Double Percolation Transition in Superconductor-Ferromagnet Nanocomposites

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A double percolation transition is identified in a binary network composed of nanoparticles of MgB_2 superconductor and CrO_2 half-metallic ferromagnet. Anomalously high-resistance or insulating state, as compared to the conducting or superconducting states in single-component systems of either constituent, is observed between two distinct percolation thresholds. This double percolation effect, which is especially pronounced at liquid helium temperatures, is controlled by composite volume fraction and originates from the suppressed interface conduction and tunneling as well as a large geometric disparity between nanoparticles of different species. We investigate the scaling behavior near both percolation thresholds and determine the distinct critical exponents associated with two different types of transitions.

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Percolation effects have been widely investigated in a variety of physical systems [1–3], with applications ranging from ferromagnetic or superconducting solid materials, such as composites [4,5], or polycrystalline samples [6,7], to soft matters, such as polymer blends [8]. In addition to the fundamental importance of understanding phase transitions, the corresponding mechanical, electronic, transport, and magnetic properties of percolating networks are often strongly affected by the system percolation. In spintronics applications, for example, percolation is often associated with large magnetoresistance [4] and may play an important role in the physics of colossal magnetoresistive oxides [9]. In most model systems that have been studied extensively, only one percolative network is considered, with the corresponding percolation theory well established [1,2,5,10]. For instance, the classical percolation problem of electrical conductance is usually featured by a conductor-insulator (or conductor-superconductor) transition in a two-component composite, where one of the constituents provides a conducting (superconducting) path through the insulating (normal) matrix [1,2,5,7], so that the percolation behavior is uniquely determined by a single conducting (superconducting) constituent. It would be of fundamental importance to understand percolation behavior in real multicomponent systems, where multiple percolative networks can potentially be formed, and to explore new effects associated with their unique material properties and functionalities. Since a general case of arbitrary coupling and variable interaction between various types of constituents may be prohibitively complicated, it is instructive to first construct and study a special well controlled case, where different percolation networks can be identified and studied independently [11].

In this Letter we report a new type of double percolation transition, observed in a binary system where both constituents can form independent percolative networks. A remarkable feature of this system is the existence of two separate thresholds, each corresponding to conductor-insulator or superconductor-insulator transition, but in two different media that are conducting or superconducting on their own in a single-component state. The system we study is based on cold-pressed powders of CrO_2 and MgB_2 mixture, with the percolation path arising through contacts between individual nanoparticles. The two materials are well suited for this experiment: CrO_2 is a half-metallic ferromagnet where the conduction band is fully spin polarized [15–19], whereas MgB_2 is a superconductor with a fairly high bulk critical temperature of 39 K. We find that the interface conduction between CrO_2 and MgB_2 particles is strongly suppressed compared to that of CrO_2/CrO_2 or MgB_2/MgB_2 interfaces, especially below the superconducting transition [20]. The percolative networks from the two constituents can then be effectively separated, yielding two distinct percolation thresholds. We can thus identify an anomalous conductor-insulator-superconductor transition attributed solely to the double percolation phenomenon, which is controlled not only by the volume fraction of the composite but also the size and shape contrast of the constituent particles.

We study a wide range of composite powders, where a weight fraction x of CrO_2 was mixed with the corresponding fraction $1 - x$ of MgB_2. This mixture of commercial CrO_2 and MgB_2 powders was ground in a controlled humidity environment, with the humidity not exceeding 30%. Disks with a diameter of 5 mm and thickness of 1–2 mm were cold pressed at a pressure of 10 GPa. Samples with 23 different compositions with x varying from 0 to 1 were prepared. Immediately after fabrication, the samples were mounted for four point transport measurements. Both particle size and average particle distribution were monitored by scanning electron microscopy (SEM).

In Fig. 1(a) we show a typical particle distribution in a composite sample with $x = 0.4$, corresponding to the volume fraction $p = 0.26$ of CrO_2 as obtained from SEM energy dispersive spectrometry mapping of elemental Mg and Cr. The SEM images of the original CrO_2 and MgB_2 powders are given in Figs. 1(b) and 1(c), respectively. The typical length L of a CrO_2 rodlike particle is about 300 nm

and the width d is about 40 nm. The MgB_2 particles are polydispersed, with approximately spherical shape and the average diameter D of about 500 nm. The typical packing densities are about 46% for pure CrO_2 and 62% for pure MgB_2.

The electrical resistance for the samples of various compositions (i.e., volume fractions) has been measured at different temperatures; see Fig. 2. In the inset we show the resistance of the samples prepared in the same fashion from pure MgB_2 (which has a superconducting transition of around 37 K) and pure CrO_2 whose resistance is fairly flat except for the lowest temperatures, where the activation-type behavior is observed, due to the presence of a nanometer thick Cr_2O_3 insulating layer at the surface of CrO_2 [21]. The resistance of the composite samples, which is negligible ($\approx 0.05\ \Omega$ at 37 K) for pure MgB_2, $p = 0$, and approximately 50 Ω at 2 K for pure CrO_2, $p = 1$, attains maximum values at fairly narrow intermediate composition range $0.22 < p < 0.34$, with the low-temperature peak value of the resistance about 3 orders of magnitude higher than that of the pure CrO_2 sample (the maximum resistance at 2 K is 450 Ω for $p < 0.22$ and 900 Ω for $p > 0.34$). We attribute this behavior to a double percolation effect, where two separate percolative networks with conductive or superconductive paths develop at different thresholds for the two constituents $p_c^{CrO_2} \simeq 0.34$ and $1 - p_c^{MgB_2}$ ($\simeq 1 - 0.78 = 0.22$). The corresponding transitions are not symmetric; i.e., the thresholds are not the same, due to the different sizes and shapes of the constituent particles, as will be addressed below. The transition is also significantly sharper at low temperatures on the MgB_2 side, where the percolative path represents an insulator-superconductor transition.

We expect these surprising results to be closely connected to the anomalously high resistance at the MgB_2/CrO_2 interface and the formation of two separate percolation clusters by the MgB_2 and CrO_2 nanocomponents. The anomalous behavior at such heterogeneous interface is verified by independent measurements of the resistance in a sandwich structure composed of two cold-pressed layers, one of pure MgB_2 and the other of pure CrO_2 nanoparticles, otherwise prepared under the same conditions and in the same geometry. The resistance of such a structure turns out to be about 1 kΩ at 2 K, 20 times higher than the resistance of the pure CrO_2 layer (see the insets of Fig. 2). These results clearly indicate that the MgB_2/CrO_2 interface resistance is at least an order of magnitude larger than that of CrO_2/CrO_2 or MgB_2/MgB_2 interfaces, particularly at low temperatures.

It can be anticipated that the path maximizing the overall interface region between MgB_2 and CrO_2 clusters would lead to the highest resistance. The perimeter of either of those clusters close to a percolation transition can be estimated as [1] $t_S \sim S(1-p)/p + c_0 S^{\zeta}$, where c_0 is a constant, the critical exponent $\zeta = 1$ (for $p < p_c$) or $1 - 1/d$ (for $p > p_c$ in d dimensions), and S is the cluster size (or mass) which scales as $(p - p_c)^{-1/\sigma}$ with σ, another critical exponent, for the "critical" clusters dominating the system properties. Thus maximum cluster perimeter (and hence maximum heterogeneous interface) will be reached when $p \to p_c$. For the current binary composite where both conducting constituents can percolate, the new effect of high sample resistance can only occur before the appearance of a percolation cluster (either conductive or superconductive), but close enough to both percolation transitions to maximize the MgB_2/CrO_2 heterogeneous interfaces. This leads to a maximum resistance (or insulating) state in between the two thresholds, as demonstrated in Fig. 2.

To further illustrate the existence of such double percolation effect, we examine in Fig. 3 the scaling behavior of the resistance of the binary composite near the two percolation thresholds. Based on the standard percolation theory

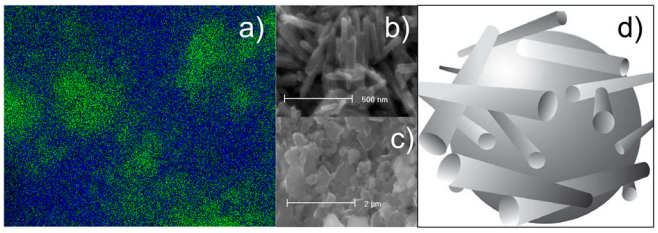

FIG. 1 (color online). (a) Energy dispersive spectrometry image of a CrO_2/MgB_2 sample with $p = 0.26$ (just below the percolation threshold), showing the distribution of Mg [light (green)] and Cr [dark (blue)]. (b) SEM image of pure CrO_2 powder. The length of typical particle nanorods is about 300 nm, with approximately 7.5:1 aspect ratio. (c) SEM image of pure MgB_2 powder. The typical particle size is about 500 nm, with roughly spherical shape of particles. (d) The schematics illustrating effective caging of spheres by nanorods.

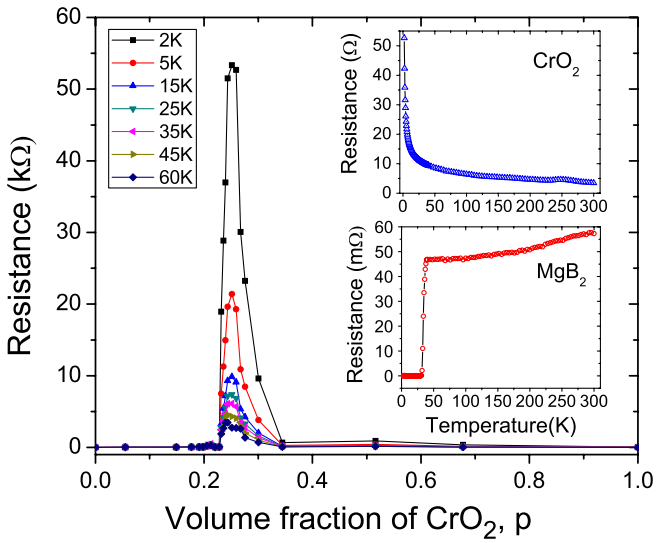

FIG. 2 (color online). Resistance of CrO_2/MgB_2 samples as a function of volume fraction p at different temperatures. Inset: Temperature dependence of the resistance for cold-pressed samples of pure CrO_2 (top) and pure MgB_2 (bottom).

[1,2,5], a power law behavior for resistance R is expected while approaching each transition threshold $p_c^{(i)}$ (with (i) referring to CrO_2 or MgB_2 network), i.e., $R \sim |p - p_c^{(i)}|^{-\mu}$, where the critical exponent μ depends on the dimensionality and the intrinsic conducting property of the system; e.g., in three-dimensional (3D) conductive networks, $\mu \simeq 2$ for lattice percolation [22] and $\mu \simeq 2.38$ for continuum percolation (the Swiss-cheese model) [5], while in 3D lattice of superconductivity μ (usually denoted as s) is about 0.75 for a conductor-superconductor transition [23]. Such scaling behavior has been confirmed in our experimental results for both MgB_2- and CrO_2- dominated networks, as shown in Figs. 3(a) and 3(b), respectively. As we approach the threshold from the CrO_2 side of the insulator-conductor transition, the data rescaling presented in Fig. 3(a) yields $\mu = 2.16 \pm 0.07$, which is between the theoretical values of 2 and 2.38 as given above. For the MgB_2 side of the superconducting network at low temperatures, a different critical exponent of $s = 1.37 \pm 0.05$ is identified from Fig. 3(b). This exponent deviates from the known theoretical result ($s \simeq 0.75$), which might be attributed to the fact that although the system here is composed of superconducting (MgB_2) and conducting (CrO_2) constituents, the effective transition is actually between superconducting and insulating states due to the anomalous interface effect identified above, possibly influenced by a proximity effect from the magnetic CrO_2 nanoparticles on superconductivity in MgB_2.

We note that the experimental value obtained here for the percolation threshold of the CrO_2 network ($p_c^{CrO_2} \simeq 0.34$) is close to the theoretical threshold of 3D site percolation in simple cubic lattice ($p_c \simeq 0.31$) or that of 3D continuum percolation model ($p_c \simeq 0.28$) [1,2]. This can be understood if one considers the large shape and size contrast of the two constituents: Although the length of an individual CrO_2 rod is about half of the diameter of MgB_2, it is very thin, with the length-to-width aspect ratio of about 7.5:1, and thus its volume is only about 0.5% of that of a spherical-like MgB_2 particle; hence, small CrO_2 particles can be effectively treated as in a continuum matrix, with $p_c^{CrO_2}$ consistent with the theoretical results. On the other hand, this approximation apparently cannot hold for the opposite case of a MgB_2 percolating network, for which our measured threshold of $p_c^{MgB_2} = 0.78$ is far from the theoretical values. However, it is important to note that $p_c^{MgB_2}$ measured experimentally is the volume fraction of MgB_2 and needs to be converted to the spatial occupation or probability fraction $P_c = p_c f$ [24], where f is the filling factor or the packing density of the system particles. The filling factor measured at threshold is $f = 0.811$, and hence we have $P_c = p_c^{MgB_2} f = 0.633$, a value that is compatible with the theoretical range of 0.16–0.64 for a hard-core sphere system embedded in a continuum medium [3].

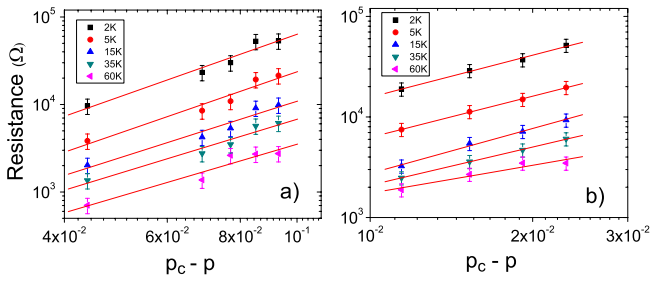

FIG. 3 (color online). Scaling behavior of the resistance near the two percolative thresholds, at various temperatures as listed in Fig. 2. (a) The CrO_2 side of the transition, with $p_c^{CrO_2} = 0.34$, and (b) the MgB_2 side, with $p_c^{MgB_2} = 0.78$.

While such effective P_c observed here for MgB_2 is very close to its random close packing limit for spheres (64%), in our system the contact between adjacent particles is established and maintained by cold-pressing the samples, and hence the value of P_c might be expected to be much lower than the packing limit [25], perhaps even approach the Scher-Zallen value of 0.16 [24]. This latter argument based on geometric contact is consistent with the known experimental results for critical thresholds of, e.g., MgB_2 and $YBa_2Cu_3O_7$ superconductor systems [6,26] or granular metal films [27], which are in the range of 0.2–0.5, but apparently differs dramatically from our current result for the MgB_2 network. We argue that this discrepancy can be attributed to the new binary (spheres-sticks) packing phenomenon appearing in our samples, particularly the unique feature of a large geometric contrast between the two components. The cold-pressed very thin and short CrO_2 sticks can very effectively fill the voids between large MgB_2 spheres [see Fig. 1(d)], as reflected in the high total measured packing density of $f = 81.1\%$. At the same time, those thin sticks can very efficiently screen the superconducting MgB_2 spheres, bringing their P_c up to the close packing limit. This can be understood by means of the concept of excluded volume [28]. The excluded volume V_{ex} of a stick or sphere binary composite is given by [29] $V_{ex} = (\pi/4)D^2L + (\pi/6)D^3$ in the limit of thin sticks, i.e., for $d/D \ll 1$, with d and D the diameters of the stick and the sphere, respectively, and L the length of the stick. In the case of short and thin sticks that are very effective in caging spherical particles, see Fig. 1(d) (in our experimental system $L \simeq D/2$), we can adopt a rough estimation [30] that the number of spheres (MgB_2) at percolation $N_c \sim V_{sys}/V_{ex}$, where V_{sys} is the total system volume. Thus the threshold for MgB_2 is estimated as $P_c = (N_c V_{sp})/V_{sys} \sim V_{sp}/V_{ex} \sim 4/7 = 57.1\%$ (with V_{sp} the volume of a MgB_2 sphere), a value that is consistent with our experimental result of 63%.

To further validate this interpretation, we annealed CrO_2 particles under vacuum (following the procedure described in Ref. [4]) to convert conducting ferromagnetic CrO_2 into insulating antiferromagnetic Cr_2O_3. This approach allowed us to repeat the measurements in the MgB_2/Cr_2O_3 composite with the same particle geometries. Quite naturally this system has only a single percolation threshold

(for MgB_2), $\tilde{p}_c^{MgB_2} = 0.76$, which is close to the value measured in the double-percolating system with CrO_2 ($p_c^{MgB_2} = 0.78$), thus confirming that p_c is determined by the geometric constraints.

While percolative thresholds for each constituent are system dependent, we expect the observed phenomenon to be robust, as long as the percolation thresholds for the two media, I and II, satisfy the condition $p_c^{I} + p_c^{II} > 1$. If this inequality holds, we can identify a region where neither constituent percolates, resulting in the double percolation effect described above. We note that the above condition is quite unexpected in 3D (for which p_c is small and generally <0.5), and is very sensitive to the shape and size of the two constituents. As our experimental results demonstrate, a large disparity in particle sizes and shapes drives the percolation threshold of at least one constituent (MgB_2) sufficiently high to satisfy the stated inequality. Additionally, the nanocrystalline nature of the components is also expected to play an important role. As discussed above, the anomalous conducting transition can be attributed to the interface effects of individual grains of MgB_2 and CrO_2. Such effects are known to be of increasing importance for gradually decreasing grain size, particularly at the nanoscale where the thickness of the interface region may approach the individual particle size. In this case the influence of interface tunneling, which is expected to be the main mechanism underlying the anomalous interface conducting observed in Fig. 2, will be dominant, especially at low temperatures. This interface-controlled conductance would be analogous to that seen in other percolative systems of nanocrystalline composites, such as Li_2O(conductor)/B_2O_3(insulator) composites [31,32], though the opposite effect of conductivity enhancement at interfaces was reported there.

In summary, our study of the transport properties of a half-metallic ferromagnet-superconductor system reveals the presence of a double percolative transition. Both transitions obey the conventional scaling laws of percolation, but are characterized by different critical exponents and thresholds, thus leading to an anomalous conductor-insulator-superconductor crossover behavior. While here we refer specifically to MgB_2/CrO_2 composites, the study is applicable to other ferromagnet-superconductor systems and, more generally, to a broad class of systems satisfying the double percolation criteria identified above. An important aspect of these studies is the establishment of a nontrivial connection between the system properties, such as conductivity, scaling effects, and critical exponents, and geometric or structural parameters. While our understanding of these phenomena is by no means complete, we expect that these surprising results will stimulate both theoretical and experimental exploration of percolation effects in complex multicomponent systems with arbitrary coupling and geometry, particularly at the nanoscale.

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