Giant Hall effect of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) nanogranular films at percolation threshold

Zhiming Wang\(^a\)\(^b\)\(^c\), Qingyu Xu\(^d\), Qiang Zhao\(^b\)\(^c\) & Yulu Che\(^e\)

\(^a\) Institute of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
\(^b\) Laboratorium voor Vaste-Stoffysica en Magnetisme & IKS KULeuven, Celestijnenlaan 200 D., B-3001 Leuven, Belgium
\(^c\) Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
\(^d\) Department of Physics, Southeast University, Nanjing 21189, China
\(^e\) Department of Physics, The Ohio State University, 191 West Woodruff Avenue Columbus, Ohio 43210-1117, USA

Published online: 17 Jul 2012.

To cite this article: Zhiming Wang, Qingyu Xu, Qiang Zhao & Yulu Che (2013) Giant Hall effect of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) nanogranular films at percolation threshold, Phase Transitions: A Multinational Journal, 86:6, 561-569, DOI: 10.1080/01411594.2012.702280

To link to this article: http://dx.doi.org/10.1080/01411594.2012.702280
1. Introduction

Granular films are composite materials where small metal granules, typically a nanometer to tens of nanometers in size, are randomly dispersed in an insulating matrix. Most of these composite films are fabricated by using co-sputtering and plasma assisted deposition techniques. They comprise an important class of inhomogeneous materials in which their physical properties, such as the transport property, the magnetic and optical phenomena, are the subjects of extensive studies [1–7]. Recently, it was found that in the magnetic Co-SiO$_2$ and (NiFe)-SiO$_2$ granular films [8–12], the extraordinary Hall coefficient was enhanced by about 3 orders of magnitude depending on the quality of granular films and the range in vacuum equipment when the metal volume fraction was reduced from 1 to the percolation threshold of $x_c \sim 0.53$ (volume proportion). The enhancement of the Hall coefficients was much greater than what could be counted from the percolation mechanism, which had therefore been named the Giant Hall Effect (GHE) [13–16].

In the granular films, the extraordinary Hall effect occurs in the spin-dependent scattering or spin-dependent tunnelling inhomogeneous structure systems. As is well known, Hall effect in magnetic materials consists of two parts. The ordinary
spin-independent Hall resistivity is due to the Lorentz force and is proportional to the magnetic field \( B \). While the spin-dependent or the extraordinary Hall resistivity is due to the skew scattering or the side jump effects of polarized electrons, and hence is proportional to the magnetization. In the magnetic granular films with a conducting matrix, the saturated Hall resistivity is about \( 10^{-2} \) to \( 10^{-1} \text{\mu\Omega}\text{cm} \), similar to that of pure ferromagnetic films. For magnetic granular films with an insulating matrix, when the metal atomic percentage \( x \) of the films was decreased to around the conduction percolation threshold \( x_p \), the saturated Hall resistivity \( \rho_{xy} \) was increased to about 2–4 orders of magnitude larger than that of the pure ferromagnetic films [17–21]. It was found that both the ordinary and extraordinary parts of the Hall effect display a huge increase when compared to the value measured in the metallic regime [20]. Although the GHE in non-magnetic granular systems have been successfully accounted for within the local quantum interference model, the understanding of the GHE in magnetic granular materials is still far from complete [13,22]. To gain more understanding of GHE in the magnetic materials, the correlative investigation including the exact composition fraction is necessary and essential. In this article, we report the GHE of the series of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) Metal–Insulator nanogranular films in order to substantiate the metal–insulator fraction of percolation threshold in GHE. The maximum of the saturated Hall resistivity of about \( 4.32 \text{\mu\Omega}\text{cm} \) was observed in composition of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) (atom proportion) at room temperature.

2. Experimental details
A series of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) nanogranular films of about 0.5–0.6μm thick were deposited on glass substrates by the RF magnetron sputtering system with a base pressure of \( 2.5 \times 10^{-8} \text{torr} \). The pressure of sputtering gas, argon, was 3 mtorr. A relevant mosaic target was employed, and small pieces of NiCo were adhered compactly on the SiO\(_2\) plate target around the effective sputtering region. The deposition rate was 160 Å/min for NiCo, 30 Å/min for SiO\(_2\) respectively. The distance between the target and the substrate was about 65 mm. The film thickness was determined by X-ray reflectivity (XRR) with a scan from 0.2\(^\circ\) to 4\(^\circ\) with a step size of 0.01\(^\circ\). Cu-K\(\alpha\) radiation was used and the apparatus was BRUKER D8-discover.

Generally, the positions of interference fringes observed in a reflectivity curve are used to determine the film thickness by the modified Bragg equation:

\[
L = D \sqrt{1 - \frac{(1 - n^2)}{\sin^2 \theta_m}}
\]  

where \( L = \frac{m\lambda}{2 \sin \theta_m} \). In general, the dispersion part of the complex refractive index is \( \delta \sim 10^{-5} \) for hard X-ray, so one can reasonably consider \( 1 - n^2 \approx 2\delta \). Then, it can be seen that Equation (1) is in accordance with the equation used by Kiessig [23,24]. Plotting \( L^2 \) versus \( \sin^{-2}\theta_m \), therefore, one can conveniently determine not only the film thickness by extrapolating the line at the \( L^2 \) axis but also the mean refractivity from the slope [23,24]. The film thickness also was calibrated in good accuracy by using an \( \alpha \)-step profiler (scanning length 5000 Å, speed 50 Å s\(^{-1}\), accuracy 0.1 Å) averaged for five measurements (and proofread by Rutherford backscattering i.e. RBS). After deposition, the exact atomic fraction of the deposited film was determined by RBS channelling method. \( M–H \) curves were measured with a vibrating sample magnetometer (VSM, LakeShore.
Cryotronics, Inc). The Hall resistivity was measured using a conventional four-terminal method with an applied magnetic field perpendicular to the film plane at room temperature. It was also repeatedly measured thrice a sample in the disparate region and in the direction of the film in order to confirm its experimentally measurable numerical value. The correlative error statistical analysis was made out of the label bars of the figure. Two Hall voltages were measured, either by rotating the film by 180° in a fixed field or by reversing the field direction to remove the offset voltage due to the asymmetric Hall terminals. Surface pattern analyses of nanogranular films were performed by field emission scanning electron microscope (FE-SEM) (QUANTA FEG 250 FEI Inc).

3. Results and discussion

Figure 1 shows the random and aligned RBS spectra of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) sample and the glass substrate. As is well known, Rutherford backscattering (RBS, channelling) is a good technique to characterize composition, thickness and interface of films directly and non-destructively. When the ion beam is directed along a high-symmetry crystal direction, a phenomenon called ‘channelling’ will occur. The incident ion beam undergoes a series of correlated small angle scatterings and consequently the backscattering events are significantly reduced compared to the backscattering events when the ion beam is directed in a random direction. In the backscattering spectrometry, the composition and depth profile of the layer on the glass substrate could be determined. Our RBS measurement was done with NEC Pelletron model 5SDH-2 on IKS, K.U. Leuven University, Belgium. The red dot on Figure 1 shows a simulation of the random spectrum given by the RUMP program [25]. It is revealed that the \((\text{Ni}_{90}\text{Co}_{10})(\text{SiO}_2)\) layers have a thickness of 50–60 nm and the composition is accurately \(\text{Ni}_{49.5}\text{Co}_{5.5}\text{Si}_{15.3}\text{O}_{30.6}\), i.e. \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) (atom proportion), which is close to the percolation threshold \((x_c \sim 0.53\) volume proportion\).

Figure 2 shows the magnetoresistivity curves of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) film samples as representative of two series that possess the characteristic of tunnelling magnetoresistance, with a magnetic field applied perpendicular to the film plane. The MR ratio is defined as \(\Delta \rho / \rho = [\rho(H) - \rho(0)]/\rho(0)\), where \(\rho(0)\) is the resistivity at zero field, while \(\rho(H)\) is the
resistivity at magnetic field \( H \). It is believed that the great MR effects in these systems originate from the spin-dependent tunnelling of electrons between the isolated metal particles. Figure 2 showed the resistivity and the MR versus the applied magnetic field curves of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) samples in the series. The different branch lines originate from the Joule effect of the electric current on whole cycles of measure.

Figure 3 shows the Hall resistivity of series of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) granular film sample with different fraction at 12,500 Oe applied field. The inset graph shows the Max. coefficient of Hall effect vs. Ni\text{90}Co\text{10} proportion in atomic fraction.

Figure 2. The magnetoresistivity curves of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) of the series granular films sample with a magnetic field applied perpendicular to the film plane.

Figure 3. Hall resistivity of series of \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) granular film sample with different fraction at 12,500 Oe applied field. The inset graph shows the Max. coefficient of Hall effect vs. Ni\text{90}Co\text{10} proportion in atomic fraction.
resistivity at magnetic field $H$. It is believed that the great MR effects in these systems originate from the spin-dependent tunnelling of electrons between the isolated metal particles. Figure 2 showed the resistivity and the MR versus the applied magnetic field curves of (Ni$_{90}$Co$_{10}$)$_{55}$(SiO$_2$)$_{45}$ samples in the series. The different branch lines originate from the Joule effect of the electric current on whole cycles of measure.

Figure 3 shows the Hall resistivity $\rho_{xy}$ as a function of the applied magnetic fields $H$ for a series of (Ni$_{90}$Co$_{10}$)$_x$(SiO$_2$)$_{1-x}$ films at room temperature. The Hall resistivity is negative in the positive field. The extraordinary Hall resistivity could be characterized by its absolute value at saturations $\rho_{xys}$, which could be determined by a linear extrapolation of the data at high fields to $H = 0$. The saturated Hall resistivity $\rho_{xys}$ of the pure ferromagnetic metal film is about $10^{-2}$ to $10^{-1}$ $\Omega$ cm. The maximum of saturated Hall resistivity occurred at atomic fraction (Ni$_{90}$Co$_{10}$)$_{55}$(SiO$_2$)$_{45}$ in the series of (Ni$_{90}$Co$_{10}$)$_x$(SiO$_2$)$_{1-x}$ films is 4.32 $\Omega$ cm. When compared to typical ferromagnetic metal film, this extraordinary Hall effect is enhanced by about 3 orders of magnitude. Note that in Figure 3, the curve of Hall resistivity against the field $H$ presents the characteristic of Hall effect. Figure 4 representatively shows the typical $M–H$ magnetization curve of (Ni$_{90}$Co$_{10}$)$_{55}$(SiO$_2$)$_{45}$ nanogranular sample, the two different branch lines originate from the coercive force. Since the extraordinary Hall coefficient is much greater than the ordinary Hall coefficient, the curves of the Hall resistivity against the magnetic field are S-shaped, similar to magnetization curves, with a finite slope after saturation fields. In addition, the mechanism of the extraordinary Hall coefficient is different from that of the giant magnetoresistance, so the composition of the largest Hall resistivity is not consistent with the composition of the largest magnetoresistance film samples. Figure 5 shows the FE-SEM image of the as-deposited sample (Ni$_{90}$Co$_{10}$)$_{55}$(SiO$_2$)$_{45}$. From the exhibited image, NiCo particles embedded in SiO$_2$ matrix are smaller than 30 nm, and almost are connected into a network. The FE-SEM image further demonstrated that the volume fraction of NiCo in these granular films is near percolation threshold and GHE originates from the percolation of magnetic metal and nonmagnetic insulator granular film. It is reasonable to attribute this GHE to the enhanced electron–electron interaction and the decrease of electron density $n$ when the atom fraction of magnetic metals is near percolation threshold.

At the point of view of Hall component application, in order to endure harsh weather conditions or a possible temperature increment from Joule effect of current, the nanogranular films should have a good thermal stability, which ensures the Hall voltage numerical value and the function of its component under normal. Figure 6 shows the
saturated Hall resistivity measured at room temperature for \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) nanogranular films annealed at different temperatures up to 300°C. Even at annealing temperature as high as 300°C, the saturated extraordinary Hall resistivity did not decrease much. The thermal stability of Permalloy \((\text{Ni}_{90}\text{Co}_{10})\) insulator nanogranular films is favourable for temperature as high as 300°C, and thus it might be considered as information storage technology or a magnetic field sensor for operating temperatures below 300°C.

The enhancement in Hall coefficient is much larger than what expected by the classical percolation theory, where the maximum predicted enhancement factor at the percolation threshold is on the order of \((\frac{t}{a})^\gamma\), where \(t\) is the thickness of the film, and \(a\) is the size of granules. Here, \(g\) is the critical exponent of three-dimension Hall resistivity, and \(n\) is the exponent for the three-dimension correlation lengths. The ratio \(g/n\) is approximately given by 0.4/0.9–0.45 [26,27]. By taking \(t = 0.5–0.6\ \mu\text{m}\), the thickness of our films, and a minimum value of \(a\) – the order of nm – the largest possible Hall coefficient enhancement is less than 30 [13,14]. Besides the magnitude of the enhancement factor, another intriguing feature is that the maximum Hall coefficient does not occur at the percolation threshold, \(x_c = 0.43\), but rather at a higher value of \(x = 0.53\) (volume proportion), which is unexpected within the classical picture. GHE is an inherent quantum effect, which is considered to be correlative with the magnetic scattering, disordered structure and heterogeneous through from the metal to insulator nanogranular film phase transition. The MR effect of Figure 2 had indicated the characteristic of before-mentioned magnetic scattering, the magnetic scattering originated from \((\text{Ni}_{90}\text{Co}_{10})\) of the nanogranular film \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) system, which provided with the maximal anisotropic magnetoresistance effect in the Permalloy [28]. The series \((\text{Ni}_{90}\text{Co}_{10})_x(\text{SiO}_2)_{1-x}\) granular film could be bit by bit close to quantum percolation threshold by modulating the proportion of metal \((\text{Ni}_{90}\text{Co}_{10})\) and insulator \((\text{SiO}_2)\). The quantum percolation threshold was experimentally made certain by the max. coefficient of Hall effect, then the correlative proportion of metal \((\text{Ni}_{90}\text{Co}_{10})\) and insulator \((\text{SiO}_2)\) is accurately ascertained by the experimental data of Rutherford backscattering and a simulation analyses of the random spectrum given by the RUMP program. As previously mentioned, RBS identifies \(x_c = 0.55\) (atom proportion) to be close to the quantum percolation threshold. (It is common in

![Figure 6. The saturated extraordinary Hall resistivity of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) films at different annealing temperature.](image-url)
granular systems to see insulating temperature variation at low temperatures and metallic behaviour at high temperatures, for metal concentrations that fall between the quantum and classical percolation thresholds. This is due to an increased local quantum interference effect at low temperatures, associated with the increased dephasing length. Thus, at \( T = 0 \) K, the conductivity threshold should be at the quantum percolation threshold, whereas, at \( T = \infty \) K, the conductivity threshold should be at the classical, or geometric (connectivity), threshold [13].

Near the percolation threshold, the electron transport is limited to the channel of very small width, which is likely to lead to electronic coherence length approaching the width of the channel. The electrons are not only taken as particles, but also as the wave, and there is electronic interference between the wave functions, thus causing GHE to occur. From Figure 5, FE-SEM image in the order of 10 nm, with the metal-insulator inlay framework one another had been favoured this viewpoint. The saturated extraordinary Hall resistivity decreased with the annealing temperature as seen from Figure 6. After annealing, the metal granule grows, the electronic interference between the wave functions weakens, GHE vanishes when the metal granule overruns the electronic coherence length.

Generally, the interference component increases as \( x \) approaches the quantum percolation threshold, at or close to the point where the interference-induced wave function localization occurs (at the Fermi level). As the quantum percolation threshold is above the classical percolation threshold, it follows that the GHE does not keep to the classical \( x_c \) but rather peaks at or close to the quantum percolation threshold. Below the quantum percolation threshold, the interference has the effect of changing the localization length. Local interference was also expected to affect the resistivity by modifying the two-component composite picture to one that has a distribution of local conductivities [13].

4. Summary

The series of \((\text{Ni}_{90}\text{Co}_{10})_c(\text{SiO}_2)_{1-x}\) metal-insulator nanogranular films were fabricated using the magnetron sputtering technique, and their compositions in the atomic fraction were accurately characterized by the Rutherford backscattering (RBS) channelling technique. The saturated Hall resistivity of about 4.32 μΩ cm of \((\text{Ni}_{90}\text{Co}_{10})_{55}(\text{SiO}_2)_{45}\) at the quantum percolation threshold for the as-deposited sample was observed at room temperature. The results of atomic fraction were essentially coincided with the volume fraction of quantum percolation threshold. The SEM image of the as-deposited sample \((\text{Ni}_{90}\text{Co}_{10})_c(\text{SiO}_2)_{1-x}\) shows the shape the atom fraction of NiCo relative to SiO\(_2\) near the percolation threshold and substantiated the volume fraction of GHE percolation threshold on the side. Generally, the GHE is correlative with the enhanced electron–electron interaction and the decrease of electron density \( n \) when the atom fraction of magnetic metals was near percolation threshold [13]. We reckon that the signal level of the GHE could be improved by precisely controlling the metal-insulator atomic fraction to the appropriate percolation region or by producing some artificial meshwork structure that makes the magnetic metal particles nano-contact but avoids separating.

Acknowledgements

The work was supported by National Laboratory of Solid State Microstructure of Nanjing University (LSSMS) under Grant No. M 23005, Department of Personnel Jiangsu Six Talent Fund under Grant No. AD 41118, and Top-Grade CNC Machine Tools and Basic Manufacture Projects under Grant No. 2010ZX04004-116.
References


