$NbNi_{2.38}Te_3$, a New Metal-Rich Niobium Telluride with a "Stuffed" $TaFe_{1+x}Te_3$ Structure

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In the last few decades early transition metal chalcogenides received the attention of many scientists, both physicists and chemists, because of their diverse and unusual physical and chemical properties. Superconductivity[1] and charge density wave (CDW) behavior[2] as well as anisotropic electrical and optical properties[3] have been observed for many of these materials. These phenomena originate in the electronic structure of this class of compounds, which is characterized by incompletely filled conduction bands. Most of these materials have low dimensional structures leading to a rich intercalation chemistry,[4] and potential applications in battery systems or as lubricants.

Originally, almost all studies were concentrated on sulfides and selenides, whereas the tellurides were neglected. Only the last few years saw an uprise in early transition metal telluride chemistry. This led to the discovery of numerous new binary and ternary phases with unique structures. For example, Ta_6Te_5,[5] $MM'Te_5$ (M = Nb, Ta; M' = Ni, Pd, Pt),[6] $Ta_{1.09}Fe_{2.39}Te_4$,[7] $M_4M'Te_4$ (M = Nb, Ta; M' = Si, Cr, Fe, Co),[8] $M_3M'Te_6$ (M = Nb, Ta; M' = Si, Ge),[9] Ta_4BTe_8,[10] and $MGeTe_4$ (M = Zr, Hf)[11] all have no counterparts among the sulfides and selenides. The origin of the different behaviour of sulfides and selenides on one hand and tellurides on the other hand is not yet clear. Neither packing considerations nor electronic reasoning based on band structure calculations on the extended Hückel level allows for a reliable differentiation between the tellurides and their lighter homologues. Indeed, we have recently succeeded in the synthesis of $Ta_2Ni_3Se_5$,[12] the first ternary tantalum selenide with an existing Te-analog, $Ta_2Ni_3Te_5$.[13] This result shows that further experimental work is needed to obtain a satisfactory understanding of the differences and similarities in sulfide/selenide and telluride chemistry. Here we report the synthesis, structure and electrical properties of the new metal-rich telluride $NbNi_{2.38}Te_3$.

Table 1. Crystallographic Data for $NbNi_{2.38}Te_3$

$NbNi_{2.38}Te_3$	fw = 615.6 gmol^{-1}
a = 7.405(2) Å	space group $P2_1/m$ (No. 11)
b = 3.7623(5) Å	T = 298 K
c = 10.005(2) Å	λ = 0.71073 Å
β = 105.70(2)°	$\varrho_{calc.}$ = 7.619 g/cm^3
V = 268.34(10) Å^3	μ = 26.160 mm^{-1}
Z = 2	R^a = 0.025
	R_w^b = 0.031

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum(w|F_o|)^2]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] (Å^2) for $NbNi_{2.38}Te_3$

atom	Wyckoff site	x	y	z	U_{eq}
Nb	2e	0.70807(8)	1/4	0.20502(6)	0.0108(1)
Ni(1)	2e	0.0996(1)	1/4	0.58824(8)	0.0126(2)
Ni(2)	2e	0.5468(1)	1/4	0.92849(8)	0.0114(2)
Ni(3)[b]	2e	0.7157(3)	1/4	0.5044(3)	0.0152(7)
Te(1)	2e	0.08252(6)	1/4	0.32876(4)	0.0130(1)
Te(2)	2e	0.21765(6)	1/4	0.99465(4)	0.0116(1)
Te(3)	2e	0.46571(6)	1/4	0.66100(4)	0.0122(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupancy 0.382(6).

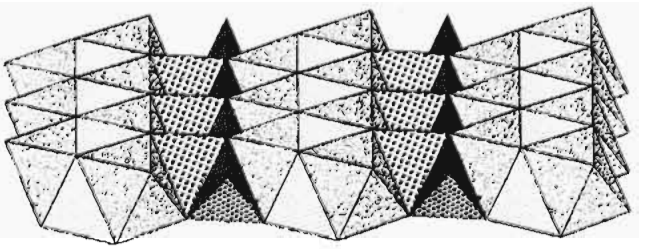

Figure 1. Polyhedral representation of a $NbNi_2Te_3$-layer ($NbTe_6$-octahedra: random dot pattern, $NiTe_4$-tetrahedra: crossed (Ni(1)), tetrahedral sites of type *B*: regular dot pattern Ni(2)). Ni(3) atoms are situated in the square hollows formed by three Ni(1)Te_4-tetrahedra and one $NbTe_6$-octahedron.

Experimental Section

Synthesis. $NbNi_{2.38}Te_3$ was synthesized by heating the elements—Nb powder (Starck, 99.99%), Ni powder (Alfa, 99.9%) and Te powder (Merck 99.9%)—in a ratio of Nb:Ni:Te = 1:2:2 in a sealed evacuated silica tube (length approx. 20 cm, diameter 18 mm). Doubly sublimated iodine (approx. 2mg/cm^3) was added as a mineralizer. The tube was placed into a two-zone furnace with a temperature gradient from 850 to 700 °C with the charge at the hot end. After 14 days long flat crystals (single phase material, EDAX on several crystals: Nb, Ni, Te) showing metallic luster were formed at the cold end of the tube (yield approximately 60%). Elemental analysis yielded a bulk composition of $Nb_{0.99(3)}Ni_{2.39(4)}Te_{3.00(2)}$. X-ray structure refinements on several single crystals from batches with different starting compositions showed variations of the sample composition according to a formula $NbNi_{2+x}Te_3$ ($x \approx 0.2-0.4$).

X-ray Powder Diffraction. The samples were examined using an Enraf-Nonius Fr 552 vacuum Guinier camera with monochromated

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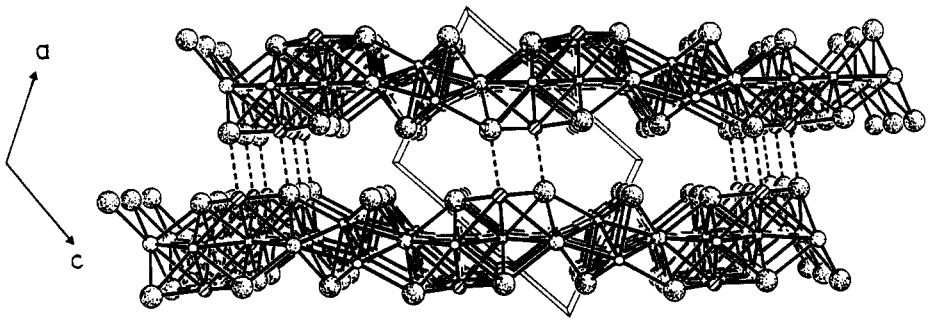

Figure 2. Projection of the structure of $NbNi_{2.38}Te_3$ along [010] (Te, large, heavily dotted circles; Nb, medium, light dotted circles; Ni(1), small open circles; Ni(2), dotted circles; Ni(3), hatched circles).

Table 3. Important Interatomic Distances (Å) for $NbNi_{2.38}Te_3$

Nb−Ni(1)	2.872(1) (2×)	Ni(1)−Ni(1)	2.725(1) (2×)
Nb−Ni(2)	2.742(1) (2×)	Ni(1)−Ni(3)	2.738(3)
Nb−Ni(2)	2.700(1)	Ni(1)−Ni(3)	2.637(2) (2×)
Nb−Ni(3)	2.980(3)	Ni(1)−Te(1)	2.579(1) (2×)
Nb−Te(1)	2.714(1)	Ni(1)−Te(1)	2.565(1)
Nb−Te(2)	2.903(1) (2×)	Ni(1)−Te(3)	2.610(1)
Nb−Te(3)	2.815(1) (2×)		
		Ni(3)−Ni(1)	2.738(3)
Ni(2)−Ni(2)	2.570(1) (2×)	Ni(3)−Ni(1)	2.637(2) (2×)
Ni(2)−Te(2)	2.539(1) (2×)	Ni(3)−Te(1)	2.685(2) (2×)
Ni(2)−Te(2)	2.693(1)	Ni(3)−Te(3)	2.622(2) (2×)
Ni(2)−Te(3)	2.579(1)	Ni(3)−Te(3)	2.730(3)

$CuK\alpha_1$ radiation (λ = 1.540 56 Å) and quartz as an internal standard. The experimental powder patterns were in almost perfect agreement with those calculated from the single-crystal data using the program Lazy-Pulverix.[14]

Structure Determination. Preliminary checks of crystal quality and Laue symmetry using film methods indicated monoclinic symmetry. Overexposed Weissenberg photographs gave no indications for superstructure formation. Single crystal studies were carried out on a flat needle-shaped crystal (dimensions 0.005 × 0.02 × 0.2 mm) using a Syntex $P2_1$ four-circle diffractometer equipped with graphite monochromator (Mo Kα radiation, λ = 0.710 73 Å) and a scintillation counter. Relevant crystallographic data are listed in Table 1. All calculations were performed with the SHELXTL/PC program system.[15] A total of 2595 reflections were collected ($4° \le 2\theta \le 70°$; $\pm h$, $+k$, $\pm l$), of which 1322 were unique (R_{int} = 0.033) and 1130 considered observed ($F > 4.0\sigma(F)$). Conventional atomic scattering factors were used and anomalous dispersion corrections were applied.[16] The processed data were empirically corrected for absorption effects using the program XEMP. Systematic extinctions led to the possible space groups $P2_1/m$ (No. 11) and $P2_1$ (No. 4). The choice of the centrosymmetric space group $P2_1/m$ (rather than $P2_1$) was proved to be correct based on the refinement results. Direct methods yielded the positions of three Te atoms, one Nb atom, and two Ni atoms. The additional, partially occupied Ni site was located from subsequent difference electron density maps. Anisotropic refinement with a free occupancy parameter for the partially occupied Ni site resulted in R = 0.025 (R_w = 0.031) and a composition of $NbNi_{2.382(6)}Te_3$ in excellent agreement with the analytical data. Atomic parameters and important interatomic distances are compiled in Tables 2 and 3. Further information on the crystal structure analysis is available as supplementary material.

Resistivity Measurements. A flat needle-shaped crystal (dimensions 0.03 × 0.5 × 3 mm) was mounted on a sample holder and four gold leads were attached along the needle axis using silver epoxy. The resistivity was measured as a function of temperature from 290 to 5 K and reverse at increments of 2 K. The absolute values of resistivity are only approximate due to difficulties in measuring the crystal dimensions accurately.

Results and Discussion

The structure of $NbNi_{2.38}Te_3$ is built up by layers of composition $NbNi_2Te_3$ which are linked by Ni atoms located at the layer surfaces. Figure 1 gives a polyhedral representation of a $NbNi_2Te_3$ layer, whereas a projection of the complete structure along the crystallographic *b*-axis is shown in Figure 2. The layers are stacked along $[10\bar{1}]$. Each slab consists of $[Nb_2Te_6]$ double chains of edge sharing octahedra which are interconnected by $[Ni_2Te_4]$ double chains of edge-sharing tetrahedra to give layers of composition $[(Nb_2Te_2Te_{4/2})(Ni_2Te_{4/2})] \equiv NbNiTe_3$. In fact, the $NbTe_6$ octahedra are heavily distorted ($d_{Nb-Te(1)}$ = 2.714(1) Å; $d_{Nb-Te(2)}$ = 2.903(1) Å (2×); $d_{Nb-Te(3)}$ = 2.815(1) Å (2×); $d_{Nb-Te(2)}$ = 3.672(1) Å) resulting in a 5-fold rather than 6-fold Te-coordination of niobium. Thus, the idealized picture of $NbTe_6$ octahedra is chemically not correct, but it facilitates discussion and clearly shows the structural relationship between $NbNi_{2.38}Te_3$ and $TaFe_{1+x}Te_3$.[17] Each $NbNiTe_3$ layer additionally contains two types of tetrahedral voids which, judged by their size, could be filled by 3d-metal atoms: site *A* is formed by two edge-sharing octahedra and one tetrahedron, while site *B* is formed by three edge-sharing octahedra. Both types of tetrahedral voids occur in a 1:1 ratio. Occupation of both sites by Ni atoms leads to a (hypothetical) compound of composition $NbNi_3Te_3$, whereas a composition of $NbNi_2Te_3$ results for a compound with only one type of tetrahedral void filled. Finally, if both sites *A* and *B* remain unoccupied, the composition is $NbNiTe_3$. The latter type of structure is realized in $TaFe_{1+x}Te_3$[17] and the corresponding niobium phase,[18] while in the $NbNi_{2.38}Te_3$ structure the *B* sites are filled with Ni atoms. Thus, $NbNi_{2.38}Te_3$ can be regarded as stuffed variant of $TaFe_{1+x}Te_3$. Additional octahedral, tetrahedral, and square-pyramidal vacancies are found in the interlayer region, of which only the latter are partially occupied by 3d-metal atoms. The electronic factors responsible for the partial occupation of these sites are not yet understood. In contrast to the octahedral and tetrahedral voids in the interlayer region the occupation of the square-pyramidal sites leads to various short metal−metal contacts ($d_{Ni(3)-Ni(1)}$ = 2.637(2) Å (2×); $d_{Ni(3)-Ni(1)}$ = 2.738(3) Å (1×); $d_{Ni(3)-Nb}$ = 2.980(3) Å (1×)). Therefore, we conclude that metal-metal bonding is one important reason for the occupation of this site.

Furthermore, numerous short Nb−Ni and Ni−Ni contacts can be found within a $NbNi_{2.38}Te_3$ slab. Ni(1), which is located at the centers of the cross-hatched tetrahedral sites (Figure 1), has two Nb and up to five (note the statistical occupation of the Ni(3) site) Ni neighbors, while Ni(2), occupying the tetrahedral

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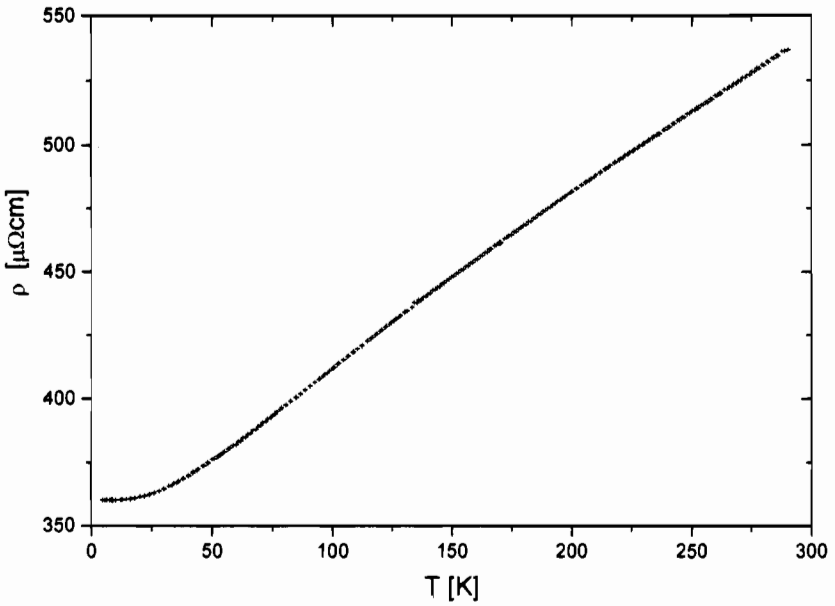

Figure 3. Plot of the specific resistivity as a function of temperature (cooling and heating cycle) of a needle-shaped $NbNi_{2.38}Te_3$-crystal measured along the needle axis.

sites of type *B* (regularly dotted in Figure 1) has three neighboring Nb and two neighboring Ni atoms. Finally, each Nb atom is surrounded by six Ni atoms (for bond distances see Table 3). Compared with the Nb−Ni distances in $NbNi_3$[19] and in ternary early transition metal tellurides such as $NbNiTe_2$[20] the corresponding distances in $NbNi_{2.38}Te_3$ (approximately 2.7 Å) have to be regarded as strongly bonding. Band structure calculations on these and similar compounds show that metal−metal bonding interactions between early and late transition metals are of crucial importance for the electronic stability of these structures.[21] The observed Ni−Ni distances (2.57−2.74 Å) are typical for Ni cluster compounds such as $[Ni_8S(SC_4H_9)_9]^{-}$ [22] or $[Ni_4Se_2(CO)Br(CpMe)_3]$[23] for which significant metal−metal bonding has been discussed. According to the computational results on related compounds[21] these distances should be considered weakly bonding. The shortest Nb−Nb distance is 3.762(1) Å, while the closest inter- and intralayer Te−Te contacts are 3.740(1) and 3.74(1) Å, respectively. To a first approximation these contacts can be considered nonbonding.

The occupation of type *B* tetrahedral sites formed by Nb_2Te_6 double chains of edge-sharing octahedra results in the formation of rhombuslike Nb_2Ni_2 clusters which are linked via common edges to form a one-dimensional infinite chain. Such $M_2M'_2$ clusters (M = Nb, Ta; M′ = Fe, Co, Ni, Pd) are a common structural feature in many metal rich niobium and tantalum tellurides such as TaM'_2Te_2 (M′ = Co, Ni),[21a,b] MM′Te_2 (M = Nb, Ta; M′ = Fe, Co, Ni),[3,20,21b,c,24] and $Ta_2M'_3Te_5$ (M′ = Ni, Pd).[13,21d] The occurrence of this type of cluster has been related to the electronic stabilization gained by the formation of strong bonds between electron-rich and electron-deficient transition metal atoms.[21,25] Similar factors are expected to be important for the electronic stability of the $NbNi_{2.38}Te_3$ structure as well. Unambigous assignment of oxidation states for the atoms in $NbNi_{2.38}Te_3$ is not possible, but for a metal-rich compound the occurrence of metal atoms in low oxidation states resulting in partially filled d-bands is anticipated. Therefore, $NbNi_{2.38}Te_3$ is expected to be a metallic conductor. Indeed, the results of four-probe resistivity measurements (Figure 3) indicate metallic behaviour for $NbNi_{2.38}Te_3$ in the temperature range from 5 to 290 K.

In conclusion, ternary niobium and tantalum tellurides can be modified by interstitial atoms on vacant lattice sites of the parent structure. This principle might be extended to other early transition metal chalcogenides with appropriate structural features such as $Ta_4Pd_3Te_{16}$[26] or $Ta_4Co_2PdSe_{12}$.[27] The importance of metal−metal bonding in early transition metal tellurides is confirmed.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, interatomic distances and angles (5 pages). Ordering information is given on any current masthead page.

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