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19. ABSTRACT

Experimental and theoretical studies have been carried out relevant to the structural, lattice, electronic, magnetic and superconducting properties of synthetic metals prepared by intercalating graphite. New synthesis methods have been developed for preparing magnetic transition metal chloride and potassium-hydrogen graphite intercalation compounds. The use of ion implantation to enhance intercalation has been explored and promising results have been obtained. Structural studies using high resolution x-ray scattering and transmission electron microscopy have been applied to study two-dimensional structural phase transitions such as the commensurate to incommensurate stripe phase transition in bromine intercalated graphite and the commensurate to glass phase transition in antimony pentachloride intercalated graphite. The construction of a Raman microprobe allows study of the spatial homogeneity (to 2 micron resolution) of the staging in specific intercalated graphite samples. Electrical and thermal transport studies have been carried out, providing new information on the dominant scattering mechanisms. "The high field magnetoresistance anomaly in graphite identified with a charge density wave has been further explored with particular emphasis given to the role of impurities in pair breaking phenomena and pulsed electric fields in non-linear non-ohmic effects. Experimental and theoretical studies of two-dimensional magnetic phenomena have been successfully carried out in magnetic intercalation compounds. The theoretical model developed to explain the superconducting behavior in the first stage alkali metal compounds has guided studies on superconducting graphite intercalation compounds with higher transition temperatures with particular relevance to their superconducting behavior and their related Fermi surface and phonon mode properties.

Semi-Annual Report to the <u>Air Force Office of Scientific Research</u> for research on Structure-Property Relationships in Intercalated Graphite

AFOSR Contract #F49620-83-C-0011 for the period October 1, 1984 — March 31, 1985

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1 Overview

This Semi-annual report contains a restatement of the proposed research under the contract and reports the current state of the work.

1.1 Abstract of Objectives

Experimental and theoretical studies have been carried out relevant to the structural, lattice, electronic, magnetic and superconducting properties of synthetic metals prepared by intercalating graphite. New synthesis methods have been developed for preparing magnetic transition metal chloride and potassium-hydrogen graphite intercalation compounds. The use of ion implantation to enhance intercalation has been explored and promising results have been obtained. Structural studies using high resolution x-ray scattering and transmission electron microscopy have been applied to study two-dimensional structural phase transitions such as the commensurate to incommensurate stripe phase transition in bromine intercalated graphite and the commensurate to glass phase transition in antimony pentachloride intercalated graphite. The construction of a Raman microprobe allows study of the spatial homogeneity (to 2 micron resolution) of the staging in specific intercalated graphite samples. Electrical and thermal transport studies have been carried out, providing new information on the dominant scattering mechanisms. The high field magnetoresistance anomaly in graphite identified with a charge density wave has been further explored with particular emphasis given to the role of impurities in pair breaking phenomena and pulsed electric fields in non-linear non-ohmic effects. Experimental and theoretical studies of two-dimensional magnetic phenomena have been successfully carried out in magnetic intercalation compounds. The theoretical model developed to explain the superconducting behavior in the first stage alkali metal compounds has guided studies on superconducting graphite intercalation compounds with higher transition temperatures with particular relevance to their superconducting behavior and their related Fermi surface and phonon mode properties.

1.2 Statement of Work

Statement of work in AFOSR contract #F49620-83-C-0011 on Structure-Property Relationships in Intercalated Graphite.

- Derive techniques for improved methods for the preparation and characterization of specific graphite intercalation compounds.
- Synthesize new intercalated systems and study their structure.
- Study in-plane structure and phase transitions in the intercalate layers with electron diffraction, lattice fringing, real space electron microscope imaging, and high resolution x-ray scattering.
- Deduce structural phase diagrams for specific graphite intercalation compounds.
- Investigate in detail commensurate-incommensurate phase transitions.
- Study lattice modes by infrared and Raman spectroscopy, and inelastic neutron scattering.
- Derive models for the phonon dispersion relations throughout the Brillouin zone, and apply these models to interpret lattice mode studies.
- Model the electronic dispersion relations and apply these models to interpret the experimental results relevant to the electronic properties.
- Measure and model thermal transport phenomena in intercalated graphite.
- Measure the temperature and field dependence of the magnetic susceptibility and heat capacity of magnetic graphite intercalation compounds and to construct magnetic phase diagrams for these systems.
- Study the superconductivity of specific graphite intercalation compounds.

2 Current Status of Research Effort

A summary of the current status of the research effort on the structure-property relationships in intercalated graphite is presented here following the listing given in the statement of work (section 1.2). In presenting the summary, we refer by number (#n) to the publications for the nine month period October 1, 1984 to June 30, 1985 following the publication numbers which are listed in section 3.1.

2.1 Synthesis and Compositional Characterization of Graphite Intercalation Compounds

2.1.1 A New Method for Synthesis of Potassium-Hydrogen Graphite Intercalation Compounds

A new method recently developed for the synthesis of potassium-hydrogen graphite intercalation compounds, based on the direct intercalation of KH (#20) has now been extended to synthesize the corresponding compounds with deuterium. The method has also yielded a well-staged KH compound of high stage (stage 4). Further emphasis is given to the preparation of higher stage compounds. The KH-GIC samples have been characterized for staging homogeneity by (00 ℓ) x-ray diffraction and for in-plane structure by transmission electron microscopy (TEM) (#20). Raman microprobe studies have given information about staging homogeneity (#19).

2.1.2 Implantation-Enhanced Intercalation

We have shown that if a graphite sample is first ion implanted, then the ability to intercalate certain species is greatly enhanced. This concept has been applied to enhance the intercalation of sodium, which does not readily intercalate graphite (#8,#14). Since the implantation of carbon and argon into graphite also enhances the subsequent intercalation of sodium, we conclude that implantation-enhanced intercalation is due to a defect mechanism rather than to a catalytic process. The extension of the implantation-enhanced intercalation concept to other intercalants has had limited success. This study was the topic of the M.S. thesis of H. Menjo.

2.1.3 Use of Rutherford Backscattering for the Characterization of Graphite Intercalation Compounds

The Rutherford backscattering (RBS) technique has been applied to provide unique information on the structure of GICs. Conventional RBS studies have yielded information on the depth distribution of the chemical constituents (#18) in both air stable and reactive GICs. With the RBS channeling spectra, unique information has been obtained with regard to interplanar alignment and the effect of structural phase transitions on this alignment. The Rutherford backscattering experiments were carried out at Bell Laboratories in collaboration with Drs. T. Venkatesan and B. Wilkens.

2.2 Structural Studies

2.2.1 High Resolution Structural Studies Using Electron Microscopy

High resolution Transmission Electron Microscopy (TEM) studies have been carried out on well staged SbCl₅-GIC (#17, #26, #30, #41) samples and KH-GIC (#20, #28, #40) samples based on both single crystal "kish" graphite and highly oriented pyrolytic graphite (HOPG) host materials. For the SbCl₅-GIC system, \Box transition from a commensurate intercalate phase at room temperature to a glassy phase is readily observed below ~ 150K (#22) using transmission electron microscopy techniques. This phase transition is very unusual insofar as the low temperature phase is the glassy phase. High resolution x-ray studies were carried out to identify this transition more fully, but no such transition could be observed with x-ray scattering using both kish and vermicular graphite host materials. Detailed TEM results show that the glassy phase is induced by the electron beam irradiation through a radiolysis mechanism. The dependence of the critical electron dose necessary to induce the glass phase has been determined as a function of electron beam energy and sample temperature. The activation energy for the formation of the glass phase changes dramatically from ~ 0.11 eV above ~ 150 K to ~ 0.01 eV below ~ 150 K. Models for the structure of SbCl₅ - GIC are suggested using computer image simulations of high resolution lattice images as a function of transmission electron microscope parameters, e.g. defocus.

For the KH-GICs, lattice fringe imaging techniques have been used to obtain unique information about the c-axis structure on an atomic level (#20, #28, #40). In addition to the c-axis repeat distances observed in (00*l*) x-ray diffraction, a variety of other structures are observed. Some structures are related to hydrogen-deficient regions separating KH-GIC regions from K-GIC regions, and other structures related to a periodic arrangement of KH and K heterostructure superlattices. Unique information on the in-plane structure has likewise been obtained, showing the (2×2) structure to be dominant for samples prepared at high temperature (e.g., 490 °C) and the $(\sqrt{3} \times \sqrt{3})$ structure dominant for samples prepared at lower temperatures (e.g., 260°C). In a complementary (00*l*) x-ray study (#41), the kinetics of the formation of the KH compounds has been investigated. The results show that with the direct KH intercalation method, a stage *n* K-GIC is rapidly formed, and subsequently over a relatively long time additional K and H species are intercalated to form the final KH compound of stage *n*, where n = 1, 2. This kinetic process was independently found by Guérard and coworkers in France.

2.2.2 High Resolution X-Ray Scattering Studies

To explain the unusual low temperature glass phase in $SbCl_5$ -GICs, high resolution x-ray studies were carried out from 14 K to 300 K in search of the glass phase. To determine whether sample thickness could be related to the observation of a glass phase, experiments were carried out using both kish and vermicular graphite host materials. The failure to observe the glass phase in high resolution x-ray experiments under a wide variety of conditions provided an essential step in the identification of the glass phase formation with an electron beam irradiation mechanism.

High resolution x-ray studies are now being initiated to determine whether the mechanism responsible for the stabilization of the superconducting transition temperature in KHg-GICs by

hydrogen doping is structural or non-structural. A major high resolution x-ray study of KH-GICs including the in-plane structure and intercalation kinetics is being initiated.

2.2.3 Model for Staging in Intercalated Graphite

A model for staging has been developed (#22) based on an evaluation of the partition function for attractive in-plane and repulsive interplanar interactions. Mixed staging is found at high temperatures below the disordering temperature. This study is being carried out in collaboration with Professor David Adler and his graduate student J.C. Schön.

2.3 Lattice Mode Studies

2.3.1 Raman Microprobe Studies

A Raman microprobe has been set up for particular application to the study of the Raman spectra in ordered and disordered graphites and graphite intercalation compounds. (#3,#12) The availability of this new instrument has enabled us to use our knowledge of the phonon dispersion relations of GICs to characterize the spatial homogeneity of the staging in GIC samples (to ~ 2μ m resolution).

2.3.2 Raman Characterization of Potassium-Hydrogen Intercalated Graphite.

The Raman shifts of the E_{2g_2} modes in KH – GICs were determined and compared with binary K – GICs and ternary KHg – GICs (#19,#42). The strong electron affinity of hydrogen plays an important role in shifting the E_{2g_2} mode of stage-1 KH – GICs to higher wavenumbers than for the stage-1 alkali-metal GICs. Of particular interest also is the drastic change in lineshape from that for the stage 1 K–GIC which shows a strong Breit–Wigner line to that for the stage 1 KH–GIC which is Lorentzian, consistent with a large reduction in the graphite-intercalate layer coupling as electrons are transferred to the hydrogen from the potassium and graphite π -bands.

2.4 Electronic Structure

2.4.1 Charge Transfer Mechanism in Acceptor-GICs

Fundamental differences between the charge transfer mechanism in acceptor and donor compounds are identified (#36). A new bard structure mechanism is proposed for charge transfer in an acceptor compound, valid for molecular acceptor compounds (such as Br_2 -GICs) which exhibit a commensurate intercalate layer with long range in-plane coherence. For acceptor compounds such as the Br_2 -GICs, defect mechanisms such as disproportionation and intercalate island structures cannot account for charge transfer.

2.4.2 On the Occupation of the Intercalate Bands in Stage 1 Alkali Metal-GICs

A review is presented of the experimental evidence relevant to the occupation of the intercalate bands in the stage 1 compounds C_8K , C_8Rb , and C_8Cs (#11), a point of current controversy.

Although the evidence is not conclusive, various experiments to clarify this important point are suggested.

2.4.3 Shubnikov-de Haas Effect in the KH-GIC System

Results on the Fermi surface for KH-GICs have been obtained using the Shubnikov-de Haas effect (#29, #42). Characteristic Shubnikov-de Haas frequencies have been observed for stage 1, 2 and 4 KH-GICs. Each of the spectra have been analyzed in terms of the rigid band model, but it is only for stage 4 that good agreement is obtained with the model, as would be expected since stage 1 and stage 2 should not be well described by the dilute limit model. The interpretation of the Shubnikov-de Haas results assumes full occupation of the hydrogen levels, consistent with the strong electron affinity of hydrogen.

2.5 Transport Properties

2.5.1 High Field Magnetoresistance Anomaly in Graphite

The role of impurities and charge imbalance in the high field magnetoresistance anomaly in graphite was recently studied and modeled (#4), showing that the detailed behavior at the magnetoresistance anomaly is highly sensitive to the concentration of charged impurities, which give rise to the breaking of pair states. By measuring the magnetoresistance with pulsed currents, it was shown that the magnitude of the anomaly exhibits a non-linear dependence on the electric field (#13). In this work it was also established that the charge density wave occurs in the basal I lane (#7) and not along the c-axis as had been proposed by Yoshioka and Fukuyama. A detailed experimental determination down to ~ 0.3 K of the field dependence of the transition temperature showed deviations from the theoretical prediction (#23).

2.5.2 Magnetic Phase Transitions in C_6Eu observed by High Field Magnetoresistance

The magnetic phase transitions in the donor compound C_6Eu , previously observed in the magnetization by Suematsu et al., have been verified in high field magnetoresistance measurements, including transitions from a triangular planar spin arrangement to a ferrimagnetic spin arrangement, to a canted spin phase, to a ferromagnetic phase (#15, #38, #45). The high field magnetoresistance measurements clearly show an additional canted spin phase. Monte Carlo spin simulation calculations have been used to identify the magnetic phases.

2.6 Magnetic Studies in Graphite Intercalation Compounds

2.6.1 Zero Field Susceptibility of Finite Size Kosterlitz-Thouless Systems

To explain the experimental susceptibility measurements in $CoCl_2-GICs$, finite size effects have been considered from a theoretical point of view (#2, #5, #34). In particular, finite size effects in the Kosterlitz-Thouless transition have been investigated using the renormalized spin wavevortex gas method. By imposing an upper limit on the length scale and a lower limit for the spin wave integral, the finite size rounding of the susceptibility in the 2D-XY model is obtained. The differential magnetic susceptibility is calculated numerically by integrating the spin-spin correlation function and the result is normalized to the high temperature series expansion for the classical 2D-XY model. Application of this theory has been made to the CoCl₂-intercalated graphite system.

2.6.2 Competing Field Induced Transitions in the Two-Dimensional XY Model

In studying the magnetic properties of CoCl₂-GICs, two symmetry breaking fields are present: the in-plane 6-fold crystal field and the external magnetic field. In this connection the ferromagnetic two-dimensional XY model with a p-fold symmetry-breaking field H_p , subjected to an in-plane external field H applied at an angle ω ($0 \le \omega \le \pi/p$) with respect to the p-fold axis, has been analyzed exactly at zero temperature. (#24, #25). A spin-flip type transition occurs at a critical field $H_C = p^2 H_p$ and at a critical angle $\omega_0 = \pi/p$. At this critical point, the parallel differential susceptibility, χ_{\parallel} , (where the probing field h_{\parallel} is parallel to H), jumps discontinuously to zero and the perpendicular differential susceptibility, χ_{\perp} , (where the probing field h_{\perp} is perpendicular to H), diverges like $(H_C - H)^{1/2}$. A self consistent harmonic approximation is applied for the low temperature analysis and numerical results for the magnetization, the parallel susceptibility and the perpendicular susceptibility are obtained. The singularities of the zero temperature analysis are retained when random averages are taken numerically over the angle ω for the parallel susceptibility and magnetization. These concepts have been applied to measurements of the magnetic properties of two-dimensional systems.

The 2D-XY model calculation consists of a generalization of the José, Kadanoff, Kirkpatrick and Nelson(JKKN) model to multiple symmetry-breaking fields using the classical 2D-XY model. The calculation applies symmetry arguments to the renormalization group equations. The generalized model is analyzed using a renormalized spin wave-vortex gas technique, with finite size effects included. Numerical results for the generalized model have been obtained for the case of a classical 2D-XY model with a 1-fold symmetry-breaking field and a 6-fold symmetry-breaking field. Applications of the generalized JKKN model have been made to the susceptibility measurements on CoCl₂-intercalated graphite.

2.6.3 Temperature Dependence of the Magnetic Susceptibility of CoCl₂-GICs

Previously measured differential magnetic susceptibility data for stage 1, 2 and 3 CoCl₂-GIC camples have been analyzed using the high temperature series expansion of the classical spin model in two dimensions, yielding conclusive evidence for a classical 2D-XY model description of the magnetic properties of CoCl₂-GICs (#35). Deviations from the high temperature series analysis have been studied using the theory of the finite size Kosterlitz-Thouless transition, with size as an adjustable parameter. The results indicate that the island size in the CoCl₂-intercalate layer is of the order of 60 × 60 to 80 × 80, consistent with the recent findings using transmission electron microscopy (#37). The effect of the symmetry-breaking field has been analyzed using a generalized JKKN model. A qualitative understanding of the susceptibility anomalies in CoCl₂-GICs is achieved. It is found that the CoCl₂-GICs are approximately a classical 2D-XY system with a ferromagnetic exchange coupling $J_{eff} = 7.125 K$. A Kosterlitz-Thouless transition takes places at $T \approx 10 K$ and the divergent susceptibility is rounded off by finite size effects as well as the

effects of the probing field. The initial decrease in the susceptibility for $T \leq 10$ K is a result of the in-plane 6-fold symmetry-breaking field as well as the interplanar coupling; the low temperature phase is consistent with the picture of ferromagnetic layers of XY spins coupled antiferromagnetically. The model Hamiltonian that describes the magnetic properties of CoCl₂-GICs is given by four terms (#9, #10). The dominant term is the classical 2D-XY Hamiltonian. The perturbations consist of a 1-fold symmetry-breaking field with Zeeman coupling to the external field, a six-fold symmetry-breaking field corresponding to the phenomenological six-fold in-plane anisotropy, and an antiferromagnetic inter-planar coupling. This magnetic Hamiltonian is used to interpret the experimental susceptibility and magnetization for CoCl₂-GICs (#6, #44).

2.6.4 Two-Dimensional Spin-Flop Transition in CoCl₂-GICs

Two field-induced susceptibility anomalies are observed in the quasi two-dimensional spin system of $CoCl_2$ -intercalated graphite (#21, #44). These anomalies are explained using the Landau free energy functional applied to the magnetic Hamiltonian of $CoCl_2$ -intercalated graphite. The low field anomaly at $H_{AS}(T) \approx 160$ Oe is identified with a two-dimensional antiferromagneticspin-flop first-order transition. The high field anomaly at $H_{SF}(T) \approx 300$ Oe is identified with a spin-flop-ferromagnetic second-order transition. The low temperature properties of these three phases in the stage 1 $CoCl_2$ -GIC are analyzed using the transfer matrix method for their *c*-axis ordering. A comparison of the theory with experimental data indicates that the antiferromagnetic coupling between $CoCl_2$ layers and the 6-fold in-plane anisotropy are approximately 160 Oe and 10 Oe respectively. Since the magnetic islands contain about 4000 spins, the $CoCl_2$ system is particularly well suited to a Monte Carlo calculation of the spin states in the magnetic phase diagram. Such a Monte Carlo calculation has been carried out and has been especially helpful in identifying the spin arrangements in the low temperature magnetically ordered phases.

2.6.5 Magnetic Donor GICs

The only donor magnetic GIC that has been prepared in a form suitable for magnetic measurements is the first stage compound C_6Eu . We have studied the magnetic phase diagram for this compound using high field magnetoresistance techniques, employing the highest fields available with the hybrid magnet at the Francis Bitter National Magnet Laboratory. Monte Carlo spin simulation calculations initially developed to explain the magnetic phases in the CoCl₂-GIC system have been extended to C_6Eu . These calculations have been useful in identifying a new magnetic phase transition with a canted spin phase. In addition, the calculations have indicated the presence of a 6-fold in-plane symmetry breaking field (#45).

2.7 Superconductivity Studies in Graphite Intercalation Compounds

2.7.1 Superconductivity in KHg-GICs

The relation between the synthesis conditions, the in-plane structure and the superconducting transition temperature T_c and width ΔT_c are under investigation (#16, #43). Of particular interest is the wide range of superconducting transition temperatures that have been reported (0.72 < T_c <

1.55 K) for the stage 1 compound, and the observation that T_c for the stage 1 compound is lower than that for the stage 2 compound, though heat capacity measurements indicate a higher density of states for the stage 1 compound.

2.7.2 Superconductivity in Hydrogenated KHg-GICs

When stage 1 KHg-GICs are doped with hydrogen, the transition temperature was found to rise to the maximum observed value of $T_c \approx 1.55$ K, independent of the transition temperature prior to the hydrogenation (#27,#32). In the hydrogenation process, the transition width ΔT_c is also greatly narrowed. The physical basis for this stabilization of the superconducting transition by the addition of hydrogen is under investigation using high resolution x-ray scattering techniques to look for structural effects relating to this stabilization of the superconducting phase transition.

2.8 Review Articles and Plenary Invited Talks

A short review article has been prepared for the Materials Research Encyclopedia, and has been published by Pergamon Press (#1). An invited plenary paper for the European Physical Society on recent advances in research on GICs was presented (#31). An article for Physics Today has been prepared for publication based on the retiring APS presidential address in which research on GICs was discussed.(#33) In response to a request to highlight the research opportunities in graphite intercalation compounds at the Fourth International Conference on Intercalated Graphite at Tsukuba, Japan (1985), a review article has been prepared.(#39)

3 Reports and Publications

3.1 Publications

- 1. "Intercalation Compounds", M.S. Dresselhaus, Materials Research Encyclopedia, Pergamon Press (in press).
- "Kosterlitz-Thouless Phase Transitions in Finite Size Systems: Application to CoCl₂-Graphite Intercalation Compounds", K.Y. Szeto, M. Elahy, S.T. Chen and G. Dresselhaus, Bull. APS <u>29</u>, 293 (1984).
- "Raman Microprobe Studies of the Structure of SbCl₅-Graphite Intercalation Compounds", L.E. McNeil, J. Steinbeck, L. Salamanca-Riba and G. Dresselhaus, Bull. APS <u>29</u>, 253 (1984).
- 4. "The Effect of Impurities on the Electronic Phase Transition in Graphite Under Strong Magnetic Field", Y. Iye, L.E. McNeil, and G. Dresselhaus, *Phys. Rev.* B<u>30</u>, (in press).
- 5. "Kosterlitz-Thouless Transition for Finite Size Systems", K.Y. Szeto and G. Dresselhaus, Phys. Rev. B(accepted).

- 6. "CoCl₂-Intercalated Graphite: A Quasi-Two-Dimensional Magnetic System", M. Elahy and G. Dresselhaus, *Phys. Rev. B* <u>30</u>, 7225 (1984).
- "The Electronic Phase Transition in Graphite Under Strong Magnetic Field", Y. Iye, L.E. McNeil, G. Dresselhaus, G. Boebinger, and P.M. Berglund, Proceedings of the 17th Conference on the Physics of Semiconductors, Aug. 6-10, 1984, San Francisco, edited by J.D. Chadi and W.A. Harrison, Springer-Verlag, N.Y., p. 981 (1984).
- 8. "Intercalation of Ion Implanted Graphite", H. Menjo, B.S. Elman, G. Braunstein, and M.S. Dresselhaus, J. de Chimie Physique <u>81</u>, 835 (1984).
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- 13. "Non-Ohmic Transport in the Magnetic-Field-Induced Charge Density Wave Phase of Graphite", Y. Iye and G. Dresselhaus, *Phys. Rev. Letts.* <u>54</u>, 1182 (1985).
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- 24. "Two-Dimensional XY Model with Multiple Symmetry-Breaking Fields", K.Y. Szeto and G. Dresselhaus, *Phys. Rev. B* 30, (1985). (in press).
- 25. "Competing Field Induced Transitions in the Two-Dimensional XY Model", K.Y. Szeto and G. Dresselhaus, Submitted to J. Phys. C, (1985).
- "High Resolution Electron Microscopy Studies of SbCl₅-GIC", L. Salamanca-Riba, J.M. Gibson and G. Dresselhaus, Extended Abstracts of the 17th Biennial Conference on Carbon, June 16-21, 1985, University of Kentucky, p. 204.

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- "Enhanced Superconductivity in Hydrogenated Potassium-Mercury Graphite Intercalation Compounds", G. Roth, A. Chaiken, T. Enoki, N.C. Yeh, G. Dresselhaus and P.M. Tedrow, Phys. Rev. B (in press).
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- 34. "Zero Field Susceptibility of Finite Size Kosterlitz-Thouless Systems", K.Y. Szeto and G. Dresselhaus, *Phys. Rev.* B, (in press).
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- 36. "Charge Transfer Mechanism in Acceptor-GICs", M.S. Dresselhaus and G. Dresselhaus, Synth. Metals (accepted).
- 37. "Magnetic Phase Transitions in CoCl₂-Graphite Intercalation Compounds", G. Dresselhaus, S.T. Chen and K.Y. Szeto, Synth. Metals (accepted).
- "Magnetoresistance and Magnetic Phase Transitions in C₆Eu", H. Suematsu, H. Minemoto, K. Ohmatsu, Y. Yosida, S.T. Chen, G. Dresselhaus and M.S. Dresselhaus, Synth. Metals (accepted).
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- "High Resolution Electron Microscopy Studies on KH_z and KD_z Intercalated Graphite", M. Endo, L. Salamanca-Riba, N.C. Yeh, T. Enoki and M.S. Dresselhaus, Bull. APS <u>30</u>, 240 (1985).
- "Electron Beam Induced Commensurate to Glass Phase Transition on SbCl₅-GIC", L. Salamanca-Riba, J.M. Gibson, G. Roth, A.R. Kortan, G. Dresselhaus and R.J. Birgeneau, Bull. APS 30, 240 (1985).
- 42. "The Intercalation Mechanism, Raman Characterization, Electronic Structure and Magnetic Susceptibility in KH_x and KD_x Intercalated Graphite", N.C. Yeh, T. Enoki, G. Roth and G. Dresselhaus, *Bull. APS* <u>30</u>, 240 (1985).
- 43. "Structural and Superconducting Properties of KHg-GICs", A. Chaiken, G. Roth, N.C. Yeh, T. Enoki, M.S. Dresselhaus and P.M. Tedrow, Bull. APS 30, 283 (1985).
- 44. "Magnetic Phase Transitions in CoCl₂-Graphite Intercalation Compounds", S.T. Chen, K.Y. Szeto and G. Dresselhaus, Bull. APS <u>30</u>, 284 (1985).
- 45. "Electrical Resistivity and Magnetoresistance in Graphite Intercalation Compounds C₆Eu", K. Sugihara, S.T. Chen and G. Dresselhaus, Bull. APS <u>30</u>, 331 (1985).

3.2 Advanced Degrees

• "Two-Dimensional XY Models and Its Application to Graphite Intercalation Compounds",

K.Y. Szeto, Ph.D., Physics, January 1985.

- "Ion Implantation Enhanced Intercalation in Graphite", H. Menjo, M.S., Department of Materials Science and Engineering, June, 1985.
- "Structural Studies of Graphite Intercalation Compounds and Ion Implanted Graphite",
 L. Salamanca-Riba, Ph.D., Physics, July 1985.

4 Personnel Involved with Research Program

- Mildred S. Dresselhaus Principal Investigator Responsible for the research and the direction of all aspects of the program. The study of intercalated graphite is the major research activity in the research group.
- Gene Dresselhaus Co-Principal Investigator Responsible together with the principal investigator for the research and the direction of all aspects of the program.

Gerhard Roth - Postdoctoral Fellow
 Responsible for high resolution x-ray measurements and for the synthesis and measurements
 of superconducting properties of graphite intercalation compounds. (Left June 1985 to take
 an R & D position at Bruker Industries, Karlsruhe, West Germany).

• Ko Sugihara - Research Staff

Responsible for modeling transport properties of GICs and of scattering processes in magnetic intercalation compounds.

• Alla Antonious – Research Assistant Responsible for setting up system for infrared spectroscopy studies in graphite intercalation compounds.

- Alison Chaiken Research Assistant and Graduate Fellowship Student Responsible for superconductivity studies in intercalated graphite, including setting up a ³He refrigeration system.
- Shyng-Tsong Chen Research Assistant and Graduate Fellowship Student Responsible for the synthesis of magnetic intercalation compounds, for high precision measurements of the magnetic susceptibility and magnetization of these compounds as a function of temperature and external magnetic fields. Is also responsible for modeling spin ordering using Monte Carlo techniques.

• Ali Kazeroonian – Research Assistant

Responsible for high resolution x-ray measurements of structure of graphite intercalation compounds, with special emphasis on the possible connection of structure to the stabilization of the superconducting transition.

- Hiroshi Menjo Fellowship Student Responsible for synthesis and measurement of the Na-GICs using ion implantation to enhance the intercalation process. Completed M.S. Thesis in May, 1985.
- Lourdes Salamanca-Riba Research Assistant Responsible for structural studies of intercalated graphite using x-ray diffraction, real space imaging and lattice fringing, with particular emphasis on phase transitions. Completed Ph.D. Thesis in July, 1985.
- Kwok-Yip Szeto Research Assistant and Graduate Fellowship Student Responsible for extension of two-dimensional xy model to calculate susceptibility for magnetic GIC including finite domain size effects, magnetic phase diagrams and spin flop transitions. Completed Ph.D. Thesis in January, 1985.
- Nai-Chang Yeh Research Assistant Responsible for the synthesis, characterization of KHg and KH_x graphite intercalation compounds, and measurement of the Fermi surface, transport properties and magnetic susceptibility.

• Maria Kudisch – Undergraduate Student Has been assisting with synthesis of KHg-GICs and superconductivity measurements. Completed B.S. Thesis in May, 1985.

4.1 MIT and Other Collaborators

- D. Adler Professor, Electrical Engineering, MIT Collaborates on models for the intercalation mechanism for graphite intercalation compounds.
- S. Berko Professor, Physics, Brandeis University Collaborates on positron annihilation studies of intercalated graphite.
- R.J. Birgeneau Professor, Physics, MIT Provides expertise and equipment for carrying out high resolution x-ray scattering experiments.
- W. Cooke Research Staff, Los Alamos Scientific Laboratory
 Collaborates on μ spin rotation studies of CoCl₂ intercalated graphite.
- P.C. Eklund Associate Professor, Physics, University of Kentucky Collaborates on lattice mode studies of intercalated graphite.
- J. Murray Gibson Research Staff, AT & T Bell Laboratories, Murray Hill, NJ Collaborates on high resolution microscopy studies of intercalated graphite.
- L. Hobbs Associate Professor, Materials Science and Engineering, MIT Provides expertise in the electron microscopy measurements.
- Y. Iye Research Staff, AT&T Bell Labs., Murray Hill, NJ Collaboration on studies of high magnetic field anomaly in graphite.
- P.A. Le⁻ Professor, Physics, MIT Provides expertise on theory of two-dimensional magnetism and high magnetic field anomaly in graphite.
- P.M. Tedrow Staff Member, Francis Bitter National Magnet Laboratory Provides expertise in superconductivity and equipment for carrying out measurements in the millikelvin range.
- T. Venkatesan Research Staff, Bell Communications Research, Murray Hill, NJ Collaborates on Rutherford Backscattering studies of intercalated graphite.

4.2 Coupling Activities – Seminars and Invited Conference Papers

The MIT group is strongly coupled to international activities on graphite intercalation compounds. Below are listed titles of seminars, invited talks and symposia given over the nine month October 1, 1984 to June 30, 1985 period relevant to the work supported under this contract.

- October 10, 1984, University of Massachusetts, Amherst MA, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- November 21, 1984, McMaster University, Hamilton, Ontario, Physics Colloquium, "Two-Dimensional Physics In Graphite Intercalation Compounds", (MSD).
- January 7, 1985, Solid State Physics Division Seminar, Oak Ridge National Laboratory, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- January 16, 1985, University of West Virginia, University Lecture, "Science Education for this Decade", (MSD).
- January 17, 1985, University of Toronto, Toronto, Canada, Physics Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- January 23, 1985, University of California, Berkeley, California, Physics Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- January 31, 1985, Stanford University, Stanford, CA, Materials Science Colloquium, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- February 1, 1985, University of California, Berkeley, Quantum Electronics Seminar, "New Materials for Applications in Quantum Electronics and Superconductivity", (MSD).
- March 20, 1985, European Physical Society, Invited Plenary Lecture, Berlin, West Germany, "Layered Crystals and Intercalated Compounds", (MSD).
- March 26, 1985, American Physical Society, March Meeting, Baltimore, MD, "Perspectives on the Presidency of the American Physical Society", (MSD).
- April 12, IBM Research Laboratory, San Jose CA, Laboratory Seminar, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (MSD).
- April 25, AFOSR, Bolling Air Force Base, Washington, DC, "Opportunities and New Directions In Graphite Intercalation Compounds", (MSD).
- May 17, Xerox Research Laboratory, Palo Alto, CA, Laboratory Seminar, "Two-Dimensional Magnetism In Graphite Intercalation Compounds", (GD).
- May 18, 1985, University of California, Berkeley, CA, School of Engineering, Commencement Address, "The Challenge of Youth", (MSD).

• June 19, 1985, Invited talk, CRDC Scientific Conference on Obscuration and Aerosol Research, June 17-21, 1985, Aberdeen Proving Grounds, MD, "Intercalated Fibers Derived from Benzene", (MSD).

5 New Discoveries, Patents or Inventions

None.

