TWO-DIMENSIONAL METAL-AMMONIA-SOLUTIONS IN GRAPHITE

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Abstract - The preparation structural properties and electrical properties of metal-ammonia-solutions intercalated into graphite are briefly reviewed. It will be shown that the metal-ammonia-solutions in graphite are both the two-dimensional structural and electrical analogues of the more familiar bulk three-dimensional metal-ammonia solutions. These conclusions are supported by the results and interpretations of a number of physical measurements including elastic X-ray and neutron scattering, anisotropic transport studies and optical reflectivity studies.

1. Introduction.

Lamellar solids are characterized by pronounced anisotropy in the interatomic forces which bind them such that the forces between atoms lying in the layer planes are considerably stronger than the forces between the planes themselves.¹ This bonding anisotropy gives rise to corresponding anisotropies in the physical properties of lamellar solids, the most dramatic of which is the property of intercalation.¹⁻⁴ When intercalation occurs one or more foreign or guest species is inserted into the galleries between the host layers in such a manner as to leave the layers themselves essentially undistorted.

The prototypical lamellar solid is graphite which, in its pristine form, is a monatomic semimetallic solid whose hexagonal structural form⁵ is shown in Fig. 1. Notice from Fig. 1. that the interatomic distance within the graphitic planes is 1.42Å whereas the interplanar distance is more than twice as large, 3.35Å. Thus while graphite is harder than diamond with respect to intralayer tensile forces, its interlayer bonding is of the Van der Waals type and is therefore quite weak.

Graphite, like other lamellar solids, forms a wide variety of intercalation compounds referred to as GICs (for graphite intercalation compounds) but GICs

Fig. 1. The crystal structure of hexagonal graphite. Both solid and open circles correspond to carbon atoms. The lattice parameters are $a_0=2.45\text{\AA}$ and $c_0=6.70\text{\AA}$

exhibit two properties which are novel if not unique. First, because graphite is amphoteric its layers can accept electronic charge from or donate charge to the intercalated species. This charge exchange process is a collateral requirement for intercalation in graphite in contrast to most other lamellar solids, e.g. layered aluminosilicate clays, where intercalation merely involves ion exchange at fixed host layer charge.¹ When an electron donor such as one of the alkali metals is intercalated into graphite a donor GIC is formed whereas electron acceptors such as AsF_5 form acceptor GICs. A second novel property of GICs is staging. Graphite can form compounds in which every interlayer gallery space contains guest species, or every other gallery, every 3rd gallery, or every n^{th} gallery to form, respectively, a stage-1, stage-2, stage-3, stage- n GIC. This property of staging in GICs is illustrated schematically in Fig. 2. Note that the guest layer depicted in Fig. 2. has a variety of structural and chemical forms. If it contains only one species a binary (B) GIC is formed. Ternary (T) and higher order GICs are also quite common. The guest layers may also be crystalline and either commensurate or incommensurate to the host or they may exhibit various disordered forms including, liquid, glass and lattice gas.³

Fig. 2. A schematic representation of the property of staging. The solid lines represent the carbon layers and indicate the lateral displacements of the carbon atoms (full circles). The broken lines represent the intercalated layers.

One of the most interesting classes of GICs are the alkali-ammonia TGICs, $M(\text{NH}_3)_x\text{C}_y$, where M is an alkali metal. Although these compounds were first synthesized by Rudorff and coworkers⁷ in the early 1950's it was not until the mid 1980's that Solin and coworkers⁸⁻¹² began extensive physical investigations of them with particular emphasis on the potassium-ammonia compounds, $\text{K}(\text{NH}_3)_x\text{C}_{24}$, $0 \leq x \leq 4.38$. Solin suspected that the K-NH_3 monolayers in graphite might constitute the 2D analogue of the famous bulk metal ammonia solutions¹³ whose properties, particularly the metal-nonmetal transition, are so fascinating. Accordingly, the purpose of this brief review is to demonstrate that these suspicions were indeed well founded and to briefly review the evidence that justifies such a conclusion.

II. Synthesis.

Rudorff synthesized metal-ammonia TGICs by direct immersion of graphite powder into the bulk metal-ammonia solutions. This led to rapid exfoliation of the host which rendered the materials unacceptable for accurate physical measurements. To overcome this problem York and Solin⁸ developed a gentle

sequential intercalation method in which the stage-2 binary compound KC_{24} was exposed to NH_3 vapor under controlled conditions of temperature and pressure. Using this method and both gravimetric and volumetric measuring techniques, York and Solin⁸ have studied the room temperature ammonia absorption isotherm of stage-2 potassium-graphite. The results of their measurements of the dependence of x on ammonia pressure for $K(NH_3)_x C_{24}$ are shown in Fig. 3

Fig. 3. The variation in x with NH_3 pressure for the TGIC $K(NH_3)_x C_{24}$. The experimental points indicated by circles correspond to volumetric data. Full circles represent the initial intercalation of NH_3 ; those indicated by open circles are for de-intercalation. Gravimetric data are shown as open triangles.

which atypically spans fully five decades of both pressure and mole fraction of ammonia absorbed. The isotherm shown in Fig. 3 is characterized by three regions of pressure, a very low pressure plateau followed by a step-like increase in composition at $P_{\text{NH}_3} \approx 10^{-3} \text{ atm}$, a second plateau in the range $10^{-3} \text{ atm} \leq P_{\text{NH}_3} \leq 1 \text{ atm}$ with a step increase to a third quasi saturation plateau at about 1 atm. It should be noted from Fig. 3 that the ammoniation of KC_{24} is irreversible and that when the ammonia is gradually pumped off in a manner which avoids exfoliation, a residue TGIC is formed with variable but typical composition $\text{K}(\text{NH}_3)_{1.8}\text{C}_{24}$. According to York and Solin⁸ the residue results from a binding of the ammonia to the K^+ ions at defects in the host graphite. Complete reversibility is obtained for cycling between the residue compound and the maximal composition $\text{K}(\text{NH}_3)_{4.38}\text{C}_{24}$ which is the limiting value determined by the vapor pressure of ammonia at room temperature, 9.5 atm.¹⁴

III. Structure.

In addressing the structural properties of lamellar solids it is convenient to subdivide them into two categories, the c-axis stacking arrangements and the inplane structure of the guest layers. One can then treat the interplay between these categories. Consider first the dependence of the interplanar or stacking arrangements on the ammonia vapor pressure. The dependence of the c-axis structure of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ on composition was ascertained from pressure-dependent in-situ (001) X-ray diffraction measurements such as those shown in Fig. 4 which are from the work of York and Solin.⁸ Those measurements correspond to the reversible ammoniation path indicated by the open circles in Fig. 3 and show the desorption-induced transition from a pure stage-1 ternary phase (panel a) through an admixture of stage-1 and stage-2 ternary phases (panels b and c) to an essentially pure stage-2 ternary phase with a slight admixture of BGIC's on the surface of the compound. Notice that the (001) reflections in Fig. 4 are very sharp and, in the case of the pure stage-1 phase (panel a), resolution limited. This indicates a c-axis extended correlation length in excess of 5000 Å which is unusually large for GIC's in general^{2,15} and TGIC's in particular.

In-situ X-ray measurements carried out during the initial ammoniation of KC_{24} provide an explanation of the absorption isotherm of Fig. 3. According to York and Solin⁸, the low pressure plateau in Fig. 3 represents a region in which a small number of NH_3 defects are present in the potassium filled galleries of KC_{24} . The step at $\approx 10^{-3} \text{ atm}$ corresponds to an activation region in which considerably more ammonia enters the stage-2 structure which persists to a pressure of $\approx 1-3 \text{ atm}$. In that ammonia pressure range, the second step-like rise in composition occurs and it is associated with a stage-2 to stage-1 phase transition. During the whole process of ammoniation, the K/C ratio is constant but at the staging phase transition, the potassium layer stoichiometry transforms from KC_{12} to KC_{24} . It is

important to note for the subsequent discussion that the staging phase transition occurs at $x = 4.0$ and that further ammoniation up to $x = 4.38$ leads to increased ammonia inplane density but not to further stacking changes.

Fig. 4. The evolution of the (00l) X-ray diffraction patterns of $\text{K}(\text{NH}_3)_x \text{C}_{24}$ with ammonia pressure, P_{NH_3} : (a) $P_{\text{NH}_3} = 9.5 \text{ atm}$; (b) $P_{\text{NH}_3} = 1.6 \text{ atm}$; (c) $P_{\text{NH}_3} = 0.11 \text{ atm}$; (d) $P_{\text{NH}_3} = 10^{-3} \text{ atm}$. Reflections associated with the stage-n TGICs are labeled $n(00l)$ while those associated with potassium binary compounds are labeled $nK(00l)$.

Fig. 5. The variation in the c-axis repeat distance of the stage-1 component of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ with ammonia pressure. The solid line and circles correspond to pressurization. The dashed line and solid triangles refer to depressurization. The lines are a guide to the eye.

In order to probe the limits of the ammoniation of KC_{24} Qian and Solin⁹ used a modified diamond anvil high pressure technique to study the diffraction at ammonia pressures up to 11kbar. In their experiments, the ammonia served as both the pressure transmitting medium and the intercalant. They found that at pressures above 10bar the pure stage-1 TGIC evolved into an admixture of stage-1 and stage-2 components with saturation NH_3 compositions of $x=4.5$ and 5.4, respectively. The ammonia pressure dependence of the c-axis repeat distance of the stage-1 component observed by Qian and Solin⁹ is shown in Fig. 5. Similar results were observed for the stage-2 component. The discontinuities at about 3.5 and 8.0kbar were attributed to inplane coordination changes in the K/NH_3 ratio.

Solin and coworkers have carried out extensive investigations of the inplane structure of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ using diffuse elastic X-ray¹⁰ and neutron¹¹ scattering methods coupled with computer simulations of the diffraction patterns. The observed inplane diffuse X-ray and neutron patterns are shown as solid lines in Figs. 6 (a) and (b), respectively. The dotted lines in that figure correspond to computer simulations based on a structural model with the following features:^{10,11}

Fig. 6. X-ray (a) and neutron (b) elastic diffraction patterns of $\text{K}(\text{NH}_3)_{4.33}\text{C}_{24}$ and $\text{K}(\text{ND}_3)_{4.33}\text{C}_{24}$, respectively. The solid lines are experimental measurements and the broken lines are simulated patterns based on computations described in the text.

1. The K^+ ions and the NH_3 (ND_3) molecules were treated as hard infinitely thin discs oriented with their planes parallel to the carbon planes and located at the mid-point of the gallery along the graphite c-axis.

2. The radii of the K^+ discs were identical and fixed at a value of $1.46\text{\AA}$ which gave the best fit to the X-ray diffraction pattern consistent with the charge exchange to the graphite layer.

3. The radii of the ammonia discs were variable and depended on the basal plane projection of the ammonia cross-section. The distribution of ammonia radii $P(r)$ was modeled on the basis of NMR measurements¹⁶ to be

$$P(r) = C \left\{ e^{\left[-\frac{(r-r_{\min})^2}{(\delta r)^2} \right]} - e^{\left[-\frac{(r_{\max}-r_{\min})^2}{(\delta r)^2} \right]} \right\} \quad (1)$$

where C is a constant, $r_{\max} = 2.00\text{\AA}$, $r_{\min} = 1.30\text{\AA}$, and $0 \leq \delta r \leq 0.3\text{\AA}$.

4. The 2D liquid was assumed to contain two types of ammonia molecule, those which are 4-fold coordinated to potassium ions and those which are dynamically unbound. The 4-fold coordinated K-NH_3 (K-ND_3) clusters which resulted were assembled in a symmetric configuration so that the lines connecting the center of the K^+ disc to each of the NH_3 (ND_3) discs in a cluster made equal angles of $\pi/2$.

5. The computer-generated collection of K-NH_3 (K-ND_3) clusters and free discs was assembled in such a way as to maximize the in-plane density. The model contained 500 K^+ discs and 2165 NH_3 (ND_3) discs satisfying the stoichiometry $\text{K}(\text{NH}_3)_{4.33}\text{C}_{24}$ where $2165/500 = 4.33$.

6. The effect of the graphite substrate potential on the structure of the liquid was ignored.

In addition to the 4-fold coordinated cluster distribution referenced in item 4 above, other distributions with 3-fold and 0-fold coordination were tested by Qian et al.¹⁰ but were found to give inferior results. The mathematical details of the calculations of the diffraction patterns shown in Fig. 6. are extensively described elsewhere^{10,11} and need not be reiterated here.

As can be seen from Fig. 6 the amplitudes, positions, and widths of the dominant experimental features have been reasonably accounted for with the model which has very few adjustable parameters. These results show that the dominant structural features of the potassium ammonia monolayers in graphite are that they are 2D liquids at room temperature and that the potassium ions are 4-fold coordinated to the ammonia molecules. For $x > 4$ the added molecules can be characterized as spacers. Note that potassium in the bulk (3D) potassium-ammonia solution is 6-fold coordinated to ammonia.¹³ However, such an octahedral cluster is too large to fit in the measured basal spacing/gallery height of the intercalation compound. But if the apical molecules of the octahedral cluster are removed, the residual 4-coordinated unit fits nicely into the graphite host. Thus the potassium-ammonia monolayers are indeed the 2D structural analogue of bulk potassium-ammonia solutions.

IV. Electronic Properties and the metal-nonmetal transition.

The ammoniation of KC_{24} to form $\text{K}(\text{NH}_3)_x\text{C}_{24}$ has a pronounced effect on the distribution of electronic charge in the layered system for values of $x > 4$. In the binary compound KC_{24} the charge exchange, f , from the potassium layer to the carbon layers is ≈ 1 . York and Solin⁸ showed from X-ray studies of the x -dependence of the basal spacing of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ that

$$f = \begin{cases} 1 \\ 1 - \gamma(x-4) \end{cases} \text{ for } \begin{cases} x \leq 4 \\ x \geq 4 \end{cases} \quad (2)$$

where γ is a constant. The physical meaning of Eq. (2) is that as ammonia molecules are inserted in the graphite gallery they contribute to the formation of the 4-fold clusters around the potassium ions. Once this clustering is complete, i.e. at $x = 4$, additional molecules create solvation sites with the clusters and these sites promote a backtransfer of electron charge from the graphite layers to the potassium-ammonia layers. This charge backtransfer is linear with x as can be seen from Eq. (2). According to Huang et al.¹⁷ the most probable form of the solvation site is a sandwich in which the electron lies between back-to-back planar triads of hydrogens one triad being from the spacer molecule and one from a molecule on the 4-fold cluster.

Solin and coworkers¹² reasoned that at sufficient levels of charge backtransfer the electrons in the potassium-ammonia layers might become delocalized in which case these guest layers would undergo a composition (x) driven metal-nonmetal transition akin to the transition observed in bulk 3D metal-ammonia solutions.¹³ To test this notion Huang et al.¹⁷ studied the composition dependence of the electronic transport in $\text{K}(\text{NH}_3)_x\text{C}_{24}$ along the c -axis direction and in the basal plane. Their measured inplane and c -axis relative resistance ratios R/R_0 are shown in Fig. 7. Here R_0 is the resistance at $x=0$. The c -axis data of Fig. 7. exhibit three plateau-like regions which are separated by two step-like rises at ammonia pressures of approximately 0.003atm and 0.2atm. The pressure dependence of $(R/R_0)_c$ is very similar to the absorption isotherm given in Fig. 3. Accordingly, Huang et al.¹⁷ have attributed the two observed steps to ammoniation of the stage-2 TGIC and to the stage-2 to stage-1 phase transition. They argued that the increase in gallery height which results from ammoniation reduces the c -axis electronic wave function overlap and thus increases the resistance in the c -axis direction. This increase is small in the region of the mild ammoniation of the stage-2 TGIC but is pronounced at the staging phase transition when ammonia becomes the dominant species in all of the galleries.

In contrast to the c -axis data, $(R/R_0)_a$ the a -axis data as measured by Huang et al.¹⁷ exhibits only a single step-like rise at about 2.0atm which corresponds to a

composition of $x = 4.0$. This rise is followed by a noted but shallow drop which has been interpreted as evidence for the metal-monmetal transition in the metal-ammonia monolayers.¹⁷ Specifically, Huang et al.¹⁷ note that the charge which is initially back-transferred to the metal-ammonia layers for $x < 4$ reduces the carrier density and thus the in-plane conduction contribution of the carbon layers. However, when the charge per unit area is below the threshold for a metal-monmetal transition, the back-transferred charge is localized in solvation cages in the metal-ammonia monolayers in analogy with the 3D solvation in bulk metal ammonia liquids.¹³ According to Huang et al.¹⁷ and to Solin¹⁸ this solvated

Fig. 7. The $T = 300\text{K}$ c-axis (o) and a-axis ($\square$) relative resistance ratios of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ as a function of NH_3 vapor pressure or x : (a) $\log_{10}[(R/R_0)_a]$ and $\log_{10}[(R/R_0)_c]$; The insets in (a) indicate the structure and composition ($\bullet \rightarrow \text{K}^+$; $\Delta \rightarrow \text{NH}_3$) in the region of the corresponding plateau while the inset in (b) depicts parallel conduction in the C (graphite) and potassium-ammonia layers. The solid lines are a guide to the eye.

charge does not produce a parallel conduction contribution from the metal ammonia layers so the net effect of ammoniation for $x < 4$ is an increase in a-axis relative resistance as is observed. But when ammoniation is sufficient to produce an areal electron density in the metal ammonia layers which exceeds the threshold for a 2D metal-nonmetal transition, the metal ammonia layers conduct and their parallel contribution to the a-axis relative resistance results in a drop in $(R/R_0)_a$ as is observed in Fig. 7 for $x > 4$.

Fig. 8 The room temperature optical reflectance (solid lines in insets) and Kramers-Kronig derived imaginary part of the dielectric function $\epsilon_2(0, \omega)$ (solid lines in main figures) of $K(NH_3)_x C_{24}$ for several values of x . The broken curves are obtained from the solid curves by subtracting the dotted curves which are Lorentzians.

Optical studies of the complex dielectric function by Huang et al.^{17,19} and by Zhang et al.²⁰ provide direct confirmation of the metal-nonmetal transition as do their quantitative calculations. The optical data are shown in Fig. 8 and reveal a narrow absorption band at 1.85eV which grows in intensity with ammonia content until $x = 4$ at which value its intensity drops precipitously. Huang et al.^{17,19} attributed this band to a localized state of the solvated electron²¹ which loses oscillator strength when delocalization occurs at the metal-nonmetal transition. In a calculation which is based on the 2D analogue of the Mott criterion²² for a metal-nonmetal transition, Huang et al.¹⁷ showed that the transition in $K(NH_3)_x C_{24}$ occurred at the predicted value of the critical areal electron density n_c given by $(n_c)^{1/2} a_H = 0.31$ where a_H is an effective Bohr radius. Thus the metal-nonmetal transition in potassium-ammonia TGICs is indeed analogous to the corresponding transition in bulk metal-ammonia solutions. Note, however, that the transition occurs with increasing ammoniation in contrast to the metal-nonmetal transition in bulk metal-ammonia fluids which occurs with decreasing ammonia content. Finally, the data of Fig. 7 can be used together with the known electrical anisotropy of KC_{24} to deduce the anisotropy of the potassium-ammonia TGIC which for $x > 4$ is as high as 5×10^5 . This is one of the highest anisotropies ever measured for a donor GIC and is further confirmation of the 2D character of the metal-nonmetal transition in potassium-ammonia-graphite.

V. Summary and concluding remarks.

We have focused here on the potassium-ammonia TGIC because this is the most thoroughly studied system and because space is limited in this brief review. It is important to note, however, that clear evidence exists for similar composition driven metal-nonmetal transitions in both $Cs(NH_3)_x C_{24}$ and $Rb(NH_3)_x C_{24}$. The physical properties of other (non-alkali) metal-ammonia TGICs such as those formed with europium have not yet been investigated. Nevertheless, one suspects that these systems will also exhibit a 2D metal-nonmetal transition and that such behavior is a universal characteristic of metal-ammonia TGICs.

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