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HOMOGENEITY AND PERCOLATION IN CERAMIC HIGH TEMPERATURE SUPERCONDUCTORS

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The main results of systematic investigation of the electric transport properties and ac susceptibility of ceramic high temperature superconductors (HTS) are presented. An effort has been made to deduce a suitable description for these properties. Due to the presence of the weak links at the grain boundaries the superconducting and the normal state properties of these systems deviate strongly from those of the corresponding homogeneous compounds. Becasue of this, ceramic HTS can be modeled as the two phase systems consisting of grains and 3D disordered array of intergrain links. The variation in the strength of the coupling between the grains determines the bulk critical currents (I_c) of these systems. A more detailed analysis shows that properties of ceramic HTS depend strongly on density and the ratio between the dimensions of the sample and the grain size. Therefore only some properties of fine-grained dense samples can probably be described by averaging the local properties over the volume of the sample. In contrast to that, the resistivity at lower densities, the diamagnetic transition below T_c and the transition to the dissipative state above I_c all exhibit the percolation effects.

1. Introduction

The discovery of quantum mechanics enabled the understanding of the condensed matter. Indeed the basic understanding of the electronic transport, heat capacity and magnetism of solids was perhaps the most prominent early sucess of a new theory. Later work, in which Prof. I. Supek and his coworkers participated[1) lead to a rather detailed (quantitative) understanding of many subtleties of above mentioned properties of solids. More importantly however Prof. Supek realized the importance of this research and together with Prof. M. Paić initiated the research in condensed matter physics in our country.

We note however that the success of application of the contemporary methods of theoretical physics on the condensed matter systems depends to a large extent on whether the material is ordered or disordered. Indeed a quantitative description is primarily achieved for a pure and ordered solids (such as single crystals) whereas many aspects of the disordered condensed matter systems are still not properly explained. At the same time liquids and disordered solids are common in nature and, perhaps more importantly, are among the most promising new materials (amorphous solids, new ceramic materials).

In this paper we wish to discuss the effects of disorder on some properties of special ceramic systems. The ceramic (granular) systems consist of at least two phases (grains and voids) with different properties. In general both these phases are disordered in the sense that there is a variation in position, size and shape of the entities of particular phase throughout the material. Complexity of the problem is probably best illustrated by the fact that most of the contemporary calculations still consider such simple systems as those consisting of spheres (3D), cylinders (2D/3D) or discs (2D). Even in the case of property which may depend on one phase only (as is often the case with electrical conductivity) the disorder in both positions (sites) and contacts (bonds) between the entities of the same phase makes the exact calculations for the real materials impossible.

In general two types of approach are used in order to explain the properties of such systems. The more classical homogenization approach is based on averaging of the (exact) local properties of an inhomogenous system. This basically perturbative approach applies well when the representative volume over which the averaging must be performed is small enough and the system is stable against a small perturbation. In the opposite case the other approach based on the concept of percolation seems more appropriate. Within this approach the system is often treated in terms of an incomplete lattice (missing bonds) and the approach is apparently well suited to some general features of the transition phenomena[2)].

The ceramic high temperature superconductors (HTS) are probably more complex than the ordinary granular systems. In particular HTS are in general strongly anisotropic and the properties of the integranular contacts (weak links) differ in general from those of grains. Because of this we will limit ourselves to an attempt to deduce which property and in what range of parameters is better described in terms of one or another approach mentioned above. Furthermore we shall mainly discuss the critical currents (I_c) of these systems and the occasional discussions of other properties will merely serve to clarify or support our analysis. Although our analysis will mainly be based on the results for $YBa_2Cu_30_{7-x}$ compound (for which the data are most detailed), judging by the similarities in the behaviours of all known HTS, the conclusions reached will probably apply to other ceramic HTS too.

2. *Experimental procedures*

The synthesis of HTS compounds were produced by the usual solid state reaction[3]. The ceramic pellets were obtained by sintering pressed (reacted) powder at predetermined temperature (depending on specific compound YBaCuO or BiCaSrCuO and other requirements) for specified time (usualy 12 hours). The sintering was performed either in air or other controlled atmosphere depending again on the compound selected and special requirements. The standard characterisation of the pellets included X-ray diffraction study, sometimes electron micro-probe analysis of the metal stochiometry was performed. For some samples the morphology and the average size of the grains was studied by the electron microscopy (Fig. 1).

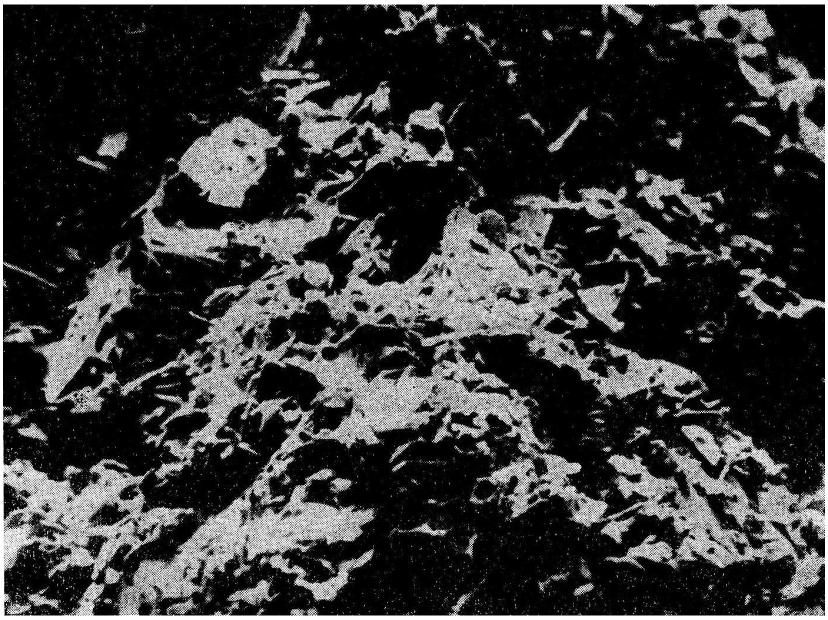

Fig. 1. SEM of a BiPbSrCaCuO *sample showing complex morphology of ceramic superconductors.*

The samples for the actual measurements were in the form of rectangular rods (typically $1 \times 1.5 \times 13$ mm) cut from the central portion of the pellet. The same sample was used for all measurements (resistivity, V-I curve, ac susceptibility and sometimes magnetization). The resistance was measured by a standard ac technique. The V-I curves (in the current range up to 10 A) were measured in a single-shot half-sinusoidal current pulse with width varying from $0.02-12$ s. The critical current I_c was determined from the first non-zero voltage (the voltage resolution was 0.1 μV). This ensured that the effective resistivity of the sample remained below that of Cu at 77 K even for the lowest I_c values[4]. The V-I curves were also measured in magnetic field ($H \leq 4000$ A/m). Such low field ensured negligible penetration into the grains of sample. In V-I determinations temperatures in the range 63 − 90 K were achieved with sample immersed in cryogenic bath consisting of either pumped liquid nitrogen ($T < 77$ K) or appropriate mixture of liquid nitrogen and oxygen ($T > 78$ K). The ac susceptibility was measured with special set-up[5)] at 28.4 Hz with the amplitudes of ac field varying from 0.8 A/m to 4000 A/m. A dc field in the same range ($H \leq 4000$ A/m) could have been superposed on ac field. The sample was mounted on monocristalline saphire sample holder which ensured both good thermal contact and no parasitic signal.

3. Results and discussion

3.1. Resistivity, diamagnetism and the nature of superconducting transition

All known HTS were first obtained in ceramic form. The reason was simplicity of the preparation techniques and the fact that desired (optimal) stochiometries were not known in the advance. This however raised a question[3)] whether, or to what extent, the properties of ceramic samples resemble those of a pure ordered compound (it is interesting to note that this question was raised before the results for YBCO single crystals became available). In an attempt to answer this question, we performed the systematic studies of the density (D) dependence of the resistivity, temperature (T_c) and width (ΔT_c) of the superconducting transition, upper critical field (H_{c2}) and ac susceptibility[6)] of $YBa_2Cu_30_{7-x}$ (hereafter YBaCuO) ceramic samples. For these samples, prepared under practically identical conditions, except for the T_c, all the other properties exhibited some variations with density.

Particularly interesting was the variation of resistivity which both immediately above T_c ($T = 95$ K) and room temperature decreased rapidly with increasing D. Recently much the same resistivity variation was observed in BiPbCaSrCuO ceramics. Although a non-linear variation of resistivity with density is expected for inhomogeneous materials, the observed variations (Fig. 2) are much stronger

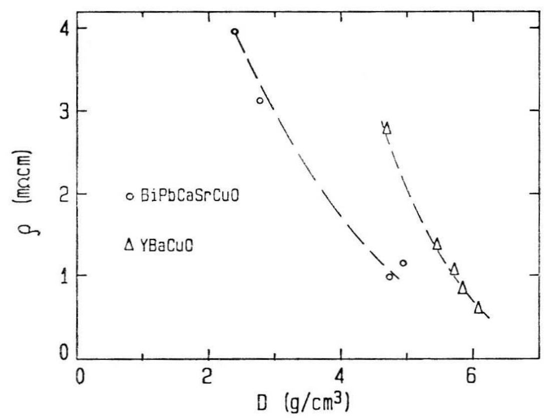

Fig. 2. Variation of resistivity at 300 K *with density for ceramic* YBaCuO (△) *and* BiPbSrCaCuO (○) *samples.*

than that expected for model systems consisting of conducting spheres or cylinders embedded in medium with different conductivity[7)]. Particulary strong deviation of the experimental results from the model predictions[7)] at lower density seem to suggest a percolative nature of conductivity already at these relatively high densities. (The effect of missing links between the entities of conducting phase on the conductivity of material should become more pronounced on approaching the percolation (connectivity) threshold.)

Although sizable percolation effects at relatively high densities (compared to the X-ray densities of given compounds) seem unlikely, the other simple explanations of the observed resistivity variation in terms of impurities or other electronic mean-free-path effects seem to be at variance with other results. In particular the X-ray diffraction patterns did not indicate the impurity phases, whereas neither resistivity (ρ) at elevated temperature (where it varies linearly with temperature) obeyed Matthiessen's rule ($d\rho/dT$ independent of ρ) nor H_{c2} exhibited a square-root variation with ρ, as they probably should if the observed variation of ρ was the mean free path effect. At the same time we note that neither the value of the connectivity threshold nor the variation of conductivity with fraction of conducting phase (thus also D) need be the same for anisotropic granular material as for isotropic one. Because of this the experiments on low-density weakly-sintered YBCO ceramics (similar to those performed[8)] on fine grained Ag ceramics) are required in order to elucidate the variation of resistivity with density in ceramic HTS samples. Such experiments would be of great importance, because they can show whether the connectivity in granular systems is merely geometrical problem (thus solvable in terms of classical percolation theory[9)]) or not.

Already the discovery of the high temperature superconductivity in LaBaCuO indicated a percolative transition to the superconducting state[10)]. In that case however very broad and irregular resistive transition was due to the fact that material consisted of several phases, most of them not superconducting. Later experiments on presumably pure ceramic $La_{2-x}Sr_xCu0_{4-\delta}$ samples indicated strong dependence of the superconducting and normal state parameters on the microstructure[11)] (in particular the average grain size) of the sample. This was a clear indication that the disorder in the system of grains (and perhaps more importantly the associated disorder in the intergrain links) governs the superconducting transition. Later on an approximately log-normal distribution of the grain sizes was deduced and the correlation between the grain size distribution (GSD) and superconducting parameters suggested[12)]. Similar conclusions have also been reached from the study of voids and grains in two, unfortunately impure, YBaCuO samples[13)].

However our experiments[3,6)] on better prepared YBaCuO samples have shown that neither T_c nor ΔT_c determined via resistivity measurements show any larger variation with the density of the sample. Moreover the resistivity variation over most of the transition region ($T \to T_c$) can be rather well described in terms of superconducting fluctuations in a 3D system[14)]. We note however that the above findings do not prove that superconducting transition in ceramic HTS is not percolative but merely reflect the fact that resistive measurements of the transition poorly represent the bulk behaviour of a dense material. (Indeed a single superconducting tread runing accross the sample is sufficient to give zero resistance.) At the same time the Aslamazov-Larkin variation of resistivity[14)] over most of the transition range shows that much of the resistivity decrease is due to superconducting transition in grains what further limits the feasibility of investigation of the propagation of superconductivity through the system of intergrain links via the temperature dependence of resistivity close to T_c.

Apparently more representative of the bulk behaviour is the development of the diamagnetism within the sample. However, even for single crystals of YBaCuO the interpretation of the measurements of the Meissner effect is complicated because of complex pattern of the flux penetration into HTS compounds[15)]. For ceramic samples a finite magnetic field used in these measurements affects strongly the superconductivity in the intergrain links, thus the results are more representative of the system of grains than of the whole sample. Because of this the simplest solution is to use ac susceptibility measurements which can be performed with very low amplitude of the exciting field. The variations of the real part of the ac susceptibility χ' with temperature shown in Fig. 3 show clearly that full diamagnetic shielding is established over a narower temperature interval for a denser sample thus confirm the percolative nature of this phenomenon. The technique employed reflects however the diamagnetic screening of the sample by the superconducting shielding currents rather than bulk diamagnetism and Meissner effect. In particular $\chi' = -1$ strictly means that entire sample is diamagnetically shielded by non-disipative ($\chi'' = 0$) surface current. Nevertheless, the above conclusion about the percolative nature of the superconducting transition remains apparently correct.

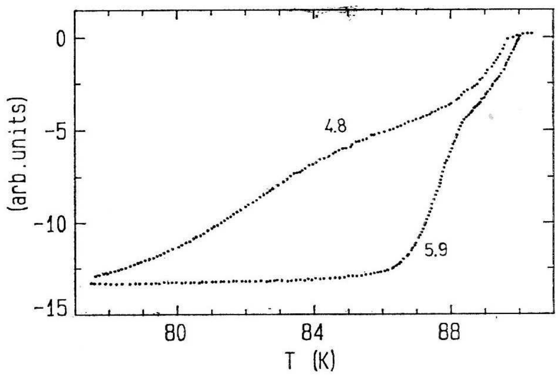

Fig. 3. AC susceptibility of YBaCuO *samples with different densities (4.8 and 5.9* $\mathrm{g\,cm^{-3}}$*, respectively) as a function of temperature.*

The χ' curves in Fig. 3 show that a diamagnetic screening in ceramic HTS occurs in two steps[6,16)], one associated with the system of grains (step at higher temperature) and the other with screening of the entire volume of the sample (thus with flow of shielding currents between the grains). Indeed the first step remains practically unchanged in powdered samples[6)] whereas the other one (absent for isolated grains) reflects the approach to the phase coherence in the network of links between the grains. Therefore these results allow the definition of the phase coherence temperature (T_{cs}) signifying the transition of the whole sample to non-disipative state ($\chi'' = 0$). Indeed later measurements of the remanent magnetization have proven the existence of the persistent integranular currents[17)] below T_{cs}, thus confirming the existence of such state in ceramic HTS. Such behaviour is analogous to that observed in conventional composite superconducting materials, such as the superconductor-normal metal composites[18)], but in ceramic HTS two phases: grains and disordered 3D network of weak links between these grains are made out from the same material. As in conventional composites the latter phase determines the bulk superconducting properties and is in particular responsible for several orders of magnitude lower critical current densities (J_c) in random (non-textured) HTS ceramics than those in single crystals (also grains) or epitaxial thin films[19)] of the same compounds. The methods for separation of the intra- and intergrain effects and in particular intra- and intergranular critical currents from the ac susceptibility and/or magnetization measurements have been discussed elsewhere[16,20,21)].

3.2. Intergranular (bulk) critical currents and the nature of weak links

According to above, the intergrain critical currents are related to the strength of coupling between the grains. Therefore the homogenization type of approach would seem appropriate in order to provide an explanation of the magnitude and variations of bulk (intergranular) critical currents in ceramic HTS. In particular, one has to find out the nature of the intergrain links and then model the system as a 3D network of links with suitably varying strengths. Already first microwave experiments on ceramic YBaCuO, in addition to showing that the electron pairing is responsible for superconductivity, indicated the existence of the Josephson junctions presumably at the grain boundaries. Indeed the observed variation of bulk critical current (irrespective whether it was determined from transport measurements or deduced via the Bean model from the magnetization measurements) with magnetic field (Fig. 4) is reminiscent of the Fraunhoffer diffraction pattern,

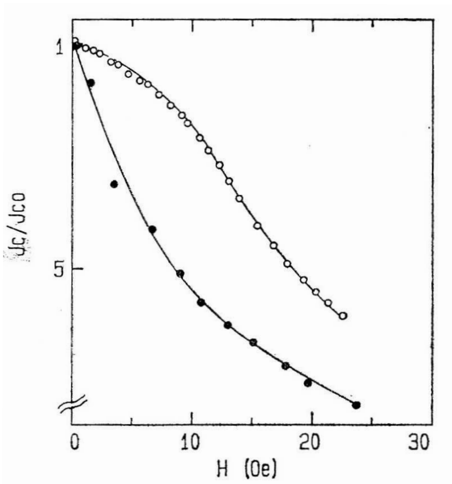

Fig. 4. Variation of critical current at 80 K *(normalized to its value in zero applied field) with magnetic field* (1 Oe = 79.5 A/m) *for two ceramic* YBaCuO *samples exhibiting self-field limited* (○) *and intrinsic* (●) *behaviour, respectively.*

$I_c \sim |\sin(\pi B/B_0)/(\pi B/B_0)|$ with B_0 in resonable agreement with one for planar Josephson junction, where $B_0 = (\Phi_0/(\tau + 2\lambda)d)$ (Φ_0 is the flux quantum, τ is the thickness of the insulating layer, λ is the London penetration depth and d is the length of the junction-comparable with the grain size). Subsequently a simple homogenization approach[22] (the averaging over an assumed Gaussian distribution of the junction parameters) was shown to yield the variation of I_c with magnetic field (H) rather similar to the observed ones. The observed quasilinear or slightly concave (upwards or downwards) variation of I_c with temperature (Fig. 5) were also consistent with those predicted for different types of Josephson junctions[23] (SIS, SNIS etc, where S denotes superconductor, I is an insulator and N normal metal).

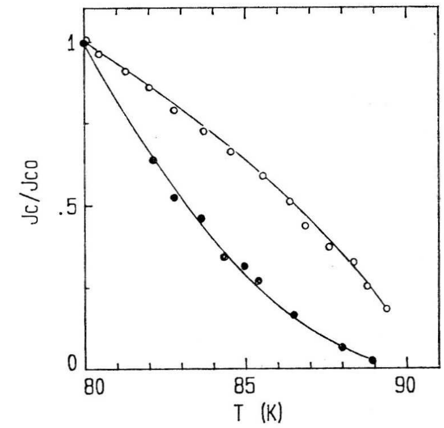

Fig. 5. Variation of normalized critical current with temperature for two ceramic YBaCuO *samples exhibiting self-field limited* (○) *and intrinsic* (●) *behaviour, respectively.*

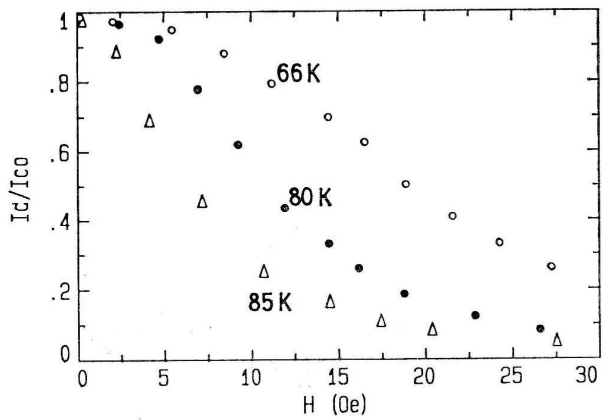

Fig. 6. Vairation of normalized critical current with magnetic field (1 Oe = 79.5 A/m) *for an* YBaCuO *sample exhibiting the self-field limited behaviour at different temperatures.*

However the magnitude of bulk critical current densities J_c for ceramic YBaCuO samples were sizably lower than those obtained from the model-based estimations[24)] or from direct measurements of current between two grains in a thin film[25)]. Furthermore, the observed variation of J_c (or I_c) with H depends strongly on temperature. In particular B_0 increased strongly on decreasing temperature (Fig. 6). This would not be expected for the Josephson junctions in which B_0 depends on d and λ only, and λ is practicaly insensitive of temperature for $T/T_c > 0.9$.

The simplest explanation of the observed behaviour (Fig. 6) is that I_c is limited by its own magnetic field. Indeed the self-field, H_s of the current is proportional to current itself and the effect of an external field H on the self-field limited I_c becomes significant when the amplitude of H exceeds or becomes comparable to H_s. The concave upward variation of I_c with T at lower temperature is similarly explained: when full H_s (characteristic of a given sample) is reached, I_c tends to saturate (Fig. 5). Simultaneously, the investigation of the influence of reduction in the cross section of a given sample[26,27)] on its J_c gave a direct evidence that in majority of ceramic YBaCuO samples J_c is self-field limited. The observed variation $J_c \sim r^{-1}$ (r is the radius for cylindrical sample) is indeed the evidence that I_c is limited by its self-field ($I_c = 2r\pi H_s$). The above findings reopened the question of the actual (intrinsic) variations of J_c with H and T (i. e. those which are not affected by the self-field or measuring field inherent to determinations of I_c from transport or magnetization measurements) and thus of the nature of weak links. (Suprisingly, this was overlooked by other scientists.)

Indeed the investigations of I_c through single intergrain boundary did not give clear answer about the nature of the junction[25)] (SIS or SNS). The SIS type seemed to be preferred but we note that even I_c through single junction can be self-field limited (depending on actual J_c) and that the effects of H_s produce the variations of I_c which are similar to those expected for SIS type of junction. At the same time, high resolution electron microscopy (HREM) showed that most of the grain boundaries are clean and showed no larger variations in stochiometry accross the grain boundary. Thus SNS junctions should dominate in single phase ceramic YBaCuO samples.

In order to assess the intrinsic critical current and the nature of weak links in YBaCuO ceramics one has to measure I_c in as low field as possible. The technique ideally suited for this purpose is high resolution ac susceptibility. A straightforward application of the Bean model[28)] shows that the initial linear variation of χ' with the ac field amplitude reflects the intrinsic I_c[29)]. The measurements in different dc magnetic fields (H) and temperatures enable the determination of intrinsic variations of I_c with H and T. Such measurements[30)] yield for clean (monophasic) YBaCuO ceramics $I_c(H) \sim (1 - T/T_c)^2$ for $T \to T_c$. The same variation of I_c with T was recently deduced from the measurements of I_c across a single grain boundary[31)]. The above variations are consistent with those observed for thick SNS junctions[32)]. This outcome seems plausible considering very short coherence length and quite large λ of YBaCuO.

A more detailed evidence that self-field effects mask the intrinsic variation of

I_c was recently obtained[33] by measuring the behaviour of I_c in a sample with very low J_c ($J_c = 20$ A/cm^2). In that case critical currents through the intergrain links would be to low to produce sizable field and hence the intrinsic behaviour of bulk (transport) I_c may be observed. Indeed the observed magnetic field (Fig. 4) and temperature (Fig. 5) dependences of transport I_c were consistent with those deduced from high-resolution ac susceptibility measurements[30], thus with thick SNS junctions. Moreover, the determinations of J_c of the same sample by means of ac susceptibility measurements (using both the initial linear variation of χ' and the relation between the maximum in χ'' field for full penetration in the sample and I_c[33]) gave practically the same values and variations of I_c as the transport measurements.

3.3. Effects of disorder: the onset of dissipation, percolation and critical current distributions

The description of weak intergrain links in terms of thick SNS junctions explains qualitatively very low and strongly field and temperature dependent critical currents in ceramic YBaCuO samples. For a more detailed understanding of these materials one has to investigate the effects of disorder, i.e. the variation in the strength of intergrain coupling within the sample. The conceptual difficulties associated with such studies have been illustrated in the introduction and here we show that experimental investigations are also non-trivial. In particular the transport critical current is defined by the onset of dissipation which is apparently associated with the least strong active (i.e. those through which the current actually flows) intergrain links. Therefore the transport I_c (or J_c) is not directly related to total variation in the intergrain coupling within the sample and hence cannot be simply related to the bulk properties of the sample[34]. Similarly, J_c determined from the initial variation of χ', although practically unaffected by the magnetic field, is also limited by the weakest intergrain junctions along the path of the current. Some knowledge about the variation in the strength of intergrain coupling could however be obtained from the accurate investigation of V-I curves over a broad current range[30,34].

Only a few reasonably accurate measurements[35,36] of the onset of dissipation (V) in ceramic HTS have been reported. (High resolution SQUID voltmeters are not readily usable with ceramic HTS.) Typical results for granular YBaCuO are shown in Fig. 7. The observed V-I curves are similar both to those for conventional type II superconductors[37] and conventional normal metal-superconductor (S-N) composites[18]. However, whereas the depinning of vortices causes the dissipation in type II superconductors, in composites this occurs due to the resistive transition of weak links in which current exceeds the local critical current. Since according to Sect. 3.2 there is no essential difference between the behaviour of HTS and S-N composites the same mechanism may explain their V-I curves. This suggests the explanation of the initial part of V-I curve in terms of classical percolation

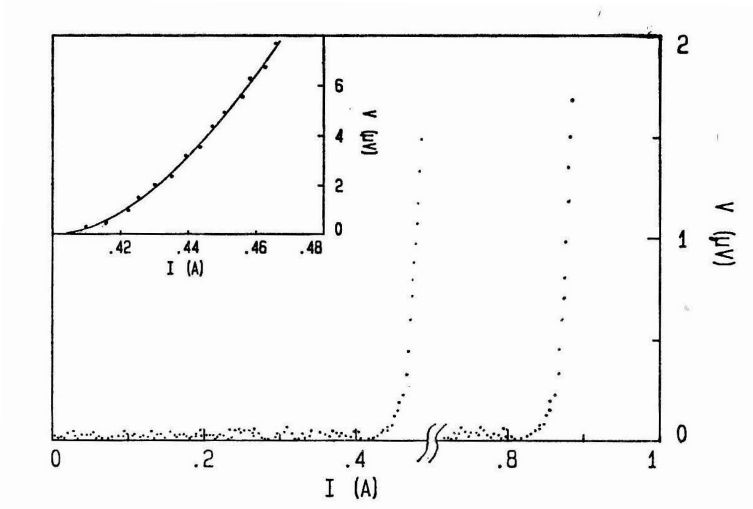

Fig. 7. Initial parts of V-I curves for an YBaCuO *sample at two different temperatures (80* K *and 70* K*, respectively). The inset: A fit of the experimental points to the power law* $V(I) \simeq (I - I_c)^n$.

approach such as that used for the explanation of random resistor or better still diode networks[9)]. In particular, diodes can be replaced with superconductors and the variation in voltage thresholds (v_g) with that in critical currents (i_c) of individual superconductors (bonds). For such array the overall V-I characteristic will exhibit three regimes:

i) At low currents, i.e. I lower than some threshold value I_c the current flow across the lattice will be nondissipative ($V = 0$).

ii) At sufficiently large currents, $I > I_{c\,max}$ a linear (ohmic) variation of V with the coefficient equal to effective resistance of a given array of (now) resistors will be established.

iii) At intermediate currents, $I < I_c < I_{c\,max}$, the increase of V will be nonlinear due to progressive enrichement of dissipating elements (bonds) as I increases.

In the regime iii) a small increase in I (dI) beyond I_c causes corresponding increase in the number of dissipating elements (dn). Realizing that corresponding increase in resistance is also proportional to dn follows

$$V \sim (I - I_c)^2. \tag{1}$$

Our results for a typical YBCO sample (Fig. 7) also exhibit an initial power law variation

$$V = k(I - I_c)^n, \tag{2}$$

but with the exponent typically in the range 2 to 2.8, i.e. close but somewhat larger than that predicted by Eq. (1). The exponent n is practically insensitive to temperature ($66 < T < 85$ K) and magnetic field ($H < 2500$ A/m). Similar results have been reported for polycrystalline Bi-Sr-Ca-Cu-O films[36)], where from 20 − 74 K the data are fitted by Eq. (2) with n in the range 2 to 3. This self-similarity in I-V onsets (Eq. 2) demonstrates that, once the critical current of the random weak link network has been exceeded, the dissipation is primarily a function of the excess current, and depends only weakly on temperature and magnetic field. Therefore the initial parts of I-V curves of ceramic HTS seem to exibit some universal features characteristic for percolative transition. We note here that the existence of power law behaviour (in contrast to for example, an initial exponential variation of V in conventional type II superconductors[37)]), i.e. Eq. (2) rather than $n = 2$ (Eq. (1)) is the indication of the percolative transition. Indeed $n = 2$ in Eq. (2) was the consequence of assumed random (uniform) distribution of i_c's which we have taken over from the analogy with diode network with uniform distribution of v_g's. Different distributions of critical currents (thus of the strengths of the intergrain couplings) will apparently produce different exponent n in Eq. (2).

According to the above, the knowledge of actual distribution of critical current within the ceramic HTS sample is very important. Fortunately the statistical method which allows the determination of critical current distribution (CCD) within the superconducting sample from the experimental V-I curve has been found a long time ago[38)]. Although derived for conventional type II superconductors, where the local variation in I_c is associated with that in pinning force of the vortices, this method is applicable to any system in which there is a local variation in I_c[39)]. thus to ceramic HTS samples too[34)]. For the sake of clarity we shall briefly review the basic relations relating V-I and CCD curve.

The potential difference developed across the sample[38)] is:

$$V(I) = A \int_0^I (I - I')f(I')\mathrm{d}I', \tag{3}$$

where I' is the local critical current, $f(I')$ is the normalized distribution of I' in the sample and A is the factor describing the dissipation process in the portions of sample where $I > I'$. The effective resistance is:

$$R(I) = A \int_0^I f(I')\mathrm{d}I'. \tag{4}$$

At elevated currents, the integral in Eq. (4) becomes one. In this regime (described in ii) above), the effective resistance (called the differential or slope resistance R_f) is equal to A. Accordingly the dissipating (resistive) fraction of the sample at a given current is $FD(I) = R(I)/R_f$. (For ceramic superconductor $FD(I)$ refers to intergrain junctions rather than whole volume of the sample.) The CCD curve is than obtained by differentiating $FD(I)$ with respect to I,

$$f(I') = (1/R_f)(\mathrm{d}^2V/\mathrm{d}I^2). \tag{5}$$

The CCD curve for the sample from Fig. 7 is shown in Fig. 8.

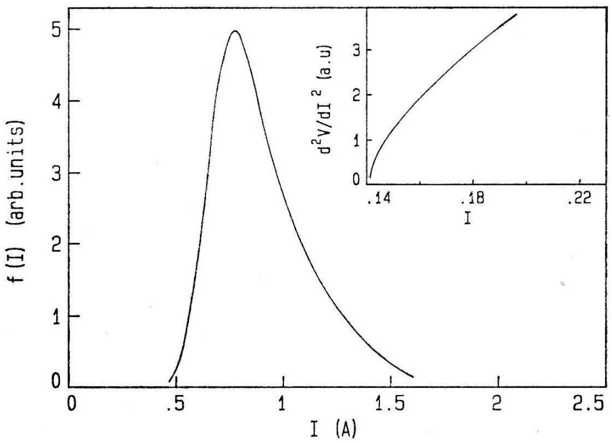

Fig. 8. Critical current distribution (CCD) for YBaCuO *sample from Fig. 7 at 80* K. *The inset: initial part of CCD curve for the sample at 85* K *shown in an expanded scale.*

The assymetric bell-shaped CCD curve shown in Fig. 8 is clearly a consequence of the disorder in 3D network of weak links between the grains. Indeed the grain size distributions[12)] (GSD) and CCD curves for ceramic YBaCuO samples have very similar shape and seem to be described rather well with the log-normal distributions[40)]. Unfortunately no measurements of GSD and CCD curves for the same sample exist so far. Therefore one cannot investigate in a more detail this similarity. Since the GSD is closely related to preparation conditions, such studies would be both conceptually and technologically very important.

The parameters characterising the CCD curves of ceramic YBaCuO samples (i.e., I_{cp}, $\langle I_c \rangle$ and I_{cm} denoting the most probable, average and maximum critical current for a given distribution, respectively) as well as their dependences on magnetic field and temperature have been discussed elsewhere[30,34,40)]. The magnetic field affects most strongly the initial part of CCD curve, thus I_c (the weakest links) whereas its effect on I_{cm} (the strongest links) is much reduced, which supports the relation of a non-linear part of V-I curve (Eq. (3)) to the variation in the strength of intergrain coupling within the sample. The maximum critical current density J_{cm} (corresponding to I_{cm} in the CCD curve) depends on the sample but does not exeed about 1000 A/cm^2 for non-textured ceramic YBaCuO at 80 K. This gives a little hope for the high-current applications of such samples. The CCD curves of ceramic YBaCuO-Ag composites have also been investigated[41)]. Such composites often show an increase of J_c in respect to that of a pure YBaCuO sample prepared under the same conditions. However CCD curves revealed that Ag shifts somewhat the initial part of the CCD curve to higher current (thus improves J_c) but does not affect its high current side (thus J_{cm}). Therefore such composites do not provide a solution for the large scale applications of YBaCuO. Because of this the solution should be sought in specially prepared grain-oriented polycrystalline samples which poses a rather difficult technological problem.

Above I_{cm}, V-I curve becomes linear with a slope R_f. The ratio R_f/R_n (where R_n is the resistance at 95 K, just above the superconducting transition of a whole sample) is particularly important because it can reveal the nature of the dissipation (intergrain junctions being driven normal for $I > I_{cm}$) and the resistive properties of weak link network (the grains remain superconducting above I_{cm}, thus do not contribute to the resistance). The relation of R_f to the actual weak link network has been recently[42] clearly shown by studying the variation of R_f/R_n with the average grain size (AGS) in ceramic YBaCuO samples. The AGS of these samples varied from 10 to 100 μm. A strong non-linear decrease of R_f/R_n on increasing AGS consistent with the assumption that weak link network determines R_f, has been observed. Of course the variation in AGS also affects the corresponding CCD curves of these samples too. In particular the CCD curves for samples with larger AGS were relatively broader than those for smaller one as could be expected on the ground of broader GSD in coarse grained samples. Perhaps even more important was the observation that the ratio between the AGS and the thickness (t) of the sample determines ultimately the behaviour of J_c and the overal CCD in these samples. In particular the behaviour of J_c and CCD changes around specific value of t/AGS. (The most prominent feature of this change is the saturation of J_c below certain value of t/AGS.) This is the clear indication of the percolative nature of the processes involved in I_c of ceramic HTS. The above findings (presently subject of intense investigation) clearly show that, in spite of little if any perspective for the large scale applications of non-textured ceramic HTS, these materials present a great chalenge for the contemporary science.

Finally we briefly outline the relation between the percolative onset of dissipation (iii) and Eq. (2) and the corresponding CCD curve (Fig. 8). The data from Fig. 8 show rather clearly that the initial part of CCD curve (thus presumably the probability density of dissipating bonds) although smeared due to disorder is not constant (the distribution of I' is not uniform) but increases with I. This results in $n > 2$ in Eq. (2). In turn one may obtain a more precise information about the initial variation of CCD by inserting V-I variation from Fig. 7 in Eq. (5). (We note that full CCD requires a measurements over a broad current range which causes a lesser accuracy and therefore lack of details, in particular those conserning the beginning and the end of $f(I')$. The result is shown in the inset of Fig. 8. We note rather sharp onset of $f(I')$ followed by somewhat slower variation at currents still close to I_c. Such variation of $f(I')$ seems to suggest that dissipation is associated with the almost simultaneous transition of sizable fraction of weak links. Therefore it is reminiscent of the results of numerical investigation of I_c in a model polycrystalline HTS thin film (2D system) which indicate that a continuous line of resistive bonds running across the sample appears at I_c[43]. In analogy with this result (which however requires direct experimental verification) one can imagine that resistive area running across the bulk ceramic HTS sample forms at I_c. The arguments for the percolation theory can be used in order to deduce the actual shape and location of this normal interphase. Indeed our recent experiments on YBaCuO sample supplied with three voltage contacts along its length indicate rather localised transition to dissipative state. Apparently more detailed experiments along these lines are highly desirable.

4. Conclusion

Ceramic high temperature superconductors (HTS) are complex granular systems which could be considered as consisting of two phases (grains and intergranular links, respectively). Both these phases are disordered and although made out of the same material (in clean samples) have distinctly different superconducting properties. The above makes the theoretical treatment of these materials very difficult and the achievement of solution for some property is in general impossible. Whereas in the normal state the properties of ceramic HTS sample depend in general on both phases, some superconducting properties (in particular bulk critical currents) due to a large difference in the relevant parameters for two phases depend primarily on the actual 3D-disordered array of intergranular (weak) links.

However, this fact is not sufficient in order to obtain the exact description of their superconducting properties.

The purpose of this paper has been to test the applicability of two approaches commonly used for the description of granular systems[9)] to ceramic HTS and at the same time to present some new results indicating percolative nature of the transport properties and superconducting transition in these systems. Apparently the homogenization approach (see Introduction) should apply well when "the building blocks" of the material are small enough compared to the dimensions of the sample. This in case of ceramic HTS suggests rather dense samples with rather narrow grain size distribution (GSD) and the average grain size (AGS) much smaller than the smallest dimension of the sample. The above approach also requires the exact knowledge of the building blocks of the material, in particular the nature of weak links in ceramic HTS. This however is not an easy task due to fact that the outcome depends on actual preparation conditions for a given sample and because of self-field (due to flow of current through the sample) effects on the measured (bulk) critical current and its variations with the magnetic field and temperature. However even when these obstacles can be solved the homogenization approach (based on averaging) cannot give an adequate explanation of the transition phenomena in these systems (such as the transition from conducting to an insulating state or from superconducting to resistive (dissipative) state). These phenomena are associated with percolation in a disordered inhomogeneous system and therefore cannot be explained by simple averaging procedure. The results presented in this paper support the above assumptions.

In particular, the resistivity in the normal state as well as the differential resistance (a slope of V-I curve well above I_c but below T_c) of dense fine-grained ceramic HTS samples can presumably be described by suitable averaging over the local properties of a sample. However a strong increase of resistivity on decreasing density seems to indicate the approach to percolation already at densities which are considerably higher than the coresponding ones for conventional granular (3D) systems[8)]. This could be related to strong conductivity anisotropy inherent to HTS compounds.

Whereas a large contribution of superconducting fluctuations in the resistivity of grains tends to mask the nature of resistive transition in dense ceramic HTS samples, the development of diamagneitism clearly shows the percolative nature of the superconducting transition. Moreover the temperature at which the phase coherence in a disordered 3D network of weak links establishes becomes progressively lower in less dense samples. The ac susceptibility measurements also enable the determination of intrinsic critical current densities (i.e. those which are not affected by self-field or trapped field) which is not possible with other methods (such as transport or magnetization measurements). The J_c values obtained by this method are however also limited by the weakest intergrain links and therefore are not directly related to the bulk (average) properties of the sample.

The critical current distributions (CCD) deduced from the V-I curves measured over a broad current range characterise probably the best ceramic HTS samples. Broad bell shaped CCD curves are reminiscent of the grain size distributions (GSD) in these samples and are apparently related to the variation in the coupling strength within the disordered 3D array of the weak links in a given sample. The parameters deduced from these curves are related both to the average properties of the sample (the average $\langle I_c \rangle$ and the most probable I_{cp} critical current) and to the limiting coupling strengths (the lowest I_c and the maximum I_{cm} critical current) within the sample. Because of this CCD curves have both the scientific and technological relevance (i.e. they may provide the most detailed information about the progress made in preparation of the sample). From the scientific point of view perhaps the most interesting is the initial part of V-I curve (the onset of dissipation). The power law behaviour of V observed so far for all ceramic HTS samples is not consistent with the flux creep (which causes the onset of dissipation at finite temperatures in conventional type II superconductors[37)]) but merely reflects the percolative nature of the transition to dissipative state in these samples. Moreover, rather low values of the exponents ($2 < n < 3$) observed both by us and other researchers[36)] seem to indicate that this transition occurs rather abruptly probably at some specific area intersecting the sample.

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HOMOGENOST I PERKOLACIJA U KERAMIČKIM VISOKOTEMPERATURNIM SUPRAVODIČIMA

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Prikazani su rezultati sistematskih istraživanja elektronskih transportnih svojstava i inicijalne (ac) susceptibilnosti keramičkih visokotemperaturnih supravodiča (VTS). Načinjen je pokušaj da se odredi najprikladniji opis tih svojstava. Keramički VTS mogu se opisati kao dvofazni sistemi sastavljeni od zrna dotičnog spoja i neuređene trodimenzijske (3D) mreže spojeva među zrnima. Raspon u jačini vezanja među pojedinim zrnima određuje ukupne kritične struje (I_c) u tim sistemima. Detaljnija analiza ukazuje da svojstva keramičkih VTS jako ovise o gustoći i omjeru između dimenzija zrna i dimenzija uzorka. Zbog toga se samo neka svojstva gustih, sitnozrnatih uzoraka mogu opisati postupkom homogenizacije tj. usrednjenjem lokalnih svojstava po volumenu uzorka. Nasuprot tome električna otpornost pri nižim gustoćama, dijamagnetski prijelaz i prijelaz u disipativno stanje iznad I_c su perkolativne pojave te se ne mogu opisati postupkom homogenizacije. Posljedica toga je, naprimjer, da napon na manjim gustoćama u neposrednoj blizini I_c slijedi zakon potencija, sa eksponentom praktički neovisnim o temperaturi i primjenjenom magnetskom polju.