Giant Hall effect in nonmagnetic Mo/SnO_2 granular films

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We have measured the resistivities and Hall coefficients, R_H, of a series of nonmagnetic $Mo_x(SnO_2)_{1-x}$ nanogranular films with the Mo volume fraction x ranging from ~0.29 to 1. We found that the magnitude of $R_H(2\ \mathrm{K})$ largely increased by a factor of ~800 as x was reduced from ~0.8 to ≃0.36. Then, it slightly decreased with a further decrease in x down to ≃0.32, which was determined to be the classical percolation threshold, x_c, from the resistivity dependence on x. This nearly 3 orders of magnitude enhancement in R_H at a metal volume fraction $x > x_c$ is explained in terms of the recent theoretical concept of the local quantum-interference effect induced giant Hall effect in granular systems.

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Over decades, the physical properties of metal-insulator composite systems have attracted considerable theoretical and experimental attention due to the nanoscale feature and rich fundamental phenomena in the presence of structural inhomogeneities.[1] Among the electrical-transport properties, the Hall effect near the percolation threshold is of particular interest.[2–8] In the 1990s, it was found that the ordinary Hall coefficient was enhanced by a factor of $\sim 10^3$ in magnetic Ni-SiO_2,[2] (NiFe)-SiO_2,[4] Fe-SiO_2,[5] and Co-SiO_2 (Ref. 6) granular films near the classical percolation threshold, x_c, and in the magnetic saturation region. Subsequently, Zhang *et al.*[3] observed that the Hall coefficient, R_H, of nonmagnetic $Cu_x(SiO_2)_{1-x}$ granular films also increased by nearly 3 orders of magnitude with decreasing Cu volume fraction x (the so-called giant Hall effect, GHE). Moreover, they found that the R_H magnitude peaked at an $x > x_c$. Wan and Sheng[7] immediately proposed a local quantum-interference theory to successfully explain the experiment of Zhang *et al.* They also predicted that the x value corresponding to the maximum R_H is the quantum percolation threshold, x_q. While x_c is fully determined by the geometrical connectivity in a granular system, x_q is sensitive to the quantum-mechanical nature of the transmitting electronic waves. Wan and Sheng argued that the presence of abounding small substructures in granular films will lead to profound wave scattering and interference within a spatial regime of $\sim L_\phi^3$, where L_ϕ is the electron dephasing (phase-coherence) length. As a consequence, the effective carrier density $\langle n \rangle$ of a three-dimensional (3D) sample with linear dimensions $L_x, L_y, L_z \gg L_\phi$ may be markedly reduced, causing a greatly enhanced R_H. The effect of the local quantum interference on the Hall effect was further theoretically elaborated and verified by Xie and Sheng[8] very recently. Experimentally, it is a pity that the GHE has not been reported for more nonmagnetic granular systems other than the Cu-SiO_2 composites.[3] Therefore, both the characteristics of the GHE and the validity of the local quantum-interference theory remain to be further tested.

In this Brief Report we report our experimental results of R_H and resistivity as functions of Mo volume fraction, x, in *nonmagnetic* $Mo_x(SnO_2)_{1-x}$ (hereafter, denoted as Mo-SnO_2) nanogranular composites. We find that the resistivity of this composite system can be well described by the classical percolation theory with a classical percolation threshold of $x_c \simeq 0.32$. Most noteworthy, the magnitude of R_H increases by a factor of nearly 3 orders of magnitude as x is decreased from ~0.8 to a critical value of $x_q \simeq 0.36$, the quantum percolation threshold. Notice the unambiguous inequality $x_q > x_c$.

A series of Mo-SnO_2 granular films with different metal volume fractions were deposited onto glass substrates held at ~50 °C by the cosputtering method. A Mo and a SnO_2 targets both of 60 mm in diameter were used as the sputtering sources. Two sputtering guns, connected with dc and rf power supplies, respectively, were both positioned at an angle of 45° to the sample holder, and the distances from the centers of the targets to the substrates were both ~90 mm. The base pressure of the vacuum chamber was better than 1×10^{-4} Pa before the sputtering process was initiated. An argon flux of 40 SCCM (standard state cubic centimeter per minute at STP) was applied to maintain a pressure of 0.8 Pa during the deposition process. By regulating the sputtering powers in the two targets, we obtained a series of Mo-SnO_2 granular films with x ranging from ~0.29 to 1. For resistivity and the Hall effect measurements, strip-shaped samples (1.5 mm wide) with four side arms (typically, ~2 mm long and ~0.5 mm wide for each arm) were defined by using mechanical masks.

The thicknesses of our films, ranging from 280 to 350 nm, were determined by a surface profiler (Dektak, 6 m). The Mo volume fraction x in each sample was obtained from the energy-dispersive x-ray spectroscopy analysis. The microstructures of the films were characterized by transmission electron microscopy (TEM, Tecnai G2 F20). The resistivities and magnetoresistivities were measured by using the standard four-probe technique. The Hall-effect measurements were performed on a physical property measurement system (PPMS-6000, Quantum Design) by employing the four-contact method. In order to cancel out any misalignment voltages and the thermomagnetic effect, a square-wave cur-

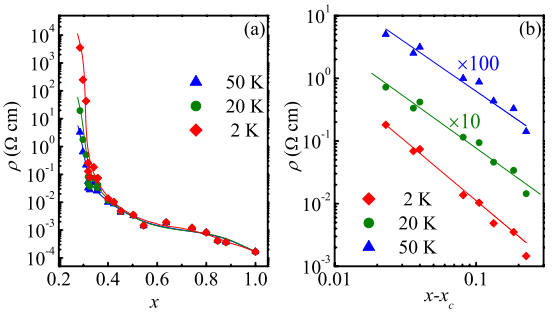

FIG. 1. (Color online) (a) Resistivity as a function of Mo volume fraction for Mo-SnO_2 granular films at three temperatures, as indicated. The solid curves are guides to the eye. (b) Log-log plot of resistivity versus $x-x_c$ at the same three temperatures as in (a). The straight solid lines are least-squares fits to Eq. (1). For clarity, the data at 20 (50) K have been shifted up by multiplying a factor of 10 (100).

rent operating at a frequency of 8.33 Hz was applied and the magnetic field was regulated to sweep from −2 to 2 T in a step of 0.05 T.

Figure 1(a) shows the variation in sample resistivity ρ with x at three measurement temperatures, as indicated. At a given temperature, ρ increases with decreasing x, especially when x is reduced to below ~0.4. Also, the increase in ρ for a given x is larger at lower temperatures. Theoretically, ρ as a function of x in a 3D metal-insulator composite system in the vicinity of percolation threshold can be written as[9,10]

$$\rho = \rho_0 (x - x_c)^{-t}, \quad x > x_c, \tag{1}$$

where ρ_0 is a constant, x_c is the classical percolation threshold mentioned above, and t is a critical exponent. Our experimental data in Fig. 1(a) were least-squares fitted to Eq. (1) and plotted in double-logarithmic scales in Fig. 1(b). Figure 1(b) clearly illustrates that Eq. (1) can well describe our experimental data with the value of $x_c = 0.32 \pm 0.01$. Since both Mo and SnO_2 in our films are amorphous (see below) and strong correlations exist between them, a value of x_c higher than that (≈0.15) for a 3D continuum model is thus expected.[9] At 2, 20, and 50 K, our fitted values of t are 1.90 ± 0.03, 1.71 ± 0.03, and 1.56 ± 0.03, respectively. The value of 1.9 obtained for 2 K is close to the theoretical prediction of $t=2$ for an ideal metal-insulator composite system having $\sigma_M/\sigma_I \gg 1$, where σ_M (σ_I) is the conductivity of the metal (insulator) constituent.[11] At higher temperatures, the condition $\sigma_M/\sigma_I \gg 1$ is not fully satisfied and thus the extracted t value will be reduced from 2.[10] It should be stressed that if we were to use a differing value of x_c to describe our data, the power-law behavior of Eq. (1) could not hold as well, strongly suggesting that ≃0.32 is indeed the classical percolation threshold of our Mo-SnO_2 granular films.

Figure 2 shows the variation in R_H with x for a series of samples at 2 and 50 K, as indicated. All samples (including the pure Mo) reveal positive R_H at our measurement temperatures. Notice that the magnitude of R_H(2 K) increases with decreasing x, reaching a maximum value of 1.6×10^{-8} m^3/C at $x \simeq 0.36$. Then, it slightly decreases with a further decrease in x. In particular, as x decreases from ~0.8

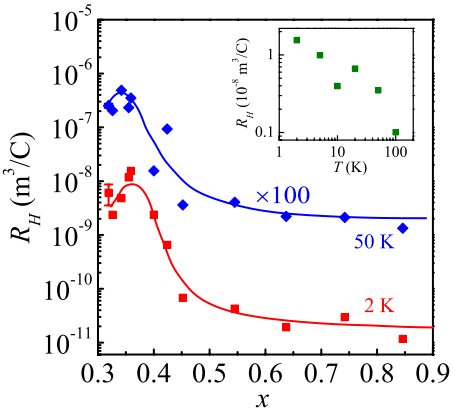

FIG. 2. (Color online) Hall coefficient versus x for Mo-SnO_2 granular films at 2 and 50 K, as indicated. For clarity, the data at 50 K have been shifted up by multiplying a factor of 100. The solid curves are guides to the eye. Inset: Hall coefficient as a function of temperature for the $x \simeq 0.36$ sample.

down to ~0.36, the magnitude of R_H(2 K) greatly increases by a factor of ~800.[12] Such a huge enhancement by a factor of nearly 3 orders of magnitude is far larger than that previously observed in Al-Ge,[13] Au-SiO_2,[14] and Al (Ref. 15) granular films, where enhancement factors of less than 100 were reported. Another significant feature manifested in Fig. 2 is the fact that the R_H magnitude peaks at a Mo volume fraction of $x \simeq 0.36$. This x value is definitely higher than the classical percolation threshold of $x_c \simeq 0.32$ determined above. This particular metal volume fraction corresponding to the maximum R_H is the quantum percolation threshold, x_q. Interestingly, our result of $x_q \simeq 0.36$ in Mo-SnO_2 is in line with the theoretical value (≈0.37) predicted for the simple cubic lattice model with the filling factor being taken into account.[16] However, this coincidence may be incidental. In any case, the true percolation threshold is not a universal value[7] and should be determined experimentally.

According to the 3D classical percolation theory,[17] the maximum enhancement in R_H should occur at $x=x_c$, and the enhancement factor be on the order of $(d/s)^{g/\nu}$, where d is the thickness of the film, s is the size of metallic granules, g is the critical exponent of Hall resistivity, and ν is the exponent of the correlation length. Taking $g/\nu \sim 0.45$,[17] the maximum value of $d=350$ nm, and the minimum value of $s \approx 0.7$ nm (see below), we obtain $(d/s)^{g/\nu} \sim 16$ for our films. This classical value is a factor of 50 smaller than our experimental value of ~800. Hence, our observed huge enhancement in R_H at $x_q \simeq 0.36$ in Mo-SnO_2 granular films can in no way be explained by the classical percolation theory.

The inset of Fig. 2 shows the temperature dependence of R_H for the $x \simeq 0.36$ sample. Notice that R_H decreases monotonically from 1.6×10^{-8} to 1.0×10^{-9} m^3/C as the temperature increases from 2 to 100 K. This result implies that the enhancement factor in R_H is reduced from ~800 at 2 K to ~50 at 100 K. At this latter temperature, the enhancement factor is still somewhat larger than the classical value. On the other hand, in those samples with higher values of $x > x_q$, we found that the R_H magnitude did not vary much with temperature between 2 and 100 K.

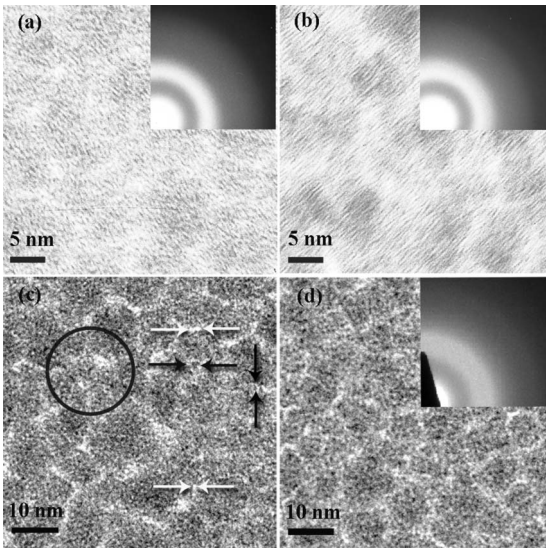

FIG. 3. TEM images and SAED patterns (insets) of Mo-SnO_2 samples with (a) $x \approx 0.29$, (b) 0.33, (c) 0.36, and (d) 0.42. The arrows in (c) indicate the small substructures of insulating and metallic particles with feature sizes of ~0.7 to ~3 nm. The circle indicates roughly the size of a footprint of the electron dephasing length at 2 K.

Figures 3(a)–3(d) show the TEM images for four representative films with values of x as indicated in the caption to Fig. 3. The dark regions correspond to the Mo particles and the bright regions the SnO_2 matrix. These images indicate that the boundaries between Mo particles and SnO_2 particles are not distinct, except that they are somewhat sharper in the $x \approx 0.33$ sample. Inspection of Figs. 3(c) and 3(d) indicates that the Mo and SnO_2 particle sizes in the $x \approx 0.36$ and ≈ 0.42 films vary notably with linear dimensions (the feature size ξ) varying from ~0.7 to ~3 nm. The selected-area electron-diffraction (SAED) patterns (insets of Fig. 3) and x-ray diffraction patterns (not shown) indicate that both Mo and SnO_2 particle in our films are amorphous.

Recently, Wan and Sheng,[7] and Xie and Sheng[8] have theoretically studied the electronic transport properties of granular films, focusing their attention particularly on samples with metal volume fractions near x_q. They realized that granular systems often contain inhomogeneous small substructures, which in turn cause effective multiple electron scattering and result in profound local quantum-interference effect. They found that the sample resistivity and R_H are to be determined by three characteristic length scales: L_ϕ, ξ, and the separations between the metallic and insulating particles. When L_ϕ is less than ξ, the quantum-interference effect occurs within a single feature size (in either the metallic or insulating particle), and the classical percolation picture is valid. In the opposite regime of $L_\phi > \xi$, the local quantum-interference effect will play a decisive role in the charge transport processes, leading to the ~3 orders of magnitude enhancement in R_H, i.e., the GHE.

We have measured the magnetoresistances in our Mo-SnO_2 composites at low temperatures to extract L_ϕ. Figure 4(a) plots the normalized magnetoresistance, $\Delta\rho(B)/\rho^2(0) = [\rho(B) - \rho(0)]/\rho^2(0)$, versus magnetic field B

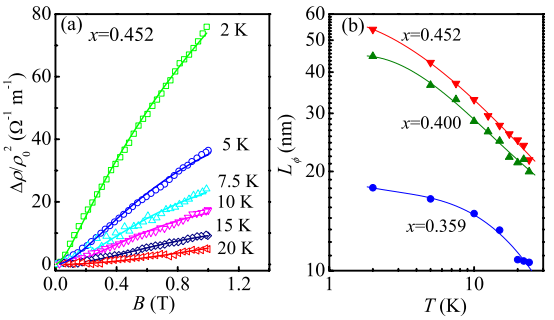

FIG. 4. (Color online) (a) Normalized magnetoresistance as a function of magnetic field for the $x \simeq 0.45$ sample at six temperatures, as indicated. The solid curves are least-squares fits to the 3D weak-localization theory, as described in the text. (b) Electron dephasing length as a function of temperature for three samples, as indicated. The solid curves are guides to eye.

for the representative $x \approx 0.45$ sample at six temperatures, as indicated. Our measured magnetoresistances were least-squares fitted to the 3D weak-localization theory, by taking the spin-orbit scattering and the Maki-Thompson superconducting fluctuation effect into account.[18–20] (Pure Mo has a superconducting critical temperature of 0.92 K, and it is moderately heavy.) Figure 4(a) indicates that the theoretical predictions (the solid curves) can well describe our experimental data. Therefore, L_ϕ at every given temperature can be reliably extracted. In Fig. 4(b), we plot L_ϕ as a function of temperature for three representative samples lying near the quantum percolation threshold. This figure shows that L_ϕ is roughly of the order of a few tens of nanometer long. In particular, in the $x \simeq 0.36$ sample, L_ϕ decreases from ~20 nm at 2 K to ~10 nm at 25 K. That is, $L_\phi > \xi$, and the local quantum-interference effect as proposed by Wan and Sheng,[7] and Xie and Sheng[8] should be responsible for our observed GHE, Fig. 2. In this regard, the monotonic decrease in R_H with increasing temperature (the inset of Fig. 2) can be readily understood as arising due to a decrease in L_ϕ or the ratio $L_\phi(T)/\xi$. At 100 K, the enhancement factor is still ~3 times the classical enhancement factor, as mentioned. This result may imply that L_ϕ(100 K) is still of a few nanometers long (so that $L_\phi > \xi$), or that some modification or extension of the local quantum-interference theory is needed. For instance, how the enhanced Coulomb interaction due to granularity might affect the Hall transport in the vicinity of the percolation threshold deserves further theoretical investigations.[21]

To double check that the R_H magnitude peaks at the quantum percolation threshold, we evaluate the value of x_q in our Mo-SnO_2 granular films in an alternative manner.[22] We use the free-electron model to calculate the Fermi wave number $k_F = (3\pi^2\langle n \rangle)^{1/3}$, where $\langle n \rangle$ is the effective carrier concentration which can be determined from the measured $R_H = 1/(\langle n \rangle e)$ (e being the electronic charge). Then, let the electron mean-free path $l \approx \xi$, we obtain the value of $k_F l = 1.6$, 3.0, and 10 in the $x \simeq 0.36$, 0.40, and 0.45 samples, respectively. Considering that an accurate estimate of the $k_F l$ value in an inhomogeneous sample is not straightforward, our result of $k_F l = 1.6$ already provides a strong indication that the quantum percolation threshold in Mo-SnO_2 must lie very

close to $x_q \approx 0.36$. Therefore, the maximum R_H does occur at an x value near x_q ($>x_c$).

The reason that the resistivity [Fig. 1(b)] appears to be uninfluenced by the quantum interference, and thus $x_c < x_q$, can be explained as follows. At finite temperatures, hopping conduction between localized states (with long localization length close to the quantum percolation threshold) would occur. Therefore, ρ does not really diverge at x_q in a finite sample. Instead, a nominal divergence occurs at x_c, according to Eq. (1), which was derived without considering any quantum-interference effect. On the other hand, if one were concerned with an infinitely large sample and at zero temperature, a resistivity divergence at x_q should be expected.[3] The respective temperature effects on ρ and R_H deserve further experimental studies.

It is worth noting that the maximum enhancement factor in R_H is $\sim$700 in the Cu-SiO_2 granular films reported by Zhang *et al.*,[3] which is $\sim$23 time as large as that would be expected by the classical percolation theory. In our Mo-SnO_2 granular films, the experimental enhancement factor of $\sim$800 corresponds to a factor of $\sim$50 times higher than the classical prediction. Therefore, the GHE observed in the present work represents the largest enhancement factor in R_H ever found in *nonmagnetic* nanogranular films. (Our films were made to be $\sim$3 times thinner than the Cu-SiO_2 films of Zhang *et al.*, facilitating a larger enhancement in R_H, as compared with the classical value.)

In summary, the electrical resistivities and Hall coefficients of a series of Mo-SnO_2 nanogranular films have been investigated. The classical and quantum percolation thresholds are clearly determined to be $x_c \simeq 0.32 < x_q \simeq 0.36$. The Hall-effect measurement indicates that R_H is enhanced by a factor of nearly 3 orders of magnitude near the quantum percolation threshold. Our overall observations support the recent theoretical concept of the local quantum-interference effect induced GHE.

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