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THERMOELECTRIC POWER OF A LOCAL PAIR MODEL AND ITS APPLICABILITY TO $YBa_2Cu_3O_7$*

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A formula of thermoelectric power (TEP) for the local pair model has been derived. It has been found that from T_c to about 125 K the TEP data of $YBa_2Cu_3O_7$ (Y-123) can be described by this formula. We have also found that the formula of the diffusion thermoelectricity in the free electron approximation can be used to express the TEP data of Y-123 in the region of 220 to about 300 K. It seems that a general transition occurs in the intermediate temperature region, that is from the regime in which the local pair subsystem is dominating to the regime in which the itinerant carrier subsystem is dominating.

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I. INTRODUCTION

There has been a great deal of recent interest in the anomalous behaviour of the TEP, S, of the high-T_c oxide superconductor (HTOS).[1−7] TEP is a very useful property in studying HTOS as it sheds light on both the fundamental information concerning the charge carriers and the superconducting mechanism of HTOS. It appears from the experiment that there is a common behaviour in S associated with the CuO_2 planes of HTOS.[2] Just below the superconducting transition temperature (T_c), S increases sharply with increasing temperature to a peak with positive value at a temperature T_m, then, S falls approximately linearly with increasing temperature and changes sign to the negative values at some higher temperature. Some suggestions have been made to interpret some of these features. Kaiser *et al.*[8] argued that the thermopower of HTOS could be understood in terms of metallic-diffusion thermopower theory with the anomalously large size of electron-phonon enhancement effect. However, there is no appearance of the sharp S peak near T_c in their theoretical curves. Devaux *et al.*[9] put forward a two-band model, however, the sharp peak in S is assumed to be the consequence of some additional trapping mechanism. Weeks *et al.*[10] have pointed out that the Hubbard model in its present state[11−13] cannot explain the TEP in HTOS. For other early models one can see Ref.[1] and the comment.[14] Among many other possible models we call your attention to the large bipolaron model proposed by Emin[15], who has suggested that the strange behaviour of TEP of HTOS can be described with the large

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bipolaron model together with the assumption that a domain of negative mass states arises at high temperatures for the bipolarons. However, it is noteworthy that there are many experimental evidences for the coexistence of two kinds of carriers in HTOS[16-19]: one is the itinerant carrier and the other is the nearly localized-carrier with some kind of local pair correlation. Zhang[20] and Robaszkiewicz *et al.*[21] separately introduced, for the first time, $-U(U>0)$ centers (or bipolarons) into the stidies of HTOS in 1987. It has been proposed that[20,21] a model having two subsystems (or two components as proposed by Bar-Yam[22]) with hybridization between them (the combining picture[23]) is a possible model for HTOS. One of them is assumed to be the free carrier (or nearly free carrier) subsystem and the other subsystem is the negative correlation energy centers of the nearly localized carriers. Bianconi *et al.*[16,17] have given experimental evidences for the itinerant hole in the oxygen derived band (ligand hole) in Y-123 and for the strong correlation between the local Cu3d and itinerant ligand holes. Sugai *et al.*[19] have pronounced the most direct evidence that there is the coexistence of the itinerant large polarons and the localized pairs in $Ba_xK_{1-x}BiO_3$ from the detailed analysis of Raman spectra. We have used this two-subsystem model to explain the properties in the superconducting state of HTOS.[20,23,24] The paper by Eagles[25] discusses more recent developments along this line. In view of the above-mentioned situations, in this paper, we wish to discuss the TEP of HTOS within the framework of the two-subsystem model. In section II we derive the formula for TEP in a local pair system of two dimensions, and study the possibility to use this formula to describe the in-plane TEP data of Y-123 in the low-temperature region. In section III the discussions of describing the in-plane TEP data of Y-123 in the high-temperature region ($T \geq 220\,\mathrm{K}$) and in the intermediate temperature region are made. The results give some valuable information concerning the competing process between the local pair subsystem and the itinerant carrier subsystem. In section IV a brief conclusion is given.

II. THE FORMULA OF TEP FOR THE LOCAL PAIR SYSTEM

Now, we derive the formula for TEP in a local pair system of two dimensions. To be specific, let N_A be the number of sites in a square lattice, and N electrons are distributed among the N_A sites, assuming $N<2N_A$. Let ν be the average population of electron pairs per site. The Hamiltonian describing the local pair problem, as we utilized the negative $U(U>0)$ model, is given by

$$H = -U\sum_i a_{i\uparrow}^+ a_{i\uparrow} a_{i\downarrow}^+ a_{i\downarrow} + t\sum_{ij\sigma} a_{i\sigma}^+ a_{j\sigma} \,. \tag{1}$$

In Eq.(1), $-U$ represents the negative correlation energy of the two electrons with opposite spins in a local pair, while the second term in Eq.(1) represents near-neighbour hopping. We assume the narrow band approximation ($t<U$). On condition that the number of the

singly occupied sites is much smaller than ν, the chemical potential of the local electron pair is given by[26]

$$\mu = -U + k_B T \ln \frac{\nu}{1-\nu} . \tag{2}$$

The diffusion thermopower is given by[27]

$$S = \frac{1}{qT} \frac{\int (\varepsilon - \mu)(-\frac{\partial f_0}{\partial \varepsilon})\sigma(\varepsilon)\mathrm{d}\varepsilon}{\int (-\frac{\partial f_0}{\partial \varepsilon})\sigma(\varepsilon)\mathrm{d}\varepsilon} , \tag{3}$$

where q, ε, and f_0 are the charge (with sign), energy and the distribution function of the carrier, respectively, $\sigma(\varepsilon)$ is a conductivity-like function for carriers of energy ε. In our case, the carrier is the local electron pair, so $q=-2e$; and we have

$$f_0 = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] - 1} . \tag{4}$$

Taking $\sigma(\varepsilon) \approx$constant for the narrow band approximation, and using Eqs.(2), (3) and (4), we obtain the following expression of TEP for the local pair system:

$$S = -\frac{k_B}{2e}\left\{\frac{x}{\sinh x}[-a + \cosh x + \frac{1}{x}(\frac{1}{2}(a + 1/a) - \cosh x)\ln\frac{ae^x - 1}{ae^{-x} - 1}] + \ln a\right\} , \tag{5}$$

where

$$x = W/2k_B T , \tag{6}$$

$$a = \frac{1-\nu}{\nu} e^x , \tag{7}$$

W represents the bandwidth of the electron pair subsystem. In the limiting case $T \to \infty$, we have $x \to 0$ for the finite value of W, then the formula (5) reduces to

$$S = -\frac{k_B}{2e} \ln \frac{1-\nu}{\nu} , \tag{8}$$

which is in agreement with the result by Chaikin et al.[12] The relation between ν and T is given by

$$\nu = (1 - e^{-U/k_B T}) , \tag{9}$$

since we have ν=1 in the ground state and the probability of breaking a local pair at finite T to single particle excitations is proportional to $\exp(-U/k_B T)$. For the same Hamiltonian as given above, Kulik[26] derived the formula of T_c as

$$k_B T_c = W \frac{1-2\nu}{\ln(1/\nu - 1)} ; \tag{10}$$

therefore, x can be written as

$$x = \frac{1}{2t}, \frac{\ln(\nu/(1-\nu))}{2\nu - 1} , \tag{11}$$

where $t' = T/T_c$.

From the two-component theoretic point of view, the local pairs exist above T_c. However, the local pair-breaking process grows with increasing temperature, and then this effect enhances the concentration of the itinerant carriers. Thus, the values of U change with the temperature due to the variation of the screening effect as the local pair-breaking proceeds successively with the change of temperature. At any fixed temperature, we can imagine a fictitious system with a constant value of U, which is equal to the value of U of the practical system to be studied at that temperature. For the fictitious system, starting with the Hamiltonian (1), we can obtain the results of Eqs.(5), (9) and (10). In the same way we can have a series of these fictitious systems corresponding to the various temperatures. The constraint condition that the series of these fictitious systems can describe the behaviour of the same practical system to be studied is that the value of T_c in Eq.(10) must be the same value as our discussed practical system. Using the above-mentioned ideas, now we try to use the formulae (5), (7), (9) and (11) to describe the experimental data of the TEP of Y-123 in the low-temperature region ($T_c < T \leq 125\,\mathrm{K}$). Empirically, it has been found that the following relation is approximately available near T_c:

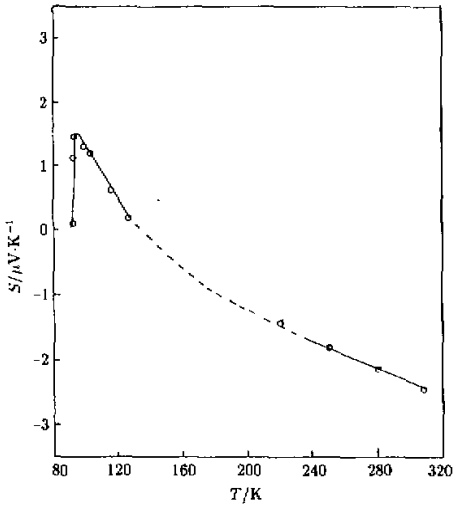

Fig. 1. Theoretical thermopower curve $S(T)$ from Eqs.(5) and (13) (solid line) in comparison with the experiment[2] (○); Dashed curve is drawn to guide the eye.

$$U - W = C(T - T_x)\,, \qquad (12)$$

with C=1.4062, T_x=92.309 K, and the unit of U and W is K in this formula. On the right side of the sharp peak (S_m) of TEP, the formula (12) with different values of C and T_x is still available up to about 125 K (C=0.53210, T_x=91.497). For $T \leq 125\,\mathrm{K}$, the theoretical value of S can then be obtained using Eqs.(5), (7), (9), (11) and (12), as shown by the smooth curve in the low-temperature region in Fig.1. Overall, the above-mentioned theoretical results of $S(T)$ for $T \leq 125\,\mathrm{K}$ are consistent with experiments. On the left side of the sharp peak (S_m) of TEP, it approaches to zero rapidly with decreasing temperature. On the right side of S_m, there is an approximately linear relation between S and T.

III. DISCUSSION

First, we make some discussions about the temperature region of about 220 to 300 K

and the intermediate temperature region (~130 to 220 K). We have found that the formula of the diffusion thermoelectricity in the free electron approximation can be used to express the experiment of S in the temperature region of about 220 to 300 K,

$$S = -\frac{k_B}{e}\frac{\pi^2}{2}\frac{k_B T}{\zeta_0}\ (\mu V \cdot K^{-1})\ , \tag{13}$$

where ζ_0 is the thermodynamic potential of the itinerant electron system for T=0 K. It is determined to be 4.9 eV from the experiment of S at T=220–300 K. The theoretical results from Eq.(13) are consistent with the experiment of S in this temperature region, as shown in Fig.1. This fact shows that a gradual transition occurs in the intermediate temperature region which ranges from about 130 to about 220 K, i.e., from the regime in which the local electron pair subsystem is dominating to the regime (T>220 K) in which the itinerant electron subsystem is dominating. Accompanied with the decrease of ν with increasing temperature, the contributions to S from the local pair subsystem decrease. That S changes sign (from positive to negative) at T ~130 K marks the ceasing to be in the leading role of the local pair subsystem in the contributions to S. However, from about 130 to 220 K, the two subsystems still compete with each other. The TEP in this intermediate temperature region is the weighted sum

$$S = \left(\frac{\sigma_p}{\sigma}\right)S_1 + \left(\frac{\sigma_s}{\sigma}\right)S_2\ , \tag{14}$$

where σ_p and σ_s are the conductivities of the local pair subsystem and the itinerant carrier subsystem, respectively (with total conductivity $\sigma = \sigma_p + \sigma_s$), and S_1 and S_2 are the contributions to S from Eqs.(5) and (13), respectively. The detailed calculation of σ, σ_s and σ_p needs further work. However, because the contribution from S_1 is already negligibly small in comparison with S_2 from below near 130 K, as a rough estimation, it has been found that the values from $S \approx (\sigma_s/\sigma)S_2$ are at least correct in the order of magnitude in the intermediate region.

From our analysis of the TEP data of Y-123, we have found that the value of U of each local pair is small (only about 250 K on the average) in the region of about 125–220 K. However, the values of U increase rapidly with decreasing temperature near T_c (e.g. U ≈550 K at T=92.5 K). The bandwidth of the local pair system can be obtained from Eq.(10). It becomes narrower as the temperature is higher and in the region of higher temperatures (about 130 K) the role that each local pair acts as a local center is strengthened.

IV. CONCLUSSION

In summary, using the formula of TEP for the local pair model we have succeeded in describing the TEP of Y-123 in the low-temperature region ($T \leq$125 K). In the higher temperature region (T ≈220–300 K) the TEP of Y-123 is consistent with the diffusion thermo-

electricity in the free electron approximation. From our point of view, there is a competing process between the two subsystems (i.e., the local pair subsystem and the itinerant carrier subsystem) as the temperature varies, especially for the region of $125\,\mathrm{K} \leq T \leq 220\,\mathrm{K}$.

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