Nb_2Te_3, a niobium sesquitelluride with Te_2^{2-} groups

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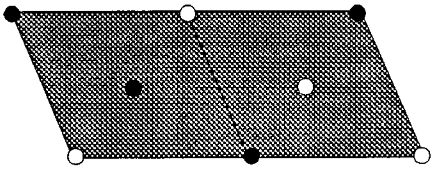
Received (in Cambridge, UK) 8th March 1999, Accepted 18th May 1999

The new binary compound Nb_2Te_3 was synthesized by reduction of $NbTe_2$ with Ga metal; different from the formally analogous Ta_2Te_3 it crystallizes in the Mo_2As_3 structure type; based on the results of band structure calculations Nb_2Te_3 is metallic with quasi one-dimensional metal electronic properties.

In spite of the spectacular progress made in fields such as supramolecular[1] or nanochemistry,[2] new binary and seemingly simple compounds still continue to be found. Typical examples are early transition metals chalcogenides: about ten new binary phases such as TaS_3,[3] Ta_6Te_5,[4] Ta_3S_2,[5] Ta_2Se,[6], Hf_3Te_2,[7] and $Ti_{11}Se_4$[8] have been reported during the past decade; all of them display a unique structure type. At first sight it may seem surprising that binaries of such simple compositions have escaped detection until recently.

Even more surprising is that these compounds challenge our basic assumptions about the chemistry of the early transition elements and our chemical understanding in general. The chemistries of Zr and Hf are considered nearly identical,[9] and the situation is similar for their Group 5 congeners, Nb and Ta. Furthermore, the opportunity for metal segregation in mixed-metal systems allows the formation of pseudobinaries such as $Nb_{1.72}Ta_{3.28}S_2$[10] which have no counterpart in the binary systems.[11] The existence and structure of none of the above compounds could be predicted *a priori* and a rationalization of their structures *a posteriori* does not give conclusive hints why the binary chalcogenides of the early transition metals display as many differences as they do, even after accounting for differences in metal–metal bond strengths.[12]

In the quest for new metal-rich early transition metal cluster compounds with interstitial atoms we have investigated reactions in the system M/A/Q (M = Nb, Ta; A = B, Ga, C, Si; Q = S, Se, Te). Nb_2Te_3 was prepared by reducing $NbTe_2$ with Ga at 1000 °C.[13] According to the results of the X-ray structure determination† Nb_2Te_3 crystallizes in the Mo_2As_3 structure type.[14] The unit cell contains eight metal atoms (two crystallographically different metal atoms per asymmetric unit) in a distorted octahedral Te coordination. The basic motif of the structure are double chains of edge-sharing $NbTe_6$ octahedra, **1**.



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Motif **1** is a common fragment in structures derived from the NiAs or CdI_2 tye, but it is also encountered in the structures of metal oxide bronzes[15] and chalcogenides such as Nb_3Q_4[16] (Q = S, Se, Te) and Nb_2Se_3.[17] Most of these compounds have intriguing physical properties, because they represent borderline cases between metallic and non-metallic behavior.[15] Each octahedron of **1** shares one common face with the octahedron of an adjacent double chain. A view of the structure along the short axis *b* is provided in Fig. 1. A special feature of the structure is that four of the twelve octahedral voids in the unit cell remain empty; the empty holes are compressed in such a way as to give rise to the formation of Te_2 pairs with Te–Te distances of 2.915(3) Å, As a result, one third of the Te atoms are involved in Te–Te bonding. Moreover, the cations are shifted from the centers of the octahedra in such a way as to give rise to zigzag Nb–Nb chains along the *b* direction. The Nb(1) atoms are moved off their ideal positions by *ca.* 0.6 Å in the direction of one octahedral face. In this way, Nb(1)–Nb(1) chains are formed with metal–metal distances of 3.001(5) Å, which are only 5% longer than those in Nb metal. Nb(2) atoms also form chains along the *b* direction, but in these chains the Nb(2)–Nb(2) distances are, at 3.095(3) Å, considerably longer. Formally, Nb_2Te_3 may be viewed as $(Nb^{2.5+})_4(Te^{2-})_4(Te_2^{2-})$.

In contrast to the homologous Ta_2Te_3,[18] which crystallizes in a peculiar layer structure, Nb_2Te_3 adopts the Mo_2As_3 structure. The sesquiselenides Nb_2Se_3 and Ta_2Se_3 crystallize in another unique structure type,[17] whereas the corresponding sulfides are unknown. It is established that metal tellurides are distinctly different from the sulfides and selenides[19] because Te has a higher tendency to form chalcogen–chalcogen bonds;[20] still, it seemed to be a general rule that in metal chalcogenides with a metal/non-metal ratio > 2 no chalcogen–chalcogen bonds are formed. Thus, several questions need to be answered: (i) why does Nb_2Te_3 crystallize in the Mo_2As_3 structure type, *i.e.* what is the reason for the partial oxidation of Te in Nb_2Te_3? (ii) What are the electronic properties of Nb_2Te_3? (iii) Why are Nb_2Te_3 and Ta_2Te_3 structurally so different? We cannot answer the latter question; a general answer to (i) might be given in terms of 'redox competition'.[20] The lower electronegativity of Te compared to its lighter group homologues leads to a partial overlap of the metal d block and the Te centered valence band. As a result, there is an electron transfer from Te to the metal, *i.e.* Nb is reduced at the expense of Te. In order to probe the electronic structure of Nb_2Te_3 we have performed tight-binding band calculations.[21] Fig. 2 shows the t_{2g} subbands of Nb_2Te_3 along the symmetry lines corresponding to the *a*, *b* and *c* directions. The energy bands are flat along X–Γ, moderately

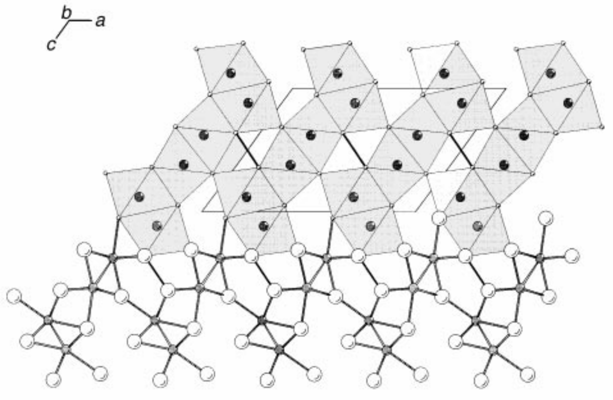

Fig. 1 View of the Nb_2Te_3 structure along *b*. Selected distances (Å): Nb(1)–Te(1) 2.883(3) (2×), Nb(1)–Te(2) 2.865(3), Nb(1)–Te(3) 2.738(3), Nb(1)–Te(3) 2.765(3) (2×) Nb(2)–Te(1) 2.904(3) (2×), Nb(2)–Te(2) 2.759(4) (2×), Nb(2)–Te(2) 2.776(3), Nb(2)–Te(3) 2.924(3), Te(1)–Te(1) 2.915(3), Nb(1)–Nb(1) 3.095(5) (2×), Nb(2)–Nb(2) 3.001(3) (2×).

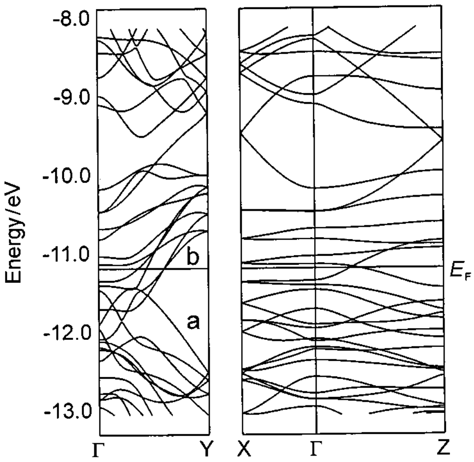

Fig. 2 Low-lying d-block bands of Nb_2Te_3: (a) along the chain direction Γ–Y; (b) along the main directions X–Γ–Z perpendicular to the chain direction. The Fermi level for Nb_2Te_3 is indicated by the horizontal bar.

disperse along Γ–Z, and highly disperse along Γ–Y. The Fermi level cuts through the middle of several steep bands; consequently, we expect metallic properties. The electronic structure may be understood in terms of the building blocks **1**, Nb_2Te_6 chains. Each of the chains **1** leads to six low-lying d block bands which originate from the t_{2g} levels of each metal. The lowest two of these bands have Nb–Nb bonding character, the two highest bands are Nb–Nb antibonding, and the remaining two bands are non-bonding with respect to the metal atoms. The unit cell of Nb_2Te_3 contains four of these chains, consequently, there must be eight bonding (labeled a in Figure 2), eight non-bonding (labeled b) and eight antibonding bands (not shown). For a $d^{2.5}$ electron count the lowest two bands of subset b are filled, and strongly anisotropic behavior is expected for Nb_2Te_3. If the bands are half-filled, a Peierls distortion may be expected. This situation is encountered for Tc_2As_3 (d^3),[22] which exhibits a superstructure of the Mo_2As_3 type and undergoes a displacive phase transition at high temperatures.

In summary, we have prepared niobium sesquitelluride, Nb_2Te_3, a new binary phase whose structure is distinctly different from those of the other known Group 5 sesquichalcogenides. It is the first early transition metal chalcogenide whose structure contains a dichalcogenide group. It is predicted to be a low-dimensional metal. For a half-filled t_{2g} subband (as observed for Tc_2As_3) a Peierls-distorted system is expected.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are indebted to Heraeus Quarzschmelze Hanau (Dr. Höfer) for a generous gift of silica tubes.

Notes and references

† *Crystal data* for Nb_2Te_3 at 25 °C: monoclinic, space group *C*2/*m* (no. 12), a = 15.073(2), b = 3.610(1), c = 10.775(2) Å, β = 126.59°, V = 470.76(10) Å, Z = 4, λ = 0.71073 Å, D_c = 8.022 g cm^{-3}, μ(Mo-Kα) = 22.77 mm^{-1}, crystal needle-like, dimensions 0.004 × 0.004 × 0.2 mm, θ_{max} = 54°, data collected at 25° on a Nicolet $P2_1$ four circle diffractometer, number of reflections, 1902, unique data with $F_o > 4\sigma(F_o)$, 767, number of variables, 32. Structure solved and refined using the SHELXTL program system. A numerical absorption correction was applied to the data (min., max. transmission, 0.86, 0.93). Final R, R_w = 0.070, 0.052. CCDC 182/1263.

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13 In a typical reaction, 2 mmol (0.696 g) of $NbTe_2$ were reacted with 1 mmol Ga (0.070 g) at 1000 °C for 3 weeks in an evacuated quartz tube which had been dried *in vacuo* at 1000 °C before loading the starting components. The reaction products were Nb_2Te_3 and GaTe. Single crystals for the X-ray structure determination were obtained from the product mixture. Attempts to prepare single phase material from the elements or by reduction of $NbTe_2$ with Nb in the temperature range 500–1200 °C failed and lead to the formation of mixtures of $NbTe_2$ and Nb_3Te_4 instead. Similarly, attempts to grow single crystals of Nb_2Te_3 by vapor transport with halogens of TeX_4 (X = Cl, Br, I) only led to the formation of $NbTe_2/Nb_3Te_4$ mixtures.
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Communication 9/01822K