行政院國家科學委員會專題研究計畫　成果報告

利用磁性元素參雜研究金屬-非金屬與超導體-非導體相變

(3/3)

計畫類別：個別型計畫
計畫編號：NSC93-2112-M-009-003-
執行期間：93 年 08 月 01 日至 94 年 10 月 31 日
執行單位：國立交通大學電子物理學系(所)

計畫主持人：許世英

報告類型：完整報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國 95 年 6 月 30 日

行政院國家科學委員會補助專題研究計畫期中報告

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※利用磁性元素參雜研究金屬−非金屬與超導−非導體相變(3/3)※
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計畫類別：■個別型計畫　　□整合型計畫
計畫編號：NSC93－2112－M－009－003
執行期間：93 年 8 月 1 日至　94 年 10 月 31 日

計畫主持人：許世英
共同主持人：
計畫參與人員：
鐘廷翊（博士班二年級生）
劉凱銘（博士班二年級生）
王聿宸（碩士班一年級生）

本成果報告包括以下應繳交之附件：
□赴國外出差或研習心得報告一份
□赴大陸地區出差或研習心得報告一份
■**出席國際學術會議心得報告及發表之論文各一份**
□國際合作研究計畫國外研究報告書一份

執行單位：國立交通大學電子物理系

中　華　民　國　95　年　01　月　27　日

行政院國家科學委員會專題研究計畫成果報告

利用磁性元素參雜研究金屬-非金屬與超導-非導體相變

Metal-Insulator and Superconductor-insulator transitions in the magnetic materials

計畫編號：NSC 93-2112-M-009-003

執行期限：93 年 8 月 1 日至 94 年 10 月 31 日

主持人：許世英　　國立交通大學電子物理系

一、中文摘要

在二氧化矽與鈷共濺鍍的厚膜系統，藉由二氧化矽與鈷兩者的相對濺鍍速率控制，我們可以調變樣品內的金屬體積百分率，使樣品無序程度由弱到強分布；尤其在靠近金屬與絕緣相變間，此顆粒結構樣品展現非常有趣的行為，除了之前所探討的電阻率對溫度有異常 $\ln(T)$相關性，遲滯的磁電阻變化率與無序程度相關，然由於不同的顆粒成長機制，隨著樣品無序程度增加，樣品的遲滯磁電阻率變化率有上升的趨勢，在金屬-絕緣相變附近的樣品磁電阻由自旋相關散射的 GMR 效應主導，而且直接與電阻率對 $\ln(T)$的變化率成正比。

我們也藉由樣品加熱來微調顆粒幾何結構的分佈，探討其對電性傳輸、遲滯電阻率、與異常霍爾效應影響，深入探討導致金屬與絕緣相變的物理機制。

關鍵詞：量子干涉效應、無序程度、磁矩、異向性磁組、鐵磁。

Abstract

We have measured the magnetization and magneto-transport in a series of 3D magnetic $Co_x(SiO_2)_{1-x}$ samples to study the metal-insulator translation. By controlling the sputtering rates of Co and SiO_2, the degree of disorder of $Co(SiO_2)$ can be made from weakly disordered to strongly disordered. However, the really interesting behavior of the granular material is when the material is metaalic, but just barely metallic above the metal-to-insulator transition. From the previous studies, resistivity of samples in this regime demonstrates the anomalous $\ln(T)$ dependence and hysteresis MR ratio depends on degree of disorder of sample. It has been known that the magnetoresistance is due to spin-dependent scattering effect and the magnitude of GMR ratio increases with increasing resistivity. Here, we found that MR ratio depends nearly linear with $d\rho(T)/d\ln(T)$, characterizing the degree of disorder of sample.

Besides, we also studied resistivity, magnetoresistivity, and the anomalous Hall effect for samples near metal-to-insulator transition upon thermal annealing. Experiments on our samples provide important insights into the mechanisms driving the metal-insulator transition (MIT).

Keywords: quantum interference effects, disorder, magnetic moment, anisotropic MR, ferromagnetism, percolation.

二、緣由與目的

Magnetic granular samples, consisting of nanometer scale metal particles embedded in a nearly immiscible insulating medium, have attracted much attention in the last couple decades and continue to be an active research topic. Recent interest is due to discover of giant magnetoresistance (GMR) in magnetic-nonmagnetic binary metal granular samples.[1] We would like to take consideration of magnetic moment into problem of disordered tuned phase transition to understand how it influence the dominant mechanisms that drives the transition.

In the previous projects (1/3 & 2/3), we concluded that the evolution of temperature dependent resistivity with increasing disorder in granular $Co_x(SiO_2)_{1-x}$ sample is similar to that observed in non-magnetic CuGe systems. However, MR due to quantum interference effects is greatly decreased because that magnetic moment in each grain is detrimental to the quantum interference effects. Near the metal-insulator transition with a $\ln(T)$ dependent resistivity, scattering length of electron is more than numerous of gain distance, MR can be described by the two-current model as in multilayer systems. The magnitude of MR ratio is in the range of 0.05%~2% at 10K and scales nearly linear with disorder ρ_{10K}. For sample in strongly disordered region, MR comes from spin-dependent tunneling effect. The magnitude of MR ratio is in the range of 2%~10% at 10K. Negative MR due to quantum interference in hopping regime become importance and is comparable to spin-dependent MR.

Here, we carefully examined much more samples near the MIT to explore the physical origin for the occurrence of MIT.

三、實驗結果

(I) Granular $Co_x(SiO_2)_{1-x}$ samples

As reported before, the behaviors of these samples can be cataloged into three regimes. Sample with ρ_{10K} <500μΩcm, low temperature transport $\Delta\rho(T) \propto -T^{1/2}$. For sample with 500μΩcm<ρ_{10K}<100mΩcm, close to MIT, $\Delta\rho \propto \ln(T)$ is better than any other form to describe the transport behavior.[2,3] For sample with ρ_{10K} >100mΩcm, ρ becomes much more sensitive to temperature and follows the hopping mechanism resulting in the form that $\Delta\rho \propto \exp[1/T^{1/2}]$. [4] Figure 1 shows the temperature dependence of the normalized resistivity for 5 representative samples near metal-insulator transition. The temperature dependence of resistivity at low temperature shows a gradual evolution. As illustrated in fig.2 for numerous samples with 0.8mΩcm <ρ_{300K}<50mΩcm, a $\ln(T)$ dependent resistivity is very common in granular system near MIT.[2,3]

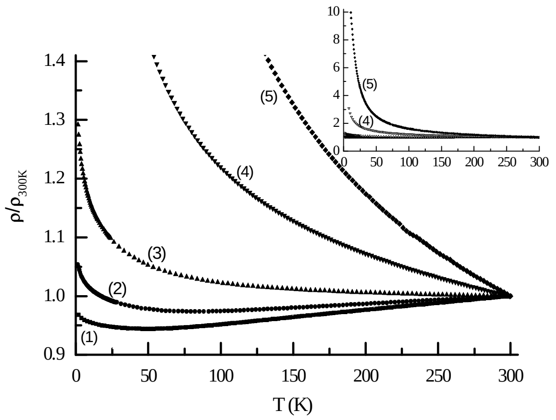

Fig.1. Temperature dependences of normalized resistivity for 5 $Co_x(SiO_2)_{1-x}$ samples near the MIT. ρ_{300K} are (1)0.9, (2)3.5 (3)6.2, (4)22, (5)79 mΩcm, respectively.

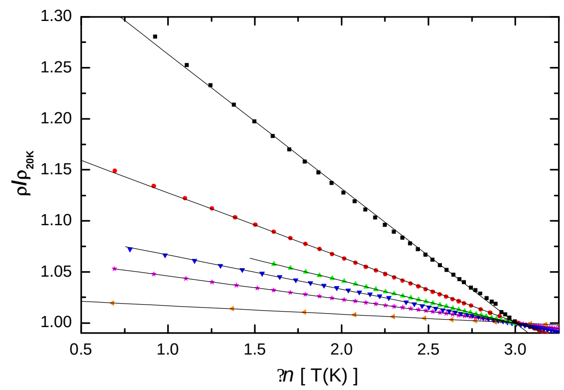

Fig.2. Normalized resistivity as a function of $\ln(T)$ for several samples near MIT at temperature range from 1.5K to 45K. Lines are least square fits to data.

The explanations in terms of either weak localization or electron-electron interaction have a limited applicability. Beloborodov *et al.* have attributed this logarithmic behavior to charging effect in grains as an evidence of granular structure of doped high-Tc cuprates. It was expected that the conductivity change in a granular sample at low temperatures follows, [5]

$$\Delta\sigma(T) = \sigma_o\left(1 - \alpha \ln\left(\frac{gE_c}{T}\right)\right)$$

where E_c is the charging energy. Our data agree with the above equation. By taking s as the normalized slope of data shown in fig.2, $d[\rho(T)/\rho_{20K}]/d[\ln(T/20)]$, s increases with disorder (resistivity) nearly linearly.

The magneto-transport of all samples demonstrates a clear hysteresis loop. This behavior was certainly not observed in CuGe samples. From DC magnetic moment measurements using PPMS we found that the MR curve is consistent with MH data. We believe the structure of magnetic Co grains can successfully explain data with the two spin current model. This is similar to that found in magnetic/metal multilayer systems. We define the value of MR_{max} as the maximum of value, $(R(H)-R(H_{sat}))/R(H_{sat})$. MR is about 0.6% for sample shown in the inset of fig.3. We plot MR_{max} vs. s that is obtained from the logarithmic temperature dependence of resistivity for all samples near MIT in fig.3. As shown, MR_{max} increases with s (disorder) nearly linearly. Despite the concentration x, there is a correlation between the zero field electric transport and magneto-transport. The origin can be the coupling between grains that correspond directly to s (degree of disorder). MR_{max} increases slowly in the hopping regime where the multiple tunneling effects dominate.

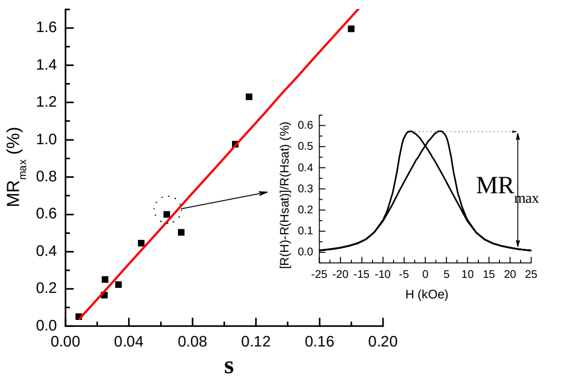

Fig.3. The maximum MR versus s (disorder) for numerous $Co(SiO_2)$ samples at T=10K. Line is a least square fit to data. Inset is magnetoresistance as a function of applied magnetic filed for one sample at 10K. Direction of field is perpendicular to film plane.

(II)Effects of Annealing

We also studied resistivity, magnetoresistivity for some disordered granular Co/SiO_2 samples upon thermal annealing. Samples were prepared by magnetron sputtering system and then were ex situ annealed at 150, 200, and 250^{o}C for seven hours in vacuum. The target temperature is not high enough to change the phase of the sample, while the distribution of the grain size is slightly changed.[6]

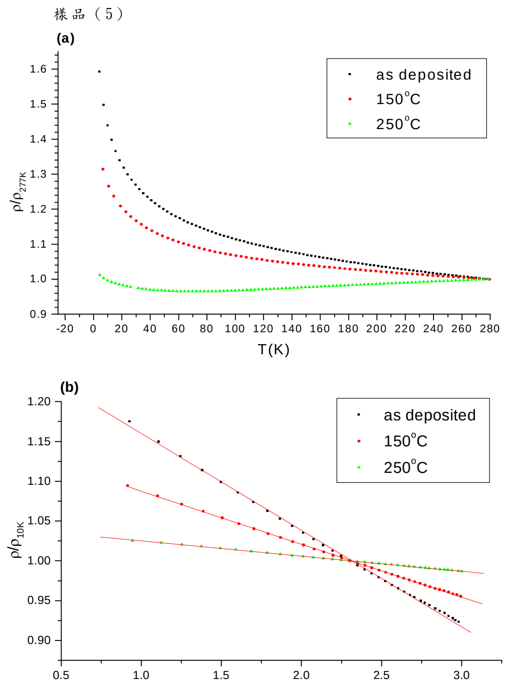

Fig.4. Normalized resistivity versus (a) temperature and (b) logarithmics of temperature for $Co(SiO_2)$ samples annealed at different temperatures. The room temperature resistivity for the as-deposited sample is 13.6mΩcm and it is near MIT.

Fig.4 shows normalized resistivity at zero field as a function of temperature for samples annealed at different temperatures. As seen, the temperature dependences of resistivity are still close to logarithmic, with the slope decreasing with increasing annealing temperature. Overall, the higher annealing temperature the sample has been through, the more metallic the sample is, the smaller of the slope of resistivity versus logarithmics of temperature.

This trend is associated with changes in grain size distribution. In the as-deposited sample, the current flows via channels formed mainly by small grains. Upon annealing, the small grains disappear and collapse into slightly bigger grains. According to the classical percolation theory, the resistivity would decrease with increasing grain size based on the classical finite-size scaling.[7] Meanwhile, the - ℏ(T) dependent contribution to resistivity is decreased.

Other work in the Hall resistivity measurements for these Co(SiO_2) is under investigation. A specific feature of ferromagnetic metals is that $\rho_H = R_H H + R_s 4\pi M$ possesses two components, the first term (normal part) is due to the Lorentz force and the second term is related with the influence of the spin-orbit interaction on the spin-polarized electrons. The second term is much greater than the first term for granular system, and usually is referred as anomalous Hall effect (AHE). [2,8] This AHE was also observed in our samples near the MIT.

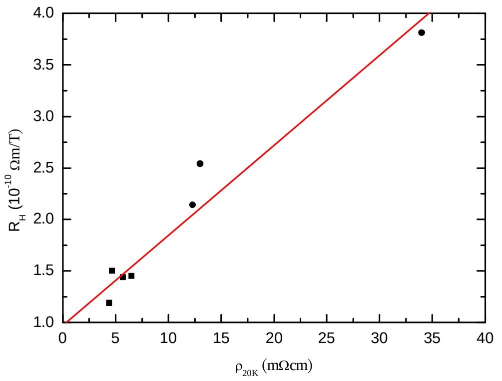

Fig.5. Hall resistivity versus resistivity for Co(SiO_2) samples annealed at different temperatures. The room temperature resistivities for the as-deposited sample (●) and (■) are 22.2 and 6.2 mΩcm, respectively.

We plot Hall resistivity for numerous samples in Fig.5. As shown, the more disorder sample has the bigger value of R_H. Moreover, Hall resistivity decreases upon annealing in consistence with the classical percolation theory.

四、結論

From the studies of $Co_x(SiO_2)_{1-x}$ systems, MIT can occurs by adjusting the relative concentrations between Co and SiO_2. The evolution of temperature dependent resistivity with increasing disorder is similar to that observed in non-magnetic composite or binary systems. The classical percolation theory can be used to describe the metal-to-insulator transition. The ℏ(T) dependent resistivity observed in samples near MIT is evident for the grain structure and is attributed to the DOS correction due to electron-electron interaction. Resistivty and Hall resistivity for samples near MIT upon annealing further support the classical percolation model. The MR demonstrates hysteresis behavior due to the magnetic couplings between grains. Near MIT, scattering length of electron is more than couples of grain distance and scattering of up and down spins through grain channels depends on whether parallel or anti-parallel alignment of magnetic moments of all grains. MR_{max} increases with s (disorder) nearly linearly. Despite the concentration x, there is a correlation between the zero field electric transport and magneto-transport.

五、參考文獻

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[8] C. Wan and P. Sheng, PRB**66**, 075309 (2002).

國外會議：

1. S. Y. Hsu, Y. T. Cheng, and C. H. Chang, "Electrical transport of granular Ferromagnets near metal-to-insulator transition", oral presentation, "Twelfth annual international conference on composites/nano Engineering", August 1-6, 2005.

參加 2005 年第十二屆國際合成材料與奈米工程會議(ICCE12)心得報告

一、會議日期：8/1~8/6

二、會議地點：Canary Island, Spain

三、報告者：許世英

四、方式 ： 口頭報告(Oral)

五、題目：

Electrical transport of granular Ferromagnets near metal-to-insulator transition

六、 會議概況：

第十二屆國際合成材料與奈米工程會議於西班牙的加那利島舉行，從八月一日到八月五日，為期五天。此會議涵蓋奈米材料、磁性材料、氧化物、等特殊材料的研發、基礎科學研究、與科技應用探討，跨物理、化學、材料、電機、機械、能源、與生物科學領域，參與的人員來自歐洲、美國、亞洲等。同時段有 4 個 parallel sections，而且從早上 8:00 到晚上 10:00，行程排得相當緊湊，與會人員應有 500 人以上，日本、大陸參與的人數頗多。

七、 參加會議過程：

7/31 由於加那利島並不在西班牙本島，而在靠西非海岸，所以旅程有些複雜，去程先搭華航從台灣到德國法朗克福國際機場，再轉銜德航到西班牙巴賽隆那機場，然後再接西班牙航空到加那利島的北部 Tenerife 機場，從 7/30 晚上 7:00 出發到達旅館已是當地 7/31 晚上 11:00，(當地與台灣時差 6 小時)。由於隔日就必需報告，盥洗後隨即倒頭就寢，

08/01 第一天在早上 8:00~10:00 期間即已安排大會演講，雖然經一天飛了半個地球的旅途勞累，仍然秉持戰戰兢兢態度，起個大早，準時到會場報到。順便熟悉場地，因為在第二場 10:30AM 就要作研究成果報告，20 分鐘的口頭報告。期間有 3~4 位者提問，同場一位做金薄膜電子表面散射造成的霍爾效應研究的智利學者，對相關物理機制頗熟悉，因此問了一些提到的 Beloborodov *et al.* 的理論，另外材料背景的希臘和西班牙學者較關心我們樣品的微結構。

08/02~08/04 除了一大早的跨領域的大會演講廣泛地瞭解生物與工程研究學者眼中的微觀世界與科技發展的遠景，其他時間主要都是聽 nano 和 magnetics 兩 sections 的演講，

期間認識來自 U. of Proto, Portugal 的理論物理學者 Dr. Yuri Pogorelov，他對於一些 spin-valve 元件的相關散射機制導致的 MR ratio 有些見解，同時也對我們的數據有興趣，會場中曾花一個多小時彼此介紹研究成果。

另外，印象較深刻的就是很多作材料或化學的研究群可利用不同的化學方式製作各式 nano 或多層特殊元件，物理機制的探討較少，畢竟這會議屬於跨領域應用範疇，偏工程。

日本的 AIST 的 Y. Tanaka 談了以 multilayer Cuprate superconductor 發展新量子電子元件，另外，K.Endo 談了氧化薄膜做為未來奈米元件的遠景，開闊了基礎科學研究對尖端科技潛力的視野。

08/05 由於班機銜接問題的緣故，因此必須提早離開會場，早上聽了一個 section，隨即趕回旅館打包，打道回府。班機於傍晚離開加那利島，到馬德里國際機場，提領行旅之後就已約半夜，而隔天到法蘭克福機場的班機又是一大早 5:00，只好就地在機場小憩，其實沒多久就被一波波人雜聲所吵醒，一下子機場又充斥著人群，搭早班機飛往德國，然後轉搭華航班機直飛台北，回到台北已是 8/07。

會議論文

ELECTRICAL PROPERTIES OF GRANULAR FERROMAGNETS NEAR METAL-TO-INSULATOR TRANSITION

<u>Shih-ying Hsu</u>, Y.T. Cheng, and C.H. Chang

Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan

Introduction

Disordered samples have a long history as systems in which new and interesting phenomena can be studied and uncovered. The different physical behaviors due to the evolution of wave function from extended to localized in two extremes were well understood. Recent interest is due to discover of giant magnetoresistance (GMR) in magnetic/nonmagnetic binary metal granular samples. With the introduction of magnetic element in disordered systems, we can investigate the influence of local electronic spin to the dominant mechanisms in phase transitions such as quantum interference and electron-electron interaction effects. We have performed careful experiments on co-sputtering $Co_x(SiO_2)_{1-x}$ disordered samples to elucidate the physical effects behind the profound. Co seems form grains embedded in SiO_2 sea and giant MR due to the couplings of magnetic moments between grains appears in these samples. Experiments on our samples provide important insights into the mechanisms driving the metal-insulator transition (MIT).

Experimental

The samples were obtained by co-sputtering of Co and SiO_2 onto Sapphire substrates in 7.4mTorr of Argon. The base pressure of the chamber was less than 7×10^{-7} Torr. Deposition rate of each material was adjusted by controlling sputtering power. The thickness of each composite sample is about 150~300nm. By this method we have successfully fabricated a series of magnetic granular samples with disorder spanning from weakly to strongly disordered regions. The room temperature resistivity ρ_{300K} changes from couple 0.1mΩcm to 10^3mΩcm. The relative concentration is unknown and however, is not important according to the following analyses.

Four terminal measurements of longitudinal resistance were performed in a pumped ^{4}He cryostat. Sample was placed in the center of a 9Tesla superconducting solenoid magnet.

Results and Discussion

Figure 1 shows the temperature dependence of the normalized resistivity for 5 representative samples near metal-insulator transition. The temperature dependence of resistivity at low temperature shows a gradual evolution. In the weakly disordered sample, the increase of resistivity with decreasing temperature follows that $\Delta\rho\propto T^{1/2}$ that can be attributed to the quantum interference effects in the extended states. In the strongly disordered sample, the resistivity becomes much more sensitive to temperature and follows the hopping mechanism resulting in the form that $\Delta\rho\propto\exp[1/T^{1/2}]$.

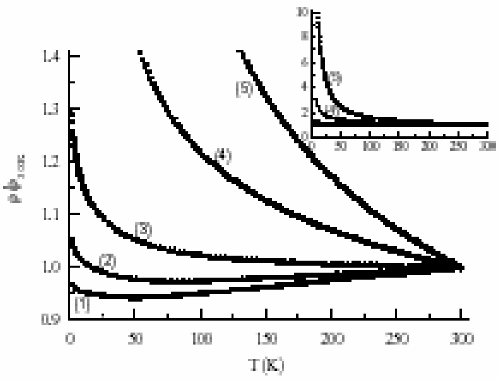

Fig.1. Temperature dependences of normalized resistivity for 5 $Co_x(SiO_2)_{1-x}$ samples. ρ_{300K} are (1)0.9, (2)3.5 (3)6.2, (4)22, (5)79 mΩcm, respectively.

However, as the sample is close to the metal-insulator transition(MIT), the form that $\Delta\rho\propto\ell n(T)$ is better than any other form to describe the transport behavior, as illustrated in fig.2 for numerous samples with 0.8mΩcm $<\rho_{300K}<$50mΩcm . A ℓn(T) dependent resistivity is very common in granular system near MIT.[1] The explanations in terms of either weak localization or electron-electron interaction have a limited applicability. Beloborodov *et al*. have attributed this logarithmic behavior to charging effect in grains as an evidence of granular structure of doped high-Tc cuprates. It was expected that the conductivity change in a granular sample at low temperatures follows, [2]

$$\Delta\sigma(T) = \sigma_o\left(1 - \alpha\,\ell n\left(\frac{gE_c}{T}\right)\right)$$

where E_c is the charging energy. Our data agree with the above equation. By taking s as the normalized slope of data shown in fig.2, $d[\rho(T)/\rho_{20K}]/d[\ell n(T/20)]$, s increases with disorder (resistivity) nearly linearly.

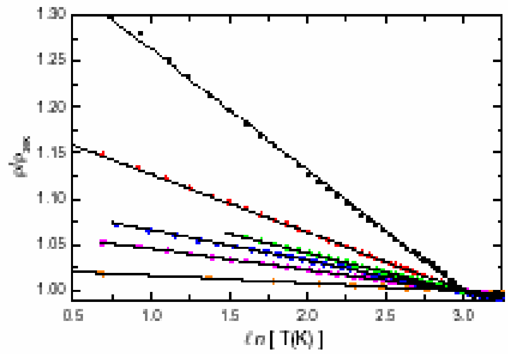

Fig.2. Normalized resistivity as a function of ℓn(T) for several samples near MIT at temperature range from 1.5K to 45K. Lines are least square fits to data.

The change of magnetoresistance of one sample is plotted in the inset of figure 3 with the applied field direction perpendicular to film plane at T=10K[3]. As seen, data demonstrates a clear hysteresis loop. This result was certainly not observed in non-magnetic binary samples such as Cu/Ge, Cu/SiO_2,…etc. From DC magnetic moment measurements using PPMS we found that the MR curve is consistent with MH data. When the magnetic field is applied in film plane, magnetoresistance demonstrate similar results. Except the Hp at maximum MR is smaller than that with field perpendicular to plane, size of MR is about the same. It is easy to figure out since grain has non-symmetric shape. Magnetic moment is easier to rotate and align in plane than out of plane. Coercive field is weaker in the former than in the latter. As the same size of MR, it is evidence that sample is three dimensional. We believe the structure of magnetic Co grains can successfully explain data with the two spin current model. This is similar to that found in magnetic/metal multilayer systems.

We define the value of MR_{max} as the maximum of value, $(R(H)-R(H_{sat}))/R(H_{sat})$. MR is about 0.6% for sample shown in the inset of fig.3. We plot MR_{max} vs. s that is obtained from the logarithmic temperature dependence of resistivity for all samples near MIT in fig.3. As shown, MR_{max} increases with s (disorder) nearly linearly. Despite the concentration x, there is a correlation between the zero field electric transport and magneto-transport. The origin can be the coupling between grains that correspond directly to s (degree of disorder). MR_{max} increases slowly in the hopping regime where the multiple tunneling effects dominate.

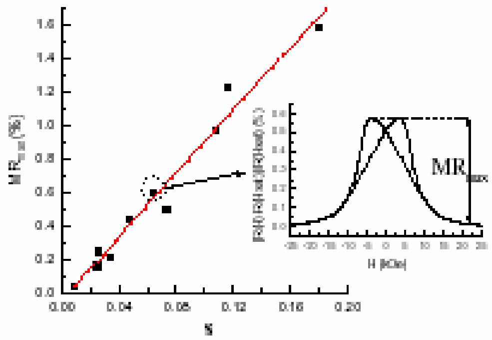

Fig.3. The maximum MR versus s (disorder) for numerous $Co(SiO_2)$ samples at T=10K. Line is a least square fit to data. Inset is magnetoresistance as a function of applied magnetic filed for one sample at 10K. Direction of field is perpendicular to film plane.

Conclusion

From the studies of $Co_x(SiO_2)_{1-x}$ systems, MIT can occurs by adjusting the relative concentrations between Co and SiO_2. The evolution of temperature dependent resistivity with increasing disorder is similar to that observed in non-magnetic composite or binary systems. The MR demonstrates hysteresis behavior due to the magnetic couplings between grains as an evidence of the formation of magnetic Co grains. Near the metal-insulator transition with a ℓn(T) dependent resistivity, scattering length of electron is more than couples of grain distance and scattering of up and down spins through grain channels depends on whether parallel or anti-parallel alignment of magnetic moments of all grains.

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