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SUPERCONDUCTIVITY AND METAL INSULATOR TRANSITIONS IN LAYERED SOLIDS:

HIGH T OXIDES AND GRAPHITE INTERCALATION COMPOUNDS

By

Yiyun Huang

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

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DOCTOR OF PHILOSOPHY

Department of Physics

SUPERCONDUCTIVITY AND METAL INSULATOR TRANSITIONS IN LAYERED SOLIDS: HIGH T_ OXIDES AND GRAPHITE INTERCALATION COMPOUNDS

by

Yiyun Huang

Field and temperature dependent levitation properties of high temperature superconducting copper oxide compounds were studied over the ranges $1 \le H \le 10 \text{kG}$, $0 \le \partial H / \partial z \le 0.77 \text{kG/mm}$ and $4.2 \text{K} \le T \le 300 \text{K}$. A novel cryogenic levitometer was developed for these experiments. For all of the specimens studied the levitation height shows a threshold temperature T_L above which the specimen will not levitate, and a dramatic slope discontinuity at a temperature T_J which is associated with the onset of the phase coherence between Josephson weakly linked grains. A linear relationship between T_L^2 and the inverse field gradient was theoretically derived and found to be in excellent agreement with experiment for both the Y and Bi based compounds. The magnetization properties revealed by the levitation experiments were also examined using a SQUID susceptometer. A least squares fit using these data yielded parameters which agree well with a Ginzberg-Landau model of the temperature dependence of the penetration depth, $\lambda(T)$.

We have also carried out systematic resistance measurements in order to study the kinetic and electronic properties of potassiumammonia graphite intercalation compounds. The time dependence of c-axis resistance measurements reveals the kinetics of the ammoniation of KC24 to form the ternary graphite intercalation compounds (GIC) K(NH3) C24, 0<x<4.38. These results provide the first evidence of two dimensional diffusion limited intercalation kinetics that are governed by the growth of planar quasicommensurate domains. A least squares fit of our data, using a 2D model, yields a diffusion constant of the order $10^{-9} \text{cm}^2/\text{sec}$. This is in agreement with known values of gaseous diffusion into solids. The a-axis resistivity measurements exhibit an intriguing metal-nonmetal transition at x>4. This transition is attributed to a 2D Mott type transition in the intercalated K-NH, liquid monolayer. The electrical anisotropy of the ternary GIC $K(NH_3) C_{24}$ at x=4 is found to be about 5x10⁴ which is the highest yet reported for a stage-1 donor GIC. Other alkali metal ammonia intercalation GICs such as $Rb(NH_3)_{x^{24}}$ and $Cs(NH_3) \underset{x^{24}}{C}$ were also studied in order to explore ion size effects. An empirical relationship between the saturation resistance and ionic parameters has been found.

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LEVITATION STUDIES OF HIGH TEMPERATURE SUPERCONDUCTORS

PART I

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CHAPTER ONE

Overview

Since the discovery of superconductivity in mercury in 1911, the spectacular physical properties of superconductors have attracted many physicists to explore this mysterious state and to search for new materials with even higher transition temperatures (or critical temperature) T_c . In 1933, Meissner and Ochsenfeld discovered that a magnetic field (provided that it is not too strong) cannot penetrate into the interior of a superconductor, that is to say superconductors exhibit perfect diamagnetism¹. This effect is named the Meissner effect. Perfect electrical conductivity and perfect diamagnetism are two independent signatures of the superconductivity. Another striking feature of a superconductor is an energy gap of width 2A centered about the Fermi energy in the set of allowed one-electron levels.

More than twenty metallic elements have been found to become superconducting at very low temperature (see table 1.1). Meanwhile, a few thousands of alloys and compounds have also exhibited superconducting properties² which have been extensively studied. Among this group of superconductors, the highest T_c has been found in the 70's³ to be 23K. In spite of the low transition temperature, many practical applications have been found in various fields. One of the

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|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| u | Be | | | | | | | | | | | 8 | С | N | 0 | F | Ne |
| Na | Mg | | | - | | | | | | | | AI | si | P | 5 | CI | Ar |
| ĸ | Ca | Sc | ті | v | Cr | Mn | Fe | Co | NI | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Te | Ru | Rh | Pd | Ag | Cd | In | Sn | SP | Te | I | Xe |
| Cı | Ba | Lu | Hf | Ta | w | Re | Os | Ir | Pt | Au | Hg | ТІ | РЬ | Bi | Po | At | An |
| Fr | Ra | | | | | • | | | | | | | | | | | |

| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | ТЪ | Dy | Ho | Ēr | Tm | Yb | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|--|
| Ac | Th | Pa | U | Np | Pu | | | | | | | | | |

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AI Si

Superconducting

Superconducting under high pressure or in thin films

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Table 1.1Superconducting elements. After G. Gladstone et al.reference 4

most important applications is in high magnetic fields. Superconducting coils which provide several Tesla magnetic fields have been widely used in cyclotron in nuclear and high energy physics experiments. Another important application is the detection of very small signals. The superconducting quantum interference device (SQUID) can detect a voltage difference⁵ as small as 10^{-15} V, and a magnetic field as small as 10^{-9} G.

To date, most superconducting devices are operated in liquid helium with increasing costs. Many applications are limited due to the low critical temperature T_c of conventional superconductors. Bednorz and Müller recently introduced a new class of superconductors which are copper oxides with a layered perovskite-like crystal structure⁶. Their work has generated a wave of intense excitement and activity which brought the transition temperature T_c from 20K to 125K in a year or

so⁶⁻⁹. This revolution in high temperature superconducting materials may bring us to a new era of technology and open whole new applications of superconductivity such as high speed superconducting computers and large scale superconductive magnetic energy storage (SMES). The study of this new class of superconductors has become extremely attractive not only because of the potential technical applications, but also because these new materials may exhibit a new mechanism for superconductivity. A full understanding of the mechanism may offer a new direction in looking for other types of superconductors with higher T_c .

In general, superconductors can be classified in two types, namely type I and type II. For type I superconductors, they undergo a transition from the normal state to the Meissner state at a certain

critical temperature T_. In the ideal Meissner state (ignoring Londonlike flux penetration at the surface), all flux is expelled from the superconductor when it is exposed to a weak magnetic field. The magnetic induction field \vec{B} inside the superconductor is zero. This is true until the external applied field reaches the so called critical field H_c, after which the sample goes into the normal state and \vec{B} increases linearly with the applied field \vec{H} as shown in figure 1.1a. Meanwhile, the magnetization increases linearly with \vec{H} until H₂, after which it jumps to zero. In contrast, type II superconductors exhibit a vortex state between the normal state and the Meissner state. In the vortex state, some flux penetrates into the material and forms vortices. Figure 1.1c shows the flux penetration for these three states. If we look at magnetization versus magnetic field, for an isotropic type II superconductor the linear relationship between the two quantities ends at the so called lower critical field H_{cl} where the superconductor enters the vortex state from the Meissner state. The magnetization then decreases with the applied field until the field reaches the upper critical field H_{c2}. Above this field, the material becomes normal. The schematic behavior of magnetization and magnetic induction for type II superconductors is plotted in figure 1.1b. The new class of layered oxides has been found to be type II superconductors. Unlike the conventional type II superconductors, the upper critical fields of these new materials are so high that they have not been directly measured to date. The ratio of H_{c2} to H_{c1} can be as high as tens of thousands while



Figure 1.1 (a) and (b) are schematic phase diagrams for type I and type II superconductors, respectively. The relations between the external field H, the magnetic induction field B and the magnetization M for each state are also shown in the figure. (c) shows the flux penetration for the three states.

it is only an order of ten for most conventional type II superconductors.

The high temperature materials include single-layered La_{2-x} M_x CuO_{4- δ} (M=Ba, Sr, Ca, Na, ...) compounds⁶, double-layered RBa₂Cu₃O_{7- δ} (R=Y and a lanthanide element except Ce, Pm, or Tb) compounds⁷ and multi-layered Bi-Ca-Sr-Cu-O⁸ and Tl-Ca-Ba-Cu-O⁹ compounds. In the crystal structure of each of the above species, one or more CuO, layers have been found by independent X-ray and neutron diffraction studies 10-12. As a representative, the orthorhombic structure of a yttrium-barium-copper oxide compound is shown in figure 1.2. The unit cell consists of two dimpled CuO, planes separated by a yttrium layer which contains no oxygen and inserted with two BaO and one CuO layers (containing Cu-O chains). Strong anisotropy has been observed in the lower critical field and in the critical current density¹³. These measurements have suggested that the "good" conducting directions are along the Cu-O planes. The CuO, plane, which is referred as the ab plane, has become a major focus of many theoretical and experimental studies due to its important role in high temperature superconductivity. It is generally believed¹⁴ that the supercurrent is localized in the CuO₂ planes and that the spins which are associated with the holes on the copper site are responsible for antiferromagnetism in the normal state.

Optical studies¹⁵⁻¹⁷ have demonstrated that various kinds of flat defects exist in the high temperature oxide superconductors $YBa_2Cu_3O_{7-6}$



Figure 1.2 The unit cell of $YBa_2Cu_3O_7$. The \vec{c} axis is along the direction which is perpendicular to the copper oxide plane, \vec{b} is parallel to the plane and along the copper oxide chain and \vec{a} is perpendicular to both \vec{b} and \vec{c} .

(hereafter denoted by 123), Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O. The three most commonly seen defects are twin planes in the 123 compounds¹⁸, strip domains in Bi based copper oxide superconductors¹⁷, and stacking faults in both Bi based and Tl based copper oxide superconductors¹⁶. The twin planes are a direct consequence of the very slight difference between the lengths of a and b axes in the 123 materials and are referred to as antiphase domain boundaries¹⁸. In figure 1.3, \vec{a} and \vec{b} are interchanged in the two adjacent striations. Light microscopy studies¹⁵ have shown that small grains (typical size 5µm or less) are unidirectional grains i.e. the twin planes in these grains are aligned in one direction. On the other hand, large grains have a multi-directional domain structure and contain different twin plane orientations.

Although twin planes are not found in Bi (or Tl) based copper oxide compounds, stacking faults are almost inevitable. These compounds form a hierarchy of structures which differ in the number of CuO_2 planes and number of perovskite layers n (see figure 1.4). The generic chemical formula can be written as $Bi_m Ca_{n-1} Sr_2 Cu_n O_{2n+m+y}$ or $Tl_m Ca_{n-1} Ba_2 Cu_n O_{2n+m+y}$. The critical temperature T_c increases as the number of CuO_2 planes n increases and the Cu-O distance decreases. The low binding energy of this structure leads to stacking errors in the number of perovskite layers between the two metallic layers as has been shown by using transmission electron microscopy¹⁶. The lattice constants of Bi-Ca-Sr-Cu-O compounds have been found to exhibit ratios



Figure 1.3 A schematic diagram showing a twin plane boundary. and b are interchanged in the two adjacent striations. Note that the orientation are orthogonal in (a) and (b). The boundaries between the striations are referred to as twin planes. They are along the (110) direction. From reference 18.



B: metallic layer

Figure 1.4 The orthorhombic structures of the Bi-based or Tlbased high temperature copper oxide superconductors. T_c (in brackets) increases as the number of perovskite layers, R. increases.

which are similar to those of some mineral materials. The structure is called an aurivillius phase where a, b, and c can be expressed in terms of a characteristic length a_p as follows: $a=\sqrt{2}a_p$, $b=5\sqrt{2}a_p$, and $c=8a_p$. For the Bi high T_c compound a_p is equal to 3.8Å. Capponi et al. have shown, using lattice fringe images, that the lengths along the b-axis are incommensurate¹⁷. The periodicity in the b direction varied from $4\sqrt{2}a_p$ to $6\sqrt{2}a_p$ instead of being exactly $5\sqrt{2}a_p$. This is shown in the images taken along the c-direction. These mass density modulations along the b-axis are referred to as stripe domains¹⁷.

An understanding of the perturbative role of flat defects and the link strength between and within grains may reveal properties that have important consequences in the design and fabrication of practical superconducting devices. An example is field induced orientation. Solin et al. ¹⁹⁻²¹ have reported the first preparation of oriented bulk polycrystalline specimens aligned at T < T_c. They have shown that twin planes have a marked effect on the macroscopic magnetic properties of YBa₂Cu₃O_{7-δ}. They also demonstrated the alignments along the [110] axes with an applied weak magnetic field at T < T_c while others²²⁻²³ obtained alignment of the c-axes with a strong field at T > T_c.

Vierira et al.²⁴ have reported a simple levitation experiment soon after the discovery of the 90K superconductors. They have immersed a permanent magnet in a liquid nitrogen dewar. Superconducting particles were then dropped from the top of a glass tube which was inserted between the two magnet poles. They have found that larger particles (>50µm) experienced a greater force and actually levitated while small particles (20μ m or less) collected at the bottom of the sample tube. All of these particles were known to be superconductors from independent SQUID measurements of the magnetization. It was found that if the small particles were then pressed into a single pellet, the pellet also levitated. Their results served as an another example of the impact of the grain morphology and their orientation on the properties of high temperature superconductors. The simple explanation of their results is that small particles are single grained and have a unidirectional twin plane domain structure. They therefore can adopt a unique alignment with the magnetic field which minimizes the flux expulsion and thus the magnetic force. However, large particles are multigrained and have no unique alignment direction. Therefore, they experienced a larger magnetic force and levitated. Their experiments were performed at fixed field and fixed temperature. In addition, their samples were immersed in the liquid nitrogen, the buoyant force of which could not be ignored. In this part of my dissertation. I will present the results of variable field and variable temperature levitation studies which explore the levitation/orientation phenomenon quantitatively and thus elucidate the influence of intergranular weak links in high temperature superconductors.

CHAPTER TVO

Variable Temperature and Variable Field Levitometer

2.1 Introduction

Since the discovery of the Meissner effect, levitation experiments have been widely used to demonstrate superconductivity²⁵, and to develop the possible applications, particularly levitated trains²⁶. Many other potential applications including frictionless bearings²⁷, levitated coil for multipole fusion²⁸, and pressure gauges which operate by diamagnetic suspension in the Brownian-motion²⁹ have been envisioned. The basic principle of magnetic levitation is to balance the magnetic force and the weight of the superconductor. Therefore, the levitometer can also be used as a magnetic balance. Conversely, one can find the magnetic force from the known gravitational force, and hence determine the related magnetization and susceptibility.

Following the reports of the 90K high temperature superconductors, the levitation experiment was immediately repeated by many groups all over the world. The common configuration of their experiments consisted of a permanent magnet and a high temperature superconducting pellet. The superconducting pellet is immersed in a small cup of liquid nitrogen. After the pellet is cooled and enters the superconducting state, one carefully puts a small permanent magnet onto the pellet and the magnet will levitate on the top of the superconduting pellet. This simple setup gives a clear view of the Meissner effect in the high temperature superconductors. But it cannot give any quantitative measure of the levitation. Meanwhile, Vieira et al.²⁴ introduced the idea of separating superconducting particles and non-superconducting particles as noted above. Again, their levitometer only works at fixed magnetic field with a permanent magnet and only at liquid nitrogen temperature. Unlike the other levitation devices, the variable temperature and variable field levitometer we designed provides the capability of accomplishing quantitative studies of the magnetization and direct visual access to the magnetic field induced alignment of individual particles. In this chapter, I shall first give a detailed description of our levitometer and then discuss the application of the device.

2.2 Apparatus details

Figure 2.1 is a schematic diagram of our levitometer. In order to achieve magnetic levitation, a non-uniform magnetic field is essential. A cryogenic levitation chamber is also required to provide a low temperature environment for the sample entering the superconduting state. Finally, a cathetometer and other accessories are used to make quantitative measurements of the levitation height. Figure 2.1 shows these important components.

We use an Alpha Scientific model 4800 electromagnet to obtain the desired magnetic field. This is a 4" magnet which is small enough to



Figure 2.1 A schematic diagram of the temperature and field variable levitometer.

mount on a platform or a table. The two poles are facing each other in the horizontal direction. The minimum air gap between the two pole caps is determined by the diameter of the levitation chamber and associated cryogenic equipment (see discussion below). The magnetic field strength can be as high as 20kG when the air gap is set as 0.6". This is the upper limit of the magnetic field strength in our levitometer. Clearly. one can increase the maximum operating magnetic field by decreasing the air gap between the pole caps and later I shall discuss this in detail. Between the pole caps is the cryogenic levitation chamber. We have modified the magnet frame from 90° upright to 45° mounting in order to allow the levitation chamber to pass through the magnet. Tapered pole caps have been chosen to provide an increasing field gradient which is the driving force of levitation. For best results, we have machined the caps until the diameter of the pole end is slightly larger than the air gap. Further sharpening the pole caps will decrease the field strength and hence the field gradient. This is because decreasing the area of the pole caps is equivalent to increasing the distance between the - · · · · · poles.

The cryogenic levitation chamber is made of double walled glass tubing with a vacuum jacket to stop heat flow. To reduce heat radiation, the glass wall is coated with silver leaving a 5mm wide uncoated strip to allow for visual access. The lower end of the cryogenic levitation chamber is immersed in a liquid helium dewar underneath the magnet. Cold helium vapor flows through the levitation chamber for cooling. The cooling rate can be controlled by the pressure relief valve shown in the figure 2.1. By completely closing the valve, the pressure of helium vapor will build up in only a few minutes. The

liquid helium level can be raised as high as the sample region. The sample temperature drops to 4.2K immediately under this maximal cooling condition. Leaving the pressure valve slightly opened, one can reduce the liquid helium boiling rate and provide much longer running time using only limited liquid helium. On the other hand, a certain helium pressure is required for cooling. Insufficient cooling will cause a temperature gradient along the inner tubing. The pressure valve is used to optimize both aspects. Under our experimental conditions, two liters of liquid helium can last for six hours. Since helium can easily diffuse through glass tubing when the temperature is above liquid nitrogen temperature (77K), activated charcoal is placed in the vacuum jacket to absorb helium and maintain good vacuum insulation of our levitation chamber. This helps maintain the levitometer in good working condition and effectively increase the length of the period that one has before re-evacuation of the vacuum jacket is required.

The sample, is confined in another glass tube which is co-axial with the double wall tubing. The bottom of the inner tubing is sealed to prevent the sample from being exposed to helium vapor flow directly. But a small hole on the side of the inner tubing ensures helium gas exchange and heat convection. This helps cool more effectively and allows a more uniform temperature over the whole sample levitation region. For most of our experiments, the maximum temperature difference is about one or two degrees. Also a copper tube, used as a heat bath, is tightly fitted to the outside of the inner tubing. A slot along the copper tubing was machined to allow visual access to the inner tubing. GE varnish was used to fill the gap between the copper tubing and the inner glass tubing to ensure good thermal contact. Three Gallium-Arsenide diode temperature sensors are attached on the bottom, the middle and the top of the copper tubing to monitor temperature. The reason we choose a GaAs sensor is because the I-V curve of the GaAs diode varies little under the influence of a magnetic field. A heater wound at the bottom of the copper tubing provides accurate temperature variation/control. The temperature range of our levitometer is from 4.2K to room temperature or even higher. The heater is double wound to eliminate the solenoid effect that will affect the magnetic field distribution. The dimensions of the temperature sensors, copper temperature sink, and inner glass tubing limit the minimum size of the chamber and the air gap between pole caps. We have used rectangular tubing to reduce the air gap from 0.8° to 0.5°. This leads to a considerable increase in the field gradient. The maximum value is as high as 8kG/cm.

Ice is very harmful since it will not only freeze the sample at some height, but also destroy superconductivity. Therefore, the levitometer must be a frost free system. This is accomplished by putting all components together with o-ring seals and using homemade feedthroughs for sensor and heater wires.

With a sliding seal at the upper portion of the inner tubing, one is able to move the inner tubing up and down without bringing in moisture. Because of hysteresis in type II superconductors³⁰, the initial position of the inner tubing is important. It corresponds to different initial conditions of the measurement. By varying the initial condition, one can study not only levitation but also suspension. Our levitometer serves both purposes.

To make quantitative studies, we should first find the field strength and field gradient. Magnetic fields were mapped in detail by using a Hall probe. Figure 2.2 shows a typical field distribution as a function of position for a magnet current of 25 amps. The open circles in the figure are the actual measured values. Similar curves are measured for other magnet currents such as 10A, 15A, 20A, 30A, etc. The position of the probe is recorded by a HEERBRUGG model KM-325 cathotometer with an accuracy $\pm 50\mu$ m. The levitation height is also read by this cathotometer. A polynomial least squares fit has been used to approximate the position dependence of the field strength H_y(z). The solid line in figure 2.2 is a fit using a sixth order polynomial

$$H_{y}(z) = \sum_{i=0}^{6} a_{i} z^{i}.$$
 (2.2.1)

By taking the derivative of this function, one can find the field gradient as a function of position. To obtain an accurate field gradient from fitting and differentiation, one should choose an appropriate order polynomial fit. We found that lower order polynomials do not fit the field strength well. On the other hand, a polynomial with additional terms does not significantly alter the quality of the fit. Rather it introduces many oscillations in the field strength curve which suggest incorrect field gradient. A sixth order polynomial turns out to be a good choice. The dashed line in figure 2.2 is the field gradient given by differentiation of equation (2.2.1). It has the form

of



Figure 2.2 The magnetic field and field gradient distribution in the levitometer. The field strength data are measured at a magnet current of I=25A, and are accurate to 50G.

$$\frac{\partial H_{y}(z)}{\partial z} = \sum_{i=1}^{6} ia_{i} z^{i-1}$$
(2.2.2)

The optimum values of the a's from the fitting procedure are listed in table 2.1.

One can also use a differential Hall probe to measure the field gradient. A differential Hall probe is constructed from two regular Hall probes with fixed separation (e.g. 1mm). The difference between the response of the two probes divided by the separation gives the field gradient. One must be very careful to ensure that the two probes are parallel to each other and the separation must be small.

Up to now, I have described in detail the components of our unique levitometer. I shall now discuss the operation of this device.

2.3 Operation of the levitometer

As noted earlier, the initial condition is very important in the levitation measurement. One should thus initiate levitation under consistent conditions. To accomplish this, the following experimental scheme was used.

Starting from room temperature, the inner tubing was pulled to well above the electromagnet. The sample is at zero field or at the earth's magnetic field, and in this state the flux in the sample is essentially zero. Then, the pressure valve is closed. Helium vapor pressure quickly builds up and sample temperature is lowered to 5K in just a few minutes. After the sample is cooled, the electromagnet is turned on and the magnet current is increased to the desired value. When the field is
| a ₀ | a ₁ | a2 | a ₃ | a4 | a ₅ | a ₆ |
|-------------------|----------------------------|-------------------|-------------------|---------------------------|---------------------------|----------------------------|
| 6.97 | 1.71 | 4.05 | -1.94 | 5.68 | 9.49 | 9.06 |
| x10 ⁻² | x 1.0 ⁻¹ | x10 ⁻⁴ | x10 ⁻⁵ | x 10 ⁻⁷ | x 10 ⁻⁹ | x 10 ⁻¹¹ |

Table 2.1The optimum coefficients a yielded by the leastsqures fit of the polynormials to the magnetic field
strength.

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below the sample's lower critical field, there is no flux inside of the sample since it is in the Meissner state and is completely diamagnetic. When the field strength is stronger than the lower critical field. some flux penetrates the sample. The stronger the field is. the more the flux penetration. Some flux will be trapped in the sample when one tries to reduce magnetic field. Therefore, the key point in this scheme is to monotonically increase the magnetic field. Since the sample is well above the magnet pole pieces, the magnetic field is very weak. The sample is still seated at the bottom of the inner tubing. At this time. the inner tubing is slowly lowered with continuous vibration. The sample then enters the stronger field and higher field gradient. At some point, the levitation force would be strong enough to lift the sample. After that, the sample would stay at the same height while the operator keeps lowering the tubing until the bottom of the tubing passes through the pole caps. The height of the sample was recorded as the first data point. The pressure valve is then opened slightly at this time to select the desired cooling rate. Now one is ready to measure the temperature dependence of the levitation height and hence the magnetization. The heater is activated and the sample temperature is increased step by step. The levitation height is then recorded at each fixed temperature by using the cathotometer described in the previous section.

The magnetization can be found from the levitation height by using the equations below. Since the magnetic force balances the gravitational force when the sample is at rest, we have

$$F_{mag.} = F_{gra.} = \rho g V \tag{2.3.1}$$

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Also,
$$F_{mag.} = \frac{1}{2} \frac{\partial H_y(z)}{\partial z} V$$
 (2.3.2)

where M(z) is the magnetization when the sample is at the height z^{19} . Thus, $M(z) = \frac{2\rho g}{[\partial H_{-}(z)/\partial z]}$ (2.3.3)

Note that the magnetization of the sample depends on its density and not on its volume. As temperature increases, the magnetization will decrease. To keep the product of magnetization and field gradient constant, the sample will drop closer to the edge of pole caps where the field gradient is higher. Therefore, we did make measurements with ever increasing field strength as we intended. The susceptibility as a function of temperature can also be found using

$$\chi(T,H(z)) = \frac{M(T,z)}{H(z)}$$
(2.3.4)

To test our levitometer, we have measured the temperature dependent levitation height of a conventional superconductor. Figure 2.3 shows the measured results for a $Nb_{0.78}(Al_{0.78}Ge_{0.22})_{0.22}$ sample. Each curve corresponds to a selected magnet current and certain field strength and gradient distribution. The levitation height decreases as the sample temperature increases just as we expected. Also, a higher magnet current produces a stronger magnetic field and field gradient. As a consequence, the magnetization will decrease as illustrated in figure 1.1b. The product of the magnetization and field gradient determines the absolute levitation height. Using equations (2.3.1)-(2.3.4), one can find the susceptibility and compare these results with SQUID (Superconducting Quantum Interference Device) measurements which are



Figure 2.3 The levitation height of Nb_{0.78}(Al_{0.78}Ge_{0.22})_{0.22} measured as a function of temperature and magnet current. The conventional superconductor was used here to verify the reliability of levitometer. Note that the data are taken at very low temperature and the temperature uncertainty is ±0.5K. The levitation height Z is accurate to 1mm.



Figure 2.4 The susceptibility of the Nb_{0.78}(Al_{0.78}Ge_{0.22}) sample measured using a SQUID susceptometer. The temperature uncertainty is <u>+</u>1K. The susceptibility measured by the SQUID susceptometer is accurate to one-thousandth of its value.

shown in figure 2.4. Since the field strength changes in each levitation curve while field is fixed in the SQUID measurements, we can not directly compare these two sets of data. Instead, the results of the two methods are compared in table 2.2. They agree well with each other.

2.4 Concluding Remarks

We have developed a unique variable field and variable temperature levitometer which can accomplish the measurements of magnetization and susceptibility. Although the levitometer is not as accurate as a commercial SQUID susceptometer, it provides magnified direct visual access of the orientation of superconducting particles in a magnetic field. Magnetic force and field induced alignment of individual particles ranging in size from 10 μ m to 3mm can be measured simultaneously. This levitometer is thus complementary to a commercial susceptometer.

| Field | Т | SQUID M/d(emu) | Levitometer M/d(emu) |
|--------------------|------|-------------------|-------------------------|
| 1.0kG | 6.2K | 8.32 | 8.6±0.9 |
| 1.2 k G | 6.7K | 7.80 | 7.3±0.7 |
| 1.8 k G | 7.6K | 5.1 | 4.9±0.5 |
| | | | |

Table 2.2A comparison of the results of levitation and SQUID
measurements for Nb
0.78 (A1
0.78 Ge
0.22)0.22

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CHAPTER THREE

Levitation Studies of High T Superconductors

3.1 Introduction

High temperature copper oxide superconductors were first prepared by solid state diffusion techniques. This was followed by sintering in an oxygen environment at about 900° C for several hours⁶⁻⁷. Müller et al. have pointed out that the sintering process used to prepare these oxide systems yielded granular materials⁶. These materials can be described as systems which are formed from many anisotropic grains. The granularity of these materials strongly affects a number of their magnetic properties. In this chapter, I will discuss levitation studies on these granular high temperature superconductors.

3.2 Experiments and Results

The yttrium-barium-copper oxide superconductor samples used in our experiments were synthesized using a solid state diffusion method⁷. Yttrium oxide (Y_2O_3) , cupric Oxide (CuO), and Barium carbonate (BaCuO₃) powders were first dried at 100° C and then were mixed with a ratio of approximately 2:4:7. In order to enhance solid state reaction, the powders were well mixed and tightly packed into a crucible. After firing at 800°C for 12 hours under flowing oxygen, the black color single phase $YBa_2Cu_3O_{7-\delta}$ was formed. The greenish nonsuperconducting phase could always be eliminated by repeated firing.

Bulk $YBa_2Cu_3O_{7-\delta}$ samples were ground into powders in a ball mill and passed through selected sieves. Powders with a dimension of less than 20µm were selected and pressed into a pellet using a WABASH Hydraulic Press. Figure 3.1a shows that homemade die parts used in this press. Two hardened steel pistons of identical diameter (A and B) were fit into another hardened steel cylinder C. The surfaces of piston A and piston B were polished using a HRIRG Surface Grinder. The longer piston A was first placed into cylinder C and then the sample powders were added. The shorter piston B was inserted in C on top of the sample. By turning B, powders were uniformly spread between the two of faces of A and B. This would set the powder into an evenly packed layer and yield a pressed pellet which was uniform. The whole assembly was then placed in the center of the WABASH press and pressed to the desired pressure (Figure 3.1b). To remove the sample pellet, piston B was pressed into C from the bottom side of A as shown in figure 3.1c. A set of die with sizes from 3/8" to 1.5" allowed us to obtain pellets with desired diameters. The amount of powder we used determined the thickness of the pellet.

The actual levitation experiments were performed using our variable temperature and variable field levitometer described in chapter two. Figure 3.2 is a schematic diagram showing the magnetic configuration of a twinned single grain disc. The axes 2 and 3 refer to the ab planes while 1 refers to the c axis. θ and ϕ are the conventional Euler



Figure 3.1 A schematic diagram of the pellet press. (a) shows the die parts used in making the pellet. (b) and (c) show the direction of the force applied to the die in the two steps of the pellet preparation.



Figure 3.2 A schematic diagram showing the relevant axes for the levitation of a twinned single crystal. The axes 2 and 3 refer to the ab plane while 1 refes to the c-axis. θ and φ are the conventional Eular angles. Lines across the sample represent twin planes. angles. Lines across the sample represent twin planes. The most general case is that the susceptibility in each direction is different. In other words, the sample is completely anisotropic. We also assume that the demagnetization factors are also fully anisotropic. The magnetic energy of the levitated grain can then expressed as follows³¹:

$$U = \frac{1}{2} \int_{V} \vec{H} \cdot \vec{H}_{o} dV = \frac{V}{2} \sum_{j=1}^{3} A_{j} H_{oj}^{2} \qquad j=x,y,z \qquad (3.2.1)$$

$$A_{j} = \frac{X_{j}}{1 + N_{j} X_{j}}$$
 (3.2.2)

Here \vec{M} is the magnetization of the sample while H_{oj} , N_j , and χ_j are, respectively, the jth components of the applied field, demagnetization factor and the susceptibility. Table 3.1 lists the values of χ_j , A_j , and the net field strength H_j for the three typical states of a type II materials. The superconducting state corresponds to complete isotropic flux exclusion and the susceptibility is $-1/4\Pi$ in all three directions. The normal state is also isotropic with approximately zero susceptibility and the field in the sample is equal to the applied field. The displacement derivative of magnetic energy gives the magnetic forces while the angular derivatives yield the magnetic torques. These relations are expressed in (3.2.3)-(3.2.5) for the components which are relevant to our levitometer.

$$F_{z} = -\frac{\partial U}{\partial z}$$
(3.2.3)
$$T_{\theta} = -\frac{\partial U}{\partial \theta}$$
(3.3.4)

| STATE | Xj | Aj | Hj |
|----------|--|--|--------------------------------------|
| Veissner | $-1/4\pi$ | $\frac{1}{N_j - 4\pi}$ | $H_{oj}/(1-\frac{N_j}{4\pi})$ |
| Vortex | н <mark>ј</mark> - <u>4</u> πн _ј | - ^{Η^j_{c1} 4πη_{oj}} | $H_{oj} + \frac{N_j}{4\pi} H_{c1}^j$ |
| Normal | 0 | 0 | H _{oj} ' |

Table 3.1A list of the values of χ_j , A_j , and H_j for the
Meissner state, the vortex state and the normal
state. j denotes one of the Cartesian coordinates
(x, y, or z). See text, equation 3.2.2.

$$\tau_{\phi} = -\frac{\partial U}{\partial \phi}$$
(3.2.5)

The z component of the magnetic force balances the gravitational force in levitation while the torques will orient the sample in the magnetic field.

Figure 3.3 shows the levitation height as a function of temperature for a $YBa_2Cu_3O_{7-\delta}$ pellet. This data was taken by strictly following the procedure described in chapter two. Each curve corresponds to one magnet current. The higher current yields greater field gradient at the same height and thus greater magnetic force. As a result, the pellet is levitated higher. The center of the pole faces is at $z_0=697$ mm.

We know from chapter two that the levitation height will decrease as the temperature increases. This is because more flux will penetrate the sample at higher temperature. Figure 3.3 clearly shows this feature. We have defined a so called levitation temperature (T_L) which is the highest temperature that can be obtained before levitation ceases. This temperature increases as the magnet current increases. A plot of the square of levitation temperature versus the inverse field gradient at the height the levitation ceased (Z_L) is shown in figure 3.4 which clearly exhibits a linear relationship between these two quantities. A linear least squares regression fit has been used to determine the slope and intercept on the T_L^2 axis. It is found that the straight line can be expressed

$$T_{L}^{2} = 6537 - 1424 \left[\frac{1}{\frac{\partial H}{\partial z}} \right]$$
(3.2.6)



Figure 3.3

The levitation height as a function of temperature of a $YBa_2Cu_307_5$ pressed pellet. Each curve corresponds to a fixed magnet current. AT, AZ are typical error bars of the measurements.



Figure 3.4 A plot for $YBa_2Cu_3O_{7-\delta}$ of the square of the levitation temperature (T_L^2) vs. the inverse field gradient where levitation ceased.

A detailed discussion of this linear form will be given in the next section.

Another interesting feature shown in figure 3.3 is the kink around 20K for all five currents. To verify that these kinks do not result from a nonuniform magnetic field, magnetization verses temperature is plotted in figure 3.5 using our knowledge of the field gradient at height z and formula (2.3.3). Clearly, the kinks remains in the plot. Moreover the kink-like feature has been observed in more than ten specimens which have been examined. This suggests a discontinuity in the derivative of the magnetization, which is related to a transition at 20K as will be discussed below.

A more accurate measurement of the temperature dependence of the magnetization was carried out on the same pellet using an SHE SQUID. The results are plotted in figures 3.6 and 3.7. Data were also acquired by zero field cooling and field heating. Figure 3.7 is a plot of the magnetic moment versus temperature at five different field strengths. The temperature dependence of the magnetization can be obtained by multiplying the ordinate of this plot by the density of the sample. The kinks observed in our levitation experiments were once again present around 20K (Fig. 3.7). In addition, the magnetic moment is essentially independent of magnetic field above that temperature. This field independent magnetization is not observed in conventional superconductors as evidenced by figure 3.8 which shows the results of the same measurement on Nb_{0.78} (Al_{0.78} Ge_{0.22})_{0.22}. At temperature below the kink, the magnetization strongly depends on the field strength. In general, the slope decreases as the field increases with the exception



Figure 3.5 The magnetization of YBa₂Cu₃O₇₋₆ deduced from levitation height measured using our levitometer. d is the density of the sample. The relative errors of the magnetization are less than 0.1. The temperature uncertainty is ±1K.



Figure 3.6 The susceptibilities of YBa₂Cu₃O₇_5 as measured using a SQUID susceptometer. The same pressed pellet was used as that used in the levitation experiments. The error bars are smaller than the symbols used in the figure.



Figure 3.7 The corresponding magnetization of $YBa_2Cu_3O_7_{-}\mathcal{S}$ as measured by a SQUID susceptometer. The error bars are smaller than the symbols used in the figure.



Figure 3.8 The magnetization of the conventional superconductor Nb0.78(Al0.78Ge0.22)0.22. d is the density of the sample. The temperature uncertainty is \pm 1K, while the magnetization is accurate to one-thousandth of its value.

of the 1kG field. The susceptibility of the $YBa_2Cu_3O_{7-\delta}$ pellet is plotted in figure 3.6. At very low fields (250G, 150G in the figure), the susceptibility is independent of field indicating a Meissner state with complete flux exclusion. From figure 3.6, we have found that the ransition temperature T_c of our sample is about 89K and the lower critical field H_{c1} is about 300G. The levitation experiments were performed with the sample in the vortex state, i.e. the field is above the lower critical field H_{c1} and below the upper critical field H_{c2} .

The same levitation experiments were repeated using a sintered pellet which is fired at $950^{\circ}C$ for four hours . Similar results are obtained and are plotted in figure 3.9. From the kinks shown again at 20K, we can conclude that the slope discontinuity occurs at the same temperature for both sintered pellets and unsintered ones. Comparing the scale in figure 3.9 and figure 3.3, it is evident that there is a dramatic slope difference in the slope discontinuity before and after the sintering process. Since the sintering process enlarges the grain size in a pellet, this experiment gives us a clue to the grain size effect of the transition at 20K. This will be discussed in detail in the next section.

Another family of high temperature superconductors is the Bi or Tl based copper oxides. They have a similar orthorhombic structure to that shown in figure 1.4. This class of materials can achieve even higher T_c than the 123 materials. It is interesting to study the difference between these two classes of materials.

The temperature dependent levitation height of a $Bi_2Sr_2Ca_{n-1}Cu_nO_v$



Figure 3.9 The levitation results for a sintered pellet of $YBa_2Cu_3O_{7-\delta}$. The temperature uncertainty is $\pm 1K$ and the levitation height uncertainty is ± 0.1 mm.

pressed pellet has been measured using the same methods as for the 123 material. A plot of the levitation height versus temperature for the Bi material is shown in figure 3.10. The overall behavior is the same as for the 123 compounds. The levitation height decreases as temperature increases until levitation ceased at a temperature T_L . The sample levitates higher at higher magnet current. The data for the Bi material also exhibits a pronounced kink but at about 15K which is significantly lower than the corresponding temperature for the YBa₂Cu₃O₇₋₆ pellets.

The square of the levitation temperature T_L^2 verse field gradient at the threshold levitation height z_L is plotted in figure 3.11. Like the Yttrium-Barium-copper oxide pellet, a linear behavior is also observed within experimental error. In this case a linear regression fit yields the expression

$$T_{L}^{2} = 7917 - 2848x \left[\frac{1}{\partial H/\partial z} \right]$$
 (3.2.7).

The experimental error arises from uncertainties in the polynomial fit to find the field gradient, from the error in the determination of the levitation height, and also from a small temperature gradient which introduces ±1K error in the measurement of specimen temperature (see chapter two).

3.3 Discussions and Analysis

In order to interpret the linear behavior shown in figures 3.4 and 3.11, the critical fields were first considered. One of the most unusual features of the new oxide superconductors is their extremely



Figure 3.10 The levitaion results for a Bi2Sr2CunOy pressed pellet. The temperature and the levitation height uncertainties are <u>+</u>1K and <u>+</u>0.1mm respectively.

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Figure 3.11 The square of the levitation temperature versus the inverse of the field gradient for Bl₂Sr₂Ca_{n-1}Cu_nO_y.

high upper critical fields H_{c2} . As noted in chapter one, there are no direct measurements of H_{c2} available to date. It is generally believed that the H_{c2} is as high as a few hundred kilogauss. Meanwhile, the lower critical field H_{c1} is quite low as suggested by our SQUID measurement of $H_{c1}^{||} = 300$ G (figure 3.6). If one examines the magnetization with respect to the applied field such as shown in figure 1.1b, magnetization decreases to zero gradually over the large range of $H_{c1}^{--}H_{c2}^{-}$. Therefore, it is reasonable to assume that the magnetization remains constant when the applied field is in the range $H_{c1}^{||,|} \cdot L < H_{c1}^{||,|} \cdot L < H_{c2}^{||,|}$ and equals the value at the lower critical field $H_{c1}^{||,|}$, where ||, and | refer, respectively, to fields in and normal to the ab plane of a single crystal specimen i.e.

$$\mathbf{H}^{||, \perp}(\mathbf{T}, \mathbf{H}) = \chi^{||, \perp}_{\mathbf{H}_{c1}^{||, \perp}}(\mathbf{T}) = -\frac{1}{4\pi} \mathbf{H}_{c1}^{||, \perp}(\mathbf{T})$$
(3.3.1)

This is exactly what we have seen from the SQUID measurement (figure 3.7) of the previous section. The magnetization does not show any appreciable dependence on the magnetic fields over a wide range from 1kG to 6.5kG when the temperature is higher than the temperature where the kink in the magnetization occurs. Since the levitation experiments were carried out in a similar region, formula 3.3.1 is valid in our analysis. Substituting this equation into equation 2.3.3, one finds

$$-\frac{1}{4\pi} \times H_{cl}^{\parallel,\perp}(T) = \frac{2\rho g}{\frac{\partial H_{oy}^{\parallel,\perp}(z(T))}{\partial z}}$$
(3.3.2)

Empirically³², the temperature dependence of the lower critical field can be expressed as

$$H_{c1}^{eff}(T) = H_{c1}^{eff}(0) \mathbf{x} \begin{bmatrix} 1 - \frac{T^2}{T_c^2} \end{bmatrix}$$
(3.3.3)

where H_{cl}^{eff} is the effective lower critical field associated with the orientational averaging over the distribution of grain alignments in the pellet. Since the pellets consist of many random oriented grains and these grains can not align with the magnetic field, neither the parallel nor perpendicular values of H_{cl} are applicable. Note that $H_{cl}^{eff}(0)$ is the lower critical field at zero degrees. Combining Eqs.3.3.2 and 3.3.3, one has

$$-\frac{1}{4\pi} \times H_{cl}^{eff}(0) \times \left[1 - \frac{T^2}{T_c^2}\right] = \rho g \left[\frac{\partial H_{oy}(z)}{\partial z}\right]^{-1}$$
(3.3.4)

After further manipulation and using the levitation temperature T_L , Eq. 3.3.4 becomes

$$\mathbf{T}_{\mathrm{L}}^{2} = \mathbf{T}_{\mathrm{c}}^{2} - \left[\frac{8\Pi\rho g \mathbf{T}_{\mathrm{c}}^{2}}{H_{\mathrm{c1}}^{\mathrm{eff}}(0)}\right] \mathbf{x} \left[\frac{\partial H_{\mathrm{oy}}(z)}{\partial z}\right]_{z=z_{\mathrm{L}}}^{-1}$$
(3.3.5)

Equation 3.3.5 gives us a linear relationship between T_L^2 and the inverse of the field gradient at the temperature where the levitation ceases. The intercept with the ordinate gives T_c^2 and the slope yields the zerotemperature lower effective critical field. Now we can understand the straight line form exhibited in figures 3.4 and 3.11. The values of $H_{cl}^{eff}(0)$ for the 123 and Bi compounds deduced from Eqs.3.2.6 and 3.2.7 in light of Eq.3.3.5 are 90G±15G and 50G±15G respectively. We also find T_c values of 81K and 89K respectively for the 123 and Bi compounds. These results are just a few degree lower than those obtained directly from SQUID measurements (figure 3.6 and 3.7).

The small error in the levitation measurement of T_c results from the approximation $M=H_{c1}^{||\cdot|}/4\Pi$ in the calculation. If we examine the magnetization with respect to the applied field for most type II superconductors it has a form shown in figure 3.12. The small drop in magnetization near $H_{c1}^{||\cdot|}$ can be accounted for if we modify Eq.3.3.2

$$-\frac{1}{4\pi} \mathbf{x} \operatorname{H}_{cl}^{\text{eff}}(T) + \Delta = \frac{2\rho g}{\partial H_{ov}(z(T))/\partial z} \Delta > 0. \qquad (3.3.6)$$

Equation (3.3.4) becomes

$$\frac{1}{4\pi} \mathbf{x} \mathbf{H}_{cl}^{eff}(0) \mathbf{x} \left[1 - \left(\frac{\mathbf{T}}{\mathbf{T}_{cA}} \right)^2 \right] + \Delta = \frac{2\rho g}{\partial \mathbf{H}_{oy}(z(\mathbf{T}))/\partial z}$$
(3.3.7)

where T_{CA} is the actual transition temperature.

Thus

$$\mathbf{T}_{\mathbf{L}}^{2} = \mathbf{T}_{\mathbf{cA}}^{2} (1 - \Delta') - \left[\frac{8\pi\rho g \mathbf{T}_{\mathbf{c}}^{2}}{H_{\mathbf{c1}}^{\mathbf{eff}}(0)} \right] \mathbf{x} \left[\frac{\partial H_{\mathbf{oy}}(z)}{\partial z} \right]_{z=z_{\mathbf{L}}}^{-1}$$
(3.3.8)

where $\Delta' = \Delta x 4 \pi / H_{cl}^{eff}(0)$ and

$$T_{cA} = T_{c} / (1 - \Delta')^{1/2}$$
 (3.3.9)

From Eq.3.3.9 and the values of T_c and T_c^A determined from levitation



Figure 3.12 A schematic diagram of the field dependent magnetization for most type II superconductors

and SQUID measurements we find that $\Delta = 20.7(\frac{1}{4\pi}G) = 1.65G$ and $\frac{1}{4\pi}$

 $10(\underline{1}_{G})=0.78G$ respectively for the 123 and Bi compounds. 4Π

We now consider the origin of the kinks shown in figures 3.3, 3.7, and 3.10. The "double transition" like behavior shown in these figures is similar to the one previously observed in weakly coupled granular superconductors³³. The first transition at around 90K is the conventional normal state to superconducting state transition which is associated with the individual grains becoming superconductors. The second transition at around 20K for $YBa_2Cu_3O_{7-\delta}$ and 15K for the Bi compounds is associated with the onset of phase coherence of Josephson weakly linked grains. This transition temperature is denoted as T_J . When the specimen temperature is below T_c , but above T_J flux is expelled by individual grains, but is able to penetrate through the boundaries between these grains. When the temperature is lower than T_J , supercurrents bridge the intergranular Josephson weak links. Flux is then expelled by the whole sample.

To quantitatively examine this transition, we first consider the London-like flux penetration in an ideal plate-like grain of thickness a. The magnetization for applied fields parallel to the plate can be expressed in terms of the penetration depth λ as

$$M(T) = M_{O} \left[1 - \frac{\tanh(a/\lambda)}{a/\lambda} \right]$$
(3.3.10)

where the penetration depth λ is a function of temperature. Figure 3.13 shows the typical behavior of this function for several different a/λ

values labeled for each curve. As a/λ increases, the curve steepens and the transition sharpens eventually yielding a step function as a/λ goes to infinity. The penetration depth λ increases as temperature increases. There are several models to deal with this relationship. These models can generally be written in the form

$$\lambda = \lambda(0) \left[1 - \left(\frac{T}{T_c}\right)^{\alpha} \right]^{-1/\beta} \qquad T \le T_c \qquad (3.3.11)$$

where $\lambda(0)$ is the penetration length at zero kelvin. The parameters α and β take different values for different models. Table 3.2 lists the values which are used in the Casimir-Gorter, Ginsberg-Landau, ordered 3D XY and disordered 3D XY models. By substituting Eq.3.3.11 into Eq.3.3.10, the magnetization can be expressed as a function of grain size a, and temperature T.

$$M(T)=M(a,\lambda(T,\alpha,\beta))$$
(3.3.12)

A five parameter $(a/\lambda, M_0, T_c, \alpha, \text{ and } \beta)$ least squares fit was used to fit the measured magnetization above the phase coherence transition temperature T_{τ} . The error is

$$\boldsymbol{\epsilon}_{k} = \mathbb{M}(\mathbf{T}_{k}) - \mathbb{M}^{\text{fit}}(\mathbf{T}_{k})$$
(3.3.13)

where $M(T_k)$ is measured value at the temperature T_k and $M^{fit}(T_k)$ is calculated value from the fit function (3.3.7). The mean square error function is defined as

$$\xi = \frac{1}{N} \left[\sum_{k=1}^{N} \epsilon_k^2 \right]$$
(3.3.14)

where N is the number of the observed points. Obviously, the larger N



Figure 3.13 The temperature dependence of the magnetization obtained from Eqs. 3.3.10 and 3.3.11 using $M_0=1$, $T_c=90K$, $\alpha=1$, and $1/\beta=0.5$. Note that the transition sharpens as the ratio of the grain size to the penetration length a/λ_0 increases.

| MODEL | α | 1/ β |
|------------------|---|-------------|
| Casimir Gorter | 4 | 0.5 |
| Ginzberg-Landau | 1 | 0.5 |
| Ordered 3D XY | 1 | 1/3 |
| Disordered 3D XY | 1 | 0.7 |
| | | |

The parameters α and $1/\beta$ used in the four different models in the expression of the temperature dependence of the penetration depth. Table 3.2

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is, the better the fit one will achieve. Recalling that in the temperature range $T_J < T < T_c$, the magnetization is independent of the magnetic field, all data points of the five curves in figure 3.7 were used and yielded T equals 91K. Since the function is very complicated, it may have several minima in the mean square error function ξ. Different initial values for the five fitting parameters will result in a different minimum or divergence. The absolute minimum was selected from all the minima obtained. A very good fit was obtained and is plotted as a solid line in figure 3.14. The fitting parameters derived from the fit are also listed in that figure. Comparing the α and β values with the corresponding ones in table 3.2, we can see that a Ginsberg-Landau model gives the best fit. This is consistent with other measurements³⁴ of the granular high T_{sup}erconductors. Thus although it is not surprising that we obtain a good fit to the data of Fig.3.14 using as many as five parameters, the best fit yields values for those parameters which make very good physical sense.

When the temperature is below T_J , the magnetization curves are separated by the applied magnetic field as shown in figure 3.7. The slope decreases as the field increases [with the exception of the case for H=1kG (see discussion below)]. This is because the magnetic field alters the Josephson coupling energy. The stronger the magnetic field, the weaker the coupling. The transition is not as sharp as in lower field. The transition temperature T_J is also slightly shifted to lower temperature as field increase. This is not very clear in our measurements since the field strengths are relatively strong and the



Figure 3.14 A least square fit of the magnetization versus temperature data for YBa₂Cu₃O₇₋S. The data measured at H=6.5kG, 5kG, 3kG, and 2kG are marked with open circles, X's, open diamonds and squares, respectively, in the plot. The solid line is the fitting result. The mean square error of the fit $(\{[\Sigma(M_{measured}-M_{fit})^2]/N\})$ is less than 10^{-5} .
change of temperature T_J is essentially saturated in such strong fields. Dubson et al. have also observed a similar "double transition" in their resistivity measurements of $YBa_2Cu_3O_{7-\delta}^{35}$. Their experiments were done at fields of mG which is well below the lower critical field $H_{c1}^{||,|}$. They have shown that the transition temperature changes over the field range from zero field to 50G. Extrapolating their result, one finds a value of T_J =20K when the field is several kilogauss which agrees with our measurements.

There are two reasons for the nonsystematic behavior of the H=1kG data. One is that the signal is small when the field is low. This could be improved by using larger samples. But for directly comparing levitation data and SQUID data, we used the same samples for which the maximum size is limited by the levitometer to be 3mm. Another reason is connected with the behavior of the magnetization with respect to the applied field. If one examines the magnetization curves for all other conventional type II superconductors³⁰, one can find an overshoot of the magnetization M in the region immediately above the lower critical field $H_{c1}^{||,|}$. M will keep increasing as the field increases at a decreasing rate until the field H_p^{30} . The more dislocations found in the sample, the higher H_p . This overshoot of the magnetization is one of the signatures of granular superconductors. The abnormal behavior observed at H=1kG reflects this overshoot and suggests that for our specimens H_p

is greater than 1kG. Therefore, the absolute value of the magnetization at H=1kG is smaller than expected.

Equation (3.3.10) suggests that a sharper decrease in magnetization with temperature occurs for larger a/λ . This is confirmed by comparing the levitation results shown in figures 3.3 and 3.9 in the previous section. To see this more clearly, levitation data for a pressed pellet, a sintered pellet, and a single crystal were plotted on the same scale in figure 3.15. The results behaves just as we expect. Note that for T<T_T the slope of the levitation curve increases as a/λ increases.

It is well known³⁶ that the average grain size grows in the sintering process. Thus, a/λ is larger in a sintered pellet than in a pressed but unsintered pellet. Therefore the observed slope increases from a pressed pellet to a sintered pellet. Moreover a single crystal is essentially one grain. It thus has the largest ratio a/λ and the largest levitation curve slope as shown in figure 3.15.

Figure 3.15 also shows a much lower levitation temperature, T_L , (30K) for the single crystal sample whereas the levitation temperatures are about 60K for both the pressed and sintered pellet which have the same composition as the single crystal. This difference results because the single crystal uniquely aligns with the external magnetic field to minimize the magnetic force. For a pellet, the orientation of the composite grains is random. The ab planes in these grains do not adopt a specific direction relative to the magnetic field. Therefore they experience a stronger magnetic force and the levitation temperature T_L is much higher than for the single crystal.



Figure 3.15 A comparison of the levitation results for YBa₂Cu₃O₇₋₅ in the form of a pressed pellet (circles), a sintered pellet (squares) and a single crystal (diamonds). The temperature and the levitation height uncertainties are +1K and ±0.1mm, respectively.

3.4 Summary and Concluding Remarks

In this chapter, I have presented evidence of intergranular weak links and phase coherence in granular high temperature superconductors using the simple levitation experiments. A least squares fit of our data to equation 3.3.12 has yielded parameters which agree well with a Ginzburg-Landau model of the temperature dependence of the penetration depth, $\lambda(T)$. The levitation temperature T_L defined in the levitation experiments was found to be inversely proportional to the field gradient $\partial H/\partial z$ at the height levitation ceased. The lower critical field H_{c1}^{eff} for Y-based and Bi-based high T_c materials has been derived from equation (3.3.5). The critical temperature T_c could be found from the intercept on the T_L^2 axis in a plot of T_L^2 verse $(\partial H/\partial z)^{-1}$. Our experimental results have shown that the magnetization of high temperature oxide superconductors is nearly independent on the external magnetic field in the range of $H_{c1}^{[1],1]} < H^{[1],1]} < H_{c2}^{[1],1]}$ and $T_J < T < T_c$.

Finally, we consider further the kink in the 123 single crystal levitation curve shown in figure 3.15. We have argued that the kink is associated with the onset of the phase coherence of Josephson weakly linked grains. But the single crystal itself is normally one grain. Therefore, the curve representing the single crystal data should be smooth and absent of kinks. This is not what we observed. The answer to this question may be related to twin planes. The YBa₂Cu₃O_{7-δ} single crystal which we studied is heavily twinned and is composed of several

unidirectional domains within each of which the twin plane striations are aligned. The boundaries between these domains may constitute <u>intra</u> granular weak links which give rise to the observed kink in the levitation curve. Additional studies are required to clarify this part. LIST OF REFERENCES

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PART II

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RESISTIVITY STUDIES

OF

ALKALI-METAL ANMONIA GRAPHITE INTERCALATION COMPOUNDS

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CHAPTER ONE

OVERVIEW

It has been known for hundreds of years that solid carbon displays many structural phases such as diamond, amorphous carbon, and graphite. In this part of the dissertation, the hexagonal graphite phase of carbon will be our main focus. Graphite is a prototypical layered solid. Its schematic structure is shown in figure 1.1. Carbon atoms are bound in a hexagonal lattice plane. These planes are then stacked in the \vec{c} axis direction in a sequence which for hexagonal graphite is ABAB... as shown in figure 1.1. The second layer of carbon atoms (B) is eclipsed relative to the first layer (A). The whole plane is shifted by a displacement \vec{a}_1 which is the unit vector of the four index hexagonal crystal cell (not primitive cell). The carbon atoms on the third layer are located directly above those in the first, and atoms in the fourth directly above those in the second and so on. The repeat distance in the \vec{c} direction is 6.7Å. The interplane distance is 3.35Å, half of the c-axis repeat distance. The nearest carbon-carbon (C-C) distance within the plane is 1.42Å. The bond between the hexagonal lattice planes is so weak that one can peel the layers of the carbon lattice easily. In fact, the samples used in our experiments are cleaned by cleaving off the top layers of carbons. The weak bonds between planes are of the Van



Figure 1.1 The structure of hexagonal graphite. The graphite planes are stacked in the sequence ABAB.

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de Waals type. In contrast, the bonds within the hexagonal lattice plane are covalent and are thus much stronger than those in the \vec{c} direction. This anisotropy in interaction strength induces many interesting phenomena such as intercalation discussed in this dissertation.

Intercalation is a term describing the insertion of guest species into a host structure such that the structural features of the host are maintained¹. The guest is called the intercalant². Intercalation was first discovered in graphite since the interplane Van de Vaals bonds are so weak that many guest atoms can easily break the bonds. Small alkai ions and large molecules can both be intercalated into graphite under appropriate conditions. The products of the intercalation process are called graphite intercalation compounds (GICs).

Many graphite intercalation compounds have been synthesized and studied. They have been classified in several ways which emphasize different aspects of their properties. Given the observation that the intercalation process is always accompanied by a charge transfer between the guest layer and the host layer, GICs can be classified according to the direction of charge transfer. If the intercalant donates electrons to the host layer, the corresponding graphite intercalation compounds are called donor GIC's. If the charge transfer is in the reverse direction, the intercalant accepts electrons and the resultant GIC is called an acceptor GIC. Table 1.1 lists some commonly studied donor and acceptor intercalants. GICs can also be classified by the number of cointercalated species. Binary GICs refer to those containing one intercalant, while ternary GICs are those intercalated with two distinct

| Donors | Acceptors | |
|----------------------------|---|--|
| Li, K, Rb, Cs, Ba, Eu, Yb, | $NiCl_2$, $CoCl_2$, $MnCl_2$, $FeCl_3$, | |
| Sr, Sm, Ca | AsF ₅ , HNO ₃ , SoCl ₅ | |

Table 1.1A list of some commonly used donor and acceptor
intercalants in graphite.

species. Potassium-ammonia graphite³ is one of the most interesting of the ternary GIC's, and is one of the main subjects of this thesis. Other ternary GIC's such as $K_{1-x}Rb_xC_8^{4-7}$, $KCsC_{16}^8$, $CoCl_2$ -FeCl_3-GIC⁹, and many more have also been extensively studied. The ternary GICs can also be classified into three subgroups such as homogeneous, heterogeneous, and localized ternary GIC's depending on whether the two species are mixed within each gallery, segregated into different galleries, or mixed but chemically similar such as SbCl₃ and SbCl₄⁻. $K(NH_3)_xC_{24}$ falls into the homogeneous subgroup³. The most heavily studied binary compounds are the alkali-metal GICs and particularly KC_{24} which is the parent compound for the study of the K-ammonia ternary that is the focus of this part of my thesis.

The subject of graphite intercalation compounds has recently become a large research field due to the prominent potential which these compounds have for applications and as a result of their unusual properties the most striking of which are the staging phenomena and the quasi-two-dimensional physical phenomena. The staging phenomenon refers to the formation of structures in which the intercalate layers are periodically arranged between graphite layers in a stacking sequence with long range order. The stage number n denotes the number of host layers between adjacent intercalate layers. Figure 1.2 schematically shows the stage-1 to stage-4 GICs. In a stage-n compounds, there are n graphite layers in between the two neighboring intercalant layers. Therefore, the repeat distance in the c-direction (I_c) can be expressed

a s



(ALKALI METAL ATOM)

Figure 1.2 A schematic representation of the stage-1 to stage-4 graphite intercalation compounds. The solid lines represent the carbon layers and the dots represent the intercalant.

$$I_{c} = nc_{o} + d_{i} = (n-1)c_{o} + d_{s}$$
 (1.1)

where c_0 is the distance between adjacent graphites and $d_s = c_0 + d_1$ is the thickness of graphite-intercalant-graphite sandwich. Using (OOL) x-ray scattering techniques, Hennig¹⁰ has shown that c_0 is approximately independent of the stage number n and is equal to 3.35Å which is the interplane distance in pristine graphite. Alkali-metal GICs with a stage index as high as 10 have been reported².

Synthesis of GIC's is usually carried out using a so-called twobulb method¹¹⁻¹². Glass tubing with a bulb at each end is placed in a two zone oven which maintains each bulb at a set temperature. One bulb contains a pristine graphite is set at the higher temperature and the other bulb with an alkali-metal is set at a lower temperature. By controlling the temperature difference between the two bulbs, one can obtain different stage alkali-metal binary GICs. The measured K/C ratio of the K-GIC versus the bulb temperature difference ΔT is plotted in figure 1.3. The step-like plateau clearly indicate the formation of distinct stages. When ΔT is less than 100°C, the composition ratio of potassium to carbon gives the molecular formula KC₈ which corresponds to

a stage-1 GIC. When ΔT is between 100°C and 170°C, KC_{24} is obtained representing a stage-2 GIC. A pure high stage sample is difficult to synthesize since the proper temperature range is very narrow. While the temperature difference is critical in determining the stage of the GIC, the absolute temperature is also important for optimizing the reaction rate and uniformity of intercalation. The temperature ranges used in



Figure 1.3 The potassium to carbon composition ratio versus the temperature difference $T_G - T_A$ between graphite and the alkali metal intercalant. The plateaus indicate the stage n=1, 2, 3, respectively. After Nixon and Parry. reference 12

preparing our precursor binary GIC samples are listed in table 1.2.

Staging phenomena have been found in all graphite intercalation compounds including both donor and acceptor GICs independent of the inplane structure of the intercalant layer. These stage transitions are essentially a unique property of graphite intercalation compounds. Much theoretical and experimental attention has been given to the interpretation of such a spectacular phenomenon. It is generally believed that an elastic strain field introduced by the insertion of each intercalant layer and an electrostatic field produced by the ionized intercalant are responsible for the formation and stabilization of the stages¹³. The elastic field generates a strong attractive intercalant-intercalant interaction within the same guest plane while the long range electrostatic field gives rise to a repulsive force between intercalants in different layers. The attractive intraplanar interaction results in clustering of intercalate atoms in the galleries between graphite planes which lowers the strain energy associated with the elastic field. Therefore, a closed-packed in-plane intercalant arrangement is the most stable structure. For a fixed intercalant the repulsive interlayer interaction is minimized by having the largest average separation between intercalant layers. This condition obtains when staging occurs.

The stage transition is quite intriguing. If whole intercalant layers must be removed and re-inserted in a stage transition which is from an odd number to an even number stage, the energy required for this transition should be much higher than the observed values. To solve this dilemma, Daumas and Herold proposed a so called DH domain

| | $K T_{A} = 250^{\circ}C$ | $Rb \\ T_{A} = 208^{\circ}C$ | Cs $T_{A} = 194^{\circ}C$ |
|-------------|-------------------------------|-------------------------------|------------------------------|
| Stage | $T_{G}(^{\circ}\mathrm{C})$ | $T_{g}(^{\circ}\mathrm{C})$ | $T_{G}(^{\circ}\mathrm{C})$ |
| l 2 3 | 225-320 350-400 450-480 | 215–330 375–430 450–480 | 200–425 475–530 550 |

Table 1.2 A list of temperature ranges used in the binary sample preparation. T_G denotes the temperature of the graphite and T_A is the temperature of the alkali metals.

model¹⁴⁻¹⁵ which is illustrated in figure 1.4 for a stage-3 GIC. Instead of being single domain as in figure 1.4a, the graphite layers exhibit "kinks" due to intercalation (figure 1.4b). These kinks will not be reflected in (00L) x-ray diffraction patterns since the planes are flat between the kinks, the kink densities are very low and the dimensions of the kinks are small ≤ 100 Å. In the DH model every gallery is occupied and the staging phase transition results from lateral intercalant motion associated with kink propagation as shown in figure 1.4c. Therefore, the staging phase transition is not accompanied by a complete emptying of the intercalant layer.

In addition to the staging phenomena, quasi-two-dimensional (2D) behavior is another attractive feature of graphite intercalation compounds. Although this dissertation will touch upon the staging phase transition, the main focus will be on 2D phenomena observed in $K(NH_3)_{\tau}C_{24}$ ternary GIC's.

Since the Van de Waals interaction between graphite planes is weak, the intercalant layers can be treated as a good approximation of a 2D system under appropriate conditions. Qian and coworkers¹⁶⁻¹⁷ have shown that the potassium-ammonia graphite intercalation compound is one of the most interesting examples of a quasi-2D GIC.

The key effort for obtaining a quasi-2D system is to eliminate the interplanar interactions including the host-guest interaction and the interaction between different guest layers. The latter can be achieved by increasing the stage number so that the separation between intercalant layers is significantly increased. The former is achieved



Figure 1.4 (a) single domain model of the stage-3 GIC. (b) DH domain model for a stage-3 GIC. (c) migration of DH domain walls in a stage-3 to stage-4 transition. by the sequential intercalation of NH_3 into KC_{24} to form ternary $K(NH_3)_xC_{24}$, $0 \le x \le 4.38$.

In the earlier stage of K-NH3-graphite studies, samples were prepared using the Rudorff-Schultze method¹⁸ in which a graphite sample is immersed into a potassium-ammonia liquid after which residual ammonia is pumped off. This method causes severe exfoliation of the graphite sample which results from the pumping off process. The mosaic integrity of the pristine sample is almost completely destroyed when exfoliation occurs. After York and Solin¹⁹ developed a well controlled procedure to synthesize the ternary K-NH3-GIC, this system has become particularly suitable for studying quasi-2D phenomena. In their method, binary potassium GICs are exposed to ammonia vapor at fixed pressure. The ammonia composition in the ternary GIC is fully controlled by the ammonia pressure. The inserted ammonia can be removed without exfoliation by very slowly reducing ammonia pressure. It is found that the maximum ammonia composition is x=4.38 at an ammonia pressure P=10atm with the sample at room temperature. A further increase in ammonia pressure causes the condensation of liquid ammonia at the sample surface due to the saturation vapor pressure at room temperature. Thus, the $K(NH_3)_{x}C_{24}$ GIC's are studied in the range $0 \le x \le 4.38$.

A computer generated 4-fold coordinated cluster model of the inplane structure of the K-NH₃ layers in $K(NH_3)_xC_{24}$ has been proposed by Qian and coworkers¹⁶⁻¹⁷ and used to calculate the in-plane diffraction pattern. The calculated results are in excellent agreement with

experiment. The ammonia molecules are treated as hard planar discs. These discs are time average of the projection of the actual molecules in ab-plane (see figure 1.5). The tilt angle between the molecular c, axis and the graphite c axis is denoted α in figure 1.5a. The radii of the planar projection (figure 1.5b) r has a distribution P(r) shown in figure 1.5c, which corresponds to the tilt angle distribution obtained from NMR experiments²⁰. Figure 1.6a shows the seed clusters which consist of four ammonia discs symmetrically attached to each potassium K^+ ion with a radius randomly generated according to the probability function, P(r). Figure 1.6b shows a computer generated K-NH, inplane 4fold K-NH, homogenous liquid structure. Not only the x-ray scattering but also the neutron diffraction obtained from this simulation yielded excellent fits with experimental results²¹. Further studies have revealed that correlations between the intercalant layers are absent even in a stage-1 $K(NH_3)_{4,3}C_{24}$ where the intercalant layers are only one graphite layer apart. The interaction between graphite carbon layers and the K-NH₂ intercalant layers is thus very weak. This guarantees that the properties studied here indeed represent a manifestation of a 2D system.

The rest of this thesis is organized as follows: In chapter two, a two-dimensional diffusion model will be given to account for the intercalation kinetics of the potassium-ammonia GIC. The theoretical fit with the time dependence of the c-axis resistance data gives the first quantitative verification of diffusion-limited intercalation in a



Figure 1.5 (a) schematic diagram of an ammonia molecule in graphite. The ammonia rotates rapidly about its symmetry axis C_3 . The tilt angle α is the angle between the C_3 axis and the graphite c-axis. (b) the planar projection of the ammonia molecule. (c) the radii of the projection have the same distribution P(r) as the tilt angle α obtained in NMR measurements. (reference 20)



Figure 1.6 (a) schematic representation of the potassiumammonia seed cluster. (b) computer generated K-NH₃ inplane 4-fold coordinated K-NH₃ homogenous liquid structure. After Qian et al. Ref. 16. GIC. In chapter three, an unusual 2D metal-insulator transition will be discussed. A comparison between the corresponding 3D transition and a generalized 2D Mott transition condition will be given. We shall end this dissertation with a qualitative explanation of the ion size effect on the resistivity of alkali-ammonia GICs.

CHAPTER TWO

Two-Dimensional Diffusion-Limited Kinetics

2.1 Introduction

Kinetic effects in layered systems have been the subject of great interest for both experimental and theoretical solid state physicists over the last decade²²⁻²⁸. Systems, such as graphite intercalation compounds (GIC's), with competing intralayer and interlayer interactions exhibit a rich variety of phases in which the physical behavior is dominated by topological features such as dislocations and domain valls²⁹. In particular, the staging phenomenon which is unique in GIC's, offer a great deal of opportunity to investigate the effect of spatial dimensionality, d, via the crossover from three-dimensional to two-dimensional interactions.

Recently, extensive studies of domain-ordering kinetics in structures with nonequilibrium interfaces, have been reported. One case of special interest is the multidegenerate system (i.e. a system having several equivalent ground states). Theoretical analyses of this system include Monte Carlo computer simulations of the Q-state Potts model³⁰⁻³¹, and analytic variants of the time-dependent Ginzberg-Landau formalism²⁷⁻³². These studies show that there are two types of time evolution ranging from "fast" kinetics where the degeneracy Q is small, to slower growth of domains in the limit of large Q.

To date, experimentally, the focus has been on kinetic processes 33-36,15 which are dominated by the growth and coalescence of intercalate domains of which two types have been considered; namely. multidegenerate in-plane two-dimensional domains and the so called Daumas-Herold¹⁴⁻¹⁵ three-dimensional stacked columns of planar domains whose 2D structure is unspecified. For example, the domain-growth kinetics³⁵ and critical behavior³⁷ of adsorption systems (e.g. 0/W(110). O/Ru(0001)) have been studied by the use of low-energy electron diffraction (LEED). However, the influence of the multi-scattering of electrons on the reliability of the determination of critical exponents and domain-growth laws has been a matter of controversy³⁸. It is obvious that x-ray scattering and neutron scattering are of limited use in such systems due to the lack of scattering intensity. Therefore, graphite intercalation compounds, which are free from this disadvantage. are employed for such studies as an alternative. The stage 3 SbCl_s-GIC which is known to have a multi-degenerate Q=7 ground state has been studied by time resolved x-ray scattering³⁶ in order to test the ordering kinetics of degenerate 2D systems. This study shows that the superlattice ordering exhibits temporal scaling consistent with an algebraic domain-growth law.

For the DH domains, the earlier real-time in situ x-ray scattering $^{23-24}$ of alkali-graphite intercalation compounds indicates that in the region of growth during a stage n to a stage n±l transition

the two dimensional diffusion of potassium is proportional to the square root of time, i.e. $t^{1/2}$, in the initial period of the stage transformation. The kinetics of the transformation indicates that the staging process is nucleation rather than diffusion controlled. These studies provide neither evidence of stage disordering nor of intermediate structures during the stage transformation. More recent high resolution x-ray scattering³⁹ shows that there is stage mixing during the stage transformation when n>2, which can be interpreted in terms of the growth of DH domains. However, in neither of the above cited experiments was a quantitative analysis of the kinetic effects provided. Clearly, a quantitative study of stage kinetics is not only warranted, but also would best be conducted using those GIC's which do not suffer from the severe complications associated with multidegenerate (MD) in-plane 2D domain structures.

The ammoniation of KC_{24} to form ternary potassium-ammonia graphite compounds involves a kinetic process of staging transformation from the stage-2 binary compound to the stage-1 ternary compound⁴⁰⁻⁴¹. Moreover, this system does not suffer from the many complications associated with a MD 2D domain structure. Therefore, it provides a suitable arena with which to study the staging kinetics which are governed by a simple mechanism from the initial state to the nearly saturated region of ammoniation. Nevertheless, one would expect that the ammoniation of KC₂₄ would be dominated by either diffusion of the guest species to the domain surface (diffusion limited) or by the rate of incorporation of guest species at the domain surface (reaction limited or nucleation limited). In this chapter I shall describe the former process we have observed and quantitatively verify the first definitive example of variable composition diffusion-limited intercalation of GIC's for a large range of the ammonia composition, 0<x<4.38.

2.2 c-axis Resistivity Measurements of K-NH3-GIC's

In experimental c-axis resistivity studies, samples of binary stage-2 KC₂₄ of typical dimension 5.2X3.5X0.5mm were prepared from highly oriented pyrolytic graphite (HOPG)⁴² using the standard two-bulb method⁴³. The temperature difference between the bulbs is set to obtain the desired stage. The staging purity of the samples was confirmed by (001) x-ray diffraction patterns using Mo K α radiation from a Rigaku 12kW rotating anode source, together with a vertically bent graphite monchromoter, a Huber 4-circle diffractometer, and a NaI detector. Pure stage-2 samples were removed from their glass ampoule in an ultra high purity (0, content less than 0.3ppm) glove box and transferred to a stainless steel sample cell with vacuum feedthough to which four platinum wires were soldered. Specimens were mounted by platinum wires, using flexible silver paint. Micro-circuits SC12 silver paint was chosen because of its stability in an ammonia atmosphere. Purified methyl-ethyl ketone ($CH_3COC_2H_5$) has been used as a solvent due to its fast drying and its weak oxidation. Four leads, each with a separate silver paint dot, made contact to the two c-faces of the sample. Two leads were on each side, one opposing pair for current and the other

pair for voltage. The configuration is shown in the inset of figure 2.1. Since graphite is a highly anisotropic material, the conductivity along the graphite plane is much higher than the conductivity perpendicular to the plane. Therefore, the equipotential lines are parallel to the graphite planes as desired. The stainless steel cell was connected to one end of a pyrex U-tube through a metal-glass joint. The other end of the U-tube was pre-filled with purified liquid ammonia. The sample was separated from the ammonia by a teflon valve (V1 in figure 2.1) with EP 0-rings, which do not react with ammonia. Another teflon valve (V2) was used to seal the sample and protect against from exposure to air.

The purified ammonia was obtained by removing water and oxygen from commercial grade NH₃. The ammonia was first condensed onto sodium metal

with liquid nitrogen and then warmed up to -70°C with a dry ice/alcohol mixture to allow reactions with impurities to take place. The solution was again frozen and any residual gas was pumped out. This "freezepump-thaw" procedure⁴⁴ was repeated until the vacuum thermocouple gauge indicated no evolution of residual gas.

To begin our experiments, the sample end of the pyrex U-tube was first evacuated to be free of the helium gas which comes from the glove box. The other end of the tube was filled with purified ammonia and was inserted into a home-made simple cryostat whose temperature range runs from 77K to 300K. The schematic diagram of this cryostat is shown in figure 2.1. A massive chunk of copper (2" in diameter) was soldered to a long copper rod (1/4" in diameter) to serve as a temperature sink. The rod was immersed into a 2-liter dewar filled with liquid nitrogen



Figure 2.1 A sketch of the experimental set up for the resistivity experiments. The two sample holders are designed for c-axis and a-axis measurements respectively (see text).

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for cooling. The large copper block was wound with a heater, insulated by styrofoam and seated on top of the cap of the dewar. Thermocouples and ammonia tubing were inserted through the opening on top of the copper block. The hole was filled with copper powder to ensure good heat contact and accurate reading of temperature from the thermocouples. Temperature was controlled by a EUROTHERM temperature controller with a Chromel-Alumel thermocouple. The saturated vapor pressure of ammonia can be simply determined from the temperature of the ammonia reservoir using equation (2.2.1) below 4^{5} . This equation is valid in the range 195K<T<340K, which covers most of our experiments.

$$\log_{10}P_{\rm NH_3}^{(T)=27.376004-\underbrace{1914.9569}_{T}-8.45983 \log_{10}T$$

+2.39309x10⁻³T+2.955214x10⁻⁶T² (2.2.1

(2.2.1)

The pressure P is in atmospheres (atms). Below 195K, the pressure was extracted from a plot of vapor pressure versus temperature obtained from known data⁴⁶. Figure 2.2 is a typical plot with the known data marked. In our experimental set up, the ammonia temperature could be varied from 77K to 300K. Therefore, the ammonia vapor pressure could be controlled over a range from 10⁻¹³ atm to 10 atm by accurately controlling the temperature of the ammonia reservoir. When the temperature of the liquid ammonia reached equilibrium, the valve V2 was closed and V1 was opened to expose the sample to ammonia vapor. Since the sample cell is small, the response time for equilibrium pressure to be reached is very short, ≤ lsec. Heat absorbed from the vaporization of liquid ammonia did not make an observable change in the temperature of the liquid



Figure 2.2 The saturated ammonia vapor pressure versus temperature. The open circles represent reported data. see ref. 46.

ammonia reservoir. As noted, the time required to achieve equilibrium pressure was negligible. This was confirmed by monitoring the output of a thermocouple attached to the ammonia tubing.

The ternary $K(NH_3)_{x}C_{24}$ was formed after the binary compound KC_{24} was exposed to ammonia vapor. Figure 2.3 shows the ratio of the saturated isothermal c-axis resistance of $K(NH_3)_{x}C_{24}$ to the resistance of KC_{24} as function of ammonia pressure. Data were taken with a stepwise increase of ammonia vapor pressure from very low pressure $(10^{-4}$ atm. at about 140K). After the saturation value was reached at a fixed pressure, the valve V1 was closed to isolate the specimen from the ammonia liquid. The temperature of the liquid ammonia reservoir was then raised to the next desired value. The valve V1 was re-opened at the equilibrium temperature and the ammonia pressure at the sample site jumped from P_{i-1} to P_i .

There are two plateaus shown in figure 2.3. Comparing these results with measurements completed by York et al.⁴⁰ on the pressure dependence of the mole fraction of intercalated ammonia, a clear correspondence is found between the resistance curve and the intercalate mole fraction curve. When the ammonia pressure is below 10^{-3} atm., little intercalation takes place. The relative resistance of K(NH₃)_xC₂₄ to KC₂₄ remains 1 until a pressure 10^{-3} atms is reached. The first small step indicates that there is enough energy to overcome the activation barrier associated with separating the graphite layers to allow a small amount of NH₄ to enter. The intercalated ammonia expands


Figure 2.3 The ratio of the saturated isothermal c-axis resistance of $K(NH_3)_XC_{24}$ to the resistance of KC_{24} as a function of ammonia pressure. The instruments' error bars are smaller than the dots used in the figure.

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the gallery height between the graphite layers and reduces the overlap of the electronic wavefunction in the c-direction. This leads to a small increase in resistance. In addition, charge back-transfer from the carbon layer to the K-NH₃ layer is another accountable reason for the increase in resistance. As more and more ammonia is intercalated into the gallery of the graphite layer, additional delocalized charge in the carbon layer of KC₂₄ transfers to localized states in the

intercalate layers of $K(NH_3)_x C_{24}^{40}$ and causes a decrease in free electron density so that the c-axis resistance increased. At this plateau, the structure of the binary compound KC_{24} remains unchanged as schematically shown in figure 2.4b. The rapid increase of resistance at about 0.1 atms. reflects a sudden influx of ammonia into the graphite gallery and an associated stage-2 to stage-1 transformation⁴⁰⁻⁴¹. In this transition, potassium and ammonia re-distribute so that every gallery of the graphite is filled with the intercalate (see figure 2.4c). The electrical consequences of ammoniation of KC_{24} are discussed in detail in the next chapter.

To explore the kinetics of the ammoniation of KC_{24} , the time dependence of the c-axis resistance has been measured. Figure 2.5 shows the results measured at two different pressures. In the figure, $R_i(t)$ is the c-axis resistance at time t which is the exposure time of the specimen to an ammonia pressure P_i . $R_{i-1}(sat)$ is the saturation value of the resistance following exposure to the preceding pressure $P_{i-1} < P_i$. Figure 2.5a was taken at P=0.0045atm. while figure 2.5b was taken at







Figure 2.5

Time dependence of the c-axis resistance ratio $g(t)=R_i(t)/R_{i-1}(Sat)$. Panels (a) and (b) correspond to ammonia pressure $P_{NH_3}=0.0045$ atm. and 0.25 atm. respectively. The solid lines are the two parameter least squares fit and the dashed lines are the fit with the third parameter — dwell time. The yielded parameters are: Panel (a), solid line: $D=8.49 \times 10^{-9} \text{ cm}^2/\text{sec}$, f=1.87, $t_d=0$; dashed line: $D=8.69 \times 10^{-9} \text{ cm}^2/\text{sec}$, f=1.90, $t_d=2.08$ hr. Panel (b), solid line: $D=8.20 \times 10^{-9} \text{ cm}^2/\text{sec}$, f=43.21, $t_d=0$, dashed line: $D=6.65 \times 10^{-9} \text{ cm}^2/\text{sec}$, f=46.39, $t_d=29.8$ hr. (see text). The instruments' error bars are smaller than the symbols used in the figure.

P=0.25atm. They are at the onset pressure of the two plateaus in figure 2.3, respectively. Two different forms of the relative resistance, $g(t)=R_i(t)/R_{i-1}(sat)$, are required to describe the two curves. One increases monotonically as in figure 2.5a and the other shows distinct inflection at the first period of intercalation as in figure 2.5b. To understand these two behaviors is the main task of the next section.

2.3 Two dimensional diffusion-limited intercalation kinetics.

Consider a rectangular parallelepiped as an ideal mathematical model for our layered sample. This is a good approximation if the height of our sample, c, is much less than the c-face dimensions a and b. We also assumed that the ammonia vapor could intercalate only through the edge of the sample. In addition, Qian and coworkers have reported that the intercalated ammonia and potassium form a two-dimensional potassium-ammonia liquid¹⁶⁻¹⁷. Therefore, the problem can be treated as a simple 2D problem. Let $n(\vec{r},t)$ be the concentration of intercalant in the sample at position \vec{r} and time t. More precisely, $n(\vec{r},t)$ is the area number density of ammonia in the specimen. The diffusion equation for $n(\vec{r},t)$ is as follows:

$$\frac{\partial n(\vec{r},t)}{\partial t} = D\nabla^2 n(\vec{r},t) \qquad (2.3.1)$$

where D is the diffusion constant. Since the sample was exposed to ammonia at fixed pressure, the boundary conditions can be expressed as:

$$n(\vec{r},t) = n$$
 at $r_{x} = \pm a/2$ and $r_{y} = \pm b/2$ (2.3.2)

where a and b are the length and width of our sample, respectively. The initial condition of is

$$n(\vec{r},0)=0$$
 (2.3.3)

that is to say there is no intercalation at t=0. In fact, $n(\vec{r},0)$ can have a constant difference which does not affect the solution of the problem. For example, if $n(\vec{r},t)=n_0$, we can always find $n'=n-n_0$ which obeys the same diffusion equation as n and the initial condition becomes $n'(\vec{r},0)=0$. Therefore, the boundary value problem given above is suitable to describe our system without loosing generality. Using the standard separation of variables technique, the solution of the above problem is found following some mathematical derivation.

$$n(\vec{r},t) = n_0 \{1 - \phi(\frac{x}{\bar{a}}, \frac{Dt}{\bar{b}\bar{z}}) \phi(\frac{y}{\bar{b}}, \frac{Dt}{\bar{b}\bar{z}})\}. \qquad (2.3.4)$$

where

$$\phi(\xi, \tau) = \frac{4}{\pi} \sum_{\nu=0}^{\infty} \frac{(-1)^{\nu}}{2\nu+1} e^{-\tau q^2} \cos(q\xi) \qquad (2.3.5)$$

and

$$q=(2\nu+1)\Pi$$
 (2.3.6)

Using the data of x versus $P_{\rm NH_3}$ reported by York et al.⁴⁰ and the measured $R_i(\text{sat})/R_o$ versus $P_{\rm NH_3}$ (Fig. 2.3), we have plotted $\log[R(\text{sat})/R_o-1]$ as a function of log x in figure 2.6. The relation between ammonia area number density n and the composition x of the ternary $K(\rm NH_3)_x C_{24}$ is given by x=24n/n_c where n_c is the areal density of carbon atoms in the specific pristine graphite specimen from which the



Figure 2.6 The composition dependence of the function $[R_i(sat)/R_0-1]$. The data points in this figure are numerically labeled for reference in the text.

intercalation compound was prepared. Thus, $n_c = M_c A/(12ab)$ where M_c is the mass of graphite in our specimen, A is Avogadro's number, and 12 is the atomic weight of carbon. Since the concentration of ammonia n is proportional to x, figure 2.6 also reflects the characteristic of $log[R_i(sat)/R_o - 1]$ verses log n, except for a constant shift along the resistance axis direction. The data points fall into two sets of straight lines in the figure. For two neighboring points, we have

$$R_{i}(sat) = R_{i-1}(sat) \left[1 + (f-1) \left(\frac{n_{i}(sat)}{n_{i-1}(sat)} \right)^{p} \right]$$
(2.3.7)

where

$$f = R_i(sat)/R_{i-1}(sat)$$
 (2.3.8)

and the power p is the slope of the straight line in the plot of $log(R_i(sat)/R_o^{-1})$ vs. log x. It is equal to 0.77 and 1.41, respectively for the two sections of the curve. The higher power corresponds to the composition range 0.07<x<4.3 which spans the staging phase transition (data points 10 to 14 in figure 2.3 and 2.6), while the lower power corresponds to the composition range 0<x<0.07 where ammonia is intercalated into the expanded graphite gallery (data points 5 to 10). For any intermediate point between i-1 and i, we have a similar formula to equation (2.3.7) except that $n_i(sat)$ is replaced by the density at the point n' and $R_i(sat)$ is also replaced by R' which is the resistance when the equilibrium ammonia density is n'. This is warranted by the straight line fits to the data in figure 2.6. Before the intercalation process reaches equilibrium, the density of ammonia is not uniform in the entire sample and formula (2.3.7) can not be applied. But in each infinitesimally small area, ammonia density can be treated as spaciously uniform at time t. Therefore, formula (2.3.7) is valid for the small area around each point \vec{r} in the sample. The local conductance is easily obtained by inversion of the local resistance. Then, we added up all segments by integrating over \vec{r} through the whole area to obtain

$$\frac{1}{R(t)} = \frac{1}{R_{i-1}(sat)} \frac{1}{ab} \int \frac{d^2r}{\{1+(f-1)[n(\vec{r},t)]^p\}}$$
(2.3.8).

Substituting equation (2.3.4) into equation (2.3.8), and using a=5.2mm, b=3.5mm which are the sample length and width, respectively, a least squares fit was applied to figure 2.5a and 2.5b. The diffusion constant D and saturation resistance ratio f are fitting parameters. The best fit yields f=1.87 and D=8.49x10⁻⁹ cm²/sec for figure 2.5a and f=43.21 D=8.20x10⁻⁹ cm²/sec for 2.5b. The solid lines in figure 2.5 are calculated results with the above parameters. The fits are quite good in most regions of time. But a deviation appears in the small time region in figure 2.5a.

Hooly's work⁴⁷ gives a clue to understanding this deviation. He reported in 1973 that intercalation in GIC's takes place only when the basal surface and side surface are both exposed to intercalant vapor allowing intercalant to invade the interior of specimens through the edges. This phenomenon was interpreted as surface adsorption⁴⁸. Before intercalating, there must be surface adsorption to create a localized charge density wave distortion so that interlayer bonding is weakened and hence intercalates have access to the graphite gallery through the edges. From this view, the deviation between theoretical calculation and experimental data can be corrected by introducing a dwell time which is associated with the surface adsorption. The same procedure of least squares fitting with the introduction of a third parameter, t_d, was again applied to the data in figure 2.5. The dashed lines shown in figure 2.5a and 2.5b are results of this least square fit which yield t₁=2.08hrs and -29.8hrs for figures 2.5a and 2.5b, respectively. As we can see, the fit for Fig.2.5a was greatly improved and the resulting diffusion constant and saturation resistance ratio change by only 22 relative to those calculated without the inclusion of a dwell time. In contrast, an unphysical negative dwell time for figure 2.5b was obtained by the same procedure. Also for figure 2.5b, the new diffusion constant generated is 25% less than the originally calculated diffusion constant and the saturation resistance ratio f is 7% higher. In addition, the fit is not improved at all. These results imply that the dwell time from surface adsorption is insignificant for the intercalation process described by figure 2.5b, which is associated with the staging transition.

The sample dimension ratio $\lambda=a/b$ was also varied in calculating the numerical solution of equation (2.3.8). The results turned out to be very insensitive to the value of λ . This insures that any inaccuracies in the measurement of sample dimension will not introduce significant error into the fit.

In our diffusion theory, the yielded saturation resistance ratio f is equal to 1.90 and 43 for figures 2.5a and 2.5b, respectively. The measured values in the experiments, as shown in the figure, are 1.33 and 39. One of the reasons for the discrepancy is under-saturation in our experiments. Complete saturation will be reached only in the limit of infinite time, theoretically speaking. It is very hard to keep samples fresh for very long periods such as four months, since the alkali metal GICs are very active materials. Moreover, a more detailed description of the physical mechanism of the time delay might result in a more accurate theory of the diffusion process in intercalation.

Finally, it is worthwhile to mention that the diffusion constant changed from 8.69×10^{-9} cm/sec for figure 2.5a to 8.20×10^{-9} cm/sec for figure 2.5b. The difference is within 67 which shows the consistency of the fitting. These values are also typical of diffusion constants for gas diffusing into solids⁴⁹. The essential physics of our result is that the ammoniation process in the K(NH₃)_xC₂₄ system is 2D diffusion-limited intercalation.

2.4 Conclusion

In this chapter, we have presented the results of c-axis resistivity studies of $K(NH_3)_xC_{24}$. The correlation between mole fraction of intercalated ammonia and c-axis resistance has been discussed. Both quantities exhibited two step-like plateaus as the ammonia pressure varied from 10^{-3} atm to 10 atm. The first one at low pressure is linked with the incorporation of ammonia into the expanded galleries of KC_{24} . The second one at P=0.5atm. is associated with a stage-2 to stage-1 phase transition.

We have employed a two-dimensional diffusion model to the

ammoniation process of KC_{24} to form the ternary $\text{K(NH}_3)_{\mathbf{x}}C_{24}$, $0 < \mathbf{x} < 4.38$. It has been found that kinetics of ammonia intercalation of the K-NH₃ ternary GIC is 2D diffusion-limited in contrast to binary graphite intercalation compounds in which the intercalation kinetics is governed by the growth of planar multidegenerate domains.

Finally, a dwell time which was attributed to surface absorption was introduced to correct the deviation between the theoretical results and measured data. The results have shown that surface absorption is irrelevant for the intercalation in association with the staging transition. Otherwise, it is necessary to include the dwell time imposed by surface absorption in consideration of the intercalation kinetics.

CHAPTER THREE

Two Dimensional Metal-Nonmetal Transition

3.1 Introduction

Since 1970, bulk three dimensional metal ammonia solutions have been one of the most interesting topological disordered condensed matter systems⁵⁰. The composition dependent metal-insulator transition which these systems exhibit has been thoroughly studied. When the concentration of metal is low (less than 72 mole metal), the metal ion and its detached electron are both solvated by an enveloping cluster of ammonia molecules⁵⁰. A narrow optical absorption band has revealed that the solvated electron is localized. As the metal concentration increases, the wavefunctions of the solvated electrons begin to overlap and form delocalized bands which sustain conduction. This is the socalled metal to non-metal transition. Potassium in ammonia forms an example of this kind of solution. The effect of dimensionality on the properties of the metal ammonia solution is obviously an intriguing subject. In this chapter, I will focus on the two dimensional metalinsulator transition in potassium-ammonia-graphite intercalation compounds.

It has been known for several decades that metal-ammonia solutions could be intercalated into graphite and form a ternary graphite

intercalation compound. A new wave of intense excitement and activity has been generated by the recent discoveries of the novel properties $^{40,16-17}$ of the ternary compounds of $K(NH_3)_{4,3}C_{24}$. Neutron scattering²¹ and x-ray diffraction¹⁶⁻¹⁷ have shown that the in-plane structure of $K(NH_3)_{4,3}C_{24}$ is a two-dimensional liquid which can be described by a model in which four ammonia molecules are associated with a single K ion and the rest of the ammonia molecules are "free". Inelastic neutron scattering measurements⁵¹ indicate that the liberation of the ammonia molecule splits the acoustic phonon branch in the [001] direction. The quasi-elastic neutron scattering 52 shows that there are three different diffusion modes in the liquid layer. First, the ammonia molecule undergoes translational diffusion in the intercalant layer. Second, the ammonia molecule spins about its C3-symmetry axis giving a very broad peak with an extended background due to the fast time scale of motion. Finally, the reorientation of ammonia about the K^+ ion yields the main peak in the spectrum. In addition, proton NMR spectra have indicated that the molecular three-fold symmetry axis, on average, lies in the basal plane of the graphite with some distribution about this ecuilibrium value⁵³. These results indicate that the in-plane structure of this compound is the 2D analogue of the well studied threedimensional (3D) bulk potassium-ammonia solutions. The electrical and optical studies of $K(NH_3)_{r}C_{24}$ discussed in this chapter will demonstrate that there is a corresponding 2D electronic analog of the 3D metalinsulator transition in bulk potassium-ammonia solutions.

3.2 a-axis Resistivity studies of K(NH₃)_xC₂₄

In order to study the in-plane properties of the ternary $K(NH_3)_{C_{24}}$ GIC, we have designed an experiment which measures the pressure dependence of the a-axis resistivity. The samples used in these experiments were prepared from individual methane-derived fibers which were heat treated to $3000^{\circ}C^{54}$. The structure of these fibers is shown in figure 3.1 which exhibits a cylindrical onion skin morphology. All of the cylindrical graphite planes are approximately coaxial. The c-axes of the graphite planes are in the radial direction while the aaxes are along the cylindrical axis. The typical dimension of the fiber samples is 0.1mm in diameter and 8mm in length which is much smaller than the HOPG sample used in c-axis measurements discussed in the previous chapter. Their high aspect ratios make them ideal materials to carry out a-axis resistance measurements. The disadvantage of the fiber host is that it is chemically unstable and decomposes after several days following maximum ammoniation. Thus, the data were taken "on the fly" over a period of two days. Fortunately, the fibers exhibit a faster kinetic response than HOPG due to their small size. This ensures that the "on the fly" data represent an equilibrium result.

The x-ray characterization of stage purity in small fiber based GIC's is extremely difficult since they are weak scatterers and the meager scattering which they do produce is masked by a strong background from the glass encapsulation ampoule. In order to solve this problem, we have modified the glass tubing used in the standard two-bulb method for preparing pure stage-2 KC_{24} graphite intercalation compounds. The



Figure 3.1 The onion skin like structure of the graphite fibers used in the a-axis resistivity studies.

graphite end of the glass tubing was pulled to a needle like capillary with a very thin glass wall (0.2mm or less). It was capped with a removable tubing to protect the capillary tubing in sample preparation (figure 3.2). The samples in the thin wall capillary tubing were then characterized by x-ray diffraction after being thermally processed in the dual oven until a blue color characteristic of stage-2 KC24 was observed. Figure 3.3 shows the (OOL) x-ray scattering results for a stage-2 KC₂₄ fiber in a standard ampoule and in our specially prepared capillary tubing. Clearly, the ratio of Bragg diffraction to background has been significantly improved. The basal spacing of pure stage-2 KC24 potassium binary GIC was 8.74Å as determined from the (OOL) diffraction pattern. Similar x-ray scattering experiments were also performed on the pristine fiber and the stage-1 ternary GIC $K(NH_3)_{4.33}C_{24}$ and yielded the basal spacings of 3.35\AA and 6.64\AA respectively (figure 3.4). These results indicate that compounds prepared from graphite fibers have the same Gibbs phase diagram as those based on HOPG⁵⁵.

The sample cell used for the a-axis resistance measurements is the same as the one used in the c-axis resistance studies, although the four platinum wires soldered onto the vacuum feedthrough were bent in an alternate way in order to hold the fiber. We first laid the fiber on a ceramic support which was pre-plated with four silver strips. Each strip was connected to a platinum wire using silver paint. The fiber also made good electrical contact with the strips through the silver paint. It turned out that this configuration would give false results for resistance measurements. This is because a layer of ammonia foam







Figure 3.3 The (OOL) x-ray scattering results for a stage-2 KC₂₄ fiber in a standard glass ampoule (a) and in the

specially prepared thin wall capillary tubing (b). Note that the Bragg peak are much more prounced in (b) although the dwell time used is less than onetenth of the one used in (a).



Figure 3.4 The (00L) x-ray diffraction pattern of (a) a pristine graphite fiber, (b) the same fiber as in (a) after intercalation with potassium to form the binary stage-2 GIC KC_{24} , and (c) the same fiber after ammoniation to form the ternary GIC $K(NH_3)_{4.3}C_{24}$.

forms on top of the ceramic. This ammonia solvates some potassium from the potassium intercalated GIC and forms a potassium-ammonia liquid on the ceramic. This liquid foam became a good conductor and shorted the four leads when a sufficient amount of potassium was solvated. Therefore, the fiber had to be suspended in the ammonia vapor. To do this. the four platinum wires were bent like hooks arranged in a straight line. The stage-2 KC24 fiber was then seated on the four hooks in the glove box and affixed on the platinum hooks by silver paint (inset of figure 2.1). The sample cell was then sealed to the Pyrex Utube described in the previous chapter. The entire procedure must be done in the glove box as usual, since the stage-2 KC₂₄ GIC is very reactive with oxygen and water vapor. Since the fiber is very small relative to HOPG. surface oxidation is much more deleterious in the former. To prevent the fiber from oxidizing, pure potassium was poured onto a piece of aluminum foil in the glove box. The potassium acts as a purifier/getter since it is more active than KC24. Thus we could keep the fiber "fresh" by transferring it from the glass tubing to the measurement cell in a few minutes. The Pyrex U-tube and the stainless steel cell were all baked dry before use. This could significantly reduces the outgasing and prevent the sample from oxidizing throughout the entire experiment (two days).

In situ electrical measurements were first carried out using a DC four probe technique. Figure 3.5 shows the room temperature isothermal a-axis relative resistance $(R(P)/R_0)$ as a function of the ammonia pressure. R(P) is the a-axis resistance at ammonia pressure P and R₀ is



Figure 3.5 The room temperature isotherm a-axis relative resistance $(R(P)/R_0)$ versus the ammonia pressure. The instruments' error bars are smaller than the symbols used in the figure.

the a-axis resistance of the pure stage-2 KC₂₄ before exposure to the ammonia atmosphere. Comparing this to a similar plot of c-axis relative resistance eg. figure 2.3, we note that the first step increase in resistance at 0.0045atm does not appear in the a-axis relative resistance curve. This is to say that the a-axis resistance remains unchanged even after some ammonia intercalates into the interior of the sample. This result can be understood by treating the graphite layer and the intercalate layer as conductors in parallel for a-axis conduction. When a small amount of ammonia intercalates the interior of the sample, the basal spacing along the c-direction expands. But the charge back transfer from the carbon layer to the intercalate layer is negligible². Also, the charge transfer from the potassium intercalate layer to the graphite layer yields a carbon layer conductance in the adirection which is much larger than the conductance of the potassium intercalate layer. Therefore, at very low ammonia concentrations the caxis conduction change is notable while that in the a-axis direction is negligible.

A more significant observation from this data is the precipitous drop in relative resistance $(R/R_0)_a$ at about 2.5atm. From the measurements by York et al.⁴⁰, we know that the ammonia composition x in $K(NH_3)_xC_{24}$ is about 4 at this pressure. The stage-2 to stage 1 phase transition has taken place before this composition has been reached. Thus, the observed resistance drop is at fixed stage. To our knowledge, there is no other GIC reported to date that displays such a decrease in a-axis resistance with increasing intercalation at constant stage. To verify this unusual behavior, more than twenty specimens have been examined. All of them showed this drop at about the same pressure, although the magnitude of this drop varied from sample to sample. An AC LOCK-IN four probe technique was also used to eliminate all possible noise and circuit induced measurement errors. The resistance drop at x=4 has been found in all our measurements. A similar experiment was repeated on a pristine fiber and the drop was not observed. Since it is well known that ammonia hardly intercalates into pristine graphite, the observed drop in resistance of $K(NH_3)_{x}C_{24}$ can be attributed to ammoniation.

Another important phenomenon obtained from figure 3.5 is the conduction anisotropy of the stage-1 $K(NH_3)_xC_{24}$. Figure 3.5 shows that the maximum a-axis resistance increases by only a factor of 4, while figure 2.3 shows that the c-axis resistance increases by a factor of 200 which is accomplished by both expansion of the basal spacing in the c-direction and the staging phase transition. It is obvious that the anisotropy has been magnified after ammonia intercalates into KC_{24} .

Using the known conductivities of the stage-2 KC_{24}^2 binary GIC and the relative resistances shown in figures 2.3 and 3.5, one can show that

$$(\sigma_{a}/\sigma_{c})_{t} = \left[\frac{(\sigma_{a})_{b}}{(R/R_{o})_{a}}\right] / \left[\frac{(\sigma_{c})_{b}}{(R/R_{o})_{c}}\right] = 2.5 \times 10^{4} \text{ at } x \neq 4 \quad (3.2.1)$$

where t represents ternary compounds and b represents binary compounds. This is the highest anisotropy yet reported for a stage-1 donor GIC^{32} and provides strong evidence for the 2D character of the conduction process in $K(NH_3)_{x}C_{24}$. 3.3 Two Dimensional Metal-Insulator transition in K(NH₃) C₂₄

In order to interpret the observed unusual electrical features of $K(NH_3)_x C_{24}$, vis-a-vis the structure and properties we refer again to the bulk potassium-ammonia solution. It is known that the solvated potassium ion and ammonia form a six fold coordinated octohedral structure. Six ammonia molecules surround the potassium ion or the detached electron from top, bottom, left, right, front and back respectively. The rest of the ammonia molecules are free. The electron appear to be localized as evidenced by a narrow optical absorption band at 0.8ev. This band has been attributed⁵⁰ to a 1s-2p transition of the solvated electron in the spherical potential of a 6Å diameter solvent bubble. When the concentration of potassium is high enough so that the wavefunctions of the solvated electrons overlap each other, the solution undergoes the metal-insulator transition. The conductance of the solution was found to increase by three orders of magnitude⁵⁰.

X-ray and neutron scattering have shown that the structure of the intercalate layer of $K(NH_3)_xC_{24}$ is a 2D potassium ammonia solution. Instead of being solvated in the six fold ammonia cluster, potassium atoms are surrounded by four ammonia molecules and form a square planar four fold structure^{16-17,21}. This is because the basal spacing of the carbon layer limits the height of the cluster. Therefore, the top and the bottom ammonia present in the bulk octohedral cluster are not seen in the clusters of the 2D potassium-ammonia liquid. The structural

analog between the intercalate layer of the 2D K-NH₃ liquid and the 3D bulk K-NH₃ promotes the association of the a-axis resistance drop with a 2D metal-nonmetal transition. To further verify this transition, the optical absorption bands were examined.

Figure 3.6 shows the x-dependence of the reflectance $R(\omega)$. Light beams were incident on an intercalated HOPG sample in a near-normal direction to the carbon planes. The obtained c-face reflectance spectra were subsequently transformed by the Kramers-Kronig relations⁵⁶⁻⁵⁷.

$$n(\omega) = 1 + P \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \cdot \frac{k(\omega')}{\omega - \omega'}$$
(3.3.1)

$$k(\omega) = -P \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \cdot \frac{n(\omega') - 1}{\omega' - \omega}$$
(3.3.2)

where P is a principle value integral. The a-plane complex dielectric functions $\epsilon_2(0,\omega)$ were then calculated through the relation

$$\epsilon = (n+ik)^2 \tag{3.3.3}$$

The results are shown in figure 3.7 (solid lines). The composition x=0 corresponds to the pure stage-2 KC₂₄ compound. Its complex dielectric

function has been measured by other groups² and agrees well with the data shown here. $\epsilon_2(0,\omega)$ can be decomposed into a free carrier absorption and an interband absorption. The free carrier absorption obeys an ω_p^2/ω^3 law and vanishes very quickly when the light frequency exceeds the plasma frequency ω_p . The increase in $\epsilon_2(0,\omega)$ is due to interband absorption which can be further decomposed into a narrow band at 1.85ev and a broader contribution which resembles a typical threshold



Figure 3.6

The composition dependence, x, of the reflectance $R(\omega)$ of potassium-ammonia-GIC's.



Figure 3.7 The Kramers-Kronig derived imaginary part of the dielectric functions $\epsilon_2(0,\omega)$ (solid lines). The

functions are subsequently decomposed into the Lorentzian oscillator (dashed line) and a broader contribution (dash dot line). (see text)

for the graphite $\pi - \pi^*$ transition⁵⁷. Clearly, the narrow band is most pronounced when the ammonia composition x equals 4.1. The full width at half maximum (FWHM) is 0.4ev for this composition. As more and more ammonia intercalates into the interior of the specimen, the oscillator strength (the narrow band peak at 1.85ev) increases at first and then exhibits a sharp drop when x exceeds 4.1. This behavior is plotted in figure 3.8 for clarity. When the concentration of intercalated ammonia is low and thus x << 4, the inserted NH₃ leads to gallery expansion and participates in the cluster formation. Therefore, the concentration of the spacer ammonia ("free" ammonia) is zero. Also the back-charge transfer $\delta f=0$. When the ammonia composition x in ternary $K(NH_3)_{x}C_{24}$ is close to 4, some newly intercalated ammonia will enter the spacer's position since almost all potassium present in the sample is bound with ammonia in a four fold cluster. When x>4, all the newly entered ammonia are spacers which promote solvation and thus give rise to an increases in δf . These spacer ammonia molecules will back transfer charge from the carbon layer to intercalate layer since they trap electrons in a hydrogen cage formed by a spacer and a cluster NH3. This is consistent with figure 3.8.

When x increases from zero to 4, more and more K-ammonia four fold clusters are formed but the back transferred electrons are localized so that the 1s-2p bound state oscillator strength increases as does the resistivity. Further increases in ammonia composition leads to the increase of spacer ammonia concentration and charge back transfer to the metal ammonia layer. The concentration of this back transferred charge can become so dense that the in-plane wavefunctions of the charge



Figure 3.8 A plot of the Lorentzian oscillator strength versus the ammonia composition x in $K(NH_3) x^{C}_{24}$.

overlap and form band-like extended states. As a result, the metal ammonia layer becomes a conductor and the a-axis resistivity decreases. These back transferred charges become delocalized and the oscillator strength decreases as x increases from 4.1 to 4.3. This is the socalled metal-insulator transition. Under this transition, localized charges have become delocalized charges.

The size of the potassium-ammonia clusters in graphite intercalation compounds is small compared to the size of the bulk six fold cluster since the former is confined between carbon layers while the latter is in free space. The Heisenberg uncertainty principle in quantum mechanics dictates $\Delta x \cdot \Delta p > h$. The smaller the cavity size Δx , the larger momentum Δp and hence the larger the band energy. Therefore, we have seen an upshift of the band from 0.8ev for the 3D bulk metalammonia solution to 1.85ev for 2D K-NH₃ solution.

We suggest that this metal-nonmetal transition is a Mott transition 58. A criteria for a three dimensional Mott transition is

$$n_c^{1/3}a^*=0.26$$
 (3.3.4)

where n_c is the critical electron volume density. Now a* can be expressed in terms of the Bohr radius $a_o=0.529 \text{\AA}$, the static dielectric constant ϵ , and the effective mass m^{*}

 $a^{*}=[\epsilon/(m^{*}/m_{o})]a_{o}$ (3.3.5)

where m is the mass of a free electron. Using dimensionality arguments, we find that the 2D Mott condition is

$$n_{c}^{1/2}a^{*}=A_{2D}=constant$$
(3.3.6)

where n_c is the critical electron areal density. A self-consistent value for n_c and x_c can be determined with the aid of a 2D Clausius Mossotti equation which was calculated for an ellipsoidal cavity in a dielectric.

$$\frac{(\epsilon-1)}{(\epsilon+1)} = 2\pi N\alpha \tag{3.3.7}$$

Here N is the molecular number density in a 3.28\AA^{0} thick ²¹ ammonia layer. The area of twenty-four carbon atoms is calculated to be 62.86\AA^{2} . Thus,

$$N = [x/(62.86X3.28)]^{0^{-3}}$$
(3.3.8)

Using ϵ =25 and ρ =0.817gm/cm³ for liquid NH₃ at -77°C⁵⁹, the static polarizability α is found to be 7.36Å³ from equation 3.3.7. Combing equation 3.3.5 — 3.3.8, n_c can be expressed as a function of the effective mass, and composition. We write

$$n_{c} = f_{1}(m^{*}/(m_{o}A_{2D}), x_{c})$$
 (3.3.9)

A linear model is expressed in Eq.3.3.10 below and is used to relate the back charge transfer to the spacer ammonia concentration.

$$\delta f = \begin{cases} 0 & x < 4 \\ \gamma(x-4) & x \ge 4 \end{cases}$$
(3.3.10)

where γ is a constant and is equal to 0.2/0.38 in this case^{21,20}. Thus,

$$n_{c} = f_{2}(x_{c}) = \underbrace{\begin{array}{c} 0.2(x_{c}-4) \\ 0.38X62.86 \end{array}}_{0.38X62.86}$$
(3.3.11)

Setting the two functions f_1 and f_2 equal to each other, a cubic equation will be obtained with only one solution which has physical meaning. A reasonable estimate of A_{2D} is obtained by comparing the 2D and 3D Fermi wavevectors which depend on electron density.

$$A_{2D} = \{(3\pi^2)^{1/3}/(2\pi)^{1/2}\}A_{3D} = 0.31$$
(3.3.12)

From equation (3.3.6)-(3.3.12), we find that

Knowing that the effective mass for a bulk 3D metal ammonia solution is between 1.5 and 4.04⁵⁰, we find that the results obtained in equation (3.3.12) are consistent with an upper bound of 10 on m^*/m_0 . The stronger the lattice interaction, the larger the effective mass of the electron will be. We expect that the effective mass of an electron in the 2D metal ammonia liquid of a ternary GIC should be larger than that of an electron in a 3D liquid. Therefore, we conservatively set the upper limit of m^*/m_0 to be ten. The x_c calculated was indeed found to be in right range.

3.3 Conclusion

Resistivity studies of the potassium-ammonia-graphite intercalation compound have shown that these compounds exhibit the highest anisotropy of any GIC.

The pressure dependence of the isothermal a-axis relative resistance of $K(NH_3)_{rC_{24}}$ shows an unusual decrease which could be

attributed to a 2D metal insulator transition. This system is the first reported graphite intercalation compound that displays such an decrease in a-axis resistance with increasing intercalation at fixed stage.

This 2D metal-insulator transition is accompanied by charge back transfer which has been confirmed by light reflectance studies. The complex dielectric constant ϵ obtained from a Kramers-Kronig transformation was decomposed into a free carrier absorption, graphite π - π^* transition, and a narrow band at 1.85ev which is associated with the localized electrons. The oscillator strength of this band increases as the ammonia composition increases indicating the formation of potassium and ammonia four fold clusters. This continues until the ammonia composition x reaches 4. The intercalated spacer ammonia promotes charge back transfer and the metal-insulator transition. The oscillator strength subsequently decreases.

Finally, we have argued this metal-insulator transition is a 2D Mott transition. The 3D Mott condition was generalized and applied to a two dimensional phase transition. Self-consistant calculations have found that the critical composition x_c is in the range (4.09 $\leq x_c \leq$ 4.39) which is in good agreement with experimental observation.

CHAPTER FOUR

Ion Size Effect of

Alkali-Metal Annonia Graphite Intercalation Compounds

4.1 Introduction

In the previous two chapters, we have shown that the potassium ammonia ternary graphite intercalation compound constitutes a novel system to study physics in lower dimensions. This system does not suffer from the complications brought by the two dimensional multidegenerate domains (MD) which are observed in all binary GICs. This is because the the intercalate-substrate interactions which cause MD domains are rather weak. The dominant interaction is the intercalate-intercalate interaction. The unique properties of K-NH₃ ternary GICs have qualified them to be the first suitable specimens in a quantitative study of the intercalation kinetics. In addition, this system has manifested an interesting two dimensional metal insulator transition which is analogous to the one observed in a bulk 3D metalammonia liquid. We now explore this system more thoroughly by substituting different size alkali metal ions for potassium.

4.2 Experiments and Results

Similar c-axis and a-axis resistance measurements were preformed respectively on the ammoniation of rubidium and cesium pure stage-2 binary graphite intercalation compounds. The reason for choosing Rb and Cs is that they have the same atomic structure as potassium. Moreover, they form a family of GIC's with the form MC_8 (M-K, Rb, Cs) for the stage-1 compounds and MC_{24} for the stage-2 intercalation compounds.

The two bulb method is equally applicable for the preparation of the three types of specimen. The only difference lies in the temperature difference between the two bulbs. Cs-GIC's require the highest temperature difference (300°C) for stage-1 formation while K-GIC's require only a 100°C differential. Care must be taken in preparing Cs-GIC's, since cesium will melt when the temperature is slightly higher than room temperature. If melted cesium flows to the graphite side, intercalation will start immediately. This intercalation is extremely non-uniform and incomplete. Although heat treatment is able to correct this nonuniformity, exfoliation of the graphite will inevitably occur and result in an undesirable mosaic. In addition, the room temperature vapor pressure of the cesium is high enough to initiate intercalation. Therefore, the stage-2 sample must be kept cool in order to prevent a stage change. The stage purity of the Cs and Rb GIC's was re-checked using (001) x-ray diffraction each time before starting a resistivity experiment.

The experimental set up and the sample cell are the same as that described in chapter two and chapter three. The samples used for c-axis experiments were HOPG with a mosaic of less than 0.5° . Figure 4.1 shows
the c-axis relative resistance $(R/R_0)_C$ measured with a DC four probe technique. The symbols used are similar to the ones used in chapter two. R_0 is the resistance of a pure stage-2 sample while R=R(P) is the resistance at ammonia pressure $P_{\rm NH_2}$ and c represents the c-axis.

Although the step-like rise for the K^+ compounds at 0.0045atm. is not pronounced for Rb and Cs samples, the rapid increase in resistance at about 0.2atm. is observed for all of the three specimens. Given our understanding of the potassium-ammonia GIC's, we associate this step with the stage-2 to stage-1 structural phase transition. Following this transition, the resistivity saturates at high ammonia pressure. The saturation values show a systematic decrease as the alkali-ion size increases. This point will be further illustrated below.

Figure 4.2 shows the AC a-axis relative resistance $(R/R_0)_a$ for the three alkali-ammonia GIC's as a function of ammonia pressure. The two dimensional metal-insulator transition is also observed in the Cs and Rb ternary GIC's. The resistance increases followed by a slight decrease with increasing ammonia pressure. Notice that the behavior of Rb compound is quite different from the other two species. This may be caused by the inplane superlattice structure of the stage-2 RbC₂₄. It

has been found that the stage-2 Rb GIC exhibits a $p(\sqrt{7}x\sqrt{7})R19.1^{\circ}$ superlattice structure⁶¹ and the other two do not. The in-plane CsC₂₄ structure is incommensurate⁶²⁻⁶³ while KC₂₄ shows a mixed in-plane structure².



Figure 4.1 The c-axis relative resistance (R/R_0) for potassium (solid circle), rubidium (triangle), and cesium (square) ammonia graphite intercalation compounds. R_0 is the resistance of the sample before the ammoniation. The instruments' error bars are smaller than the symbols used in the figure.



Figure 4.2 The a-axis relative resistance $(R/R_0)_a$ for the three alkali metal GIC. The instruments' error bars are smaller than the symbols used in the figure.

4.3 Discussion

Solin et al.⁶⁴ have measured the ammonia weight uptake of the potassium, rubidium, and cesium ternary GIC's. Their results show that the weight uptake depends on the cube of alkali-metal radius. In order to interpret their observation they have developed a 3D model in which they have claimed that the cluster formation in ammoniation does not affect the composition of the ternary GIC⁶⁴. The maximum ammonia uptake obtained from their measurements together with the basal spacing of the final product of ammoniation, and the ionic radius are listed in table 4.1. An empirical relationship between the saturation resistance and the saturation NH₃ composition has been found and expressed through the ionic radius in equation 4.3.1

$$\ln\{(R/R_{o})_{c}\}_{max} = B - \frac{x_{max}^{d}c}{r_{m}^{2}} + A.$$
 (4.3.1)

Here x_{max} is the maximum ammonia mole fraction, d_c is the c-direction basal spacing of the stage-1 $M(NH_3)_x C_{24}$, and r_m is ionic radius the alkali metal. Figure 4.3 shows the straight line in a semi-log plot of the saturated relative resistance $(R/R_0)_c$ against to xd_c/r^2 . A linear regression fit of this straight line has yielded A=0.580 and B=0.296.

Although we are not able to derive equation (4.3.1), we can qualitatively understand the relationship. First, the increase in the basal spacing will cause a decrease in the overlap of wavefunctions in

| к 4.33±0.05 6.62 | | resistance (R/R ₀) |
|-------------------|--------------|--------------------------------|
| | 0±0.005 1.33 | 220±25 |
| Rb 4.10±0.05 6.64 | 0±0.005 1.46 | 75±5 |
| Cs 3.65±0.05 6.67 | 1±0.005 1.67 | 24±5 |

| Table 4.1 | A list of parameters and properties of the stage-1 |
|-----------|--|
| | alkali-metal ammonia GIC. x is the maximum |
| | ammonia uptake at an ammonia pressure of 10atm. |

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Figure 4.3 The plot of the maximum relative c-axis resistance $(R/R_o)_{max}$ versus the ionic parameters $x_{max} \cdot (d_c/r^2)$

the c-direction and a corresponding resistivity increase. Since the amplitude of the wavefunction exponentially decreases with increasing distance (e.g. the wavefunction of the hydrogen ground state

$$\psi_{100}(r,\theta,\phi) = \left[\frac{z^3}{\pi a^3}\right]^{1/2} \exp\left[-\frac{2r}{a}\right], \text{ one can expect the conductivity}$$

(proportional to $|\psi|^2$) to decrease exponentially with an increase in separation of the carbon layers d_c. Secondly, we know from chapter two that ammonia intercalation causes charge back transfer from the carbon layer to the intercalate layer (metal-ammonia liquid layer). The decrease in delocalized electron density caused by this charge backtransfer leads to an increase in c-axis resistance. The amount of charge back transferred is strictly controlled by the ammonia content. Thus, the saturation relative resistance increases with ammonia content. Thus, the saturation relative resistance increases with ammonia the value of x_{max} . This is reflected in the empirical formula (4.3.1) which shows that the relative resistance increases with decreasing r_m^2 .

In conclusion, the size of the metal ion has a dramatic influence on both the c-axis and a-axis resistivity. While a quantitative understanding of the ion size effect is not available, a qualitative understanding could be obtained from equation (4.3.1). The ion size determines the amount of a given molecule that can be cointercalated into an alkali binary GIC, the basal spacing of the parent compounds, and subsequently the c-axis resistivity. The ion size effect on the critical ammonia composition \mathbf{x}_{C} for a 2D metal-insulator transition is also observed.

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TEMPERATURE DEPENDENT LEVITATION STUDIES OF HIGH TEMPERATURE SUPERCONDUCTORS

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It is generally assumed that high T_c materials are simple bulk anisotropic superconductors (BAS) although the mechanism responsible for the bulk character is not yet definitively established. Additional common assumptions are that <u>intragranular</u> flat defects such as [110] twin boundary planes in the Y based compounds, c-axis interstratifications in the Bi and Tl based compounds and stripe domains in the Bi compounds are either irrelevant or act as weak-links as do the <u>intergranular</u> boundaries which are present in polycrystalline specimens but presumed absent in single crystals. The effect of flat defects and "links" on the superconductivity of high T_c materials has been probed in several experiments on YBa₂Cu₃O_{7-x} and

 $Bi_2Sr_2Ca_{n-1}Cu_no_y$, n = 1,2,3. These include temperature/fielddependent studies of X-ray diffraction, magnetic levitation, and magnetic susceptibility of random and field-aligned powders as well as pressed pellets, sintered pellets, multidirectional twinned single crystals and unidirectional twinned single crystals.

As an example of our results, we show in Fig. 1 the temperature dependent studies of the levitation properties of a pressed (unsintered) pellet of $YBa_2Cu_3O_{7-x}$ for various fields (various magnet currents). This data was acquired in equilibrium after time dependent

magnetization changes [1] had saturated. In addition to the noticeable kink in all the levitation curves at ~ 20 K, one observes that the temperature at which the pellet no longer levitates, T_r, is

field (gradient) dependent. We have shown previously [2,3] that if buoyant forces are negligible, the levitation condition for a horizontal magnetic field and a vertical gravitational field ($||z\rangle$) is

$$(V/2)M \left[\frac{\partial H}{y}(z)/\partial z\right] = \rho g V \qquad (1)$$

where V is the sample volume, M is the magnetization, ρ , is the mass density and g is the acceleration due to gravity.

The essential quantity of interest in Eq. (1) is, of course, the magnetization. In this regard, one of the most distinguishable features of high T materials relative to normal superconductors is

the high ratio of upper to lower critical fields, i.e. $H_{c2}^{j}/H_{c1}^{j} > 1000$,

j = $||, \perp$ relative to the ab planes. As a result, in the range $H_{cl}^{j} < H << H_{c2}^{j}$ the vortex state susceptibility can be approximated as

$$x_{j} = (-1/4\pi) H_{c1}^{j}(T)/H.$$
 (2)

If we employ the relation $H_{cl}^{j}(T) = H_{cl}^{j}(0)[1 - T^{2}/T_{c}^{2}]$ then Eqs. (1) and (2) can be combined to relate the maximal levitation temperature to the inverse field gradient and

$$T_{L}^{2} = T_{c}^{2} \{1 - \frac{8\pi\rho g}{H_{c1}^{eff}(0)} [1/(\partial H_{y}(z)/\partial z)]\}$$
(3)

where $H_{cl}^{eff}(0)$ is an effective lower critical field which results from the orientational distribution of the grains. A plot of T_L^2 vs. inverse gradient for $YBa_2Cu_3O_{7-x}$ is shown in Fig. 2 and presents clear verification of the linear relation defined in Eq. (3). From the slope of this line, we find $T_c = 88 \pm 4$ K in agreement with susceptibility measurements on this specimen and $H_{cl}^{eff}(0) = 90 \pm 15$ G which, as expected, is less than, but of the same order as, $H_{cl}^{||}(0) =$ 270 ± 50 G [3,4].

The kink in the magnetization and levitation data at 20K is, we believe, due to the onset of intergranular phase coherence which results in a field-dependent magnetization for T < 20K. Several models are available to explain such intergranular effects [5,6] including one which treats the onset of intergranular phase coherence as a 3D XY problem [6], but further work is necessary to identify the correct model. Note, however, that independent of the particular model which is applicable, the temperature at which the levitation kink occurs provides a quantitative measure of the intergranular coupling strength, an important parameter. Preliminary levitation results [7] on an admixed $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ compound with n = 2,3 show that these materials exhibit the same type of levitation behavior as evidenced by the Y compounds.

The dramatic slope discontinuities in levitation and magnetization data which we observe in pressed pellets are also clearly observable with single crystals which, by inference contain weak-links, too.

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Fig. 1 Zero-field-cooled (ZFC) Levitation height of $YBa_2Cu_3O_{7-1}$ vs. temperature and magnet current. The center of the magnet is at a height $Z_0 = 697$ mm.



Fig. 2 Maximum levitation temperature vs. inverse gradient for $YBa_2Cu_3O_{7-x}$. The solid line is a linear least-squares fit to the data using Eq. 3 of the text and yields the values $T_c = 88 \pm 4K$ and $H_{cl}(0) = 90 \pm 15G$.

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Two-Dimensional Diffusion-Limited Kinetics in a Ternary Graphite Intercalation Compound

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The kinetics of the ammoniation of KC₂₄ to form the ternary graphite intercalation compound (GIC) K(NH₃)_xC₂₄, $0 \le x \le 4.38$, has been studied by monitoring the time dependence of the c-axis resistance. Our results are in quantitative agreement with a two-dimensional (2D) diffusion model which yields diffusion constants -10^{-8} cm²/sec. In contrast to binary GIC's which exhibit intercalation kinetics that may be limited by the growth of planar multidegenerate domains, the K-NH₃ ternary

system provides a clear example of 2D diffusion-limited intercalation.

Kinetic effects in layered systems, and in particular graphite intercalation compounds (GIC's), have been the subject of intense recent experimental 1^{1-3} and theoretical 4^{-7} interest. To date the focus has been on kinetic processes which are dominated by the growth and coalescence of intercalate domains of which two types have been considered; namely, multidegenerate (MD) in-plane two-dimensional (2D) islands 8 and the so-called Daumas-Herold (DH)⁹ 3D stacked columns of planar domains whose 2D structure is unspecified. There is evidence 8,10 that MD 2D domains are prevalent in binary GIC's and that their formation constitutes a theoretically complex step in the kinetics of both in-plane ordering and staging. (A stage n GIC contains a regular c-axis stacking sequence in which nearest pairs of guest layers are separated by n graphite host layers.) Moreover, the traditional^{11,12} and still popular¹³ approach to kinetic studies of GIC's ignores the complexities of MD domains and quantitatively addresses only that small part of the kinetic process which exhibits a (supposedly) diffusionlimited $t^{1/2}$ variation of intercalatant concentration with time.

The kinetics of in-plane diffusion¹⁴ and in-plane ordering¹ (at constant stage and constant composition) and of staging^{2,3} (variable composition) in binary GIC's have been recently probed by real-time in-situ neutron and x-ray diffraction studies. However, very similar experiments on staging kinetics in potassiumgraphite yielded conflicting qualitative conclusions.^{2, 3} Clearly, a quantitative study of staging kinetics which accounts for both the $t^{1/2}$ and saturation regions of the intercalation process is warranted. Furthermore, this study

would best be conducted using GIC's which do not suffer from the severe complications¹⁵ associated with MD 2D domain structures. Until now, such studies were apparently precluded by the lack of suitable specimens.

We have recently shown that unlike binary GIC's, the alkali-ammonia ternary GIC $K(NH_3)_x C_{24}, 0 \le x \le 4.38$, forms an intercalate that is a simple 2D metal-ammonia liquid, the structure of which 16,17 is the planar analog of the structure of the famous 18 bulk 3D metalammonia solutions. While the substrate potential is of course "felt" by the K-NH3 liquid, its structure is dominated by intercalate-intercalate interactions rather than by intercalate-substrate interactions which generate MD 2D domains in binary GIC's. Modern X-ray techniques are not sufficiently sensitive for direct detection of DH domains 9 and electron microscopic methods are incompatible with a high-pressure ammonia environment. Nevertheless, one would expect that ammonia intercalation in the alkali-ammonia GIC's would be governed by the formation of 3D DH domains the growth rate of which could be kinetically constrained by diffusion of guest species to the domain surface (diffusion-limited) or by the rate of incorporation of guest species at the domain surface (reaction/nucleation-limited). In this letter we show that the former process obtains and we quantitatively verify the first definitive example of variable composition diffusion-limited intercalation of a GIC from induction to near-saturation.

Samples of binary stage-2 KC₂₄ of typical

dimension 5.2 x 3.5 x 0.5 mm were prepared from highly oriented pyrolytic graphite (HOPG) for a 4-probe DC resistance measurement. After x-ray characterization, the encapsulated samples were placed in a high-purity glove box (0, 1evel <

0.5 opm), removed from their glass ampoules and affixed with four platinum wires using flexible silver paint that was pretested and found to be impervicus to attack by ammonia. Two leads, each with a separate silver paint dot, made contact to the two c-faces of the sample, one opposing pair for surrent and one for voltage. The anisotropy of the resistivity ensures that the equipotential lines are parallel to the graphite planes as desired. The sample assembly, which consisted of a vacuum feedthrough to which the four platinum leads were soldered, was sealed to one end of a Pyrex U-tube, the other and of which was filled with purified liquid ammonia and isolated by a Teflon isolation valve (TIV). By accurately controlling the temperature of the ammonia reservoir ($\pm 0.5K$) in the range 77K to 300K the vapor pressure could be controlled to better than =3% over the range 10⁻⁹ atm. to 10 atm. All measurements reported here were carried out with the sample held at

room temperature. To assess the intercalation process with very high sensitivity (-1 part in 10^4), we monitored the time dependence of the c-axis resistance of $K(3H_3)_{x}C_{24}$ as a function of ammonia pressure (or x) using a sequential pressure up-quenching technique as follows. With the TIV closed and the sample space evacuated to a pressure P_0 (corresponding to a KC_{24} c-axis resistance of R_0) the temperature of the ammonia reservoir was adjusted for a pressure P_1 . At time t = 0, the TIV was opened and the c-axis resistance of the sample $R_{1}(t)$ was monitored until the measured resistance appeared to be time independent and equal to R_i (sat) (points 3-5, 7-10, and 12-14 in Fig. 1) or until sufficient near-saturation data was acquired to analytically determine (see below) the saturation resistance R_i (sat). Then the TIV was closed, the reservoir pressure was raised to P2, the TIV was opened and $R_2(t)$ and $R_2(sat)$ were determined in the same way. This process was repeated until a pressure $P_n = -10$ atm was reached. The measurement apparatus was designed so that a negligible time was required to achieve pressure equilibrium following an opening of the TIV. The room temperature resistance isotherm of

the c-axis saturation resistance of $K(NH_3)_xC_{24}$ relative to the resistance of KC_{24} is shown in Fig. 1. The data of Fig. 1 mimic previous studies²⁰ of the dependence of the composition (or x value) of $K(NH_3)_xC_{24}$ on ammonia pressure and exhibit step-like plateaus, with onset pressures of -10⁻³ atm. and -0.5 atm.,





respectively. From previous x-ray studies²⁰ it is known that the step at -10^{-3} atm. corresponds to the incorporation of ammonia into the expanded galleries of KC₂₄ while the step at -0.5 atm. corresponds to an n=2-to-n=1 staging phase transition in which the potassium and ammonia redistribute to fill every gallery. The exact pressures at which the plateaus in Fig. 1 occur are sample dependent. Therefore, we were unable to successfully acquire data in the mid-region of the step itself. Moreover, the ammoniation of KC₂₄ is not reversible²⁰ and on depressurization a residue compound forms with R_{residue}/R₀ -

 10^2 . To explore the kinetics of the ammoniation of KC₂₄, we have monitored the time dependence of the resistance ratio $g(t) = R_i(t)/R_{i-1}(sat)$ for several of the intervals between the labeled points of Fig. 1. The results for i = 6 and 11 are shown in Fig. 2. We will now show that the form of g(t) is well described by a model of 2D diffusion-limited intercalation kinetics.

Consider a rectangular parallelepiped sample with c-faces of dimensions a and b and height c << a,b. We assume that the specimen is bathed in vapor at pressure P_1 and that this vapor can intercalate only through the edge faces by the process of 2D diffusion. Let $n_{(i-1)+i}(\vec{r},t)$ be the areal number density (hereinafter called the density) of ammonia in the specimen at position \vec{r} at time t following an increase in ammonia pressure from P_{i-1} to P_i

and assume that $n_{(i-1)+1}(r,t)$ obeys the diffusion equation:

$$\frac{\partial n_{(i-1)+i}(r,t)}{\partial t} = D \nabla^2 n_{(i-1)+i}(r,t). \quad (1)$$

The boundary condition which expresses the fact that the density is constant at the edge faces $r_{\chi} = \pm a/2$ or $r_{\psi} = \pm b/2$ is

$$n_{(i-1)+i}(r,t) = n_i(sat)$$
 (2)

where n_i (sat) is the saturation density corresponding to the pressure P_i . The initial condition for $|r_y| < a/2$ or $|r_y| < b/2$ is

$$a_{(i-1)+i}(\vec{r},0) = 0.$$
 (3)

We may neglect the initial density of ammonia since $n_{i-1}(\operatorname{sat})/n_i(\operatorname{sat})$ is small, of the order of 0.01 for the transitions at i = 6 and 11. Equivalently, we may regard $n_{(i-1)+i}(\hat{r}, t)$ as the change in the density of ammonia compared to $n_{i-1}(\operatorname{sat})$.

We have determined the solution to the boundary value problem represented by equations (1)-(3) to be

$$n_{(i-1)+i}(r,t) = n_i(sat) \{1 - \phi(\frac{x}{a}, \frac{Dt}{a}) + \phi(\frac{y}{b}, \frac{Dt}{b})\},$$

where

and

$$\phi(\xi,\tau) = \frac{4}{\pi} \sum_{v=0}^{\infty} \frac{(-1)^{v}}{2v+1} e^{-\tau q^{2}} \cos(q\xi), (5)$$

$$q = (2v + 1)\pi.$$
 (6)

A comparison of our previous measurements²⁰ of x vs. P_{NH_3} for $K(NH_3)_xC_{24}$ with the data of Fig. 1 yields a plot of log $[(R_1(sat)/R_0) - 1]$ vs. log x as shown in the inset of Fig. 1. Here the composition x is proportional to the ammonia areal number density, n and is given by x = $24n/n_e$ where n_e is the areal density of carbon atoms in the specific pristine graphite specimen from which the intercalation compound was and temporally. Nevertheless, in an incrementally small neighborhood of area d^{2+} at r the density can be treated as spatially uniform. Moreover, the conductance per unit area corresponding to the case of uniform density is simply $\frac{1}{ab} R_i^*(sat)$ where $R_i^*(sat)$ is given by Eq.

(7). For the nonuniform density $n_{(i-1)+i}(\vec{r},t)$, the conductance per unit area is locally given by the same formula with $n_{(i-1)+i}(\vec{r},t)$ replacing $n_i^*(\text{sat})$. Then the conductance of the entire sample is obtained by integrating the <u>local</u> conductances per unit area over \vec{r} ; that is,

$$\frac{1}{R_{i}(t)} = \frac{1}{R_{i-1}(sat)} \frac{1}{ab} \int \frac{d^{2}r}{\{1 + (r-1) [n_{(i-1)+i}(r,t)]^{p}\}} .$$
 (8)

(4)

prepared. Thus $n_c = M_c A/(12 \text{ ab})$ where M_c is the mass of graphite in our specimen, A is Avagadro's number, and 12 is the atomic weight of carbon. [The very small change in the inplane lattice parameter of the carbon layers²² as annonia is introduced into the galleries is negligible.] Notice from the inset of Fig. 1 that the saturation resistance varies as a power of composition over the ranges 0 < x < 0.07 and

The solution for $R_i(t)$ given in Eq. (8) involves three dimensionless parameters; namely, f, D, and $\lambda = a/b$.

For $\lambda = 1.47$ corresponding to the measured dimensions of our specimen, we have performed least squares fits to the data of Fig. 2a) and b) using Eq. (8) with p = 0.77 and 1.41, respectively and with f and D treated as adjustable parameters. The results of these fits are shown

RY GRAPHITE INTERCALATION COMPOUND 471 0.07 < x < 4.3, the latter of which spans the staging phase transition. Straight line fits to

the data of Fig. 1 inset indicate that for a <u>uniform intermediate</u> density, say $n_1^*(sat)$, in the range between data points 5 and 6 or between 10 and 11, the intermediate saturation resistance $R_1^*(sat)$ is of the form

$$R_{1}^{*}(sat) = R_{1-1}^{*}(sat) [1 + (f - 1)(\frac{n_{1}^{*}(sat)}{n_{1}^{*}(sat)})^{p}].$$
 (7)

Here $f = R_i(sat)/R_{i-1}(sat)$ and p is the slope of the curve of log $(R_i(sat)/R_0 = 1)$ vs. log x. From Fig. 2 we estimate that p = 0.77 between data points 5 and 10, and p = 1.41 between data points 10 and 14. The observed nonlinear dependence of $R_i^*(sat)$ on x is presumed to result from both weight gain and basal spacing expansion.

Now Eq. (7) gives the relation between the intermediate saturation resistance $R_{i}^{*}(sat)$ and the uniform saturation density $n_{i}^{*}(sat)$. But when the pressure is changed from P_{i-1} to P_{i} , the actual density, $n_{(i-1)+i}(r,t)$ given by Eq. (4) is not uniform but evolves both spatially



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Time dependence of the ratio g(t) -Fig. 2 $R_i(t)/R_{i-1}(sat)$ (solid circles). Panels (a) and (b) correspond to pressures $P_6 = 4.5 \cdot 10^{-3}$ atm. and P_{11} = 0.25 atm., respectively. The dashed (solid) line is a least squares fit using Eq. (8) with (without) a dwell time and yields the following fitting parametears: panel (a), solid line: D = $3.49 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, f = 1.87, t_d = 0; dashed line: $D = 8.69 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, f =1.90, $t_d = 2.08$ hr. Panel (b), solid line: $D = 8.20 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, f = 43.21, $t_{d} = 0$; dashed line: D = $6.65 \cdot 10^{-9} \text{ cm}^2/\text{sec}, f = 46.39, t_d = -$ 29.8 hr.

as solid lines in Fig. 2 which evidences good agreement between theory and experiment. It is particularly gratifying that the values of D we obtain, $8.49 \cdot 10^{-9} \text{ cm}^2/\text{sec}$ and $8.20 \cdot 10^{-9} \text{ cm}^2/\text{sec}$ for Figs. 2a and b, respectively, are typical of gas diffusion in solids.²³ There are small deviations between theory and experiment in the small time region, especially in Fig. 2a where the diffusion theory rises faster than the data. Therefore, we also attempted to fit the data by introducing one additional parameter, a dwell time t_d.²⁴ For the data of Fig. 2a, the introduction of a dwell time (dashed lines of Fig. 2) improved the fit with t_d optimized at 2.08 hours

and D and f at $8.69 \times 10^{-9} \text{ cm}^2/\text{sec}$ and 1.90, respectively. However, the same procedure when

applied to Fig. 2b yielded an unphysical <u>nega-</u> tive dwell time $t_d = -29.8$ hours with $D = 6.65 \times 10^{-10}$

 10^{-9} cm²/sec and f = 46.39. Moreover, the introduction of a dwell time in Fig. 2b had a negligible effect on the fitting parameters D and f. Therefore, we justifiably infer that t_d

= 0 for Fig. 2b.

We suggest that the dwell time may be associated with surface adsorption. It has been known for some time²⁵ that intercalation in GIC's cannot occur unless the basal surfaces of the specimen are exposed even though access to the specimen interior is through its edges.

This has been attributed 26 to surface adsorption which produces a localized charge density wave distortion that weakens the interlayer bonding and promotes access to the gallery through the edges. Note that the diffusion constant associated with the staging transition, a structurally disruptive process, is slightly smaller than that for absorption at constant stage. For intercalation accompanied by staging, the dwell imposed by surface absorption is apparently insignificant as in Fig 2b.

We allowed the saturation resistance ratio f to be a free parameter in fitting the diffusion theory to the experimental results. The saturation resistance ratios obtained from the fits of the time dependence of $R_i(t)$ are ap-

proximately f = 1.9 for i = 6 and f = 43 for i = 11. The corresponding measured values shown in Fig. 2 are 1.33 and 39, respectively. Part of the difference between theory and experiment may be attributed to some undersaturation in the experimental measurements. In addition, the time dependence of the diffusion theory does differ somewhat from the observed time dependence in the case of i = 6, even when a time delay is naively included; this is reflected in an artificially large fitted value of f. A more detailed knowledge of the physical mechanism responsible for the time delay might make possible an even more accurate description of the diffusion process.

The numerical solutions of Eq. (8) were found to be very insensitive to 1. The quality of the fits obtained for the data of Fig. 2 was also very insensitive to the value of the parameter p in Eq. 8 as was the diffusion constantant deduced from Fig. 2a) which changed by only +4% when p was changed +30% from .77 to 1. However, the diffusion constant deduced from Fig. 2b) was more sensitive to the parameter p and changed by +73% when p was increased by +41% from 1 to 1.41. Note that it is the quality of fit and not the exact value of D which is important here. Therefore, the essential physics of our results still obtain: in GIC's, which are not structurally dominated by MD 2D domains, the intercalation process itself is apparently governed by the formation of 3D DH islands whose growth rate, in the case of potassium-ammoniagraphite, is kinetically limited by 2D diffusion of the intercalant to the specimen interior.

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A 2D METAL-HONMETAL TRANSITION IN

POTASSIUM-AMMONIA LIQUID MONOLAYERS IN GRAPHITE

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ABSTRACT

The x-dependence of the a- and c-axis relative resistances and of the near-normal reflectance of the metal-ammonia ternary graphite intercalation compound $K(NH_3)_x C_{24}$ has been studied in the range $0 \le x \le 4.38$. For $x \ge 4$ the a-axis relative resistance and the reflectance both exhibit unusual features which we associate with a two-dimensional Mott type metal-nonmetal transition in the intercalated K-NH₃ liquid monolayers.

Bulk three dimensional (3D) metal ammonia (MA) solutions constitute one of the most interesting topologically disordered condensed matter systems' because they exhibit a composition dependent metal-nonmetal transition (MNMT). At low concentration (< 7 mole percent metal) the metal ion and its detached electron are both solvated by an enveloping cluster of NH_ molecules. The solvated electron is adalized and exhibits a narrow optical absorption band. A MNMT occurs when sufficient metal is present in solution to cause the wavefunctions of the solvated electrons to overlap and form delocalized bands which sustain conduction. Although the possibility of studying the effect of dimensionality on the properties of MA solutions is intriguing, no such studies have been reported to date.

It has been known for several decades that MA monolayers could be periodically inserted between the host layers of graphite.³ However, interest in MA graphite intercalation compounds (GIC's) remained dormant until recent X-ray studies showed that the MA monolayers in the stage-1 compound $K(NH_3)_{4/38}C_{24}$ were the two dimensional (2D) <u>structural</u> analogue of the corresponding 3D MA solution. (In a stage n GIC, nearest pairs of guest layers are separated by n graphite host layers.) This result stimulated several other measurements of the system $K(NH_3)_{2}C_{24}$, $0 \le x \le 4.38$ including NMR, kinetics and neutron scattering studies. These studies provided information on the configuration, correlations and motions of the NH₂ molecules in the 2D liquid and showed that ammoniation of KC_{24} results in a back-transfer of electron charge, of per K ion, from the C layers to the MA liquid. Such information was prerequisite to a careful analysis of the x-dependent electronic properties of that novel liquid. Accordingly, we report here electrical and optical studies of the K-NH₂ monolayers in graphite. Our results indicate that these monolayers exhibit localized electronic states and a MNMT which may be considered the 2D electronic analogues of the unusual properties of their bulk MA counterpart.

The ternary GIC's $K(NH_3)_{xC_2}$ were synthesized by exposing KC_{24} at rodm temperature to pure NH₃ vapor. The relationship between₈x and pressure P_{NH₃} has been carefully measured.

Details of these measurements and of our synthesis procedures are given elsewhere.⁸ The compounds studied here were prepared from either highly oriented pyrolytic graphite (HOPG) or from individual methane-derived fibers heat treated to 3000C². The latter, being of much smaller dimension, exhibit a faster kinetic response. They also chemically decompose after several days following maximum ammoniation.

In situ electrical measurements were carried out using both AC and DC 4-probe techniques. Intercalated HOPG samples were used for the c-axis resistance and optical studies while fibers were used for the a-axis POTASSIUM-AMMONIA LIQUID MONOLAYERS IN GRAPHITE

measurements because of their ideal aspect ratio. Near-normal incidence in situ c-face reflectance spectra $R(\omega)$ were Kramers-Kronig (KK) transformed to obtain the a-plane complex dielectric function $\varepsilon(0,\omega)$. The c-axis resistance and optical spectra were measured in chemical equilibrium. Because of the decomposition alluded to above, a-axis resistance data were taken "on the fly" over a period of two days. Nevertheless, the enhanced kinetic response exhibited by the fibers ensures that our "on the fly" data represent an equilibrium result.

Room temperature isotherms of the c and aaxis relative resistances $(R/R_0)_{a}$ and $(R/R_0)_{a}$, respectively of $K(NH_3)_{a}C_{a}$ are shown in Fig. T. Here R₀ is the appropriate resistance of KC_{24} . The curve for $(R/R_0)_{a}$ exhipits three plateaus separated by steps at 2-10 atm and 1.2-10 atm. In the first plateau a negligible amount of NH₃ enters defect sites in the occupied galleries of KC_{24} . In the second a significant amount of NH₃ enters but the compound retains its stage-2 structure. For P_{NH₂} 2.1.2-10 atm, the system undergoes a stage-2 to stage-1 transition and NH₂ becomes the domina- constituent while the K in-plane density falls by a factor of 2 as the number of galleries which contain K doubles.





Fig. 1. The T = 300K c-axis () and a axis ([]) relative resistance ratios of $K(NH_3)_x C_{2k}$ as a function of NH_3 vapor pressure or x. Insets in the upper panel $(\log_{10}(R/R_0))$ indicate the structure and composition in the region of the corresponding plateau while the lower panel $((R/R_0)_3)$ inset depicts parallel conduction in the carbon and metal-ammonia layers. The solid lines are a guide to the eye.

extended plateau that is terminated by a step at 1 atm which is upshifted in pressure from the onset of the staging transition. But $(R/R_0)_{atm}$ shows no sign of the step at $2 \cdot 10^{-3}$ atm in $(R/R_0)_c$. More significant is the precipitous drop in $(R/R_0)_a$ at x = 4. While the magnitude of this drop is sample dependent, it has been observed in more than twenty specimens which we have examined. To our knowledge, no other GIC displays such a decrease in R_a with increasing intercalation at fixed stage.

In Fig. 2 we display the x-dependence of the reflectance $R(\omega)$ and the KK-derived values of $c_2(0,\omega)$. Our x = 0 result is in excellent agreement with previous work¹. The $c_2(0,\omega)$



$K(NH_3)_{X}C_{24}$

Fig. 2. The T = 300K optical reflectance (solid lines, insets) and Kramers-Kronigderived imaginary part of the dielectric function $c_2(o,\omega)$ (solid lines, main panels) of $K(NH_3)_{x}C_{24}$ for several values of x. The dashed curve (x-2-4) is obtained from the solid

dashed curve (---- -) is obtained from the solid curve by subtracting the dotted (.....) Lorentzian curve (see text). Vol. 64, No. 4

decrease near the plasma frequency, $\omega_{\rm p}$, as - $\omega_{\rm z}^2/\omega^3$ due to free carrier absorption, followed ω^2/ω^2 due to free carrier absorption, followed by a rise caused by interband absorption. This interband absorption has been decomposed into a narrow band at 1.85 eV (FWHM - 0.4 eV) plus a broader contribution which resembles a typical threshold for graphitic π - π transitions. The motivation for this decomposition comes from the $x = 4.1 \in (0, \omega)$ data in which the band is most pronounced. For the compositions x = 1.9 and 4.3 the same energy and FWHM were used and the strength was adjusted to the maximum value which still ayoided introducing a notch at 1.85 eV in the $\pi-\pi$ threshold. The x-dependence of the oscillator strength of the band reveals (Fig. 3.) an increase up to x = 4.1 followed by a sharp drop at higher x values.

The results shown in Figs. 1-3 are closely related to the x-dependent structure of the K-NH₃ liquid and to δf . The liquid structure is dominated by planar K(NH₃)₄ clusters⁴ (inset Fig. 3) while we associate δf with spacer molecules. These spacers may provide the stuructural configurations (eg. a hydrogen cage formed by a spacer and a cluster NH2) which trap electrons. For x < 4 the inserted NH, causes gallery expansion but only participates in cluster formation; thus, of = 0. When $x \leq 4$ some added NH,'s enter as spacers and backtransfer commences while for x > 4, NH, enters only as spacers which further increase of. A linear model: of = 0, x < 4; of = Y(x-4), $x \ge 4$ (Y = const.) has been found to be compatible

with X-ray intensity measurements of $K(MH_3) C_{24}$. When NH₄ is ingested at - 2.10⁻³ atm, the resultant gallery expansion causes a reduction in the electronic wavefunction c-axis overlap which results in the step-like increase in



Fig. 3 Dependence of the oscillator strength of the 1.85 eV absorption band (see Fig. 2) of $K(NH_3)_{2}C_{24}$ on x. The solid lines are a guide to the eye. Inset - the computer generated planar structure of the K-NH, liquid monolayers (from ref. 4). the solid circles (), open circles () and hatched circles () represent respectively K ions, bound NH_3 molecules, and unbound NH_3 spacer molecules.

 $(R/R_0)_c$. At and above 0.12 atm, the onset of the staging transition, the wavefunction overlap is even more drastically reduced as complete filling/expansion of all of the galleries is achieved. As a result, (R/R_0) rises by about two orders of magnitude and levels off when significant WH, uptake ceases to occur with increased $P_{\rm MH}$. This leveling commences at increased $P_{NH_3}^{0.5}$. This leveling commences at - 0.8 atm, well below the pressures of -1 atm at

which of becomes significant and 6 atm at which the staging transition is complete. We attribute this lag to the inhomogeneous c-axis distribution of NH, which forms an intercalation front that migrates from the surfaces and edges of the specimen towards the interior during the stage transformation. Thus the c-axis resistance of the outer galleries, which are ammoniated well before the staging transition is complete, rises drastically and dominates the "series" resistance of the bulk specimen.

For a-axis conduction, the MA layers and the C layers conduct in parallel as indicated in Fig. 1. Expansion of the galleries should not directly effect this conduction process so there is no change in (R/R_0) until charge back-transfer is initiated at $x \leq 4$. This backtransfer causes a drop in the a-plane C layer conduction which is not compensated for by increased MA layer conduction because the charge which is received is localized. But as x increases further, the trapped electrons become sufficiently dense for their in-plane wavefunctions to overlap and form band-like extended states. The MA layers then conduct and $(R/R_0)_a$ drops. Additional increases in P_{NH}.

result in minimal weight gain and minimal change in in-plane conduction.

The 1.85 eV band in the data of Fig. 2 is direct evidence for localized electronic states in the MA layers. Similar bands (FWHM - 0.5 eV) have been observed at lower energy (0.2 eV ') in 3D MA solutions and have been attributed² to a solvated electron 1s-2p transition between states which form in a ~ 64 diameter solvent, bubble. It is clear from the work of Jortner² and from studies of other solvents $\frac{1}{2}$ that the and from studies of other solvents solvation band energy increases with decreasing cavity size. The cavities formed in the K-NH layers would be smaller than those in the bulk fluid and thus give rise to an upshifted band. The drop in the oscillator strength of that band at x = 4 is consistent with the drop in (R/R_0) once it is recognized that the band strength is proportional to the concentration of localized electrons. These localized electrons are lost to the newly formed conduction band arising from the MNMT.

The low energy optical data were also subjected to a Drude analysis to determine a carrier relaxation time and $w_{\rm c}$ from which if could be obtained. Details of this analysis will appear elsewhere. Of significance here is the fact that ω_{1} is found to be essentially constant at 3.3 \pm 0.1eV as the strength of the 1.85 eV band decreases by a factor of -3. The corresponding drop in (R/R_0) is -10%. Since $\omega_c^2 - \sigma_{dc}$, one would expect a -5% increase in ω_c^2 le. $\delta \omega_c^2 = -0.15$ eV. The anticipated change is therefore only slightly larger than the estimated experimental error in w. We have isscribed the MNMT in our specimens

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as a Mott transition¹⁴. This description is justified as follows. It can be shown from dimensional and/or energy arguments that the Mott condition for the critical electron areal density n, in 2D is n'a = A_{2D} = const. where a = $[c/(m/m_0)]a_0$. Here c is the static dielectric constant, a is the effective mass, m is the free electron mass, and a = 0.529A. Although the quantity in square brackets is difficult to calculate for MA GIC's we can still determine a set of self-consistent values for n (or x). We obtain c from a 2D Clausius Mossotfi (CM) relation (c - 1)/(c + 1) = 27Ng which was calculated for an ellipsoidal cavity in a dielectric. Here N = [x/(62.86-3.28)]A is the number density of a 3.28A thick NH₃ layer where 62.86A² is the area of 24 C atoms. The static polarizability a = 7.36A³ is computed from the 3D CM equation using c = 25 and p = 0.817 gm/cm² for liquid NH₃ at = 77 C³.

By combining the Mott condition with the 2D CM equation we obtain $n_{c} = f_{1}(m_{c}/(m_{A_{2D}}), x_{c})$. But the linear model yields $n_{c} = f_{1}(x/62.36) \cdot (x_{c} = 4) = f_{c}(x)$ where $Y = 0.2/0.38^{+}$. Setting $f_{1} = f_{2}$ we obtain a cubic equation the three solutions of which are the self-consitent values of x_{c} . Only one of these solutions is physically significant and it is bounded: for $0 \le m_{c}/(m_{A_{2D}}) \le -, 4 \le x_{c} \le 4.47$. By comparing the 2D and 3D Fermi wavevectors which depend on electron density one obtains a reasonable estimate of $A_{2D} = \{(3\pi^2)^{1/2}/(2\pi)^{1/2}\}A_{3D} = .31$. Now a delocalized electron in an MA layer must be heavier than a free electron as evidenced by the fact that m /m₀ is between 1.5 and 4.04 for 3D_MA solutions. If we reasonably limit (m /m₀) to 10, the applicable range of x is 4.09 s x 3 4.39 for 1 s m /m₀ s 10. This range of x overlaps closely the region in which (R/R₀) and the 1.85eV band intensity drop preclpitously. Thus, the MA layers should indeed conduct for x \geq 4. This conclusion does not depend on A_{2D} the value of which merely rescales m /m₀. Finally, we can compute the Fermi temperature T_c = (h πn)/(m k) which for m /m₀ = 10 and T = 300K gives (T/T₁) = 2.94. Therefore, our measurements are at "high temperature" and Σ_{m} << L where L_{Th} is the (Thouless) effective scale size for quantum interference and L is our sample size. Thus, quantum interference effects are negligible and the MNMT in the K-NH layers is of the Mott type.

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TWO DIMENSIONAL METAL-INSULATOR TRANSITIONS IN ALKALI-AMMONIA TERNARY GRAPHITE INTERCALATION COMPOUNDS

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ABSTRACT

The composition dependence of the c-axis and a-axis resistance of the alkali-ammonia ternary graphite intercalation compounds $M(NH_3)_xC_{24}$, M = K, Rb, Cs and 0 \leq x \leq x_{max} has been measured at room temperature for x_{max} values of 4.33, <u>4.10</u>, and <u>3.65</u> corresponding respectively to, K Rb, and Cs. The c-axis resistances relative to that of MC_{24} exhibit features which we associate with the onset of a stage-2 to stage-1 structural phase transition whereas the a-axis relative resistances exhibit features which we associate with a metal-insulator transition in the metal-ammonia intercalate layers. For some vales of x the alkali-ammonia ternary GIC,s exhibit electrical anisotropies which are among the highest yet reported for stage-1 donor GIC's.

INTRODUCTION

Bulk metal-ammonia (MA) solutions have been the subject of intense study over the past several decades [1] primarily as a result of the composition dependent three dimensional (3D) metal-insulator transition (MIT) which they exhibit when an alkali metal is added to the insulating ammonia fluid. In a chemical synthesis effort unrelated to the conducting properties of bulk MA solutions, Rudorff and coworkers [2] showed that an alkali metal and ammonia could be cointercalated into powdered graphite to form binary monolayers in the host galleries. Following a three decade period of underwhelming interest in ternary MA GIC's, renewed interest in those materials developed when York and Solin[3] pointed out that MA monolayers in graphite might be the 2D analogues of the bulk MA solutions and thus may exhibit a host of interesting physical properties.

• Invited paper.

During the past half decade the research efforts on ternary MA GIC's have been focussed on the potassium compounds $K(NH_3)_{\chi}^{\circ}_{24}$, $0 \le x \le 4.38$ and many composition dependent measurements have been made on those materials. These measurements include x-ray studies, [3] elastic, inelastic and quasi elastic neutron diffraction studies, [4] nuclear magnetic resonance studies, [5] optical reflectivity and absorption studies, [6] absorption isotherm measurements [3] and measurements of the a-axis and c-axis resistance. [6] Naturally such studies have generated a wealth of knowledge about the K-NH₃ ternary GIC's. Most significantly, we now know that:

1. The MA monolayers in $K(NH_3)_{x}C_{24}$, $x \ge 2$, are the 2D <u>structural</u> analogue of the 3D MA solution. These intercalated layers possess a 2D fluid structure in which the K ions are 4-fold coordinated to NH_3 molecules whose C_3 axes are tilted by approximately 90° with respect to the graphite c-axis so that the nitrogen lone pair electrons point towards the potassium cation. To satisfy the stoichiometry for x > 4, "spacer" ammonia molecules which are dynamically uncoupled from a K ion are also present in the fluid.

2. The MA monolayers in potassium-ammonia-graphite are the <u>electrical</u> analogue of the corresponding 3D MA solutions and exhibit a composition dependent MIT. For the potssium compound, this transition obeys a 2D Mott condition [6] for the critical concentration namely,

$$n_c^{1/2}a_h = 0.31$$
 (1)

where n_{C} is the critical areal electron density at which the MIT takes place and a_{h} is an effective-Bohr radius for the system.

To date only the potassium-ammonia ternary GIC has been probed for a MIT and attendant properties. In this paper we report the first corresponding studies of the electrical behavior of the Rb and Cs alkali-ammonia ternary GIC's. These studies also yield evidence for a MIT in the Rb and Cs compounds the electrical behavior of which is similar to that of the potassium compound. Moreover, we will show that there is a systematic relationship between the c-axis resistance at maximal ammonia concentration and the physical properties, e.g. the ionic radius, of the alkali species in $M(NH_3)_{\nu}C_{2\mu}$.

EXPERIMENTAL METHODS

The intercalation procedures employed by Rudorff [2] invariably caused drastic exfoliation of the host material. To avoid this undesirable morphological effect, York and Solin [3] developed sequential intercalation methods in which binary alkali GIC,s prepared from highly oriented pyrolytic gaphite (HOPG) could be ammoniated and partially reversibly deammoniated without

exfoliation. To prepare and study the in situ electrical properties of $M(NH_3)_xC_{24}$, stage-2 MC_{24} was exposed to purified ammonia vapor the pressure of which was controlled by adjusting the temperature of an ammonia resevoir that was attached to the sample tube through a valved off side arm. The absorption isotherm which relate composition, x, to ammonia pressure, P_{NH_3} , has been thoroughly studied for $K(NH_3)_xC_{24}$ but only the saturation composition corresponding to the vapor pressure of ammonia at room temperature, ~ 10 atm, has been determined for the Rb and Cs compounds. The results of these composition measurements together with x-ray derived basal spacings and other physical parameters which are relevant to further discussions in this paper are summarized for the alkali-ammonia ternary GIC's in TABLE 1. Further details of the sequential sample intercalation method are given elsewhere.

TABLE 1

Parameters and properties of the stage-1 alkali-ammonia ternary graphite intercalation compounds, $M(NH_3)_xC_{24}$ for $x = x_{max}$ corresponding to an ammonia pressure of - 10 atm

| alkali ion | x [7] max | basal spacing [7] d _c (A) | ionic radius [7] (A) | saturation relative resistance $(R/R_0)_c$ | |
|---------------|--------------|---|-------------------------|--|--|
| к | 4.33±0.05 | 6.620±0.005 | 1.33 | 220±25 | |
| Rb | 4.10±0.05 | 6.640±0.005 | 1.46 | 75±5 | |
| Cs | 3.65±0.05 | 6.671±0.005 | 1.67 | 24±5 | |

For the c-axis resistance measurements, HOPG specimens were employed whereas benzene derived fibers which had been heat treated to 3000 °C were used for the a-axis measurements. Conducting epoxy contacts which were pretested and found to be impervious to attack by high pressure ammonia were used for the HOPG measurements while mechanical contacts were used for the fiber measurements. All of the electrical transport studies reported here were carried out using a four-probe configuration with both AC and DC detection.

RESULTS AND DISCUSSION

The dependences of the c-axis relative resistances $(R/R_0)_c$ on ammonia pressure (or equivalently on composition, x) for the three alkali-ammonia GIC's studied are shown in Fig. 1. Here R_0 is the corresponding resistance of the stage-2 binary alkal; GIC.



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Fig. 1. C-axis Relative Resistance of $M(NH_3) \propto_{24}^{C}$ as a Function of Ammonia Pressure.

Each of the c-axis relative resistance curves of Fig. 1 exhibit a step-like rise at an ammonia pressure of about 0.3 atm. This step is preceded and followed by plateau regions in which the resistance is essentially independent of pressure. Given our understanding of the potassium-ammonia GIC's we associate this step with a stage-2 to stage-1 structural phase transition in which ammonia enters all available galleries and becomes the dominant guest species. This ingestion of ammonia causes a drastic expansion of the gallery height and the resultant reduction in the overlap of electron wave function along the c-axis direction gives rise to the observed increase in $(R/R_0)_c$. The curve for $K(NH_3)_{x}C_{24}$ also exhibits a step-like rise at a lower pressure of - 4.5X10⁻³ atm. which is associated with the uptake of small ammounts of ammonia into the stage-2 galleries which are already occupied by potassium.

Notice from Fig. 1 that there is a systematic decrease in the maximum value of the $(R/R_0)_c$ with increasing ionic radius. This point is further illustrated in TABLE 1 where we have catalogued the maximum c-axis resistance with other parameters of the alkali ion. We have noticed that there is an imperical relationship between the saturation resistance and the ionic parameters:

$$\ln\{(R/R_0)_c\}_{max} = B + \frac{xd_c}{r^2} + A$$
 (2)

where R is a constant and all of the other parameters in Eq. (2) have been previously defined. From Fig. 2 which shows a straight line semilog plot of Eq. (2) using the appropriate parameters from TABLE 1 we find a value of A = 0.580 and B = 0.296.



Fig. 2. The Experimental (.) and Theoretical (-) Variation (see text) of the C-axis Relative Resistance of $M(NH_3) x^{C}_{24}$ as a Function of Composition and Ion Parameters.

Although we cannot derive Eq. (2) a priori, we can understand it on a qualitative basis. The c-axis wave function overlap integral which influences conduction can be expected to decrease exponentially with increasing separation of the carbon layers, thus the resistance ratio should increase exponentially with d_c as observed. Moreover, the ammonia content controls the amount of charge which is backtransferred from the carbon layers of MC₂₄ to the M-NH₃ layers so the resistance should increase with x_{max} and decrease with the area of the alkali ion, r_m^2 , because this area sterically limits the value of x_{max} .

In Fig. 3 we show the a-axis relative resistances $(R/R_0)_a$ for the three alkali-ammonia GIC's as a function of ammonia pressure. As in the potassium



Fig. 3. a-axis Relative Resistance of $M(\rm NH_3)_{\rm x}C_{\rm 24}$ as a Function of Ammonia Pressure.

case which has been previously studied the Rb and Cs compounds exhibit a marked rise in $(R/R_{n})_{a}$ followed by a slight decrease with increasing ammonia pressure.

This decrease in resistance or increase in a-axis conduction with intercalant weight gain at constant stage is unique to the alkali-ammonia ternary GIC's and is associated with a 2D MIT in the MA monolayers.

As ammonia is inserted with increasing pressure, a value of P_{NH_3} is reached at which additional ammoniation results in the back transfer of charge from the carbon layers to the MA layers. Initially this charge is localized in the MA layers and the reduced carrier density in the C layers which conduct in parallel causes the rise in a-axis relative resistance. However, when sufficient charge backtransfer occurs to produce wave function overlap in the a-plane, a MIT occurs in the MA layers and their parallel contribution to the conduction causes the a-axis relative resistance to drop. Note that this drop is not a manifestation of the staging phase transition since it does not occur at an ammonia pressure at which the c-axis relative resistance shows a sharp rise.

It is known from optical [6] and NMR measurements [5] that the potassiumammonia GIC's are donor compounds and the same can be reasonably assumed for the Rb and Cs species with ammonia. From a knowledge of the electrical anisotropies of the MC_{24} binary GIC's and the data of Figs. 1 and 3, one can deduce that the MA ternary GIC's exhibit some of the highest anisotopies yet reported for stage-1 donor compounds. For example, at an ammonia pressure of about 1 atm the potassium compound has an anisotropy of 1.6×10^5 which is a factor of a thousand higher than that of a typical stage-1 donor GIC. The extreme anisotropy of the MA GIC's provides additional confirmation of the 2D nature of the conduction process in those novel materials.

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EVIDENCE FOR A 2-DIMENSIONAL METAL-INSULATOR TRANSITION IN POTASSIUM-

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We have studied the ammonia pressure dependence and composition dependence of the a-axis electrical resistivity of the potassium-ammonia ternary graphite intercalation compounds $K(NH_3)_{x}C_{2x}$, 0 < x < 4.33. Our results show evidence of the 2D analog of the well-studied bulk 3D metal-insulator transition [1] in bulk K-NH₃ solutions.

In order to probe the electrical properties of the intercalate layer in K(NH₃) C_{2*} , we measured the in-plane a-axis resistivity as a function of ammonia pressure [2]. For convenience, we used a benzene-derived onion skin-like graphite fiber [3] rather than HOPG. Thus, the fiber axis is approximately coaxial with the cylindrical graphite planes. From the (001) x-ray diffraction patterns of a single fiber (see Fig. 1) we determined the basal spacing of the pristine fiber (d = 3.35Å), of stage-2 KC_{2*} potassium binary GIC (d = 8.74Å) and of the stage-1 ternary GIC K(NH₃)₄₋₃C_{2*} (d = 6.64Å). These results indicate that the graphite fiber has the same Gibbs phase diagram [4] as HOPG.

A four-probe measurement technique was developed for monitoring the pressure dependence of the a-axis relative resistance (R/R_{-}) of $K(NH_{3})_{-}C_{2*}$, using a pressure up-quenching technique. [Here $R(R_{-})$ is the a-axis resistance of the ammoniated (KC_{2*}) compound.] The result is plotted in Fig. 2. Note that the relative resistance ratio remains a constant below one atmosphere and then starts to increase in the stage-2 to stage-1 phase transition region at =0.5 atm. [5]. The increasing resistivity in a stage-2 to stage-1 phase transition is a common feature of binary GIC's [5]. But when NH, is added to KC_{2*} , some delocalized electrons in the carbon layer are back-transferred to the intercalate layer [6] so that the conductivity of the carbon layers decreases. However, R/R_{-} starts to decrease dramatically at about 3-4 atm. at which pressure x Is greater than four [6]. This phenomenon may be a consequence of a 2D metal-insulator transition. When x = 4, there are enough NH₃ molecules to completely solvate potassium and form a 4-fold coordinated K-NH₃ clusters [7]. Higher NH₃ concentration leads to a sufficient amount of electron back-transfer



Fig. 1. The (001) x-ray diffraction patterns of (a) a single pristine cylindrical onion skin-like graphite fiber, (b) the same fiber as in (a) after intercalation with potassium to form the binary GIC KC_{2*}, and (c) the same fiber as in (b) after ammoniation to form the ternary GIC K(NH₃)_{h 3}C_{2*}. The diffraction patterns were recorded at room temperature using MoKa radiation. The background continuum is diffuse scattering from the glass envelope and from air in the beam path.



Fig. 2. The room temperature relative resistance a-axis ratio R/R of potassium-ammonia-graphite as a function of ammonia pressure. Here R and R correspond respectively to the resistance of KC_{24} and $K(NH_{24})_{1}C_{24}$.

from the graphite layers to the intercalate layers to induce a hopping-type metal-insulator transition [8]. When there is sufficient solvation to cause in-plane overlap of the electron wave function, the intercalate layer starts to conduct in parallel with the carbon layers and the a-axis resistance drops as is observed in Fig. 2. The study of the composition dependence of the dielectric constant of $K(NH_3)_{x}C_{2x}$ also provides evidence of a metal-insulator transition at x = 4.

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OPTICAL AND ELECTRICAL MEASUREMENTS OF POTASSIUM-AMMONIA-GRAPHITE: EVIDENCE FOR A METAL-NON METAL TRANSITION

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The potassium-ammonia ternary graphite intercalation compound, $K(NH_3)_x c_{24}$, $0 \le x \le 4.38$, has been shown to have intriguing properties such as a staging phase transition [1,2] and a simple unmodulated 2D metal-ammonia liquid structure of the intercalate layer [3]. These properties induce more extensive studies of metal-ammonia GIC's. Here we will report the results of electrical resistance measurements of potassium-ammonia graphite in both the c-axis and a-axis directions. We also report optical reflectivity measurements carried out with the incident light approximately normal to the basal planes.

The samples that we used in the c-axis measurements were prepared from highly oriented pyrolytic graphite (HOPG). Pure binary stage-2 KC_{pu} was exposed to ammonia vapor the pressure of which was controlled by cotrolling the temperature of an attached ammonia reservoir. A four-probe method was employed in the resistance experiment. By stepwise increasing the ammonia pressure, we obtained the c-axis relative resistance ratio R/R_0 of $K(NH_3)_x C_{24}$ versus ammonia pressure as shown in Fig. 1a. Here, ${\rm R}_{\rm o}$ is the resistance of the binary $KC_{2\mu}$ compound and R is the saturation resistance of the ammoniated compound at various ammonia pressures. Clearly, the c-axis relative resistance ratio exihibits two step-like plateaus at ammonia pressures of approximately 5 x 10^{-3} atm. and 0.5 atm. The first plateau with a resistivity increace of 10% is due to the ammonia weight gain of KC_{24} at a constant stage-2 composition. The sample expanded macroscopically as ammonia entered the potassium-occupied galleries between the carbon layers, and this expansion is the source of the small c-axis resistance increase. In contrast, the second plateau with a 100-fold relative resistance ratio increase is associated with a stage-2 to stage-1 phase transition which has been studied by (001) x-ray diffraction. Besides the expanding gallery, the charge back-transfer from the carbon layers to the intercalate layers through this transition [1] also contributes to the large c-axis relative resistance ratio increase.

We also measured the a-axis relative resistance ratio of potassiumammonia graphite using individual graphite fibers with a cylindrical onion skin morphology and four-probe AC and DC techniques. The results of this measurement are plotted in Fig. 1b. Compared with c-axis measurement, the inplane relative resistance ratio also increases at the staging phase transition, but by only a factor of approximately 3. Moreover, it shows a significant decrease at an ammonia pressure corresponding to a composition of $x \sim 4$ while the c-axis ratio is essentially flat in that composition range. In analogy with the famous metal-insulator transitions in the bulk 3D metalammonia solutions [4], we suggest that the drop in the a-axis relative resistance ratio is associated with a metal-nonmetal transition in the 2D potassium-ammonia liquid layer.

Optical reflectivity measurements also provide evidence for this metalinsulator transition. In Fig. 2 are shown composition_dependent plots of the imaginary part of the complex dielectric constant of $K(NH_3)_x C_{24}$ (derived from the optical reflectivity using a Kramers-Kronig analysis) as a function of incident photon energy. The sharp peaks at -2eV in the x = 4.1 and x = 4.3spectra have never before been observed for any GIC, the typical optical response of which is shown for KC_{2h} in the inset of Fig. 2. These peaks can be accounted for phenomenologically by adding a Lorentzian oscillator contribution at 1.85 eV to ε_2 as shown schematically in Fig. 2. We associate this Lorentzian oscillator with an optical transition of the localized solvated electron in the potassium-ammonia layer, again in analogy with bulk potassium-ammonia solutions [4]. Note, however, that the oscillator strength of the 1.85 eV excitation decreases with increasing ammoniation in the composition range x > 4.0. This decrease results from the wave function overlap and delocalization of the electron charge that is back-transferred to the K-NH, layers. The reduction in the bound/localized state density and concommitant charge delocalization in the intercalant layer also generates the observed decrease in the a-axis relative resistance ratio.

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Fig. 1. Relative resistance ratio R/R_0 of $K(NH_2) C_{24}$ as a function of ammonia vapor pressure (P_{NH_2}) . (a)c-axis ratio (b) in-plane (a-axis) ratio.



Fig. 2. The imaginary part of the complex dielectric constant of $K(NH_3) \propto_{24} vs.$ incident phonon frequency for x = 4.1 and x = 4.3. The corresponding plot for the pure stage-2 KC_{24} is shown in the inset.