Isolated and Condensed M_2Co_2 Clusters (M = Nb, Ta) in the Layered Tellurides $Nb_2Co_2Te_4$ and $TaCo_2Te_2$

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The new ternary layer compounds $Nb_2Co_2Te_4$ and $TaCo_2Te_2$ have been prepared by reaction of the elements at high temperature; isolated and condensed M_2Co_2 (M = Nb or Ta) clusters are the structural key features of these unusual layer compounds, tight-binding band structure calculations indicate the importance of Nb–Co(Ta–Co) and Nb–Nb(Ta–Ta) interactions for the electronic stability of the structures.

During the past two decades the early transition metal chalcogenides have been studied extensively because of their intriguing and often unusual physical properties such as superconductivity,[1a] anisotropic optical and electrical behaviour[1b] or charge density wave phenomena.[1c] Moreover, many of these materials are of potential technological interest, *e.g.* as synthetic conductors, reversible battery electrodes for energy storage[1d] and heterogeneous catalysts.[1e] Most of the previous investigations in this area have been concerned with sulphides and selenides. Almost no attention has been given to the tellurides, although the composition of the known binary phases indicates that the tellurides should be interesting in their own right. Thus, the chalcogen rich phases MQ_3 (M = Ti, Zr, Hf, Nb, Ta; Q = S, Se) are well known compounds,[2] but MTe_3 (M = Nb, Ta) do not exist. On the other hand, MTe_4 (M = Nb, Ta)[3] are extremely well characterized materials, but the corresponding MQ_3 phases are not known. Initially, the question arising from these facts was whether chemical modification of the binary tellurides through reaction with 3d metals might be possible. The subsequent investigations resulted in the synthesis of several novel layer compounds $Cu_{1.86}Zr_2Te_6$,[4] $Cu_{0.67}MTe_2$ (M = Nb, Ta),[4] $M_2M'Te_4$ (M = Nb, Ta; M' = Cr, Fe),[4] $M_2Ni_2Te_4$ (M = Nb, Ta),[4,5] and $Ta_2M'_3Te_5$ (M = Ni, Pd).[4,5] The synthesis of the two unusual layer compounds $Nb_2Co_2Te_4$ and $TaCo_2Te_2$, which is the subject of this communication, is an indication of the rapidly growing chemistry in this area of solid state research.

$Nb_2Co_2Te_4$ and $TaCo_2Te_2$ are synthesized from the elements in the appropriate stoichiometric ratios in evacuated sealed silica ampoules at 1000 °C. Both materials crystallize as well-developed metallic plates up to several mm in size. A comparison of the X-ray powder patterns for the materials produced suggested that they were unique. An EDAX (energy dispersive analysis of X-rays) analysis showed the presence of Nb(Ta), Co and Te.

The structure of $Nb_2Co_2Te_4$[‡] (Fig. 1) consists of layers stacked along [010] and held together by van der Waals contacts only, the shortest interlayer Te–Te distances being 3.808 Å.

The Te atoms of each layer are part of a hexagonal close-packed arrangement with Nb atoms in the octahedral interstices. This description considers the $NbTe_2$ section of the structure in terms of layers sliced from an NiAs-type lattice. The $NbTe_6$ octahedra share faces along [001] and edges along [100]. The Nb atoms are shifted off the centres of the octahedra in a pairwise fashion. This shift changes the Te coordination of Nb from six to four (+ two) ($\bar{d}_{Nb-Te}$: 4× 2.810, 2× 3.217 Å), the Nb–Nb distances change from approximately 3.1 Å (2×, across faces) and 3.6 Å (2×, across shared edges) in the NiAs type structure to 3.217 Å (2×, across shared faces), 4.66 and 3.214 Å (across shared edges). Furthermore, this atom shift increases the size of one half of the tetrahedral voids (A); correspondingly, the size of the remaining half (B) is reduced. The A-type cavities take up the Co atoms, the B-type cavities remain empty. The centres of two neighbouring tetrahedral voids (d_{Co-Co}) are 2.521(3) Å apart, in addition we find four close Nb–Co contacts [$\bar{d}_{Nb-Co}$: 2.632 (2×), 2.868 Å (2×)]. A view at the metal sublattice (which is sandwiched between Te atom layers) is very instructive (Fig. 2). Each

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[‡] *Crystal data* for $Nb_2Co_2Te_4$: orthorhombic, space group *Cmca*, a = 7.836(1), b = 14.437(2), c = 6.279(1) Å, V = 710.33 Å^3, D_c = 7.612 g cm^{-3}, μ(Mo-Kα) = 23.65 mm^{-1}, Z = 4, λ = 0.71073 Å, crystal platelet shape, dimensions 0.015 × 0.035 × 0.08 mm^3, R = 0.039, R_w = 0.036, for 711 unique reflections with $I > 2\sigma(I)$, empirical absorption correction, data collected at room temperature (298 K) on a Siemens R3 four-circle diffractometer; structure solved and refined using the SHELXTL PLUS program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1. Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-55579, the names of the authors, and the Journal citation.

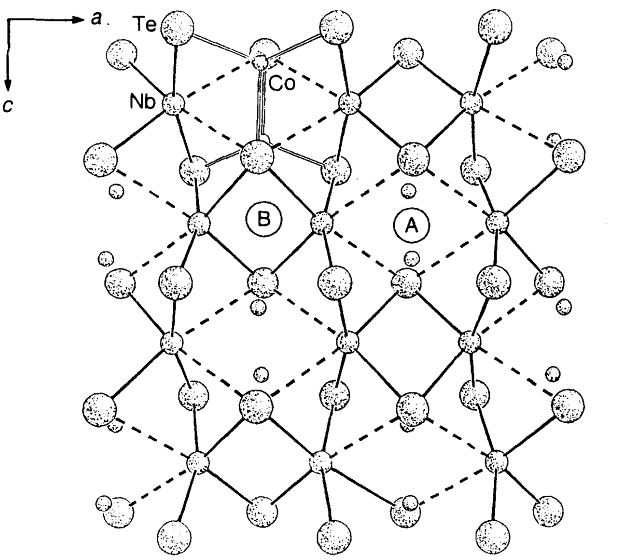

Fig. 1 A view of a layer of the structure of $Nb_2Co_2Te_4$ viewed along [010] (small circles: Co atoms, medium circles: Nb atoms, large circles: Te atoms)

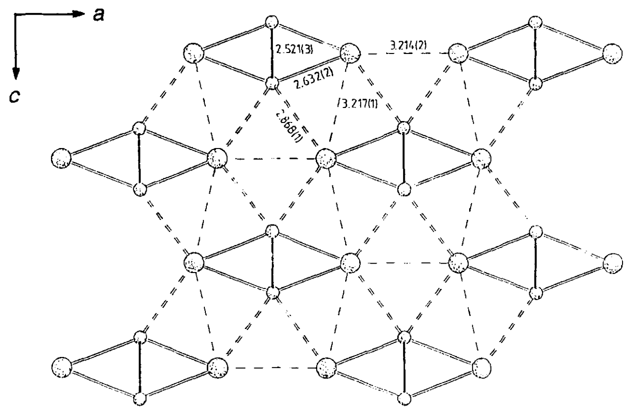

Fig. 2 A view of the metal sublattice within a layer of the structure of $Nb_2Co_2Te_4$ viewed along [010] (small circles: Co atoms, large circles: Nb atoms)

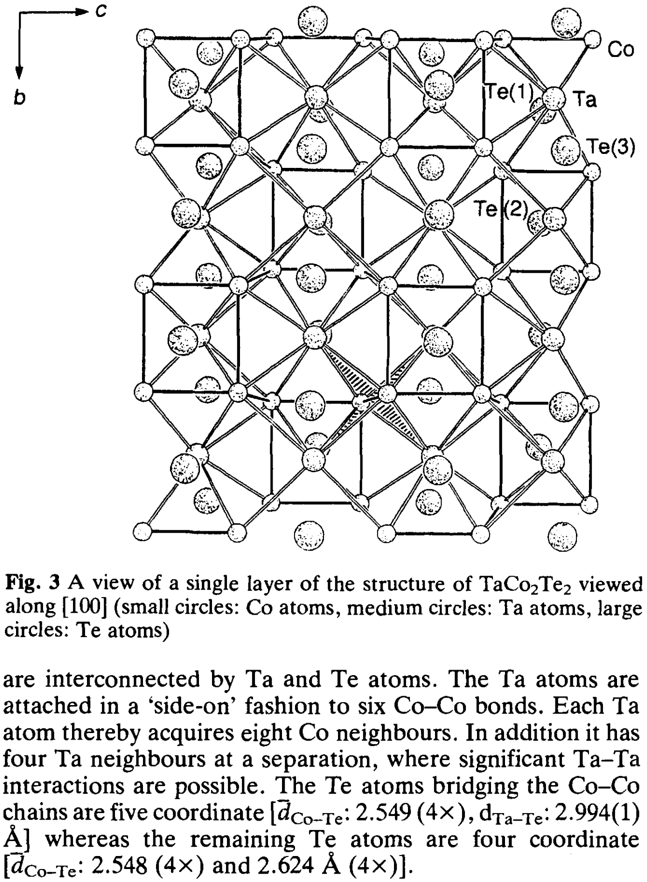

Fig. 3 A view of a single layer of the structure of $TaCo_2Te_2$ viewed along [100] (small circles: Co atoms, medium circles: Ta atoms, large circles: Te atoms)

layer contains rhomboid-like Co_2Nb_2 clusters, which are interconnected by a number of weaker Co–Nb ($\bar{d}_{Nb-Co}$: 2.868 Å) and Nb–Nb links ($\bar{d}_{Nb-Nb}$: 3.216 Å) to a two-dimensional metal–metal bonded network.

The unusual $TaCo_2Te_2$ structure§ is more complex. Again the structure is built up from layers stacked along *a*, which are held together by van der Waals contacts only, the shortest interlayer Te–Te distances being 3.849 Å. One possible description starts from the naked metal framework (Fig. 3). Each layer consists of a slightly puckered square net of Ta atoms [d_{Ta-Ta}: 3.312 Å (4×)]. This square net is interpenetrated by a second net built of Co_2 dumbbells [d_{Co-Co}: 2.557(1) Å], which are tilted in an alternating fashion with respect to the Ta net.

The tilt of the Co_2 dumbbells reduces the idealized symmetry of the Ta net from tetragonal (4 mm) to orthorhombic (2 mm). Each Ta atom acquires eight Co neighbours [d_{Co-Ta}: 2.718(1) (4×), 2.647(1) Å (4×)], while the Co atoms have four Ta neighbours [2.718(1) (2×), 2.647(1) Å (2×)] and three Co neighbours [2.557(1) Å (dumbbell), 2.599(2), 2.852(2) Å].

An alternative description starts from Co–Co *cis–trans* chains running parallel to the crystallographic *a* direction. The Co–Co distances within these chains are 2.557 and 2.599 Å and, thus, are comparable with the Co–Co distances in Co metal,[6] pentlandite (Co_9S_8)[7] and in several molecular Co cluster compounds such as $[Co_3Ni_3C(CO)_{20}]^{3-}$,[8] and $[Co_6Ni_2C_2(CO)_{16}]^{2-}$.[9] The shortest Co–Co distances between the chains are 2.852(2) Å. In addition, the Co–Co *cis–trans* chains are interconnected by Ta and Te atoms. The Ta atoms are attached in a 'side-on' fashion to six Co–Co bonds. Each Ta atom thereby acquires eight Co neighbours. In addition it has four Ta neighbours at a separation, where significant Ta–Ta interactions are possible. The Te atoms bridging the Co–Co chains are five coordinate [$\bar{d}_{Co-Te}$: 2.549 (4×), d_{Ta-Te}: 2.994(1) Å] whereas the remaining Te atoms are four coordinate [$\bar{d}_{Co-Te}$: 2.548 (4×) and 2.624 Å (4×)].

A comparison of the metal frameworks of $Nb_2Co_2Te_4$ and $TaCo_2Te_2$ is helpful at this stage. Both structure types have a common structural motif: they contain rhombic $Ta(Nb)_2Co_2$ metal clusters (highlighted by the shaded area in Fig. 3 for $TaCo_2Te_2$), but in $TaCo_2Te_2$ two of the clusters share a common Co_2 axis and four of them share a common Ta vertex. Finally, the Te atoms sandwiching the metal layers are added. They are placed from top and bottom over the smallest hollows of the metal layer. Te(1) is capping one Ta [$d_{Te(1)-Ta}$: 2.815(1) Å] and four Co [$d_{Te(1)-Co}$: 2.619(1) (2×), 2.629(1) Å (2×)], Te(2) four Co only [$d_{Te(2)-Co}$: 2.545(1) (2×), 2.551(1) Å (2×)], and Te(3) is bridging two Ta [$d_{Te(3)-Ta}$: 2.826(1), 2.994(1) Å] and two Co atoms [$d_{Te(3)-Ta}$: 2.550(1), 2.547(1) Å].

A formal oxidation state assignment for $Nb_2Co_2Te_4$ and $TaCo_2Te_2$ is not helpful in understanding their electronic structures. Both materials are probably best considered as two-dimensional metals. The metallic character of both

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§ *Crystal data* for $TaCo_2Te_2$: orthorhombic, space group *Pnma*, $a = 17.781(3)$, $b = 6.608(1)$, $c = 6.579(1)$ Å, $V = 773.01$ Å^3, $D_c = 9.520$ g cm^{-3}, μ(Mo-Kα) = 51.01 mm^{-1}, $Z = 8$, $\lambda = 0.71073$ Å, crystal thin platelet, dimensions 0.015 × 0.20 × 0.082 mm^3, $R = 0.036$, $R_w = 0.039$, for 1659 reflections with $I > 2\sigma(I)$, numerical absorption correction, data collected at room temperature (298 K) on a Siemens R3 four-circle diffractometer; structure solved and refined using the SHELXTL PLUS program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1. Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-55579, the names of the authors, and the Journal citation. The formula $Nb_2Co_2Te_4$ (instead of $NbCoTe_2$) was used in order to give the cluster formal recognition as well.

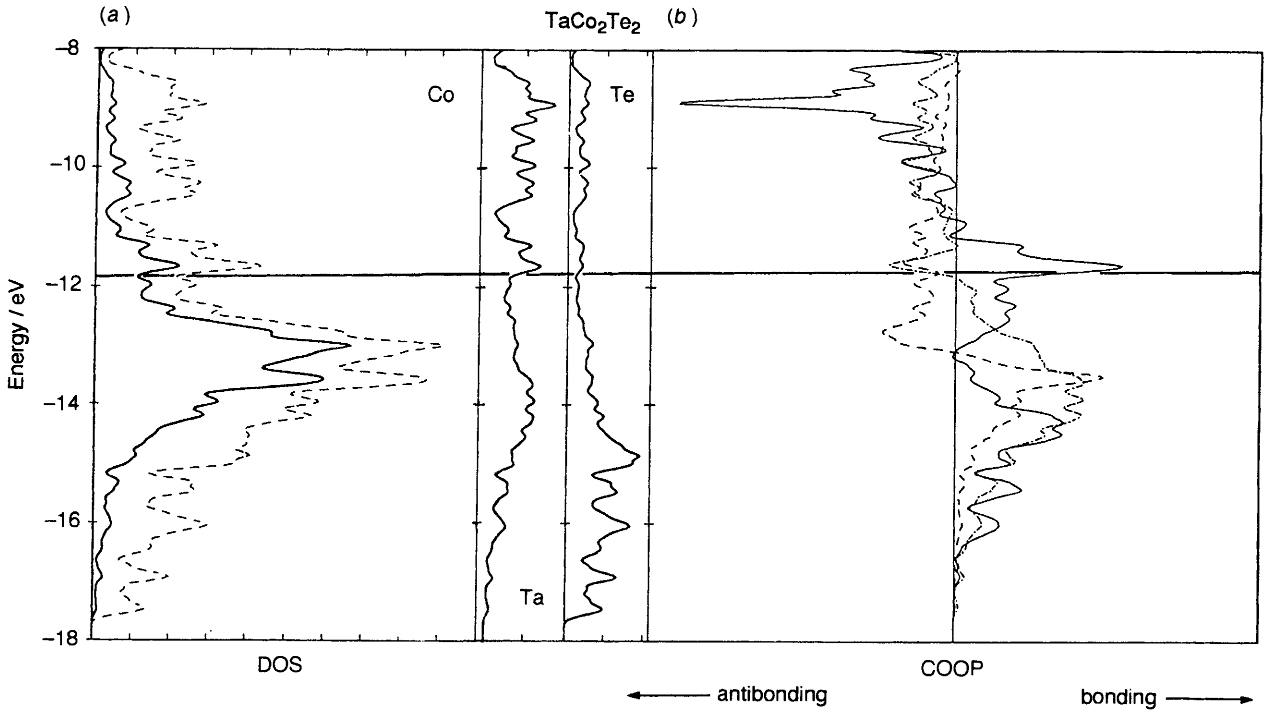

Fig. 4 (*a*) Density of states plot (DOS) for $TaCo_2Te_2$; left panel: total DOS (dashed line) with Co contribution (solid line); middle: Te contribution, right panel: Ta contribution. (*b*) COOP-curves. Solid line: Ta–Ta, dashed line: Co–Co (average of 3 Co–Co bonds), dashed–dotted line: Ta–Co. The Fermi level is marked by a horizontal bar.

compounds is indicated by preliminary resistivity measurements[4,10] and the results of tight-binding band-structure calculations.[11] The computed density of states (DOS) and the crystal orbital overlap population (COOP) curves for $TaCo_2Te_2$ are given by Fig. 4. The position of the Fermi level (indicated in Fig. 4 by a horizontal bar) clearly predicts metallic properties for this material.

The highly covalent character in the bonding is indicated by the wide and overlapping tellurium 5p and metal d bands. According to our calculations little electron density is even transferred from the most electronegative bonding partner Te to Co. The calculated atomic net charges are $[Ta(1)^{0.30-}][Ta(2)^{0.45-}][Co(1)^{0.13-}][Co(1)^{0.17-}][Te(1)^{0.39+}][Te(2)^{0.36+}][Te(3)^{0.30+}]$. The most interesting point comes from the computed Co–Co and Co–Ta overlap populations. Although there are numerous short Co–Co contacts, the net Co–Co overlap population is calculated to be quite small (0.048). The reason simply is, that Co–Co bonding states are filled, but most of the Co–Co antibonding states are filled as well. The major part of the electronic stabilization by metal–metal bonding in these structures is carried through Ta–Ta and Co–Ta bonds. This result is consistent with Brewer's rules,[12] which state that a strong affinity exists between d-electron-poor ('Lewis acids') and d-electron-rich metals ('Lewis bases').

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