Superconductivity of Metal-Graphite (MG)

Masatsugu Sei Suzuki and Itsuko S., Suzuki
Department of Physics, SUNY at Binghamton.
Binghamton. New York

(Date: November 25, 2021)

1. Introduction

During the period between 2002 and 2006, we studied the physical properties of metal-graphite (MG) experimentally, in collaboration with Dr. Jűrgen Walter of the Osaka University, Osaka, Japan. By metal-graphite (MG), we mean that single kind of metal atoms (such as Bi, Pd, Sn, Ta, Ru, Rh) are inserted (or intercalated) between graphite layers, forming an ideal two-dimensional lattice of single metals. In such a metal layer, there may occur the 2D-like superconductivity, 2D ferromagnetism and so on, depending on the kind of metals, whose properties are expected to be rather different from bulk metals. Before doing on this research, we have been studying the magnetic properties of magnetic graphite intercalation compounds (GIC's) such as stage-2 $CoCl_2$ GIC (2D XY system), stage-2 $MnCl_2$ GIC (frustration effect on the triangular lattice), and so on, using SQUID magnetometer. In these GIC's, the intercalants [$CoCl_2$ and $MnCl_2$ (insulators)] are intercalated between the interlamellar space between adjacent graphene layers.

We have studied on the physical properties of MG from 2002, when I met Dr. Jűrgen Walter at the International Symposium on Graphite Intercalation Compounds at Okazaki, Japan (Institute of Molecular Science). I heard from him that he succeeded in synthesizing MG's for the first time. That was a big surprise to me since we struggled in synthesizing such MG's for long times. While talking with him at the conference, I noticed that he wanted to collaborate with us on the research on superconductivity and magnetism. Dr. Walter got a Ph.D. in the University of Munich under the instruction of Prof. Hanns P. Boehm (the name of Prof. Boehm is well-known over the world in the field of chemistry of graphite intercalation compounds).

Since 2002, Dr. Walter continued to send us various kinds of MG's. In our laboratory, we enjoyed in measuring the magnetic properties (DC magnetization and AC magnetic susceptibility) and the electrical resistivity of these MG's, by using our SQUID magnetometer. While doing measurements, it occurred to us that MG's with appropriate metal atoms may be possible high temperature superconductors. It was amazing to us that MG's such as Bi-MG, Pd-MG, Sn-MG, Ta-MG, show Meissner effect at low temperatures. Note that in 2009, it was shown that CaC_6 is type-II superconductor with $T_c = 11.5$ K. This critical temperature is the highest for this class of materials (MG's).

REFERENCES

((Reserachgate))

Jurgen Walter's research while affiliated with Osaka University and other places
https://www.researchgate.net/scientific-contributions/Juergen-Walter-64000741

((**Researchgate**))
Masatsugu Sei Suzuki
https://www.researchgate.net/profile/Masatsugu-Suzuki-3

2. NSF Proposal (2004)

Here we put my proposal on the study of MG's in 2004 (as a Part II), which was submitted to National Science Foundation (NSF) in order to get a grant. Recently, we found this proposal in my old hard disc by accident. We almost forgot the significance and motivation of our reserch around 2004. We were very impressed with this old proposal when we read it again after 17 years later. In the proposal we explained how important this research was. In order to convince Referees of our NSF proposal, we spent a lot of times to write a good proposal. Unfortunately, no grant was awarded from NSF. Our research on the superconductivity of MG's faded away because of lack in resources after 2006. In spite of our unsuccess in getting a NSF grant, we still believe that this proposal deserves to putting in our website (Bingweb). This may be useful to researchers on the superconductivity in metal atoms inserted between graphene sheets.

PROPOSAL DESCRIPTION

Study on Physical Properties in Metal Layer Sandwiched between Graphene Sheets

Principal Investigator: Masatsugu Suzuki
Co-Principal Investigator: Itsuko S. Suzuki

I. 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.[1-3] 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.

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[4,5] 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 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. 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.

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.[4,5] 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.

Some of MG's are commercially available from Alfa Aesar (Johnson Matthey) under the name of Graphimets.[6] Fe-, Ni-, Cu-, Rh-, Pd-, and Pt-Graphimets can be prepared by low temperature reduction of the corresponding metal chloride GIC's with lithium biphenyl. Pt-Graphimet, for example, is prepared by reduction of $PtCl_4$ GIC at 223 K with lithium biphenyl under a He gas atmosphere. These compounds show a high catalytic activity in hydrogenation reactions. The names of such Graphimets as products are denoted as Cu-5 (5 %), Fe-5 (5%), Rh-1 (1%), Pt-5 (5%), Ni-75 (75%), and Pd-1 (1%), depending on the amount of percentage and kinds of metal species. It is claimed that Graphimets contain atomically dispersed metal between adjacent graphene sheets. As far as we know, there have been a series of studies on the sample characterization of Graphimets mainly by chemists since 1986, using XPS (x-ray photoelectron spectroscopy), TEM (transmission electron microscopy), XRD (x-ray diffraction), DSC (differential scanning calorimetry), and isothermal chemisorption techniques.[7-17] It is no doubt that in some Graphimets such as Rh-, Pt-, and Ni-Graphimets the metal layers are sandwiched between adjacent graphene sheets, although they are far from ideal MG systems. Some Graphimets contain detectable metallic particles only on the surface of the graphite flakes. The size and the distribution of metal nanoparticles are greatly influenced by the method of preparation and metal species. In 1996, Touzain et al.[18] 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 CoC_2 from the intensity ratio of the observed x-ray (001) and (002) Bragg intensities. The in-plane structure of CoC_2 is a commensurate structure where Co atoms are situated in the center of each graphite hexagon. This structure is similar to that of superconductor MgB_2 (T_c = 39 K).

In 1998-2003, one of our collaborators (Jürgen Walter, a chemist at 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.[19-23] This method of synthesis is rather different from that used by Vol'pin et al.[4,5] Our recent studies have revealed that the physical properties of MG's are completely different from those of the corresponding bulk metals.[24-29] For example, Bi-MG is a superconductor,[24] while the pristine Bi shows no superconductivity. Ru-MG is ferromagnetic, while the pristine Ru is paramagnetic.[25] Pd-MG shows superconductivity,[27] while the pristine Pd is paramagnetic. Sn-MG shows a quasi 2D superconductivity.[28] 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 this project 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: Zn, 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 exten-

sively. Only with very clean samples in respect to chemistry and structure will they have the required success.

The experimental techniques to be used will 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).

In the current trend of solid state physics, we have seen many cases, in which a material which happened to be discovered by chance opened a new area, for example, fullerenes, high T_c superconductors, MgB_2, and so on. We think that MG's will also be a candidate of such key material. In the present stage, we do not have enough information on their properties, though several unconventional features have been revealed mainly by us. Researches on MG's are expected to involve a large variety of issues from basic science to applications, such as low dimensional physics, nanoscience and nanotechnology, superconductivity, ferromagnet, magnetic fine particles, and so on. MG systems are also important from a technical point of view since their physical properties can be better tuned and specifically designed than in their bulk form. Best examples are semiconductor quantum well and quantum dot structures, as well as ferromagnetic GMR (giant magnetoresistance)-materials. The obtained results will allow one to optimize the parameters of technological process for production of MG nanocomposite structures and provide the necessary energy of reproducibility and stability of their functional characteristics. Metal layers in MG's are intriguing as possible future device applications: hydrogen sensor,[30] hydrogen activated switch, cluster protection, nano-ball-bearings, nano-optical-magnetic devices, and catalysis.

II. PREVIOUS RESULTS

Since 1999 we have been studying on the superconductivity and magnetism of MG's. These researches are funded by the Research Foundation of State University of New York at Binghamton. 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. Our previous results are presented below. Five papers on Bi-MG,[24] Ru- and Rh-MG's,[25,26] Sn-MG[28], and Ta-MG[29] have been published in Phys. Rev. B, Physica C (Superconductivity), J. Phys. Chem. B, and Solid State Commun., respectively. One paper on Pd-MG,[27] which has been submitted to J. Phys. Condensed Matter, can be seen in arXiv.org. e-Print archive.

A. Superconductivity in Bi-MG[24]

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 1 shows a typical example of the T dependence of the zero-field cooled (ZFC) susceptibility χ_{ZFC} and field-cooled (FC) susceptibility χ_{FC} at a magnetic field $H = 100$ Oe for $H \perp c$ (c: c axis). Both χ_{FC} and χ_{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 χ_{FC} is almost the same as that for χ_{ZFC}. The insets of Fig.1 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 ρ_a around H_c (= 25 kOe) for both $H \perp c$ and $H // c$. Such behaviors

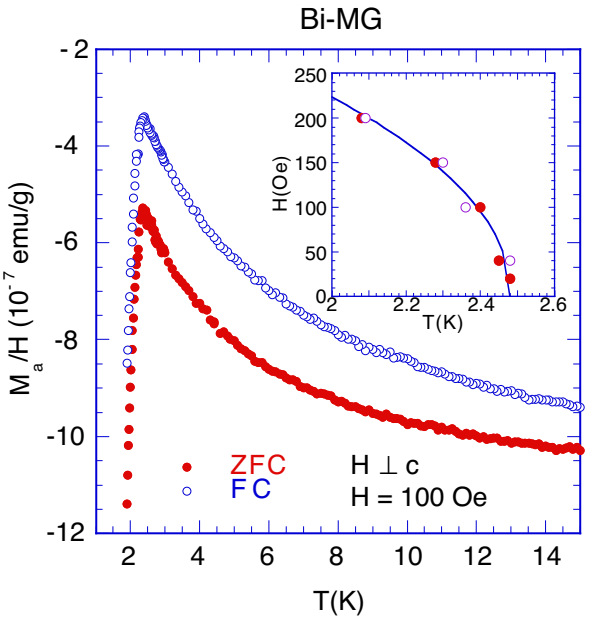


Fig.1 T dependence of ZFC and FC susceptibilities of Bi-MG based on HOPG. H = 100 Oe. $H \perp c$.[11] The inset shows the magnetic phase diagram of H vs T for $H \perp c$, where the peak temperatures of ZFC and FC susceptibilities are plotted as a function of H (Ref. 24).

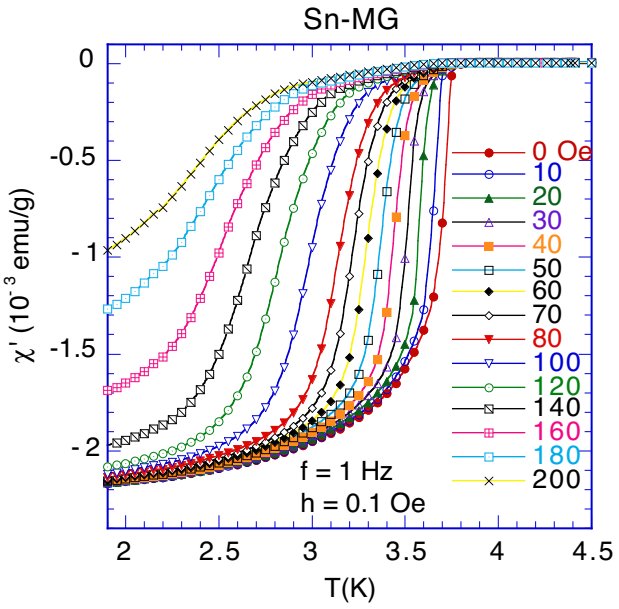


Fig.2 T dependence of χ' at various H for Sn-MG. $h = 0.1$ Oe. $f = 1$ Hz. The solid lines are guides to the eyes (Ref. 28).

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 ρ_a for $H \perp c$ ($0 < H < 3.5$ kOe) and a logarithmic divergence in ρ_a with decreasing temperature for $H // c$ ($H > 40$ kOe) are observed, suggesting the occurrence of 2D weak localization effect.

B. 2D superconductivity in Sn-MG: vortex glass phase[28]

Sn-MG has a unique layered structure where Sn metal layer is sandwiched between adjacent graphene sheets. This compound undergoes a superconducting transition at $T_c = 3.75$ K at $H = 0$. Figure 2 shows the T dependence of the dispersion χ' at various H, respectively, where $f = 1$ Hz and $h = 0.1$ Oe. The AC response to such a small h is found to be linear in the whole range of temperatures and fields. The derivative $d\chi'/dT$ shows a sharp peak at T_c at $H = 0$, shifting to the low-T side with increasing H. The peak temperature for $d\chi'/dT$ vs T plotted as a function of H in the H-T diagram shown in Fig. 3, which is similar to that of a quasi 2D superconductors. The phase boundaries of vortex liquid, vortex glass, and vortex lattice phase merge into a multicritical point located at $T^* = 3.4$ K and $H^* = 40$ Oe. There are two irreversibility lines denoted by H_{gl} (de Almeida-Thouless type)[31] and H_{gl}' (Gabay-Toulouse type),[32] intersecting at $T_0' = 2.5$ K and $H_0' = 160$ Oe.

C. Coexistence of superconductivity and spin-glass like behavior in Pd-MG[27]

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

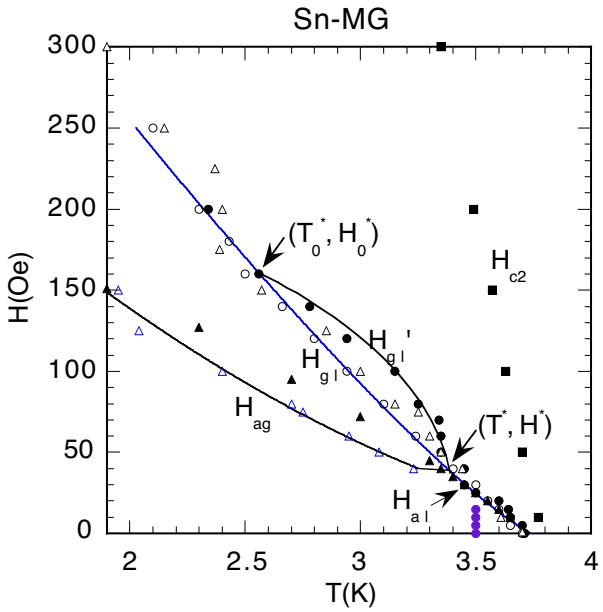


Fig.3 *H-T* diagram for Sn-MG. The vortex lattice (Abrikosov lattice), vortex liquid, and vortex glass phases are separated by the lines H_{al}, H_{ag}, H_{gl}, and H_{gl}'. These lines merge at the multicritical point located at ($T^* \approx 3.4$ K, $H^* \approx$ 40 Oe). The line H_{c2} is a crossover line (■) (Ref. 28).

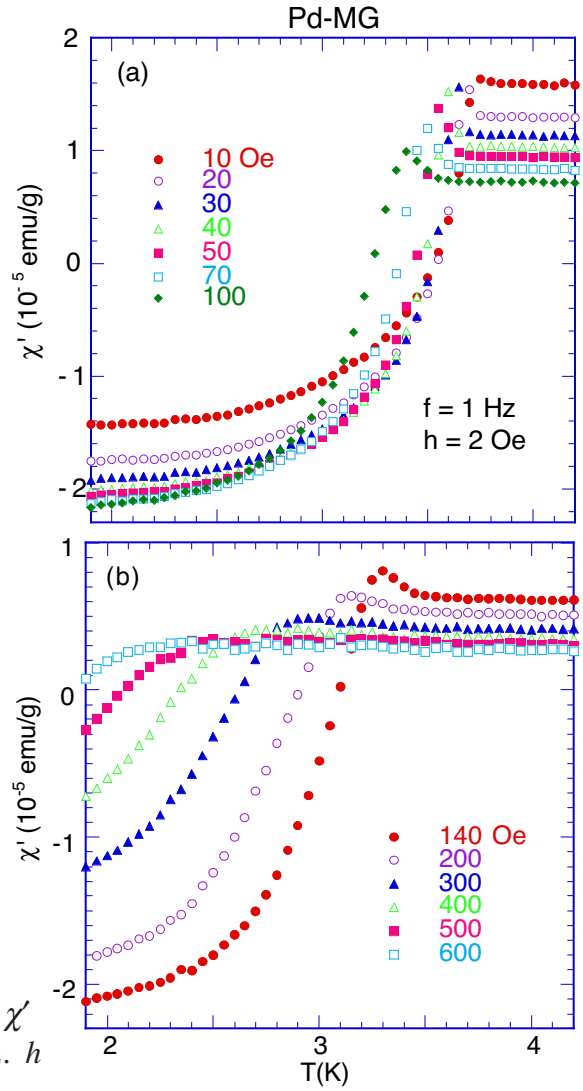


Fig.4 (a) and (b) *T* dependence of χ' for Pd-MG at various *H*. $f = 1$ Hz. $h = 2$ Oe (Ref. 27).

have been measured using a SQUID magnetometer. Figure 4 show the *T* dependence of χ' for Pd-MG at various *H*, where $f = 1$ Hz and $h = 2$ Oe. The sign of χ' changes from positive to negative below a zero-crossing temperature T_0 (= 3.45 K at $H = 10$ Oe). For $400 \leq H \leq 600$ Oe, no appreciable peak is observed in χ'. The dispersion χ' starts to decrease with decreasing *T* below T_0. The negative sign of χ' below T_0 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 ± 0.04 K). The superconductivity occurs in Pd sheets. The relaxation of M_{ZFC} (aging), which is common to spin glass systems, is also observed below T_c. The relaxation rate $S(t)$ shows a peak at a characteristic time t_{cr}, which is longer than a wait time t_w. The irreversibility between χ_{ZFC} and χ_{FC} occurs well above T_c. The susceptibility χ_{FC} obeys a Curie-Weiss behavior with a negative Curie-Weiss temperature (Θ = -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.

D. Quasi 2D magnetism in Ru- and Rh-MG's[25]

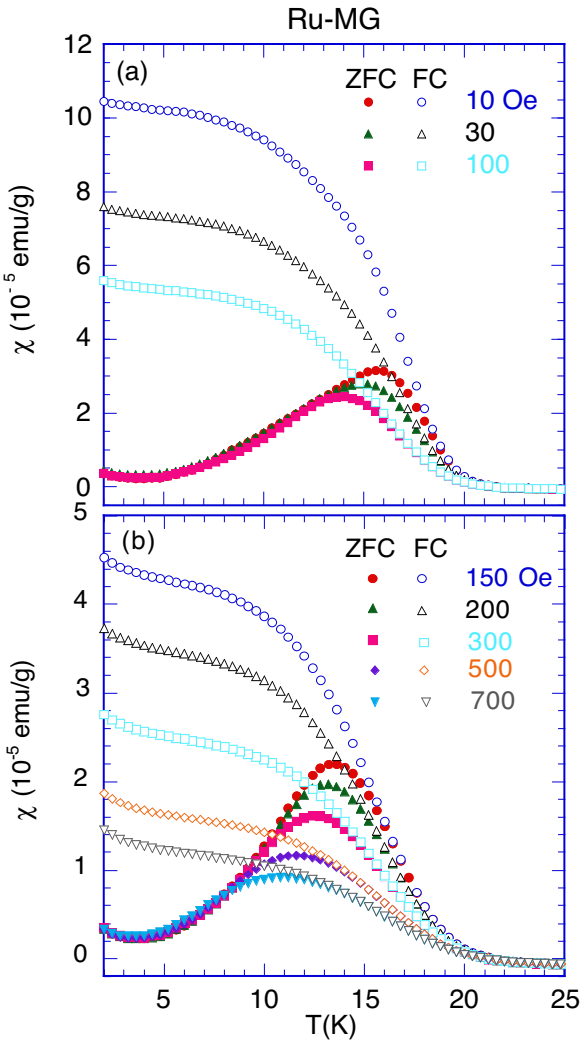


Fig.5 T dependence of χ_{ZFC} and χ_{FC} for Ru-MG at various H (Ref. 25).

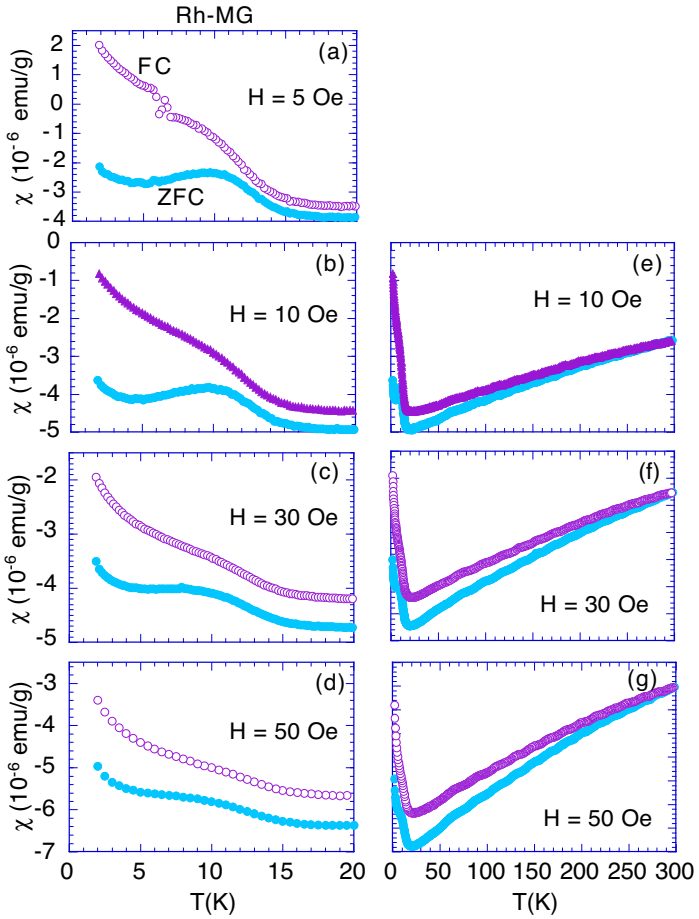


Fig.6 T dependence of χ_{ZFC} and χ_{FC} at various H for Rh-MG (Ref. 25).

4d transition metal (TM = Ru and Rh)- graphite (MG) has a unique layered structure, where TM monolayer is sandwiched between adjacent graphene sheets. The magnetic properties of TM-MG based on natural graphite are investigated using DC and AC magnetic susceptibility. (i) Ru-MG magnetically behaves like a quasi 2D ferromagnet. This compound undergoes successive magnetic phase transitions at T_{cu} (= 16.3 ± 0.2 K) and T_{cl} (= 12.8 ± 0.3 K). The origin of two phase transitions in Ru-MG is similar to that in stage-2 $CoCl_2$ GIC (T_{cu} = 8.9 K and T_{cl} = 6.9 - 7.1 K), where the ferromagnetic layers are antiferromagnetically stacked along the c axis.[33,34] The low-temperature phase below T_{cl} may be a reentrant spin-glass like phase where the antiferromagnetic phase and spin glass phase coexist. (ii) Rh-MG exhibits a superparamagnetic behavior. A ferromagnetic blocked state is formed below 9.7 K. The zero-field cooled susceptibility shows a broad peak around 9.7 K. The irreversible effect of magnetization is observed below 13.5 K. The relaxation time obeys Arrhenius law for thermal activation .

Figure 5 shows the T dependence of χ_{ZFC} and χ_{FC} for Ru-MG at various H. The measurements were carried out as follows. After the sample was cooled from 298 to 1.9 K at H = 0 (in a strict

sense, a very weak remnant field less than 3 mOe), H was applied at T = 1.9 K. The susceptibility χ_{ZFC} was measured with increasing T from 1.9 to 40 K. After the sample was annealed at 100 K for 20 minutes in the presence of H, χ_{FC} was measured with decreasing T from 40 to 1.9 K. Figure 6 shows the T dependence of χ_{ZFC} and χ_{FC} at various H for Rh-MG. The measurements were carried out as follows. After the sample was cooled from 298 to 1.9 K at $H = 0$, H was applied at T = 1.9 K. The susceptibility χ_{ZFC} was measured with increasing T from 1.9 to 298 K and sequentially χ_{FC} was measured with decreasing T from 298 to 1.9 K. The susceptibility χ_{ZFC} starts to deviate from χ_{FC} at 298 K, reflecting the frustrated nature of the system. The susceptibility χ_{ZFC} exhibits a local maximum around T_p(ZFC) = 9.7 K and a local minimum around 21 - 22 K at H = 5 and 10 Oe. This local maximum disappears at H larger than 30 Oe. The susceptibility χ_{FC} does not show any anomaly at T_p(ZFC) and increases with decreasing T. This is in contrast to the T dependence of χ_{FC} observed in a typical spin glasses (SG) system, where χ_{FC} is nearly independent of T below the spin freezing temperature T_f. A superparamagnetic behavior occurs in Rh-MG, where Rh clusters are ferromagnetically ordered.

E. Reply to criticism to our previous results

(1) Nanoparticles and nanographites

In MG's, metal sheets are sandwiched between adjacent graphene sheets. The correlation length of metal sheets and graphene sheets strongly depend on the condition of sample preparation: preparation and reduction of metal-chloride GIC's. It is experimentally demonstrated from Raman scattering and TEM of Pd-MG that metal sheets and graphene sheets are formed of metal nanoparticles and nanographites.[23] This arises partly from few charge transfer between metal and graphene sheets. The nanographites contribute to a peculiar magnetism, while the metal nanoparticles contributes to a peculiar electrical conduction. At present, we do not have any specific model for the generation of nanoparticles and nanographites. There are some reports on the magnetism of nanographites with zig-zag edge sites, in particular spin-glass like behavior at low temperatures.[35] The origin of magnetism in nanographites is theoretically predicted.[36-41]

(2) Possibility of PdH_x in Pd-MG.

Hydrogen is used in the reduction process producing Pd-MG and there are going to be cases where some hydrogen may be incorporated into the sandwiched structure, forming PdH_x compounds instead of Pd layers, importantly influencing the physical properties. For example, hydrogen loaded Pd is a known superconductor, and when one is looking for interesting properties, it will be important to know if H is floating around. In the previous works by Walter and his group,[19,21-23] it has been experimentally confirmed that there is no hydrogen atoms in PdH layers. It has been also reported that in hydrogen sorption isotherms measurement, Pd-Graphimet shows a pronounced S-shape absorption curve of hydrogen at ambient temperature H_2.[14] The atomic ratio x = 0.73 for PdH_x, which is the threshold concentration for the superconductivity of bulk PdH_x,[42] is obtained at the hydrogen pressure of P = 2 kPa = 204 Torr. However, the atomic ratio x decreases with decreasing the hydrogen pressure and become less than 0.1 at P = 0 (reversible process), suggesting no superconducting transition. Concerning the density of states at the Fermi edge of Pd-MG, we need to collaborate with a group which maintains a set-up for UPS experiments. It would be important to understand the electronic changes of Pd which occur when reducing the dimensionality.

(3) Sample characterization

Samples used in our previous work have been prepared by Dr. Jürgen Walter (chemist) who belonged to Osaka University and currently returned to Germany. He is an expert on sample prepa-

ration and characterization of GIC's and MG's (he was a Ph.D. student of Prof. H.P. Boehm at the Institut für Anorganische Chemie der Universität München). The preparation and characterization of samples used in the previous works[24-29] were carried out by Walter and his group. The detail of the preparation and characterization of samples has been reported in several papers.[19-23,26] The samples were characterized using x-ray diffraction, TEM/SAED, XPS and UPS. In spite of such characterization, however, we realize that a full characterization of our MG-samples is necessary systematically. There should be a greater emphasis on it because the properties depend on the structure and composition of the metallic layer. We think that it is the first piece of business to really pin down the conditions which produce exactly what kind of layered material. Understanding the results of the physical measurements requires knowing in detail about this. Analytical tools are used in the work proposed which address these issues. We note that the EXAFS of Rh-MG will be done in collaboration with a research group of Prof. H. Maletta at the Hahn-Meitner-Institut, Berlin, Germany.

III. PROPOSED 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 the proposed research, we propose to 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), single crystal of kish graphite (SCKG) from Toshiba Ceramics, and natural graphite from Ticonderoga, NY.

In the proposed works, we plan to 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. We hope that we will make an important contribution to adding metal-graphite to key materials in low-dimensional physics and nanoscience, on the basis of their experimental effort. We also propose to study the physical properties of MG's by SQUID DC magnetization, SQUID AC magnetic susceptibility, electrical resistivity, magnetoresistance, and Hall effect.

A. Sample preparation of GIC's and MG's

Samples of GIC's (such as $BiCl_3$-, $PdCl_2$-, $SnCl_2$-, $TaCl_5$-, $RhCl_5$-GIC's and so on) as precursors will be prepared using our existing facility including a Bridgeman furnace, single zone and two zone furnaces, Cl_2 gas handling system, and HCl gas handling system. MG samples will be prepared under varying experimental conditions. A walk-in hood, whose use is required for han-

dling Cl_2, HCl, and hydrogen gas, was already installed thanks to the support of NSF-Academic Research Infrastructure Grant-STI9415193. We have a lot of experience in preparing metal-chloride GIC's for these two decades.

There are two methods of reduction of metal chloride GIC's. For Bi-MG, for example, the reduction is made by keeping $BiCl_3$ GIC for three days in a solution of lithium diphenylide in tetrahydrofuran (THF) at room temperature. Then the samples are filtered, rinsed by THF, and dried in air. Finally the samples are annealed at 260 °C in a hydrogen gas atmosphere for one day. For Ru-MG, the reduction is made by keeping $RuCl_3$ GIC at 200°C under hydrogen gas (flow rate 300 ml per minute) for 2 hours. A hydrogen gas handling system in the latter case will be set up in this proposed research.

B. Sample characterization

The MG samples will be characterized using a variety of experimental techniques which have been already applied to Graphimets[7-17] and GIC's.[43-50] They include x-ray diffraction, neutron diffraction, SAED (selected area electron diffraction), TEM (transmission electron microscope), Raman scattering, XPS (x-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), and EXAFS (extended x-ray absorption fine structure). The neutron scattering measurement (in particular, small angle neutron scattering) will be carried out at the NIST (Gaithersburg, MD) in collaboration with Dr. D.A. Neumann at NIST. The x-ray diffraction with synchrotron radiation source and EXAFS measurement will be carried out at CHESS of the Cornell University (Ithaca, NY), which is not far from Binghamton, NY. The structures of the metal layer and graphene sheets in MG's may be sensitive to the condition of sample preparation (temperature, hydrogen gas flow rate, and reaction time). It is considered that the physical properties of MG's such as magnetism and superconductivity strongly depend on such structures. Concerning the density of states at the Fermi edge of metal layers and the in-plane structures of nanographite and nanoparticles in specific MG's such as Pd-MG, we will collaborate with a research group (Prof. H. Suematsu) at Spring-8 (synchrotron radiation source) in Japan: x-ray photoemission of novel functional nano-materials, high precision crystal structure analysis of novel nano-materials, soft X-ray spectroscopy of nanoparticles and nano-layers, and nano-aggregate analysis by a high-precise small angle scattering, and high energy inner shell photoelectron spectroscopy.

(1) Heat capacity (thermodynamics)

It is important in addition to the real structural work suggested above to get some bulk characterization of the materials. These are bulk materials, not thin films, so it should be possible to measure specific heat. There are many ways that susceptibility and resistivity measurements can not reflect bulk properties and mislead one. This is not in general the problem with specific heat, and the unusual phase diagrams shown in the proposal should be backed up with this kind of thermodynamic data.

The thermodynamic measurements are needed to underpin the phase diagrams determined via magnetic susceptibility measurements. The heat capacity measurement will be done in collaboration with a collaborator at RIKEN (The Institute of Physical and Chemical Research) in Japan. The heat capacity of MG's will be measured as a function of temperature and magnetic field: MAG Lab^{HC} microcalorimetry (Oxford Instruments). The thermal analysis of MG's at high temperatures will be also carried out using a differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-2 Instrument installed at the Department of Physics, in order to discuss the thermodynamic stability of the system such as the melting temperature of metal layers.

(2) Raman scattering

The nature of disorder generated in graphene sheets will be studied by the Raman scattering. The graphene sheets next to the metal layer may be formed of nanographites. In fact, the Raman scattering spectrum in Pd-MG reveals two broad peak around 1570 cm^{-1} and 1350 cm^{-1} which are assigned to the E_{2g2} mode and D-band (disordered induced modes) of graphite, respectively, consistent with the finite size of the particles.[35,51,52] Using the empirical formula $L_a = 4.4 \times I_{1570}/I_{1350}$, where I_{1570} and I_{1350} are the intensities of the peak corresponding to the E_{2g2} mode and the disordered induced mode, respectively, we can estimate the in-plane size L_a of nanographites.

(3) TEM

The in-plane structure of the metal layer in MG's will be studied by TEM. It is expected that the in-plane structure of metal layers in MG's depends on the metal species. The structural correlation between the metal layer and the graphene sheet will be discussed. Recent studies on Pd-MG indicate that the Pd layer is formed of Pd nanoparticles with an average lateral dimension of 530 Å.[19,21-23] The in-plane structure of Pd nanoparticles consist of two kinds of superstructures with the in-plane lattice constants close to $2x a_G$ and $3x a_G$, where a_G is the in-plane lattice constant of graphite layer. These structures are different from the commensurate structures $p(2x2)$ and $p(3x3)$ because of the different rotation angle between the guest and graphite lattices.

(4) XPS and UPS

The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from MG's. The binding energy of the peaks are characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the surface of MG's. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. The low photon energy in UPS means that deep core electron levels cannot be excited, and only photoelectrons emitted from the valence band or shallow core levels are accessible. By using a synchrotron, the relative change in photoemission cross-section for various electron states can be used to determine the partial density of states (DOS) in MG's

(5) EXAFS

The determination of the environment of the metal in MG's cannot be realized by classical characterization methods since an additional structural disorder between the graphene sheets generally occurs. The EXAFS has been confirmed to be a suitable technique to study such ill-crystallized compounds, because one of the salient features is that EXAFS does not require long range ordering. The EXAFS provides structural information on the location of the absorbing atom with respect to neighbors. The net result is a series of oscillations on the high photon energy side of the absorption edge. These oscillations can be used to determine the distance and coordination number of the atoms surrounding the element whose absorption edge is being examined. The necessity to sweep the photon energy implies the use of synchrotron radiation in EXAFS experiments. A first Fourier transform of the raw $\chi(k)$ function (EXAFS oscillations) yielded in R-space a radial distribution function (RDF) uncorrected for phase shift, and centered onto atoms. Structural information in terms of nature, number and distance of nearest cation neighbors can be derived via least-squares fitting of this partial EXAFS spectrum.

In the proposed research we plan to study the interplay between local structure and induced magnetism in Rh metal layer in Rh-MG by using the EXAFS method at the Rh-K shell (23.220 keV) within the photon energy range from 23.1 keV to 24.7 keV. The Rh-C distance also contributes to the EXAFS signal besides Rh-Rh distances. The Rh-C contribution to the EXAFS signal can be reduced by analyzing the higher k range where the backscattering amplitude of C atoms has

dropped significantly compared to the backscattering amplitude of Rh. To get a good optical resolution for the nearest neighbor distance we need data for a large range of the photon wave number ($\Delta k \approx 20$ Å).

C. 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 elements (TM = Ru, Rh, Pd) at the very end of the 4d series are likely candidates to exhibit 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.[53] 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.[54-58] The magnetic moment per atom varies between 0.6 - 1 μ_B for Rh and 1.7 μ_B for Ru. Experimentally, however, long range ferromagnetic order has never been observed in these systems.[59,60] 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.[61] 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.[62] and Krüger et al.[63] 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.[63] 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 Å) in $RuCl_3$ GIC. According to Krüger et al.,[63] the magnetic moment for d_c = 4.625 Å is about 1.9 μ_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.[25] 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_{cl} and a superparamagnetic behavior is observed in Rh-MG.

In this proposed research, we propose to 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 experimental techniques described in Sec.IVA (the irreversible effect of magnetization, the relaxation times, and the nonlinear AC magnetic susceptibility). The nature of the superparamagnetic behaviors in MG's will be discussed in the light of theories and experimental results of typical superparamagnets.[64-68]

D. 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.[69-71] 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 InO_x,[72] MoGe,[73,74] and Bi,[75] which undergo magnetic field-induced transitions from superconducting phase to insulating phase. Bi-MG is a typical 2D conductors: it shows superconductivity below $T_c = 2.48$ K. Above T_c the in-plane resistivity ρ_a of Bi-MG shows a negative magnetoresistance and a logarithmic divergence of ρ_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.[72-77]

In the proposed research, we propose to 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 $MoCl_5$ GIC,[78,79] as a typical example.

E. 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.[80-87] 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_{al}) 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.[82] 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.[28] The value of H^* is much smaller than those of high-T_c superconductors such as $YBa_2Cu_3O_7$, which is also a typical quasi 2D superconductors.[85] 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 propose to study the vortex glass phase in MG's such as Sn-, Zn-, Al-, Nb-MG's using the methods which will be described in Sec.IVA: (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 (Θ_1'/h or χ') and absorption (Θ_1''/h or χ'') of the AC magnetic susceptibility, and (iv) the nonlinear AC magnetic susceptibility.

F. Coexistence between spin-glass like behavior and superconductivity: Pd-MG

Magnetism and superconductivity are manifestations of two different ordered states into which metals can condense at low temperatures. In general these two states are mutually exclusive; they do not coexist at the same site in the system. The study of the interplay between these properties has recently been revitalized by the discovery of a family of high-T_c boride carbides RNi_2B_2C (where R is a rare-earth element).[88,89] The R-C layers separated by Ni_2B_2 sheets are antiferromagnetic ally ordered below a Néel temperature T_N, while Ni_2B_2 sheets are superconducting below T_c. Like RNi_2B_2C, Pd-metal graphite (MG) has a layered structure. Ideally, Pd monolayer is sandwiched between the adjacent graphite sheets, forming a periodic *c*-axis stacking like graphite intercalation compounds (GIC's). Each Pd layer consists of small islands formed of Pd nanoparticles with finite sizes. Pd nanoparticles would generate internal stress inside the graphite lattice, leading to the break up of adjacent graphene sheets into nanographites. Thus the Pd sheet formed of Pd nanoparticles is sandwiched between adjacent graphene sheets formed of nanographites. It is expected that 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. Such behaviors are similar to those observed in RNi_2B_2C. In this proposed research we propose to 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.[90,91] Bouarab et al.[92] 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[93] 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^+ 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[94] have shown that the AC magnetic susceptibility of low-temperature irradiated Pd is strongly reduced in comparison to the annealed Pd metal.

IV. PROCEDURES AND TECHNIQUES

A. SQUID DC magnetization and SQUID AC magnetic susceptibility

We maintain a Quantum Design SQUID magnetometer (MPMS XL-5) installed in our research laboratory in 1997 (NSF DMR-IMR 9625829). As an option, this has an ultra-low field capability, a mode of AC magnetic susceptibility, an external device control for resistivity measurement, and horizontal rotation. The specifications of MPMS XL-5 are summarized as follows: absolute sensitivity of magnetization: 1×10^{-7} emu to 1 T, 5×10^{-7} emu to 5 T, external magnetic field: $H = 0$ - 5.0 T, temperature range: 1.9 - 330 K. The remnant magnetic field can be reduced down to 3 mOe. The dispersion χ' and absorption χ'' of AC magnetic susceptibility can be measured as a function of temperature, field, frequency, and the strength of the AC field. The AC frequency range is between 0.007 Hz and 1 kHz and the strength of the AC field is between 0.2 mOe and 4.2 Oe. The sensitivity of AC magnetic susceptibility is 5×10^{-8} emu. Using these techniques, dynamic scaling and aging phenomena have been studied for 3D short-ranged Ising spin glass $Cu_{0.5}Co_{0.5}Cl_2$-$FeCl_3$ graphite bi-intercalation compound (GBIC)[95,96] and reentrant ferromagnet $Cu_{0.2}Co_{0.3}Cl_2$-$FeCl_3$ GBIC.[97]

B. Existing other facilities at SUNY-Binghamton

We maintain a comprehensive x-ray laboratory. The system consists of a high resolution x-ray (Phillips, X' pert-MPD, maximum power 2.2 kW) with a CuKα radiation source and a high resolution double-circle x-ray spectrometer with Ω: 2θ diffractometer (Huber, Model 424. maximum power 2 kW) with a MoKα radiation source. The composition of MG's can be determined by the electron probe microanalyzer (JEOL JXA-8900M) in the Department of Geological Science at SUNY-Binghamton. We maintain a helium liquefier of PSI (Process Systems International Inc.): Model 1400 (16 l/hour). This system was acquired and installed under the support of NSF-Academic Research Infrastructure Grant-STI9415193. Hence liquid He is available for the continuous operation of the SQUID magnetometer.

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 proposed 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 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_2. 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.

VI. EDUCATION AND HUMAN RESOURCES

The Ph.D. program in Materials Science and Engineering (MSE) at the SUNY-Binghamton has started from this fall in 2002. The P.I. (M.S.) is a faculty of Doctor Course of MSE as well as a faculty of Physics Department. The MSE faculties come from the Biology, Chemistry, Geology, Physics, Mechanical and Industrial Engineering, and Electrical Engineering Departments. The major areas of interest and interaction of these faculties can be grouped into four categories: new materials, materials for energy applications, electronic materials and packaging, and characterization of materials. Particular strength is brought to new synthetic approaches to materials and to their characterization. Ph.D. students in MSE, and M.S. and undergraduate students in Physics Department work in the P.I.'s research laboratory. The Co-P.I. (I.S.) is a woman scientist. She is currently a research associate at the MSE of SUNY-Binghamton and is working with the P.I. Her contributions to both experimental and theoretical works are crucial in the proposed research.

This proposal leans heavily towards the education and development of students. The graduate students in this program will be involved with all aspects of experiments including sample preparation, x-ray diffraction, XPS, UPS, EXAFS, neutron scattering, TEM, SQUID DC and AC magnetic susceptibility, resistivity, magnetoresistance, and Hall effect. The undergraduate students will be involved in sample preparation, x-ray characterization, and set-up of equipment for various kinds of measurements as their independent research projects during the summer or the academic year. Students can learn a great deal about materials, magnetism and superconductivity and how to interpret good experimental data. The results will be disseminated through complete papers and presentations at physics meetings which will improve scientific understanding. The P.I. has attracted students from underrepresented groups into this research program. During of the course of the project, the P.I. will be cognizant of the recruitment of such students.

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. J.M. Lalancetts. U.S. Patent 3.847.963, November 1974.
7. K. Aika, T. Yamaguchi, and T. Onishi, Applied Catalysis **23**, 129 (1986). "Characterization and catalytic behavior of graphite lamellar compounds of iron, nickel, and cobalt."
8. G. Sirokman, A. Mastaliar, A. Molnar, M. Bartok, Z. Schay, and L. Guczi, Carbon **28**, 35 (1990). "Structure and catalytic activity of copper, nickel, and platinum graphimets prepared from graphite intercalation compounds."
9. A. Messaoudi, R. Erre, and F. Beguin, Carbon **29**, 515 (1991). "The graphite intercalation compounds: A route to metallic supported clusters."
10. A. Mastalir, F. Notheisz, M. Bartok, Z. Kiraly, and I. Dekany, J. Molecular Catalysis A: Chemical **99**, 115 (1995). "Transformation of carbon compounds on graphimet catalysts. Part V. The effect of pretreatment on the structure and activity of Pt-graphimet catalyst."
11. Ya.V. Zubavichus, Yu.L. Slovokhotov, L.D. Kvacheva, and Yu.N. Novikov, Physica B 208&209, 549 (1995). "EXAFS study of graphite intercalated with metal chlorides."
12. J.-Y. Tilquin, R. Cote, G. Velleux, D. Guay, and J.P. Dodelet, and G. Denes, Carbon **33**, 1265 (1995). "Preparation and chemical reduction of Pt (IV) chloride-GICs: supported Pt vs Pt inclusion graphite compounds."
13. A. Mastalir, F. Notheisz, and M. Bartok, J. Phys. Chem. Solid **57**, 899 (1996). "The effect of medium-temperature pretreatment on the active site distribution of Pt-, Pd-, and Rh-graphimet."
14. Z. Kiraly, A. Mastalir, F. Berger, and I. Dekany, Langmuir **13**, 465 (1997). "Sorption and microcalorimetric investigations of palladium/hydrogen interactions on palladium-graphimet intercalation catalyst.'
15. A. Mastalir, Z. Kiraly, I. Dekany, and M. Bartok, Colloidal Surfaces A: Physicochemical and Engineering Aspects **141**, 397 (1998). "Microcalorimetric and catalytic investigations of transition metal nanoparticles intercalated in graphite."
16. A. Mastalir, Z. Kiraly, J. Walter, F. Notheisz, and M. Bartok, J. Molecular Catalysis A: Chemical **175**, 205 (2001). "Shape-selective catalysis: quasi two-dimensional Pd-particles encapsulated in graphite."
17. A. Mastalir, F. Notheisz, M. Bartok, I. Bertoti, and J. Szepvolgyi, Applied Catalysis A: General **229**, 155 (2002). "Investigation of the morphology and the active site distribution of Rh-graphimet."
18. P. Touzain, G.K. N'Guessan, D. Bonnin, P. Kaiser, and G. Chouteau, Synthetic Metals **79**, 241 (1996). "Electrochemically reduced cobalt-graphite intercalation compound."

19. J. Walter and H. Shioyama, Phys. Lett. A **254**, 65 (1999). “Quasi two-dimensional palladium nanoparticles encapsulated into graphite.”
20. J. Walter, H. Shioyama, and Y. Sawada, Carbon **37**, 41 (1999). “The generation of nanometer-size tantalum particles in a graphite host lattice.”
21. J. Walter, Adv. Mater. **12**, 31 (2000). “Template-assisted growth of hexagonal poly- or single-crystalline quasi two-dimensional palladium nanoparticles.”
22. J. Walter, Phil. Mag. Lett. **80**, 257 (2000). “Quasi-two-dimensional or hcp palladium nanoparticles with host-guest interaction prepared at room temperature.”
23. 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.”
24. 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.”
25. M. Suzuki, I.S. Suzuki, and J. Walter, “Quasi two-dimensional magnetism in Ru and Rh metal layers sandwiched between graphene sheets,” Phys. Rev. B **67**, 094406 (2003).
26. 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.”
27. M. Suzuki, I.S. Suzuki, and J. Walter, “Superconductivity and spin-glass like behavior in system with Pd sheet sandwiched between graphene sheets,” submitted to J. Phys. Condensed Matter. http://arxiv.org/abs/cond-mat/?0308292
28. M. Suzuki, I.S. Suzuki, and J. Walter, “*H-T* diagram and the nature of the vortex glass phase in a quasi two-dimensional superconductor: Sn metal sandwiched between graphene sheets,” Physica C (superconductivity) in press (October, 2003). http://arxiv.org/abs/cond-mat/?0308311
29. 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.”
30. F. Favier, E.C. Walter, M.P. Zach, T. Benter, and R.M. Penner, Science **293**, 2227. 21 September 2001 Issue. “Hydrogen sensor and switches from electrodeposited palladium mesowire arrays.”
31. J.R.L. de Almeida and D.J. Thouless, J. Phys. A **11**, 983 (1978). “Stability of the Sherrington-Kirkpatrick solution of a spin glass model.”
32. M. Gabay and G. Toulouse, Phys. Rev. Lett. **47**, 201 (1981). “Coexistence of Spin-Glass and Ferromagnetic Orderings.”
33. M. Suzuki and I.S. Suzuki, Phys. Rev. B **58**, 840 (1998). “Dynamic spin fluctuations in stage-2 $CoCl_2$ graphite intercalation compounds.”
34. M. Suzuki, I.S. Suzuki, and T.-Y. Huang, J. Phys. Condensed Matter **14**, 5583 (2002). “Non-linear dynamic susceptibility in stage-2 $CoCl_2$ graphite intercalation compounds.”
35. Y. Shibayama, H. Sato, T. Enoki, and M. Endo, Phys. Rev. Lett. **84**, 1744 (2000). “Disordered magnetism at the metal-insulator threshold in nano-graphite-based carbon materials.”
36. M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996). “Peculiar localized state at zigzag graphite edge.”
37. K. Wakabayashi, M. Sigrist, and M. Fujita, J. Phys. Soc. Jpn. **67**, 2089 (1998). “Spin wave mode of edge-localized magnetic states in nanographite zigzag ribbons.”
38. K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, Phys. Rev. B **59**, 8271 (1999). “Electronic and magnetic properties of nanographite ribbons.”

39. K. Harigaya, J. Phys. Condensed Matter **13**, 1295 (2001). “The mechanism of magnetism in stacked nanographite: theoretical study.”
40. K. Harigaya, Chem. Phys. Lett. **340**, 123 (2001). “New type of antiferromagnetic state in stacked nanographite.”
41. K. Wakabayashi and K. Harigaya, J. Phys. Soc. Jpn. **72**, 998 (2003). “Magnetic structure of nano-graphite Möbius ribbon.”
42. T. Skoskiewicz, Phys. Status Solid (a) **11**, K123 (1972). “Superconductivity in the palladium-hydrogen and palladium-nickel-hydrogen systems,”
43. T. Roisnel, A. Tressaud, J. Grannee, H. Dexpert, and S. Flandrois, Solid State Commun. **73**, 547 (1990). “EXAFS study of transition metal chlorides intercalated in graphite
44. R. Schlögl, in *Graphite Intercalation Compounds II*, edited by H. Zabel and S.A. Solin, edited by Springer-Verlag, Berlin 1992. “Electron Spectroscopy of Graphite Intercalation Compounds.”
45. Ya.V. Zubavichus, Yu.L. Slovokhotov, L.D. Kvacheva, and Yu.N. Novikov, Physica B **208&209**, 549 (1995). “EXAFS study of graphite intercalated with metal chlorides.”
46. M. Foba, K. Lochte, and W. Metz, Physica B **208&209**, 552 (1995). “XANES and EXAFS studies on the Rhenium L absorption edges of graphite intercalation compounds of $ReCl_5$.”
47. E. Bulska and H.M. Ortner, Spectrochimica Acta Part B **55**, 491 (2000). “Intercalation compounds of graphite in atomic absorption spectrometry.”
48. A.M. Danilenko, V.A. Chernov, and V.V. Kriventsov, Nuclear Instruments and Methods in Physics Research A **470**, 373 (2001). “EXAFS study of the reaction of graphite-$MeCl_2$ (Me = Ni, Co) intercalation compounds with bromine fluorides.”
49. G.E. Gadd, M. Collela, M. Blackford, A. Dixon, P.J. Evans, D. McCulloch, S. Bulcock, and D. Cockayne, Carbon **3**9, 1769 (2001). “The encapsulation of Ni in graphitic layers using C_{60} as a precursor.”
50. B. Rousseau and H. Estrade-Szwarckopf, Solid State Commun. **126**, 583 (2003), ”x-ray and UV photoelectron spectroscopy study of Na-halogen-graphite intercalation compounds. Comparison between donor- and acceptor-graphite compounds.”
51. T.C. Chieu, M.S. Dresselhaus, and M. Endo, Phys. Rev. B **26**, 5867 (1982). “Raman studies of benzene-derived graphite fibers.”
52**.** O.E. Anderssen, B.L.V. Prasad, H. Sato, T. Enoki, Y. Hishiyama, Y. Kaburagi, M. Yoshikawa, and S. Bandow, Phys. Rev. B **58**, 16387 (1998). “Structure and electronic properties of graphite nanoparticles.”
53. A.J. Cox, J.G. Louderback, and L.A. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993). “Experimental observation of magnetism in rhodium clusters.”
54. S. Blügel, Phys. Rev. Lett. **68**, 851 (1992). “Two-dimensional ferromagnetism of 3d, 4d, and 5d transition metal monolayers on noble metal (001) Substrates.”
55. 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).”
56. M.J. Zhu, D.M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991). “Rhodium monolayer on gold: a 4d ferromagnet.”
57. 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.”
58. S. Blügel, Phys. Rev. B **51**, 2025 (1995). “Magnetism of 4d and 5d transition metal adlayers

on Ag(001): dependence on the adlayer thickness."
59. 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)."
60. 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)."
61. 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."
62. 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)."
63. 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."
64. R.W. Chantrell, M. El-Hilo, and K. O'Grady, IEEE Transactions of Magnetics **27**, 3570 (1991). "Spin-glass behavior in s fine particle system."
65. M. El-Hilo, and K. O'Grady, IEEE Transactions of Magnetics **26**, 1807 (1990). "Components of magnetisation of a fine particle system."
66. E.P. Wohlfarth, J. Phys. E: Metal Phys. **10**, L241 (1980). "The magnetic field dependence of the susceptibility peak of some spin glass materials."
67. T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa, J. Phys. Soc. Jpn. **64**, 1305 (1995). "Field-cooled and zero-field-cooled magnetization of superparamagnetic fine particles in $Cu_{97}Co_3$ alloy: comparison with spin-glass $Au_{96}Fe_4$ alloy."
68. E.P. Wohlfarth, Phys. Lett. A **70**, 489 (1979). "The temperature dependence of the magnetic susceptibility of spin glasses."
69. 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 $B = 0$."
70. 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."
71. 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."
72. A.F. Hebard and M.A. Paalanen, Phys. Rev. Lett. **65**, 927 (1990). "Magnetic-field-tuned superconductor-insulator transition in two-dimensional films."
73. Ali Yazdani and A. Kapitulnik, Phys. Rev. Lett. **74**, 3037 (1995). "Superconducting-insulating transition in two-dimensional a-MoGe thin films."
74. N. Mason and A. Kapitulnik, Phys. Rev. Lett. **82**, 5341 (1999). "Dissipation effects on the superconductor-insulator transition in 2D superconductors."
75. 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."
76. D.B. Haviland, Y. Liu, and A.M. Goldman, Phys. Rev. Lett. **18**, 2180 (1989). "Onset of superconductivity in the two-dimensional limit."
77. 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."
78. M. Suzuki, C. Lee, I.S. Suzuki, K. Matsubara, and K. Sugihara, Phys. Rev. B **54**, 17128 (1996). "*c*-axis resistivity of $MoCl_5$ graphite intercalation compounds."
79. M. Suzuki, I.S. Suzuki, K. Matsubara, and K. Sugihara, Phys. Rev. B **61**, 5013 (2000). "Two

dimensional weak localization effect in stage-4 $MoCl_5$ graphite intercalation compound."
80. A.I. Larkin and Yu.N. Ovchinnikov, J. Low Temp. Phys. **34**, 409 (1979). "Pinning in type-II superconductors."
81. K.A. Müller, M. Takashige, and J.G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987). "Flux trapping and superconductive glass state in La_2CuO_{4-y}:Ba."
82. 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."
83. 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."
84. 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."
85. 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."
86. G. Menon, Phys. Rev. B **65**, 104527 (2002). "Phase behavior of type-II superconductors with quenched point pinning disorder: a phenomelogical proposal."
87. 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."
88. R. Nagarajan, C. Mazumdar, Z. Hossain, S.K. Dhar, K.V. Gopalakrishnan, L.C. Gupta, C. Godart, B.D. Padalia, and R. Vijayaraghavan, Phys. Rev. Lett. **72**, 274 (1994). "Bulk superconductivity at an elevated temperature ($T_c \approx 12$ K) in a nickel containing alloy system Y-Ni-B-C."
89. R.J. Cava, H. Takagi, B. Batlogg, H.W. Zandbergen, J.J. Krajewski, W.F. Peck Jr., R.B. van Dover, R.J. Felder, T. Siegrist, K. Mizuhashi, J.O. Lee, H. Eisaki, S.A. Carter, and S. Uchida, Nature **367**, 146 (1994). "Superconductivity at 23 K in yttrium palladium boride carbide."
90. D. Fay and J. Appel, Phys. Rev. B **16**, 2325 (1977). "Possibility of triplet pairing in palladium."
91. 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."
92. S. Bourab, C. Demangeat, A. Mokarani, and H. Dreysse, Phys. Lett. A **151**, 103 (1990). "Onset of magnetism in palladium slabs."
93. B. Stritzker, Phys. Rev. Lett. **42**, 1769 (1979). "Superconductivity in irradiated palladium."
94. J.D. Meyer and B. Stritzker, Phys. Rev. Lett. **48**, 502 (1982). "Reduced susceptibility of irradiated palladium."
95. I.S. Suzuki and M. Suzuki, "Dynamic scaling and aging phenomena in short-range Ising spin glass: $Cu_{0.5}Co_{0.5}Cl_2$-$FeCl_3$ graphite bi-intercalation compound," Phys. Rev. B **68** 094424 (2003).
96. M. Suzuki and I.S. Suzuki, "Aging, rejuvenation, and memory effects in short-range Ising spin glass: $Cu_{0.5}Co_{0.5}Cl_2$-$FeCl_3$ graphite bi-intercalation compound," submitted to European Physical Journal B. http://arxiv.org/abs/cond-mat/?0308285
97. M. Suzuki and I.S. Suzuki, "Nonlinear magnetic susceptibility and aging phenomena in reentrant ferromagnet: $Cu_{0.2}Co_{0.8}Cl_2$-$FeCl_3$ graphite bi-intercalation compound," submitted to Phys. Rev. B. http://arxiv.org/abs/cond-mat/?0308247

III. A part of Master Thesis of Robert Lee

We also put a Thesis of Master-Degree of our students, Robert Lee (Superconductivity of Bismuth Metal-Graphite) at SUNY at Binghamton. He explained in his thesis how to prepare how to prepare the sample. He learned the method of sample preparation from Dr. Jűrgen Walter.

We hope that one may understand the situation of the study on the superconductivity in MG's during the period between 2002 and 2006. It is our hope that these articles may be useful to researchers who want to have experimental works on the superconductivity of metal-graphite (single metals inserted between adjacent graphene sheets).

3. A part of Robert Lee's Mater Thesis

Robert Lee's Mater Thesis (the degree of Master of Science of Physics in the Graduate School of SUNY at Binghamton)

Superconductivity in bismuth metal layer sandwiched between graphene sheets

3.1 Preparation of Bi-MG Sample

$BiCl_3$ GIC samples as a precursor material were prepared by heating a mixture of highly oriented pyrolytic graphite (HOPG) (grade ZYA from Advanced Ceramics, Ohio) and an excess amount of $BiCl_3$ at 200 °C in a ampoule filled with chlorine gas at a pressure of 375 Torr (diagram 1,2).[9,10] The reaction was continued for three days. It was confirmed from (00*L*) x-ray diffraction (Rigaku RINT 2000 x-ray powder diffractometer) that the $BiCl_3$ GIC sample consists of stage 2 as majority phase and stage 3 and stage 4 as minority phase. The *c* axis repeat distance is 13.17 ± 60.05 Å for stage 2, 15.85 ± 0.25 Å for stage 3, and 20.22 ± 0.25 Å for stage 4, respectively. No Bragg reflection from the pristine graphite is observed.

The synthesis of Bi-MG was made by the reduction by Li-diphenylide from $BiCl_3$ GIC. $BiCl_3$ GIC samples were kept for three days in a solution of lithium diphenylide in tetrahydrofuran (THF) at room temperature. Then the samples were filtered, rinsed by THF, and dried in air. Finally the samples were annealed at 260 °C in a hydrogen gas atmosphere for one day (diagram 3). The structure of Bi-MG thus obtained was examined by (00*L*) x-ray diffraction, and bright-field images and selected-area electron diffraction (SAED) (Hitachi H-800 transmission electron microscope) operated at 200 kV. The same methods for the structural analysis were used for Pd-MG.[16–18] The (00*L*) x-ray-diffraction pattern of Bi-MG is much more complicated than that of $BiCl_3$ GIC, which makes it difficult to calculate the average particle thickness from the identity period in Bi-MG. Note that graphite reflections appear in Bi-MG, suggesting that a part of Bi atoms leaves from the graphite galleries occupied by $BiCl_3$ intercalate layers in BiC_{13} GIC during the

reduction process. Such Bi atoms tend to form multilayered Bi nanoparticles in the graphite galleries in Bi-MG. The number of Bi layers in possible multilayered structures could not be exactly determined at present. The SAED pattern of Bi-MG consists of polycrystalline diffraction rings, suggesting that there are at least four Bi layers in thickness. Reflections from Bi and graphite were observed.

As listed in Table I, all the Bi reflections were labeled and attributed to the formation of rhombohedral Bi, according to the standard ICDD PDF (Card No. 05-0519). This result indicates that Bi nanoparticles are crystallized as rhombohedral Bi phase in Bi-MG. The observed spacings of Bi-MG are 1–2% shorter than those of bulk Bi metal. The size of Bi nanoparticles distribute widely around the average size 110 Å. More than 50% of Bi nanoparticles have sizes ranging between 10 and 50 Å. The largest particle size is 750 Å (diagram 4).

1. E. Abrahams, P.W. Anderson, D.C. Licciardello, and T.V. Ramakrishnan, Phys. Rev. Lett. 42, 673 (1979).
2. 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).
3. D. Simonian, S.V. Kravchenko, M.P. Sarachik, and V.M. Pudalov, Phys. Rev. Lett. 79, 2304 (1997).
4. S.V. Kravchenko and T.M. Klapwijk, Phys. Rev. Lett. 84, 2909 (2000).
5. A.F. Hebard and M.A. Paalanen, Phys. Rev. Lett. 65, 927 (1990).
6. Ali Yazdani and A. Kapitulnik, Phys. Rev. Lett. 74, 3037 (1995).
7. N. Mason and A. Kapitulnik, Phys. Rev. Lett. 82, 5341 (1999).
8. N. Markovic, C. Christiansen, and A.M. Goldman, Phys. Rev. Lett. 81, 5217 (1998).
9. J. Walter, H. Shioyama, and Y. Sawada, Carbon 36, 1811 (1998).
10. J. Walter and H. Shioyama, Carbon 37, 1151 (1999).
11. E. McRae and J. Walter, Carbon 39, 717 (2001).
12. M. Suzuki, C. Lee, I.S. Suzuki, K. Matsubara, and K. Sugihara, Phys. Rev. B 54, 17 128 (1996).
13. M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. 65, 1920 (1996).
14. K. Wakabayashi, M. Sigrist, and M. Fujita, J. Phys. Soc. Jpn. 67, 2089 (1998).
15. K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, Phys. Rev. B 59, 8271 (1999).
16. J. Walter and H. Shioyama, Phys. Lett. A 254, 65 (1999).
17. J. Walter, Adv. Mater. 12, 31 (2000).
18. J. Walter, Philos. Mag. Lett. 80, 257 (2000).
19. D.B. Haviland, Y. Liu, and A.M. Goldman, Phys. Rev. Lett. 18, 2180 (1989).
20. B. Weitzel and H. Micklitz, Phys. Rev. Lett. 66, 385 (1991).
21. G. Deutscher, O. Entin-Wohlman, and Y. Shapira, Phys. Rev. B 22, 4264 (1980).
22. D. Saint-James and P.G. de Gennes, Phys. Lett. 7, 306 (1963).
23. S. Tanuma, in *Graphite Intercalation Compounds II*, edited by H. Zabel and S.A. Solin (Springer-Verlag, Berlin, 1992), p. 163.
24. hyperphysics.phy-astr.gsu.edu/hbase/solids/supcon.html

Step one of preparation of Bi-MG

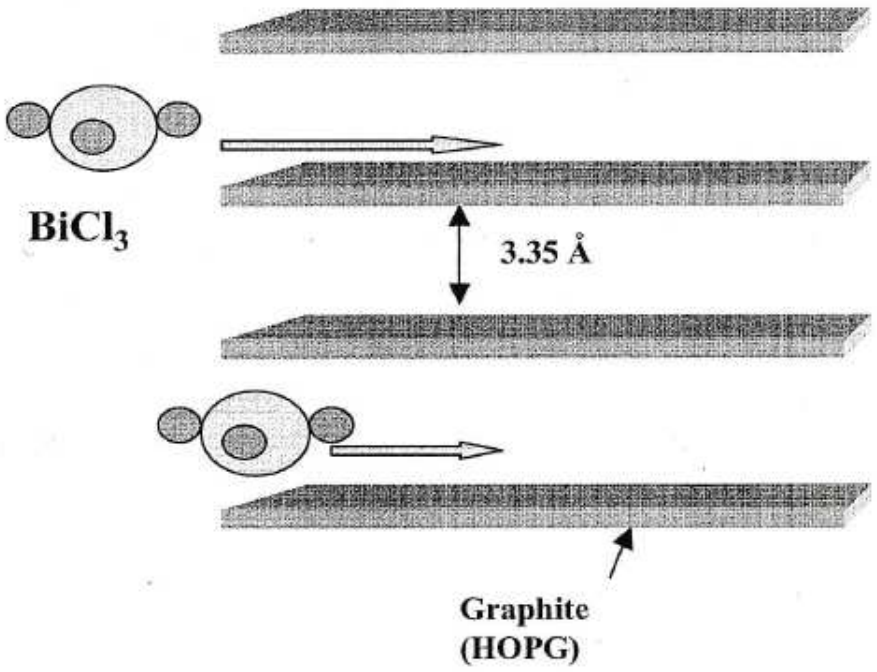
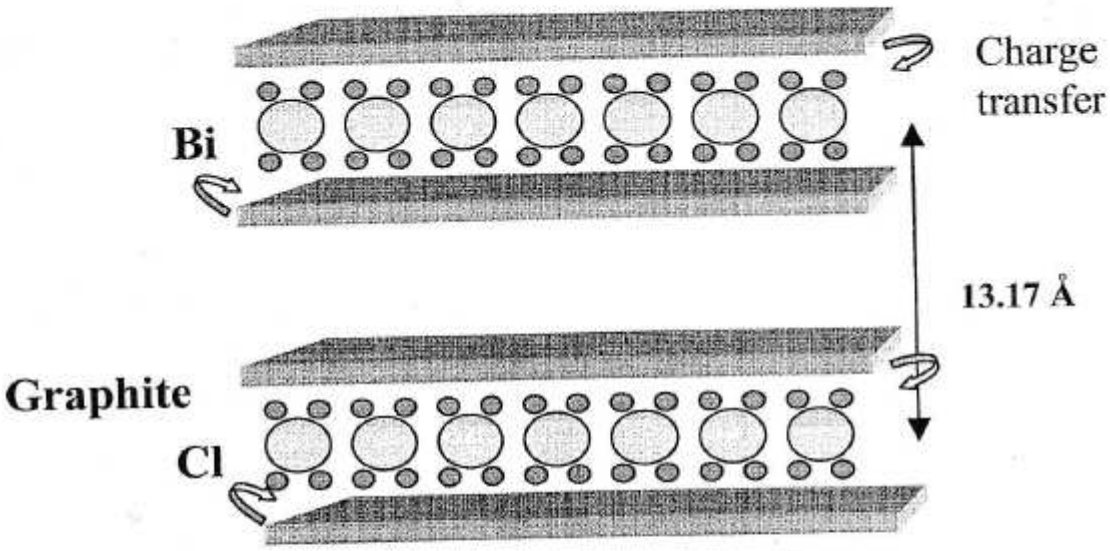


Diagram 1. Bi Cl_3 was intercalated into highly oriented pyrolytic graphite (HOPG).



State-2 $BiCl_3$ GIC (acceptor GIC)

Diagram 2. State-2 BiCl3 GIC (acceptor GIC).

Step two of preparation of Bi-MG

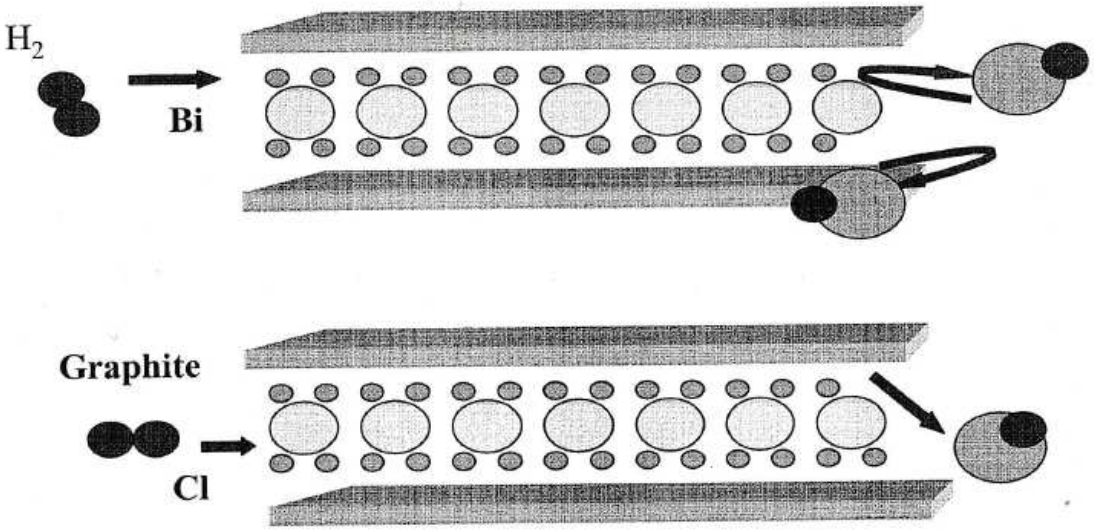


Diagram 3. **Bi-MG was prepared by the reduction of chlorine atoms from $BiCl_3$ GIC. $BiCl_3$ GIC was kept in lithium diphenylide in tetrahydrofuran (THF) at room temperature for 3 days. Then, the samples were annealed at 260 °C in a hydrogen gas atmosphere for one day.**

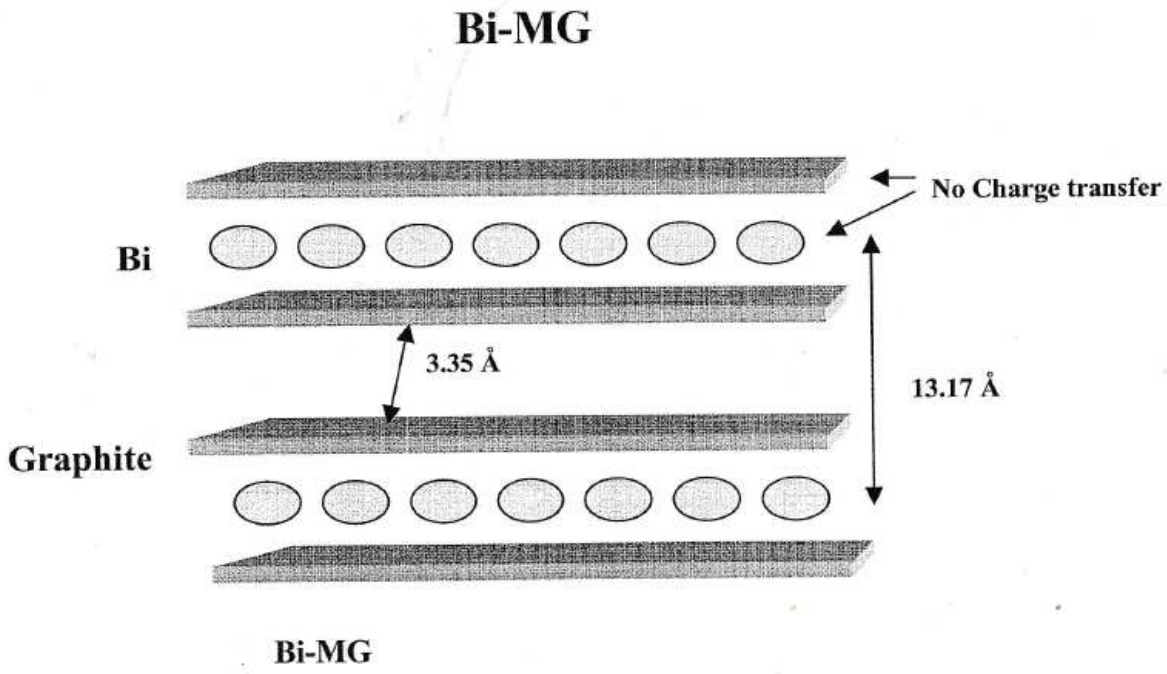


Diagram 4. **In Bi-MG, there is no charge transfer between Bi nanoparticles and nanographites. The size of Bi nanoparticles distibutes widely around the average size 110Å. More than 50 % of Bi nanoparticles have sizes ranging between 10 and 50 Å. The largest size is 750 Å**

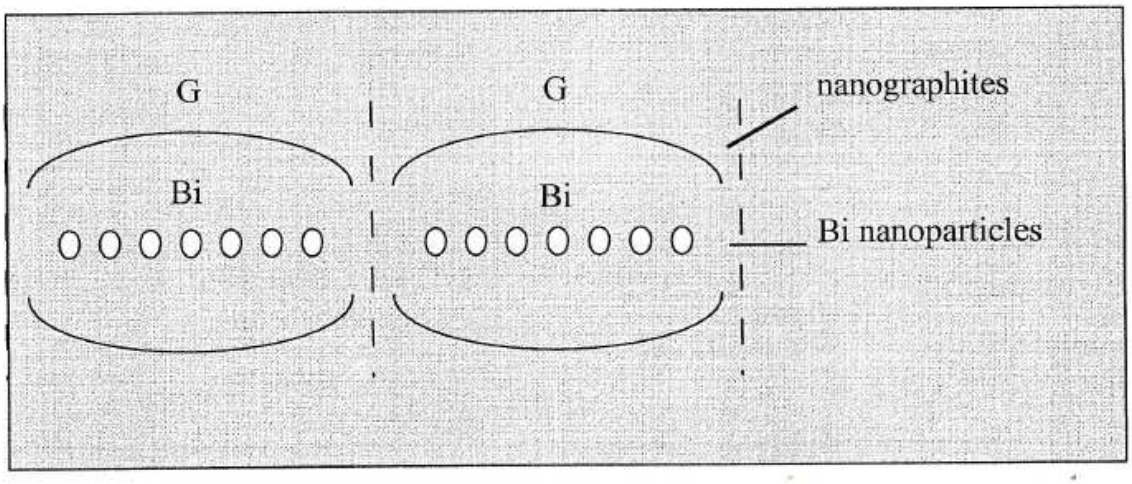


Diagram 5. **Nanographite with zigzag edges.**