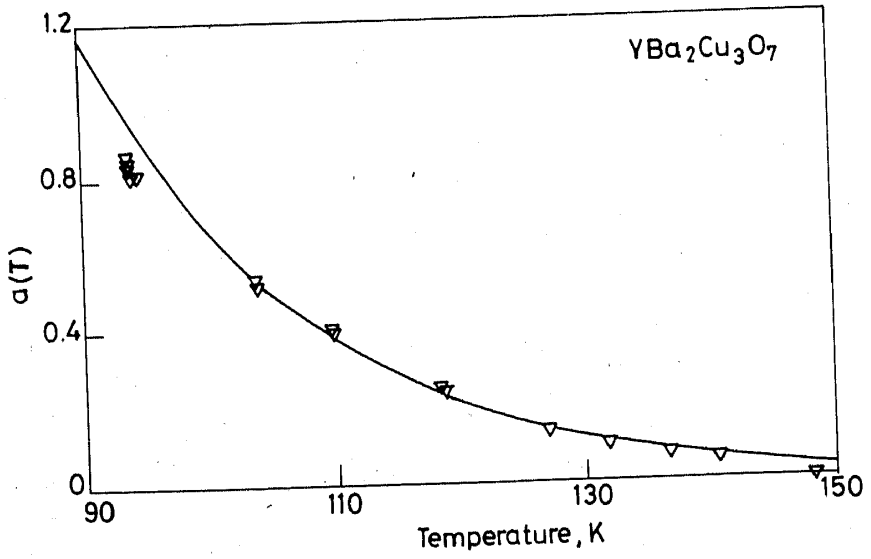

Figure 4a. Plot of enhancement factor $a(T)$ against temperature for $YBa_2Cu_3O_7$ (inverted triangles); continuous line: From equation (3).

The enhancement of the thermopower seen below 150 K is defined by the quantity $a(T) = [(S(T) - S_{ed}(T))/S_{ed}(T)]$ where the electron diffusion thermopower $S_{ed}(T)$ is in this case $0{\cdot}0171\,T$. Figure 4a shows a plot of $a(T)$ for the yttrium compound. It is seen that (i) the enhancement reaches a value of 0·8 near the superconducting transition and (ii) the enhancement decreases rapidly as the temperature increases and becomes insignificant at 150 K. For comparison the behaviour in $Cu_{1.8}Mo_6S_5Te_3$ observed by Vasudeva Rao *et al* (1984) is shown in figure 4b. It is seen that in this case the enhancement decreases from about 0·97 at 26 K to a vanishingly small value near 150 K.

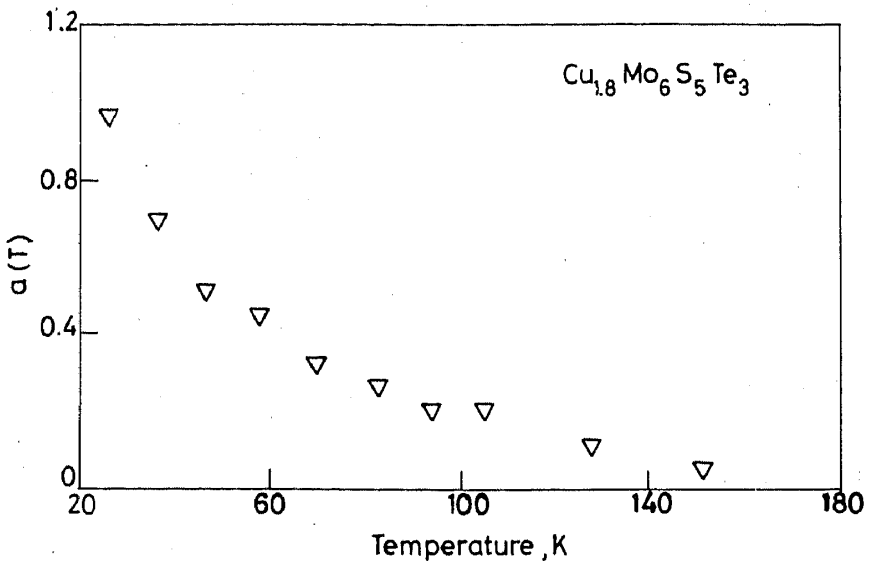

Figure 4b. Plot of enhancement factor as a function of temperature for $Cu_{1.8}Mo_6S_5Te_3$.

Kaiser (1987) has shown that the enhancement can be expressed in terms of the electron phonon mass enhancement factor and a universal function $G_s(T/T_D)$ where

$$\bar{\lambda}_s(T/T_D)=\int_0^\infty \frac{\alpha^2F(E)}{E}G_s(F/k_BT)\,dE \Big/ \int_0^\infty \frac{\alpha^2F(E)}{E}dE \tag{1}$$

where $\alpha^2F(E)$ is the Eliashberg coupling function and $G_s(E/k_BT)$ is a universal function given by

$$G_s(y)=\frac{3}{\pi^2}\int_{-\infty}^{\infty} dz\left(\frac{-\partial f}{\partial z}\right)z\int_{-\infty}^{\infty} dt f(t)y^2/[(t-z)^2-y^2]. \tag{2}$$

However, the temperature dependence of the enhancement in $YBa_2Cu_3O_7$ is too steep to be represented by the above expression assuming $\alpha^2F(E)$ is proportional to E^n, where n was taken to be 1, 2 or 3. A mechanism for electron pairing arising from local structural excitations (LSE) which can give rise to high T_c was proposed by Vujicik *et al* (1981). In this mechanism the mass enhancement factor λ_{LSE} depends on temperature as $\tanh(E/k_BT)$ multiplied by the function $G_s(E/k_BT)$ where E is assumed to be the energy difference between the two states characterizing the LSE. However, even this function does not adequately represent the dependence of $a(T)$. In fact $a(T)$ is found to vary almost exactly as

$$a(T)=189{\cdot}5\exp(-T/17{\cdot}7) \tag{3}$$

or

$$S(T)=0{\cdot}0171\,T(1+189{\cdot}5\exp(-T/17{\cdot}7)). \tag{4}$$

One may think that the enhancement could arise from phonon drag. However, the range of temperature in which the enhancement is observed does not appear to make it likely. To check this, the thermoelectric power of the erbium substituted $YBa_2Cu_3O_7$ compound was measured. It is well known and also seen in Vasudeva Rao *et al* (1984)

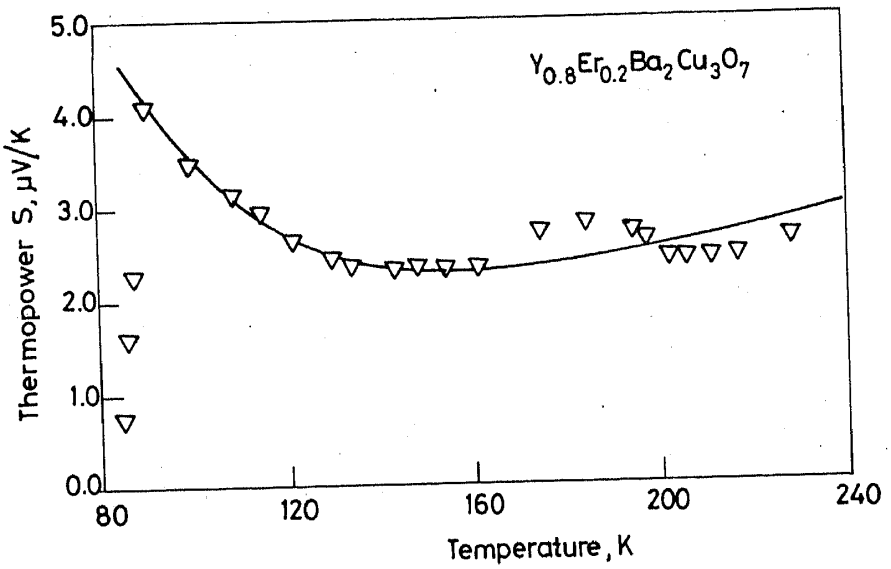

Figure 5. Variation of thermopower with temperature for $Y_{0.8}Er_{0.2}Ba_2Cu_3O_7$ (circles) with a fit to equation (5) (full line).

that alloying a given compound with a substituent drastically reduces the phonon drag effect. Figure 5 shows the thermoelectric power of the erbium substituted compound in the range 250 K to T_c. The enhancement below 150 K is still observed as strong as in the unsubstituted compound. In the range from T_c to 150 K the thermoelectric power can be well represented by the formula

$$S(T) = 0{\cdot}0124\,T(1 + 99\exp(-T/25)). \tag{5}$$

It is noteworthy that the exponential and pre-exponential factors are of the same order as in the pure yttrium compound. In the erbium substituted compound one sees a subsidiary maximum in the thermopower in the region around 185 K. The origin of this peak is not clear.

Preliminary measurements on $Y_{0.8}Ho_{0.2}Ba_2Cu_3O_7$ also showed the characteristic enhancement below 150 K. In this compound the thermopower in the region from T_c to 150 K is well represented by

$$S(T) = 0{\cdot}0248\,T(1 + 28{\cdot}9\exp(-T/28)). \tag{6}$$

Thus it is seen that in these compounds there is a characteristic exponential variation of thermopower enhancement below 150 K.

van Bruggen (1987, Private communication) has measured the thermoelectric power of superconducting $La_{1.7}Ba_{0.3}CuO_4$ pellet. From the thermoelectric power they calculated the Fermi level E_F using the expression for the thermoelectric power in a single spherical band approximation. In this approximation the thermoelectric power is inversely proportional to E_F. The calculated values of E_F were found to vary from 1 eV at 306·6 K to 0·04 eV at 52·7 K. Such a variation is indicative of thermopower enhancement. The data of van Bruggen appear to yield an enhancement $a(T)$ which varies as $66\exp(-T/49)$. The enhancement in the superconducting lanthanum compound actually varies less steeply than the variation observed in $YBa_2Cu_3O_7$.

Raychaudhri *et al* (1987) have found a significant difference in the Seebeck coefficient

of an air heated and an oxygen heated sample. The results reported in this paper are on freshly oxygen treated samples. It may happen that the thermopower behaviour may change if the samples are left in air for long periods of time. Such investigations are in progress.

Thanks are due to the Department of Science and Technology, Government of India for the award of research grant under thrust area program.

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