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Synthesis, Structure, and Physical Properties of the New Layered Ternary Chalcogenide $NbNiTe_5$

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The new ternary chalcogenide $NbNiTe_5$ has been prepared. $NbNiTe_5$ crystallizes with four formula units in a cell with dimensions $a = 3.656(5)$, $b = 13.075(16)$, $c = 15.111(19)$ Å in the orthorhombic system in space group D_{2h}^{17}-$Cmcm$. The structure has been refined to a final R index on F_o^2 of 0.037 for 25 variables and 1405 observations. $NbNiTe_5$ forms in a new layered structural type. Each layer consists of bicapped trigonal prismatic niobium atoms and octahedral nickel atoms coordinated by tellurium atoms. Electrical conductivity measurements indicate that $NbNiTe_5$ is a metal; its conductivity at room temperature is about $1.3 \times 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Magnetic susceptibility measurements show that $NbNiTe_5$ is paramagnetic ($X_{rt} \approx 1.04 \times 10^{-3}$ emu mole^{-1}).

Introduction

The known binary and ternary chalcogenides of Nb and Ta display interesting structural features and a wide assortment of important physical properties, such as superconductivity and charge density waves (*1–6*). We have recently expanded the known chemistry of such chalcogenides through the preparation of new compounds of the type $M_xM'_yQ_z$, where M = Nb or Ta, M' = Ni, Pd, or Pt, and Q = S or Se (*7–12*).

This and the vast majority of previous work on binary and ternary systems of Nb and Ta have involved sulfides and selenides. The chemistry of the tellurides, on the other hand, is undeveloped. Only three ternary niobium ($Sb_2Nb_3Te_5$ (*13*), Cu_3NbTe_4 (*14*), Ag_2NbTe_3 (*15*)) and three ternary tantalum (Cu_3TaTe_4 (*14*), Ag_2TaTe_3 (*15*), Mo_2TaTe_4 (*16*)) tellurides appear to have been prepared previously and none contains a member of the Ni triad.

Since new compounds may exhibit new structure types and interesting physical properties we have a strong impetus to investigate tellurides. On the one hand we might guess that new ternary tellurides will be isostructural with existing sulfides and selenides. Thus Cu_3NbS_4, Cu_3NbSe_4, and Cu_3NbTe_4 are isostructural (*14*). On the other hand, from the binary systems we might guess that new niobium and tantalum ternary tellurides will be very different from known sulfides and selenides. Thus among the higher chalcogenides NbQ_3 and TaQ_3 (Q = S, Se) are known, but not NbQ_4 and TaQ_4; similarly, $NbTe_4$ (*17*) and $TaTe_4$ are known (*18, 19*) but not $NbTe_3$ or $TaTe_3$. Here we report our initial investigation of ternary tellurides: the new layered ternary $NbNiTe_5$ has been synthesized and characterized.

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Experimental

Synthesis. The compound $NbNiTe_5$ was synthesized from the powders of the elements (Nb, 99.8%, ALFA; Ni, 99.9%, ALFA; Te, 99.999%, ALFA). These were loaded in a silica tube in the atomic ratio $Nb:Ni:Te = 3:1:8$ (in an attempt to make an analogue of $Nb_3Pd_{0.72}Se_7$ (*10*)). A small amount of I_2 was added as a transport agent. The tube was evacuated to $\approx 10^{-5}$ Torr and was then sealed. Next it was heated to 750°C and kept there for 10 days. The tube was then heated at 600/550°C for 14 days. Many thin needlelike crystals formed. Analysis of these crystals with the microprobe of an EDAX-equipped Hitachi S570 scanning electron microscope showed the presence of Nb, Ni, and Te. Elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN) on approximately 100 mg of sample corresponded to the composition $Nb_{1.02}NiTe_{5.19}$.

Physical measurements. Single crystals of $NbNiTe_5$ averaging in size approximately 0.015 by 0.038 by 1.2 mm were mounted with Ag paint on Al wires. Four-probe ac conductivity measurements along the needle axis a were then carried out using methods described previously (*20*). Magnetic susceptibility measurements were performed at 1 kG over the temperature range 1.99–300°K with a modified VTS-50 SQUID susceptometer (SHE Co.). Sample holders made of high-purity Spectrosil quartz were used in the susceptibility measurements.

Structure determination. Crystals of $NbNiTe_5$ exhibit Laue symmetry *mmm* on Weissenberg photographs. The systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) are consistent with the space groups *Cmcm* and $Cmc2_1$. A crystal measuring approximately 0.023 by 0.027 by 0.6 mm was mounted. The lattice parameters were determined from least-squares analysis of the setting angles of 15 reflections in the range $20° \leq 2\theta(MoK\alpha_1) < 25°$ automatically centered on a Picker FACS-1 diffractometer. Diffraction data were collected at −150°C. Table I gives details of the data collection.

All calculations were carried out on a Harris 1000 computer with programs and methods standard in this laboratory (*21*). Conventional atomic scattering factors (*22*) were used and anomalous dispersion corrections (*23*) were applied. The processed

TABLE I

Details of X-Ray Data Collection and Refinement for $NbNiTe_5$

Formula mass (amu)	789.61
Space group	D_{2h}^{17}-*Cmcm*
a (Å)	3.656(5)[a]
b (Å)	13.075(16)
c (Å)	15.111(19)
V (Å^3)	722.3
Z	4
T of data collection, K[b]	123
Radiation (graphite monochromated)	$MoK\alpha_1$ ($\lambda(K\alpha_1) = 0.7093$ Å)
Crystal shape	Needle bounded by {100} {001} (010) $(0\bar{2}1)$ (011) $(0\bar{1}2)$ (021) $(0\bar{2}\bar{1})$
Crystal volume (mm^3)	3.8×10^{-4}
Linear abs. coeff. (cm^{-1})	238.5
Transmission factors[c]	0.476–0.618
Detector aperture (mm)	Horizontal, 5.5; vertical, 5.0, 32 cm from crystal
Takeoff angle (deg)	2.5
Scan speed (deg min^{-1})	2.0 in 2θ
Scan range (deg)	1.3 below $K\alpha_1$ to 1.1 above $K\alpha_2$
2θ limits (deg)	$3 \leq 2\theta(MoK\alpha_1) \leq 83$
Background counts	10 sec at each end of scan with rescan option[d]
Data collected	$\pm h, \pm k, \pm l$
	$3° \leq 2\theta \leq 50°$
	$h, k, \pm l$
	$50° \leq 2\theta \leq 83°$
p Factor	0.04
Extinction coefficient	$2.1(2) \times 10^{-7}$
Number of data collected	4590
Number of unique data	1448
Number of unique data with $F_o^2 > 3\sigma(F_o^2)$	1202
$R(F^2)$	0.037
$R_w(F^2)$	0.070
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.024
Error in observation of unit weight (e^2)	1.13

[a] Obtained from a refinement constrained so that $\alpha = \beta = \gamma = 90°$.

[b] The low-temperature system is based on a design by J. C. Huffman, Ph.D. thesis, Indiana University (1974).

[c] An analytical absorption correction was applied with the use of the method of Tompa and de Meulenaer (*Acta Crystallogr.* **19**, 1014, (1965)).

[d] The diffractometer was operated under the Vanderbilt disk-oriented system (P. G. Lenhert, *J. Appl. Crystallogr.* **8**, 568 (1975)).

TABLE II

Atom	Wyckoff notation	x	y	z	B_{eq} (Å^2)
Te(1)	8*f*	0	0.102226(21)	0.144231(19)	0.351(5)
Te(2)	8*f*	$\frac{1}{2}$	0.107868(22)	0.575246(19)	0.400(5)
Te(3)	4*c*	0	0.175341(29)	$\frac{3}{4}$	0.449(7)
Nb	4*c*	$\frac{1}{2}$	−0.012282(41)	$\frac{1}{4}$	0.308(9)
Ni	4*a*	0	0	0	0.40(1)

data were corrected for absorption effects. The same residual of 0.033 results from averaging the inner sphere (<50° in 2θ) data with $F_o^2 > 3\sigma(F_o^2)$ in *mmm* and *mm*2 symmetry. Hence the centrosymmetric space group *Cmcm* was chosen. Initial positions for the Te atoms were determined with the direct methods program MULTAN (*24*). The Ni and Nb atoms were located in ensuing electron density maps. The final cycle of refinement on F_o^2 included anisotropic thermal parameters and resulted in a value of $R(F_o^2)$ of 0.037. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$. The final difference electron density map showed no peak greater than 1.2% the height of a Te atom. No unusual trends were found in an analysis of F_o^2 versus F_c^2 as a function of F_o^2, setting angles, and Miller indices. Intermediate calculations in which relative positional occupancies were varied provided no evidence of nonstoichiometry. Similarly, the refined values of the thermal parameters are consistent with a stoichiometric structure. Final values of the atomic parameters appear in Table II. Final anisotropic thermal parameters and structure amplitudes are given in Tables III[1] and IV.[1]

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) FOR $NbNiTe_5$

Nb–2Te(3)	2.808(3)	Te(1)–Ni–4Te(2)	95.17(7)
Nb–4Te(1)	2.852(2)	Te(2)–Ni–2Te(2)	90.51(9)
Nb–2Te(2)	2.921(3)	Te(3)–Nb–Te(3)	81.21(11)
Nb–2Nb	3.656(5)	Te(3)–Nb–4Te(2)	71.04(4)
Nb–4Ni	4.200(4)	Te(3)–Nb–4Te(1)	88.93(9)
Ni–2Te(1)	2.557(3)	Te(2)–Nb–Te(2)	129.34(8)
Ni–4Te(2)	2.574(2)	Te(1)–Nb–4Te(2)	73.63(7)
Ni–2Ni	3.656(5)	Te(1)–Nb–2Te(1)	79.70(9)
Te(1)–Te(1)	3.196(4)	Te(1)–Nb–2Te(1)	68.15(8)
Te(1)–2Te(2)	3.460(3)		
Te(1)–2Te(1)	3.656(5)		
Te(1)–2Te(2)	3.788(4)		
Te(1)–4Te(3)	3.789(3)		
Te(2)–4Te(3)	3.331(3)		
Te(2)–Te(2)	3.623(3)		
Te(2)–2Te(2)	3.656(5)		
Te(3)–2Te(3)	3.656(5)		

Results

Description of the structure. Interatomic distances and bond angles for $NbNiTe_5$ are given in Table V. $NbNiTe_5$ forms in a new layered structural type and is the first example of a layered ternary niobium telluride. A view down the *a* axis (Fig. 1) clearly shows the layered nature of the structure. The structure consists of two types of chains that run parallel to the *c* axis. Figure 2 shows the geometry around the Ni and Nb atoms. One chain consists of Ni-centered edge-shared octahedra. This type of coordination is rather common for the tellurides and is seen in $NiTe_2$ (*25*). The

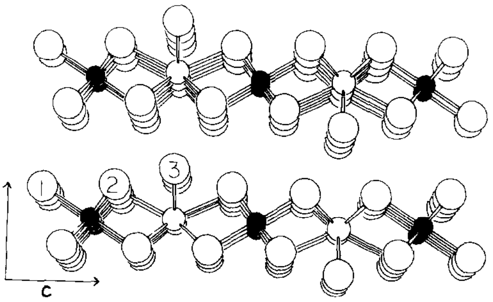

FIG. 1. View of $NbNiTe_5$ down the *a* axis. Here and in Fig. 2, small filled circles are Ni atoms, small open circles are Nb atoms, and large open circles are Te atoms.

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[1] See NAPS document No. 04503 for 7 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or $7.75 for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

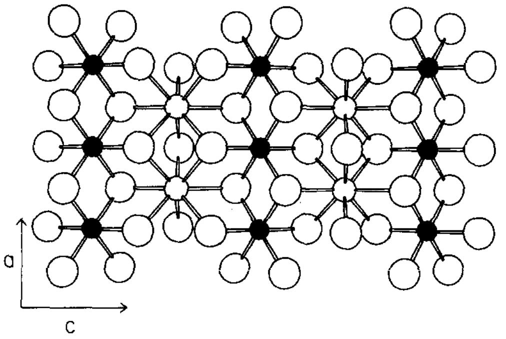

FIG. 2. View of $NbNiTe_5$ down the b axis showing the coordination around the Ni and Nb atoms.

Ni—Te bond lengths range from 2.557(3) to 2.574(2) Å. These compare well with the Ni—Te bond length in the $Cd(OH)_2$-type structure of $NiTe_2$ of 2.596(11) Å (*25*). The other chain possesses Nb-centered bicapped trigonal prisms of Te atoms that share triangular faces along the a axis. This type of coordination is unknown for binary and ternary tellurides of the group V triad where octahedral (*26*), square antiprismatic (*19*), and tetrahedral (*14*) are the usual coordination geometries of the cations.

TABLE VI

VOLUME PER Te ATOM (Å^3) FOR TELLURIDES OF NIOBIUM AND TANTALUM

Telluride	Volume	Ref.
Without Te–Te bonds		
$NbTe_2$	39.35	(*26*)
$TaTe_2$	39.48	(*26*)
With Te–Te bonds < 2.95 Å		
$NbTe_4$	36.10	(*17*)
$TaTe_4$	35.78	(*19*)
$NbNiTe_5$	36.20	—

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

However, this geometry is seen in the corresponding selenides, e.g., in Ta_2NiSe_7 (*12*) and $TaSe_3$ (*27*). The Nb—Te bonds range in length from 2.808(3) to 2.921(3) Å and may be compared with those of 2.690(7) – 2.908(7) Å in $NbTe_2$ (*26*). There are no close Nb–Ni interactions in this structure as the shortest Nb–Ni distance is 4.200(4) Å. The shortest metal–metal interactions are along the a axis, with both the Nb–Nb and Ni–Ni distances being 3.656(5) Å (the a repeat).

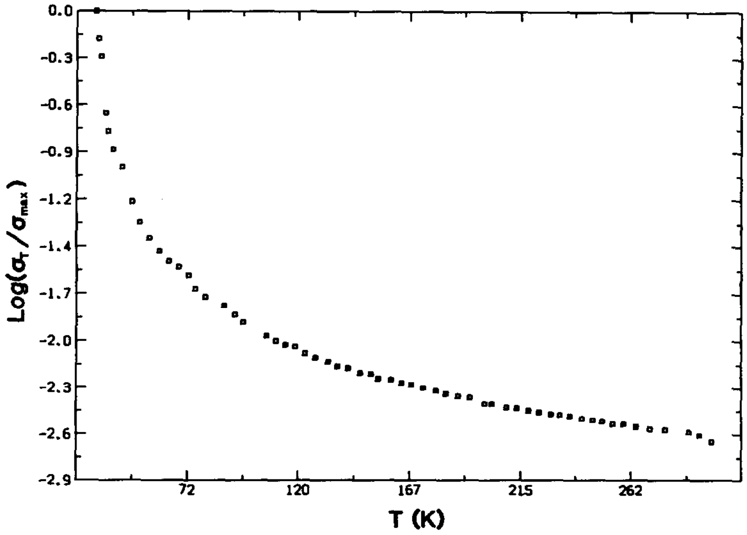

FIG. 3. Normalized conductivity vs temperature for $NbNiTe_5$ · $\sigma_{293} \approx 1.3 \times 10^4\ \Omega^{-1}\ cm^{-1}$, $\sigma_{33} \approx 5 \times 10^6\ \Omega^{-1}\ cm^{-1}$.

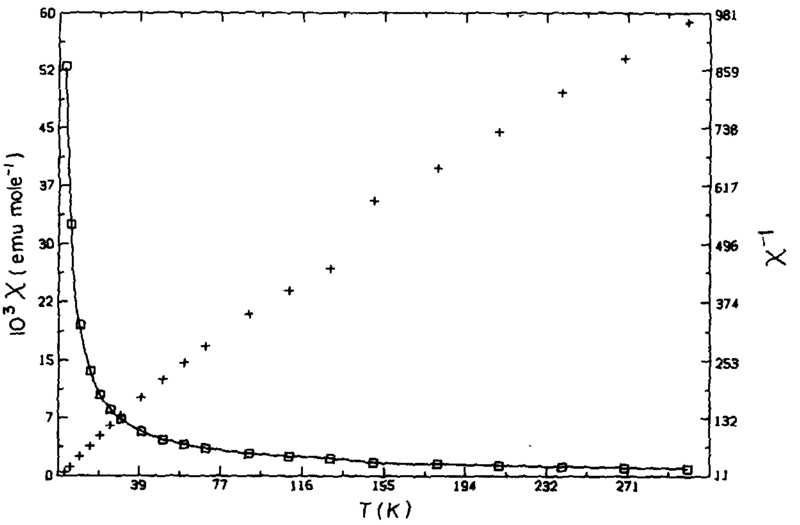

FIG. 4. Plot of χ (□) and inverse χ (+) as a function of temperature at 1 kG. The deviation at ≈130°K in the plot of inverse χ vs T probably occurred because the signal from the sample holder and sample were of approximately equal magnitude but opposite sign in this temperature region.

The shortest Te–Te interaction in $NbNiTe_5$ is 3.196(4) Å. This is significantly longer than the distance of 2.92 Å expected for a Te–Te single bond (*28*). However, the majority of the Te–Te interactions in $NbNiTe_5$ are in the range 3.19–3.79 Å, significantly shorter than twice the ionic radius of Te^{2-} (4.4 Å) (*29*). Thus, intermediate Te–Te interactions are present in $NbNiTe_5$. In fact, the volume per Te atom in $NbNiTe_5$ is very similar to those in compounds with Te—Te bonds (Table VI).

Physical properties. Four-probe single-crystal conductivity measurements along the needle axis *a* show that $NbNiTe_5$ is a highly conductive metallic material with a room-temperature conductivity of ≈$1.3 \times 10^4\ \Omega^{-1}\ cm^{-1}$. A plot of the normalized electrical conductivity over the temperature range 33–300°K is given in Fig. 3. No deviation from metallic behavior is seen.

Plots of the inverse susceptibility and the temperature dependence of the magnetic susceptibility at 1 kG are given in Fig. 4. These plots demonstrate that $NbNiTe_5$ obeys the Curie–Weiss law over the temperature range 1.99–300°K. The magnetic data were corrected for ion-core diamagnetism (*30*) and then fit by a least-squares procedure to the equation $\chi = \chi_0 + C/(T + \theta)$. The values obtained for θ, C, and χ_0 are 0.36(3) K, 0.192(2) emu K mole^{-1}, and $7.2(9) \times 10^{-4}$ emu mole^{-1}, respectively. From the formula (*31*) $\mu_{eff} = (8C)^{1/2}$ we obtain $\mu_{eff} = 1.24(1)$ B.M. From the spin-only approximation ($\mu_{eff} = (4s(s + 1))^{1/2}$ B.M. the values for μ_{eff} for Ni^{2+} and Nb^{4+} are 2.83 and 1.73 B.M., respectively, while of course they are 0 B.M. for Ni^0 and Nb^{5+}. Thus there must be some electron transfer from Te^{2-} to Nb^{5+} or Ni^0 to account for μ_{eff} and for the Te–Te interactions. A more detailed description of the bonding would require a band-structure calculation.

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