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$_2$)$_{1-x}$ granular films with the Mo volume fraction $x$ ranging from $\sim$0.29 to 1. We found that the magnitude of $R_H$ (2 K) largely increased by a factor of $\sim$800 as $x$ was reduced from $\sim$0.8 to $\sim$0.36. Then, it slightly decreased with a further decrease in $x$ down to $\sim$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.$^2,4$ 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$_2$,$^3$ Fe-SiO$_2$,$^4$ 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.$^5$ 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$^6$ immediately proposed a local quantum-interference theory to successfully explain the experiment of Zhang et al.$^5$ They also predicted that the $x$ value corresponding to the maximum $R_H$ is the quantum percolation threshold, $x_q$. While $x_q$ is fully determined by the geometrical connectivity in a granular system, $x_c$ 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 $\sim L^3_d$, where $L_d$ is the electron dephasing (phase-coherence) length. As a consequence, the effective carrier density ($n$) of a three-dimensional (3D) sample with linear dimensions $L_x, L_y, L_z \gg L_d$ 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$^7$ 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$_2$) granular 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 $x_c = 0.32$. Most noteworthy, the magnitude of $R_H$ increases by a factor of nearly 3 orders of magnitude as $x$ is decreased from $\sim$0.8 to a critical value of $x_q = 0.36$, 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 $\sim 50$ °C by the co-sputtering method. A Mo and a SnO$_2$ target 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 $45^\circ$ to the sample holder, and the distances from the centers of the targets to the substrates were both $\sim 90$ mm. The base pressure of the vacuum chamber was better than $1 \times 10^{-4}$ 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 $\sim$0.29 to 1. For resistivity and the Hall effect measurements, strip-shaped samples (1.5 mm wide) with four side arms (typically, $\sim 2$ mm long and $\sim 0.5$ 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-
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 $\rho$ with $x$ at three measurement temperatures, as indicated. At a given temperature, $\rho$ increases with decreasing $x$, especially when $x$ is reduced to below ~0.4. Also, the increase in $\rho$ for a given $x$ is larger at lower temperatures. Theoretically, $\rho$ as a function of $x$ in a 3D metal-insulator composite system in the vicinity of percolation threshold can be written as\(^{9,10}\)

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

where $\rho_0$ is a constant, $x_c$ is the classical percolation threshold mentioned above, and $\tau$ 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.\(^{9,10}\) At 2, 20, and 50 K, our fitted values of $\tau$ 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 $\tau = 2$ for an ideal metal-insulator composite system having $\sigma_M/\sigma_I \approx 1$, where $\sigma_M$ ($\sigma_I$) is the conductivity of the metal (insulator) constituent.\(^{11}\) At higher temperatures, the condition $\sigma_M/\sigma_I \approx 1$ is not fully satisfied and thus the extracted $\tau$ value will be reduced from 2.10.\(^{10}\) 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 $\approx 0.32$ 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 $R_H$ at 2 K increases with decreasing $x$, reaching a maximum value of $1.6 \times 10^{-8}$ m\(^3\)/C at $x \approx 0.36$. Then, it slightly decreases with a further decrease in $x$. In particular, as $x$ decreases from ~0.8 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, Au-SiO\(_2\), 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 $x \approx 0.36$. This $x$ value is definitely higher than the classical percolation threshold for Mo-SnO\(_2\) granular films at three temperatures, as indicated. At a given temperature, the enhancement factor be on the order of $(d/s)^{\nu}\gamma$, where $d$ is the thickness of the film, $s$ is the size of metallic granules, $g$ is the critical exponent of Hall resistivity, and $\nu$ is the exponent of the correlation length. Taking $g/\nu \approx 0.45$,\(^{17}\) the maximum value of $d = 350$ nm, and the minimum value of $s = 0.7$ nm (see below), we obtain $(d/s)^{0.45} \approx 16$ 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 $x_c = 0.36$ 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 $x \approx 0.36$ sample. Notice that $R_H$ decreases monotonically from $1.6 \times 10^{-8}$ to $1.0 \times 10^{-9}$ 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 $x > x_c$, we found that the $R_H$ magnitude did not vary much with temperature between 2 and 100 K.
Electron-diffraction patterns of H2O849 particles. When the separations between the metallic and insulating particles are not distinct, except that they are somewhat sharper in the scattering and result in profound local quantum-interference effects. Granular systems often contain inhomogeneous small substructures, as indicated in the caption to Fig. 3. The dark regions correspond to the Mo particles and the bright regions the SnO2 matrix. These images indicate that the boundaries between Mo particles and SnO2 particles are not distinct, except that they are somewhat sharper in the x=0.33 sample. Inspection of Figs. 3(c) and 3(d) indicates that the Mo and SnO2 particle sizes in the x=0.36 and x=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 SnO2 particle in our films are amorphous.

Recently, Wan and Sheng,7 and Xie and Sheng8 have theoretically studied the electronic transport properties of granular films, focusing their attention particularly on samples with metal volume fractions near x_p. 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_m, ξ, and the separations between the metallic and insulating particles. When L_m 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_m>ξ, 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-SnO2 composites at low temperatures to extract L_m. Figure 4(a) plots the normalized magnetoresistance, ∆ρ(B)/ρ^2(0)=[ρ(B)-ρ(0)]/ρ^2(0), versus magnetic field B for the representative x≈0.45 sample at six temperatures, as indicated. Our measured magnetoresistances were least-squares fitted to the 3D weak-localization theory, as described in the text. In Fig. 4(b), we plot the L_m as a function of temperature for three representative samples lying near the quantum percolation threshold. This figure shows that L_m is roughly of the order of a few tens of nanometer long. In particular, in the x=0.36 sample, L_m decreases from ~20 nm at 2 K to ~10 nm at 25 K. That is, L_m>ξ, and the local quantum-interference effect as proposed by Wan and Sheng,7 and Xie and Sheng8 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_m or the ratio L_m(T)/ξ. At 100 K, the enhancement factor is still ~3 times the classical enhancement factor, as mentioned. This result may imply that L_m(100 K) is still of a few nanometers long (so that L_m>ξ), 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_p in our Mo-SnO2 granular films in an alternative manner.22 We use the free-electron model to calculate the Fermi wave number \( k_F = \frac{3\pi^2(n)}{\hbar^2} \), where (n) is the effective carrier concentration which can be determined from the measured R_H = 1/(ne) (e being the electronic charge). Then, let the electron mean-free path \( l = \frac{k_F}{(n)e} \), we obtain the value of k_p = 1.6, 3.0, and 10 in the x=0.36, 0.40, and 0.45 samples, respectively. Considering that an accurate estimate of the k_p value in an inhomogeneous sample is not straightforward, our result of k_p = 1.6 already provides a strong indication that the quantum percolation threshold in Mo-SnO2 must lie very

FIG. 4. (Color online) (a) Normalized magnetoresistance as a function of magnetic field for the x=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.
close to $x_{c} \approx 0.36$. Therefore, the maximum $R_H$ does occur at an $x$ value near $x_{c}(>x_{c})$.

The reason that the resistivity [Fig. 1(b)] appears to be uninfluenced by the quantum interface, 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, $\rho$ does not really diverge at $x_{c}$ 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 $x_{c}$ should be expected.3 The respective temperature effects on $\rho$ 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., which is $\sim 23$ times 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 $x_{c}=0.32<x_{q}=0.36$. 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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12The magnitudes of $R_H$ for those samples with $0.7 \leq x \leq 1$ are small and hence subject to comparatively large uncertainties. Here we take an average value of $R_H=1.9 \times 10^{-11}$ m$^3$/C.