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Mercury Intercalates of Titanium Disulfide: Novel Intercalation Compounds

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Relatively little is known about the intercalation of mercury into transition metal dichalcogenides (TMDs),[1,2] even though the high volatility of Hg relative to other metallic intercalants[1-6] and its ability to form clusters[7-14] suggest that the properties of these materials may be interesting. Therefore, this initial study was undertaken to help elucidate the reaction chemistry, thermal behavior, and structural features of this relatively unexplored system. As described below, we have found that Hg_xTiS_2 is indeed an unusual intercalation compound in all these respects.

Nearly stoichiometric TiS_2 ($Ti_{1.002}S_2$) was used as the host.[15] Triply distilled Hg (<5 ppm foreign metals) and TiS_2 were loaded into quartz ampules in a drybox, evacuated to $<10^{-4}$ Torr at −196 °C, and flame sealed. The gradual uptake of Hg by the host is apparent at ambient temperature. Samples were homogenized by annealing for 2 days at 320 °C, followed by slow cooling to ambient temperature.

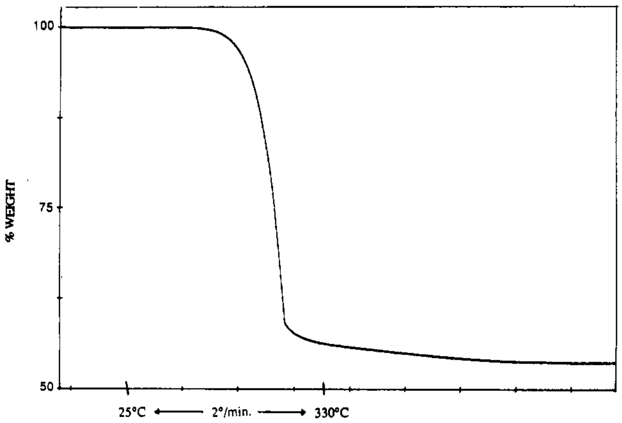

Figure 1. TGA of $Hg_{0.48}TiS_2$ using argon as the flow gas.

Sample compositions (x = 0.27, 0.48, 0.75, 1.03, 1.25, and 1.29 for Hg_xTiS_2) were determined by thermogravimetric analysis (TGA) with a 40 cm^3/min argon flow. It is interesting to note that the compositional limit of $x = 1.29$ corresponds to that expected if hexagonally-closest-packed elemental Hg monolayers completely fill the guest layers.

Both TGA and X-ray powder diffraction (XPD) demonstrate the thermal reversibility of the intercalation process. TGA of Hg_xTiS_2 shows that Hg begins to slowly deintercalate at about 170 °C, and substantial deintercalation occurs only above 250 °C and is complete at 330 °C (Figure 1). This behavior is distinct from elemental Hg, which volatilizes above 90 °C. TGA of the oxidation of the regenerated host at 900 °C reveals that it has essentially the same stoichiometry as the original host.[15,16] XPD of the deintercalated host indicates that it is also similar structurally to the original host. A slight expansion in c (0.003 Å) and some peak broadening were observed for the regenerated host, which can be attributed to slight disorder in host–layer registry.[16]

The XPD patterns observed for Hg_xTiS_2, where $1.29 \geq x \geq 1.00$, are almost identical and are characteristic of stage-one monolayer compounds having a 2.96-Å occupied layer expansion. For example, the diffraction pattern for $x = 1.25$ can be primarily indexed to a monoclinic unit cell, with a = 5.9209 (8) Å, b = 3.4074 (9) Å, c = 8.8662 (12) Å, and β = 102.352 (14)°, suggesting a change from AB to ABC sulfur stacking during intercalation. This indexing of the pattern accounted for 28 of the observed 38 reflections, which includes all of the major peaks as well as the first seven ($00l$) reflections. This cell can be viewed as a slight monoclinic distortion of a trigonal unit cell, with an 8.66-Å layer repeat distance. However, the above fit for $x = 1.25$ does not take into account reflections from an incommensurate Hg sublattice, which may be the origin of the 10 extra, relatively weak, reflections. Such incommensurability is indicated by the unusual composition observed for the fully intercalated stage-one compound ($Hg_{1.29}TiS_2$), where there are insufficient guest sites (one per Ti) to accommodate all of the guest species.

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Table I. Basal-Plane Lattice Parameter vs Guest–Host Charge Transfer for TiS_2 and Its Intercalates

compound	a,[a] Å	b,[b] Å	% charge transfer	ref
TiS_2	3.407[a]		00	(23)
$Li^+_{0.20}(NH_4^+)(NH_3)_{0.58}TiS_2^{0.22-}$	3.424[a]		22	(24)
$Li_{1.00}TiS_2$	3.452[a]		85	(21, 22)
$Hg_{1.25}TiS_2$	5.921[b]	3.407[b]	00	

[a] a is the basal plane parameter of the hexagonal cell, which is the effective host-layer sulfur diameter. [b] b is the basal plane parameter of the monoclinic cell that is equivalent to the hexagonal parameter a. It represents the closest S–S distance and hence the sulfur diameter. a is slightly larger than for the equivalent intralayer distance in TiS_2 ($a\sqrt{3}$ = 5.901 Å), suggesting the possibility of a small amount of covalent electron exchange.

XPD results for $x < 1.0$ are strongly dependent on the thermal history of the sample. In particular, ambient-temperature Hg intercalation produces a mixture of the stage-1 intercalate and the unintercalated host. However, after a 320 °C anneal and slow cooling to ambient temperature, the large d spacings and broad diffraction peak profiles observed suggest the presence of random staging. As previously observed for Hg_xTaS_2,[3] a minimum of x = 1 was necessary to induce long-range stage ordering. Above x = 0.48, no host lines were observed.

The stage-one nature of Hg_xTiS_2 for $x > 1.0$ was confirmed by high-resolution transmission electron microscopy (HRTEM) using a JEOL 2000FX microscope having 2.5-Å point-to-point resolution. By cooling $Hg_{1.25}TiS_2$ to −170 °C to avoid deintercalation in the microscope vacuum, a stage-one structure having an 8.7-Å layer repeat distance was observed (Figure 2a). Partial Hg deintercalation, induced by very slowly warming the same crystal to ambient temperature in the microscope vacuum, resulted in the randomly staged structure shown in Figure 2b.

These observations are in marked contrast to the distinct stage-one to stage-two transition observed for $Ag^+_{0.17}TiS_2^{0.17-}$ by XPD, neutron powder diffraction, and dynamic HRTEM, where apparently electrostatic interlayer guest–guest repulsions are primarily responsible for long-range stage ordering.[6,17] Clearly, the interlayer guest–guest interactions are much weaker for Hg_xTiS_2, suggesting a much lower level of guest–host charge transfer.

The thermal reversibility of Hg intercalation at relatively low temperatures also indicates unusually weak metal–host interactions, consistent with minimal Hg–TiS_2 charge transfer. These observations are contrary to the generally accepted view that guest–host charge transfer and the formation of ionic guest species are central to the metal intercalation process,[1,2,18] and prompted additional studies described below to assess the degree of guest–host charge transfer.

The ionic character of the intercalant Hg was probed by trying to ion-exchange Li^+ into Hg_xTiS_2 in an anhydrous $LiClO_4$/1,3-dioxolane solution for 3 weeks. The amount of exchanged Hg, determined by X-ray fluorescence, indicated that <0.0005 mol of Hg/mol of TiS_2 could be exchanged. This indicates essentially no Hg is individually ionized. However, the Hg guest layers could contain islands or layers that are very weakly ionized globally (i.e., Hg_n^{2+} for n large), since the ion exchange of such species may be difficult. The possible trace presence of Hg^+ ($5d^{10}6s^1$) was investigated by EPR from 4 to 480 K, but no signal was observed.

The effective host–layer sulfur diameter has been found to increase with increasing levels of guest–host charge transfer for TiS_2 intercalates, as summarized in Table I.[19,20] Since the sulfur diameters for $Hg_{1.25}TiS_2$ and TiS_2 are identical, as judged by the shortest intraplanar S–S distance, it appears that essentially no or very little guest–host charge transfer has occurred.

Further evidence consistent with diminished charge transfer comes from the ability of liquid ammonia to reduce $Hg_{0.27}TiS_2$, which is accompanied by the co-intercalation of NH_4^+. This reduction follows from the observation of N_2 evolution during intercalation and the deintercalation of NH_3 and $^1/_2H_2$ associated with the decomposition of NH_4^+.[16,25] Previous studies of TiS_2 intercalation compounds containing silver, alkali, and alkaline-earth metals indicate that ammonia can only reduce these materials if less than 0.24 ± 0.01 mol of e^-/mol of TiS_2 have been transferred to the TiS_2 conduction band.[16,24-27] Thus, any guest–host charge transfer for $Hg_{0.27}TiS_2$ is below this level.

The above observations indicate there is essentially no or very little charge transfer associated with the intercalation of Hg into TiS_2. A small amount of covalent electron exchange[1,2] is also possible based on these studies. Hence, we conclude that the primary driving force for Hg–TiS_2 intercalation is *not* the redox reaction of individual guest species with the host, as has been generally assumed for metal–TMD intercalation.

The thermal behavior of Hg_xTiS_2 was also studied by differential scanning calorimetry, and two endothermic events were observed between 30 and 360 °C. The high-temperature event, with an onset temperature of about 250 °C, is associated with the thermal deintercalation of Hg, as observed by TGA (Figure 1). The Hg deintercalation enthalpy is estimated to be 14 ± 1 kcal/mol of Hg, which is very close to the heat of vaporization for mercury in further support of weak Hg–host bonding.[28] Unlike the high-temperature event, the low-temperature transition, which occurs near 193 °C, is not associated with deintercalation and is reversible with thermal cycling below 220 °C (Figure 3). Elemental Hg, under similar conditions, shows no such transition. This transition must result from a structural rearrangement of intercalated Hg, since the transition enthalpy of 0.49 ± 0.02 kcal/mol Hg is independent of x ($0.27 \leq x \leq 1.29$) for Hg_xTiS_2. However, the nature of the rearrangement, and whether it is related to two-dimensional cluster formation[7-11] or melting, is unresolved. X-ray and neutron diffraction studies are presently underway to explore the structure of Hg_xTiS_2 both below and above the transition temperature.

In summary, we have found Hg_xTiS_2 to be a very unusual intercalation compound. Unlike other metal–TMD systems, Hg–TiS_2 intercalation is thermally reversible, and

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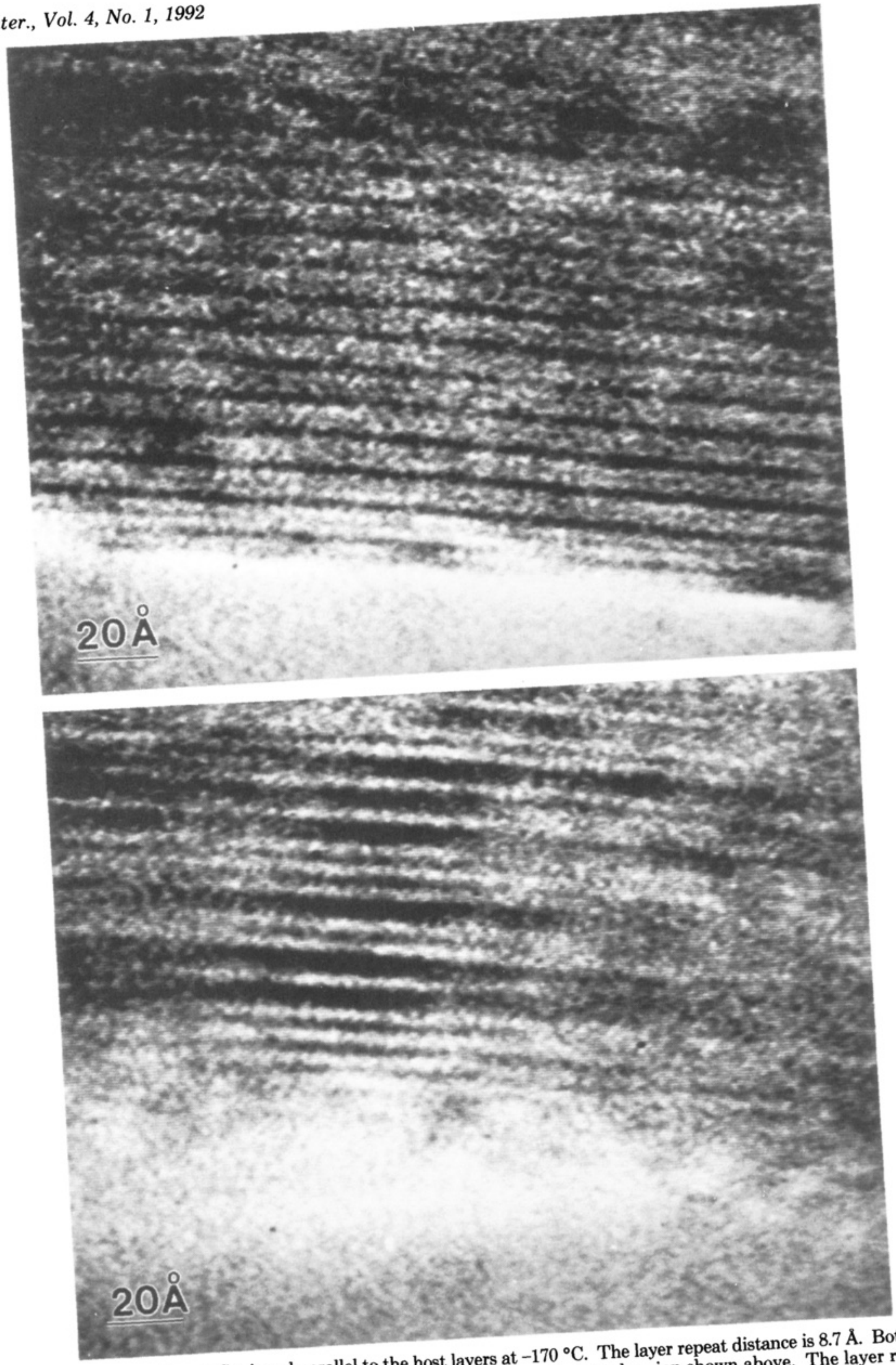

Figure 2. Top: Stage-one $Hg_{1.25}TiS_2$ viewed parallel to the host layers at −170 °C. The layer repeat distance is 8.7 Å. Bottom: randomly staged Hg_xTiS_2, $x \ll 1.25$, resulting from partial deintercalation of the same crystal region shown above. The layer repeat distances are 8.7 and 5.7 Å for the intercalated and empty TiS_2 layers, respectively. Note: There is a contrast reversal from above, which more clearly defines the layers.

the individual guest species appear to be essentially or very nearly neutral, which is contrary to the prevalent view that guest–host redox reactions and the intercalation of individual ionic guest species generally accompany metal intercalation into TMDs. Both very weak guest–host covalent electron exchange and a very small level of charge transfer, associated with globally, very weakly ionized Hg islands/layers, remain possible. Intercalated Hg also undergoes a reversible thermal transition, which may be related to cluster (island) formation or two-dimensional melting.

A detailed account of our studies for this novel system

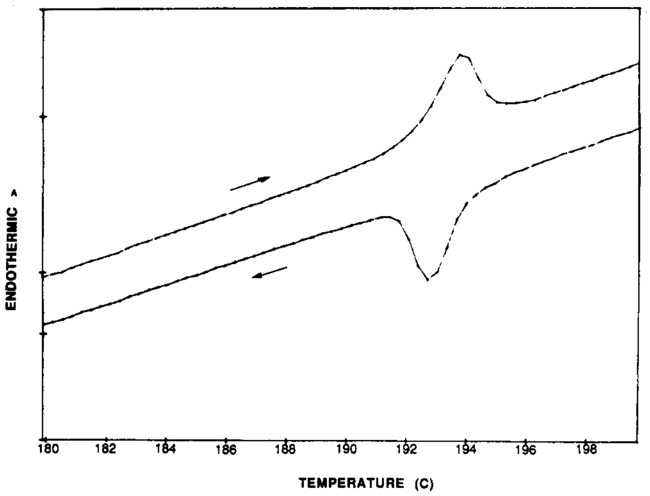

Figure 3. DSC of Hg_xTiS_2 showing the reversible thermal event near 193 °C. The event is endothermic on heating and exothermic on cooling. The absolute value of the associated enthalpy is 0.49 ± 0.02 kcal/mol of Hg and is independent of x for $0.27 \leq x \leq 1.29$.

will be published in the near future.

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Boron Nitride Fibers Processed from Poly(borazinylamine) Solutions

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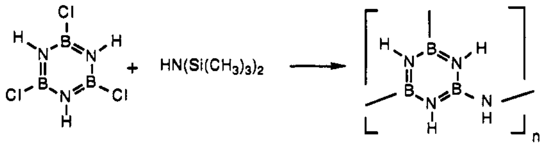
During the past 25 years, carbon fibers and filaments obtained from organic polymer solutions and melts have been intensively studied[1] due to their technological importance that is derived largely from the very high strength-to-weight properties found in carbon fiber/resin composites. Boron nitride, with a graphite-like structure, should be amenable to similar fiber and composite production with appropriate precursors. Indeed, the increasing utility of the polymer precursor approach to fiber research is illustrated by the development of other nonoxide fiber materials such as SiC,[2a-e] Si_3N_4,[2c-g] and AlN.[3] Further, the resistance of boron nitride to oxidation at high temperatures[4] and its dielectric properties offer foreseeable advantages over carbon fibers in certain applications. Despite their potential benefits, BN fibers are comparatively less studied than their carbon counterpart, and this is a direct consequence of a shortage of appropriate processible sources. However, recent progress in the development of boron nitride precursors including those obtained from decaborane cross-linked by amines,[5] nitrided poly-B_2O_3 melt-drawn filaments,[6] soluble borazinyl oligomers,[7] and poly(borazylene)[8] now permits more fruitful studies of BN fibers.

An amino-bridged borazine polymer developed in our group and illustrated in eq 1 is a useful precursor to BN



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ceramics.[9] It is soluble in liquid ammonia, and the concentrated solutions have favorable rheological properties for fiber production. Since the preceramic polymer is moisture sensitive, all manipulations of materials prior to pyrolysis were conducted under a dry atmosphere of N_2. The white gel polymer[9] was isolated by vacuum evaporation of volatiles and then transferred to a simple fiber-pulling jig. The jig consisted of a solution reservoir into which a glass rod with six drawing tips was lowered and raised on a pulley to draw fibers. A 30 wt % solution of the polymer in $NH_3(l)$ was obtained by condensation of anhydrous ammonia into the jig reservoir containing the polymer. The polymer/NH_3 solution was rapidly stirred at −78 °C, and the NH_3 was subsequently evaporated to

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