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Granularity in superconductors: intrinsic properties and processing-dependent effects

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Abstract

This contribution presents a selected set of results, obtained as part of a systematic investigation, evidencing that many effects exhibited by superconductors are distinct manifestations of granularity which, in turn, is envisaged as a break of symmetry. The Wohlleben effect, the "fishtail anomaly", the magnetic remanence exhibited by Josephson junction arrays, and the jumps on the magnetic moment of superconducting samples of mesoscopic dimensions, are examples which we briefly review and discuss taking granularity as the basic ingredient. The emphasis of the present approach is to recognize the importance of granularity in every scenario intended to explain the magnetic properties of superconducting systems.

Keywords: Granularity; Josephson junction arrays; Intrinsic properties; Critical current

1. Introduction

Due to the smallness of the coherence length, practically any imperfection may contribute to both the weak-link (WL) properties and the flux pinning in high-temperature superconductors (HTS). Such an inevitable dualism brings about a great amount of interesting peculiarities and anomalies, many of which have been tentatively explained in terms of the granular character of HTS materials. Examples of these intriguing features are the Wohlleben effect (WE) [1–3] on the field-cooled magnetization (M); the fishtail anomaly [4–11] on the magnetic field dependence of the isothermal magnetization; the magnetic remanence observed in Josephson junction arrays (JJAs) [12–14]; and the occurrence of jumps on the magnetic response of mesoscopic samples submitted to an external magnetic field (H) [15].

Since some of these anomalies were also observed in macroscopic single crystals and single-domain thin films of both high- and low-temperature superconductors (LTS) [16,17], one is compelled to consider that there might be at least two levels of granularity in HTS materials. The larger of these two scales would match the typical grain size, being responsible for intergranular effects. The other level, usually called intrinsic, would reside within the grains, being responsible for the inherent magnetic properties of such materials. Although a broad variety of alternative scenarios have been proposed by authors to explain most of these effects [18–22] (for instance, the existence of

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π-junctions or the capture of compressed flux, in connection with impurities and/or inhomogeneities, etc.), none of them embraces the complete set of oddities. This contribution presents a selected set of results, obtained as part of a systematic investigation, evidencing that, in reality, all these effects are distinct manifestations of granularity.

2. Granularity in superconductors

Granular superconductors can be envisaged as a collection of superconducting grains embedded in a weakly superconducting- or even non-superconducting matrix. For this reason, granularity is a term intimately related to HTSs, being ordinarily invoked to justify the fact that magnetic and transport properties of these materials are usually manifested by a two-component response. One of these components represents the intragranular contribution, associated to the grains which exhibit ordinary superconducting properties. The other component originates from intergranular material, being thus associated with WL superconductivity. In this sense, intragranular properties would be inherent, while intergranular, on the contrary, would be extrinsic, generating effects dependent on the processing conditions. In spite of this natural association, granularity in superconductors became a matter of study even before the advent of HTSs. For instance, pressed pellets of LTSs were used in the 1970s as a way to create defects in a controlled manner, in order to study the enhancement of the critical current (J_c) as a consequence of additional pinning centers [23–25]. Likewise, granular LTSs systems were employed in the early 1980s to form Josephson networks, in an attempt to obtain experimental data to be compared with simulation results [26] for two-dimensional Josephson junction arrays (2D-JJAs).

In fact, granularity is a key experimentally controllable parameter. For samples which are granular in the macroscopic sense, the granular fraction, f_g, is a measure of the superconducting relative volume, which can be controlled during preparation. For single crystals and other nearly perfect structures, granularity is a more subtle feature, which can also be controlled so that granularity-related effects are induced and tuned through experimentally accessible parameters. In general, granularity can be envisaged as the result of a symmetry break. Thus, one might have granularity in the nanometric scale, generated by localized defects like impurities, oxygen deficiency, vacancies, atomic substitutions and the genuinely intrinsic granularity associated with the layered structure of perovskites. On the micrometric scale, granularity results from the existence of extended defects, as grain and twin boundaries.

3. Magnetic response of a granular superconductor

We discuss now briefly the response of a granular superconductor submitted to a magnetic field of small magnitude, presumably weak enough to guarantee that the critical current of the intergranular material is not exceeded at low temperatures. In this case, after cooling the sample from above its critical temperature (T_c) with $H = 0$ (zero-field cooling process, ZFC), the magnetic response to the application of a magnetic field is that of a perfect diamagnet: intragranular screening currents prevent the magnetic field from entering the grains, whereas intergranular currents flow across the sample to ensure a null magnetic flux throughout the whole specimen. Fig. 1a is a pictorial illustration of this situation, in which the effective magnetic response might be visualized as a combination of two screening currents, both being diamagnetic. Since the intergranular material has weaker superconducting properties, the temperature T^* at which its critical current vanishes, $J_{c,\mathrm{inter}}(T^*) = 0$, is smaller than its intragranular correlate, i.e., $T^* < T_c$. Thus, the temperature dependence of the magnetic response gives rise to the well-known "double plateau" behavior for the DC susceptibility, χ, and the corresponding "double drop/double peak" for the AC susceptibility, χ_{AC} [27,28]. On the other hand, if the sample is subsequently cooled in the presence of the same magnetic field (field-cooling process, FC), the screening currents are, at temperatures immediately below T_c, restricted to the intragranular contribution, a situation that remains until the temperature reaches T^*, below which $J_{c,\mathrm{intra}}(T)$ is

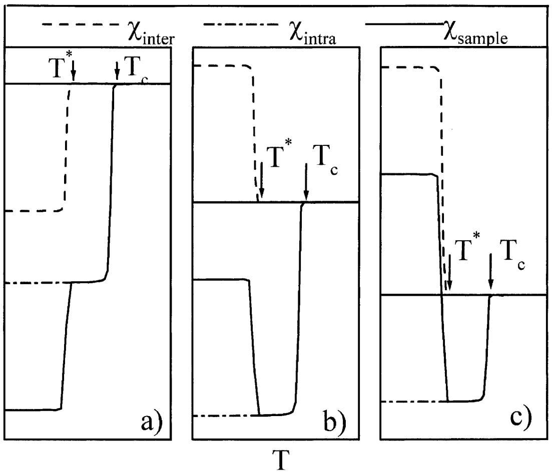

Fig. 1. Pictorial illustration of $\chi(T)$ for a two-component granular system. (a) Both components are diamagnetic, $\chi_{sample}(T) < 0$; (b) intergranular contribution is paramagnetic, yielding to reentrant yet diamagnetic χ_{sample}; (c) intergranular paramagnetic component stronger than intragranular contribution, χ_{sample} reenters and switches signal.

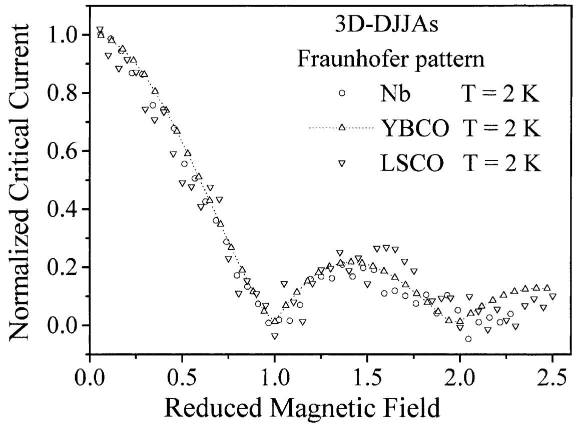

Fig. 2. Normalized critical current as a function of the reduced magnetic field for 3D-DJJAs of Nb, YBCO and LSCO. To collapse all Fraunhofer patterns into one curve, the applied field was divided by the value at which the critical current passes through its first zero.

no longer zero. Intergranular currents which develop below T^* might contribute with a signal that can be either paramagnetic or diamagnetic. Fig. 1b depicts a circumstance where the intergranular contribution χ_{inter} is positive, although smaller than $|\chi_{intra}|$. In this situation, the resulting susceptibility χ_{sample} reenters between T^* and T_c, yet remaining negative for all temperatures. An extreme situation is pictured in Fig. 1c, for which $\chi_{inter} > |\chi_{intra}|$. In this latter condition, χ_{sample} also reenters and changes sign close to T^*.

All possibilities described above have been extensively verified in a variety of experiments reported in the literature, involving both LTSs and HTSs [1–3,15]. The reentrant behavior, called here the WE, is also known in the literature as the paramagnetic Meissner effect (PME). Its occurrence has also been reported as a reentrant behavior in $\chi_{AC}(T)$ measurements of 2D-JJAs [29,30], which are particularly ordered granular systems. For small values of the excitation field h, $\chi_{AC}(T)$ resembles the conventional diamagnetic response of a superconductor in its Meissner state. However, the magnetic response becomes similar to that illustrated in Fig. 1b as h is increased in magnitude. In fact, this is not surprising if one considers that a JJA is a combination of two subsystems: a set of superconducting grains which are weakly linked through a network of regularly displayed JJs.

The WE has also been detected in tridimensional disordered JJAs, 3D-DJJAs, fabricated from granular superconductors in a controlled manner, as described elsewhere [12,13]. Fig. 2 is a collection of experimental results for the field dependence of the critical current of 3D-DJJAs. The vertical axis is the normalized critical current, obtained from the real part of χ_{AC} [29,30], whereas the horizontal axis displays reduced fields, obtained dividing the applied field by the value at which J_c passes through its first zero (a field corresponding to one flux quantum per plaquette). The plot includes low-temperature ($T = 2$ K) data for 3D-DJJAs of Nb, $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $La_{1.85}Sr_{0.15}CuO_{4+\delta}$ (LSCO), collapsed in a single Fraunhofer pattern which constitutes one of the distinctive signatures of the magnetic activity of the arrays. Data for $M(T)$ exhibiting WE has been already published for the Nb array [12], and similar results will appear soon for the other two [13,14]. In Fig. 3 we present a different approach to reveal the WE, in which the magnetic moment of a 3D-DJJA is measured immediately after the array

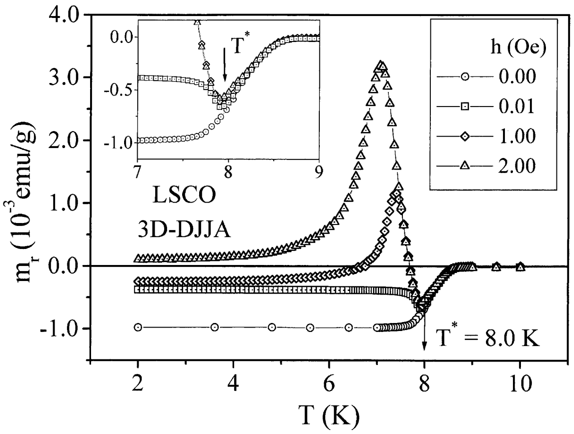

Fig. 3. WE exhibited by a 3D-DJJA of LSCO. The magnetic moment was measured after excitation of the array by an oscillating field h, which is kept off during the DC measurement.

was excited by an AC field of magnitude h, which was then kept off during the magnetic measurement. The array response (intergranular), which is superimposed to the diamagnetic moment of the superconducting grains (intragranular) is either negative or negligible for $h = 0$. For $h = 0.01$ Oe, however, the contribution originated from the array is positive up to a temperature T^*, at which it vanishes and the overall response resumes the shape observed for $h = 0$. For higher values of the exciting field, e.g., $h = 1$ and 2 Oe in the figure, the intergranular parcel becomes dramatically distinguishable. This behavior, with a positive response that increases with T, peaks and decreases to zero at T^*, is a consequence of a remanent magnetization caused by the excursion of the AC field around zero. As will be discussed in the next session, the remanence is intense in a limited window of temperatures. The inset of Fig. 3 is a blow up of the region around T^*, showing how all curves collapse for $T \geqslant T^*$.

4. Magnetic remanence in JJAs

In an attempt to model their $\chi_{AC}(T)$ measurements in a 2D-JJA of Nb–AlO_x–Nb, Araújo-Moreira and coworkers [29,30] simulated the magnetic response of a single plaquette with four identical JJs, using the Wolf and Majhofer [31] temperature dependence for the critical current, $J_c(t) = J_c(0)(1-t)^{1/2}\tanh\{1.54(1-t)^{1/2}/t\}$, with $t = T/T_c$. The authors have demonstrated that the magnetic response of JJAs could be adequately described by this single-plaquette model, pointing out that JJAs may exhibit a paramagnetic response, offering thus a plausible explanation for the WE observed not only in their arrays, but also in several samples of HTSs and LTSs. The magnetic response of the single plaquette is controlled by the the McCumber parameters $\beta_L(T) = 2\pi I_c(T)L/\phi_0$ and $\beta_C(T) = 2\pi I_c(T)C_J R_J^2/\phi_0$, where L is the plaquette inductance, $I_c(T)$ is the temperature-dependent critical current, C_J is the shunt capacitor, R_J is the shunt resistor, and ϕ_0 is the flux quantum. When both parameters are larger than 1, typically of the order of 10 or higher, the reentrant behavior is present.

Based on the same premises, we have simulated $M(H)$ curves for the single-plaquette model. An example, using $\beta_L = \beta_C = 30$, is shown in Fig. 4, for three different values of the reduced temperature, $t = T/T_c$. It is clear from the figure that, if one focus within the right temperature window (e.g., $t = 0.64$ in this case, but not too much be-

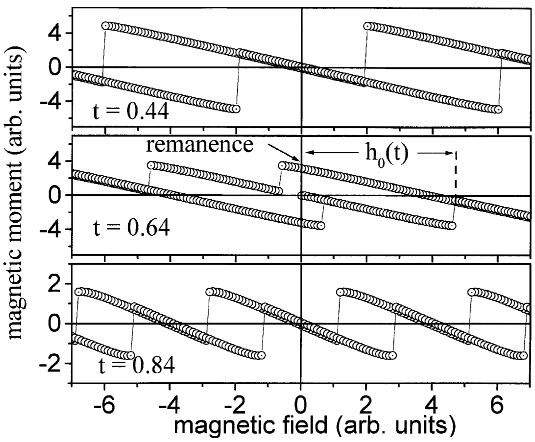

Fig. 4. Simulation results for the magnetization versus field curve of a single plaquette with four JJAs, for three values of the reduced temperature $t = T/T_c$. The remanence occurs in a restricted temperature interval, only if the excitation field exceeds the threshold value $h_0(t)$.

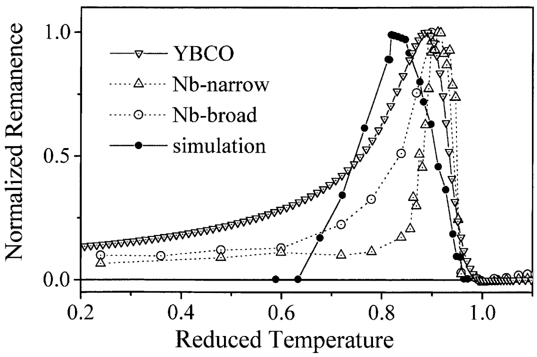

Fig. 5. Temperature dependence of the magnetic remanence measured for three 3D-DJJAs, along with a simulation curve, plotted for the sake of comparison.

low or above this value), the array will retain a magnetic moment (M_r) after been excited by a magnetic field whose value is higher than a temperature-dependent threshold value, labeled $h_0(t)$ in the figure. This behavior, which could predictably be exhibited by minimally organized granular systems, has been detected for many 3D-DJJAs of both HTSs and LTSs [12–14]. Fig. 5 includes results for $M_r(T)$ for one array of YBCO and two different arrays of Nb – one with a narrower and the other with a broader critical current distribution $N(J_c)$, as characterized previously [12]. The fourth curve in the figure is a simulation generated by the single-plaquette model for $t = 0.5$, using $\beta_L = \beta_C = 30$. What is most remarkable in this result is that the simulation can be tuned almost freely in order to recover the experimental data, using the reduced temperature as a fitting parameter and introducing, when necessary, a critical current distribution $N(J_c)$. As a matter of fact, as one can see from the curves in the figure, the temperature dependence of the remanence varies from sample to sample, being sensitive to the process used during preparation of the array and thus to $N(J_c)$. Thus, the fitting process allows for an indirect determination of $N(J_c)$.

From the facts presented above one can conclude that the occurrence of a magnetic remanence is an expected peculiarity of granular systems. In reasonably symmetric specimens with controlled granularity, the effect produced is strong enough to be readily detected.

5. Fishtail anomaly

A direct evidence of the influence of a symmetry break on the pinning ability of HTSs has been obtained in screw dislocated HTS single crystals [32,33]. A nearly linear increase of the critical current J_c with the number of dislocations was detected, as well as a substantial improvement of $J_c(H)$ in the presence of applied magnetic fields. On the other hand, dislocation networks were found to provide effective pinning centers when the characteristic length scale of the network matches that of the vortex spacing [34]. An important conclusion of that work was that, in HTSs, oxygen vacancies are effective pinning centers at low temperatures while the high-temperature spatial variation of the oxygen ordering may well account for the so-called anomalous "fishtail magnetization" (FA) feature in YBCO crystals [35–39]. In another paper, Daeumling and coworkers [35] discussed a rather intriguing correlation between defect pinning, intragrain WLs and oxygen deficiency in YBCO single crystals. In particular, they have found that, as the nominal oxygen deficiency decreases towards zero, the flux pinning declines and the crystals lose their explicitly granular signature. The above mentioned anomalous magnetic-field behavior has been attributed to a "field-induced intragrain granularity" in oxygen-depleted materials [35–39].

A phase diagram $H_m(x,T)$ demarcating the multigrain onset as a function of temperature and oxygen deficiency (x), was reconstructed by Osofsky et al. [37], confirming that their single crystals exhibit the characteristic behavior of homogeneous superconductors for $H < H_m$ and that of inhomogeneous superconductors for $H > H_m$. The granular behavior for $H > H_m$ has been related to the clusters of oxygen defects (within the CuO plane) that restrict supercurrent flow and allow excess flux to enter the crystal. The field at which FA occurs was found [34,37,38] to decrease with increasing both the temperature and the oxygen deficiency. This, in turn, suggests that the characteristic scale of the defect network structure is strongly dependent on oxygen stoichiometry. On the other hand, Ullrich et al. [40] have observed a rather substantial critical current enhancement in stoichiometric melt-textured crystallites with dislocation densities of the order of 10^{10} cm^{-2}. They argue that the strained region surrounding a dislocation can cause the FA as well. Indeed, since the strained regions near the dislocation core, as well as oxygen-deficient regions, both result in a lower H_{c2} (the upper critical field) compared to that of the YBCO matrix, they become (normal conducting) pinning centers if the external magnetic field exceeds the upper critical field.

In addition to those reports of the FA in the nanometric domain, we have also observed the "fishtail anomaly" in every 3D-DJJA sample of HTSs which we have prepared thus far [13,14]. This constitutes convincing experimental evidence that the FA is inherently related to the existence of controlled granularity in the micrometric domain. Fig. 6 is an example of the FA measured on a 3D-DJJA of LSCO, whereas a similar behavior exhibited by a 3D-DJJA of YBCO is shown in Fig. 7.

It becomes clear that, as well as the WE, the "fishtail anomaly" is a predictable feature of granular systems. Also in this case, the effect produced by reasonably symmetric specimens with controlled granularity has sufficient magnitude to be directly observed.

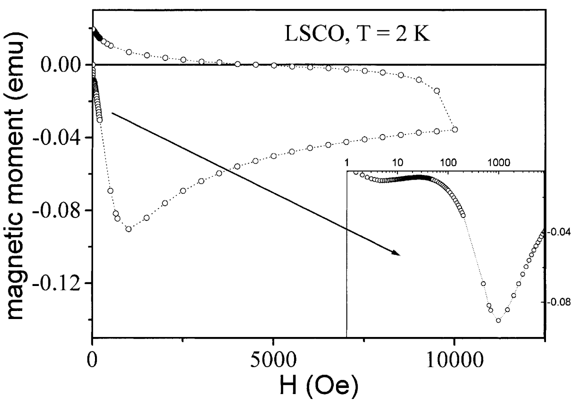

Fig. 6. "Fishtail anomaly" (second magnetization peak) measured for a 3D-DJJA of $La_{1.85}Sr_{0.15}CuO_4$. The inset shows the first branch (virgin curve) using a logarithmic scale for the field, so as to emphasize the two peaks exhibited by the magnetization versus field curve.

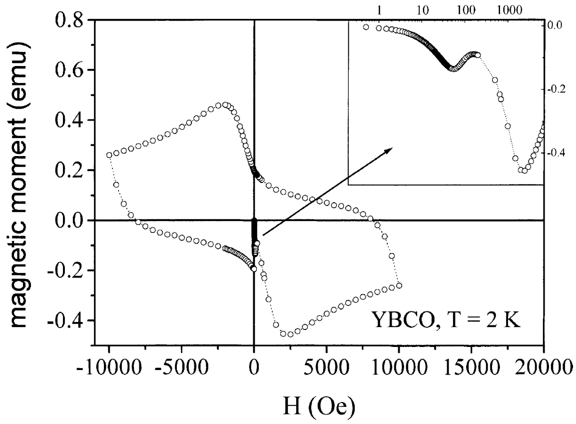

Fig. 7. "Fishtail anomaly" exhibited by a 3D-DJJA of $YBa_2Cu_3O_7$. The virgin curve is shown at the inset where a logarithmic scale for the field emphasizes the existence of two magnetization peaks.

6. Magnetization jumps in mesoscopic superconductors

The effect of a magnetic field in small superconducting samples has been studied by Geim and collaborators [15], using micrometric disks of Al and Nb, with diameters ranging from 0.3 to 3 μm and thicknesses from 0.03 to 0.15 μm. The authors have found all characteristic signatures of the WE, attributing this singular behavior to the fact that their samples were mesoscopic, what enhances the surface-to-volume ratio and, consequently, the role played by surface superconductivity. Among other important observations, the authors conclude that WE is a general property of superconductors, being due to flux capture and compression onto the sample [18–22].

Although agreeing with the general lines of the paper, we have now collected a significant number of evidences that WE is in fact a property inherent to granularity, which will manifest itself as long as the appropriate conditions are present. To further examine this aspect of WE occurring in mesoscopic systems, we have reproduced the experiments of Geim and coworkers [15] using a high quality, single-phase film of Nb having a thickness 2000 Å. All magnetic features observed in their experiments were also exhibited by our sample, including discrete jumps on the magnetic moment as a function of the applied field, $m(H)$, in a relative configuration for which the plane of the film is perpendicular to the field. This fact – that our findings are in perfect agreement with theirs – was predictable, since both experiments were conducted with mesoscopic samples comparable in sizes and quality.

It is worth stress here, however, that the same results can be interpreted in a totally different manner, using the same single plaquette with four JJs already employed earlier in this paper. Although we cannot show here the whole set of experimental data, due to lack of space, we have seen that $m(H)$ does not oscillate for $T = 5$ K and above, presenting a rather smooth response, resembling that of a regular superconductor. For lower temperatures, $m(H)$ oscillates around the regular pattern, which we can thus consider as a background that can be subtracted to evidence the unusual behavior. Fig. 8 includes $m(H)$ for the Nb film, measured at $T = 4$ K, showing the oscillating jumps, already free from the background. Simulation results are also included and compare well with the experimental data.

In reality, the existence of the typical background of a regular superconductor is an important clue to the proposed approach to the problem, as it indicates that the film responds with two distinct contributions, exactly like in a granular system. As a matter of fact, we have already studied in a previous paper the magnetic response of superconducting thin films in the same relative configuration [17], showing that it indeed behaves like a granular system, what is explained by the dendritic pattern formed by the field as it penetrates the sample [41].

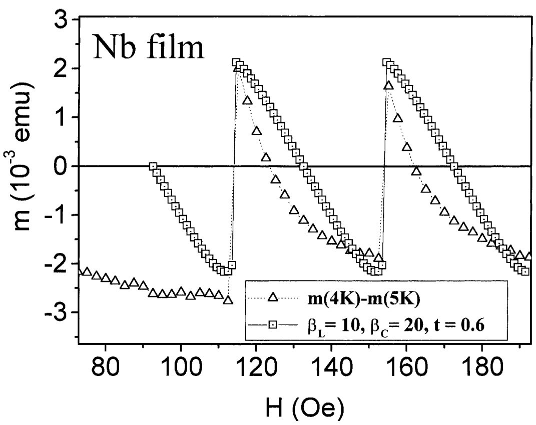

Fig. 8. Magnetization jumps measured in a thin film of Nb, compared with simulated results obtained for a single plaquette with four JJAs. The values of the McCumber parameters and of t are adequate, but were not optimized to fit the experimental data.

We return now to Fig. 8 to recognize that the magnetic responses shown represent two granular systems of similar behavior. It is remarkable that the simulation curve plotted has absolutely nothing special and, in fact, was not optimized to fit the experimental points. We thus conclude that, in spite of other existing possibilities to explain the experiments, granularity is once more a highly qualified candidate in this case.

7. Final remarks

In this contribution we have presented a number of experimental evidences accounting for the key role played by granularity on the understanding of the magnetic response of superconductors, mainly the HTSs, for which the smallness of the coherence length enhances the importance of point defects of all kinds. We have shown that effects of the same nature can be exhibited by superconducting samples having granularity scales in two domains, the nanometric and the micrometric, and that these features are really associated with the general attribute of being granular, and not to any particular difference between HTS and LTS material. Events like the WE, the "fishtail anomaly", the magnetic remanence of JJAs, and the jumps on $M(H)$ of mesoscopic systems, were briefly reviewed and discussed taking granularity as the basic hypothesis. The present approach is not intended to be the ultimate against other possible explanations to the effects accessed. However, it shows how a simple granular model, based on cells with four identical JJAs, can account for the unusual magnetic behavior of certain superconducting samples. Furthermore, it emphasizes the importance that ought to be given to granularity in every scenario intended to explain the magnetic properties of superconducting systems.

Acknowledgements

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