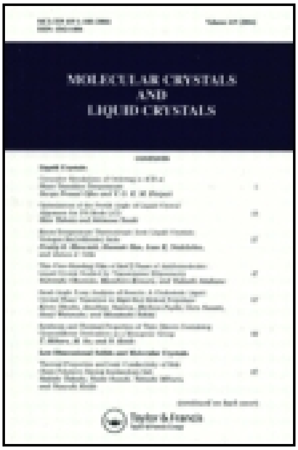

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Atomic Level Observation of Early Events in Molecular Intercalation: Preintercalation Host-Layer "Loosening" and the Role of Elastic Strain

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Atomic Level Observation of Early Events in Molecular Intercalation: Preintercalation Host-Layer "Loosening" and the Role of Elastic Strain

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Dynamic high-resolution transmission electron microscopy (DHRTEM) has been used to follow the early events in ammonia/2H-TaS_2 intercalation. This molecular intercalation process is characterized by two intriguing transient partial gallery expansions of 0.6 and 1.4 Å, prior to and during intercalation, respectively. These expansions do not persist throughout the intercalation process, eventually yielding to full gallery expansions of 3.0 Å. The former partial expansion was observed prior to intercalation during preintercalation ammonia adsorption on the basal planes and can be associated with a charge-transfer-induced host-layer "loosening" of the outermost guest gallery via octahedral-to-trigonal prismatic restacking of the adjacent host layers. The latter expansion is associated with the formation of a near planar ammonia species, which reduces the elastic strain energy for molecular intercalation.

Keywords: intercalation reaction processes; intercalation mechanisms; transition-metal disulfides; dynamic high-resolution transmission electron microscopy.

INTRODUCTION

Even though there has been widespread interest in the investigation of graphite and transition metal disulfide intercalation compounds,[1] relatively little is known about the early events that lead to intercalation and intercalation reaction mechanisms, especially at the atomic level. Such understanding is essential to understand the mechanism(s) that govern intercalation processes, chemical reactivity, and materials homogeneity and properties such as interlayer electronic and intralayer ionic conductivity.[1] In this *in situ* dynamic high-resolution transmission electron microscopy (DHRTEM) investigation, we directly observe some of the early events associated with molecular redox-rearrangement intercalation processes for the model intercalation system NH_3/2H-TaS_2. These processes result in intercalates with low levels of ammonium cointercalated with ammonia $(NH_4^+)_{y'}(NH_3)_{y''}TS_2^{y'-}$ (T=Ta, Ti and Nb and y'=0.08, 0.25, and 0.25, respectively; y' + y" can range up to 1.00, depending on the vapor pressure of ammonia over the intercalate).[2,3]

This study continues our efforts at elucidating the early events in intercalation reaction processes.[4-6] Previously, we have observed a preintercalation charge transfer state for these processes by scanning tunneling spectroscopy/microscopy.[4] In this investigation the structural effect(s) of preintercalation adsorbate charge transfer and the role of elastic strain in molecular guest deformation during intercalation are observed *in situ* via DHRTEM to provide a better understanding of the physical processes that govern intercalation reactivity.

EXPERIMENTAL

Stoichiometric 2H-TaS_2 was synthesized by direct reaction of stoichiometric amounts of the elements and handled under rigorous inert conditions, as described previously.[5] The host was characterized structurally by X-ray powder diffraction (**a**=3.315 and **c**=12.10 Å) and compositionally $(Ta_{1.000\pm0.003}S_2)$ by oxidative thermogravimetric analysis.[2,5] 99.999% ammonia was used as the intercalation reactant.

Thin crystal fragments suitable for DHRTEM were prepared by dry crushing at -196 °C in a helium containing glovebox (< 1 ppm O_2 and H_2O). The crystallites were dry-loaded on holey carbon grids in the glovebox and quickly transferred to the electron microscope column to minimize air exposure. Interlayer spacings and gallery expansions cited are the result of multiple measurements. The values presented are average values, with a statistical error of ± 0.3 Å. Outermost gallery expansions were observed to be constant over a range of focus and similar expansions were observed in internal galleries indicating any Fresnel fringe effects were minimal.[7]

DHRTEM studies were performed *in situ* using an environmental-cell equipped Philips 400T electron microscope (3.4 Å point-to-point resolution) operated at 120 kV with a Sony video-recording system (30 frames/sec). The images shown are taken directly from the videotape and view the host crystals parallel to their lamella. Reactant gas pressures were varied from 0.1 to 5 Torr and optimized to provide suitable reaction rates for DHRTEM observation.

RESULTS AND DISCUSSION

General Observations

Intercalation was only observed parallel to the host layers consistent with DHRTEM observations of $Hg_{1.24}TiS_2$ deintercalation processes[8] and macroscopic observations of the intercalation of highly-oriented pyrolytic graphite by Hooley et al.[9]

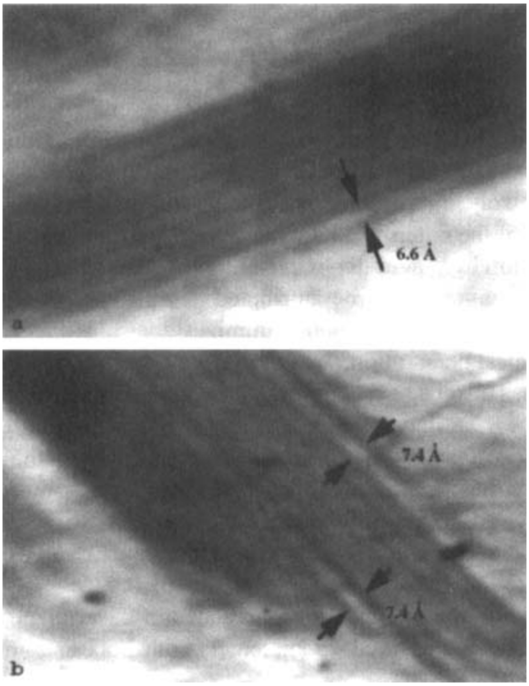

FIGURE 1 Partially expanded guest galleries: (a) basal-plane adsorption of ammonia results in expansion of the bottom gallery (6.0 to 6.6 Å host-layer repeat); (b) during intercalation, two galleries have partially expanded to host-layer repeats of 7.4 Å. The dark and light lines correspond to the host layers and galleries, respectively.

Ammonia intercalation processes were routinely observed to occur by the formation of guest-edge dislocations (GEDs) at the crystallite edges, followed by their lateral progression to fill the galleries.[5,6] The majority of these intercalation events progressed from side-to-side across the crystallite, instead of front-to-back or back-to-front, as observed by DHRTEM for $Hg_{1.24}TiS_2$ deintercalation.[8] This is associated with the dimensions of the crystallites suitable for DHRTEM study, where a less extensive GED termination front occurs for side-to-side intercalation, because the crystallites are typically much wider than they are thick. During intercalation, the GED front advances against both the host-layer separation energy and the strain activation energy associated with host-layer deformation. Hence, the intercalation activation energy should be less for a shorter GED termination front due to reduced elastic strain.

In addition to the observation of the gallery expansion of 3 Å expected for NH_3 intercalation,[5,6] two smaller partial gallery expansions were frequently observed during the early events in intercalation, 0.6 Å and 1.4 Å, as shown in Figure 1. These partial gallery expansions were generally transitory, eventually yielding to the full expected gallery expansion of 3.0 Å. The fully expanded galleries observed by DHRTEM are in good agreement with X-ray powder diffraction analysis of the 2H stage 1 intercalate (**a**=3.323 and **c**=18.20 Å) and its 3.1 Å gallery expansion.[3]

The Preintercalation State

The intercalation process was most often observed to start at the outermost galleries. This is consistent with the results obtained during the initial *in situ* DHRTEM investigations of NH_3 2H-TaS_2 intercalation, which supports a general outside-in lamellar intercalation process.[5,6] Such a process was originally suggested by Hooley, based on macroscopic observations of the intercalation of highly-oriented pyrolytic graphite that showed intercalation initially occurs in the outermost lamellar regions of the crystal, followed by the intercalation of progressively more interior lamellar regions of the crystal.[9] Enhanced reactivity of the outermost lamellar regions has also been observed for Ag/TiS_2 intercalation by Auger depth profiling.[10] The onset of intercalation in the outermost galleries can be attributed to the enhanced flexibility of the neighboring host layers, which minimizes the host-layer strain energy associated with guest penetration.

Adsorbate charge transfer has also been proposed as a possible mechanism for enhanced reactivity of the outermost galleries.[9] A recent ultrahigh vacuum scanning tunneling spectroscopy/microscopy investigation of the NH_3/TiS_2 intercalation process has identified a preintercalation state that includes pressure-independent adsorbate-host charge transfer up to the activation pressure required for intercalation to occur.[4] This state involves an ammonia-TiS_2 basal plane preintercalation charge transfer of 0.07 e^-/TiS_2 unit. Once the activation pressure for intercalation is reached, a basal plane charge transfer of 0.24 e^-/TiS_2 unit is observed, in agreement with bulk charge transfer studies.

Observations of the early events associated with the model NH_3/2H-TaS_2 intercalation process by DHRTEM often revealed a small (~10%) interlayer expansion across the outermost gallery as the initial event during the intercalation process, as shown in Figure 1a. The interlayer distance across the bottom outermost gallery has expanded 0.6 Å from the initial 6.0 Å layer repeat observed for 2H-TaS_2 to 6.6 Å. This small, but definite, gallery expansion was also observed in more internal galleries during the intercalation process, but only for galleries adjacent to at least one intercalated gallery.

Adsorbate-host charge transfer results in a partial negative charge on the host basal planes and the electrostatic repulsion of their neighboring host layers. These repulsions can be reduced by a restacking of the host layers about the outermost gallery from the octahedral stacking arrangement observed for the pristine host to a trigonal prismatic stacking of the sulfurs about the empty gallery lattice sites, resulting in a slight expansion of the gallery. Assuming the sulfur-sulfur distance across the octahedrally coordinated empty gallery for 2H-TaS_2 (**a**=3.314(1) and **c**=12.097(1)Å) [11] is similar to that for trigonal prismatic restacking of the gallery, a gallery expansion of 0.6Å is estimated, in good agreement with the observed expansion of the gallery. The observation of these small gallery expansions in internal galleries adjacent to intercalated galleries suggest the restacking process can be more generally associated with neighboring host-layer charge transfer.

Molecular Distortion of Ammonia during Intercalation

The transitory partial gallery expansion of 1.4 Å is also commonly observed during the DHRTEM observation of early intercalation processes. Figure 1b illustrates this partial expansion of the galleries early in the intercalation process for a crystallite under a pressure of 3.8 Torr. The interlayer spacing observed for these galleries is 7.4 Å. A similar phenomenon has been previously observed during an X-ray powder diffraction study of ammonia deintercalation for $Na_{0.25}^{+}(NH_3)_{y''}TiS_2^{0.25-}$, where $0.75 \geq y'' \geq 0.00$.[12] The fully intercalated material ($y''=0.75$) has an occupied gallery expansion of 3.35 Å, where the pseudo C_3 axis of the NH_3 is parallel to the host layers. Ammonia deintercalates at ambient temperature to form $Na_{0.25}^{+}(NH_3)_{0.12}TiS_2^{0.25-}$, with a dramatically reduced occupied gallery expansion of 1.32 Å, which is virtually identical to that observed for $Na_{0.25}^{+}TiS_2^{0.25-}$ (1.34 Å). To account for the observed expansion, it was proposed that ammonia must exist as a nearly planar species in the galleries, with its C_3 axis perpendicular to the host layers. This planar distortion of ammonia is apparently caused by the compressive force exerted on the galleries by the electrostatic attraction of the Na^{+} guests to the negatively-charged host layers, as the occupied gallery expansions for $Na_{0.25}^{+}(NH_3)_{0.12}TiS_2^{0.25-}$ and $Na_{0.25}^{+}TiS_2^{0.25-}$ are virtually identical.

Similarly, it may be energetically favorable for ammonia to initially adopt a distorted planar configuration during initial gallery penetration and intercalation, to minimize the elastic strain energy associated with the development and expansion of the guest-edge dislocation intercalation front within the gallery. This process should be enhanced energetically in the more rigid internal galleries, as shown in Figure 1b, where the elastic activation energy for intercalation is higher. The ability of ammonia to distort during intercalation arises from its relatively low energy of deformation compared to the observed intercalation energies. In particular, the above ammonia guest species may closely resemble the planar transition state structure associated with $NH_3(g)$ inversion, which requires 5.9 kcal/mol to occur.[13] Such a transient intercalant structure is feasible, since the distortion energy is smaller than the enthalpy decrease for ammonia intercalation (~ 8 kcal/mol NH_3).[14] Figure 2 illustrates a possible model for the transient nearly planar ammonia guest species located in trigonal prismatic gallery sites, with its pseudo C_3 axis perpendicular to the host layers.[12] N is located at the center of the trigonal prismatic sites, with the hydrogens directed at the centers of the rectangular faces of the trigonal prism. The plausibility of this near planar ammonia structure in terms of its interatomic distances has been previously discussed for ammonia in $Na_{0.25}{}^{+}(NH_3)_{0.12}TiS_2{}^{0.25-}$.[12]

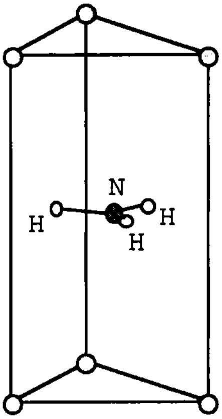

FIGURE 2 Possible model for near planar ammonia in the partially expanded (1.4 Å) galleries, in trigonal prismatic sites.[12]

Progression from Partial to Full Gallery Expansion during Intercalation

A typical progression from partial to fully expanded galleries during intercalation is shown in Figure 3. Initially, the gallery adjacent to the lower host basal plane partially expands by 0.6Å, as shown in Figure 3a. Within seven seconds, the lowest four galleries have intercalated, with the third from the bottom gallery partially expanded by 1.4 Å, as shown in Figure 3b. After eight seconds, the lower four and the upper two galleries have intercalated, with each of the galleries fully expanded with the exception of the 1.4 Å partially expanded third from the bottom gallery, as seen in Figure 3c. As the intercalation process continues, the partially expanded gallery appears to instantaneously "snap open" to the full gallery expansion of 3 Å observed in Figure 3d, consistent with the expected metastability of near-planar ammonia in the partially expanded gallery.

Although the $NH_4{}^{+}$ content in ammoniated 2H-TaS_2 is small (8%), occupying about one out of every 12 trigonal prismatic lattice sites, its relatively large ionic diameter (2.86 Å)[15] compared to the 1.4 Å partially expanded galleries suggests ammonium is not cointercalated in these partially expanded galleries. Consequently, ammonium formation/cointercalation apparently occurs during the transition between the 1.4 Å partially expanded and fully expanded (3.0 Å) galleries, together with ammonia reorientation.

The observed early events in lamellar intercalation underscore (i) the importance of physical mechanisms that govern intercalation in this and related system(s), including host-layer deformation and charge transfer and (ii)

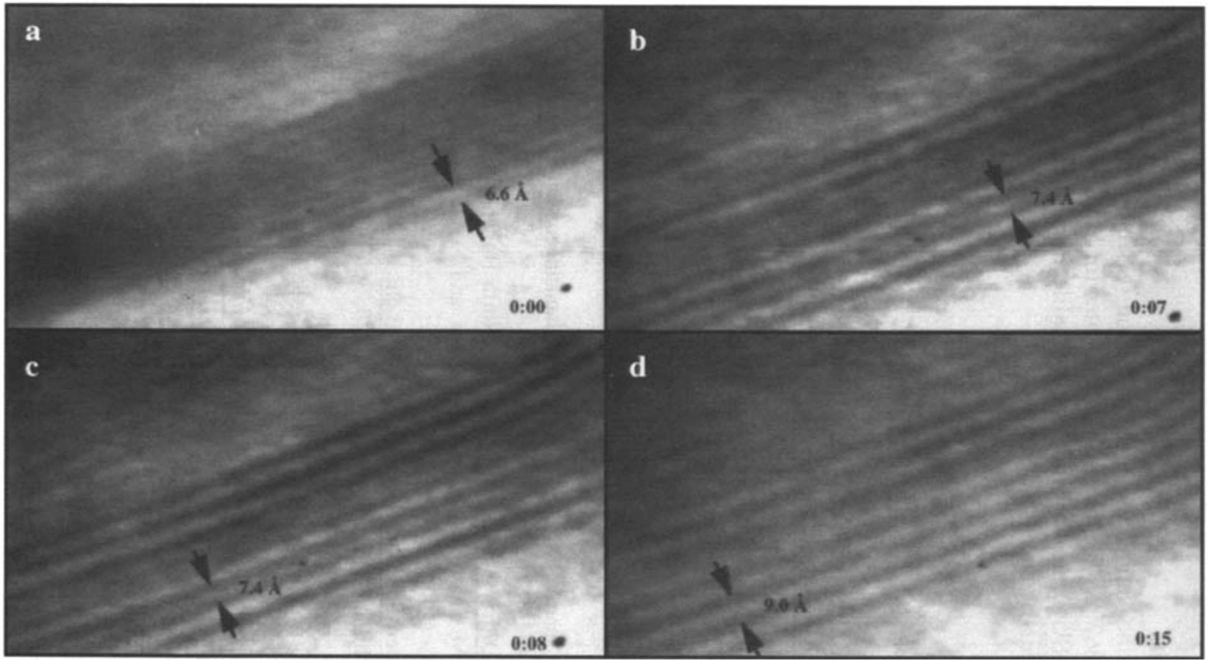

FIGURE 3 General progression of outside-in intercalation showing both partially and fully expanded galleries: (a) the lowest gallery host-layer repeat has partially expanded from 6.0 to 6.6 Å; (b) the lower four and uppermost galleries have intercalated with full gallery expansions (9.0 Å host-layer repeats), except the third from the bottom gallery has partially expanded (7.4 Å host-layer repeat); (c) the third from the bottom gallery remains partially expanded, while the second from the top gallery intercalates with full expansion; (d) the partially expanded gallery (7.4 Å interlayer repeat) "snaps" open to full gallery expansion. The dark and light lines correspond to the host layers and galleries, respectively.

that molecular guest species can deform during intercalation, enhancing their reactivity and kinetics. DHRTEM observations of the overall intercalation process, including internal and outermost gallery onset and progression, will be the subject of future publication.

Acknowledgments

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References

1. See, for example, (a) Intercalation Chemistry, M.S. Whittingham and A.J. Jacobson, Eds. (Academic Press, New York, 1982); (b) Chemical Physics of Intercalation II, P. Bernier et al. Eds. (Plenum Press, New York, 1993), and (c) Graphite Intercalation Compounds I, H. Zabel and S. Solin Eds., (Springer-Verlag, Berlin, 1990).
2. M. McKelvy and W. Glaunsinger, Annu. Rev. Phys. Chem. **41**, 497 (1990).
3. L. Diebolt, Ph.D. Dissertation, Arizona State University, 1996.
4. C. Wang, M. McKelvy and W. Glaunsinger, J. Phys. Chem. **100**, 19218 (1996).
5. M. McKelvy, R. Sharma and W. Glaunsinger, Solid State Ionics, **63-5**, 369 (1993).
6. L. Diebolt, R. Sharma, M. McKelvy and W. Glaunsinger Mater. Res. Soc. Symp. Proc., **404**, 183 (1996).
7. J.M. Cowley, Diffraction Physics, 2nd Ed., (North Holland, N.Y., 1990).
8. M. McKelvy, M. Sidorov, A. Marie, R. Sharma, and W. Glaunsinger, Chem. Mater. **6**, 2233 (1994).
9. J. Hooley, Mater. Sci. Eng. **31**, 17 (1977); Carbon, **18**, 82 (1980).
10. D. Kaluarachchi and R. Frindt, Phys. Rev. B, **28,** 3663 (1983), **31**, 3648 (1985).
11. A. Meetsma, G.A. Wiegers, R.J. Haange and J.L. deBoer, Acta Cryst, **C46,** 1598 (1990).
12. G. Burr, M. McKelvy and W. Glaunsinger, Chem. Mater., **5**, 1363 (1993).
13. C. Townes and A. Schawlow, Microwave Spectroscopy (Dover, N.Y., 1975).
14. M. McKelvy and W. Glaunsinger, J. Solid State Chem., **67,** 142 (1987).
15. Handbook of Chem. and Phys., 54th Ed., R. Weast, Ed., (CRC Press, Cleveland, 1973) p. F194.