

# Experimental Studies on Metal Graphites (MG's)

M. Suzuki and I.S. Suzuki

Department of Physics,  
State University of New York at Binghamton

(October 13, 2005)

## I. SUMMARY

Metal Metal-graphite (MG) is a novel type of layered compound, where a metal layer is sandwiched between adjacent graphene sheets. These sandwiched structures are periodically stacked along the  $c$  axis. MG's can be synthesized by the reduction of the corresponding metal-chloride graphite intercalation compounds (GIC's). The MG's are a quite extensive set of quasi-2D metallic materials with interesting and potentially quite unusual properties. They exhibit superconductivity, magnetism, weak localization, and so on, depending on the position of the metal elements in the periodic table (3d, 4d and 5d) transition metals. MG's can be a source of new issues in solid state physics. This is a strong and in many ways sufficient motivation for pursuing studies of the properties of this type of material. These materials are also very important for future industrial application.

The principal concern of our research is to prepare various kinds of MG's and to study the structural and physical properties of MG's. These physical properties of MG's are completely different from those in their bulk metal systems. Our recent studies on Pd-, Ta-, Bi-, Sn, Rh-, and Ru-MG's using SQUID magnetometer revealed the 2D superconductivity in Bi-, Sn-, and Pd-MG's, 2D ferromagnetism in Ru-MG, and superparamagnetic behavior in Rh-MG. We are studying the structure, charge transfer, superconductivity, magnetism, weak localization, magnetic-field induce transition between superconducting state and semiconducting state in

various kinds of MG's. The goals are: (i) to prepare high quality MG samples which can be used as a model system, (ii) to obtain a comprehensive overview of the structural and physical properties in MG's, and (iii) to use MG's as a testing ground for fundamental studies in 2D physics. We are using superconducting quantum interference device (SQUID) magnetometer to measure DC magnetization, AC magnetic susceptibility, electrical resistivity, heat capacity, x-ray scattering, neutron scattering, Raman scattering, x-ray photoemission, extended x-ray absorption fine structure, and transmission electron microscope techniques.

## II. INTRODUCTION

The physics of two-dimensional (2D) conducting systems has received considerable attention in recent years. These systems exhibit a number of novel behaviors such as superconductivity, magnetism, weak localization effect, charge density wave, quantum Hall effect, and so on. A wide variety of 2D metal systems have become available for detailed experimental study so that the relevance of various theoretical ideas could be assessed. A simple example of these systems is a metal monolayer attached to the surface of a bulk substrate. There are, however, various kinds of layered materials whose conduction is more or less two-dimensional. Typical examples are graphite intercalation compounds (GIC's), which have so-called staging structures along the  $c$  axis (perpendicular to the  $c$  plane). The intercalate layer is sandwiched between adjacent graphene sheets.<sup>1-3</sup> Such sandwiched structures are periodically stacked along the  $c$  axis. GIC's have proven to be extremely fruitful for fundamental studies in physics in 2D systems.

It is expected that metal GIC's provide one of the best candidates for studying the 2D metal physics, if they might be prepared. The electrical conductivity parallel to the planes of metal layer is much higher than that perpendicular to the planes. As far as we know, however, there have been no report on the successful synthesis of metal GIC's except for donor GIC's such as alkali metal (Li, K, Rb, Cs) GIC's and Eu-GIC. In alkali metal GIC's alkali metals are intercalated into the empty graphite galleries. During the intercalation process a charge is transferred from the alkali metals to the graphene sheets, forming donor-type GIC's.

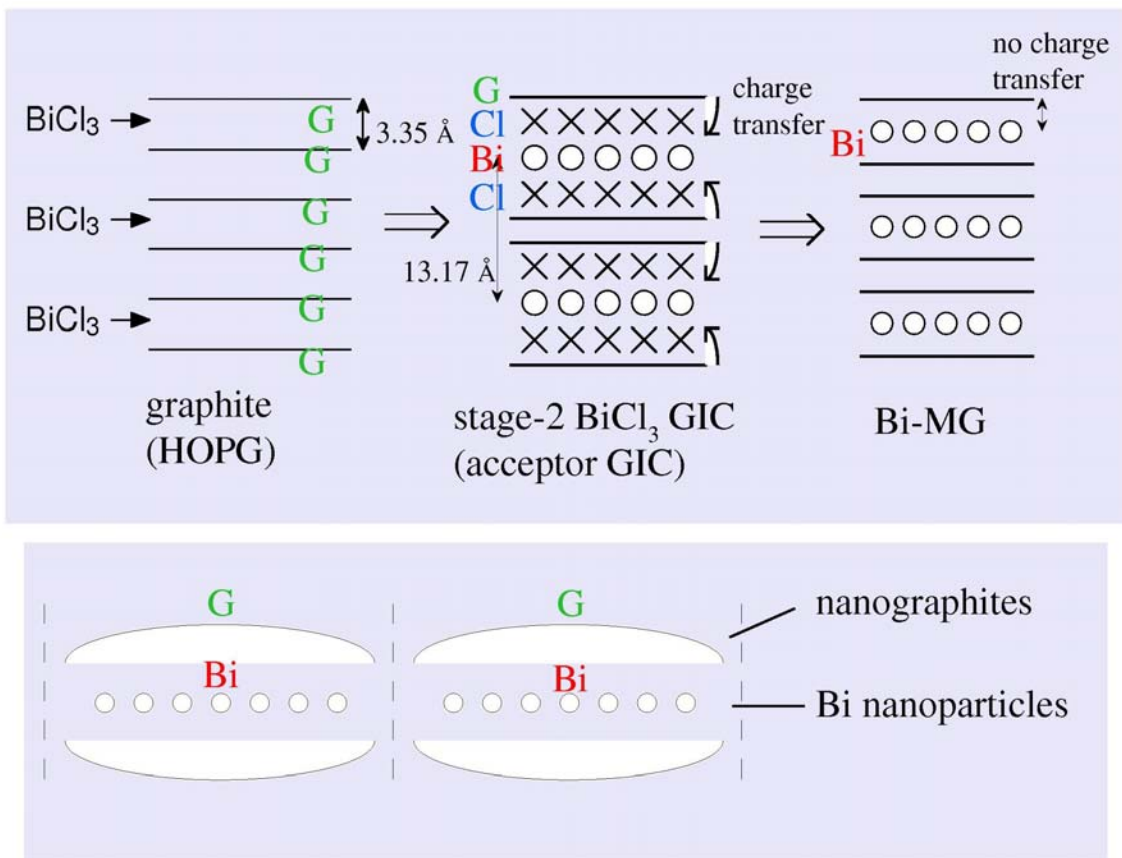


Fig. 1 Schematic diagram of the sandwich structure (G – Bi – G) in Bi-MG.

The 3d, 4d, and 5 d transition metals do not intercalate directly into graphite. These MG's can be synthesized by the reduction of corresponding acceptor-type metal-chloride GIC's<sup>4,5</sup> either by hydrogen, by alkali metal vapor, by chemical reductants, or by electrochemical methods. The physical properties of MG's are completely different from the corresponding GIC's. The metal chloride as an intercalate layer in GIC's is insulating, while the metal layer in MG's is conducting. In the acceptor-type GIC's a charge is transferred from the graphite layers to the intercalate layers. In contrast, there is few charge transfer in MG's. MG's have an unique layered structure, where the metal layer is sandwiched between adjacent graphene sheets (see Fig.1 for the schematic diagram). Like GIC's such sandwich structures would be periodically stacked along the *c* axis perpendicular to the graphene sheets. The metal layer in MG's behaves

like a 2D metal. It is expected that the 2D metal layer exhibits novel types of physical properties which have never been seen before.

The MG's have been synthesized for the first time by Vol'pin et al. in former Soviet Union in the middle of 1970's. Vol'pin et al. have succeeded in synthesizing MG's such as Fe-, Ni-, Co-, Cu-, Mo-, W-, and Cr-MG's.<sup>4,5</sup> Although they have reported interesting results on the structural and magnetic properties of these MG's, no special attention has been directed toward such studies. In 1996, **Touzain et al.**<sup>6</sup> have reported their success in the synthesis of electrochemically reduced Co-MG. The Co atoms forms island structure between adjacent graphene sheets. The stoichiometry was determined as  $\text{CoC}_2$  from the intensity ratio of the observed (001) and (002) lines. The in-plane structure of  $\text{CoC}_2$  is a commensurate structure where Co atoms are situated in the center of each graphite hexagon.

In 1998-2004, Walter (our collaborator, Osaka University, Japan) has succeeded in synthesizing eight MG's (Zn-, Mo-, Ru-, Rh-, Pd-, Sn-, Ta-, and Bi-MG's) by the reduction of the corresponding metal-chloride GIC's.<sup>7-11</sup> This method of synthesis is rather different from that used by Vol'pin et al.<sup>4,5</sup> Our recent studies have revealed that the physical properties of MG's are completely different from those of the corresponding bulk metals. For example, Bi-MG is a superconductor,<sup>12</sup> while the pristine Bi exhibits no superconductivity. Ru-MG is ferromagnetic, while the pristine Ru is paramagnetic.<sup>13,14</sup> Pd-MG shows superconductivity,<sup>15</sup> while the pristine Pd is paramagnetic. Sn-MG shows a quasi 2D superconductivity.<sup>16</sup> Because of a possible interplanar interaction between the metal layer and the graphene sheets, the in-plane structure of the metal layer is either a commensurate or incommensurate with that of the graphene sheets, leading to a drastic change of the in-plane lattice constant of the metal layer.

Recent progress in preparation of MG's makes it possible for one to study novel physical phenomena associated with characteristics of 2D metals, because of increased reliability and reproducibility of the experimental results. MG's provide an ideal system for studying the 2D superconductivity and 2D magnetism of metals. The goal of our research is to prepare various kinds of ideal MG's as model systems and to study their structural and physical properties. The

physical properties of these MG's may be classed into three groups from those of bulk metals. (i) magnetism: Cr, Mn, Fe, Co, Ni, (ii) superconductivity: Al, Nb, Mo, Sn, Ta, W, (iii) 4d metals with enhanced Stoner effect: Pd, Rh, Ru, and (iv) normal metal: Cu, Bi, Pt. One of the important difficulty in the reduction of metal-chloride GIC is to preserve the 2D structure of the compounds during the reduction process. For any class of materials to be important as a model system in this respect it is absolutely necessary that they are chemically clean, can be prepared with reasonable effort, exhibit very high structural quality, and show reproducible physical properties. So far the metal-graphite compounds do not fulfill all these conditions. We need to study the structural properties extensively only for very clean samples in respect to chemistry and structure. The experimental techniques to be used, include SQUID (superconducting quantum interference device) magnetometer, electrical resistivity, heat capacity, XRD (x-ray diffraction), neutron scattering, Raman scattering, XPS (x-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), EXAFS (extended x-ray absorption fine structure), and TEM (transmission electron microscopy).

### III. OUR RECENT RESULTS

Since 1999 we have been studying on the superconductivity and magnetism of Bi-MG,<sup>12</sup> Ru- and Rh-MG's,<sup>13,14</sup> Pd-MG,<sup>15</sup> Sn-MG<sup>16</sup>, and Ta-MG<sup>17</sup>. Through these studies we have learned the significant roles of interplay between metal layer and graphene sheets in MG's. This experience will be useful in further studying on the structural and physical properties of new types of MG's. Here our results on Bi-MG<sup>12</sup> and Pd-MG<sup>15</sup> are briefly presented.

#### A. Superconductivity in Bi-MG<sup>12</sup>

In Bi-MG, Bi layer is sandwiched between adjacent graphene sheets. While bulk Bi does not show any superconductivity, Bi-MG undergoes a superconducting transition at  $T_c = 2.48$  K. **Figure 2** shows a typical example of the  $T$  dependence of the zero-field cooled (ZFC) susceptibility  $\chi_{ZFC}$  and field-cooled (FC) susceptibility  $\chi_{FC}$  at a magnetic field  $H = 100$  Oe for

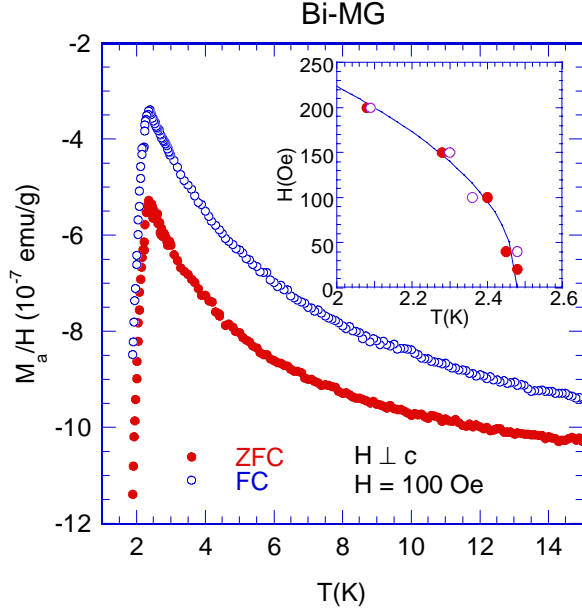


Fig. 2  $T$  dependence of ZFC and FC susceptibilities of Bi-MG based on HOPG.  $H = 100$  Oe.  $H \perp c$  ( $c$ :  $c$ -axis). The inset shows the magnetic-phase diagram of  $H$  vs  $T$  for  $H \perp c$ , where the peak temperatures of ZFC and FC susceptibilities are plotted as a function of  $H$ .

$H \perp c$  ( $c$ :  $c$  axis). Both  $\chi_{FC}$  and  $\chi_{ZFC}$  show a sharp peak around 2.5 K at  $H = 20$  Oe, which results from the competition between the diamagnetic susceptibility due to the Meissner effect and the Curie-like susceptibility. The peak temperature ( $= T_c$ ) for  $\chi_{FC}$  is almost the same as that for  $\chi_{ZFC}$ . The insets of **Fig.2** shows the  $H$ - $T$  phase diagram for Bi-MG for  $H \perp c$ .

Above  $T_c$ , a magnetic-field induced transition from metallic to semiconductor-like phase is observed in the in-plane resistivity  $\rho_a$  around  $H_c$  ( $= 25$  kOe) for both  $H \perp c$  and  $H // c$ . Such behaviors are very similar to those observed in amorphous ultrathin metal films which undergo magnetic field-induced transitions from superconducting phase to insulating phase. In addition, a negative magnetoresistance in  $\rho_a$  for  $H \perp c$  ( $0 < H < 3.5$  kOe) and a logarithmic divergence in  $\rho_a$  with decreasing temperature for  $H // c$  ( $H > 40$  kOe) are observed, suggesting the occurrence of 2D weak localization effect.

## B. Coexistence of superconductivity and magnetic short-range order in Pd-MG<sup>15</sup>

Pd-MG has a layered structure, where Pd sheets are sandwiched between adjacent graphene sheets. DC magnetization and AC magnetic susceptibility of Pd-MG based on natural graphite have been measured using a SQUID magnetometer. **Figure 3** shows the  $T$  dependence of  $\chi'$  for Pd-MG at various  $H$ , where  $f = 1$  Hz and  $h = 2$  Oe. The sign of  $\chi'$  changes from positive to

negative below a zero-crossing temperature  $T_0$  ( $= 3.45$  K at  $H = 5$  Oe). For  $400 \leq H \leq 600$  Oe, no appreciable peak is observed in  $\chi'$ . The dispersion  $\chi'$  starts to decrease with decreasing  $T$  below  $T_0$ . The negative sign of  $\chi'$  below  $T_0$  for  $H \geq 5$  Oe is related to a diamagnetic flux expulsion (the Meissner effect), giving a bit of evidence of the superconductivity at low temperatures. Pd-MG undergoes a superconducting transition at  $T_c$  ( $= 3.62 \pm 0.04$  K). The superconductivity occurs in Pd sheets. The relaxation of  $M_{ZFC}$  (aging), which is common to spin glass systems, is also

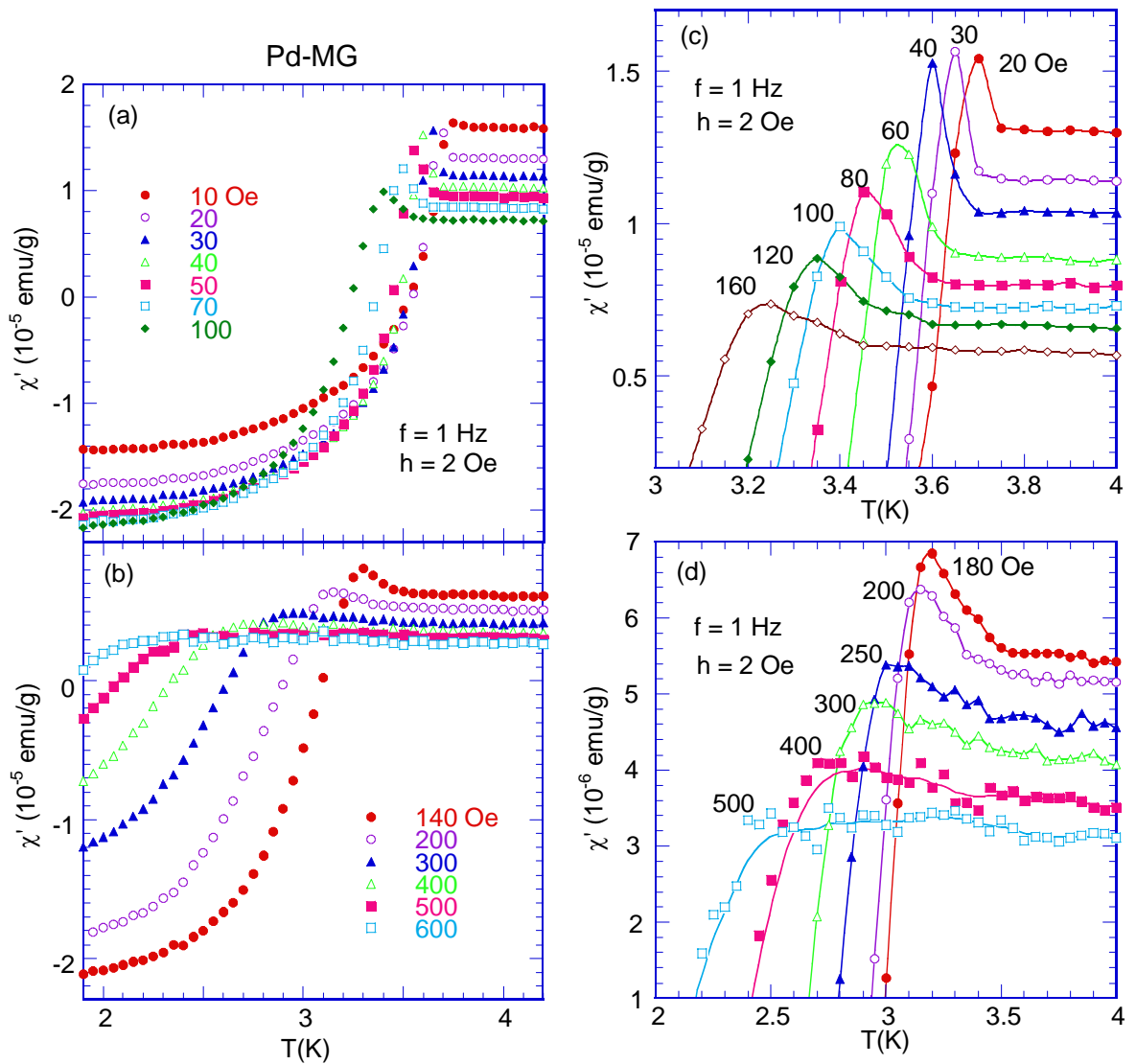


Fig.3 (a)-(d) The  $T$  dependence of  $\chi'$  for Pd-MG at various  $H$ .  $f = 1$  Hz.  $h = 2$  Oe. The solid curve in (c) and (d) are guides to the eyes [Ref. 15].

observed below  $T_c$ . The relaxation rate  $S(t)$  ( $= \frac{1}{H} \frac{dM_{ZFC}(t)}{d \ln t}$ ) shows a peak at a characteristic time  $t_{cr}$ , which is longer than a wait time  $t_w$ . The irreversibility between  $\chi_{ZFC}$  and  $\chi_{FC}$  occurs well above  $T_c$ . The susceptibility  $\chi_{FC}$  obeys a Curie-Weiss behavior with a negative Curie-Weiss temperature ( $\Theta = -5.4 - -13.1$  K). The growth of antiferromagnetic order is limited by the disordered nature of nanographites, forming spin glass-like behavior at low temperatures in graphene sheets.

#### **IV. OUR RESEARCH**

A series of our works have contributed to revealing their unconventional electronic and magnetic properties, such as ferromagnetism, superconductivity, weak localization, and so on. The properties of MG's are essentially different from the properties of GIC's, which have been intensively investigated in these three decades. From this viewpoint, we think that we contribute to open a new field of graphite- and nanoparticle- related areas in solid state physics. In the present stage, however, the electronic and magnetic properties of MG's are not well understood, and many issues, which have to be clarified, remain unsolved.

Through our recent studies on MG's, we realize that physical properties in MG's are strongly influenced by the condition of reduction from GIC's (precursors) such as temperature, reaction time, and so on. In our research we prepare various kinds of metal-chloride GIC's and the corresponding MG's under various conditions. As a host graphite material we use several kinds of graphites such as highly oriented pyrolytic graphite (HOPG) and single crystal of kish graphite (SCKG) from Toshiba Ceramics.

In our research, we comprehensively investigate the structures and properties of MG's with various metal elements. The structural properties of the resulting MG's are examined by using x-ray diffraction, neutron scattering, electron microprobe, Raman scattering, TEM, XPS, UPS, and EXAFS. We have a lot of experience of sample characterization of GIC's using x-ray diffraction and neutron scattering. We have been working on magnetism and electron transport of GIC's and



MG's using diffraction, magnetic susceptibility, magnetoresistance, and so on. It is our hope that we will make an important contribution to adding MG's to key materials in low-dimensional physics and nanoscience, on the basis of their experimental effort. We also study the physical properties of MG's by SQUID DC magnetization, SQUID AC magnetic susceptibility, electrical resistivity, magnetoresistance, and heat capacity.

#### **A. 4d metal magnetism: Rh- and Ru-MG's**

For the vast majority of elements, magnetism is found in isolated atoms, as shown by Hund's rules. In solids, however, the existence of spontaneous, long-range ferromagnetic order is restricted to only 3d-transition metals (Fe, Co, and Ni) and 4f-rare-earth metals (Gd, Tb, Dy, Ho, Er, and Tm). The electronic structure calculations now reveal the exciting perspective that more elements might be forced to conserve their atomic magnetism. The 4d transition metals (TM), which are paramagnetic in its bulk form, might have a ferromagnetic order, if properly synthesized at the nanometer scale: (i) small clusters with nanoscale size and (ii) monolayer of these elements epitaxially formed on an adequate nonmagnetic substrate. The possible ferromagnetic order in such systems is due to the reduced dimensionality, the reduced coordination number, and the enhanced lattice constant. For small clusters, for example, Cox et al.<sup>18</sup> have shown that small Rh clusters formed of a few tens of atoms exhibit a superparamagnetic behavior. The 2D ferromagnetism in 4d transition metal monolayers deposited on Ag(001) or Au(001) surfaces [or simply TM/Ag(001) or TM/Au(001)] has been theoretically predicted.<sup>19-23</sup> The magnetic moment per atom varies between 0.6 - 1  $\mu_B$  for Rh and 1.7  $\mu_B$  for Ru. Experimentally, however, long range ferromagnetic order has never been observed in these systems.<sup>24,25</sup> This is due to the possible diffusion of TM atoms into the noble metal substrate. Graphite has been suggested as an alternative substrate, because TM atoms diffuse much less into it. The graphite C(0001) surface is known to be very flat and it has only a small band overlap with the transition metal *d*-bands. Pfandzelter et al.<sup>26</sup> have reported the first observation of 2D ferromagnetic order in Ru monolayer on graphite C(0001) surface. Using

Auger electron spectroscopy, they have found that a nonzero in-plane spin polarization appears below 250 K. Motivated by this experiment, Chen et al.<sup>27</sup> and Krüger et al.<sup>28</sup> have discussed the possible 4d magnetism of the transition metal TM monolayer on the graphite C(0001) surface [simply TM/C(0001)]. They show that the magnetic properties of the system TM/C(0001) are dependent on (i) the in-plane structure of TM atoms and (ii) the TM-C interlayer distance  $d_c$ . Krüger et al.<sup>28</sup> assume a superstructure of the TM atoms which is partly commensurate with that of graphite substrate. Small magnetic moments can survive for Ru and Rh, while the magnetism of Pd is completely diminished. That only Ru and Rh are ferromagnetic could be due to the density of states (DOS) at the Fermi energy which is higher than that of the other 4d metals. So they have tendency for ferromagnetism according to the Stoner criterion. The magnetic moment in Rh/C(0001) is considerably smaller than that in the Ru/C(0001). However, the overall dependence of the magnetic moment on  $d_c$  is quite similar.

In Ru-MG, Ru monolayer is sandwiched between adjacent graphene sheets. The separation distance  $d_c$  in Ru-MG is on the same order as that ( $= 4.625 \text{ \AA}$ ) in  $\text{RuCl}_3$  GIC. According to Krüger et al.,<sup>28</sup> the magnetic moment for  $d_c = 4.625 \text{ \AA}$  is about  $1.9 \mu_B$  for the Ru site, which satisfies at least the necessary condition for the occurrence of the 2D ferromagnetism in Ru-MG. In contrast, the magnetic moment for Rh/C(0001) is considerably smaller than that for Ru/C(0001), but the overall dependence of the magnetic moments on  $d_c$  is quite similar. This prediction is consistent with the superparamagnetic behavior observed in Rh-MG. In fact, we find the 2D ferromagnetic behaviors in Ru- and Rh-MG.<sup>13</sup> These results suggest that the magnetism in these MG's is related to the in-plane structure of metal layer in MG's and the interlayer spacing between the metal layer and the graphene sheet. However, the spin orders are far from well-defined long range spin order. A re-entrant spin-glass like behavior is observed in Ru-MG below  $T_{c1}$  and a superparamagnetic behavior is observed in Rh-MG.

In our research, we study spin-glass like behavior and superparamagnetic behavior arising from spin frustration effects in various kinds of magnetic MG's (including Ru-MG and Rh-MG) by using SQUID magnetometer (the irreversible effect of magnetization, the relaxation times,

and the nonlinear AC magnetic susceptibility and aging dynamics). The nature of the superparamagnetic behaviors in MG's will be discussed in the light of theories and experimental results of typical superparamagnets.

## **B. 2D superconductivity, weak localization effect, and magnetic-field-induced transition: Bi-MG**

A weak localization theory predicts a logarithmic divergence of the resistivity in the two-dimensional (2D) electron systems as the temperature ( $T$ ) is lowered.<sup>29-31</sup> In high-mobility Si metal oxide-semiconductor field-effect transistor (MOSFET), the in-plane resistivity for a system with an electron density  $n$  larger than a critical electron density  $n_c$  decreases with decreasing  $T$ , indicating a metallic behavior. This metallic state is completely destroyed by the application of an external magnetic field ( $H$ ) applied in the basal plane when  $H$  is higher than a threshold field  $H_c$ . Such coplanar fields only polarize the spins of the electrons, indicating that the spin state is significant to the high conductivity of the metallic state. The scaling relation of the in-plane resistivity collapses into two distinct branches above and below  $H_c$ . Such behaviors are very similar to those observed in amorphous ultrathin metal films of  $\text{InO}_x$ ,<sup>32</sup>  $\text{MoGe}$ ,<sup>33,34</sup> and  $\text{Bi}$ ,<sup>35</sup> which undergo magnetic field-induced transitions from superconducting phase to insulating phase. Bi-MG is a typical 2D conductor: it shows superconductivity below  $T_c = 2.48$  K. Above  $T_c$  the in-plane resistivity  $\rho_a$  of Bi-MG shows a negative magnetoresistance and a logarithmic divergence of  $\rho_a$  with decreasing  $T$ , suggesting the occurrence of the 2D weak localization effect (WLE). Bi-MG also undergoes a transition from metallic phase to semiconductor-like phase by the application of  $H$  above 25 kOe. In this sense the universality class of Bi-MG is the same as that of amorphous ultrathin metal films.<sup>32-37</sup>

In our research, we study the transport properties of MG's such as Bi-, Zn-, Al-, and Nb-MG' which may belong to the same universality class. The in-plane and  $c$ -axis resistivity of these MG's will be measured as a function of temperature and magnetic field, using our SQUID magnetometer with an external device control as an option. The generic features of the scaling

relation for the in-plane resistivity will be examined through these studies concerning on the 2D superconductivity, the 2D weak localization effect, and a field-induced transition from metallic to semiconductor-like phase. It is interesting to compare the results of 2D WLE in MG's with those observed in the  $c$ -axis resistivity in stage-4 MoCl<sub>5</sub> GIC,<sup>38,39</sup> as a typical example.

### **C. Vortex glass phase and vortex liquid phase in superconductivity: Sn-MG**

An interplay among quenched disorder, dimensionality, and anisotropy in the mixed state of the quasi 2D superconductors leads to the complex  $H$ - $T$  diagram.<sup>40-47</sup> A typical  $H$ - $T$  diagram consists of a vortex lattice (Abrikosov lattice) phase, a vortex glass phase, and a vortex liquid phase. The boundary between the vortex lattice phase and the vortex liquid phase (the line  $H_{a1}$ ) is of the first order, while the phase boundaries between the vortex lattice phase and the vortex glass phase (the line  $H_{ag}$ ) and between the vortex glass phase and the vortex liquid phase (the line  $H_{gl}$ ) are of the second order. These boundaries merge into a multicritical point at  $T = T^*$  and  $H = H^*$ . For  $H > H^*$ , the vortices are interacting much more strongly in the planes than between the planes and they behave much more two-dimensionally. The pinning of vortices due to the quenched disorder destroys the long-range correlations of the vortex lattice, replacing it with a new vortex glass phase that has spin glass-like off-diagonal long-range order. The vortex-glass phase may occur with a freezing of vortices into a particular random configuration reflecting the positions of the randomly pinned vortices. Fisher et al.<sup>42</sup> have argued that sufficient random pinning could turn the vortex lattice phase into a vortex glass phase, where the vortices are frozen into a particular random pattern that is determined by the details of the pinning in the particular sample. This phase is named the vortex glass by analogy with the spin glass phase of random magnetic materials.

MG's such as Sn-MG provide a model system for studying the  $H$ - $T$  diagram of quasi 2D type-II superconductors. In fact, the existence of vortex glass phase has been experimentally confirmed in Sn-MG, where  $T^* = 3.4$  K and  $H^* = 40$  Oe.<sup>16</sup> The value of  $H^*$  is much smaller than those of high- $T_c$  superconductors such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, which is also a typical quasi 2D

superconductors.<sup>73</sup> This makes it much more feasible for one to study the nature of the vortex glass phase in MG's using various techniques in SQUID DC and AC magnetic susceptibilities, which are frequently used for the study on spin glass behaviors in random spin systems. We study the vortex glass phase in MG's such as Sn-, Zn-, Al-, Nb-MG's: (i) the  $T$  dependence of the magnetization ( $M$ ) in various states such as the FC, ZFC, IR, and TR states, (ii) relaxation effect from the measurement of time dependence of  $M_{ZFC}$ , (iii) the  $T$ ,  $H$ ,  $h$ , and  $f$  dependence of the dispersion ( $\Theta_1'/h$  or  $\chi'$ ) and absorption ( $\Theta_1''/h$  or  $\chi''$ ) of the AC magnetic susceptibility, and (iv) the nonlinear AC magnetic susceptibility.

#### **D. Coexistence of superconductivity and magnetic short-range order: Pd-MG**

It is expected that in Pd-MG the superconductivity occurs in Pd sheets and that the antiferromagnetic (AF) short-range order (spin-glass like behavior) occurs in graphene sheets, leading to a spin glass-like behavior. In our research we investigate the nature of spin-glass like behavior in Pd-MG from the magnetic neutron scattering which will be carried out at NIST, as well as the magnetic susceptibility measurement. The examination of magnetic Bragg reflections along the  $Q_c$  direction is a key to understanding the mechanism of the coexistence of the superconductivity and spin-glass-like behavior in Pd-MG.

As far as we know, there has been no report for the discovery of the superconductivity in the pristine Pd metal. Nevertheless, we have found the superconductivity in the Pd layer in Pd-MG. How can we understand such a difference? Pristine Pd metal has the largest Pauli susceptibility with a Stoner enhancement factor. The absence of superconductivity in the pristine Pd above 2 mK is mainly due to such strong spin fluctuations. Theoretically it is predicted that Pd without spin fluctuations should be a superconductor.<sup>48,49</sup> Bouarab et al.<sup>50</sup> have predicted (i) no magnetic moment for  $n = 1$ , (ii) ferromagnetic moment for  $n = 2 - 5$ , and (iii) no magnetic moment for  $n > 5$ , where  $n$  is the number of Pd layers. The value of the density of states (DOS) at the Fermi energy  $E_F$ ,  $N(E_F)$ , for  $n = 1$  is smaller than that in the bulk Pd. The peak of the DOS, which is much below  $E_F$  for  $n = 1$ , moves towards  $E_F$  for higher  $n$ . This prediction suggests that

the Pd monolayer may be a superconductor because of the suppression of spin fluctuations. On the other hand, Pd layers with  $n = 2 - 5$  may be a ferromagnet.

Experimentally Stritzker<sup>51</sup> has reported that pure Pd films, evaporated between 4.2 K and 300 K, can be transformed into superconductors by means of irradiation at low temperatures with He<sup>+</sup> ions. The maximum transition temperature obtained is 3.2 K. A special kind of disorder produced by low temperature irradiation may lead to a smearing of  $E_F$ , and thus to a reduction of  $N(E_F)$ . This reduction of  $N(E_F)$  leads to a decrease in the Stoner enhancement factor. As a result, the strong spin fluctuations would be reduced and superconductivity might be possible. In fact, Meyer and Stritzker<sup>52</sup> have shown that the AC magnetic susceptibility of low-temperature irradiated Pd is strongly reduced in comparison to the annealed Pd metal.

## **V. SIGNIFICANCE**

The ultimate control over the molecular structure of material will give humankind the ability to efficiently and effectively design materials with properties tailored to specific applications. Progress towards this goal must be made simultaneously on many scientific and technological fronts. Our project opens up a new class of intercalates with no charge transfer between guest and host species. The novel system of MG's could exhibit many possible new phenomena, such as 2D superconductivity, 2D magnetism, 2D weak localization, and coexistence of superconductivity and magnetism. The expected results will be a contribution to the understanding of the superconducting, magnetic, and transport of 2D metal systems in a restricted space between adjacent graphene sheets.

There is considerable current interest in MG's, because they are expected to have unique properties with considerable implications for basic science and many promising applications. One can hope that some of MG's may be a possible high temperature superconductors, partly because of the structure which is similar to that of MgB<sub>2</sub>. Metal layers sandwiched between adjacent graphene sheets are intriguing in terms of both scientific research and future device

applications, such as hydrogen sensor, hydrogen activated switch, cluster protection, nano-ball-bearings, nano-optical-magnetic devices, catalysis, and biotechnology.

## REFERENCES

1. M.S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 139 (1981). “Intercalation compounds of graphite.”
2. See, for example, *Graphite Intercalation Compounds I*, edited by H. Zabel and S.A. Solin (Springer-Verlag, Berlin, 1990).
3. T. Enoki, M. Suzuki, and M. Endo, *Graphite Intercalation Compounds and Applications* (Oxford University Press, 2003).
4. M.E. Vol’pin, Yu.N. Novikov, N.D. Lapkina, V.I. Kasatochkin, Yu.T. Struchkov, M.E. Kasakov, R.A. Stukan, V.A. Povitskij, Yu.S. Karimov, and A.V. Zvarikina, *J. Am. Chem. Soc.* **97**, 3366 (1975). “Lamellar compounds of graphite with transition Metals. Graphite as a Ligand.”
5. A.T. Shuvayev, B.Yu. Helmer, T.A. Lyubeznova, A.S. Mirmilstein, L.D. Kvacheva, Yu.N. Novikov, and M.E. Volpin, *J. Phys. France* **50**, 1145-51 (1989). “EXAFS study of graphite intercalation compounds with transition metals (Fe, Ni).”
6. P. Touzain, G.K. N’Guessan, D. Bonnin, P. Kaiser, and G. Chouteau, *Synthetic Metals* **79**, 241 (1996). “Electrochemically reduced cobalt-graphite intercalation compound.”
7. J. Walter and H. Shioyama, *Phys. Lett. A* **254**, 65 (1999). “Quasi two-dimensional palladium nanoparticles encapsulated into graphite.”
8. J. Walter, H. Shioyama, and Y. Sawada, *Carbon* **37**, 41 (1999). “The generation of nanometer-size tantalum particles in a graphite host lattice.”
9. J. Walter, *Adv. Mater.* **12**, 31 (2000). “Template-assisted growth of hexagonal poly- or single-crystalline quasi two-dimensional palladium nanoparticles.”
10. J. Walter, *Phil. Mag. Lett.* **80**, 257 (2000). “Quasi-two-dimensional or hcp palladium nanoparticles with host-guest interaction prepared at room temperature.”
11. J. Walter, J. Heiermann, G. Dyker, S. Hara, and H. Shioyama, *J. Catalysis* **189**, 449 (2000). “Hexagonal or quasi two-dimensional palladium nanoparticles-tested at the Heck reaction.”
12. M. Suzuki, I.S. Suzuki, R. Lee, and J. Walter, *Phys. Rev. B* **66**, 014533 (2002). “Magnetic-field induced superconductivity-metal-insulator transition in bismuth metal-graphite.”
13. M. Suzuki, I.S. Suzuki, and J. Walter, *Phys. Rev. B* **67**, 094406 (2003). “Quasi two-dimensional magnetism in Ru and Rh metal layers sandwiched between graphene sheets,”



14. J. Walter, S. Wakita, W. Boonchuduang, S. Hara, M. Suzuki, and I.S. Suzuki, J. Phys. Chem. B **106**, 8547 (2002). "Preparation of Rh-graphite and Rh-clay nanocomposites-model substances for nanographite and introduced magnetization in 4d transition metals."
15. M. Suzuki, I.S. Suzuki, and J. Walter, J. Phys. Condensed Matter. **16**, 903 (2004). "Superconductivity and magnetic short-range order in system with Pd sheet sandwiched between graphene sheets,"
16. M. Suzuki, I.S. Suzuki, and J. Walter, Physica C **402**, 243 (2004). "*H-T* diagram and the nature of the vortex glass phase in a quasi two-dimensional superconductor: Sn metal sandwiched between graphene sheets."
17. I.S. Suzuki, M. Suzuki, and J. Walter, Solid State. Commun. **118**, 523 (2001). "Superconductivity and magnetism in tantalum-graphite multilayers based on natural graphite."
18. A.J. Cox, J.G. Louderback, and L.A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993). "Experimental observation of magnetism in rhodium clusters."
19. S. Blügel, Phys. Rev. Lett. **68**, 851 (1992). "Two-dimensional ferromagnetism of 3d, 4d, and 5d transition metal monolayers on noble metal (001) Substrates."
20. O. Eriksson, R.C. Albers, and A.M. Boring, Phys. Rev. Lett. **66**, 1350 (1991). "Prediction of ferromagnetism and metamagnetism in 4d transition-metal overlayers on the (001) surface of Ag (4d = Tc, Ru, Rh, and Pd)."
21. M.J. Zhu, D.M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991). "Rhodium monolayer on gold: a 4d ferromagnet."
22. R. Wu and A.J. Freeman, Phys. Rev. B **45**, 7222 (1992). "Possible 4d ferromagnetism of Rh and Ru overlayers on a Ag(001) substrate."
23. S. Blügel, Phys. Rev. B **51**, 2025 (1995). "Magnetism of 4d and 5d transition metal adlayers on Ag(001): dependence on the adlayer thickness."
24. C. Liu and S.D. Bader, Phys. Rev. B **44**, 12062 (1991). "Absence of ferromagnetism in epitaxial films of ultrathin Pd, Rh, and Rh on Pd grown on Au(100)."
25. G.A. Mulhollan, R.L. Fink, and J.L. Erskine, Phys. Rev. B **44**, 2393 (1991). "Surface magneto-optics Kerr-effect probe for magnetization in monolayer p(1x1) Rh on Ag(100)."
26. R. Pfandzelter, G. Steierl, and C. Rau, Phys. Rev. Lett. **74**, 3467 (1995). "Evidence for 4d Ferromagnetism in 2D Systems: Ru monolayers on C(0001) Substrates."

27. L. Chen, R. Wu, N. Kioussis, and J.R. Blanco, J. Appl. Phys. **81**, 4161 (1997). “First Principles investigations of 4d magnetism on C(0001).”
28. P. Krüger, J.C. Parlebas, G. Moraitis, and C. Demangeat, Computational Materials Science **10**, 265 (1998). “Magnetism of epitaxial Ru and Rh monolayers on graphite.”
29. S.V. Kravchenko, W.E. Mason, G.E. Bowker, J.E. Furneaux, V.M. Pudalov and M. D’Iorio, Phys. Rev. B **51**, 7038 (1995). “Scaling of an anomalous metal-insulator transition in a two-dimensional system in silicon at  $B = 0$ .”
30. D. Simonian, S.V. Kravchenko, M.P. Sarachik, and V.M. Pudalov, Phys. Rev. Lett. **79**, 2304 (1997). “Magnetic field suppression of the conducting phase in two-dimensions.”
31. S.V. Kravchenko and T.M. Klapwijk, Phys. Rev. Lett. **84**, 2909 (2000). “Metallic low-temperature resistivity in a 2D electron system over an extended temperature range.”
32. A.F. Hebard and M.A. Paalanen, Phys. Rev. Lett. **65**, 927 (1990). “Magnetic-field-tuned superconductor-insulator transition in two-dimensional films.”
33. Ali Yazdani and A. Kapitulnik, Phys. Rev. Lett. **74**, 3037 (1995). “Superconducting-insulating transition in two-dimensional a-MoGe thin films.”
34. N. Mason and A. Kapitulnik, Phys. Rev. Lett. **82**, 5341 (1999). “Dissipation effects on the superconductor-insulator transition in 2D superconductors.”
35. N. Markovic, C. Christiansen, and A.M. Goldman, Phys. Rev. Lett. **81**, 5217 (1998). “Thickness-magnetic field phase diagram at the superconductor-insulator transition in 2D.”
36. D.B. Haviland, Y. Liu, and A.M. Goldman, Phys. Rev. Lett. **18**, 2180 (1989). “Onset of superconductivity in the two-dimensional limit.”
37. Y. Liu, K.A. McGreer, B. Nease, D.B. Haviland, G. Martinez, J.W. Halley, and A.M. Goldman, Phys. Rev. Lett. **67**, 2068 (1991). “Scaling of the insulator-to-superconductor transition in ultrathin amorphous Bi films.”
38. M. Suzuki, C. Lee, I.S. Suzuki, K. Matsubara, and K. Sugihara, Phys. Rev. B **54**, 17128 (1996). “ $c$ -axis resistivity of MoCl<sub>5</sub> graphite intercalation compounds.”
39. M. Suzuki, I.S. Suzuki, K. Matsubara, and K. Sugihara, Phys. Rev. B **61**, 5013 (2000). “Two dimensional weak localization effect in stage-4 MoCl<sub>5</sub> graphite intercalation compound.”

40. A.I. Larkin and Yu.N. Ovchinnikov, *J. Low Temp. Phys.* **34**, 409 (1979). “Pinning in type-II superconductors.”
41. K.A. Müller, M. Takashige, and J.G. Bednorz, *Phys. Rev. Lett.* **58**, 1143 (1987). “Flux trapping and superconductive glass state in  $\text{La}_2\text{CuO}_{4-y}\text{:Ba}$ .”
42. D.S. Fisher, M.P.A. Fisher, and D.A. Huse, *Phys. Rev. B* **43**, 130 (1991). “Thermal fluctuations, quenched disorder, phase transitions, and transport in type-II superconductors.”
43. L.I. Glazman and A.E. Koshelev, *Phys. Rev. B* **43**, 2835 (1991). “Thermal fluctuations and phase transitions in the vortex state of a layered superconductor.”
44. G. Blatter, M.V. Feigel'man, V.B. Geshkenbein, A.I. Larkin, and V.M. Vinokur, *Rev. Mod. Phys.* **66** 1125 (1994). “Vortices in high-temperature superconductors.”
45. P.L. Gammel, D.A. Huse, and D.J. Bishop, in *Spin Glasses and Random Fields*, edited by A.P. Young (World Scientific Publishing Co., Singapore, 1998) p.299. “Magnetic vortices in the copper oxide superconductors: observation of lattice, glass, and liquid phase.”
46. G. Menon, *Phys. Rev. B* **65**, 104527 (2002). “Phase behavior of type-II superconductors with quenched point pinning disorder: a phenomenological proposal.”
47. V.B. Geshkenbein, V.M. Vinokur, and R. Fehrenbacher, *Phys. Rev. B* **43**, 3748 (1991). “ac absorption in the high- $T_c$  superconductors: reinterpretation of the irreversibility line.”
48. D. Fay and J. Appel, *Phys. Rev. B* **16**, 2325 (1977). “Possibility of triplet pairing in palladium.”
49. F.J. Pinski, P.B. Allen, and W.H. Butler, *Phys. Rev. Lett.* **41**, 431 (1978). “Electron-phonon contribution to electrical resistivity and superconducting “*p*-wave” transition temperature of Pd.”
50. S. Bourab, C. Demangeat, A. Mokarani, and H. Dreyse, *Phys. Lett. A* **151**, 103 (1990). “Onset of magnetism in palladium slabs.”
51. B. Stritzker, *Phys. Rev. Lett.* **42**, 1769 (1979). “Superconductivity in irradiated palladium.”
52. J.D. Meyer and B. Stritzker, *Phys. Rev. Lett.* **48**, 502 (1982). “Reduced susceptibility of irradiated palladium.”