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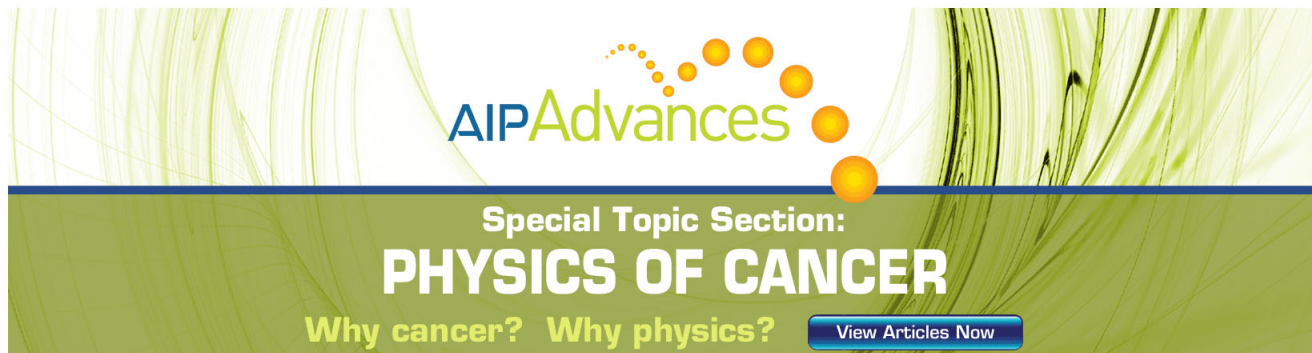
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Properties of H_xTaS_2 : Correlation between the superconducting T_c and an electronic instability in layer compounds*

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The preparation of H_xTaS_2 ($0 < x < 0.87$) is described. The compounds are only marginally stable at room temperature, slowly evolving H_2S and H_2 (and possibly H_2O in air). Magnetic susceptibility data show that a low temperature transformation in $2H \cdots TaS_2$ (at $80^\circ K$) is suppressed with the addition of hydrogen, and at the same time the superconducting transition temperature T_c rises from 0.8 to $\sim 4.2^\circ K$ at $x = 0.11$. Heat capacity measurements near this concentration show the superconductivity to be a bulk effect. Finally, by correlation of this data with susceptibility and T_c measurements in other intercalation compounds, we suggest that the rise of T_c (at low electron transfer) is due to suppression of the low temperature transformation and *not* due to an excitonic mechanism of superconductivity.

INTRODUCTION

In the past few years many compounds of layered transition metal dichalcogenides (LTMD) intercalated with electron donor atoms or organic molecules have been reported.¹⁻³ A σ donor capability appears necessary for intercalation. For organic molecules the ability to intercalate is lost if the Lewis basicity is low. For atoms the donor capability may be expressed in terms of electronegativity. Elements such as bismuth, copper, and mercury (Pauling electronegativity 1.9) are the most electronegative atoms to have been intercalated so far.¹ On intercalation with organics the superconducting transition temperature (T_c) for $2H \cdots TaS_2$ ($T_c = 0.8$) usually rises to $3-4^\circ K$, while T_c for $2H \cdots NbSe_2$ ($T_c = 7.2^\circ$) usually drops below $1^\circ K$. An adequate explanation of the effect of intercalation on superconductivity in these LTMD has not been established. Phillips suggested that the superconductivity in the organic intercalation compounds is excitonic,⁴ but Thompson *et al.* suggested that enhancement of T_c in $2H \cdots TaS_2$ (pyridine)_{1/2} is due to absence of a low temperature phase change and added electron density.⁵ This low temperature ($\sim 80^\circ K$) phase change has subsequently been shown to be a superlattice instability due to Fermi surface driven charge density waves.^{6,7} An intercalation system wherein electron donation could be continuously varied without significantly affecting other parameters, such as the crystallographic a and c axes, would be of value in establishing the role of the Fermi surface and subsequent charge density superlattice instabilities. Hydrogen intercalation compounds would be the ideal choice for such a study. Earlier it was reported that hydrogen gas would not react with $2H \cdots TaS_2$ at low temperature, and that at higher temperatures ($400^\circ C$) hydrogen sulfide and tantalum were produced.¹

In this paper we report the intercalation of hydrogen (electronegativity 2.1) by electrolysis in $2H \cdots TaS_2$, $2H \cdots NbSe_2$, $2H \cdots NbS_2$, and TiS_2 .⁸ Unsuccessful attempts were made with $1T \cdots TaS_2$, HfS_2 , ZrS_2 , and MoS_2 . We have studied hydrogen intercalates of $2H \cdots TaS_2$ in detail and find that at low hydrogen concen-

trations the compounds are superconducting, reaching a maximum T_c of approximately $4.2^\circ K$ at $x \approx 0.11$. We also present evidence that hydrogen behaves as an electron donor and that the increase in T_c is due to suppression of the instability at $80^\circ K$.

SAMPLE PREPARATION

All the LTMD used were prepared as previously described.^{1,2} Crystals of the LTMD were grown by vapor transport with hydrogen chloride or iodine. Polycrystalline powders of $2H \cdots TaS_2$ were also used. Crystals of $2H \cdots NbSe_2$ were grown in a Se atmosphere (≈ 1.5 atm pressure).

Electrolysis was carried out in a beaker of acid, using a platinum anode, and the LTMD as the cathode. Several samples intercalated with deuterium were prepared in the same manner. Compounds used for physical measurements were prepared under conditions where no hydrogen gas was evolved. Throughout this paper we use for the hydrogen stoichiometry the value calculated from the number of coulombs passed through the cell. The samples of interest contain only $\sim 0.05\%$ H so that normal adsorbed water made meaningful analysis impossible. Only an insignificant amount of sulfide could be detected in the electrolyte. Use of the calculated stoichiometry gave reproducible results showing a systematic variation in physical properties with x .

Maximum stoichiometries for H_xTaS_2 depend markedly on electrolytic conditions. With bare gold wire on the cathode a maximum hydrogen content of $x = 0.1$ is obtained, beyond which hydrogen evolution occurs at the gold. By coating the gold with black Apiezon wax higher stoichiometries are achieved. When concentrated sulfuric acid is used as the electrolyte, only hydrogen evolution occurs; while electrolysis from dilute (10% or less) sulfuric acid caused severe exfoliation due to intercalation of water as well as hydrogen. Stoichiometries up to $x = 0.87$ were obtained with 50% sulfuric acid without intercalation of water. Concentrated (38%) hydrochloric acid also gave satisfactory results.

Typical currents used to intercalate crystals of $2H \cdots TaS_2$ (15–20 mg) suspended from gold wires were on the order of 100 μA (giving a current density of $\approx 0.5 A/cm^2$, assuming that hydrogen enters only from the edge). Much lower current densities ($10^{-4} A/cm^2$) were necessary for $NbSe_2$ and TiS_2 . This difference is probably due to extensive microcracks in the crystals of $2H \cdots TaS_2$, caused by a phase change from 1T to 2H as the crystals are cooled from growth temperature to room temperature. $2H \cdots NbSe_2$ and TiS_2 do not have such cracks. These microcracks presumably provide a considerable amount of added edge area for intercalation. At moderate to high current densities, the face of TaS_2 crystals become silvery, and x-ray diffraction data shows that the surface of the crystal is high in hydrogen content (c increases from 6.05 to 6.22 \AA). After scraping the surface away with a razor blade, the material shows the blue-black color characteristic of $2H \cdots TaS_2$ and x-ray diffraction data show there is no increase in the c spacing. Apparently hydrogen is intercalated into the outer layers first, although it is not clear whether this is due to exfoliation of the TaS_2 or is intrinsic to the hydrogen intercalation process. At low current densities the hydrogen content is more uniform—but this may be an annealing effect (see later).

A particularly useful method for electrolysis of powders is to float the powder (in a pressed pellet or free flowing) on a mercury cathode. The high overvoltage for hydrogen evolution on mercury allows high stoichiometries. Samples for magnetic susceptibility and superconductivity were prepared by this method using pressed powders. Currents of 1–10 mA were used for samples of about 300 mg. The pellets were removed from the cell, washed with isopropyl alcohol, and dried under vacuum.

In order to obtain a homogeneous hydrogen distribution, the pressed pellets of H_xTaS_2 were annealed for three days under 300 torr of hydrogen at room temperature. We found it more difficult to obtain homogeneous samples using TaS_2 crystals. The best procedure for annealing crystals is to leave them in the acid electrolyte for a few days. The electrolyte appears to be necessary to transfer protons across microcracks, from layer to layer, or particle to particle. The transfer of the charge balancing electron is then quite simple due to physical (electrical) contact of the particles. The pressed powders are probably easier to homogenize because the crystallites are small ($\leq 20 \mu$) and relatively crack-free. Intercalation in the pellets proceeds throughout the sample, i.e., acid enters the pellet and, even after washing with isopropyl alcohol and drying, some electrolyte remains to assist in homogenization.

No change in physical properties was noted for samples stored in an inert atmosphere for 10 days, showing sample stability for at least that length of time. The samples are, however, only marginally stable. When powdered samples are exposed to air for a few weeks most of the hydrogen deintercalates. Pyrolysis *in vacuo* of samples at 450 $^\circ C$ gave hydrogen and hydrogen sulfide in approximately a four to one ratio. A slight odor of hydrogen sulfide emanates from the compounds even at

room temperature, possibly indicating a slow decomposition. Deintercalation occurs more readily in a pure oxygen atmosphere, presumably with formation of water. After several days at 150 $^\circ C$ in oxygen the T_c of H_xTaS_2 crystals returns to 0.8 $^\circ K$. Shorter times at lower temperatures are sufficient for powdered samples. All the measurements reported in this study were performed on samples after annealing.

MEASUREMENTS

The major part of this study concerns the properties of H_xTaS_2 . After simple characterization of H_xTaS_2 by x-ray diffraction and optical properties, we measured T_c by a two coil low frequency ac method,^{2,9} heat capacity on small samples (≈ 20 mg) between 1 to 10 $^\circ K$,¹⁰ magnetic susceptibility (χ) from 4.2 to 300 $^\circ K$ by the Faraday method,¹¹ and electrical resistivity (ρ) from 4.2 to 300 $^\circ K$. All layered compounds successfully intercalated with hydrogen were tested for superconductivity by the ac method and T_c determined if $T_c > 0.5$ $^\circ K$. In this section we present the data obtained, and discuss in more detail some of the difficulties in measuring certain properties of this system.

At low hydrogen concentrations, no change is observed in the a or c axis of powders by x-ray measurements. At the highest concentrations, $2H \cdots NbSe_2$ and $2H \cdots TaS_2$ show an increase of about 0.2 \AA in the c axis (interlayer separation) to 6.51 and 6.22 \AA from 6.27 and 6.05 \AA respectively. In addition $H_{0.87}TaS_2$ also changes to the $2H \cdots MoS_2$ layer structure. Crystals of TiS_2 intercalated with hydrogen were yellow in optical transmission (TiS_2 is purple) and the yellow TaS_2 crystals were red after intercalation (the same as WS_2).

The results of superconducting measurements are shown in Fig. 1, where the superconducting onset temperature (T_c), transition width (noted by bars), and the apparent superconducting fraction are shown. Although the apparent superconducting fraction obtained with powders by this method is reliable only to $\pm 15\%$ (assum-

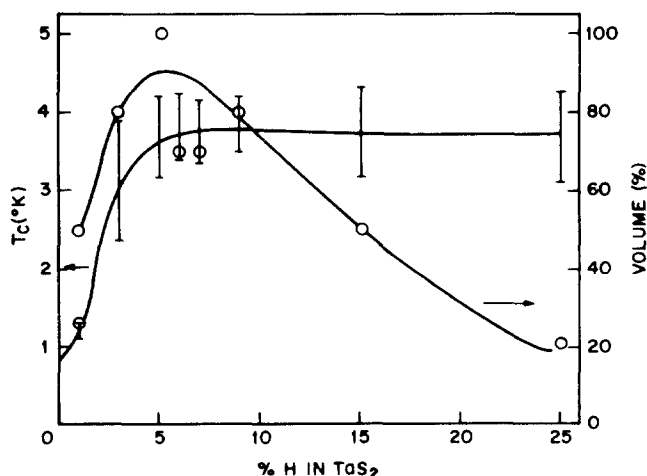


FIG. 1. Superconducting transition temperature and apparent fraction superconducting as determined by a low frequency ac method. The bars represent the transition width, while the circles are the volume % superconducting.

ing bulk superconductivity) it is clear from both transition widths and fraction superconducting that bulk superconductivity extending up to 4.0 °K occurs somewhere in the range $0.05 < x < 0.15$. At $x > 0.15$ some transition is still seen at 4.2 °K, likely due to a somewhat inhomogeneous hydrogen distribution. Early measurements on single crystals of H_xTaS_2 found T_c 's as high as 4.2 °K even for $x < 0.01$. But this was due to improper annealing and inhomogeneous hydrogen distribution as previously discussed.

None of the H_xTiS_2 samples were superconducting above 0.5 °K. $NbSe_2$ was studied only at very low x and high x . The T_c of $H_{0.01}NbSe_2$ is 7.45 °K (onset) with a width of 0.1 °K, which returns to 7.25 °K (onset) on deintercalation at 100 °C in oxygen. When $x \geq 0.2$ T_c is less than 0.5 °K. No difference could be detected between H_xTaS_2 and the corresponding deuterium compounds.

ac measurements can lead to quite erroneous results due to filamentary superconductivity; i.e., very small superconducting volume fractions may shield the entire sample if the superconducting regions are physically connected.¹² Heat capacity measurements, which detect only true bulk superconductivity, have been carried out on small samples¹⁰ of H_xTaS_2 at $x = 0.01$, 0.08, and 0.10. The sample at $x = 0.01$ was a single crystal that gave a T_c of 4.2 °K by the ac method, but heat capacity measurements showed no superconductivity to 1.1 °K, confirming only filamentary superconductivity at 4.2 °K. The results for the other two samples are shown in Fig. 2, where the data are given as C/T vs T^2 . At $x = 0.08$, from both the initial heat capacity jump ΔC and the shape of C/T vs T^2 below T_c , it is clear that a distribution of T_c 's below 4.2 °K occurs in this sample (hydrogen distribution inhomogeneous). However, at $x = 0.10$ the curve is typical of a bulk superconductor with a single T_c of 3.9 °K. When $T > T_c$ the electronic specific heat coefficient (γ) and phonon coefficient (β) (in the usual expansion $C = \gamma T + \beta T^3$) are found to be $\gamma = 8.9$ mJ/mole °K² and $\beta = 0.54$ mJ/mole °K⁴. The jump at the transition $\Delta C/\gamma T_c$ is 2.2 and compares favorably with the jump of 2.1 for the bulk super-

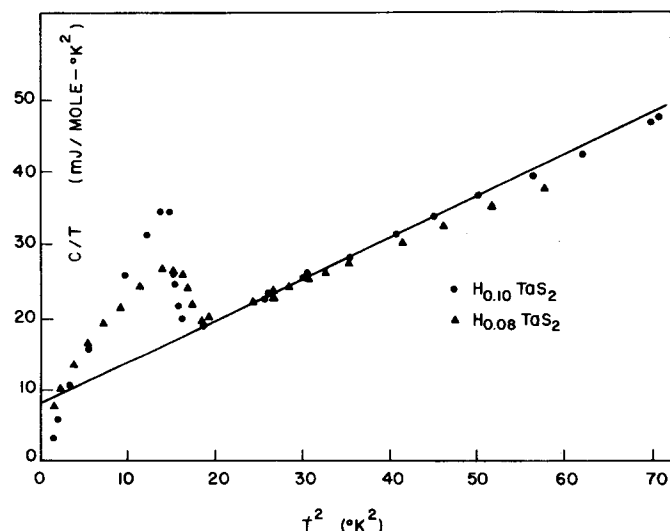


FIG. 2. Results of heat capacity measurements.

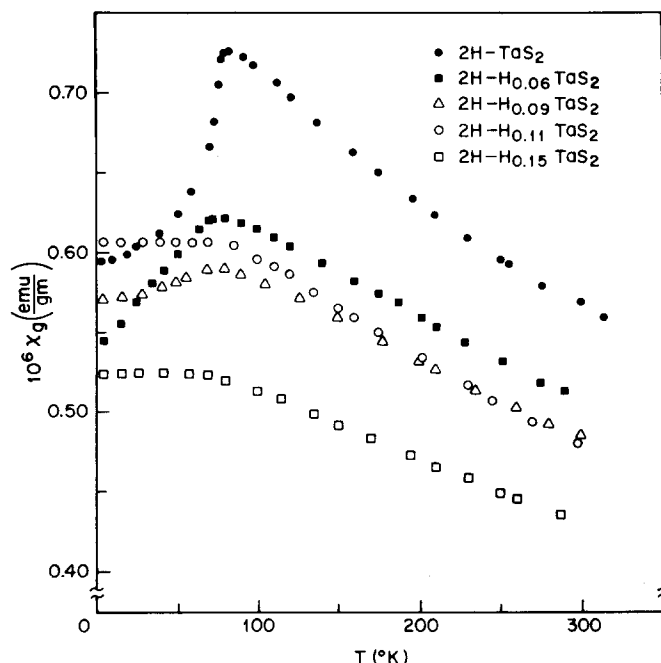


FIG. 3. Magnetic susceptibility of several H_xTaS_2 powders. The data have been corrected for both small amounts of ferromagnetic and paramagnetic impurities as described in the text. Note the shifted origin of the vertical axis.

conductor $NbSe_2$. At low temperatures C/T extrapolates to zero as it should for a 100 volume % superconducting sample. These heat capacity measurements confirm that bulk superconductivity near 4.2 °K occurs close to $x = 0.10$. Observations of T_c at 4.2 °K for x much below or above this value are due to filamentary superconductivity.

The magnetic susceptibility χ_g for H_xTaS_2 samples at low concentration are shown in Fig. 3. One effect of increasing hydrogen content is to suppress the marked decrease in χ_g , apparent in $2H \cdots TaS_2$ below 80 °K. In $2H \cdots TaS_2$ this drop is known to be caused by superlattice formation.⁷ At $x \geq 0.11$, χ_g no longer decreases at low temperatures. The data shown in Fig. 3 have been corrected in two ways. First, most of the hydrogen intercalated samples contained a small amount of ferromagnetic impurity, probably introduced by the steel die used to press the powder into pellets prior to intercalation. The ferromagnetic impurity leads to an apparent dependence of χ on the applied magnetic field (H). The ferromagnetic contribution to the susceptibility can be subtracted out by plotting the apparent susceptibility vs $1/H$ as shown in Fig. 4 for $H_{0.09}TaS_2$. The $1/H = 0$ intercept is the χ of the H_xTaS_2 alone.¹³ In all cases the ferromagnetic contamination was small enough to be accurately subtracted out in this manner. Second, samples of H_xTaS_2 for $x = 0.09$, 0.11, 0.15, and 0.87 showed a small Curie tail at low temperatures due to paramagnetic impurities. For $4.2^\circ < T < 10^\circ K$, the susceptibility can be expressed as $\chi = \chi_0 + C/T$, where χ_0 is temperature independent and the Curie term C/T is probably due to Fe impurities (~ 10 ppm). Analysis of the data between 4.2 and 10 °K gives χ_0 and C ; C/T is then subtracted from the raw data over the whole temperature

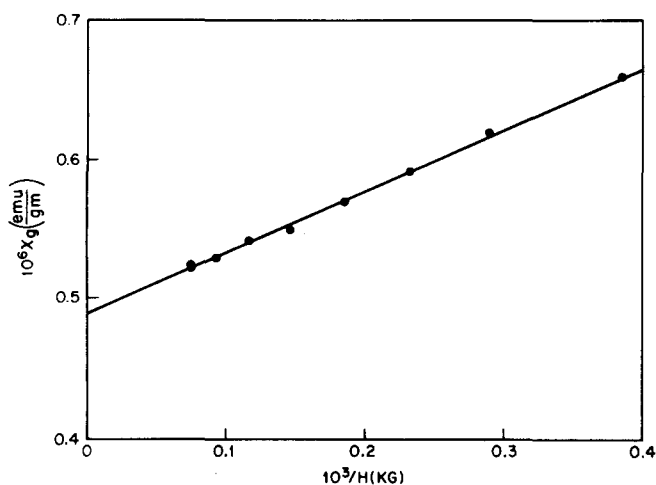


FIG. 4. $1/H$ plot at room temperature for $H_{0.09}TaS_2$, showing the method and accuracy of subtracting out the effect of a ferromagnetic impurity. The susceptibility of the $H_{0.09}TaS_2$ itself is given by the $1/H=0$ intercept.

range. Such corrections become insignificant by $50^\circ K$. The size of the tail is indicated for each sample in Table I, by giving the largest correction (at the lowest temperature, $C/4.2^\circ K$).

Since the instability of $2H \cdots TaS_2$ at $80^\circ K$ also causes a drop in the resistivity ρ , which is lost for pyridine intercalated samples,⁵ we measured resistivity by the four point method of a number of H_xTaS_2 samples. While this method is not as reliable as the van der Pauw method for determining the absolute value of the resistivity of thin irregularly shaped samples,¹⁴ we were mainly interested in determining the shape of the resistivity vs temperature curve. We had difficulty in obtaining reproducible results probably due to several factors: (1) the exfoliation of $2H \cdots TaS_2$ crystals becomes more pronounced with hydrogen content, (2) we sometimes encountered difficulty in producing crystals with homogeneous hydrogen distributions even after an anneal, and (3) the current and voltage probes were spring loaded indium contacts on the flat surface of the crystals—leading to possible difficulties in exfoliated crystals. Several features were apparent, however, which were al-

ways present in the $H_{0.11}TaS_2$ crystals. First, the resistive anomaly apparent in $2H \cdots TaS_2$ is not completely suppressed at $x=0.11$. In Fig. 5 typical results for $2H \cdots TaS_2$ (similar to those reported by Thompson *et al.*⁵) are compared to a sample of $H_{0.11}TaS_2$. The resistance ratio $\rho(4.2)/\rho(300)$ is approximately the same for both samples, but it is clear that the low temperature anomaly is reduced in $H_{0.11}TaS_2$. We also always found a larger slope in the ρ vs T characteristic above $100^\circ K$ for the hydrogen intercalated samples.

A number of observations support a charge transfer model for hydrogen intercalation, i. e., for each H intercalated the number of electrons in the Ta conduction band increases (by approximately 1). First, the change in structure in H_xTaS_2 at large x to the $2H \cdots MoS_2$ type is similar to that in $2H \cdots Ta_{1-x}W_xS_2$ or $2H \cdots Ta_{1-x}W_xSe_2$, where again the structures change from the $2H \cdots TaS_2$ type to the $2H \cdots MoS_2$ type at $x \approx 0.6$.^{10,15} Since these alloys are metallic we expect the rigid band model to apply, and see that the structure change is driven by an increasing conduction electron concentration. Second, the color of the crystals observed in optical transmission suggest, at high x , that the transition metal configuration is changing from d^n to d^{n+1} ($n=0$ for Ti, $n=1$ for Ta) consistent with a charge transfer model. Finally the diamagnetism of $H_{0.87}TaS_2$ (see Table I, here converted to molar susceptibility = -4.6×10^{-5} emu/mole) is close to that obtained in the d^{n+1} semiconductors MoS_2 (-5.8×10^{-5} emu/mole)¹⁶ or WS_2 (-1.0×10^{-4} emu/mole).¹⁶

The data given in Table I indicate that both the room temperature χ and its slope ($d\chi/dT$) decrease with increasing hydrogen content. At $x=0.11$, however, both χ and $d\chi/dT$ are higher than expected from the rest of the series. A clear trend is seen in $\Delta\chi = \chi_{(max)} - \chi_{(4.2^\circ K)}$, where $\Delta\chi$ continuously decreases with x until at $x=0.11$, $\Delta\chi=0$ within experimental error. Note also that since $\chi(4.2^\circ K)$ reaches a maximum at $x=0.11$, the electronic density of states is thus expected to reach a maximum just above that of $2H \cdots TaS_2$ (at low temperatures). This is consistent with the slightly larger γ value of $H_{0.10}TaS_2$ obtained in the low temperature heat capacity measurement as compared to that of $2H \cdots TaS_2$ powder where $\gamma = 8.5$ mJ/mole $^\circ K^2$. From this discussion and Table I it appears that T_c increases as $\Delta\chi$ decreases. How-

TABLE I.

Sample	$10^6 \chi(290^\circ K)$ emu/g	$10^6 \chi(max)$	$10^{10} d\chi/dT$ at $250^\circ K$ (emu/g $^\circ K$)	$\Delta\chi$ $\chi(max) - \chi(4.2)$	$10^6 C/4.2^\circ K$ (emu/g)	T_c ($^\circ K$)
$2H \cdots TaS_2$	+0.565	+0.725	-6.40	+0.134	0	0.8
$H_{0.06}TaS_2$	+0.515	+0.622	-4.8	+0.078	0	a
$H_{0.09}TaS_2$	+0.490	+0.590	-4.6	+0.020	+0.910	a
$H_{0.11}TaS_2$	+0.488	+0.606	-5.6	+0.002	+0.095	$4.2^\circ K$
$H_{0.15}TaS_2$	+0.435	+0.523	-4.1	-0.003	+0.089	a
$H_{0.87}TaS_2$	-0.190	...	0	0	...	< 0.5
$Ta_{1.05}S_2$	+0.410	+0.472	-3.2	+0.050	+0.080	$\approx 3.6^\circ K$
TaS_2 (collidine) _{1/6}				+0.112		1.95
TaS_2 (picoline) _{1/3}	a	a	a	+0.080	...	2.70
TaS_2 (pyridine) _{1/2}				+0.020		3.55

*See text.

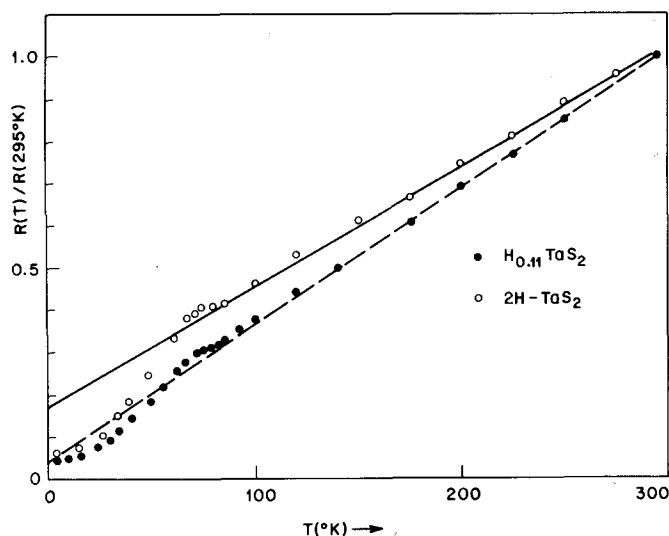


FIG. 5. The in plane resistivity of $2H \cdots TaS_2$ and $H_{0.11}TaS_2$ crystals, each normalized to the value measured at 295°K.

ever, the instability of $2H \cdots TaS_2$ is probably not completely suppressed at $x = 0.11$, just significantly reduced since, although $\Delta\chi = 0$, there is still a change in the slope of χ near 70°K and ρ still shows a (reduced) anomaly.

The absence of superconductivity in the H_xTiS_2 system is not entirely unexpected, since none of the alkali metal intercalation compounds A_xTiS_2 with $A = Li, Na, K, Rb, Cs$, and $0 < x < 1$ are superconducting.¹⁷

Intercalation with excess tantalum or organic donor molecules is known to produce effects similar to those in the H_xTaS_2 system, especially as reflected in χ .¹⁸ Previous studies indicate that a charge transfer $\bar{d} \approx 0.25$ electrons/molecule occurs in the organic intercalates.^{2,19} Using the indicated stoichiometry and the estimated charge transfer, the $\Delta\chi$ given in Table I from previous data¹⁸ are also consistent with the H_xTaS_2 data. There are some differences in behavior between the organic intercalates and H_xTaS_2 compounds, as may be expected, since the interlayer distance is hardly affected by hydrogen intercalation (< 0.2 Å) but increases dramatically for organics (3 to 6 Å in most cases). The major difference appears to be that the temperature at which the peak in χ occurs in H_xTaS_2 decreases slightly with increasing x , while in the organic intercalates the temperature at which χ (max) occurs increases with increasing organic content, to ~ 200 °K for TaS_2 (pyridine) $_{1/2}$. Consequently χ (290°K), χ (max), and $d\chi/dT$ data are not considered relevant here.

The superconducting transition temperatures of hydrogen intercalates, metal rich TaS_2 (excess Ta intercalated), and a few organic intercalates are given in the last column of Table I. The data show that T_c increases as electron donation to the d band increases and as $\Delta\chi$ decreases. This effect is seen in many other TaS_2 intercalates (both organic and inorganic), where generally T_c reaches a maximum of ~ 4 °K.^{2,3,18,20} We conclude that the major effect of intercalation by any electron donor is suppression of the charge density

wave instability of TaS_2 ($\Delta\chi$ decreases) with a resultant increase in T_c from 0.8°K to a maximum of approximately 4°K. The exact value of the maximum T_c is expected to depend somewhat on the nature of the intercalate, since T_c depends not only on the electronic density of states, but also on the phonon spectrum, which can depend on the bonding of the intercalate. In the previous cases (H, Ta, or organic intercalation), the suppression of the instability and subsequent increase in T_c appears closely correlated with the total charge transfer. It is not necessary to have charge transfer, however, to reduce $\Delta\chi$ and increase T_c . An example is given by $2H \cdots TaS_{1.6}Se_{0.4}$, where $T_c \approx 4.0$ °K²¹ and, as seen in Fig. 6, the anomaly in χ is considerably reduced. The suppression of superlattice formation by atomic disorder is also observed in nonsuperconducting TaS_2 polymorphs, such as $1T \cdots Ta_{1-x}Nb_xS_2$.⁷ From this we conclude that it is not primarily the electron donation, but rather the subsequent *suppression of the distortion* (say as seen in χ), that is related to the increase in T_c .

If such a conclusion is valid, then we expect an increase in T_c of $2H \cdots NbSe_2$ if its distortion is suppressed. The distortion in $2H \cdots NbSe_2$ at ≈ 35 °K is similar to that in $2H \cdots TaS_2$ but it is much weaker, being observable only in the Hall effect and the NMR quadrupole spectra.²²⁻²⁴ We have found, in agreement with others,²⁵ that single crystals of $NbSe_2$ grown from stoichiometric powders by iodine transport have $6.5 < T_c < 7.5$ °K. Although chemical analysis shows these crystals to be stoichiometric to 0.5%, small changes in stoichiometry are known to drastically change T_c .²⁶ However, after growth of $NbSe_2$ at 750°C in an atmosphere of Se (≈ 1.5 atm pressure), T_c was reproducible from crystal to crystal at 7.25 ± 0.05 °K. Growth in a Se atmosphere likely reduces the tendency of $NbSe_2$ to form slightly metal rich. Since the distortion is weak in $2H \cdots NbSe_2$,

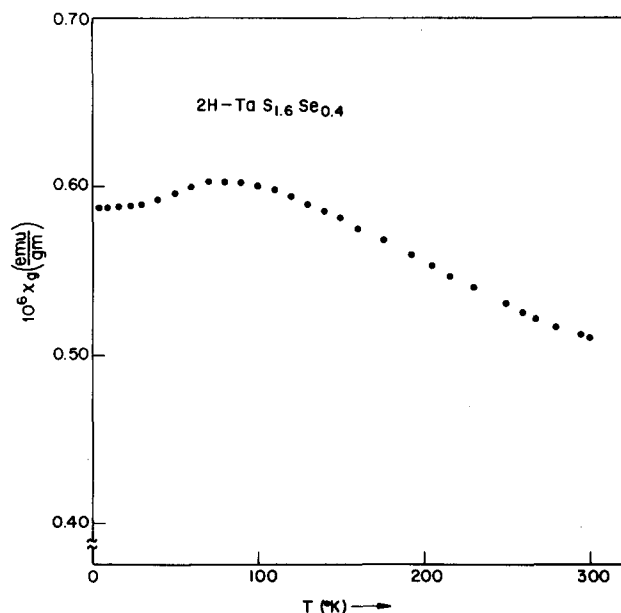


FIG. 6. Magnetic susceptibility of $2H \cdots TaS_{1.6}Se_{0.4}$ powder, showing a much smaller anomaly at low temperatures than either $2H \cdots TaS_2$ or $2H \cdots TaSe_2$. Note that the origin of the vertical axis is shifted.

we might expect only a small amount of hydrogen intercalation would be necessary to increase T_c , while further intercalation would decrease T_c . Indeed, the T_c of $H_{0.01}NbSe_2$ is 7.45 °K which returns to 7.25 °K on deintercalation. This difference in T_c (0.2 °K) is the same as that reported when the phase transformation of $NbSe_2$ is suppressed with pressure.²⁷ This result is similar to that obtained for $2H \cdots Nb_{1-x}Mo_xSe_2$ which has a maximum T_c of 7.5 °K at $x = 0.01$.²⁸ These results support the conclusion put forward to explain the increase of T_c in $2H \cdots TaS_2$ intercalation compounds.

CONCLUSIONS

The data presented here for hydrogen intercalation compel us to conclude that the bonding is due to charge transfer from hydrogen to the d band of the tantalum layer, and that the enhanced superconducting transition temperatures of $2H \cdots TaS_2$ and $2H \cdots NbSe_2$ are due to suppression of a charge density wave instability near 80 and 35 °K, respectively. Furthermore, the evidence presented here and correlated with data elsewhere on other atom and organic intercalates, as well as on mixed anion alloys, indicates that in each case enhancement in T_c is caused by superlattice suppression. This present interpretation of the relation between the increase in T_c and the suppression of the superlattice distortion is in marked contrast to the suggestion that excitonic superconductivity exists in these compounds with a maximum $T_c \sim 4$ °K for that mechanism.⁴ Allender, Bray, and Bardeen suggested that, under favorable conditions, an exciton mechanism could lead to T_c 's as high as 800 °K.²⁹ While Phillips used the properties of intercalation compound (among other arguments) to refute the possibility of the above estimated high transition temperature, we do not feel that there is any evidence for excitonic or other unusual mechanism for superconductivity in these compounds. The properties of the presently known intercalation compounds, then, do not directly bear on the question of excitonic superconductivity or of a maximum T_c for that mechanism—except to say that the mechanism has not yet likely been observed.

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¹F. J. Di Salvo, G. W. Hull, Jr., L. H. Schwartz, J. M. Voorhoeve, and J. V. Waszczak, *J. Chem. Phys.* **59**, 1922 (1973).

²F. R. Gamble, J. H. Osiecki, and F. J. Di Salvo, *J. Chem. Phys.* **55**, 3525 (1971).

³F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. Di Salvo, and T. H. Geballe, *Science* **174**, 493 (1971).

⁴J. C. Phillips, *Phys. Rev. Lett.* **29**, 1551 (1972).

⁵A. H. Thompson, F. R. Gamble, and R. F. Koehler, Jr., *Phys. Rev. B* **5**, 2811 (1972).

⁶J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Phys. Rev. Lett.* **32**, 882 (1974).

⁷J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Phys. Rev.* (to be published).

⁸Similar observations concerning intercalation of hydrogen and water by electrolysis were noted in a study of the electrochemical behavior of layered compounds and a number of elements in M. S. Whittingham, *Chem. Commun.* **1974** 328.

⁹F. J. Di Salvo, Ph.D. thesis, Stanford University (1971).

¹⁰R. Bachmann, F. J. Di Salvo, T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H. U. Thomas, and R. B. Zubeck, *Rev. Sci. Instrum.* **43**, 205 (1972).

¹¹The use and calibration of this instrument are described in F. J. Di Salvo, A. Menth, J. V. Waszczak, and J. Tauc, *Phys. Rev. B* **6**, 4574 (1972).

¹²G. Arrhenius, R. Fitzgerald, D. C. Hamilton, B. A. Holm, B. T. Matthias, E. Corenzwit, T. H. Geballe, and G. W. Hull, Jr., *J. Appl. Phys.* **35**, 3487 (1964).

¹³P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956).

¹⁴L. J. van der Pauw, Philips, *Res. Rep.* **13**, 1 (1958).

¹⁵L. H. Brixner and G. Teufer, *Inorg. Chem.* **2**, 992 (1963).

¹⁶W. Geertsma and G. Hass, *Proc. Int. Conf. Trans. Met. Comps.* 4th, Geneva, 134 (1973).

¹⁷J. F. Revelli, Ph.D. thesis, Stanford University (1973).

¹⁸F. J. Di Salvo, *Proc. Low Temperature Conference No. 13*, Boulder, Colo., 1972 (unpublished).

¹⁹A. R. Beal and N. Y. Liang, *Phil. Mag.* **27** (1973) 1397, also J. V. Acrivos and J. R. Salem, *Phil. Mag.* (to be published).

²⁰S. F. Meyer, Ph.D. thesis, Stanford University (1973); J. V. Acrivos, S. F. Meyer, and T. H. Geballe, in *Electrons in Fluids*, edited by J. Jortner and Kestner (Springer Verlag (1972)).

²¹J. F. Revelli, Jr. and W. A. Phillips, *J. Solid State Chem.* **9**, 176 (1974).

²²H. N. S. Lee, H. McKinzie, D. S. Tannhauser, and A. Wold, *J. Appl. Phys.* **40**, 602 (1969).

²³E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geballe, *J. Appl. Phys.* **42**, 1491 (1971).

²⁴M. Marezio, P. D. Dernier, A. Menth, and G. W. Hull, Jr., *J. Solid State Chem.* **4**, 425 (1972).

²⁵D. J. Huntley and R. F. Frindt, *Can. J. Phys.* **52**, 861 (1974).

²⁶E. Revolinsky, G. A. Spiering, and D. J. Beerntsen, *J. Phys. Chem. Solids* **26**, 1029 (1965).

²⁷K. Yamaya and T. Sambongi, *Solid State Commun.* **11**, 903 (1972).

²⁸F. J. Di Salvo, unpublished work.

²⁹D. Allender, J. Bray, and J. Bardeen, *Phys. Rev. B* **7**, 1020 (1973).