Superconductivity fluctuations in electrical and thermoelectrical properties of granular ceramic superconductors: Homogeneous versus fractal behavior

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(Received 12 March 1990)

Both the electrical-resistivity and the thermoelectric-power temperature-derivative divergences are examined in typical granular ceramic superconductors ($YBa_2Cu_3O_{7-y}$ and $Bi_{1.75}Pb_{0.25}Ca_2Sr_2Cu_3O_{10-z}$). Critical exponents are extracted in the region above the critical temperature. The dimensionality of anomalous superconductivity fluctuations is deduced. The same "universal" behavior is found for the excess resistivity and the excess thermoelectric power in a given system. It is shown that a homogeneous regime and a self-similar (fractal) behavior can be distinguished depending on the samples. The results are discussed in terms of superconductivity paths occurring through surface connections and of different values of the superconductivity ξ_S and percolation ξ_P coherence-length ratio.

MS code no. BQJ421 1990 PACS number(s): 64.60.Fr, 74.70.Vy, 72.15.Jf, 74.40.+k

The behavior of the temperature dependence of the thermoelectric power $S(T)$ is predicted to be intimately related to that of the electrical resistivity $\rho(T)$ (Refs. 1 and 2) but such relationships often grossly misrepresent thermoelectric-power data.[3] Even though the Matthiesen rule[4] can be applied when calculating electron-scattering cross-section contributions to the thermoelectric power, this does not imply that thermoelectric-power scattering mechanisms are additive contributions in $S(T)$ itself.[3,5] However, in the vicinity of a *magnetic* critical temperature T_c, inelastic and elastic scattering of the conduction electrons have been predicted to contribute to $S(T)$ through the same temperature dependence (in terms of critical components[6,7]). In view of the expectation that noncritical scattering process contributions can be weakly temperature dependent near T_c, a simple relationship can thus be expected between the most singular contributions to $d\rho/dT$, and to dS/dT

$$\left.\frac{d\rho}{dT}\right|_c \simeq \left.\frac{dS}{dT}\right|_c . \tag{1}$$

It can be of interest to examine whether such a proportionality holds near other critical points as well, e.g., at superconductivity transitions. Such a result if true would thus be by no means trivial since ρ and S involve different integrals of the dynamic correlation function.[6,8-10] The temperature interval on which Eq. (1) is supposed to hold is certainly material-dependent, however. An obvious restriction on Eq. (1) is that the reduced temperature interval $\epsilon=|T-T_c|/T_c$ be *"small enough."* This restriction might appear to limit the validity of Eq. (1) to the *scaling* region only. However, it might also hold in the mean-field regime if the "background" (noncritical) contribution is smooth. Therefore it is also of general interest to observe the temperature interval validity of Eq. (1) (with respect to the Ginzburg temperature value T_G or, in reduced units, to ϵ_G).[11]

In this Brief Report we complete our paper[12] on precise measurements of ρ with those on S as a function of temperature taken on samples from the same batch for two different types of granular ceramics oxides ($YBa_2Cu_3O_{7-y}$ and $Bi_{1.75}Pb_{0.25}Ca_2Sr_2Cu_3O_{10-z}$). We briefly report on experimental setups and data acquisition first. We discuss the data next and analyze the so-called excess resistivity $\Delta\rho$ and excess thermoelectric power ΔS versus the reduced excess temperature (all terms to be defined below). We show that the same behavior, i.e., the same exponent characterizes the temperature derivative of $\Delta\rho$ and ΔS divergence in a large temperature regime encompassing the critical temperature. The behavior found for the excess resistivity[12] is hereby recovered for the excess thermoelectric power ΔS though the data are (as usual) less precise. Therefore we confirm Eq. (1) in the mean-field regime as well, i.e., where superconductivity fluctuations are not necessarily highly coherent. As in Ref. 12 we thus show that the thermoelectric-power behavior is affected by the granularity of the materials and can present some fractal character (i.e., in the Bi-based sample). Finally we discuss such results in terms of relative values of the superconductivity coherence length and of some percolation coherence length as imagined in the fracton theory of Alexander and Orbach.[13] This leads to the understanding of superconductivity propagation in terms of connecting *two-dimensional* paths.

Experimental details on measurements and synthesis have been presented elsewhere.[14–17] It is necessary to recall that the resistance (R) is measured with a dc current density (I) of the order of 0.2 A/cm^2. The temperature gradient on the sample holder is less than 10^{-2} K/cm.[14] The data for $R(T)$ are highly reproducible for I being a constant. Furthermore, dR/dT is stable but not R versus T for various temperature sweeping rates. Furthermore, the thermoelectric-power (S) measuring method avoids sharp thermal gradients at contact leads.[15] In all cases much care has been taken to eliminate parasitic effects. The temperature sweep rate is low (a few K/h) such that quasistatic conditions are maintained. The sensitivity is about a few nV for voltages and a few 10^{-3} K for temperature. This allows us to take with confidence the temperature derivative of R and S (through a third-order polynomical fit).

The sample granular structure will be seen to be of interest. We do not claim to have optimized in any way the texture for the following considerations. However, the Y-Ba-Cu-O sample is markedly porous and a quasisingle phase.[14] The grains have a linear dimension about 1 μm. The small pore size distribution is peaked near 30 Å. In the Bi-based sample the grains look "more spherical," and are smaller in size with a distribution around the mean linear dimension about 0.1 μm. The sample is also more compact with both much less large and small pores.

The electrical resistance R and thermoelectric power S are similar to those reported in the literature by other authors for the same kind of compounds. The temperature dependence of dR/dT and dS/dT is shown on Figs. 1 and 2 over a temperature range encompassing the so-called "critical temperature" T_c (Ref. 11) even though some discussion may arise[11,18,19] whether such a value is identical to that derived from static properties. Some structure is found at a few degrees below T_c.

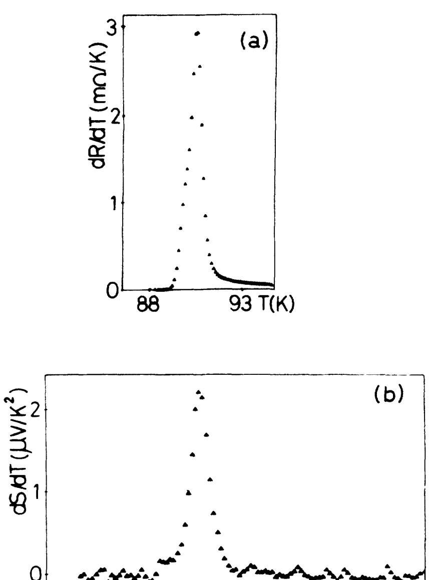

FIG. 1. Plots of (a) electrical resistance (R) and (b) thermoelectric power (S) temperature derivative versus temperature for a $YBa_2Cu_3O_{7-y}$ sample.

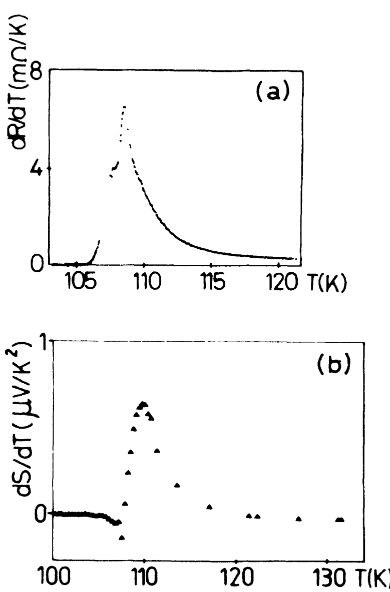

FIG. 2. Same as Fig. 1, but for $Bi_{1.75}(Pb)_{0.25}Ca_2Sr_2Cu_3O_{10-z}$ sample.

For a definite quantitative examination of Eq. (1), plots of dR/dT as a function of dS/dT in the close vicinity of T_c should be given using T as an implicit variable. However, the log-derivatives cannot be taken here since R and S almost vanish below T_c. Since each derivative is obtained in a different experimental run (and obviously this can be hardly avoided). It is necessary to interpolate one of the derivatives in order to find its "exact" corresponding values as measured at each temperature of the other run. In view of the experimental precision as discussed here above this interpolation scheme is just barely acceptable down to reduced temperatures as $\epsilon > 5\times10^{-4}$ or $\ln\epsilon > -7.6$.

It should be emphasized that the data rely then on the previous determination of a particular value for T_c which we found to be slightly varying, i.e., if determined from the maximum of the peak in dR/dT and in dS/dT. Thus much data scattering is found and cannot be totally eliminated in this procedure. On the other hand, due to the weaker precision in dS/dT only a dozen of points or so could be calculated.

Nevertheless a proportionality relation between dR/dT and dS/dT can be seen both below and above T_c, respectively, in both compounds for the whole temperature range investigated. However, visual inspection indicates much departure from linearity in such an analysis which is not thus further pursued here.

On the other hand, a log-log analysis of

$$\frac{d}{dT}(\Delta R)\bigg|_c \simeq A\epsilon^{-(\lambda+1)} \qquad 2(a)$$

and

$$\frac{d}{dT}(\Delta S)\bigg|_c \simeq B\epsilon^{-(\mu+1)} , \qquad (2b)$$

where ΔR and ΔS are the so-called excess resistance and the excess thermoelectric power, i.e., the values of R and S from which a linear background has been subtracted[14–19] leads to values of λ and μ (Figs. 3 and 4). The critical exponents are indicated on the figures. For ΔR (in fact for the excess conductivity $\Delta\sigma$, but this subtlety is not relevant here[11]) the values are predicted in the mean-field region above T_c according to landmark theories.[20–23] Already, in such a region superconductivity fluctuations are expected to be important.[24–27] It could be thought that a Maki-Thompson (MT) theory[22–24] rather than an Aslamazov-Larkin (AL) theory[20] would describe such a region, but the MT prediction only leads to a log divergence near T_c (in two-dimensions and to a very small contribution in three dimensions). However, such a MT term may be expected to be more important than an AL term at *"high temperature."*

In the AL theory, the critical exponent λ of the (excess) resistivity is related to the fluctuation dimensionality D by

$$\lambda = 2 - D/2 \qquad (3)$$

[and from Eq. (1), it is *expected* that $\lambda=\mu$]. Therefore from the values of the slopes on Figs. 3 and 4, it is found that $D=4$ for this $YBa_2Cu_3O_{7-y}$ sample above T_c (between $\epsilon=2$ and 0.07) and $D=2$ for $YBa_2Cu_3O_{7-y}$ between $\epsilon=0.07$ and 0.005. Notice that the crossover between $D=4$ and $D=2$ seems to occur at the same ϵ value in both transport properties.

On the other hand, $\lambda=\mu=\frac{5}{6}$ implies $D=\frac{7}{3}$ for the $Bi_{1.75}Pb_{0.25}Cu_2Sr_2Cu_3O_{10-z}$ sample between $\epsilon=1$ and $\epsilon=0.002$. We stress that such results are valid for *both* transport properties.

In the so-called homogeneous critical regime, i.e., below the Ginzburg temperature T_G,[11] critical exponents $\frac{2}{3}$ and $\frac{1}{3}$ (i.e., slopes $-\frac{1}{3}$ and $-\frac{2}{3}$) are, respectively, predicted to correspond to $\lambda=\mu=1$ and $\frac{1}{2}$, i.e., to $D=2$ and 3. We can only state that such values are not unlikely, and are similar for both transport coefficients R and S (see the parallelism of data on Figs. 3 and 4) but can hardly be treated with confidence here in view of the scarcity of data points. Furthermore, it is unlikely that the critical regime be attained in view of the precision of the data. Therefore we let other investigations clarify the status of Eq. (1) in such a regime, but consider that its validity is confirmed in the mean-field regime for such high-temperature superconductors.

In some sense the above results also place an upper bound on the Ginzburg temperature: T_G is estimated to be at $\ln\epsilon < -6$.[11] Notice that the impossibility to reach a temperature less than T_G can be due to the distribution of so-called critical temperatures in the samples which are just signatures of stoichiometry defects in general.

A fluctuation dimension $D=2$ can be easily understood from the anisotropic crystallographic structure of the Y-Ba-Cu-O compound. A $D=4$ value is awkward, but from Eq. (3) it appears that $\lambda=0$ then. It is known from singular function analysis that such a value indicates a "logarithmic singularity".[28] In fact, Maki and Thompson[22–24] and Lawrence and Doniach[21] have predicted such a logarithmic term for σ (thus for $d(\Delta\sigma)/dT$ and $d(\Delta R)/dT$) as arising from pair breaking-mechanisms (see also Ref. 29). Twins, grain boundaries, and other defects can thus account for such a behavior both on R and on S.

The most anomalous value ($D=\frac{7}{3}$) found in the Bi-based sample can be understood when generalizing Eq. (3) to noninteger D, i.e., when allowing for a fractal description of nonhomogeneous (granular) material. It has often been pointed out that the resistivity vanishes because the superconducting system is a percolation network indeed, i.e., superconductivity is restricted to regions where microscopic mechanisms are active in inducing the phenomenon. We observe here that the percolation mechanism can already be effective above the critical temperature in both transport properties.

According to well-known results in fractal description of percolation networks[13] a structurally quasi-three-dimensional network may behave as a lower dimensionality system from the dynamical point of view. The dynamical behavior should scale as the (so-called fracton) or spectral dimensionality which governs energy

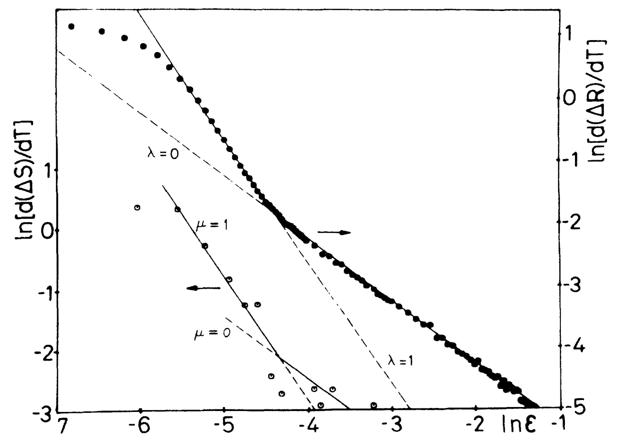

FIG. 3. Log-log analysis of the singular behavior of the excess resistance (ΔR) and excess thermoelectric power (ΔS) above T_c for Y-Ba-Cu-O. Critical exponents are indicated.

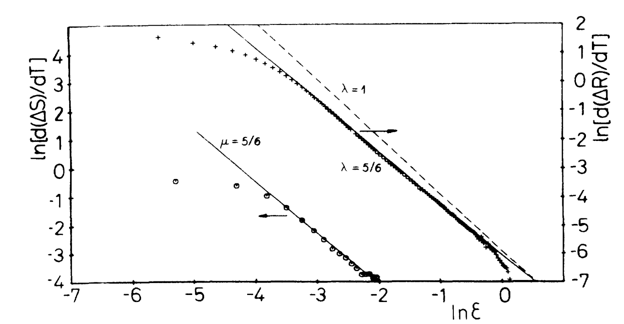

FIG. 4. Same as Fig. 3, but for $Bi_{1.75}(Pb)_{0.25}Ca_2Sr_2Cu_3O_{10-z}$. A line of slope -2 (corresponding to a critical exponent $\lambda=1$ or $\mu=1$) has been shown in order to contrast these results with those of Fig. 3.

diffusion. The (length, and consequently temperature) validity range of this description is usually unknown. However, the lower cutoff is connected to a length of the order of the mean interatomic spacing, but the maximum is as the correlation length ξ_P of the percolation network. This effect can evidently only apply if the superconductivity correlation length ξ_S is of the order *or less* than ξ_P: for larger distance scales, the system has to appear homogeneous and fractal effects disappear. The simple condition ($\xi_S < \xi_P$) for the observation of fracton contribution thus explains the fluctuation apparent difference between $YBa_2Cu_3O_{7-y}$ and $Bi_{1.75}(Pb)_{0.25}Ca_2Sr_2Cu_3O_{10-z}$ compounds. In fact, ξ_S has to be temperature dependent, while in granular materials ξ_P should depend on the grain and pore size distribution. Some crossover could be expected[30] but is not observed here. The length scale ξ_P can be set also by the dimensions of oxygen defective regions, i.e., by superconducting layers or by the carrier mean free path.[11] The granularity is also quite different in both cases indeed, and the superconductivity coherence lengths appear also to differ.[31-34] Thus samples can indeed have distinct behaviors. It remains for other investigations to discuss whether such results depend on specific sample preparations or whether they are intrinsic unavoidable properties.

Finally, notice that the values of $\lambda=\mu=\frac{5}{6}$ for the fractal regime observed in $d(\Delta R)/dT$ and $d(\Delta S)dT$ hides dimension of the fractal network. Indeed, the value $D=\frac{7}{3}$ found here above is "nothing else" than $(1+\frac{4}{3})$, where $\frac{4}{3}$ is known as the fractal dimension for linear-like percolating clusters.[13] Therefore we emphasize that the relevant phase-space dimensionality of the fluctuation spectrum of such superconductors is markedly higher by a single unit than in usual cases. Such a result indicates that the percolation backbone is more *surfacelike* than *pathlike* both in the resistivity and in the thermoelectric power.

In conclusion, we have confirmed the occurrence of similar (or "universal") behaviors between superconductivity fluctuation contributions in *different* transport properties. Fractal or homogeneous regimes can be found (even far away from the critical temperature) depending on the materials.

Finally notice that several authors claim that the fractal nature of the materials and its dynamics contribute to raise the superconducting temperature—suggesting that the selection of granule size and material composition can be optimized to reach a high-T_c value.[35,36]

This work has been financially supported by the NATO research Grant No. 890576. The authors thank Dr. C. Politis (Karlsruhe and La Jolla) for his encouragement, and for making available the Bi-based ceramics.

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[1]J. M. Ziman, *Electron and Phonons* (Clarendon, Oxford, 1960), p. 285.

[2]N. F. Mott, Proc. R. Soc. London Ser. A **156**, 368 (1936).

[3]F. J. Blatt *et al.*, *Thermoelectric Power of Metals* (Plenum, New York, 1976).

[4]K. Durczewski and M. Ausloos, J. Magn. Magn. Mater. **51**, 230 (1985).

[5]E. Gratz and H. Nowotny, Physica B **130**, 75 (1985).

[6]M. Ausloos, Solid State Commun. **21**, 373 (1977).

[7]S. Alexander *et al.*, Phys. Rev. B **13**, 306 (1976).

[8]O. Entin-Wohlman *et al.*, Phys. Rev. B **14**, 4015 (1976).

[9]J. S. Helman and I. Balberg, Solid State Commun. **27**, 41 (1978).

[10]G. Baym, Phys. Rev. A **135**, 1691 (1964).

[11]M. Ausloos *et al.*, Solid State Commun. **73**, 137 (1990).

[12]M. Ausloos *et al.*, Phys. Rev. B **41**, 9506 (1990).

[13]S. Alexander and R. Orbach, J. Phys. (Paris) **17**, L625 (1982).

[14]M. Ausloos and Ch. Laurent, Phys. Rev. B **37**, 611 (1988).

[15]Ch. Laurent *et al.*, Solid State Commun. **66**, 445 (1988).

[16]M. Ausloos *et al.*, Mod. Phys. Lett. B **2**, 1319 (1988).

[17]Ch. Laurent *et al.*, Mod. Phys. Lett. B **3**, 241 (1989).

[18]J. A. Veira and F. Vidal, Physica C **159**, 468 (1989).

[19]F. Vidal *et al.*, J. Phys. C **21**, L599 (1988).

[20]L. G. Aslamazov and A. I. Larkin, Phys. Lett. **26A**, 238 (1968).

[21]J. Lawrence and S. Doniach, *Proceedings of the XII Conference on Low Temperature Physics, Kyoto, 1970,* edited by E. Kanda (Keigaku, Tokyo, 1971), p. 361.

[22]R. S. Thompson, Phys. Rev. B **1**, 327 (1970).

[23]K. Maki, Prog. Theor. Phys. **39**, 897 (1968); **40**, 193 (1968).

[24]K. Maki and R. S. Thompson, Phys. Rev. B **39**, 2767 (1989).

[25]C. J. Lobb, Phys. Rev. B **36**, 3930 (1987).

[26]S. Hikami and A. I. Larkin, Mod. Phys. Lett. B **2**, 693 (1988).

[27]M. R. Beasley, Physica B **148**, 191 (1987).

[28]M. M. Amado *et al.*, Solid State Commun. **65** 1429 (1988).

[29]K. Maki and R. S. Thompson, Physica C **162-164**, 1441 (1989).

[30]J. M. Gordon *et al.*, Phys. Rev. Lett. **59**, 2311 (1987).

[31]T. P. Orlando *et al.*, Phys. Rev. B **35**, 7249 (1987).

[32]H. B. Liu *et al.*, Physica C (to be published).

[33]W. C. McGinnis *et al.*, IEEE Trans. Magn. (to be published).

[34]H. Kupfer *et al.*, Z. Phys. B **71**, 63 (1988).

[35]B. K. Chakrabarti and D. K. Ray, Solid State Commun. **68**, 81 (1988).

[36]M. P. Fontana and D. Cassi, Nuovo Cimento **11**, D783 (1989).