Inorg. Chem. **1985**, *24*, 3611–3614

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Structure and Physical Properties of the New Layered Ternary Chalcogenides Ta_2NiS_5 and Ta_2NiSe_5

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Received March 1, 1985

Two new ternary chalcogenides have been prepared and characterized. Both Ta_2NiS_5 (D_{2h}^{17}-*Cmcm*; a = 3.415 (1), b = 12.146 (3), c = 15.097 (4) Å) and Ta_2NiSe_5 (C_{2h}^{6}-*C*2/*c*; a = 3.496 (1), b = 12.829 (3), c = 15.641 (4) Å; β = 90.53 (1)°) crystallize as layered structures with four formula units per cell. These layers contain octahedral tantalum atoms and tetrahedral nickel atoms each coordinated by chalcogen atoms. These polyhedra join via shared edges to form zigzag chains along the c axis. Electrical conductivity and magnetic susceptibility measurements show these materials to be diamagnetic semiconductors. The description of the structures as $Ta^{4+}Ni^{2+}Q^{2-}$ (Q = S, Se) with pairing of nickel and tantalum electrons is consistent with these physical properties.

Introduction

Recently we have prepared several new compounds in the ternary systems Nb/Ta–Pd–S/Se. These compounds, which include channel[1] and layered structures,[2] display differing physical properties. A common feature of these compounds is the square-planar or square-pyramidal coordination geometry about Pd and the trigonal-prismatic geometry about Ta or Nb. These coordination geometries are known for other transition metals, so the systematic replacement of Pd or Nb/Ta has been undertaken. In particular, nickel chalcogenides with Ni in square-planar[3] or square-pyramidal[4] sites are known. Thus replacement of Pd by Ni should be possible. Yet such a simple substitution may be complicated since both tetrahedrally[5] and octahedrally[6] coordinated Ni exist in nickel chalcogenide compounds. The coordination geometry of Ta may also change when Ni is substituted for Pd. Trigonal-prismatic and octahedral Ta are of very similar stability.[7] For example, several polymorphs of TaS_2 exist with Ta in either of these two geometries,[8] and in the compound $Co_2PdTa_4Se_{12}$ both octahedral and trigonal-prismatic Ta coexist.[2a]

The only reported ternary Ni–Ta–S compound, $Ni_{1/3}TaS_2$, possesses Ni intercalated in octahedral sites within the TaS_2 framework.[9] In this paper we describe the new ternary compounds Ta_2NiQ_5 (Q = S, Se), in which Ni is tetrahedrally coordinated and Ta is octahedrally coordinated by chalcogen atoms.

Experimental Section

Synthesis of Ta_2NiS_5 and Ta_2NiSe_5. Both compounds were initially obtained by combining the elements, Ta powder (Alfa 99.9%), Ni powder (Alfa 99.9%), and S powder (Atomergic 99.999%) or Se pellets (Atomergic, 99.999%), in an evacuated silica tube ($\sim 10^{-5}$ torr) and heating for 7 days at 650 °C. Subsequent reactions have shown that crystals grow more readily at higher temperatures, 725–850 °C, with a slight excess of chalcogen (~1%). Under these conditions small shiny black needles form throughout the reaction tube. Larger crystals can be obtained with I_2 as a transport agent in conjunction with a temperature gradient (875–800 °C). There is no evidence of attack of silica during either synthetic approach. Anal. Calcd for Ta_2NiS_5: Ta, 62.30; Ni, 10.10; S, 27.60. Found: Ta, 61.07; Ni, 9.46; S, 27.99. Calcd for Ta_2NiSe_5: Ta, 44.38; Ni, 7.20; Se, 48.42. Found: Ta, 43.90; Ni, 6.90; Se, 48.20.

Physical Measurements. Four-probe single-crystal conductivity measurements along the needle axis, a, were made on both compounds with the use of previously described procedures.[10] Magnetic susceptibility measurements were made on samples of ground crystals for both compounds with a SHE 800 Series susceptometer.

Collection of X-ray Diffraction Data. The crystal structures of Ta_2NiS_5 and Ta_2NiSe_5 have been determined by single-crystal X-ray diffraction methods. The systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) as determined from Weissenberg photographs are indicative of the orthorhombic space groups *Cmcm* and $Cmc2_1$ or the monoclinic space groups *C*2/*c* and *Cc*. The relative intensities of hkl and $hk\bar{l}$ reflections did not allow for further classification based on photographic data alone. The photographs showed no evidence of crystal twinning or other abnormalities. Cell refinement on several crystals of each compound, based on diffractometer setting angles, indicated that Ta_2NiSe_5 has β = 90.53 (1)° while Ta_2NiS_5 has β = 90.04 (6)°. Diffraction data were collected on needle-shaped crystals at ambient temperature with an Enraf-Nonius CAD-4 diffractometer. During data collection six standard reflections measured every 3 h showed no significant variation in intensity. Data collection parameters and crystallographic details are given in Table I. After correction for absorption a comparison of $\{hkl\}$ and $\{hk\bar{l}\}$ reflections revealed that the selenide crystallizes with monoclinic symmetry, while the sulfide appears to possess orthorhombic symmetry.[11] Analysis of Friedel pairs resulted in residual indices R = 4.2% and 5.7% for the selenide and sulfide, consistent with the centrosymmetric space groups *C*2/*c* and *Cmcm* for the selenide and sulfide, respectively. Refinement of Ta_2NiS_5 in both *C*2/*c* and *Cmcm* gave essentially identical indices ($R(F_o^2)_{\text{mono}} = 0.0722$; $R(F_o^2)_{\text{ortho}} = 0.0716$), and bond distances calculated following these refinements were equivalent within the limits of errors. Thus the group of higher symmetry, *Cmcm*, has been assigned to Ta_2NiS_5.

Solution and Refinement of the Structures. All calculations were carried out on a Harris 800 computer with the use of programs standard in this laboratory.[12] Conventional atomic scattering factors[13] were used and anomalous-dispersion corrections[14] were applied. The structures were solved by the heavy-atom method. Initial positions for Ta and Ni atoms were determined from a Patterson synthesis, and the chalcogen atoms were located in subsequent electron density maps. Because nonstoichiometry in other ternary tantalum chalcogenides is known,[15] refinements were carried out while varying the occupancies of the Ta and Ni sites. Simultaneous refinement of Ta and Ni occupancies yielded stoichiometries $Ta_{2.03}Ni_{0.98}S_5$ and $Ta_{2.03}Ni_{1.02}Se_5$. Refinement of the tantalum occupancy led to stoichiometries $Ta_{2.05}NiS_5$ and $Ta_{2.03}NiSe_5$. These results are consistent with the formula Ta_2NiQ_5 (Q = S, Se) used in the

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(11) As examples, for monoclinic Ta_2NiSe_5 the average structure amplitude of reflections of the form $\{426\}$ is F_o = 230.4 while for $\{42\bar{6}\}$ it is F_o = 151.8 (F_c = 233.0 and 145.0 electrons, respectively). For $\{358\}$ F_o = 135.8 and for $\{35\bar{8}\}$ F_o = 182.8 (F_c = 131.4 and 180.6 electrons). Reliability indices obtained by averaging reflections ($F_o^2 > 3\sigma(F_o^2)$) equivalent under monoclinic or orthorhombic symmetry are for Ta_2NiSe_5 R_{mono} = 4.2% and R_{ortho} = 10.1% while for Ta_2NiS_5 R_{mono} = 6.7% and R_{ortho} = 7.5%.

(12) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277. We are also indebted to Dr. Reinhard Fischer at the University of Illinois at Chicago for the program STRUPLO84, a routine for plotting polyhedra.

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Table I. X-ray Data Parameters for Ta_2NiSe_5 and Ta_2NiS_5

formula	Ta_2NiSe_5	Ta_2NiS_5
M_r	815.41	580.93
space group	C_{2h}^6-$C2/c$	D_{2h}^{17}-$Cmcm$
a, Å	3.496 (1)[a]	3.415 (1)[a]
b, Å	12.829 (3)	12.146 (3)
c, Å	15.641 (4)	15.097 (4)
β, deg	90.53 (1)	90
vol, $Å^3$	701.42	626.25
Z	4	4
T, K	298	298
radiation (graphite monochromated); $\lambda(K\alpha_1)$ = 0.7093 Å	Mo $K\alpha$	Mo $K\alpha$
cryst shape	needle bound by $(0\bar{1}3)$ $(01\bar{3})$ {010} {100} {001} {011}	needle bound by {100} {010} {001}
cryst vol, mm^3	0.000 107	0.000 012 3
linear abs coeff, cm^{-1}	596.3	385.7
transmissn factors[b]	0.194–0.406	0.659–0.845
detector aperture, mm		
horiz	3.0	4.0
vert	$3.2 + 1.25 \tan \theta$	4.0
takeoff angle, deg	3.4	3.0
scan type	ω–2θ	ω–2θ
scan speed, deg min^{-1}	1.33[c]	1.07
scan range, deg	1.4 below $K\alpha_1$ and above $K\alpha_2$	0.9 below $K\alpha_1$ and above $K\alpha_2$
$\lambda^{-1} \sin \theta$ limits, $Å^{-1}$	0.0639–0.8062	0.0663–0.8538
θ limits, deg	$2.50 \le \theta$ (Mo $K\alpha_1$) ≤ 35	$2.60 \le \theta$ (Mo $K\alpha_1$) ≤ 37.5
data collcd	$\pm h,\pm k,\pm l$	$+h,+k,+l$[d]
p factor	0.03	0.03
no. of unique data	1528	947
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1221	646
$R(F^2)$	0.114	0.072
$R_w(F^2)$	0.129	0.087
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.050	0.038
error in observn of unit wt, e^2	1.87	1.16

[a] Obtained from refinements constrained in the following way: Ta_2NiSe_5 $\alpha = \gamma = 90°$; Ta_2NiS_5 $\alpha = \beta = \gamma = 90°$. [b] An analytical absorption correction was applied with use of the analytical method of Tompa and de Meulenaer (*Acta Crystallogr.* **1965**, *19*, 1014–1018). [c] Reflections with $\sigma(I)/I > 0.333$ were rescanned. [d] Data were collected on two crystals of Ta_2NiS_5. For the first crystal $\pm h,\pm k,\pm l$ were collected; on the second crystal $+h,+k,+l$ were collected. The second crystal was of higher quality, as judged by ω-scans, and the results for this crystal are presented here.

final refinements. These final refinements on F_o^2 included anisotropic thermal parameters and resulted in residuals $R(F^2) = 0.114$ and $R_w(F^2) = 0.129$ for the selenide and $R(F^2) = 0.072$ and $R_w(F^2) = 0.087$ for the sulfide (for 39 and 27 variables, respectively). The conventional index $R(F)$ for reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.038 for Ta_2NiS_5 and 0.050 for Ta_2NiSe_5. Final difference electron density maps show no features greater than 3% of the height of a Ta atom in either structure. Analysis of F_o^2 vs. F_c^2 as a function of F_o^2, $\lambda^{-1} \sin \theta$, and Miller indices reveals no unusual trends. The thermal parameters show no unexpected trends.

Final parameters are presented in Table II. Anisotropic thermal parameters and structure amplitudes for both compounds are given in Tables III and IV.

Results

Description of the Structures. Bond distances and bond angles for Ta_2NiS_5 and Ta_2NiSe_5 are listed in Table V. The structures of both compounds are virtually identical except that Ta_2NiS_5 is apparently of higher symmetry. A view of one of these structures down the a axis (Figure 1) clearly shows the layered nature of these compounds. The structure can be described as a series of zigzag chains along the c axis. These chains are composed of tetrahedrally coordinated Ni atoms and octahedrally coordinated Ta atoms where the coordination environments are determined by the surrounding chalcogen atoms. These polyhedra combine by sharing edges to form the repeat unit Ta–Ni–Ta. The Ta–Ni distance within this unit is short (2.808 (4) Å average for selenide, 2.747 (1) Å for the sulfide) while the Ta–Ta distance between adjacent units is long (>3.7 Å). These chains, which stack in the a direction, are connected via edge-shared octahedra and shared vertices of tetrahedra (Figure 2). The unit cell contains two such chains, the second displaced by $a/2$ with respect to the first. The coordination about the Ta and Ni atoms is slightly distorted from ideal geometry, but this distortion is not the result of chalcogen pairing as all Q–Q distances are consistent with Q^{2-} species (S–S = 3.36–3.65 Å; Se–Se = 3.50–3.69 Å). Metal–chalcogen and chalcogen–chalcogen distances are in good agreement with those calculated from crystal radii typical for these atoms in sulfide structures.[16] The volume per chalcogen atom is also consistent with other layered chalcogenides that do not contain Q–Q pairs (Table VI).[17,18] However, the chalcogen atoms are not closest

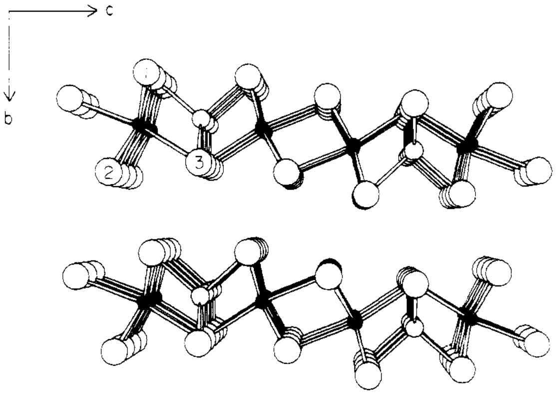

Figure 1. View of the Ta_2NiQ_5 structure down the a axis. In this figure and in Figure 2 small black circles are Ta, small open circles are Ni, and large open circles are Q. Views for Q = S and Se are indistinguishable.

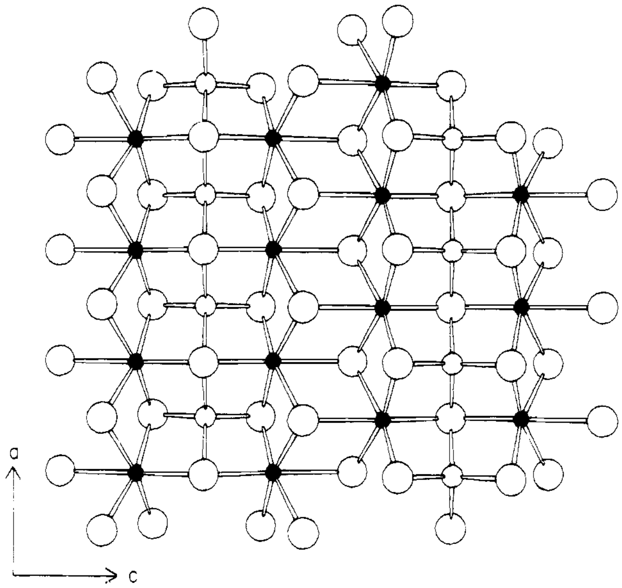

Figure 2. View of the Ta_2NiQ_5 structure in the a–c plane.

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Table II. Final Positional Parameters and Equivalent Isotropic Thermal Parameters for Ta_2NiSe_5 and Ta_2NiS_5

atom	Wyckoff notation	point symm	*x*	*y*	*z*	B_{eq}, Å^2
			Ta_2NiSe_5			
Ta	8f	1	−0.007 93 (14)	0.221 349 (37)	0.110 442 (29)	0.9
Ni	4e	2	0	0.701 13 (18)	$^1/_4$	1.0
Se(1)	8f	1	0.505 30 (34)	0.080 385 (93)	0.137 979 (74)	1.0
Se(2)	8f	1	−0.005 13 (33)	0.145 648 (92)	0.950 866 (73)	0.9
Se(3)	4e	2	0	0.327 14 (13)	$^1/_4$	0.9
			Ta_2NiS_5			
Ta	8f	*m*	0	0.220 820 (41)	0.108 793 (31)	0.6
Ni	4c	*m2m*	0	0.696 92 (20)	$^1/_4$	0.8
S(1)	8f	*m*	$^1/_2$	0.082 82 (25)	0.135 27 (20)	0.7
S(2)	8f	*m*	0	0.148 50 (24)	0.949 74 (19)	0.6
S(3)	4c	*m2m*	0	0.319 68 (35)	$^1/_4$	0.6

Table V. Bond Distances (A) and Bond Angles (deg) in Ta_2NiSe_5 and Ta_2NiS_5

Ta_2NiSe_5		Ta_2NiS_5	
Ta–Se(1)	2.523 (2)	Ta–2S(1)	2.426 (2)
Ta–Se(1)	2.581 (2)		
Ta–Se(2)	2.588 (2)	Ta–2S(2)	2.493 (2)
Ta–Se(2)	2.661 (2)		
Ta–Se(2)	2.678 (2)	Ta–S(2)	2.557 (2)
Ta–Se(3)	2.570 (2)	Ta–S(3)	2.447 (2)
Ta–Ni	2.804 (1)	Ta–Ni	2.747 (1)
Ta–Ni	2.813 (1)		
Ta–Ta	3.496 (1)	Ta–Ta	3.415 (1)
Ni–Ni	3.496 (1)	Ni–Ni	3.415 (1)
Ni–2Se(1)	2.339 (2)	Ni–2S(1)	2.218 (4)
Ni–2Se(3)	2.381 (2)	Ni–2S(3)	2.267 (3)
Se(1)–2Se(1)	3.496 (1)	S(1)–2S(1)	3.415 (1)
Se(1)–Se(1)	3.505 (2)	S(1)–S(1)	3.464 (1)
Se(1)–Se(2)	3.505 (2)	S(1)–2S(2)	3.507 (4)
Se(1)–Se(2)	3.515 (2)		
Se(1)–Se(2)	3.654 (2)	S(1)–2S(2)	3.530 (4)
Se(1)–Se(2)	3.666 (2)		
Se(1)–Se(3)	3.692 (2)	S(1)–S(3)	3.635 (5)
Se(2)–2Se(2)	3.496 (1)	S(2)–2S(2)	3.415 (1)
Se(2)–Se(2)	3.537 (3)	S(2)–2S(2)	3.614 (5)
Se(2)–Se(2)	3.559 (3)		
Se(2)–Se(3)	3.590 (1)	S(2)–2S(3)	3.487 (3)
Se(2)–Se(3)	3.635 (1)		
Se(3)–2Se(3)	3.496 (1)	S(3)–2S(3)	3.415 (1)

Ta_2NiSe_5		Ta_2NiS_5	
Se(1)–Ta–Se(1)	86.45 (4)	S(1)–Ta–S(1)	89.5 (1)
Se(1)–Ta–Se(2)	95.37 (5)	2S(1)–Ta–S(2)	90.93 (7)
Se(1)–Ta–Se(2)	92.28 (5)		
Se(1)–Ta–Se(2)	168.28 (4)	2S(1)–Ta–S(2)	168.6 (1)
Se(1)–Ta–Se(2)	167.86 (4)		
Se(1)–Ta–Se(2)	84.69 (4)	2S(1)–Ta–S(2)	85.26 (9)
Se(1)–Ta–Se(2)	83.85 (4)		
Se(1)–Ta–Se(3)	103.62 (4)	2S(1)–Ta–S(3)	101.3 (1)
Se(1)–Ta–Se(3)	103.08 (4)		
Se(2)–Ta–Se(2)	84.36 (4)	S(2)–Ta–S(2)	86.45 (9)
Se(2)–Ta–Se(2)	83.50 (4)	2S(2)–Ta–S(2)	83.45 (9)
Se(2)–Ta–Se(2)	83.59 (4)		
Se(2)–Ta–Se(3)	88.19 (4)	2S(2)–Ta–S(3)	89.8 (1)
Se(2)–Ta–Se(3)	88.02 (4)		
Se(2)–Ta–Se(3)	169.35 (5)	S(2)–Ta–S(3)	170.7 (1)
Ta–Ni–Ta	101.82 (2)	Ta–Ni–Ta	102.02 (3)
Se(1)–Ni–Se(1)	97.0 (1)	S(1)–Ni–S(1)	102.7 (2)
2Se(1)–Ni–Se(3)	116.03 (4)	4S(1)–Ni–S(3)	114.26 (6)
2Se(1)–Ni–Se(3)	117.43 (4)		
Se(3)–Ni–Se(3)	94.5 (1)	S(3)–Ni–S(3)	97.7 (2)

Table VI. Volume per Chalcogen Atom (Å^3)[a] for Layered Chalcogenides of Nb and Ta

	Without Q–Q Pairs		
$2H_a$-TaS_2	28.7	$2H_a$-$TaSe_2$	32.5
$2H_a$-NbS_2	28.2	$2H_a$-$NbSe_2$	32.2
3R-TaS_2	28.5	3R-$TaSe_2$	32.6
3R-NbS_2	28.7	3R-$NbSe_2$	32.4
1T-TaS_2	28.9	1T-$TaSe_2$	32.8
Ta_2NiS_5	31.3	Ta_2NiSe_5	35.1
	With Q–Q Pairs		
TaS_3	24.7	$TaSe_3$	29.2
NbS_3	25.3	$NbSe_3$	28.5

[a] Volume per chalcogen atom is obtained by dividing the volume of the unit cell by the number of chalcogen atoms in the cell.

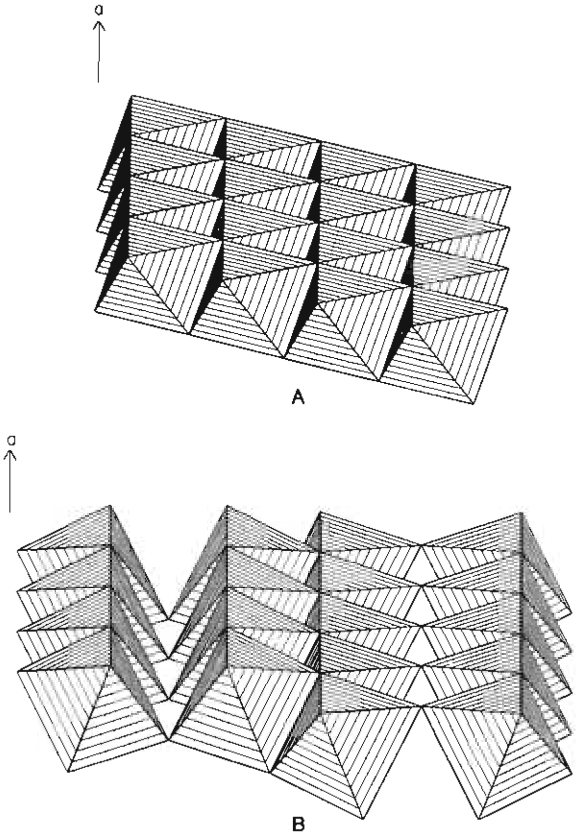

Figure 3. Polyhedral representation of one layer of (A) 1T-TaS_2 viewed along *a* and (B) Ta_2NiQ_5 viewed along *a* (only Ta octahedra shown). The 1T-TaS_2 structure is closest packed whereas the Ta_2NiQ_5 structure distorts to accommodate the tetrahedrally coordinated Ni atoms.

packed (Figure 3). This distortion from closest packing has two important consequences. First, this structural type is not seen in other compounds since most layered materials are derived from closest packing of anions.[18] Second, the sites between the layers are trigonal prismatic and octahedral as compared with octahedral and tetrahedral for layered dichalcogenides. The degradation of the cathode in Na/TiS_2 battery systems has been attributed to the distortion of the cathode framework to accommodate the preference of Na^+ for trigonal-prismatic sites.[19] This degradation

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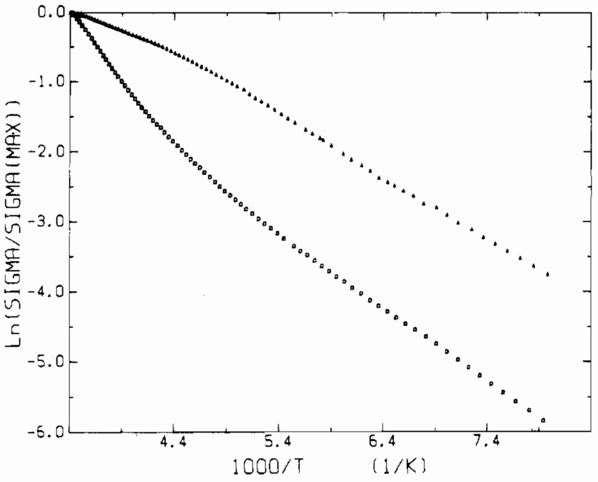

Figure 4. Plot of ln σ vs. $1/T$ for Ta_2NiS_5 (upper) and Ta_2NiSe_5 (lower). The conductivity has been normalized to the maximum conductivity for each compound.

may not occur if both octahedral and trigonal-prismatic sites are present initially.

Physical Properties. The temperature dependence of the magnetic susceptibility of Ta_2NiS_5 and Ta_2NiSe_5 was measured over the range 10–300 K. The data can be corrected for paramagnetic impurities (μ_{eff} for bulk sample 0.20 μ_B) by fitting the results at low temperature (10–50 K) to eq 1 where χ_0 is assumed

$$\chi_g = \chi_0 + \frac{C}{T + \Theta} \qquad (1)$$

to be temperature independent at low temperature. The Curie–Weiss contribution ($C/(T + \Theta)$) is then subtracted from the data. The values of χ thus obtained are constant and negative (-8.0×10^{-5} emu/mol for the sulfide and -9.9×10^{-5} emu/mol for the selenide), typical of diamagnetic materials.

Four-probe single-crystal conductivity measurements along the needle axis, *a*, show that both compounds are semiconductors over the temperature range 100–300 K with room-temperature conductivities of 4.6 and 117 Ω^{-1} cm^{-1} for the sulfide and selenide, respectively (Figure 4). These results are consistent with the magnetic measurements that indicate the absence of unpaired electrons. The band gaps at room temperature, as calculated from the slope of ln σ vs. $1/T$ between 245 and 295 K, are 0.13 and 0.36 eV for the sulfide and selenide.

Valence Description

All physical measurements are consistent with a structure containing no unpaired electrons. These results preclude the description of the structure in simple valence terms as $Ta^{4+}Ni^{2+}Q^{2-}$ since Ta^{4+} (d^1) and Ni^{2+} (d^8) ions possess unpaired electrons. The absence of unpaired electrons can be rationalized in at least two ways. One could describe the structure as containing Ni^0 and Ta^{5+} species. The octahedral coordination of Ta is typical of d^0 Ta^{5+};[7] however, compounds with Ta^{4+} in octahedral sites are also known, and the coexistence of the low oxidation state for Ni and the high oxidation state for Ta seems unlikely. A second rationalization for the absence of unpaired electrons is pairing of lone electrons from Ni^{2+} and Ta^{4+} via a Peierls' transition above room temperature. Such pairing is seen with Nb^{4+} in NbS_3[20] and may occur for Ta^{4+} in TaS_3.[21] The presence of Ta–Ni–Ta units with short Ta–Ni distances (~2.80 Å) supports this possible pairing. High-temperature conductivity and magnetic susceptibility measurements are under way to determine if a Peierls' distortion occurs above room temperature.

Acknowledgment. This work was supported by the National Science Foundation, Solid State Chemistry (Grant DMR-83-15554). Some of the measurements were carried out in the Magnet and SEM Facilities of Northwestern University's Material Research Center, supported in part under the NSF-MRL program (Grant DMR-82-16972).

Registry No. Ta_2NiS_5, 98104-46-2; Ta_2NiSe_5, 98104-47-3; Ta, 7440-25-7; Ni, 7440-02-0; S, 7704-34-9; Se, 7782-49-2.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table III) and structure amplitudes (Table IV) for both compounds (13 pages). Ordering information is given on any current masthead page.

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