Journal of Alloys and Compounds, 195 (1993) 623–626
JALCOM 7543

INFLUENCE OF THE GRANULARITY ON THE THERMOELECTRIC POWER OF POLYCRYSTALLINE $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ SUPERCONDUCTORS.

O. Cabeza, G. Domarco, J.A. Veira, A. Pomar, C. Torrón, A. Díaz, J. Maza and Félix Vidal.

LAFIMAS, Dpto. de Física de la Mat. Condens. Univ. de Santiago de Compostela. 15706 Spain.

Abstract

We first present an empirical picture of the influence of the sample structural inhomogeneities, at length scales much larger than the superconducting correlation length amplitude, on the thermoelectric power, S(T) in copper oxide superconductors. Then, we present experimental results on S(T) near the superconducting transition obtained in two polycrystalline $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ samples with different granularity. In full agreement with our empirical model, our results show that the reduced temperature (ε) behaviour of the thermopower excess near but above the transition, $\Delta S(\varepsilon)$, is the same for the two different samples. For completness we also analize the excess of the thermopower coefficient, $L \equiv S\sigma$.

1. Introduction.

The interplay between structural and compositional inhomogeneities and transport properties has been an important research subject of the metallic low temperature superconductors (LTS).[1] In the case of the high temperature copper oxide superconductors (HTSC) such an interplay is still more crucial, mainly due to their very short superconducting correlation length, $\xi(T)$, in all directions. $\xi(T)$ is given by[1]

$$\xi(T) = \xi(0)\, \varepsilon^{-1/2} \quad ,$$

where $\xi(0)$ is the correlation length amplitude (i.e., at T=0), and ε is the reduced temperature (see later). As $\xi(0)$ is of the order of the interatomic distances, the different inhomogeneities, even at very short lengths, may affect the superconducting properties.[2] In addition, due to the complexity of the chemistry of these compounds, most of real HTSC presents some type of inhomogeneities.[3] So, the studies of the micro-structure influence in the transport properties of HTSC is interesting for both, the fundamental and the practical point of view.

In this work we will study the influence of structural inhomogeneities at large length scales (i.e., at scales much bigger than the superconducting correlation length) on the thermoelectric power near but above the superconducting transition in granular copper oxide compounds. We will first propose an empirical picture to take into account the influence of these long length scale structural inhomogeneities (grains, crystallites, twins...) on the thermoelectric power, S(T), above the superconducting transition. Then, we will confront that approach with our experimental results on S(T) in two different granular $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ samples, all with almost the same composition (y ~ 10) but having different granularity characteristics. A similar study for $Y_1Ba_2Cu_3O_{7-\delta}$ granular samples has been presented previously.[4,5] One of the main interests in studying now the Bi-based system is a direct consequence of the fact that the Bi-based HTSC are much more anisotropic than the YBCO system. This anisotropy manifests directly through the behaviour of S(T) near the superconducting transition: In the mean field region (i.e., from, aproximatively, T_{CO}+1K to T_{CO}+10K) the critical part of S(T) depends as ε^{-1} in Bi-based compounds, whereas it depends as $\varepsilon^{-1/2}$ for YBCO samples[6,7], where $\varepsilon \equiv (T-T_{CO})/T_{CO}$ is the reduced critical temperature.

2. The Empirical Approach

Our main task here is to introduce an empirical relation between the measured thermopower in single phase granular samples having long length scale structural inhomogeneities, S(T), with the intrinsic thermopower in the ab plane, $S_{ab}(T)$, in an ideal single crystal of the same nominal composition. For that, it will be useful to remember first here that a relationship between the measured electrical resistivity, $\rho(T)$, and the intrinsic resistivity in the ab plane, $\rho_{ab}(T)$, above the transition may be obtained through two coefficients, p and ρ_{ct}, associated with the structural inhomogeneities at length scales much larger than the superconducting correlation

0925-8388/93/$06.00

length in all directions. The details may be seen in Refs. 7 and 8.

To obtain now a relationship between S(T) and $S_{ab}(T)$ similar to that for $\rho(T)$ and $\rho_{ab}(T)$, we may assume first that in measuring S, an intensive magnitude, the random distribution of the ab planes and c directions of the grains, crystallites and untwinned domains in a polycrystalline sample is equivalent to a sample having ab and c paths in parallel. Then, we must take into account that S is measured under the condition $J_N = 0$, where J_N is the number current density defined as in Ref. 9. So, by applying such a condition to that sample, the equivalent thermopower, S^e, is easily found to be

$$S^e = \frac{S_{ab}\sigma_{ab} + S_c\sigma_c}{\sigma_{ab} + \sigma_c} \approx S_{ab} , \quad (1)$$

where we have assumed $\sigma_{ab} >> \sigma_c$[10], whereas S_{ab} and S_c are of the same order of magnitude in Bi-based samples[11,12]. Now, the differences between S and S^e are due to the presence in the real granular sample of intergrains and interfaces having some effective thermal resistivity and thermopower. We may thus suppose that only a fraction, $p^s\Delta T$, of the temperature difference, ΔT, used to measure S drops within the intragrains, the other fraction, $(1-p^s)\Delta T$, being associated with the intergrains and interfaces. Therefore, S(T) may be crudely related to $S_{ab}(T)$ by

$$S(T) = p^s\, S_{ab}(T) + S_{ct}(T) , \quad (2)$$

where p^s $(0 < p^s \leq 1)$ is the coefficient that takes into account the relative gradient temperature distribution between intragrains and intergrains, $S_{ct} \equiv (1-p^s)S^e_{ct}$ will be the contribution to S(T) associated with the sample interdomains (grains, crystallites, untwinned regions), and S^e_{ct} is the "effective" thermopower of these sample interfaces. The possible presence of small inhomogeneities (structural or compositional) at short length scales will also arise through S^e_{ct}. Note that p^s will mainly depend on the intragrains and intergrains thermal conductivities and, therefore, p^s will have a weak T-dependence. For $T < T^S_C$ (defined by $S(T^S_C) = 0$), S_{ct} must vanish, and indeed, for a good single crystal $S_{ct} \approx 0$, and $p^s \approx 1$. On the other side, in agreement with the fact that T^S_{CI} $(\approx T_{CI})$ is almost the same for the different samples having the same nominal composition, one may assume $dS_{ct}(T)/dT << dS_{ab}(T)/dT$ near but above the transition, where T^S_{CI} is the temperature where S(T) around the transition has its inflexion point, in analogy with T_{CI} for $\rho(T)$.

So, whereas the amplitude differences between S(T) and $S_{ab}(T)$ will be due to both p^s and $S_{ct}(T)$, variations in the temperature behaviour will be mainly associated with $S_{ct}(T)$.

To analyze the rounding effects of S(T) above the superconducting transition we must introduce the measured excess thermoelectric power, $\Delta S(\varepsilon)$, defined by

$$\Delta S(\varepsilon) \equiv S_B(\varepsilon) - S(\varepsilon) \quad , \quad (3)$$

where $S(\varepsilon)$ and, respectively, $S_B(\varepsilon)$ correspond to the measured and to the background magnitudes (this last related with the normal temperature behaviour in the background region, see later). Here ε is the reduced temperature defined as

$$\varepsilon \equiv \ln\frac{T}{T^S_{CI}} \approx \frac{T - T^S_{CI}}{T^S_{CI}} \quad . \quad (4)$$

The excess of S(T) in a granular sample may be related to ΔS_{ab}, the excess in the ab plane of an ideal single crystal, by using the empirical picture presented above. First, by applying Eq.(2) to the background region, we obtain

$$S_B(T) = p^s\, S_{abB}(T) + S_{ct}(T) \quad , \quad (5)$$

where $S_{abB}(T)$ is the background thermopower in the ab plane of an ideal single crystal of the same composition. Then, by combining Eqs. (2), (3) and (5) we obtain

$$\Delta S(\varepsilon) = p^s\, \Delta S_{ab}(\varepsilon) \quad . \quad (6)$$

We see, therefore, that $\Delta S(\varepsilon)$ and $\Delta S_{ab}(\varepsilon)$ are related through a sample-dependent, but almost temperature-independent parameter, p^s. So our empirical approach predicts that the reduced temperature behaviour of $\log_{10} \Delta S(\varepsilon)$ will be close to that of $\log_{10} \Delta S_{ab}(\varepsilon)$.

3. Experimental results and Comparison with the Empirical Approach

Two different granular $Bi_{1.5}Pb_{0.5}Sr_2Ca_2$-Cu_3O_y ceramic samples with y ~10 were used. The samples were prepared by usual solid-state synthesis procedure.[13] Optical microscopy measurements and SEM show that the typical grain and crystallite size of our polycrystalline samples are 1 μm to 50 μm. The crystallites show also a high density of twin boundaries at a length scale larger than 1000 Å.

Figure 1 shows the temperature dependence of the measured electrical resistivity and thermoelectric power for one of the two samples studied here (sample Bi2) around the transition. The dependence of $\rho(T)$ between 150 K and 250 K may be fairly well approximated by a straight line, with $d\rho/dT > 0$. Such a line may be extrapolated through the transition and used as resistivity background.[6,7,8] In the case of S(T), amongst the various possible functional forms for the thermopower in the normal region, we have chosen that proposed in Ref. 12,

$$S_B(T) = \alpha T + \frac{AT}{B^2+T^2} , \qquad (7)$$

where α, A and B are free parameters. We do not

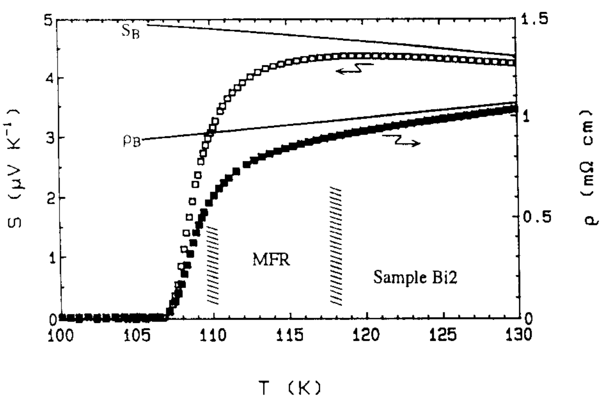

Fig. 1. Temperature behaviour of the measured thermoelectric power (open symbols) and of the measured electrical resistivity (solid symbols) for sample Bi2 near the superconducting transition. The solid lines are the extrapolation of the corresponding background functions to this region. The mean field like temperature region (MFR) is indicated.

claim this functional form to represent better than others the physics of thermopower in the normal state, but it gives a high quality fitting in a wide T-region well above the transition. As our previous $\rho(T)$ results strongly suggest that the OPF effects in Bi-based compounds are not appreciable above 140 K,[6,7,8] we have fitted Eq. (7) between 140 K and 240 K. The fit quality is excellent, the rms for the two samples being less than 3%, including the experimental errors. The mean field like region (MFR) indicated in Fig. 1 corresponds to the temperature region where the Ginzburg-Landau like approaches for the thermodynamic fluctuations of the superconducting order parameter (OPF) are supposed to be valid.

In Figure 2 we plot in logarithmic scale $\Delta S(\varepsilon)$ for the two samples studied here. The results show that the ε-dependence of $\Delta S(\varepsilon)$ is very similar for both samples, and that the amplitudes change moderately among them. These results are in full agreement with Eq. (6) and they indicate that p^s changes moderately (mainly when compared with p) from sample to sample.

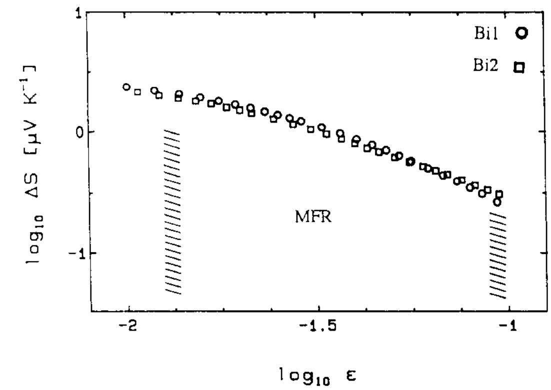

Fig. 2. Log-log plot of the excess of the thermoelectric power, ΔS, vs the reduced temperature for the two samples studied here over the mean field like region (MFR).

For completeness in Fig. 3 we present our results for the thermopower coefficient excess, $\Delta L(\varepsilon)$, defined by

$$\Delta L(T) \equiv L(T) - L_B(T) \qquad (8)$$

where L is defined as usually by $L(T) \equiv S(T)\sigma(T)$. The data in Fig. 3 full confirm our previous results for $YBa_2Cu_3O_{7-\delta}$[4,5] and $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$[5,14],

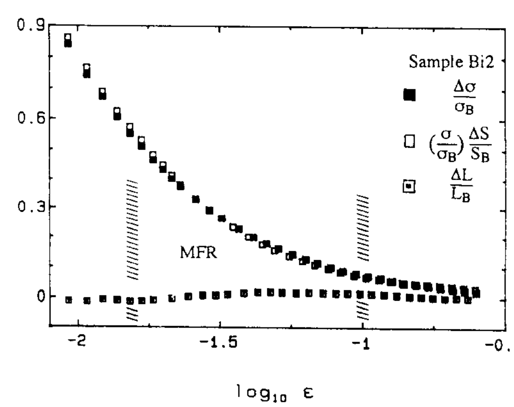

Fig. 3. Normalised excesses of the thermoelectric power (open symbols), electrical conductivity (solid symbols) and thermoelectric coefficient (dotted symbols) vs the logarithm of the reduced temperature for sample Bi2. The mean field like region (MFR) for this sample is indicated.

suggesting that $\Delta L \approx 0$, i.e., that all the critical behaviour of S(T) near T_{CI}^{S} is due to that of $\sigma(T)$. So, $\Delta L/L_B < 4$ % seems to be an intrinsic property of all the copper oxide superconductors. This conclusion seems to agree with recent theoretical results.[15]

By using now $\Delta L(T) = 0$ in Eq. (8), and with help of Eq. (2) and the corresponding for $\rho(T)$,[7,8] it is easy to obtain

$$L(T) = p^S p \, L_{ab}(T) \quad , \tag{9}$$

this expression being, indeed, applicable near the transition, in the region where ΔS and $\Delta\sigma \neq 0$.

In addition, we must note that probably Eq. (9) is more severely affected by the various simplifying approximations involved in our empirical pictures of $\rho(T)$ and S(T), due to the condition $\Delta L(\varepsilon) = 0$ used in its deduction. However, it may serve to check, at least qualitatively, these pictures. In particular, Eq. (9) predicts that, near the transition, the ε-dependence of L(T) will be the same for all the samples with similar composition, independently of their long-scale structural inhomogeneities. This prediction is fairly well confirmed by the experimental results of L(T).

4. Conclusions

We have presented an empirical picture of the influence of the sample structural inhomogeneities, at length scales much larger than the superconducting correlation length amplitude, $\xi(0)$, on the thermoelectric power, S(T). In particular, this approach predicts that the reduced temperature behaviour of the thermopower excess in the mean field region above the transition will not depend on the long length scale structural inhomogeneities. Our results for two $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ polycrystalline samples having different granularity fully confirm the predictions of that approach. Finally, we obtain that $\Delta L \approx 0$ also in this compound.

5. Acknowledgements

This work has been supported mainly by the Programa MIDAS Grant No. 89.3800, and also by CICYT Grant No. MAT 88-0769, the Fundación Ramón Areces, and the Fundación Domingo Martínez, Spain.

References

1. See, e.g., M. Tinkham, in *Electrical Transport and Optical Properties of Inhomogeneous Media*, Edited by J.C. Garland and D.B. Tanner (AIP, New York, 1978), p. 130; A. Kapitulnik and G. Deutcher, J. Phys. A **16**, L225 (1983).
2. See, e.g., J.C. Phillips in *Physics of High-Tc Superconductors*, (AT&T, Academic Press, London, 1989), p. 261.
3. See, e.g., C.H. Chen, in *Physical Properties of High Temperature Superconductors II*, Edited by D.M. Ginsberg (World Scientific, Singapore, 1990), p. 199.
4. O. Cabeza et al., Physica C **185-189**, 1897 (1991).
5. O. Cabeza et al. in *Properties and Applications of Perovskite-Type Oxides,* Eds. L.G. Tejuca and J.L. Fierro, Marcel Dekker Inc., New York (1992), Chap. 5, p. 101.
6. F. Vidal et al., Physica C **156**, 807 (1988).
7. J.A. Veira and F. Vidal, Phys. Rev. B **42**, 8748 (1990); Physica C **159**, 468 (1989)
8. C. Torrón et al., J.Phys.: Condens. Matter **4**, 4273 (1992); C. Torrón et al. (This issue).
9. H.B. Callen, in *Thermodynamics*, (John Wiley, New York, 1966). Chap. 17.
10. A. Poddar et al., Physica C **159**, 231 (1989); Physica C **169**, 43 (1990).
11. C.H. Chen et al., Mod. Phys. Letters B **3**, 295 (1989); M. Pekala et al., Solid State Comm. **76**, 419 (1990); L.M. León and R. Escudero, Physica B **165&166**, 1211 (1990).
12. L. Forro, J. Lukatela and F. Keszei, Solid State Commun. **73**, 501 (1990).
13. M.A. Señarís-Rodríguez et al., Physica C **162-164**, 85 (1989).
14. A.J. Lopez et al., Supercond. Sci. Technol. **4**, S292 (1991).
15. K. Maki, Phys. Rev. B **43**, 1252 (1991), and erratum, Phys. Rev. B **43**, 13685 (1991).