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Influence of oxygen deficiency on the thermoelectric power of $Y_1Ba_2Cu_3O_{7-x}$

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Abstract. In this paper we report measurements of the thermoelectric power on a series of $Y_1Ba_2Cu_3O_{7-x}$ specimens with varying amounts of oxygen deficiency obtained by changing the cooling rate of the sintered specimens. The specimens have been characterized by X-ray diffraction measurements, electric resistivity and oxygen contents The temperature variation of the thermopower reveals a peak just before the onset of superconducting transition We examine possible theoretical explanations of this anomaly In particular we argue that this anomaly is associated with the pairing fluctuations in the normal state close to T_c We present some theoretical results in support of this conclusion

Keywords. Thermoelectric power, oxygen deficiency, cooling rate, phonon drag, pair fluctuation, correlation effect

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1. Introduction

Even though a breakthrough in the technological use of the new 90 K superconductors (Wu *et al* 1987) is yet to be achieved, a plethora of experimental data continue to pour in. Most studies are aimed at understanding the mechanism operating in these ceramic superconductors. Studies on transport properties are particularly interesting as these give useful information regarding the nature of the carriers responsible for conduction. The peculiar problem of porosity and consequently the intergrain weak links in these ceramic materials make the interpretation of the transport properties quite difficult. Thermopower, however, could give more reliable data since the temperature drop is less serious than the voltage drop at the integrain boundaries. Moreover, the thermopower measurements have the advantage of being independent of sample geometry. In this communication we report our data on the thermopower measurements on a series of $Y_1Ba_2Cu_3O_{7-x}$ specimens with varying amounts of oxygen deficiency, which is known to have a large influence on the superconducting behaviour as well as on the transport properties of these materials in the normal state. We also give a tentative theoretical explanation for the observed behaviour of the thermopower of these materials.

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A number of papers (Raychaudhuri *et al* 1987; Srinivasan *et al* 1987; Khim *et al* 1987; Lee *et al* 1987; Mitra *et al* 1987; Henkie *et al* 1987, 1988; Trodahl and Mawdsley 1987; Crommie *et al* 1988) have recently appeared on the thermopower of $Y_1Ba_2Cu_3O_{7-x}$ superconductor prepared under varying sintering conditions. However there are many discrepancies in the magnitude of thermopower, its temperature variation and even its sign. Most of the studies reported a positive absolute thermopower barring a few exceptions Khim *et al* (1987) and Lee *et al* (1987) report a negative thermopower (S) for $Y_1Ba_2Cu_3O_{7-x}$ superconductor and for other rare earth element superconductors with a rare earth ionic radius of <0·92 Å. A positive thermopower is reported for superconductors with rare earth element of ionic radius of >0·92 Å. A negative thermopower is also reported by Raychaudhuri *et al* (1987) for their oxygen annealed $Y_1Ba_2Cu_3O_{7-x}$ specimen and a positive value for an air-annealed specimen. More recently Hankie *et al* (1988) also reported both the signs of thermopower being negative for compounds with an oxygen deficiency of 0·03 and 0·05 and positive for oxygen deficiencies of 0·17 and 0·19. Irrespective of the sign, the thermopower in all cases shows a peak between 80 and 100 K and drops to zero at a temperature close to the observed T_c value.

As regards the temperature variation of the thermopower the situation appears equally fluid. Thermopower independent or nearly-independent of temperature has been reported by Yu *et al* (1987) and by Crommie *et al* (1988) in an oxygen-deficient single crystal of $Y_1Ba_2Cu_3O_{7-x}$ along the C axis. In most other studies the thermopower is generally a slow decreasing function of temperature between 100 and 300 K. The peak values vary between 4 μV/K (Khim *et al* 1987) to 45 μV/K (Yu *et al* 1987). Yet another peak in the thermopower around 200 K was reported by Trodahl and Mawdsley (1987) in addition to the usual peak just above T_c. Srinivasan *et al* (1987) report a thermopower of the $Y_1Ba_2Cu_3O_{7-x}$ specimen which shows a minimum at 125 K and an increasing function of temperature beyond 125 K. It is, therefore, quite clear that further systematic studies of the thermopower of these materials are required.

2. Experimental details

The $Y_1Ba_2Cu_3O_{7-x}$ compound was prepared by the usual solid state ceramic technique described earlier (Sharma *et al* 1988). The preformed powder was pressed in the form of a strip (35 × 4 × 3 mm) and sintered at 920°C for 15h under flowing oxygen each time and cooled to room temperature at 60°C, 100°C, 160°C and 200°C per hour. The same specimen was also quenched to 77 K from 920°C. For thermopower measurements the bar-shaped specimen was mounted inside a vacuum can. An electric heater was wound on the lower end of the specimen whereas the top end of the specimen was fixed in good thermal contact with a copper plug welded to the lid of the can. A temperature gradient was maintained along the specimen by supplying a current to the heater A copper-constantan differential thermocouple was used to monitor ΔT between the two points about 10 mm apart on the specimen. The sample temperature was recorded with a copper-constantan thermocouple, one junction of which was fixed on to the specimen. The thermo-induced voltage ΔV was read with a Keithley nano-voltmeter with an accuracy of ±10 nV. $A\Delta T$ of 2–3 K was usually maintained throughout the measurement between 300 and 77 K. The measured thermopower ($\Delta V/\Delta T$) was suitably corrected for the thermopower of pure copper leads.

The crystal structure of all the specimens was checked by recording the room temperature X-ray diffraction peaks between the 2θ values of 20° and 70° on a Philips X-ray diffractometer. A few selected prominent peaks viz (200), (020) and (006) between $2\theta = 46$–$48°$ are well-resolved using k_α radiation Ni filter, PHD and a slow scanning at 1/8° per minute. The receiving slit was set at 0·1° and a time constant of 16 s. The lattice parameters were calculated from these peak positions to see their variation with the oxygen stoichiometry obtained by varying the cooling rate. The oxygen contents in the specimens in excess of 6·5 was estimated using a gas chromatograph (model Perkin Elmer Sigma 2000) and making use of a hot wire detection (HWD) technique.

The superconducting transition temperature was determined by measuring the electrical resistivity as a function of temperature in the range of 77 to 300 K following the usual four-probe technique. A variable temperature cryostat was used. The temperature was read with a copper-constantan thermocouple. We have used indium pressure contacts for the current and potential leads.

3. Results and discussions

The resistance versus temperature plots of all the specimens used for the thermopower measurements are shown in Figure 1. All the specimens including the quenched one show a metallic character and a linear variation of the resistivity with temperature with an average value of the slope of 17 $\mu\Omega$cm/K. The quenched sample, though metallic, does not become superconducting down to 77 K. The 100°C/h cooled specimen shows the sharpest transition but ends in a tail. The general trend seems to be an increase in the transition width with an increase in the cooling rate The onset T_c, midpoint T_c, $T_c(R = 0)$ and ΔT_c are given in table 1. The oxygen contents

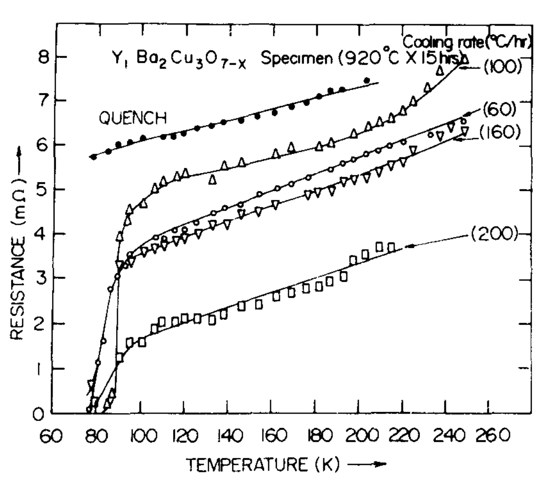

Figure 1 Resistance versus temperature plots of the $Y_1Ba_2Cu_3O_{7-x}$ specimens sintered 920° C × 15h and cooled at a rate of 60, 100, 160, 200 C/h and quenched to 77 K

Table 1. Oxygen contents (per formula unit), T_c and peak thermopower values of the $Y_1Ba_2Cu_3O_{7-x}$ specimens sintered at 920°C for 15h and cooled down at different rates

Cooling Rate (°C/h)	Oxygen content per formula unit	T_c(onset) (K)	T_c(midpoint) (K)	$T_c(R=0)$ (K)	ΔT_c* (K)	Thermopower peak value (μV/K)
60	6·914	90	83·5	77	13	10·3
100	6·88	92	90	84	8	8·0
160	—	92	83	77	7·5	7·0
200	6·76	96	86	78	18	8·2
Quenched to 77K	⩽6·5	Not SC down to 77K	—			120

$^*\Delta T_c = T_c\,(\text{onset}) - T_c\,(R=0)$

of all the specimens estimated using gas chromatography as described earlier are also given in table 1. This technique detects oxygen in excess of 6·5 only with an accuracy of 3%.

Figure 2 gives the room temperature diffraction spectra of the specimens cooled at different rates. Figure 3, on the other hand, shows the well-resolved (200), (020) and (006) reflections. The lattice parameters calculated from these peaks for the four specimens are listed in table 2. Although the changes in lattice parameters were marginally higher than the experimental error (±0·003Å) of our measurements a definite trend of relative increase in b and c parameters is observed with slower cooling rates. The a parameter of different samples remains practically unchanged.

The sample quenched to 77 K appears to be tetragonal (figure 3d) but the possibility of an additional orthorhombic phase cannot be ruled out. It is noticed from figure 2(D) that all those lines with different h and k values of the Miller indices (hkl) where splitting of lines is possible in transformation from tetragonal to orthorhombic unit cell are broad. On the other hand reflections with the same h and k values (like 113, 112 etc.) are sharp. We, therefore, conclude that the quenched sample could be partly tetragonal (as confirmed by the indexing of different reflections up to $2\theta = 80°$) and partly orthorhombic with a small magnitude of orthorhombic distortion $(b-a)$ as also indicated by a net metallic behaviour of the resistivity (figure 1). Also, the two unindexed sharp lines in figure 3(D) disappeared later in a fresh and fast-quenched sample and the 2θ positions of (200) and (006) reflections were also found to vary to a certain extent depending upon the rate of cooling. Table 3 gives the X-ray powder data for the quenched sample (shown in figure 2(D)). All the reflections are indexed on a tetragonal cell with $a = 3{\cdot}86(1)$ Å and $c = 11{\cdot}67(2)$ Å. We observe from table 2 that on increasing the cooling rate from 60°C/h to 200°C/h $(b-a)$, the measure of orthorhombicity decreases from 0·068 Å to 0·063 Å. Evaluating this data in the light of transition 'onset and end point' curves published by Takagi *et al* (1987) one expects a larger transition width with decreasing orthorhombic distortion $(b-a)$. We do observe a large transition width ΔT_c as large as 18 K in the 200°C/h specimen.

The thermopower values (S) of all the specimens are plotted against temperature in figure 4. After the preliminary results were presented at a workshop (Jha *et al* 1988) the thermopower data on the 200°C/h specimen was found to be in error when the measurements were repeated. The thermopower of other specimens also got slightly modified when corrected using a more reliable data for pure copper, even though the

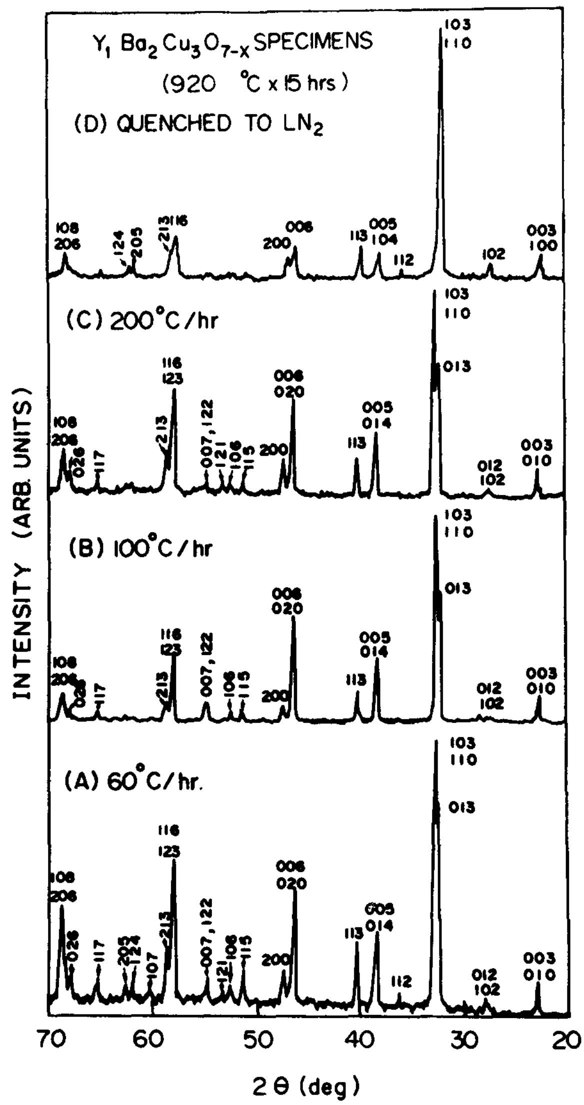

Figure 2 Room temperature diffraction spectra of the specimens cooled at the rate of 60, 100, 200°C/h (A-C) and quenched to 77K (D)

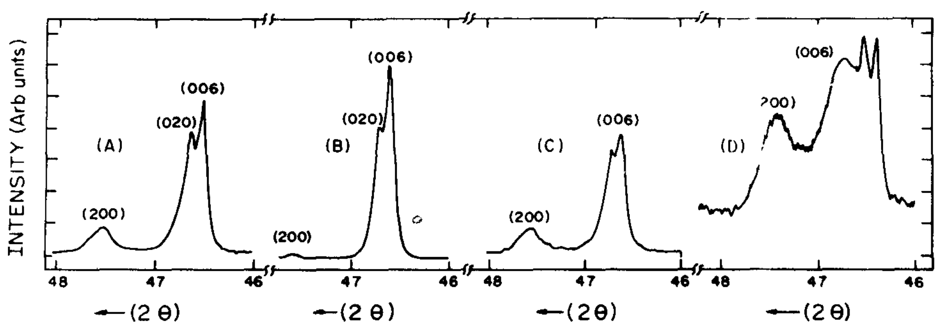

Figure 3 X-ray diffraction peaks between $2\theta = 46$–$48°$ for $Y_1Ba_2Cu_3O_{7-x}$ specimens cooled at 60°C/h (A), 100°C/h (B), 200°C/h (C), and quenched to 77 K (D)

Table 2. Lattice constants of the $Y_1Ba_2Cu_3O_{7-x}$ (920°C × 15 h) specimens as determined from the (200), (020) and (006) diffraction peaks.

Cooling Rate (°C/h)	a(Å)	b(Å)	c(Å)	$(a-b)$(Å)
60	3 892	3 824	11 713	0·068
100	3 889	3·823	11 697	0 066
200	3 887	3 824	11·690	0 063
Quenched to 77K	3 86(1)	—	11 67(2)	Tetragonal

Table 3. X-ray diffraction data for tetragonal system in quenched sample

d_{obs}(Å)	d_{cal}(Å)	hkl
5 84	5 835	002
3·86	3 890	003
	3·860	100
3 21	3 219	102
2·72	2 740	103
	2 729	110
2 34	2 334	005
	2 327	104
2 23	2 234	113
1 94	1 945	006
1 92	1 930	200
1 77	1 774	115
1 73	1 737	106
1·58	1 584	116
1 57	1 578	213
1·36	1 370	206
	1 364	108

basic character of the plots remains unchanged. As seen from figure 4, the thermopower is positive for all the specimens which is an indication of the hole conduction in these materials. The sign of the thermopower alone, however, cannot be taken as the sole criterion for the polarity of the carriers as the well-known free electron metals viz; copper, silver and gold do have a positive thermopower. The Hall coefficient measurements (Wang *et al* 1987) on this system do confirm the hole-like behaviour of the carriers. The specimen cooled most slowly (60°C/h) shows S, a decreasing function of temperature between 130 and 270 K. A braod peak ($\sim 10\,\mu V/K$) appears at around 125 K below which the thermopower drops rather sharply becoming zero at T_c. This specimen has the highest oxygen content 6·91 as seen from table 1 and a near perfect orthorhombic perovskite structure (figure 2(A)). Our thermopower curve is very similar to that reported by Crommie *et al* (1988) for a polycrystalline sample. A peak value of $12\,\mu V/K$ occurring around 125 K was reported. Above the peak the thermopower is a decreasing function of the temperature A very similar behaviour of thermopower was also observed by the same authors in single crystal sample of $Y_1Ba_2Cu_3O_{7-x}$ with temperature gradient along the $a-b$ plane. It therefore appears

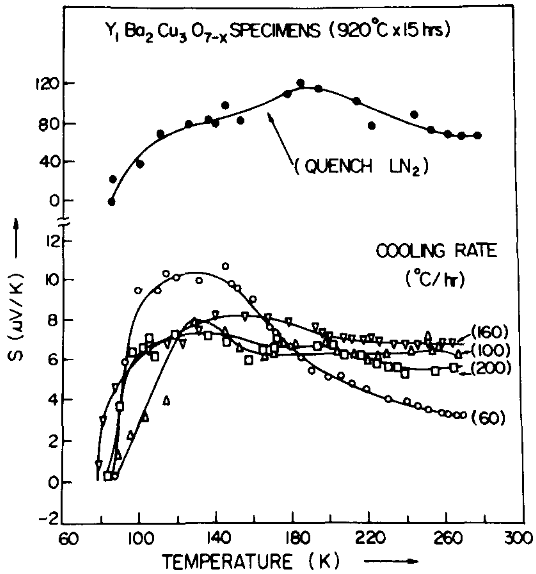

Figure 4 Measured thermopower corrected for the thermopower of pure copper leads, plotted against temperature for $Y_1Ba_2Cu_3O_{7-x}$ specimens as listed in table 1 All values are positive The quenched sample has a very large thermopower

that polycrystalline samples are dominated by the transport in the $a-b$ plane.

The other specimens (100–200 °C/h) show S values slightly larger than the 60°C/h specimen at the higher temperature side, almost independent of temperature, a peak between 120 and 150 K and dropping to zero at around 80 K. The specimens are characterized by the reduced oxygen contents (6.88–6.76) and a slow transformation from a well-ordered orthorhombic structure to a tetragonal structure as seen from the $(a-b)$ values in table 2. A gradual oxygen disorder which preferentially occurs along the Cu-O chains (Jorgensen *et al* 1987) should indeed increase the phonon scattering and bring down the phonon drag component as observed in these specimens. However, a $S \propto 1/T$ behaviour observed for the 60° C/h specimen between 125 and 180 K and expected for a phonon drag component is not well obeyed in the faster cooled specimens.

The liquid nitrogen quenched specimen (figure 4) has a positive and a large peak value of thermopower equal to 120 μV/K at 190 K. It is a slow decreasing function of temperature on the higher temperature side and drops to zero at 85 K similar to the other specimens. It is surprising that this sample, though not superconducting down to 77 K, has a zero thermopower at 85 K. As already discussed, our X-ray diffraction data do indicate the possibility of a small concentration of the orthorhombic phase. This is also corroborated by a metallic nature of the resistivity curve of this specimen. The specimens of the other two systems viz. Gd-Ba-Cu-O and Sm-Ba-Cu-O (Jha *et al* 1989) quenched to 77 K show a semiconducting behaviour of the electrical resistivity and a finite thermopower down to 77 K. Perhaps our quenching process in the present studies was not fast enough to prevent oxygen pick-up totally and the formation of a small quantity of the orthorhombic phase. The zero thermopower of the quenched specimen hints at a possibility that the precursor superconductivity is observed in the thermopower more significantly than in the resistivity behaviour.

Similar evidence of precursor superconductivity was reported by Cooper *et al* (1987) in La_2CuO_4. The thermopower which is positive and large ($\sim 300\,\mu V/K$) invariably starts to fall below 80 K even though the thermopower and the resistivity are zero only at 20 K in some samples. The doping with Sr and Ba reduces the thermopower in the normal state (50 and 100 μV/K at 300K). Thermopower is weakly temperature-dependent and zero in the superconducting state consistent with the picture of a ground state condensate. It appears from the thermopower behaviour in the normal state that it is not a characteristic feature of a normal metal.

The negligible difference in the thermopower behaviour of the specimens (100°C to 200°C/h) with oxygen contents between 6·88 and 6·76 sounds very similar to a plateau region found in the Hall Coefficient, T_c and the Meissner fraction (Wang *et al* 1987) of the $Y_1Ba_2Cu_3O_{7-x}$ specimens with oxygen contents between 6·9 and 6·5. This plateau region suggests a very small variation in the carrier density between oxygen $O_{6\cdot 9}$ and $O_{6\cdot 5}$ (per formula unit). The orthorhombic-to-tetragonal transformation has been found at $O_{6\cdot 4}$ instead of $O_{6\cdot 5}$. The thermopower behaviour observed by us appears consistent with the above experimental observations. The thermopower shows a small drop initially with the oxygen deficiency (60–100°C/h, it stays almost independent of oxygen content for specimens (100–200°C/h). The thermopower jumps to a large value for the quenched specimen where oxygen is reduced to below 6·5. The insensitivity of these transport coefficients to the oxygen deficiency in the middle range is attributed to the presence of a sink which is a narrow band of localized states and absorbs the donated electrons as oxygen deficiency increases leaving most of the transport properties in the normal and superconducting state unaffected. The sink is identified as the Cu(I) cations along the chains closest to the oxygen vacancy created. Since the O-vacancies disrupt the transport along the chains the electrons donated to the Cu(I) ions are strongly localized. Most transport properties in the middle region of the oxygen deficiency will therefore be dominated by the hole carriers in the Cu(II)-O planes. At 0-deficiency $>0{\cdot}5$ the number of Cu^{3+} ions reduces to zero pushing the system to an insulating phase.

Let us now turn to the possible theoretical explanations for the anomalous behaviour of the thermopower just before the onset of superconductivity. This anomaly is most pronounced in 60°C/h cooled specimen, where there seems to be a clear peak. This is quite reminiscent of the phonon drag peak expected at a temperature about $\theta_D/5$. Taking a reasonable value of θ_D as 400 K (Crommie *et al* 1988) the observed peak and its $1/T$ like fall are consistent with the phonon drag mechanism. The phonon drag component should, in general, be reduced with alloying due to an increase in the phonon scattering. However, Srinivasan *et al* (1987) who studied the thermopower of an alloy in which 20% yttrium was replaced by erbium, found no such reduction. In their more recent studies (Radhakrishnan 1989) with alloys in which zinc replaces copper, this point is further clarified. In this series of alloys, the transition temperature T_c changes substantially, but θ_D is not expected to vary much. The thermopower anomaly is always found to occur close to T_c.

Ausloos *et al* (1988) offered another explanation which relies on the granular nature of these materials. Assuming a fraction of the grains to be superconducting, they are able to achieve the desired form for the temperature dependence of thermopower S.

Since these superconductors have a small coherence length, we consider an alternative mechanism based on superconducting fluctuations in the normal phase. We take as a starting point, the standard text book formula for S, given by

$$S = \frac{\pi^2 k_B^2 T}{3e}\left(\frac{\mathrm{d}\ln\sigma(E)}{\mathrm{d}E}\right)_{E=E_f}, \tag{1}$$

where $\sigma(E)$ is the electrical conductivity regarded as a function of the Fermi energy E_f. Using the standard, nearly free electron expression for $\sigma(E)$, equation (1) may be written as

$$S = \frac{\pi^2 k_B^2 T}{3e}\left[\frac{\partial \ln\rho(E)}{\partial E} + \frac{\partial \ln v^2(E)}{\partial E} + \frac{\partial \ln \tau(E)}{\partial E}\right]_{E=E_f}, \tag{2}$$

where $\rho(E)$ is the single particle density of states, $v(E)$ the velocity and $\tau(E)$ the mean collision time of the carriers.

Now note that the quantity that is most sensitive to the superconducting ordering is the density of states $\rho(E)$. In the normal phase $\rho(E) \propto E^{\frac{1}{2}}$, whereas $\rho(E)$ is zero over a gap $\Delta(T)$ around E_f. Since this is a somewhat drastic effect, one expects that close to T_c, even in the normal phase, one should see some incipient effects of superconducting ordering in $\rho(E)$. Since $\rho(E)$ is directly related to $v(E)$, one expects that the first two derivatives in (2) should be strongly temperature-dependent.

In order to consider the effect of superconducting fluctuations on $\rho(E)$, one has to consider the single particle propagator $G(p, E)$ and the corresponding self-energy $\sum(p, E)$. The simplest process that incorporates the virtual pairing fluctuations in the self-energy correspond to diagrams shown in figure 5. To obtain a qualitative idea, one of us (Kumar 1989) evaluated $\sum(p, E)$ corresponding to these diagrams in the

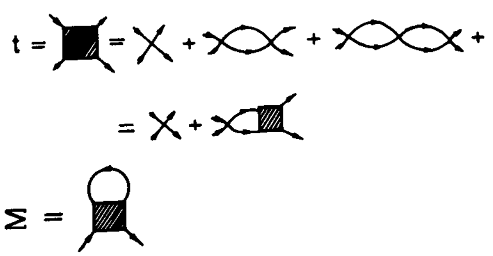

Figure 5 Self-energy and t-matrix diagrams that lead to equation (3)

interaction model (Abrikosov *et al* 1965). This calculation yields for the single particle energy E_p (measured from E_f) the following equation

$$E_p = \varepsilon_p + \sum\nolimits_p = \varepsilon_p + \frac{2\omega_0}{\pi\beta\rho_0(E_f)}\frac{\tanh(\beta\varepsilon_p/2)}{\varepsilon_p^2 + \omega_0^2}, \tag{3}$$

where $\varepsilon_p = (p^2/2m) - E_f$, $\beta = (k_B T)^{-1}$, the free particle density of states and

$$\omega_0 = \frac{2}{\pi\beta}\left(\frac{T - T_c}{T_c}\right) \tag{4}$$

with

$$k_B T_c = \frac{e_D \gamma}{\pi}\exp\left(-\frac{1}{\lambda\rho_0(E_f)}\right). \tag{5}$$

Further λ is the strength of the attractive interaction independent of the momenta of the particle, and e_D is the range in energy about E_f, in which the particle energies must lie in order to have a non-zero interaction. The density of states $\rho(E)$ can be calculated using the formula

$$\rho(E) = \frac{1}{2\pi^2 h^3} \frac{p^2(E)}{v(E)} \tag{6}$$

the velocity, $v(E) = |\vec{\nabla}_p E_p|$. From (3) one finds that the Fermi velocity $V_F = V(E_f)$ is given by the expression

$$v_F = v_F^0 \left[1 + \frac{1}{\pi \rho_0(E_f)} \frac{1}{\omega_0} \right] \tag{7}$$

According to (7) $V_F \to \infty$ as $T \to T_c$, implying that $\rho(E_f) \to 0$ as $T \to T_c$ from above. This model calculation demonstrates the qualitative remarks made above, that the gap in $\rho(E)$ can open in a continuous way. Further (2) and (3) imply (Kumar 1989) that $S \propto (T - T_c)^{-1}$.

Clearly such a singular behaviour is not seen in the experiment. There are many factors like granularity, which smother this behaviour (Kumar 1989). We do not regard the theory presented here as adequate to describe the thermopower in strongly interacting systems as its starting point is a formula based on nearly free electron model. It, however, serves to demonstrate that the thermopower measurement should be very useful to understand precursor fluctuations in the new superconductors. Clearly to achieve better comparison with experiments, the theory should include strong correlation effects and the effects due to granularity of the material.

4. Conclusions

The drastic change in the superconducting behaviour of the $Y_1Ba_2Cu_3O_{7-x}$ caused by the introduction of oxygen deficiency is amply reflected in the thermopower measurements. The peak in the thermopower above T_c appears to be caused by the pair fluctuations in the normal state rather than being a phonon drag effect.

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