Experimental Study of the Solid Solutions $Ti_xTa_{1-x}S_2$

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We have found that the substitutional replacement of Ti for Ta in TaS_2 stabilizes the octahedral $1T$ phase for x between 0.1 and 0.9. A comparison of the resistivity, magnetic susceptibility, and thermoelectric power shows that at room temperature the properties vary systematically from diamagnetic, semiconducting behavior for $1T$-TaS_2 to paramagnetic, metallic behavior for TiS_2. This interpretation of the data contradicts all previous models which treat TiS_2 as a degenerate semiconductor.

The layered dichalcogenides of the transition elements of columns IV and VB and their intercalation complexes have recently been the subject of extensive studies with special emphasis on their superconducting properties.[1] In these studies, the layers of the crystal are separated at the Van der Waals gap by organic or inorganic species intercalated between the dichalcogenide layers. Such complexes are electrically quasi-two-dimensional. The electronic and optical properties of these compounds are usually discussed in terms of empirical band models proposed by Wilson and Yoffe[2] and by Greenaway and Nitsche.[3] The electrical transport properties of TiS_2 and TaS_2 should fall within the province of these schemes but are anomalous. TiS_2 has been described as a semiconductor with a 1-eV band gap. Its high metallic conductivity is rationalized in terms of metal-rich off stoichiometry and degenerate semiconductivity. Electrical conductivity in $2H$-TaS_2 seems to be best described by a two-band model.[4] $1T$-TaS_2 presents an even more formidable problem. According to Ref. 2 it should be metallic, and yet we have found that it is metallic only above 80°C.[5,6] We believe the present study of the alloys of these compounds shows that TiS_2 is in fact a metal.

Both powder and large single-crystal materials were prepared for this study. Mixed-cation crystalline powders were obtained by mixing prereacted TiS_2 and TaS_2 powders in the proper stoichiometric ratios, and heating the pressed pellets of the mixtures to 1273°K in evacuated quartz ampules. After heating for approximately 2 weeks, the samples were annealed at 773°K for 1 week and cooled slowly to room temperature. The slow cooling and annealing should ensure that only the phase that is stable at room temperature is produced. In every case this was the $1T$ phase. The powders prepared in this way were then used as the starting materials for vapor-phase transport of single crystals. Powder x-ray diffraction studies of these materials revealed that the lattice parameters vary linearly with composition. For $1T$-TaS_2, $a=3.36$ Å and $c=5.90$ Å. For TiS_2, $a=3.410$ Å and $c=5.702$ Å. No evidence of disorder or superlattice ordering was detected in any diffractogram.

Room-temperature values of the magnetic susceptibility were taken with a Faraday balance system in fields to 7 kG. The values increase systematically from -25×10^{-8} emu/g for $x=0.1$ to $+33\times10^{-8}$ emu/g for TiS_2. The small values severely limit the accuracy of the measurement, but a definite trend from diamagnetic behavior for $1T$-TaS_2 to paramagnetic behavior for TiS_2 is detectable. The values $\pm2.5\times10^{-8}$ emu/g for $1T$-TaS_2 are anomalous because of the presence of hysteresis in an electronic transition near room temperature.[5,6]

Measurements of Hall constants did not reveal compositional trends. The values are nearly constant for all compositions. Subtle differences were possibly masked by uncertainties in the crystal-thickness measurement. The typical value of electron concentration obtained is near

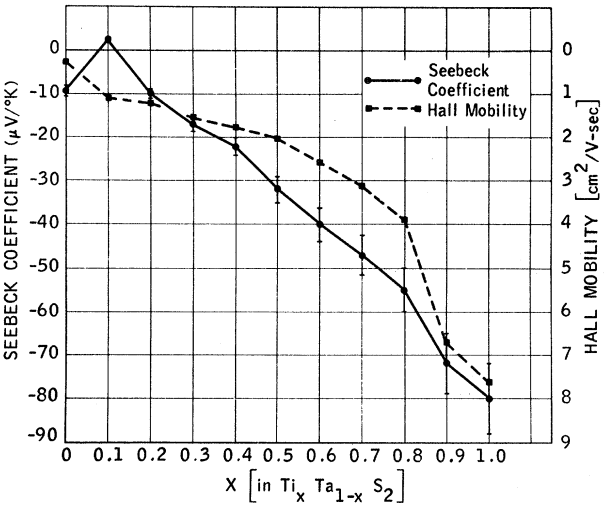

FIG. 1. Comparison of the Hall mobility and Seebeck coefficient as a function of composition at room temperature. Above 80°C the Hall and Seebeck data change monotonically.

5×10^{21} cm^{-3}. No effort was made to account for the anisotropy in the effective mass or for an energy-dependent mobility, so this carrier concentration represents a lower limit for a single-band model. This large number of carriers must be nearly constant with composition in order to give the observed nonvarying Hall values. Any observed systematic changes in transport properties at room temperature must then be closely related to changes in carrier mobility. Thus, the Hall mobility (independent of sample thickness) was compared with the Seebeck coefficient as shown in Fig. 1. All Hall mobility data were taken by the Van der Pauw technique, while the Seebeck data were taken in the steady state with indium contacts. The data displayed in Fig. 1 indicate that for $x \geqslant 0.2$ the Hall mobility calculated from a single-band model generally parallels the Seebeck coefficient. The Seebeck coefficient is an experimentally measured parameter and is independent of assumed band models. Thus, the carrier concentration is reasonably insensitive to composition, while the Hall and drift mobilities take on similar compositional dependences.

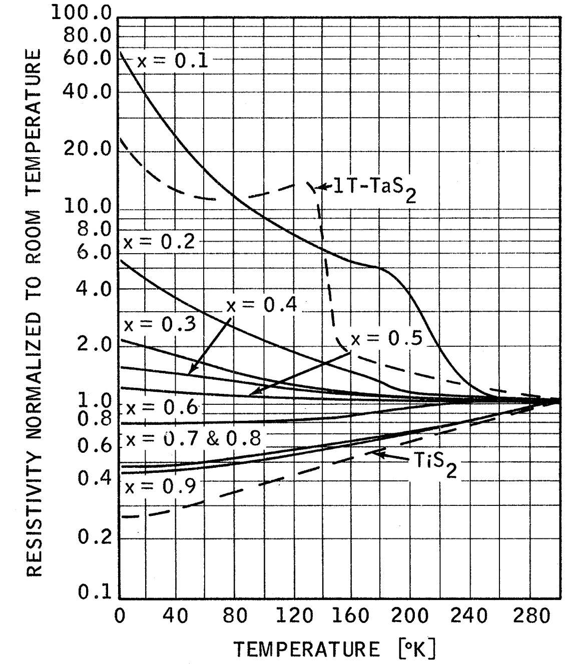

FIG. 2. Temperature dependence of the resistivity as a function of composition. The curves are normalized to room temperature where all the resisitivity values are nearly constant and equal to $\simeq 8\times10^{-4}$ Ω cm.

Trends in the temperature dependence of the resistivity are shown in Fig. 2. These resistivity data were taken by the Van der Pauw technique on single crystals. All the curves have been normalized to the room-temperature values since the actual values are similar at 300°K. The logarithm of the resisitivity has been plotted for visual clarity. The trend from negative to positive slope is clearly represented in this figure. None of the curves with negative slope fit an Arrhenius plot over any significant temperature interval. In general, the resistivity levels off at low temperature as if limited by impurity-band conduction. The presence of a phase transition in the $Ti_{0.1}Ta_{0.9}S_2$ material is apparent in the resistivity data of Fig. 2. Its presence was verified by magnetic-susceptibility measurements that show a discontinuous drop in χ as the temperature is raised through the transition. This is the low-temperature, semiconducting-semiconducting transition previously observed in $1T$-TaS_2.[5] No other phase changes were detected up to 800°K.

Some of the trends and values presented above were quite unexpected. $1T$-TaS_2 is a narrow-gap semiconductor at room temperature with an activation energy of 2×10^{-5} eV,[5] while TiS_2 has been thought to be a degenerate semiconductor.[2] Our Hall data, supported by our Seebeck results, indicate (assuming a one-band model) that the carrier concentration is quite large and nearly constant throughout the series. The small Hall mobility for TiS_2 (our value is close to that reported by Conroy and Park[7]) should suggest that a two-band model should be required. We reject this because correlation between the Hall and Seebeck data would then require an unlikely cancelation between the hole and electron bands. Also, it does not appear that TiS_2 has been convincingly identified as a degenerate semiconductor. The optical-reflection data[3] show a Drude tail up to $\simeq 0.8$ eV, the Hall mobility is near 8 cm^2/V sec, the resistivity has a metallic slope, and the Seebeck coefficient is approximately 70 $\mu V/°K$. (Compare with bismuth, a semimetal, where $S \simeq 100$ $\mu V/°K$.) Using only these data, TiS_2 could be either a highly degenerate semiconductor or a metal. However, the data presented here for the Ti-Ta alloys would be much easier to explain if TiS_2 were a metal. We have measured a Hall coefficient corresponding to almost one carrier per titanium in TiS_2. Previous authors attributed the degeneracy of TiS_2 to an excess of Ti. We have found (as did Conroy and Park[7]) that our materials are stoichiometric to within the limits of resolution of chemical analysis; approximately 0.2%. The calculated and measured mass densities agree within 0.1%. Furthermore, no additional crystalline phases could be detected via scanning electron-microscope studies. Thus, a number of carriers approaching one per titanium would be unrealistic if TiS_2 were in 1-eV–gap semiconductor.

Previous authors have based their interpretation of the electronic properties of TiS_2 either on an impirical band model[2] or on an extrapolation from the optical properties of the hafnium and zirconium disulfides.[3] However, very convincing x-ray spectroscopy studies made by Fischer[8] have shown that the bonding and antibonding Ti $3d$ and S $3p$ bands overlap. Within the resolution of these x-ray measurements (0.1 eV), a band gap at the Fermi level does not exist. These data combined with those presented in this Letter lead us to urge that TiS_2 be considered a metal or narrow-gap semiconductor with $E_g \lesssim 0.1$ eV. Measurements of the heat capacity, plasma frequency, and superconducting transition temperature below 0.4°K are being carried out by others. The plasma-frequency studies have indicated that the carrier concentration is approximately that measured by the Hall effect.[9]

The resistivity-versus-temperature data have suggested new areas for both experimental and theoretical studies. The composition intervals between $x=0.5$ and 0.6, where a material of temperature-independent resistivity may exist, and between $x=0$ and 0.2, where the $1T$-TaS_2 transitions are eliminated, should receive further experimental study.

Despite the phase transition in the $x=0.1$ material, a relationship can be drawn between the low-temperature values of resistivity for $x=0.1$ through 0.5 and the composition. For these alloys it has been found that $\ln[\ln\rho_{T<60°K}] \propto 1-x$. Assuming activated conductivity for the alloys the logarithmic relation implies that the logarithim of the activation energy (E_a) is proportional to the tantalum concentration. The activation energies calculated from an Arrhenius plot below 20°K are consistent with this conclusion. The compositional-dependent activation energy could result from a Ta-Ta interaction that is screened by the addition of Ti. The existence of this correlation between the value of the resistivity at low temperature and the composition was unexpected. The alloy with $x=0.1$ is the only one having an obvious phase transition between 20 and 300°K. The logarithmic relationship suggests, however, that all of the alloys with $x \leq 0.5$ are in the same state at low temperature. Thus, either the materials that do not show the transition must be in the low-temperature state at room temperature or the transition is so gradual as to not be detected by the techniques used here.

Pure $1T$-TaS_2 does not fit either the resistivity value or activation energy correlation at low temperature. The TaS_2 resistivity is too low to fit the logarithmic relationship. This may be the result of impurity or defect scattering in the alloy crystals. However, the TaS_2 activation energy is also too low. This anomalous behavior for $1T$-TaS_2 might have been expected since the Seebeck coefficient and magnetic susceptibility are also anomalous at room temperature. Furthermore, the $1T$-TaS_2 is the only material having a discrete metal-insulator transition just above room temperature. Comparing the $1T$-TaS_2 in its metallic state above 350°K with the remainder of the series at the same temperature removes the anomalies. In that temperature range a simple monotonic trend of all the properties from *metallic* $1T$-TaS_2 to TiS_2 is obtained. This lends further support to the conclusion that TiS_2 is a metal.

TiS_2, as we prepare it, reacts at room temperature with organic and inorganic Lewis bases as well as stronger electron donors such as the alkali metals by taking up these species between the crystal layers. In an ideal crystal the TiS_2 layers are held together principally by Van der Waals forces, and it is presumably for this reason that the crystal can be intercalated. Now the postulated degeneracy of TiS_2 is thought to arise from excess Ti atoms between the layers. Such an excess is found in crystals deliberately prepared metal rich or in material quenched from high temperature. In such materials basal cleavage is difficult and the crystals are brittle. The ease with which our materials can be cleaved and intercalated argues against interlayer Ti.

The implications of the present study extend to the interesting work of Barz *et al.*[10] on the layered compound $Li_xTi_{1.1}S_2$. A recent theoretical speculation by Phillips[11] on the superconductivity in these compounds includes the assumption that TiS_2 has a 1-eV band gap. Before meaningful theoretical considerations of these and other intercalation compounds can be made, a more careful study of the simple dichalcogenides will be required.

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[1] F. R. Gamble, F. J. Di Salvo, R. A. Klemm, and T. H. Geballe, Science 168, 568 (1970); F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. Di Salvo, and T. H. Geballe, Science 174, 493 (1971); F. R. Gamble, J. H. Osiecki, and F. J. Di Salvo, J. Chem. Phys. 55, 3525 (1971).

[2] J. S. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

[3] D. D. Greenaway and R. Nitsche, J. Phys. Chem. Solids 26, 1445 (1965).

[4] A. H. Thompson, F. R. Gamble, and R. F. Koehler, Phys. Rev. B 5, 2811 (1972).

[5] A. H. Thompson, F. R. Gamble, and J. F. Revelli, Solid State Commun. 9, 981 (1971).

[6] A. Menth, T. H. Geballe, and F. R. Gamble, Bull. Amer. Phys. Soc. 16, 403 (1971).

[7] L. E. Conroy and K. C. Park, J. Inorg. Chem. 7, 159 (1968).

[8] D. W. Fischer, Phys. Rev. B (to be published).

[9] T. H. Geballe and J. Benda, private communication.

[10] H. E. Barz *et al.*, Science 175, 884 (1972).

[11] J. C. Phillips, Phys. Rev. Lett. 28, 1196 (1972).

Evidence for the Polarization of Polyethylene from Positron Lifetimes*

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Four lifetimes have been resolved for positrons annihilating in polyethylene. The three longer lifetimes are identified with three kinds of morphologies in which the positrons annihilate. These lifetimes are observed to decrease with increase of applied static electric field across the polyethylene. This evidence and evidence from the intensities associated with these three lifetimes support the conclusion that polyethylene is polarized under the influence of a static electric field.

We have used positrons as a probe to elucidate the structure of polymeric solids and in particular to show that polyethylene, normally considered nonpolar, is polarized under a static electric field. Polarization, in this context, refers to electric-field-induced molecular alignment as well as field-induced charge separation. The results from initial experiments are reported here.

The annihilation time spectra for positrons annihilating in polymeric solids are complex and can be decomposed into exponentially decaying components. We have clearly resolved four lifetime components (Table I) by analytically representing the annihilation lifetime spectra for positrons annihilating in polyethylene by a sum of exponential functions convoluted with a prompt instrumental resolution function as described by Lichtenberger, Stevens, and Newton.[1] In agreement with other authors[2,3] we had only previously been able to resolve three lifetime components.[4] In an attempt to better characterize the annihilation mechanisms associated with each of these components we measured the lifetimes and intensities of positrons annihilating in polyethylene under the influence of a static electric field.

The polyethylene sample used has a weight average molecular weight of 41 700 and its ratio