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Effects of Intercalation on Electron Transport in Tantalum Disulfide

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Studies of the temperature dependence of the electrical resistivity, Hall effect, and magnetic susceptibility indicate that the crystallographic distortion apparent in metallic layered chalcogenides at low temperature is absent after intercalation. In the quasi-two-dimensional superconductor $TaS_2(pyridine)_{1/2}$ the measured c-axis resistivity is 10^4–10^5 times the a-axis resistivity. However, since the temperature dependence of the c-axis resistivity may be represented by a constant times the a-axis resistivity, we believe that the c-axis resistivity is significantly reduced by shorts and that the intrinsic anisotropy is greater than the measured value of 10^5.

INTRODUCTION

The superconductor $TaS_2(pyridine)_{1/2}$ is a stoichiometric crystalline-intercalation complex in which metallic planes of TaS_2 6-Å thick are separated by pyridine (py). Our study of this complex has been stimulated by the two-dimensional nature of the layered dichalcogenides and by the fact that one can increase the electrical anisotropy of these materials by intercalation of organic molecules between the layers.[1] The discoveries of a metal-insulator transition in pure $1T$-TaS_2[2] and of superconducting fluctuations far above T_c in intercalated $2H$-TaS_2[3] show that this class of compounds should be a rich subject for continued investigation. Previous studies of $2H$-$TaSe_2$, $2H$-$NbSe_2$, and $1T$-TaS_2 [1, 2, 4] suggest that the group-Vb-layered chalcogenides might all undergo a low-temperature phase change. The interpretation of these data in terms of magnetic ordering has been shown by NMR studies to be incorrect.[5] X-ray crystallographic studies show that the singularities in the resistivity and magnetic susceptibility in $NbSe_2$ are accompanied by a change in crystal structure,[6] perhaps the result of an electronic instability in a half-filled band and a high density of states at the Fermi level.

Here we report on a comparative study of the resistivity, magnetic susceptibility, and Hall Effect in $2H$-TaS_2 and in the intercalation compound $TaS_2(py)_{1/2}$. These measurements reveal a phase transition in $2H$-TaS_2 at 70 °K that is not present after intercalation. The similarity between our results for TaS_2 and those on $NbSe_2$ and $TaSe_2$ is remarkable and therefore we believe that the transition we have observed in TaS_2 is accompanied by a distortion of the hexagonal array that is common to these group-Vb dichalcogenides.

DESCRIPTION OF MATERIALS

TaS_2 crystallizes in a number of polytypes that differ in the sulfur-tantalum coordination symmetry and in the number of layers per unit cell.[2] The electronic properties of pure and intercalated $2H$-TaS_2 will be compared here. The $2H$ polytype of TaS_2 is stable at room temperature. Large black wrinkled platelike crystals of it are produced by iodine vapor-phase transport followed by slow cooling from the growth temperature.[1] In each layer of the crystal the sulfur atoms lie on the corners of a trigonal prism with a tantalum atom at the center of the prism. However, since each layer is rotated 60° with respect to the previous layer, the repeat distance is two layers. This polytype is metallic and superconducting below 0.8 °K. $TaS_2(py)_{1/2}$ is prepared by treating TaS_2 with pyridine in a sealed Carius tube at 470 °K. The insertion of the pyridine spreads the layers by 6 Å making the Ta-Ta distance 12 Å along the c axis. The exact structure of this complex is not known but it seems likely that the pyridine molecules lie in bilayers parallel to the TaS_2 layers.[7] $TaS_2(py)_{1/2}$ is metallic, at least along the layers, and superconducts below 3.5 °K.

EXPERIMENTAL TECHNIQUES AND RESULTS

The electrical resistivity has been measured on single crystals of TaS_2 and $TaS_2(py)_{1/2}$ both parallel and perpendicular to the layers. The a-axis (parallel to the layers) measurements were made via the van der Pauw technique[8] while the c-axis measurements were made by soldering two contacts to each side of the planar samples using solder with a low melting point. The accuracy of both measurements is limited by the accuracy with which the thickness

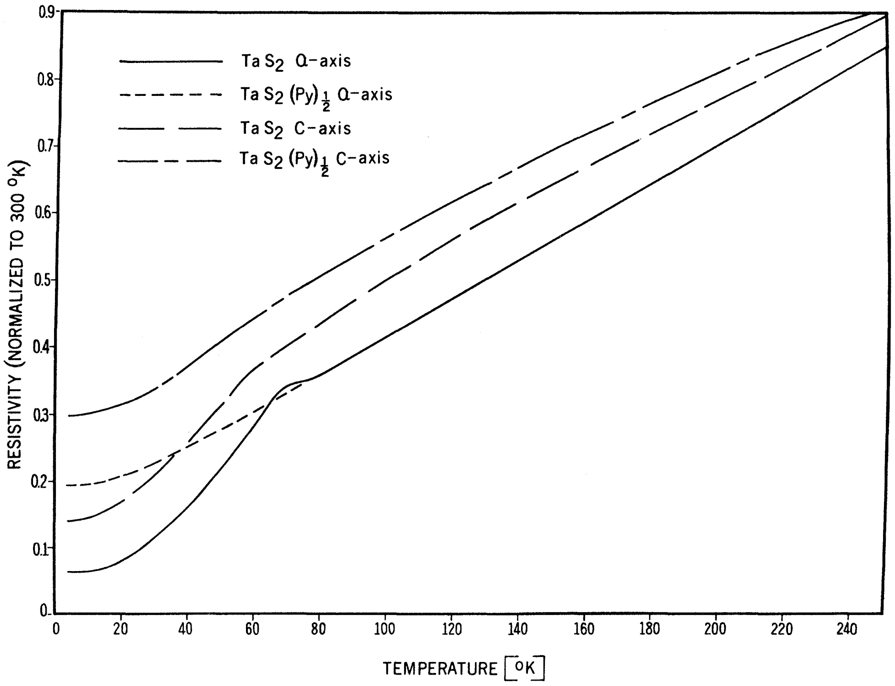

FIG. 1. Resistivity vs temperature for $2H$-TaS_2 and $TaS_2(py)_{1/2}$. The curves are normalized to the room-temperature values of the resistivity, which are $[\rho_a(300\,°K)]_{TaS_2} = 1.5\times10^{-4}\ \Omega$ cm, $[\rho_a(300\,°K)]_{TaS_2(py)1/2} = 3.0\times10^{-4}\ \Omega$ cm, $[\rho_c(300\,°K)]_{TaS_2} = 2\times10^{-3}\ \Omega$ cm, $[\rho_c(300\,°K)]_{TaS_2(py)1/2} = 20\ \Omega$ cm.

can be measured, and since the single crystals are often of nonuniform thickness the accuracy of this measurement could not be better than 10%. However, on a single crystal the resolution of the measurement as a function of temperature is limited by noise which is approximately 1% of the signal. These considerations, combined with the importance of the temperature dependence of the resistivity, dictated that the resistivities be compared on a scale normalized to the room-temperature resistivity, as shown in Fig. 1.

In Fig. 1 we compare the temperature dependence of the resistivity parallel and perpendicular to the layers, both before and after intercalation. The room-temperature values of ρ_a are $1.5\times10^{-4}\ \Omega$ cm for TaS_2 and $3.0\times10^{-4}\ \Omega$cm for $TaS_2(py)_{1/2}$. These values reflect the fact that the intercalation doubles the c-axis lattice dimension, i.e., the change in resistivity appears to be dominated by the geometrical factor introduced by spreading the metal layers apart. This result was substantiated by monitoring the a-axis resistance on a single crystal during intercalation. It was found that the resistance was constant within 5% of its starting value. Thus, the change in the conductivity of the metal layers that would be expected to occur on intercalation must be small compared to the effects of spreading the layers apart. In contrast to this result, the resistivity along the c axis, which was initially $2\times10^{-3}\ \Omega$ cm, increased to values as large as 20 Ω cm after intercalation. Various values for ρ_c were obtained between 2 and 20 Ω cm. This spread in results is probably caused by shorts inside the crystal between the layers and by uncertainty as to the true thickness of the crystal.

Despite these very large changes in c-axis resistivity, the temperature dependence of the c-axis resistivity appears to be insensitive to intercalation. The a-axis resistivities before and after intercalation have the same temperature dependence between 70 °K and room temperature. In this temperature range the resistivity is not exactly linear but tends to flatten off near 70 °K. Below 70 °K the a-axis resistivity of the unintercalated sample rapidly drops, indicating the presence of the phase transition. The c-axis cooling curves show a similar behavior: a metallic temperature dependence with a slope near that of the a-axis curve. The similarity of the a- and c-axis curves for the intercalation compound is surprising and probably results from interlayer shorts since the room-temperature values of the resistivity differ by four to five orders of magnitude. Hence, we feel that the intrinsic anisotropy of the resistivity and the correct temperature dependence for ρ_c in $TaS_2(py)_{1/2}$ have not yet been observed. The heating curves reproduced the cooling curves for both the unintercalated and the intercalated samples. Yet, while measuring the unintercalated c-axis resistivity a number of samples cleaved parallel to the planes near 70 °K. This cleaving appeared to be due to internal stress buildup near the transition temperature.

The Hall effect has been used to verify the existence of the phase transition and to give some insight

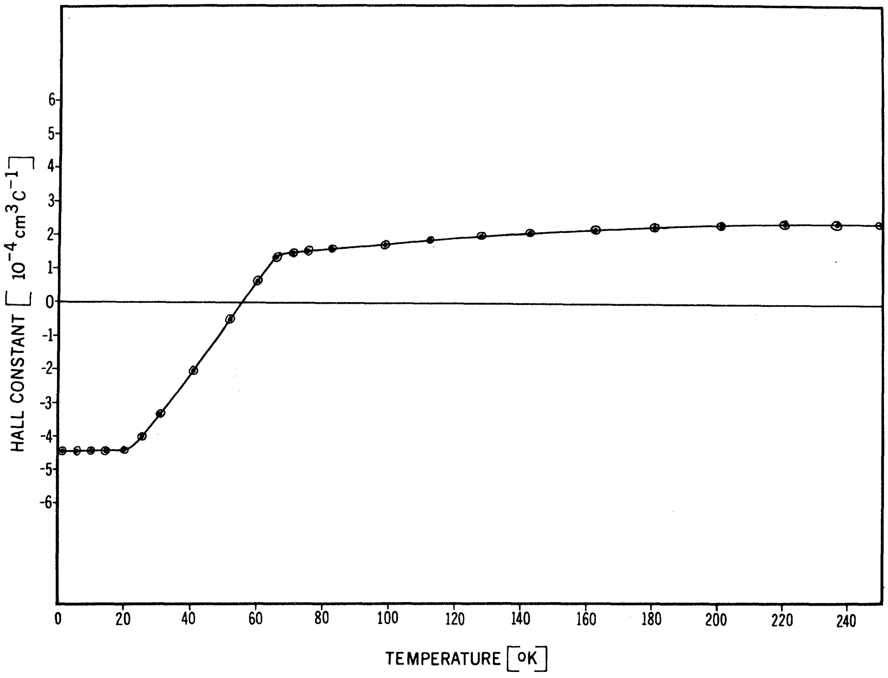

FIG. 2. Hall constant vs temperature for $2H$-TaS_2. Within the resolution of the measurement (±1%) the Hall constant is independent of temperature between 1.7 and 15 °K and between 220 and 300 °K.

into the origin of the transition. As with the resistivity measurements, the accuracy could not be better than 10% because of variations in sample thickness. Relative values are noise limited and are reproducible to approximately 2%. The data plotted in Fig. 2 were taken on pure TaS_2 during both heating and cooling cycles and no hysteresis was detected. The most striking features of these data are the change in sign at 56 °K and the broad transition between 20 and 70 °K that joins regions of nearly constant magnitude. Indeed, the Hall data give the clearest evidence for the phase transition and indicate that the change in slope of the resistivity curve is due to a transition taking place continuously between 20 and 70 °K.

Hall data were taken on the intercalated material at room temperature. In all of the samples measured, the Hall constant was positive and approximately three times larger than that for the unintercalated material. However, this value must be treated with some care. The Hall constant for the configuration used in these experiments is given by $R_H = dV_H/BI$, where d is the sample thickness, V_H is the Hall potential, I is the current, and B is the magnetic field intensity. It was shown above that the resistivity along the a axis changes by a factor of 2 on intercalation, so that only the metal planes should be considered in the contribution to the a-axis resistivity. This means that the effective thickness in the expression for the Hall coefficient is just one-half the measured value. The use of this scaling factor is at best an approximation but one that seems justified in light of the resistivity results. Inserting this scaling factor gives the effective Hall coefficient as $+4.1\times10^{-4}$ cm^3 C^{-1} for the intercalated samples at room temperature. This value is the average for a number of samples measured but the spread in values was within the experimental error, limited by the uncertainty in the thickness measurement. The Hall constant for the unintercalated TaS_2 at room temperature is $+2.5\times10^{-4}$ cm^3 C^{-1}. The Seebeck coefficient measured at room temperature was found to be $-7\pm0.5\times10^{-6}$ V/°K for both the pure and intercalated materials. The negative sign for the thermoelectric power combined with the positive Hall constant suggests an overlapping two-band model in which the number of electrons is greater than the number of holes but with the hole mobility larger than the electron mobility. The insensitivity of the Seebeck coeffecient to intercalation means that the fractional changes in the number of electrons and their mobility must be small on intercalation.

Measurements of the magnetic susceptibility have confirmed the presence of the transition in $2H$-TaS_2 and the absence of one in $TaS_2(py)_{1/2}$. These data were taken using a Faraday balance system in fields to 7 kG. Three calibration points were taken at 300, 77, and 4.2 °K followed by a continuous plot of χ vs T from 4.2 to 300 °K. The data are shown in Fig. 3. In the unintercalated material the presence of the transition is indicated by the peak in the susceptibility at 80 °K. This peak is removed on intercalation, the susceptibility is reduced by 50%, and, except for a slight drop near 4 °K probably associated with the onset of superconductivity, the curve is flat. Deintercalating the sample returns the peak and the behavior of the unintercalated material. These data on the intercalated material agree with those taken by Geballe *et al.*[3] on $TaS_2(py)_{1/2}$ when the magnetic field is parallel to the crystal planes. Our measurements were made on powders and pressed pellets in which the preferred orientation is with the layers parallel to $\vec{B}$.

DISCUSSION

In the data presented above we have shown that the phase transition in $2H$-TaS_2 at 70 °K is removed by intercalation with pyridine. Previous work on phase transitions in $1T$-TaS_2, and $2H$-$NbSe_2$ shows that these transitions are accompanied by a change in crystal structure.[2,6] The present case is remarkably similar to $2H$-$NbSe_2$ and $TaSe_2$[4] and, hence, is quite likely also accompanied by a crystal distortion.

Our data suggest that at room temperature in $2H$-TaS_2 a heavy electron *d* band overlaps the light-hole valence band. The number of holes at room temperature calculated from a one-type-of-carrier model for R_H is 2.5×10^{22} cm^{-3}. This number is double the atomic density of tantalum in TaS_2 and hence is much too large. Also, the hole mobility calculated from ρ_a and R_H is 1.7 cm^2/V sec, which is even smaller than would be expected for *d*-band conduction in TaS_2. These results indicate that a single-band model for conduction at room temperature is not appropriate. Two-band conduction is further suggested by the opposite signs for the Hall and Seebeck coefficients. Since the sign of the Hall voltage is dominated by the carrier of higher mobility, the positive sign for R_H and the negative sign for S lead one to the conclusion that a heavy-electron *d* band overlaps the light-hole valence band at room temperature.

On the other hand, a similar calculation for the electrons in the temperature region below 20 °K gives $n = 1.5\times10^{22}$ cm^{-3} and $\mu_e = 46$ cm^2/V sec for the carrier concentration and mobility, respectively. These are reasonable values for single-carrier conduction since the number of carriers that would be predicted from a calculation of the density of TaS_2 is 1.7×10^{22} cm^{-3}. Furthermore, the mobility of *d* electrons at room temperature would be expected to be approximately 10 cm^2/V sec. A value of 50 cm^2/V sec is reasonable at 4.2 °K because of the reduced lattice scattering at low temperature.

Thus, a single-band model describes the low-temperature conduction. The transition from the high- to low-temperature phases may be then accompanied by a changing band overlap. An overlapping-band model has been proposed by van Maaren and Harland[9] for TaS_2 at room temperature. In that model it is not clear which *d* band might be involved. However, in Ref. 10 it is shown by means of a molecular-orbital calculation that the nondegenerate $A_1'^*$ level, derived from the metal d_{z^2} orbital lying along the prism axis, should be the lowest lying of the *d* levels and from the experimental data it is concluded that this band overlaps the valence band in $2H$-TaS_2. It is further shown that the relative positions of the *d* bands are a sensitive function of the bond angles or, equivalently, of the c/a ratio. Thus, a crystal distortion in which c/a is changed could produce an upward shift in the energy of the lowest *d* level because

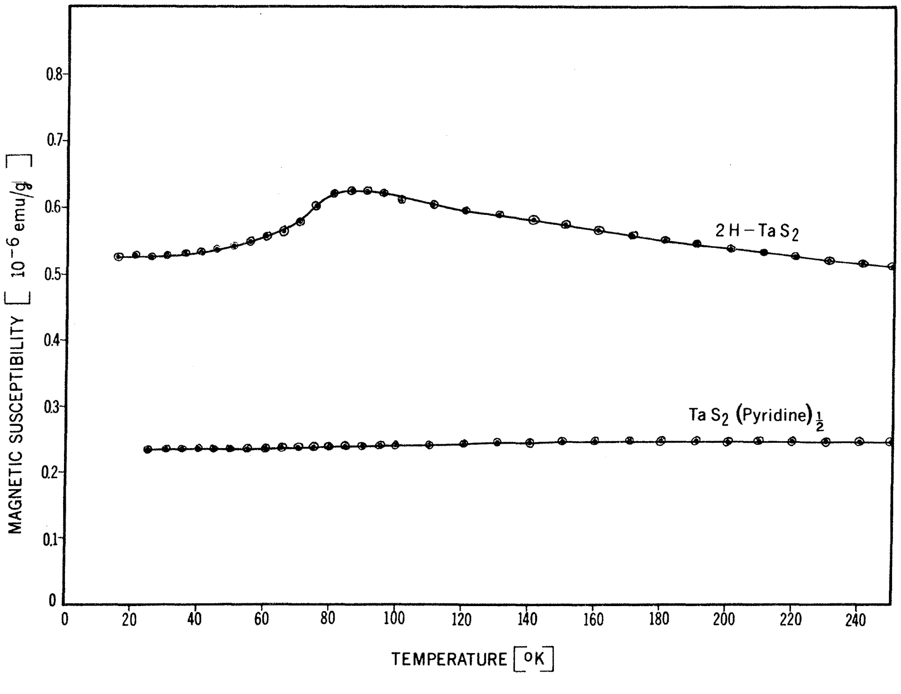

FIG. 3. Magnetic susceptibility vs temperature for $2H$-TaS_2 and $TaS_2(py)_{1/2}$. No correction has been made for the diamagnetism of the cores or of the py molecule.

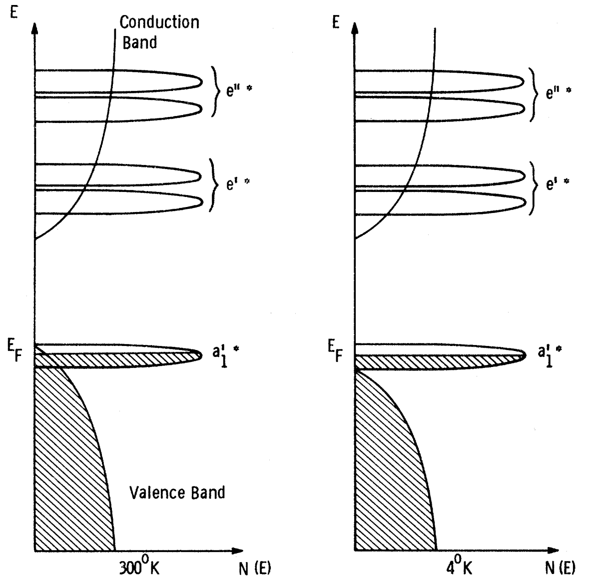

FIG. 4. Schematic energy bands for TaS_2 at room temperature and 4 °K (after R. Huisman *et al.*, Ref. 8). At 300 °K, the Fermi level lies below the top of the valence band.

of increased overlap with the ligand orbitals. For the observed transition the valence band must either remain stationary or move down relative to the *d* band so that the Fermi level, lying close to the top of the valence band at room temperature, can cross the top of the valence band.

The band-overlap model described above is supported by the magnetic susceptibility data. The temperature dependence of the magnetic susceptibility is similar to that for an antiferromagnetic transition. Previous NMR studies[5] and the small values for χ suggest that the peak in χ is associated with a change in the electronic density of states and not with magnetic ordering. This peak can be understood from the band scheme shown in Fig. 4. At room temperature the *d* conduction band overlaps the *sp* valence band such that the Fermi level lies below the top of the valence band. Some electrons from the valence band are donated to the *d* band so that the *d* band is more than half-full. Then, assuming a triangular model for the *d* band, the electronic density of states is less than the maximum density in the *d* band. Since the density of states at the Fermi level in the *d* band is much greater than the density in the valence band, the total density of states is less than some maximum value. Similarly, if the *d* band lies higher at lower temperature so that the Fermi level is above the top of the valence band, the total density of states is just that in the *d* band and is less than the density when hole states contribute to $N(E_F)$.

After intercalation the Seebeck coefficient is approximately the same as before intercalation while the Hall constant increases. Preliminary electron-spectroscopy-for-chemical-analysis data[7] suggest that the nitrogen atom in the pyridine contributes about one-fourth an electron to the TaS_2. It is also known that Lewis bases (electron donors) preferentially intercalate.[7] Thus, it appears to be established that electrons are donated to the TaS_2 by the intercalate. But if electrons are added at the Fermi level of a two-band conductor, one would expect that the positive Hall constant would decrease. However, it is also known that on intercalation the *a* axis increases by as much as 1% so that the *c*/*a* ratio and the bond angles may also change on intercalation. Thus, referring to the molecular-orbital calculation in Ref. 10, one would expect the *d* conduction band to be shifted relative to the valence band and intercalation would cause a redistribution in the number of electrons and holes, making the Seebeck and Hall results acceptable.

If, in fact, the *d* conduction band is depressed by intercalation, then intercalation could affect the low-temperature transition through both a realignment of the relevant bands and through a donation of electrons to the metal. Depression of the *d* band relative to the valence band could prevent the appearance of the transition in the electrical measurements even if it occurs crystallographically, since then the change in carrier type would not occur. The distortion of the lattice in the case of $NbSe_2$ is of the same order[6] (approximately a 1% change in lattice dimensions) as that caused by intercalation in TaS_2, so that it is not unreasonable to expect the transition to be removed by intercalation. The absence of the transition in the intercalated material should, however, be checked by an x-ray analysis.

In addition to removing the transition by intercalation we have found that certain pure TaS_2 crystals do not have the transition. A correlation has been made between the rate at which crystals are cooled from the growth temperature and the presence of the transition. Crystals cooled too rapidly do not go through the transition, are difficult to intercalate, and have a higher superconducting critical temperature. These crystals are a mixed phase, consisting of the low-temperature 2*H* phase and one or more of the high-temperature phases. Several different superconducting critical temperatures have been reported for 2*H*-TaS_2 [11] and may be related to the presence or absence of the phase transition.

Perhaps the most serious criticism of the above model for the phase transition in 2*H*-TaS_2 is that it does not seem reasonable that a transition resulting from a sensitive band overlap should be found in all of the group-V*b* dichalcogenides. However, two comments can be made that make the band-overlap model more acceptable. First, the transitions in the various materials are not identical. In niobium and tantalum diselenides either single- or double-band conduction is consistant with the data. It is not necessary to assume that the same band overlap or the same bands are involved in the observed transitions. For example, in $TaSe_2$ overlap between the metal *d* band and the anion conduction band may be important below 40 °K. The second relevant comment is that, if the low-temperature transitions are the result of an instability in a half-filled band that is characteristic of the group-V*b* hexagonal layered crystals, then the observed discontinuities in transport properties are necessary and not accidental. The temperature-sensitive overlapping bands in $2H$-TaS_2 are then a result of the instability and not the cause of it.

A number of important characteristics of the intercalated materials are evident in the resistivity-vs-temperature curves. The similarity in the slopes of the four curves in Fig. 1 is striking. Between 70 °K and room temperature the *a*-axis resistivities follow essentially identical curves. This similarity, despite the fact that the resistivity of the intercalated material is double that of the unintercalated material, suggests that the Debye temperature of the metal lattice does not change appreciably on intercalation. This result is consistent with a model in which conduction takes place in covalently bound layers separated by the intercalated molecule weakly bound to the metal. Perhaps the most surprising result in Fig. 1 is that the *c*-axis resistivity as a function of temperature is roughly proportional to the *a* axis both before and after intercalation even though the resistivity values differ by as much as 10^5. We believe that this is the result of shorts. These shorts might be crystalline imperfections in which some layers run perpendicular to the layers of the majority of the material, excess metal atoms trapped between the layers, or perhaps screw dislocations that are formed when the crystal is grown. The existence of screw dislocations in these materials has been confirmed by optical microscopy. Electrical shorts must be eliminated before the inherent anisotropy and temperature dependence of the *c*-axis resistivity can be measured. The effects of superconducting fluctuations on the low-temperature resistivity have recently been studied and will be reported elsewhere.[12]

CONCLUSION

We have reported the observance of a phase transition in TaS_2 that appears to be associated with a crystallograhic distortion of the type common among the layered chalcogenides of group V*b*. This distortion is removed by the intercalation of an organic base that is thought to donate electrons to the conduction band and influence the overlap between the *d* and valence bands. The enhancement of the critical temperature from 0.8 to 3.5 °K produced by intercalation is then most likely due to both the absence of the distortion and to the added electron density.

In view of the interest in the two-dimensional aspects of the superconductivity in $TaS_2(py)_{1/2}$, we have examined the temperature dependence of the electrical conductivity of $2H$-TaS_2 and $TaS_2(py)_{1/2}$ in the direction perpendicular to the layers. In both cases, the resistivity perpendicular to the layers is much greater than that parallel to the layers. But both before and after intercalation with pyridine we find that the resistivity in the two directions is related reasonably well at all temperatures by a scalar factor, suggesting that the measured conductance is along the planes and that paths parallel to the planes provide coupling through the crystal.

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