Conclusions

(1) The four ir-active fundamentals of the $(Nb_6Cl_{12})^{n+}$ cluster (n = 2, 3, 4) are established as 340–353, 279–302, 234–267, and 141–143 cm^{-1}. It appears likely that the three highest bands are associated primarily with motion of the halogens and the lowest band is associated primarily with a motion of the metal atoms.

(2) The M–L stretching frequencies for the (Nb_6Cl_{12})-L^n species are established as 409, 439, 200, 157, and 100 cm^{-1} for L = OH, DMSO, Cl, Br, and I, respectively.

(3) The M–L frequencies are largely independent of the nature of any other terminal ligands which may be present. For a given M, the M–L frequency depends primarily on the atom in the terminal ligand to which M is attached.

(4) There is little interaction between the M–L and M_6X_{12} modes when there is no overlap of frequencies.

(5) The terminal ligands are not appreciably dissociated when the compounds are dissolved in nitromethane solution.

(6) There are no appreciable solid-state effects on the ir spectra of these compounds.

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Electrical Properties of the Group IV Disulfides TiS_2, ZrS_2, HfS_2, and SnS_2[1,2]

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Large single crystals of TiS_2, ZrS_2, HfS_2, and SnS_2 have been prepared by the chemical transport method. All four disulfides were found to be n-type semiconductors with the CdI_2 (C6) structure. Room-temperature electrical conductivity values were 1.4×10^3 ohm^{-1} cm^{-1} for TiS_2, 7.6×10^{-1} ohm^{-1} cm^{-1} for ZrS_2, 3.0×10^{-3} ohm^{-1} cm^{-1} for HfS_2, and 9.6×10^{-9} ohm^{-1} cm^{-1} for SnS_2. Both TiS_2 and ZrS_2 exhibited typical degenerate semiconductor behavior at room temperature. Energy gap values for HfS_2 and SnS_2 were 2.1 and 2.2 eV, respectively. Magnetic susceptibility values at room temperature were 0.52, 0.61, 0.44, and 0.41 BM, respectively, for TiS_2, ZrS_2, HfS_2, and SnS_2.

Introduction

The disulfides of the group IV elements Ti, Zr, Hf, and Sn have remarkably similar properties, characterized by high metallic luster. TiS_2, ZrS_2, HfS_2, and SnS_2 all crystallize in the hexagonal (C6) CdI_2 structure[3] which consists of a hexagonal close-packed sulfide lattice with metal atoms in alternate layers of the octahedral holes. Alternatively, the structure may be described as planar sheets of MS_6 octahedra joined at their edges. The optical and electronic transport properties of this group of compounds is of interest from several aspects. (1) They exhibit pseudo-metallic properties. In addition to the metallic luster, high room-temperature electrical conductivities have been reported for TiS_2[4-6] and ZrS_2.[4] (2) They constitute a group of isostructural compounds in which one may hope to examine effects on the optical and electron-transport properties arising from the substitution of metal atoms, differing in size, nuclear charge, and d-orbital configuration, in the same anion (or nonmetal atom) lattice. Optical properties of these compounds have been reported by Greenaway and Nitsche,[7] but electrical conductivity data on single crystals have been reported only for TiS_2[6] and SnS_2,[8] and the literature lacks any data on the temperature dependence of conductivity, Hall mobility, or charge-carrier concentration of any of these compounds. This research was directed toward the characterization of single crystals of TiS_2, ZrS_2, HfS_2, and SnS_2.

Experimental Section

Materials.—Titanium metal sponge (99.99%, United Mineral and Chemical Corp.), zirconium metal sponge (99.99%, K & K Laboratories, Inc.), hafnium metal sponge (99.9%, Electronic Space Products, Inc.), purified sulfur (J. T. Baker), and purified SnS_2 (City Chemical Corp.) were employed as starting materials. Resublimed reagent grade iodine was used in the chemical transport reactions.

Preparation of Single Crystals.—Single crystals of TiS_2, ZrS_2, HfS_2, and SnS_2 were prepared by utilizing chemical transport reactions, in a procedure similar to that employed by Greenaway and Nitsche.[7,9] All reactions were carried out in Vycor tubes ranging in size from 1.5 to 2.5 cm i.d. and 10–15 cm in length, employing iodine vapor (5 mg/cm^3) as the transport agent. SnS_2 crystals were prepared from SnS_2 powder. The transition

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[1] This research is taken from the thesis presented by Kyu Chang Park to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, Aug 1967.

[2] Presented before the Division of Inorganic Chemistry at the 154th Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[3] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1962, p 512.

[4] F. K. McTaggart and A. D. Wadsley, *Australian J. Chem.*, **11**, 445 (1958).

[5] F. K. McTaggart, *ibid.*, **11**, 471 (1958).

[6] H. G. Grimmeiss, A. Rabenau, H. Hahn, and P. Ness, *Z. Elektrochem.*, **65**, 776 (1961).

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

[8] G. Domingo, R. S. Itoga, and C. R. Kannewurf, *Phys. Rev.*, **143**, 536 (1966).

[9] For a definitive review of this method see H. Schäfer, "Chemical Transport Reactions," Academic Press, New York, N. Y., 1964.

metal disulfides were prepared from the elements in the presence of iodine vapor. Metals in sponge form reacted most rapidly and smoothly.

In the case of SnS_2, the best crystals formed during transport from a 700 to a 600° zone (700→600°) and reaction times of 25–30 hr produced golden yellow single crystals of dimensions up to 13×10 mm^2 and several microns thick. For the transition metal disulfides transport from 900 to 800° for 70 hr produced crystals as large as 20×20 mm^2 of TiS_2, 20×15 mm^2 of ZrS_2, and 15×12 mm^2 of HfS_2. The transport rate increased rapidly with a small increase in iodine concentration, but only polycrystalline masses resulted when the iodine concentration substantially exceeded 5 mg/ cm^3.

Chemical Analyses. Tin Analysis.—A weighed SnS_2 crystal was dissolved in aqua regia. The cool solution was diluted to a convenient volume (250–400 ml), and hydrazine hydrochloride was added. Tin was plated on a copper-coated platinum electrode at a potentiostat-controlled voltage of −0.65 V *vs.* a standard calomel electrode.

Titanium Analysis.—A weighed TiS_2 crystal was dissolved in a mixture of 40 ml of 1:1 sulfuric acid, 20 ml of concentrated HNO_3, and 15 ml of concentrated HCl and heated to fuming temperature. A 1-ml sample of 30% H_2O_2 was added to the cooled solution, followed by dilution to 250 ml. Ti was determined colorimetrically[10] on a Bausch and Lomb Spectronic 20 at 410 mμ, using a water blank. A titanium standard solution was prepared from National Bureau of Standards TiO_2 (sample No. 154) that had been fused with $KHSO_4$ and dissolved in dilute H_2SO_4.

Zirconium Analysis.—A weighed ZrS_2 crystal was fused with $Li_2B_4O_7$ in a graphite crucible at 1040° for 20 min. The bead was dissolved in 1:1 HCl and diluted. Zr was determined colorimetrically[10,11] at 540 mμ, using alizarin dye. The standard Zr solution was prepared from $ZrOCl_2 \cdot 8H_2O$ (Sargent, CP) that was purified by successive washings with concentrated HCl, followed by washing with acetone and air drying.

Hafnium Analysis.—A weighed HfS_2 crystal was fused with $Li_2B_4O_7$ in a graphite crucible at 1040° for 20 min. The bead was dissolved in 25 ml of 1 *M* HCl, and 20 ml of 0.01 *M* EDTA was added. The pH was adjusted to 3 using 10% ammonium acetate. The solution was titrated with 0.04 *N* thorium nitrate using xylenol orange indicator.[12]

Sulfur Analysis.—Sulfur was determined by two methods on all samples. Method 1 involved oxidation in a stream of oxygen,[13] absorption of the SO_2 in water, and titration with KIO_3. Method 2 involved gravimetric determination as $BaSO_4$.

Analytical results are given in Table I.

TABLE I

ANALYTICAL DATA

Compd	% M Obsd	% M Calcd	% S Obsd	% S Calcd
TiS_2	42.7 ± 0.2	42.76	57.5 ± 0.9	57.24
ZrS_2	58.6 ± 0.2	58.72	42.1 ± 1.0	41.28
HfS_2	73.6 ± 0.2	73.57	27.3 ± 1.0	26.43
SnS_2	64.7 ± 0.3	64.92	34.8 ± 0.7	35.08

X-Ray Diffraction.—Powder diffraction data were recorded with a Philips Type 12045 B diffractometer. Single-crystal rotation photographs were also employed to determine the *c*-axis parameter. Copper Kα radiation was employed throughout.

Electrical Resistivity and Hall Effect.—Measurements of the specific resistivity and Hall effect were made using the four-probe method of van der Pauw,[14] over the temperature range 77–650°K, approximately. This method allows both measurements to be made on a flat sample of arbitrary shape. High-temperature measurements were made in a dry argon atmosphere and low-temperature measurements were carried out under vacuum. The crystal holder and cryostat are diagrammed in Figure 1. Electrical contacts were made with silver paint (Sc 12) on high-resistance samples and with rose metal (low temperature) or platinum paint (high temperature) on the low-resistance samples. Hall coefficient measurements were made with a Varian electromagnet in a 13-kgauss field and checked with a 5.2-kgauss permanent magnet.

Magnetic Susceptibility.—Magnetic susceptibility measurements were carried out on powdered samples by the Gouy method. Freshly ground crystals of the samples prepared by chemical transport were used. Measurements were made at fields of 5120 and 8060 gauss, using $HgCo(SCN)_4$ as the calibration standard.

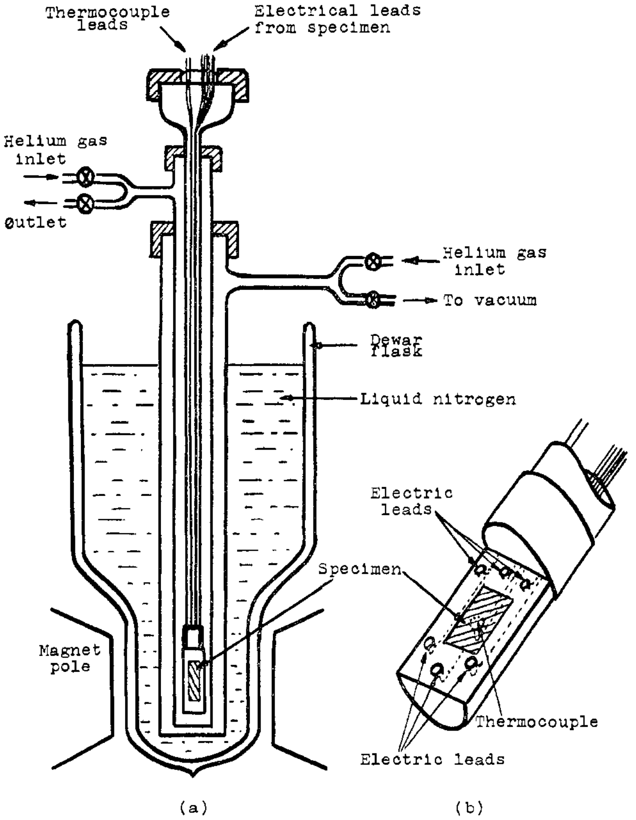

Figure 1.—Cryostat (a) and crystal holder (b) for resistivity and Hall effect measurements.

Results and Discussion

The group IV disulfide crystals were produced by chemical transport in the form of very thin platelets several microns thick and 1.3–3 cm^2 in area. The TiS_2 crystals were brass colored, ZrS_2 brown-violet, HfS_2 purple, and SnS_2 gold-colored. All exhibited a pronounced metallic luster. X-Ray diffraction examination showed all to have the C6 cadmium iodide structure. The lattice parameters are listed in Table II, along with previously reported values.

The electrical conductivity data are plotted as a function of temperature for the four disulfides in Figures 2–5. All measurements were made on plane-parallel platelets perpendicular to the crystallographic *c* axis. Thermal probe tests of the Seebeck voltage

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[10] See I. M. Kolthoff and P. Elving, Ed., "Treatise on Analytical Chemistry," Vol. 5, Interscience Publishers, Inc., New York, N. Y., 1961, Part II, p 26.

[11] G. Charlot, "Colorimetric Determination of Elements," Elsevier Publishing Co., New York, N. Y., 1964.

[12] L. J. Ottendorfer, *Chemist Analyst*, **48**, 97 (1959).

[13] A. C. Holler, R. Klinkenberg, and C. Friedman, *Anal. Chem.*, **26**, 1658 (1954).

[14] L. van der Pauw, *Philips Res. Rept.*, **13**, 1 (1958).

TABLE II

UNIT CELL DIMENSIONS OF GROUP IV DISULFIDES

a, Å	c, Å	c/a	Ref
	TiS$_2$		
3.402 ± 0.004	5.698 ± 0.004	1.675	This work
3.405 ± 0.005	5.687 ± 0.005	1.670	Greenaway and Nitsche[7]
3.4048	5.6904	1.671	Benard and Jeannin[a]
3.4080 ± 0.0002	5.7014 ± 0.0003	1.673	Bartram[b]
3.39	5.70	1.68	McTaggart and Wadsley[4]
	ZrS$_2$		
3.661 ± 0.004	5.825 ± 0.004	1.591	This work
3.66 ± 0.030	5.85 ± 0.030	1.598	Greenaway and Nitsche[7]
3.660	5.825	1.592	LaPlaca[c]
3.662	5.809	1.586	Bracuti[d]
3.662	5.813	1.587	McTaggart and Wadsley[4]
	HfS$_2$		
3.625 ± 0.006	5.846 ± 0.006	1.612	This work
3.622 ± 0.003	5.88 ± 0.030	1.623	Greenaway and Nitsche[7]
3.635	5.837	1.606	McTaggart and Wadsley[4]
	SnS$_2$		
3.644 ± 0.004	5.884 ± 0.004	1.615	This work
3.639 ± 0.005	5.884 ± 0.005	1.617	Greenaway and Nitsche[7]
3.639	5.868	1.613	Wyckoff[e]

[a] J. Benard and Y. Jeannin, "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 191. [b] S. Bartram, Dissertation, Rutgers University, New Brunswick, N. J., 1958. [c] S. LaPlaca, X-Ray Powder Data File 11, American Society for Testing of Materials, Philadelphia, Pa., 1959, p 679. [d] A. Bracuti, Dissertation, Rutgers University, New Brunswick, N. J., 1958. [e] R. W. G. Wyckoff, "Crystal Structures," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963.

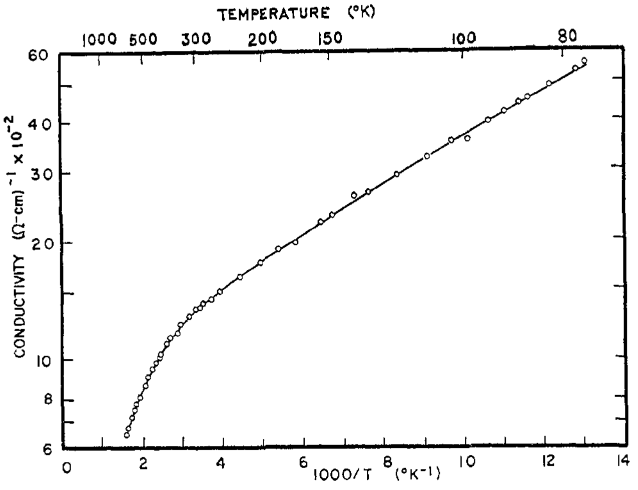

Figure 2.—Electrical conductivity as a function of temperature for TiS$_2$ single crystal.

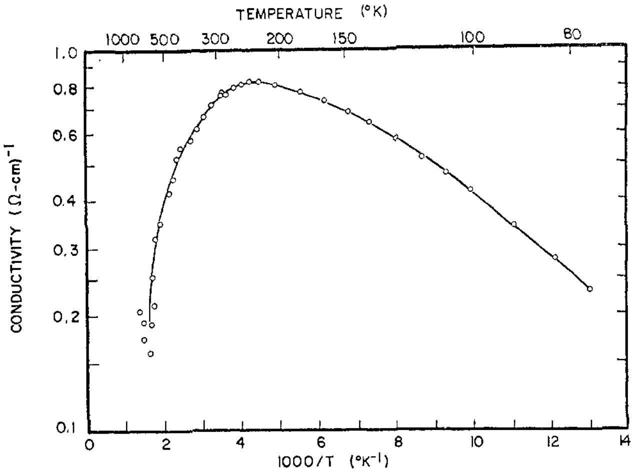

Figure 3.—Electrical conductivity as a function of temperature for ZrS$_2$ single crystal.

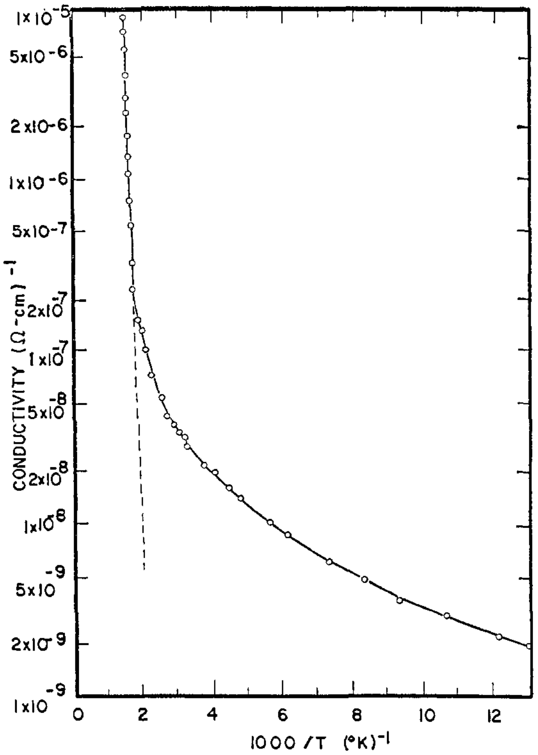

Figure 4.—Electrical conductivity as a function of temperature for HfS$_2$ single crystal.

indicated all four compounds to be n type. The Hall mobility data on TiS$_2$ and ZrS$_2$ are shown in Figures 6 and 7 and the carrier concentration for ZrS$_2$ is shown in Figure 8. The room-temperature value 1.4 × 10^3 ohm^{-1} cm^{-1} for TiS$_2$ is in good agreement with the value of 10^3 ohm^{-1} cm^{-1} reported by Grimmeiss, Rabenau, Hahn, and Ness[6] measured on small crystals and is in fair agreement with the 1.3 × 10^2 ohm^{-1} cm^{-1} value of McTaggart and Wadsley[4] measured on compressed powders. The previous studies of McTaggart and Wadsley[4] and Benard and Jeannin[15] indicate that TiS$_2$ is always sulfur deficient when prepared from the elements at atmospheric pressure, and our data support these observations. Attempts to anneal TiS$_2$ crystals in sulfur vapor for periods of 10–20 days at 500° produced a somewhat increased resistivity; however, the annealing was primarily a surface effect because measure-

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(15) See footnote a of Table II.

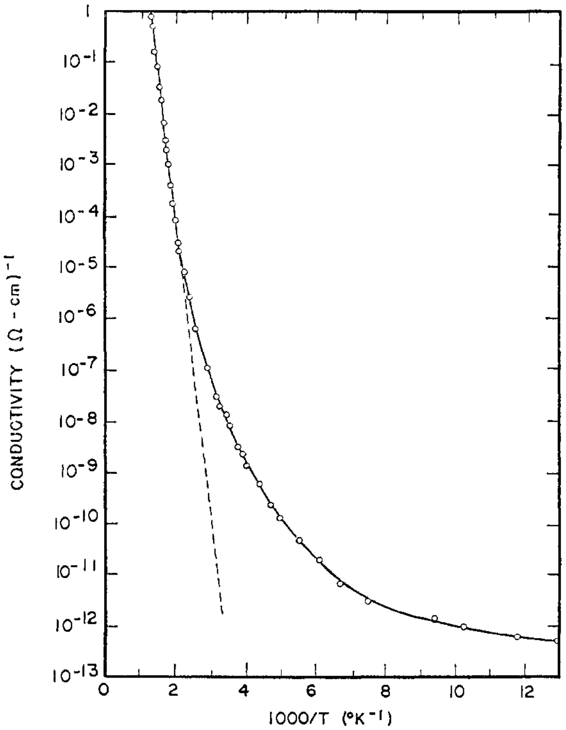

Figure 5.—Electrical conductivity as a function of temperature for SnS_2 single crystal.

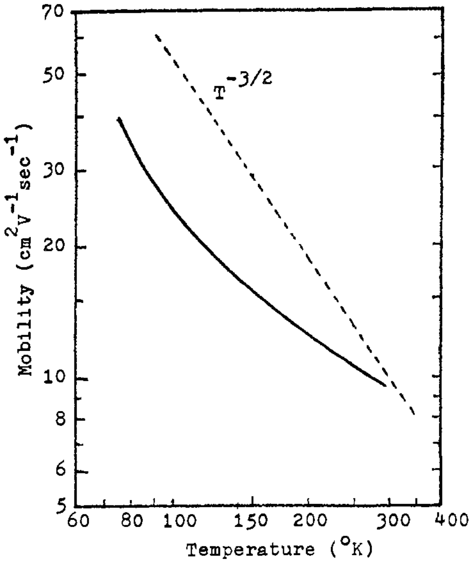

Figure 6.—Temperature dependence of Hall mobility for TiS_2

ments on freshly cleaved surfaces of annealed crystals yielded conductivities very close to those for the unannealed samples. The carrier concentration of TiS_2 (9×10^{20} cm^{-3}) is temperature independent over the range measured. The mobility data in Figure 6 show a strong temperature dependence. The dotted line in that figure indicates the slope of a $T^{3/2}$ dependence for comparison. Such behavior is indicative of lattice scattering as the predominant factor throughout the measured temperature range. All of these data characterize TiS_2 as a highly degenerate semiconductor.

The electrical data on ZrS_2 indicate a more typical semiconductor behavior than that shown by TiS_2.

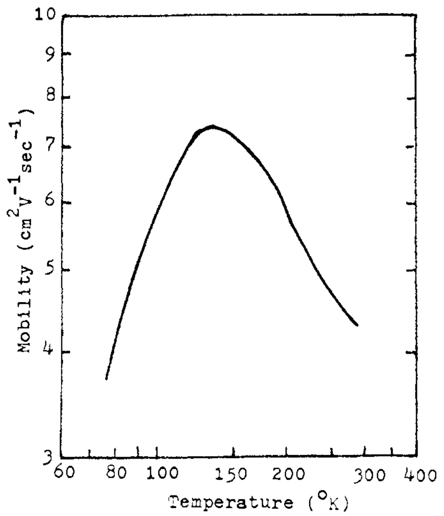

Figure 7.—Temperature dependence of Hall mobility for ZrS_2.

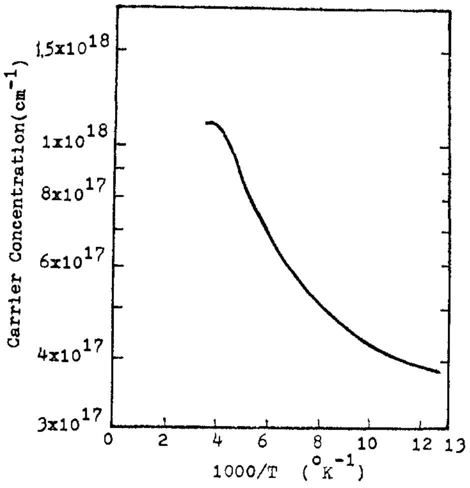

Figure 8.—Temperature dependence of carrier concentration for ZrS_2.

The room-temperature conductivity value of 7.6×10^{-1} ohm^{-1} cm^{-1} is close to the value of 10^{-1} ohm^{-1} cm^{-1} reported by McTaggart and Wadsley[4] for freshly prepared ZrS_2 powders. We observed no change in the conductivity of our crystals upon exposure to oxygen over periods of 50 hr, in contrast with the report of McTaggart and Wadsley that the resistivity of their powders increased 2000-fold within 24 hr after exposure to air. A typical exponential rise of carrier concentration in the impurity range is observed for ZrS_2 in Figure 8 with the room-temperature value being near 1.1×10^{18} cm^{-3}. The carrier mobility is 4.3 cm^2/V sec at 25° and its temperature dependence follows roughly a $T^{3/2}$ curve from liquid nitrogen temperatures to 130°K, indicating ionic impurity scattering; whereas between 130 and 300°K the mobility varies roughly as $T^{-3/2}$, a behavior characteristic of lattice scattering.

The conductivities of HfS_2 and SnS_2 place them in the near-insulator class. Attempts to measure carrier concentrations and mobilities of these compounds by both ac and dc techniques were not successful. Energy gap values of 2.1 eV for HfS_2 and 2.2 eV for SnS_2 were obtained from the slopes of the conductivity curves in the intrinsic region, as shown by the extended dotted lines in Figures 4 and 5. Compared with the 10^{-9} ohm^{-1} cm^{-1} value reported by McTaggart and Wadsley[4] for HfS_2 powder, our single-crystal data yield 3×10^{-8} ohm^{-1} cm^{-1} at room temperature. Our room-temperature value of 9.6×10^{-9} ohm^{-1} cm^{-1} for SnS_2 can be compared with a recently reported value by Domingo, Itoga, and Kannewurf[8] of 10^{-7} ohm^{-1} cm^{-1} on single crystals. There appear to be no data in the literature on the temperature dependence of conductivity for HfS_2 and SnS_2, so comparisons with our data cannot be made.

The magnetic susceptibility data on the four disulfides are summarized in Table III. Here the $\chi_{M'}$ value has been corrected for diamagnetic contributions to $10^6\chi_M$ of -5, -10, -16, $+16$, and -32 for Ti^{4+}, Zr^{4+}, Hf^{4+}, Sn^{4+}, and S^{2-}, respectively. The only literature value available for comparison is that for TiS_2, reported as 0.47 BM at 300°K by Ehrlich.[16] The possibility of iodine impurities being incorporated into crystals prepared by this method was investigated. No iodine was detectable in the chemical analysis procedures nor in optical measurements that were performed on the same crystals used in the electrical measurements reported here. The chemical and optical procedures could have detected iodine concentrations of 10^{17} I atoms cm^{-3}. Tracer studies using I^{131} indicated iodine concentrations ranging from 5×10^{14} to 3×10^{15} I atoms cm^{-3} in HfS_2 samples. No correlations between the iodine concentrations and electrical resistivity were evident in these samples, the conductivity values differing by no more than 20% and in a random manner. Iodine concentrations no larger than 10^{17} atoms cm^{-3} are too low to account for the carrier concentrations observed in TiS_2 and ZrS_2. In the case of HfS_2 and SnS_2, assuming a mobility of the order of 10 cm^2/V sec^{-1} would require a carrier concentration of only about 10^9 cm^{-3}; thus compensation by iodine atoms could be an important factor affecting the carrier concentration and/or mobility.

TABLE III

MAGNETIC SUSCEPTIBILITIES OF GROUP IV DISULFIDES AT 23°

	$10^6\chi_g$	$10^6\chi_M$	$10^6\chi_{M'}$	μ, BM
TiS_2	0.408	45.8	116	0.52
ZrS_2	0.535	83.2	158	0.61
HfS_2	0.005	1.2	82	0.44
SnS_2	−0.058	−10.6	71	0.41

The wide range of electrical properties exhibited by this group of isostructural compounds would not be anticipated and is not explained by the data accumulated in this research. The most likely explanation for the relatively high conductivities of TiS_2 and ZrS_2 is that they are the results of deviations from stoichiometry, probably in the sulfur-deficient direction. Excess metal atoms could then contribute electrons to bands formed from empty (ionic model) or partially empty (covalent model) d orbitals of the transition metal, producing typical impurity-type semiconducting properties. This argument would then require that our HfS_2 be very nearly perfectly stoichiometric, so that the available d bands are only sparsely populated by electrons from impurity levels. The low conductivity of SnS_2 could arise from either good stoichiometry, *i.e.*, low impurity level, or lack of suitably low empty orbitals in the d^{10} configuration. Our attempts to prepare deliberately nonstoichiometric SnS_2 by chemical transport gave no evidence of success, so that we are still unable to eliminate one of the possibilities. We plan to try diffusion of Sn vapor into our transport-grown crystals as the next step. In view of the wide range of electrical conductivities exhibited by these disulfides, the luster of these compounds cannot be attributed to delocalized electrons in conduction bands, but rather is a result of the high polarizability of this type of sulfur atom lattice. Attempts to grow crystals of FeS_2 in the pyrite structure by chemical transport were not successful; so comparisons between the two disulfide types of crystals of similar perfection and purity are not available.

Acknowledgment.—It is a pleasure to acknowledge the support of this research by the U. S. Army Research Office (Durham).

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(16) P. Ehrlich, *Z. Anorg. Allgem. Chem.*, **260**, 1 (1949).