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Intercalation Complexes of Lewis Bases and Layered Sulfides: A Large Class of New Superconductors

Abstract. *Exploration of the generality of the recently discovered reaction whereby certain organic molecules can be inserted between the metallic layers of the superconductors tantalum disulfide and niobium disulfide revealed that a large variety of organic and inorganic molecules can penetrate between the crystalline layers of a number of transition metal dichalcogenides and that the resulting complexes are superconducting if the layered chalcogenide from which they are formed is superconducting. The critical temperatures of the 50 new superconductors we report depend on the nature of the intercalate but are insensitive to a separation of the superconducting planes of up to 57 angstroms.*

The compound $TaS_2(C_5H_5N)_{1/2}$ is a crystalline superconductor (critical temperature $T_c = 3.5°K$) in which metallic TaS_2 planes 6 Å thick are separated by layers of pyridine 6 Å thick (*1*). This structure was originally derived from x-ray diffraction data and has now been confirmed and extended by Fernández-Morán *et al.*, using electron microscopic imaging techniques [see (*2*)]. The pyridine complex and similar complexes that we report on here are probably the most anisotropic superconductors known. They are also the only crystalline metallic systems that are in large part organic, and, consequently, they offer us a unique opportunity to examine a number of speculations regarding interactions between conduction electrons and molecular electrons which might result in new kinds of superconductivity (*3*). As one should expect from their remarkable structure, such superconductors possess a number of unique superconducting properties. For instance, the depression of the critical temperature with magnetic field (dT_c/dH) is less in these materials than in any other known superconductor. Fields of 60 kilogauss applied parallel to the layer depress the critical temperature by only half a degree (*4*). Another unique feature of these superconductors is the apparent formation of evanescent Cooper pairs at temperatures in excess of ten times the critical temperature. A small diamagnetic contribution to the susceptibility is observed even above 50°K and grows slowly in a Curie-like manner as the temperature is lowered (*5*). It appears that constraining the electrons to motion along the TaS_2 planes in these crystals has enhanced the stability of evanescent Cooper pairs with the result that they are observed at higher temperatures than ever before. These results, the novelty of the materials, and the hope that some of the speculations regarding higher critical temperatures in such systems might be well founded have encouraged us to try to define the limits and nature of this new class of materials by examining TaS_2 and other layered chalcogenides and intercalates other than pyridine. In particular, we wished to determine whether the superconducting critical temperature could be affected in an understandable or dramatic way by varying the intercalate and whether the superconducting properties would be altered by increasing the distance between superconducting planes.

There are about 40 binary layered chalcogenides (*6*). We have prepared intercalation complexes of many of them. Some, however, are considerably more difficult to prepare and to characterize than others. Here we report only on our studies of the intercalation complexes of the group IV b and V b disulfides, especially TiS_2, NbS_2, and TaS_2. Titanium disulfide is a degenerate semiconductor, whereas NbS_2 and TaS_2 are superconducting metals. All three compounds are composed of parallel layers in which a plane of metal atoms is sandwiched between two planes of sulfur atoms. The atoms in each plane are arranged in a hexagonal array. Both NbS_2 and TaS_2 are polymorphic. Here we shall be concerned only with the 2H-phase of each. In the 2H-phase, the sulfur atoms in the two planes within the sandwich superpose and the metal atoms are found at the center of half the trigonal prisms formed by the sulfur. On the basis of the notation for the closest packing of spheres, the structure of 2H-TaS_2 and 2H-NbS_2 is *AbACbC*, where the capital letters refer to the sulfur atoms and the lowercase letters refer to the metal atoms. In TiS_2 the sulfur planes do not superpose. The structure is *AbCAbC*, and the titanium is in an octahedral environment. Bonding within the layer is strong and primarily covalent, whereas that between layers is mainly van der

Table 1. Chemical analysis of some complexes.

Complex	Percentage (by weight) found						Percentage (by weight) calculated					
	Nb/Ta	S	C	H	N	P	Nb/Ta	S	C	H	N	P
$NbS_2(\text{aniline})_{1.0}$	36.8	25.4	28.8	3.10	5.85		37.1	25.6	28.8	2.82	5.60	
$NbS_2(\text{tributylphosphine})_{1/8}$	51.0	35.0	9.86	1.94		2.03	51.0	35.2	9.88	1.87		2.11
$TaS_2(\text{TMPD})_{1/4}$*	63.6	22.6	10.3	1.40	2.41		63.3	22.4	10.5	1.39	2.44	
$TaS_2(\text{tributylphosphine})_{1/8}$	67.3	23.9	6.50	1.31		2.08	66.9	23.7	6.66	1.26		1.43

* TMPD = tetramethyl-*p*-phenylenediamine.

Table 2. Comparison of complexes formed with different layered sulfides; δ, increase in interlayer spacing.

Intercalate	Chalcogenide	Molecules per formula unit*	Reaction time (days)	Reaction temperature (°C)	a (Å)	c (Å)	δ (Å)	Onset temperature (°K)
Ammonia	TaS_2	1	1	25	3.324	2 × 9.07	3.03	4.2
Ammonia	NbS_2	1	3	80		? × 9.2	3.15	2.0
Ammonia	TiS_2	1	1	25		? × 8.90	3.21	
Ammonia	ZrS_2	1	2	100		? × 8.95	3.14	
Pyridine	TaS_2	1/2	1	200	3.326	2 × { 11.85† 12.02	{ 5.81† 5.98	3.5
Pyridine	NbS_2	1/2	30	200	3.34	2 × 11.84	5.89	4.0
Pyridine	TiS_2‡	1/2	1	90	3.426	3 × 11.71	6.02	
Aniline	TaS_2	3/4	16	150		? × 18.15	12.11	3.1
Aniline	NbS_2		23	170		? × 18.1	12.1	4.0
Aniline	TiS_2‡		60	170	3.40	? × 17.5	11.8	
Tributylphosphine	TaS_2	1/8	11	200	3.318	2 × 10.50	4.46	2.0
Tributylphosphine	NbS_2	1/8	30	200		2 × 10.42	4.48	3.5
Tributylphosphine	TiS_2	1/8	60	200	3.41	3 × 10.15	4.46	
s-Collidine	TaS_2	1/6	13	160	3.319	2 × 9.67	3.63	2.0
s-Collidine	NbS_2	1/6	23	200		? × 9.74	3.79	3.5
s-Collidine	TiS_2	1/6	60	200	3.413	3 × 9.41	3.72	
s-Collidine	$Ta_{0.8}W_{0.2}S_2$	1/6	20	200	3.29	2 × 9.642	3.65	
s-Collidine	$Ta_{0.3}W_{0.7}S_2$	1/6	5	200				

* The number of intercalate molecules per formula unit was determined from the weight increase of the dichalcogenide and corresponded to the rational numbers given, to within 5 percent. † Two intercalated phases are present. ‡ These samples were first intercalated with ammonia and then deintercalated.

Waals attraction and thus weak enough to permit intercalation.

The disulfides TiS_2, NbS_2, and TaS_2 form a set of analogous complexes with a variety of molecules, but most readily with strong Lewis bases. These Lewis bases react with the sulfides to give complexes whose stoichiometry and interplanar spacing depend only on the intercalate. We have measured the unit cell dimensions, determined the composition in some cases, and measured the superconducting critical temperatures of the TaS_2 and NbS_2 complexes.

Both powders (200 mesh) and crystals of the layered materials, prepared as previously described (*1*), were used for intercalation. The complexes prepared from either material were of identical structure and composition. The critical temperature of 2H-TaS_2 prior to intercalation is about 0.8°K; that of 2H-NbS_2 is about 6°K.

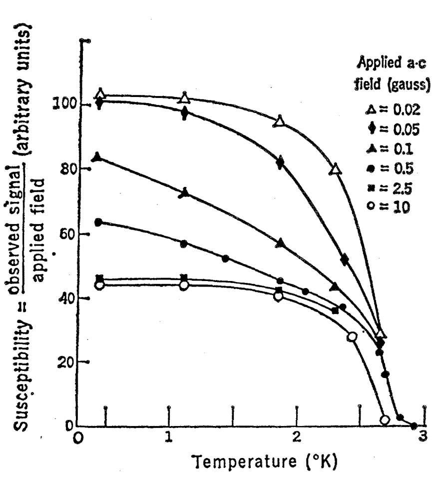

Fig. 1. The a-c magnetic susceptibility in arbitrary units as a function of temperature with the magnitude of the excitation as a parameter. The apparent width of the transition depends on the excitation.

Intercalation was accomplished either by mixing the reactants in sealed Pyrex tubes as described in detail elsewhere (*7*) or by stirring a suspension of the chalcogenide in a solution of the intercalate. The reaction rates increased rapidly with temperature, and, depending upon the intercalate, the time needed for completion of the reaction varied from minutes at room temperature to many days even at 200°C. Completion of the reaction was indicated by the cessation of a quite remarkable swelling of the layered material and by the attainment of a constant limiting weight. The complexes were exposed to the atmosphere as little as possible because certain of them (the TaS_2 aliphatic amines, especially) proved to be unstable to such exposure.

We detected the onset of superconductivity in the samples by measuring the low-frequency (18 hz) a-c magnetic susceptibility, a measurement which reflects the high electrical conductivity of the sample when superconducting (*8*). The transitions of the unintercalated TaS_2 powders were less than 0.2°K wide. In every TaS_2 complex measured the transition was broader, between 0.5° and 1°K wide, depending on the strength of the a-c excitation. The NbS_2 crystals, which contained a small amount of the 3R polytype in addition to the 2H-phase, had transitions about 1°K wide, as did their intercalation complexes. In this report we define a "critical temperature" as that temperature at which shielding currents could first be detected. At this temperature approximately 1 percent of the sample is shielded. The measurements of the susceptibility below T_c in pressed powder samples were complicated by the fact that the apparent volume of super-

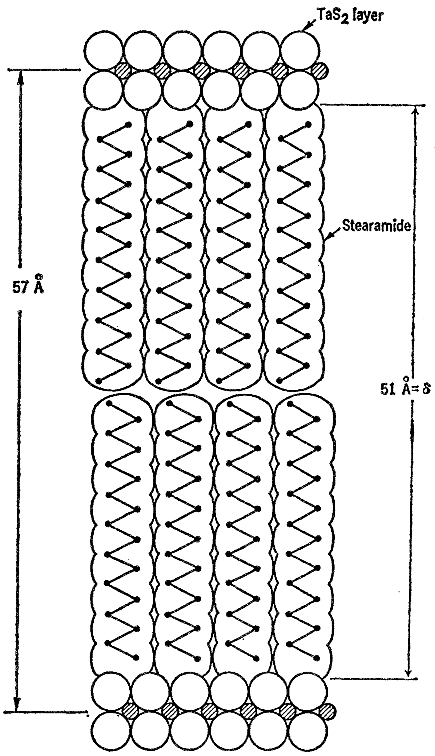

Fig. 2. Schematic representation of the structure of the TaS_2 stearamide complex. The large open circles represent the sulfur atoms. The shaded circles represent the tantalum atoms.

conducting material was a function of the applied a-c magnetic field. The apparent volume of superconducting material is plotted as a function of temperature in Fig. 1 for a typical sample with a-c field amplitude as a parameter. The curves are enveloped by two limiting cases, that for weak excitation and that for strong excitation. If the powders were dispersed in oil or if their surfaces were heavily oxidized, this effect was not observed. Apparently in the pressed powders, particle-to-particle contact is strong enough to allow weak superconducting currents, which in low a-c fields can shield the entire sample volume including voids.

We report the number of intercalate molecules per metal atom for some of the complexes. These data were obtained from chemical analysis (Table 1) and from measurement of the weight gained by the chalcogenide. Stoichiometries were not determined for all the complexes prepared because these data were difficult to obtain. X-ray diffraction data provided proof of intercalation and were considerably easier to obtain. Unit cell dimensions were calculated from x-ray powder diffraction data gathered with the use of CuK radiation and a recording diffractometer.

In a previous study of intercalation complexes of TaS_2 and substituted pyridines (*7*), we showed that the base strength of the molecule could be used as an index whereby one could separate molecules that would form stable intercalation complexes from those that would not. In that group, all molecules that formed isolatable intercalation complexes were Lewis bases with pK_a's greater than 4. Although it is not likely that such a simple index as this would provide a universal cutoff, the idea that Lewis basicity is the controlling factor in intercalation has proved useful for the compounds we have investigated.

Among the intercalates that we have found most satisfactory from the standpoint of speed of reaction and stability in the presence of the disulfides are ammonia, aliphatic amines, pyridine, similar compounds, and, to some extent, aniline. In Table 2 we have tabulated the unit cell dimensions, stoichiometries, and, where appropriate, the critical temperatures of TiS_2, NbS_2, and TaS_2 complexed with ammonia, pyridine, *s*-collidine, tributylphosphine, or aniline. The stoichiometry and the increase in interplanar spacing depend only on the intercalate. The number of transition metal layers per unit cell depends on the starting material. Intercalation complexes of 2H-TaS_2 have two layers per unit cell as in the starting material. The TiS_2 complexes have three layers in the cell despite the fact that TiS_2 has only one layer. In some complexes the registry of the layers is too poor to permit an assignment of the number of layers in the cell. On intercalation the *a* axis increases but only by about 0.01 Å (*9*). These data suggest that the structure of the layers in the intercalated crystal is very close to that of the layers in the unintercalated crystal, especially since a given intercalate produces the same dilatation of the interlayer (basal) spacing regardless of the structure of the layer and the initial distance between metal planes.

Weiss and Ruthardt reported that TiS_2 forms intercalation complexes with aliphatic amides (*10*). Although the amides are only weakly basic, we

Table 3. Different intercalates in TaS_2; δ, increase in interlayer spacing.

Intercalate*	Time†	Temperature (°C)	a‡ (Å)	c§ (Å)	δ (Å)	T_c (°K)
Amides						
Butyramide	21 days	150		? × 11.0	5.0	3.1
Valeramide	21 days	150		? × 11.0	5.1	2.9
Hexanamide	21 days	150		? × 11.2	5.2	3.1
Caprylamide	21 days	150		? × 10.9	4.9	
Stearamide (stage I)	10 days	150		? × 57.0	51.0	3.1
Stearamide (stage II)	4 days	150		? × 63.2	51.2	3.0
Thiobenzamide	8 days	160		? × 11.9	5.9	3.3
Phenylamines						
Aniline	16 days	150		? × 18.15	12.11	3.1
N,*N*-Dimethylaniline	3 days	170		? × 12.45	6.41	4.3
p-Phenylenediamine ‖	4 hr	140	3.318	? × 13.34	7.30	3.3
p-Phenylenediamine ‖	4 hr	140	3.318	? × 12.04	6.00	2.9
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	13 days	200	3.335	2 × 9.66	3.62	2.9
Heterocyclic amines						
4,4′-Dipyridyl	21 days	160	3.316	2 × 12.08	6.04	2.5
Quinoline	6 days	160		? × 12.08	6.04	2.8
Isoquinoline	28 days	160		? × 12.85	6.81	2.5
Pyridine-*N*-oxide	8 hr	100	3.335	? × 11.97	5.93	2.5
Pyridinium chloride	4 days	170	3.329	? × 9.30	3.26	3.1
Hydroxides¶						
NH_4OH	30 min	25	3.326	2 × 9.10	3.06	3.3
CsOH	30 min	25	3.330	2 × 9.28	3.24	3.8
RbOH	30 min	25	3.325	2 × 9.10	3.06	4.3
KOH	30 min	25	3.328	2 × 9.02	2.98	5.3
LiOH	30 min	25	3.330	2 × 8.92	2.88	4.5
NaOH	30 min	25	3.326	2 × 11.86	2.82	4.8
Triton B	30 min	25	3.331	2 × 11.98	5.94	5.0
Alkylamines#						
Ammonia	3 days	25	3.328	2 × 9.22	3.17	4.2
Methylamine	30 days	25	3.329	2 × 9.37	3.32	4.2
Ethylamine	30 days	25	3.334	2 × 9.58	3.53	3.3
Propylamine	30 days	25	3.330	2 × 9.66	3.61	3.0
Butylamine	30 days	25		? × 9.73	3.68	2.5
Amylamine	30 days	25				2.2
Tridecylamine	30 days	25	3.322	? × 40.5	36.4	2.5
Tetradecylamine	30 days	25	3.325	? × 46.2	40.1	2.4
Pentadecylamine	30 days	25	3.328	? × 45.1	39.0	2.8
Septadecylamine	30 days	25		? × 48.5	43.4	2.7
Octadecylamine	30 days	40		? × 56.1	50.0	3.0
Tributylamine	7 days	200		2 × 10.28	4.23	3.0
Dimethylethylamine	30 days	25	3.326	2 × 9.80	3.75	
Miscellaneous						
Ammonium acetate	1 hr	150	3.330	? × 9.08	3.04	2.0
Hydrazine	10 min	10	3.334	? × 9.16	3.12	4.7
Potassium formate	1 hr	200	3.334	? × 9.05	3.01	4.7

* The intercalate listed should be considered the nominal intercalate unless a chemical analysis is given. In most cases, the chemical analyses are in accord with the nominal intercalate listed. † The time given is one that is sufficient or more than sufficient for the reaction to go to completion. ‡ The *a*-axis spacing was computed only if sharp mixed reflections (10*l*) were present. The error is then approximately 0.003 Å. § The number of layers in the unit cell could be determined only if 10*l* reflections were present; 2H-TaS_2 always yielded layers per unit cell. ‖ The lesser *c*-axis was obtained by heating the TaS_2 with only a quarter equivalent of *p*-phenylenediamine, that is, 0.25 mole of *p*-phenylenediamine for each mole of TaS_2. ¶ The hydroxides were intercalated from aqueous solution. Some water was undoubtedly intercalated at the same time. # *N*-Alkylamines from dodecylamine on were intercalated from benzene. The x-ray diffraction pattern of alkyl amines from C_5 to C_{11} showed a large amount of disorder, and reliable *c* and *a* spacings could not be obtained.

Table 4. Comparison of first- and second-stage complexes; *n*, number of layers per unit cell; *d*, interlayer distance.

Intercalate	Chalco-genide	$d_0 = c/n$ (chalco-genide)	$d_1 = c/n$ (first stage)	$d_2 = c/n$ (second stage) (Å)	$d_0 + d_1$	T_c (first stage)	T_c (second stage)
Pyridine*	TaS_2	6.05	11.9	18.0	18.0	3.5	2.5
Stearamide†	TaS_2	6.05	57.0	63.2	63.1	3.1	3.0
Ammonia‡	TiS_2	5.69	8.90	14.8	14.6		

* The second-stage compound was prepared by treating the TaS_2 with a quarter equivalent of pyridine, for 30 days at 200°C, that is, 0.25 mole of pyridine per mole of TaS_2, half the amount absorbed in the presence of excess pyridine. † The second-stage compound was formed after a brief treatment with excess intercalate (see Table 3). ‡ The second-stage compound was prepared by heating the first-stage compound briefly at 100°C in a vacuum.

have succeeded in preparing complexes of amides and TaS_2. However, these reactions proceed very slowly and only at high temperatures with some degradation of the amide and production of ammonia. Ammonia is intercalated in these layered materials quite rapidly even at room temperature, and its presence along with the amide was indicated on the basis of chemical analysis and the mass spectra of the complexes. We have found it very difficult to assign reliable stoichiometries to these amide complexes. In fact, we believe that the stoichiometries assigned by Weiss and Ruthardt to their amide complexes of TiS_2 may be incorrect since they cannot be reconciled with the interlayer spacings, which are probably reliable. Even though the composition of the amide complexes is not determined, the layers are quite uniformly separated and a case is included in which the layers are separated by as much as 57 Å (see Fig. 2 and Table 3). The interlayer spacing for shorter chains is fairly constant and is consistent with a structure in which the molecules are parallel to the layers. The interlayer spacing of the stearamide TaS_2 complex (57 Å) is naturally rationalized on the assumption that the TaS_2 layers are separated by a molecular bilayer in which the chain axis is perpendicular to the layers.

In Table 3 we present the unit cell dimensions, preparative conditions, and critical temperatures of intercalation complexes of TaS_2 and a variety of compounds, both organic and inorganic. With the interesting exception of pyridinium chloride, the intercalates are all bases. These data show the generality of the intercalation phenomenon in these materials, show how insensitive T_c is to spacing, and finally demonstrate that T_c can be manipulated chemically. The insensitivity of the critical temperature to spacing suggested that the superconductivity might be that of an impurity phase. This possibility has been eliminated. Low-temperature, heat-capacity measurements of a number of these samples show that the superconductivity is a bulk property of the metallic TaS_2 layers and is not due to impurity phases. The transition we measure by the a-c susceptibility technique corresponds satisfactorily to the observed bulk heat-capacity transition in every case where the two have been compared (*11*).

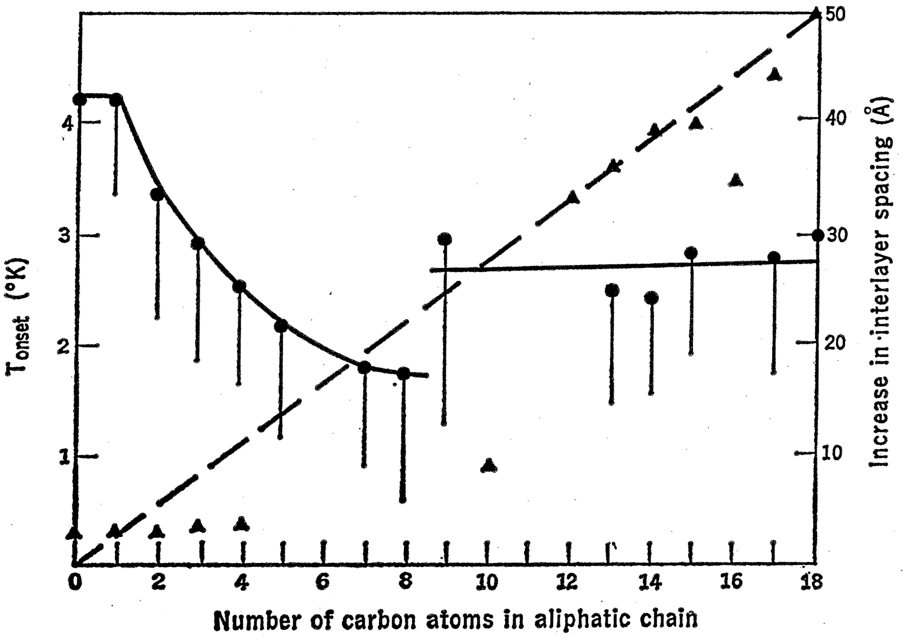

Fig. 3. The onset temperature of superconductivity (●) and the increase in the interlayer spacing (▲) as a function of the number of carbon atoms in the *n*-alkyl amine intercalates in TaS_2.

In an earlier paper (*7*) we suggested that the critical temperature of the intercalation complexes of TaS_2 depended on the strength of the base and on the number of bonds between the intercalate and the layer. This suggestion was borne out to some extent by a rather crude correlation between the critical temperature and the stoichiometry of TaS_2-substituted pyridine complexes, the critical temperature increasing with increasing number of molecules per "molecule" of TaS_2. We have now confirmed these notions by examining the complexes of TaS_2 and *n*-alkyl amines. We find that an increase in the chain length from ammonia to octylamine causes the critical temperature to drop in a monotonic fashion from 4.2° to 1.8°K. The critical temperature for *n*-nonylamine is near 3°K and it remains the same, with some small variation, up to octadecylamine (see Fig. 3). The interlayer spacing increases only slightly with increasing chain length for small chain lengths, an indication that the chains lie parallel to the layers. In this configuration increasing the chain length reduces the number of amine groups per TaS_2. The parallel configuration eventually gives way to a perpendicular configuration in which the stoichiometry does not vary with chain length but the interplanar spacing increases. The rate of intercalation, which was satisfactorily rapid even at room temperature, was always faster for amines with an even number of carbons than for amines with an odd number of carbons.

In the complexes there is a tendency for the intercalate to penetrate every other layer if one does not treat the layer crystal long enough or with sufficient intercalate. Such second-stage complexes have been prepared but they are usually difficult to isolate. X-ray powder diffraction patterns frequently suggest the presence of such complexes along with the regular first-stage complex and the unintercalated material. Only in a few cases have we obtained fairly pure second-stage complexes. [The structures suggested by the x-ray diffraction data and by the stoichiometries have been confirmed and elaborated by the electron microscopy reported in (*2*)]. In second-stage complexes the *c*-axis parameter is approximately the sum of the *c*-axis parameter of the first-stage complex and that of the unintercalated material. These data are presented in Table 4 where the critical temperature of the first and second stages are compared. In the second-stage complex $TaS_2(C_5H_5N)_{1/4}$ the critical temperature is lower than that of $TaS_2(C_5H_5N)_{1/2}$ by an amount which might have been estimated from the crude relationship we have already established in complexes of TaS_2 and the substituted pyridines (*7*). The critical temperatures of the first and second stages of the stearamide complex of TaS_2 are nearly identical.

We proposed earlier that the interaction responsible for the stability of these intercalation complexes was a bond between the layer and the intercalate involving the lone-pair electrons of the intercalated Lewis base and a partially filled band with significant amplitude on the sulfur atom. This proposal is supported by measurements of the Hall effect (*12*) which are in accord with a band structure for TaS_2 suggested by van Maaren and Harland (*13*) in which the conduction band overlaps the valence band. When the conduction band is filled, as it is in the semiconductors WS_2 and MoS_2, stable intercalation complexes of Lewis bases have not been isolated. In TiS_2 the band picture is altered because of the octahedral coordination of the metal, but we believe that the same arguments hold.

In considering the mechanism of intercalation in a layered material such as 2H-TaS_2 we have found it convenient to assume that one of the initial steps involves nucleophilic attack by the intercalate on the interlayer S–S "bonds." Reactions of S_8 are rationalized by postulating that an initial nucleophilic attack is required to open the S_8 ring. The activation energy for such reactions has been correlated with bond distances, and, by analogy, since the interlayer S–S "bonds" are rather long, the activation energy for intercalation should be relatively low and intercalation should proceed readily with suitable nucleophiles. Nucleophiles such as ammonia, trialkylated phosphines, OH—, and RSO_2— were intercalated with facility even at room temperature. The charged, rather weak nucleophile RSO_2^- intercalates most readily from solvents, such as dimethyl sulfoxide and dimethylformamide, known to accelerate reactions in which the transition state involves a complex of the anion. (The products of the sulfinate intercalations were not homogeneous and therefore are not described in the tables.)

The critical temperature of intercalated TaS_2 can be as low as 1.6°K and as high as 5.3°K, depending on the intercalate. In contrast, the critical temperature is quite insensitive to the distance between the tantalum layers as this parameter is varied from 9 to 57Å. This insensitivity to interlayer spacing prompts us to think of the superconductors as two-dimensional in some sense; that is, the interlayer coupling is unimportant to the stability of the superconducting state and the attractive electron-electron interaction giving rise to the superconductivity is confined to the metallic disulfide layers. We believe both from chemical and structural considerations and from studies of the heat capacity and magnetization that a large fraction of the entropy is removed by intraplanar electron correlations as the sample is cooled into the superconducting region. Thus the crystal complexes can be properly described as two-dimensional superconductors in the same sense that $KMnF_4$ crystals are termed two-dimensional antiferromagnets (*14*).

Part of our interest in the intercalation complexes derives from the notion that one might find in them a new mechanism for superconductivity and perhaps use this to prepare materials with higher critical temperatures. The systematics of the variation in critical temperature with variation of intercalate are not completely worked out as yet. Thus far it seems likely that they will be understood in terms of the usual mechanisms. Charge transfer from the bases to the layer probably effects most of the enhancements or depressions of T_c noted. Yet all of the intercalation complexes examined thus far contain molecules whose electronic excited states are in the ultraviolet region. Some of the schemes for the attainment of higher superconducting critical temperatures in which interactions between conduction electrons and molecular electrons are used require molecules with lower-lying electronic excited states. Whether these considerations prove fruitful or not, intercalation of such molecules should yield qualitatively different materials. The mild conditions under which many intercalations proceed and the large number of basic functional groups that can be used to carry a molecule between the layers suggest that molecular species of almost any description can be designed to form intercalation complexes with certain of the layered sulfides.

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