Simulation and study of the percolation effect in the magnetic susceptibility of high-temperature superconducting composites

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A simple model is proposed to analyze the relationship between susceptibility and composition in superconducting composites. The model is based on a random distribution of superconducting and nonsuperconducting phases and on the occurrence of shielding when a nonsuperconducting area is encapsulated by superconducting material. A three-dimensional simulation based on percolation theory is in agreement with our experimental data on a series of MgO-superconductor composites. A predicted percolation effect was observed and a maximum in shielding efficiency was determined.

I. INTRODUCTION

An important problem hampering the widespread application of bulk polycrystalline high-temperature superconductors (HTSC's) in large scale systems is related to their poor mechanical qualities. However, these can be improved by the addition of reinforcing material.[1,2] On the other hand, the presence of a disperse phase is bound to change the superconducting properties of the material. The understanding of the mechanism of this influence is of primordial interest for future applications.

Whereas percolation of the resistivity of superconductors is a well-known phenomenon,[3–6] studies on the percolation of magnetic properties as a function of the composition are rather scarce.[7–9] In this context, we studied the variation of the magnetic properties as a function of the percentage superconducting Bi 2223 phase in a series of composites.

In the first part of this paper we report the results of ac susceptibility measurements of Bi-Sr-Ca-Cu-O (BSCCO)/MgO composites and a model for this magnetic behavior is suggested. After a brief overview of the relevant aspects of percolation theory, a three-dimensional simulation based on this model is presented.

II. EXPERIMENTAL DETAILS

Polycrystalline Bi-based high-temperature superconductors were prepared by spray drying a solution of nitrates and subsequent calcination and sintering as previously reported.[10] Using x-ray diffraction (XRD),[11] the high-T_c phase $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) was determined to be the major phase, representing 75% of the grain volume; approximately 25% is made up of the low-T_c phase $Bi_2Sr_2Ca_1Cu_2O_x$ (2212) and traces of $Ca_{2.3}Sr_{2.6}CuBi_{0.33}Pb_{3.44}O_x$. Mixtures of manually ground superconducting powder and MgO powder with volume fractions between 10 and 100% were uniaxially cold pressed into rectangular bars at a pressure of 600 MPa and subjected to a resintering process for 60 h at 860 °C under static air. The composites all exhibit a porosity of approximately 25%. According to XRD and IR, no chemical reactions occurred during resintering.

Susceptibility measurements were performed on rectangular composite bars with the approximate dimensions of $2\times2\times13$ mm, using a Lake-Shore 6000 Series Susceptometer. The screening properties were determined at 100 A/m alternating field and 125 Hz. The direction of the applied field was parallel with the longest dimension of the zero-field-cooled bars. No demagnetization effects were considered.

III. RESULTS AND DISCUSSION

The composition of the composites can be defined as a function of the volumes of BSCCO and MgO grains used to make the initial mixture. In reality, the sintered composite is composed of MgO grains, BSCCO grains (both 2223 phase and 2212 phase) and pores. In this paper, we will define the concentration as the percentage 2223 phase, i.e., the volume percentage HTSC's used to make the composite corrected for porosity and from which the volume fraction 2212 phase was substracted. We consider the 2212 phase as an inert phase because our earlier magnetic studies[11] on powdered samples of this composition never revealed a noticeable transition due to the presence of the low-T_c phase in the temperature range considered here.

Figure 1 shows an overview of the ac measurements as a function of the temperature. We observe an increasing susceptibility with the vol. % 2223 phase, until almost perfect diamagnetism is obtained at 40 vol. % 2223 phase.

From these ac data, the susceptibility χ' was plotted as a

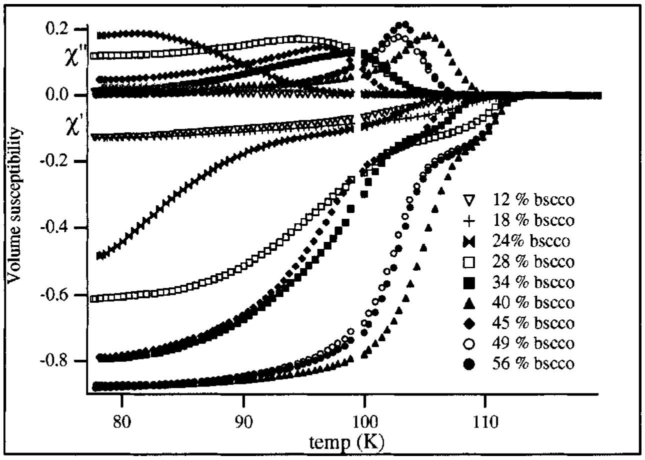

FIG. 1. ac volume-susceptibility in function of temperature for 12–56 vol. % 2223 phase.

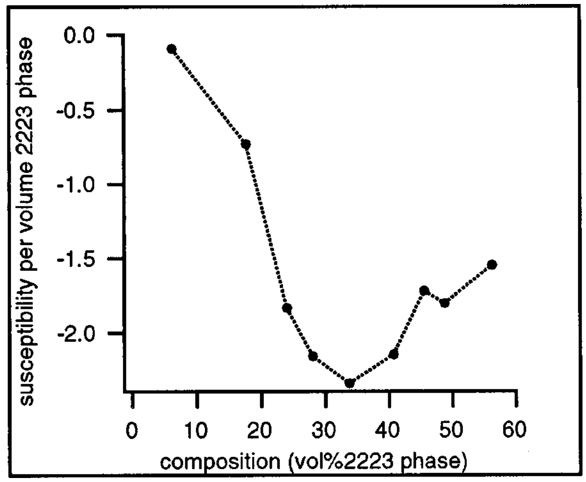

FIG. 3. Susceptibility per volume 2223 phase as a function of vol. % 2223 phase at 80 K.

function of the composition for different temperatures. A percolation effect is observed in the range between 20 and 40 vol. % depending on the temperature. Due to the variation of the intergrain contacts this percolation shifts to higher concentrations of 2223 phase with increasing temperature, as is shown in Fig. 2. An increasing temperature results in a dilution of the weak links and a decrease in the screening properties. For intermediate concentrations this transition is spread out over a broad temperature range, while for higher concentrations the decline is concentrated in a narrow temperature range. The screening is almost constant until the number of weak links reduces to a critical value. This is in accordance with the findings of Dubois *et al.*[8] for variation of susceptibility with applied field strength.

The susceptibility per volume 2223 phase is shown in Fig. 3. In this case the susceptibility at 80 K was divided by the true volume fraction of 2223 phase in the composite. From this graph we can deduce that the superconducting material introduced into the composite has the largest screening efficiency between 30 and 40 vol. %. Higher and lower concentrations seem to be less remunerative for screening properties.

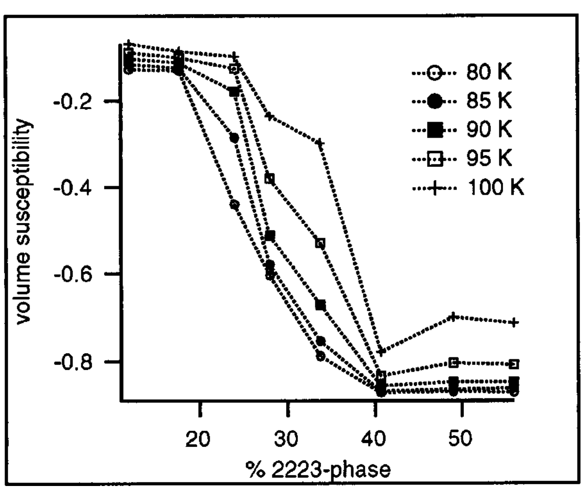

FIG. 2. Volume susceptibility in function of composition for various temperatures. (Lines are a guide for the eye).

IV. MODEL

These phenomena can be explained within the following model. We consider that, with an increasing amount of superconductor, three possible mechanisms can occur:

(a) The added material is isolated from other superconducting domains by a nonsuperconducting matrix and contributes to the total susceptibility of the sample, according its own volume.

(b) The added grains form the ''missing link'' required to shield a certain inner volume. In this case the whole shielded volume will contribute to the susceptibility.

(c) The new material ends up inside an already shielded volume; in this case the total susceptibility of the sample will not change upon the addition of superconducting material.

Each of the three possibilities can occur at any concentration; but the statistical probability to occur is determined by the amount of superconducting material already present.

The results can be understood as follows: at low concentrations, the added material will be isolated and the susceptibility of the sample increases in proportion to its own volume. With increasing concentrations the probability of encapsulating a volume of nonsuperconducting material raises. The susceptibility of the specimen increases proportionally to the shielded area, so the efficiency of the added grains is much increased, we call them ''superefficient.'' This effect leads to the steep increase in the susceptibility per unit volume noted in Fig. 3 above 10 vol. %. This phenomenon occurs until a concentration of approximately 35 vol. % 2223 phase is reached. We can explain this by assuming that the volumes of the encapsulated bodies increases between 10 and 35 vol. %, and the fraction of superefficient grains increases with respect to the total number of grains. For higher concentrations, the volume of the composite will be almost completely shielded. The probability for an added grain to encapsulate a nonshielded area decreases. New material will most likely end up in a region that was already shielded, consequently the total susceptibility of the specimen will not change. If the grain ends up on the outside of a shielded area, it will contribute to the total susceptibility according its own volume. In both cases the susceptibility per volume 2223 phase in the composite will decrease, because the relative

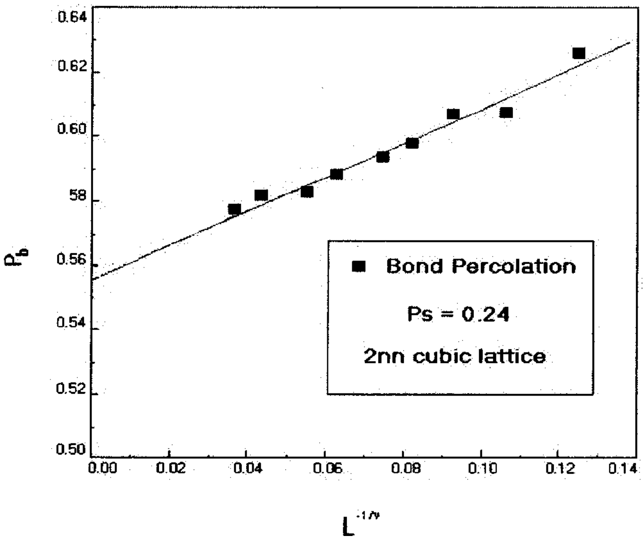

FIG. 4. Finite-size scaling plot for the site-bond percolation model with $p_s = 0.24$.

amount of superefficient grains decreases. This can be seen in Fig. 3, where at concentrations above 35 vol. % the susceptibility per volume superconducting phase clearly decreases.

V. PERCOLATION THEORY

Percolation theory, introduced in 1957 by Broadbent and Hammersley,[12] is now a well-established tool to tackle a wide variety of phenomena and it has been extensively reviewed.[13–22] It deals with the effect of random dilution of elementary geometrical objects (spheres, squares, cubes, sites, bonds, etc.) located in lattices or in the continuum. Upon dilution a very sharp transition occurs in the connectivity of the system. The percolation threshold is defined as the minimum concentration at which an infinite cluster of occupied elements spans the system. The percolation model has many generalizations that represent different physical situations and it has been applied in a great variety of fields, for example porous media, polymers gels, fragmentation and fractures, dispersed ionic conductors, ionic glasses, galaxies, forest fires, epidemics, etc.

The percolation problem can be described in a general way as a site-bond percolation model. Let us briefly describe the *site* percolation model in a square lattice. In this problem each site on the lattice is chosen to be occupied randomly with a probability p_S or empty with probability $q_S = 1 - p_S$. Two sites that are occupied belong to the same cluster if they are connected through a path of nearest-neighbors occupied sites. For an infinite system, as p_S increases the average size of the clusters grow until a critical concentration p_S^C is reached. Below this concentration, only finite sizes exist and above this, an infinite cluster is formed. In the *bond* percolation problem, we consider that all the sites are occupied and that the units that link them (bonds) are occupied randomly with a probability p_B or empty with probability $q_B = 1 - p_B$. Two sites belong to the same cluster if they are connected through a path of occupied bonds, there is also a critical concentration p_B^C below which there are only finite clusters and above there is an infinite spanning cluster.

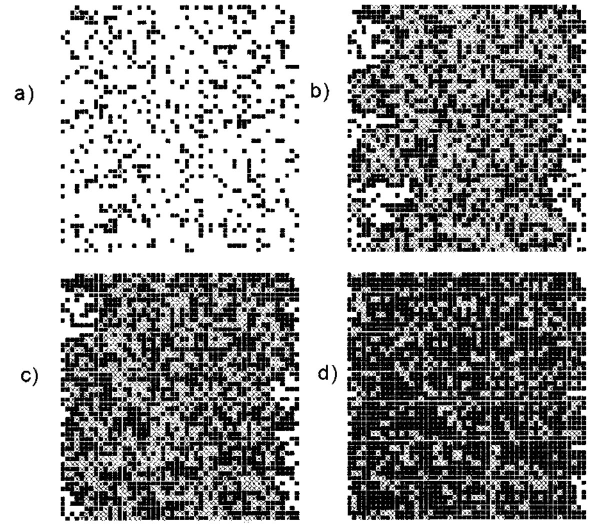

FIG. 5. Two-dimensional representation of the model. The solid squares represent the superconducting grains, the open squares are nonsuperconducting grains and the gray areas are entrapped in a closed volume of superconducting material. The density of HTSC is 0.20, 0.40, 0.60, and 0.80 for (a), (b), (c), and (d), respectively.

The *site-bond* percolation is the more general case where sites are connected to each other if they are both occupied and they are connected through a path of occupied sites and bonds. From Monte Carlo simulations, series expansions, and a few analytical calculations, it is well known that the percolation threshold depends on both the space dimensions and the coordination number z. Very recently Galam and Mauger have reported universal formulas which with great accuracy give the site and bond percolation thresholds in regular lattices at dimensions $d < 7$ (Ref. 23) and anisotropic and nonperiodic lattices at dimension $d = 2.3$.[24]

We will focus on the site bond problem for the superconducting-nonsuperconducting transition and we will look to the volume of entrapped material (the fraction of nonoccupied sites not connected to the outside) in order to simulate the evolution of the susceptibility as function of concentration.

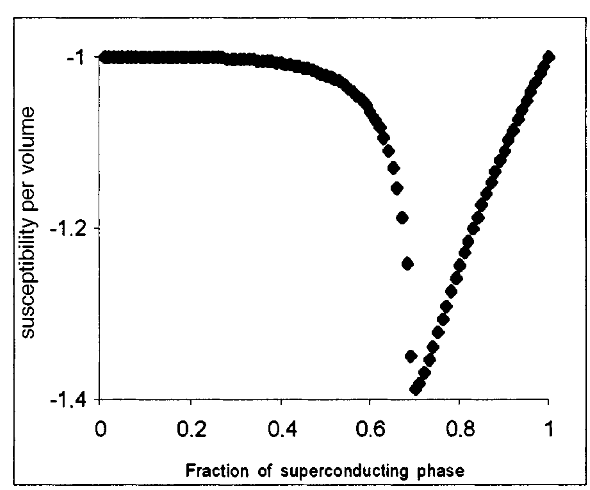

FIG. 6. Simulation of the susceptibility per volume 2223 phase as a function of vol. % 2223 phase, at low temperature.

VI. SIMULATION

We simulate this process in a three-dimensional lattice, neglecting influence of grain size and demagnetization. The fraction of superconducting bonds present in the samples was established from resistivity measurements. The room-temperature isolator-conductor percolation is determined to be at approximately 13% conducting phase. This value is quite close to the percolation threshold for the cubic lattice with next-nearest neighbors ($p_S^C = 13.7\%$). However, from measurements of the resistivity as a function of temperature we see that the percolation threshold for transition to zero resistivity rises up to 24% superconducting phase. This suggests that at low temperatures not all the electrical contacts between neighboring superconducting grains became superconductive themselves.

We use a three-dimensional cubic lattice of $L \times L \times L$ sites with each site being occupied with probability p_S and each bond with probability p_C. We fixed the probability $p_S = 0.24$ according with the experimental results and then we look for the fraction of bonds needed to have the spanning cluster.

Since the lattices prepared with the computer are finite in size we have to use finite-size scaling to determine the percolation threshold on an infinite system. The percolation threshold for the finite-size system depends on the value of L.[13] The average threshold for a lattice of size L, at a fixed value of p_S, approaches the true value according with the scaling law

$$p_B^{\mathrm{AV}} - p_B^C \sim L^{-1/v},$$

where V is a critical exponent of the correlation length, that diverges at p_C. The root-mean-square deviation (rms) of the threshold also scales with system size. Using the scaling law stated above and taking the universal and exact value $v = 4/3$, we can extrapolate the percolation threshold for the infinite lattice. We plot the calculated thresholds p_B^{AV} versus $L^{-1/v}$ and extrapolate to the interception by letting $L \to \infty$. In our calculations different values of L ($L = 16$, 20, 24, 28, 32, 36, 48, 64, and 80) were used to obtain a good statistical accuracy see Fig. 4. The value found for the fraction of bonds that become superconducting when cooled down is $p_B^C = 0.5558 \pm 0.0027$.

To model the magnetic susceptibility we calculated the total fraction of empty sites that become isolated from the outside of the volume. A two-dimensional representation is shown in Figs. 5(a)–5(d), the solid squares represent the superconducting grains whereas the open squares represent the nonsuperconducting areas and the gray areas are the grains confined in a closed volume, the fraction of superconducting grains in the figure are 0.20, 0.40, 0.60, and 0.80. The total magnetic susceptibility of the sample will be proportional to the number of superconducting grains plus the volume of nonsuperconducting material that is entrapped into the superconducting phase and is not in contact with the outside through a nonsuperconducting path. Figure 6 shows the susceptibility per volume as a function of the fraction of superconducting material in the volume. No scaling was done and the largest size of the system compatible with the computer resources available was used, $L = 128$ and the properties were calculated after 20 000 simulations, periodic boundary conditions were used in the x and y directions.

VII. DISCUSSION

The model correctly describes the major features of the system, exhibiting percolation in the susceptibility of the samples and a maximum in screening efficiency. The overall behavior of the system is the same, however, the minimum in the volume susceptibility is shifted to a higher concentration of superconductor than the experiments.

This shift can be due to many sources such as the omission of demagnetization effects and the simplicity of the geometrical model (number of neighbors). A discrepancy between measurement and calculation in the low concentration region of the susceptibility per volume HTSC is expected to be related to the effect of the penetration depth. For single grains at low temperature and field, the variation of the susceptibility with the concentration is expected to be $\chi' = -1.5.\phi$ (ϕ is the fraction superconducting phase).[25] From the ac measurements we deduce a $\chi' = -0.95\phi$ dependency. We therefore conclude that the effective volume of each grain is only about 60% of its actual volume due to the penetration of the magnetic field. With a penetration depth of approximately 200 nm, we would need a grain size of about 1.2 μm to account for the observations, which is nicely confirmed by optical microscopy. This loss in effective volume thus accounts for the small measured value for the susceptibility per volume 2223 phase at low concentration, in contrast to the model, where it is assumed that each grain is perfectly diamagnetic ($\chi' = -1$).

VIII. CONCLUSIONS

A percolation effect in the variation of screening properties with the concentration of HTSC phase is observed. Maximum values in magnetic shielding are reached at 30–40 vol. % 2223 phase. These values may be indicative of loadings in future technological applications of magnetic screening using superconducting composites. The correlation between susceptibility and composition is explained in terms of random distribution of superconducting and nonsuperconducting phases and the occurrence of intergrain coupling effects. We tested these assumptions using a simple three-dimensional percolation model and we found that it properly describes all the major features of the observed relationships. The remaining discrepancies can undoubtedly be attributed to the lack of detail in the geometry of the model used here and the unaccounted occurrence of demagnetization effects. In addition, the presence of magnetic penetration is supposed to strongly reduce the magnetization of the smaller particles.

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