X-ray Powder Diffraction as a Tool for Facing Twins: The Case of the Monoclinic $NbCoTe_2$ and $TaCoTe_2$ Phases

**Jing Li,[*,1a] Frank McCulley,[1a] Susan L. McDonnell,[1a] Norberto Masciocchi,[1b]
Davide M. Proserpio,[1b] and Angelo Sironi[*,1b]**

Department of Chemistry, Rutgers University, Camden, New Jersey 08102, and Istituto di Chimica
Strutturistica Inorganica, Università di Milano, via Venezian 21, 20133 Milano, Italy

Received February 2, 1993[⊗]

$TaCoTe_2$ has been synthesized from the elements at 900 °C in evacuated silica tubes; the crystals of $TaCoTe_2$ are monoclinic, space group $P2_1/c$ (No. 14), with $a = 8.1524(6)$ Å, $b = 6.2649(4)$ Å, $c = 7.7945(5)$ Å, $\beta = 116.789(4)°$, and $Z = 4$, and appear to be heavily twinned about the (100) plane. Therefore, powder diffraction data and Rietveld refinement were used to assess the correct stereochemistry of the atoms of this new compound. In addition, the already reported $NbCoTe_2$ compound has been found to be, in the bulk, monoclinic [$a = 8.1612(4)$ Å, $b = 6.2976(3)$ Å, $c = 7.8518(4)$ Å, $\beta = 117.487(3)°$], rather than orthorhombic, and isostructural to $TaCoTe_2$. The stereochemical interpretation of this change of crystal symmetry is given in terms of a significant asymmetrical bending of one tellurium atom toward one Nb (or Ta) atom, making these metals five-, rather than six-, coordinated.

Introduction

Single-crystal X-ray diffraction analysis has been often considered the ultimate tool for assessing with certainty the crystal (and molecular) structures of crystalline materials. There are, however, cases where single crystals are not available or cannot be properly grown. For example, for many organic and organometallic polymers, the low solubility and/or the poor thermal stability hamper the use of common methods of crystal growth, such as slow diffusion, gel permeation, evaporation techniques, and crystallization from the melt. In this case, if the unit cell volumes are not too large (typically <2000 Å^3 for "low"-symmetry systems), powder diffraction data from conventional laboratory equipment can undoubtedly help in assigning (and refining) the correct model. Accordingly, we recently reported[2] the *ab initio* structure determination and refinement of the only known binary metal carbonyl polymer, $[Ru(CO)_4]_n$, from X-ray powder diffraction (XRPD) data only.

Some samples may inherently suffer of heavy twinning problems, making the structure determination difficult and unreliable even from "single"-crystal data of (apparent) good quality. For such cases powder diffraction is well suited because the individual twins are treated as *independent* crystallites with their diffraction peaks lying at the very same θ values. As a consequence, the presence of twinning does not affect the powder spectra.

A fairly large number of studies have been conducted recently on the solid-state ternary telluride systems, especially on the metal-rich compounds.[3–7] These metal-rich phases usually contain atoms that form highly covalent bonded frameworks and often possess low-dimensional structures such as the chain or layer type. Most of them exhibit unusual structural features and deserve further investigation. One interesting class is $M_xM'Te_{2x}$, where M is Nb or Ta and M′ stands for Fe, Co, or Ni for $x = 0.5$ and 1[3g,4–7] or Si and Ge for $x = 3$.[3a,b,d] We have found that compounds of this type behave quite differently from the corresponding sulfides. Starting with MTe_2 ditellurides, addition of a third element (M′) causes an *intra*layer insertion and M′ enters positions within a layer. This is in contrast with the disulfide derivatives, for which an *inter*layer insertion takes place and intercalation products result almost exclusively. In this paper we report the synthesis of $TaCoTe_2$ and $NbCoTe_2$, two new monoclinic structures belonging to the $M_xM'Te_{2x}$ family, and the crystal structure (Rietveld) refinement of these two phases from conventional XRPD. The stereochemical interpretation of their nature, in comparison with the already reported orthorhombic phases of $NbCoTe_2$,[4] $NbFeTe_2$,[4a] $Ta_{0.77}Fe_{0.9}Te_2$,[5] $Nb_{0.89}Fe_{0.93}Te_2$,[5] $TaNiTe_2$,[6] and $NbNiTe_2$,[6b,7] will also be discussed. A summary of crystal data for several *independent* determinations for $MM'Te_2$ compounds (M = Nb, Ta, and M′ = Fe, Co, Ni) is reported in Table I.

Experimental Section

Sample Preparation. Powder samples of $TaCoTe_2$ and $NbCoTe_2$ were prepared from high-temperature solid-state reactions at 900 and 925 °C, respectively. The elements Nb (99.98%, Strem Chemicals, Inc., Newburyport, MA) or Ta (99.9%, Aldrich Chemical Co., Inc., Milwaukee, WI), Co (99.999%, Johnson Matthey, Inc., Seabrouck, NH), and Te (99.999%, Aldrich Chemical Co., Inc) were mixed in 1-g amounts with a molar ratio of Nb (or Ta):Co:Te = 1:1:2. The mixture was transferred to a 6-in. long fused silica tube (10-mm ID) and sealed under vacuum. The reaction containing tantalum was then heated from room temperature to 900 °C within 12 h and was kept at this temperature for 48 h. The niobium sample was heated to a slightly higher temperature, 925 °C, in 12 h and remained at 925 °C for 3 days. After slowly cooling to room temperature, the reaction containers were removed from the furnaces. Fine, dark powders were formed which showed metallic luster. Single

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

(1) (a) Rutgers University. (b) Università di Milano.

(2) Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 471.

(3) For example: (a) Li, J.; Badding, M. E.; DiSalvo, F. *J. Less-Common Met.* **1992**, *184*, 257. (b) Li, J.; Carroll, P. *Mater. Res. Bull.* **1992**, *27*, 1073. (c) Badding, M. E.; Li, J.; DiSalvo, F.; Zhou, W. *J. Solid State Chem.* **1992**, *100*, 313. (d) Li, J.; McDonnell, S. L.; McCulley, F. *J. Alloys Compounds* **1993**, *191*, 187. (e) Monconduit, L.; Evain, M.; Boucher, F.; Brec, R.; Rouxel, J. *Z. Anorg. Allg. Chem.* **1992**, *616*, 1. (f) Tremel, W. Habilitationsschrift, University of Munster, 1991. (g) Tremel, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 217. (h) Badding, M. E.; DiSalvo, F. *Inorg. Chem.* **1990**, *29*, 3952. (i) Li, J. Presented at the 204th National Meeting of the American Chemical Society, Washington, DC, Aug 23–28, 1992; paper INOR 290. Li, J. Manuscript in preparation. (j) Mar, A.; Ibers, J. A. *J. Solid State Chem.* **1992**, *97*, 366. (k) Mar, A.; Ibers, J. A. *Ibid.* **1991**, *92*, 352. (l) Mar, A.; Ibers, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 639. (m) Liimatta, E. W.; Ibers, J. A. *J. Solid State Chem.* **1989**, *78*, 7.

(4) (a) Li, J.; Badding, M. E.; DiSalvo, F. *Inorg. Chem.* **1992**, *31*, 1050. (b) Huang, B.; Shang, M.; Huang, J. *Jiegou Huaxue (J. Struct. Chem.)* **1988**, *7*, 133. (c) Tremel, W. *J. Chem. Soc., Chem. Commun.* **1991**, 1405.

(5) Neuhausen, J.; Stork, K. L.; Potthoff, E.; Tremel, W. *Z. Naturforsch.* **1992**, *47B*, 1203.

(6) (a) Tremel, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 840. (b) Huang, J.; Liu, S.; Huang, B. *Sci. China, Ser. B* **1991**, *34*, 666. (c) Huang, B.; Huang, J.; Liu, S. *Jiegou Huaxue (J. Struct. Chem.)* **1989**, *8*, 145.

(7) Huang, J.; Huang, B. *Jiegou Huaxue (J. Struct. Chem.)* **1988**, *7*, 214.

0020-1669/93/1332-4829$04.00/0

Table I. Lattice Parameters for $MM'Te_2$ Compounds (M = Nb, Ta; M' = Fe, Co, Ni)

compd	ref	space group	a, Å	b, Å	c, Å	β, deg
$NbCoTe_2$	4a	$Cmca$	7.840(1)	14.431(2)	6.237(1)	90
$NbCoTe_2$	4c	$Cmca$	7.836(1)	14.437(2)	6.279(1)	90
$NbCoTe_2$	4b	$P2_1/c$	8.197(2)	6.258(1)	7.816(3)	118.48(2)[a]
		$Cmca$[b]	7.816	14.410	6.258	90
$NbCoTe_2$	this work	$P2_1/c$	8.1612(4)	6.2976(3)	7.8518(4)	117.487(3)
		$C112_1/a$[c]	7.852	14.483	6.298	91.26 (γ)
$TaCoTe_2$	10	$P2_1/c$	8.207(2)	6.232(2)	7.764(3)	118.17(3)[a]
		$Cmca$[d]	7.764	14.470	6.232	90
$TaCoTe_2$	this work	$P2_1/c$	8.1524(6)	6.2649(4)	7.7945(5)	116.789(4)
		$C112_1/a$[c]	7.794	14.562	6.265	91.75 (γ)
$NbNiTe_2$	6b,7	$Pm2a$	7.955(1)	7.203(2)	6.258(1)	90[e]
$TaNiTe_2$	6a	$Pmna$	7.897(1)	7.228(1)	6.230(1)	90
$TaNiTe_2$	6b,c	$Pm2a$	7.914(1)	7.236(1)	6.237(1)	90[e]
$NbFeTe_2$	4a	$Pmna$	7.922(1)	7.239(1)	6.243(1)	90
$Nb_{0.89}Fe_{0.93}Te_2$	5	$Pmna$	7.951(1)	7.241(1)	6.233(1)	90
$Ta_{0.77}Fe_{0.90}Te_2$	5	$Pmna$	7.890(2)	7.252(2)	6.192(2)	90

[a] Monoclinic lattice parameters can be transformed into a *C*-centered orthorhombic lattice. [b] The refined atomic coordinates in $P2_1/c$ can be transformed consistently with the *Cmca* structure proposed by ref 4a. [c] Nonprimitive monoclinic lattice related to orthorhombic *Cmca*. [d] The absence of published atomic coordinates leaves undefined the full assignment of the space group. [e] Originally determined as *Pma*2.

Table II. Crystal Data for $TaCoTe_2$ and $NbCoTe_2$

formula	$CoTaTe_2$	$CoNbTe_2$
fw	495.08	407.04
cryst system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.1524(6)	8.1612(4)
b, Å	6.2649(4)	6.2976(3)
c, Å	7.7945(5)	7.8518(4)
β, deg	116.789(4)	117.487(3)
V, Å^3	355.37(4)	358.00(3)
Z	4	4
D_{calc}, g cm^{-3}	9.25	7.55
$F(000)$	816	688
μ(Cu Kα), cm^{-1}	2223.3	1921.2
T, K	298(1)	298(1)
R_p[a]	0.120	0.122
R_{wp}[a]	0.155	0.163
R_{Bragg}[a]	0.046	0.040

[a] $R_p = \sum|y_{i,o} - y_{i,c}|/\sum y_{i,o}$, $R_{wp} = \sum w_i(y_{i,o} - y_{i,c})^2/\sum w_i y_{i,o}^2$, and $R_{Bragg} = \sum|I_{i,o} - I_{i,c}|/\sum I_{i,o}$, where y_i and I_i are the (observed or calculated) *profile* and *integrated* intensities, respectively, and w_i is a statistical weighting factor, taken as $1/y_{i,o}$.

crystals of $TaCoTe_2$ were grown from chemical transport reactions using $TeCl_4$ as transport agent. Approximately 10 mg of $TeCl_4$ was weighed and added to the Ta/Co/Te mixture under an inert atmosphere. The reaction tube was evacuated and placed in a Kanthal furnace and heated slowly to 900 °C for 5 days. Shiny, thin platelike crystals were found both at the cool end of the tube and within the bulk. They are stable in air for a long period of time.

XRPD Structure Determination. The samples of $NbCoTe_2$ and $TaCoTe_2$ were gently ground in an agate mortar and then filtered through a 37-μm sieve in order to remove the largest particles. The fine powders were then cautiously deposited with the aid of a binder (5% collodion in amyl acetate) onto a silicon wafer cut perpendicularly to the [511] direction (supplied by The Gem Dugout) in order to minimize scattering from the substrate. X-ray powder diffraction data were taken on a Rigaku D/Max horizontal-scan diffractometer operated in the θ:2θ mode, with Cu Kα radiation (λ = 1.5418 Å), parallel Soller slits, and a pyrolytic graphite monochromator in the diffracted beam. A Na(Tl)I scintillation detector was used, coupled with pulse height discrimination for noise removal. The samples were continuously rotated at about 70 rpm around the scattering vector in order to minimize preferred orientation effects. Scan conditions for both compounds were $5 < 2\theta < 85°$, step scan with $\Delta 2\theta = 0.02°$, t = 15 s, DS = 0.5°, AS = 0.5°, and RS = 0.15°.

The recorded powder patterns of the two samples were very similar and clearly indicated the isomorphous nature of the two compounds. The monoclinic unit cell parameters found for $TaCoTe_2$ on the (pseudo) single crystals (*vide infra*) were also detected *ab initio* by TREOR,[8] when the lowest θ peak positions, located by standard peak search methods, were fed into its trial and error indexing routines, with the following figures of merit:[9] $M(16) = 31$, $F(16) = 43$ (0.013,28). Similar cell parameters were found for the Nb compound and resulted in $M(17) = 45$ and $F(17) = 61$ (0.007, 40). No rational transformations of these unit cells into higher symmetry metrics were found.

Systematic absences uniquely indicated the $P2_1/c$ (No. 14) space group, later confirmed by successful refinement of the structure. Similar cell parameters and space group were derived earlier by Huang et al.[10] on single crystals of $TaCoTe_2$, but no further structural details are available. Owing to the similarity of the cell parameters found by Huang[4b,10] for the single crystals of the Nb and Ta compounds (which, however, should have been correctly described within an orthorhombic *Cmca* space group after a proper transformation; see Results and Discussion), the starting model of our refinements was taken from that paper.[4b] Refinement was conducted with the Rietveld technique using the DBW 3.2 program,[11] locally modified in order to allow an empirical surface roughness correction, as described by Masciocchi *et al.*,[12] which becomes necessary in the case of highly absorbing powders. The background was refined using a polynomial fit, while a Pearson VII function[13] best described the observed peak shape. The angular dependence of the peak widths was modeled using the standard Caglioti dependence.[14] A total of 34 independent parameters, including lattice parameters, zero angle shift, peak asymmetry, and preferred orientation corrections, were refined. Final R_p, R_{wp}, and R_{Bragg} values, defined in Table II (see also ref 11), are 0.120, 0.155, 0.046 and 0.122, 0.163, 0.040 for the Ta and Nb compound, respectively. A summary of the crystal data is presented in Table II; Table III contains the final values of the fractional atomic coordinates, while the relevant internuclear distances for the title compounds are collected in Table IV. Plots of the observed and calculated XRPD spectra for both compounds are reported in Figure 1.

Results and Discussion

Crystallography. The crystals of $TaCoTe_2$, of evident metallic luster, appear as very thin platelets, in agreement with the layered structures of a number of ternary tellurides reported in the literature.[3-7] Independent of the actual thickness of the chosen samples, all (apparently single) crystals mounted on a four-circle diffractometer gave intense Bragg reflections and a unit cell similar to that of the reported Nb analogue[4a] but with very poor esd's.

---

(8) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(9) De Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108. Smith, G. S.; Snyder, R. L. *J. Appl. Crystallogr.* **1979**, *12*, 60.

(10) Huang, J. L.; Huang, B. Q. *Acta Crystallogr., Sect. A* **1990**, *46* (*Suppl.*), C-287.

(11) Young, R. A.; Mackie, P. E.; Von Dreele, R. B. *J. Appl. Crystallogr.* **1977**, *10*, 262. Wiles, D. B.; Young, R. A. *J. Appl. Crystallogr.* **1981**, *14*, 149.

(12) Masciocchi, N.; Toraya, H.; Parrish, W. *Mater. Sci. Forum* **1991**, *79–82*, 245.

(13) Hall, M. M.; Veeraraghavan, V. G.; Rubin, H.; Winchell, P. G. *J. Appl. Crystallogr.* **1977**, *10*, 66.

(14) Caglioti, G.; Paoletti, A.; Ricci, F. P. *Nucl. Instrum. Methods* **1958**, *3*, 223.

Table III. Fractional Atomic Coordinates and B (Å^2) Values for $TaCoTe_2$ and $NbCoTe_2$ with Esd's in Parentheses

	x		y		z		B	
atom	Ta	Nb	Ta	Nb	Ta	Nb	Ta	Nb
M	0.4904(4)	0.4908(5)	0.4846(6)	0.4857(7)	0.1994(4)	0.2011(4)	1.3(1)	1.3(1)
Co	0.3985(11)	0.3853(7)	0.6526(13)	0.6496(8)	0.4442(11)	0.4378(8)	1.3(3)	1.1(2)
Te(1)	0.1804(4)	0.1786(3)	0.7501(10)	0.7517(6)	0.0910(5)	0.0914(3)	0.38(12)	0.46(8)
Te(2)	0.7276(4)	0.7274(3)	0.7431(9)	0.7434(5)	0.6378(5)	0.6332(3)	0.81(14)	0.42(9)

Table IV. Relevant Bond Distances (Å) for $TaCoTe_2$ (**1**, This Work), $NbCoTe_2$ (**2**, This Work), and Orthorhombic $NbCoTe_2$ (**3**)[4a]

	compd		
	M = Ta (**1**)	M = Nb (**2**)	M = Nb (**3**)
Co–M	2.569(11)	2.596(8)	2.641(1) (×2)
	2.647(9)	2.672(7)	
	2.704(10)	2.777(7)	2.845(1) (×2)
	2.888(9)	2.941(7)	
M–M	3.217(5) (×2)	3.228(6) (×2)	3.204(1) (×2)
	3.188(5)	3.235(5)	3.187(1)
Co–Te1	2.589(8)	2.534(6)	2.534(1) (×2)
	2.584(11)	2.562(8)	
Co–Te2	2.479(8)	2.558(5)	2.552(1)
	2.649(10)	2.609(6)	2.587(1)
M–Te1	2.818(6)	2.831(5)	2.819(1) (×2)
	2.842(5)	2.837(4)	
M–Te2	2.854(5)	2.842(4)	2.766(1) (×2)
	2.778(6)	2.806(5)	
	2.973(6)	3.014(5)	3.234(1) (×2)
	3.476(5)	3.439(4)	
Co–Co	2.419(11)	2.514(7)	2.499(2)

A closer look at the most intense peaks revealed, however, that they were narrow in θ, but several degrees wide in ω, and (for some classes) possessed a double-maxima nature. On selection of a coherent set of maxima, a monoclinic unit cell (7.79 × 6.26 × 8.15 Å, $\beta = 116.8°$) was determined. Analogously, the very same cell was found on using the setting angles of the other peak components. This refined lattice metric was similar to the cell parameters proposed for $NbCoTe_2$ by Huang *et al.*,[4b] [$a = 7.816(3)$, $b = 6.258(1)$, $c = 8.197(2)$ Å; $\beta = 118.48(2)°$]. A simple mathematical cell transformation[15] of Huang's monoclinic lattice parameters, however, generated a C-centered orthorhombic cell, and an orthorhombic phase could indeed be successfully refined.[4a,c] On application of the same transformation to the monoclinic cell of our $TaCoTe_2$ sample, only a nearly orthorhombic (C-centered) cell could be found ($a = 7.794$, $b = 14.562$, $c = 6.265$ Å; $\gamma = 91.75°$). This led to the conclusion that all crystals of $TaCoTe_2$ tested on the four-circle diffractometer were twinned samples of a truly *monoclinic* phase. Since the two differently oriented reciprocal lattices give rise to double diffraction spots, the twinning belongs to the TLQS (twinned-lattice quasi-symmetry) class with $\omega = 1.75°$ (see for example ref 16). We decided therefore to overcome the twinning problem by using powder diffraction methods, which are, by definition, unaffected by the presence of (random macro) twins. To test the reliability of XRPD refinement, we reran the Nb analogue on our powder diffractometer and, to our surprise, we found that the bulk material conforms to the monoclinic symmetry and that no trace of the orthorhombic phase previously described could be detected. This disagrees with the earlier report[4a] on the consistency between the observed powder spectrum and that calculated from the orthorhombic structure. *A posteriori*, we think that, possibly because of the natural tendency to prefer results in agreement with preconceived ideas, the comparison of the powder spectra was done in a rough way and the monoclinic splitting of some peaks went unobserved. In addition, (i) three *independent* reports are consistent with the very existence of the orthorhombic phase of $NbCoTe_2$ and (ii) $TaCoTe_2$ too has been claimed to be isostructural to $NbCoTe_2$. All "single-crystal" samples, however, were obtained in the presence of $TeCl_4$ as a transport agent, and transport reactions are known to produce, in some cases, different phases. Accordingly, our observations of *monoclinic* $TaCoTe_2$ single crystals and of the *monoclinic* XRPD spectra for $NbCoTe_2$ *and* $TaCoTe_2$ do not contradict the previous results. In fact, all the monoclinic crystals appear to be heavily twinned (*vide supra*), hence normally rejected for a standard X-ray analysis. The self-selecting procedure of searching for *good* single crystals has certainly driven past researchers toward the few (untwinned) orthorhombic crystals present in their samples. However, we failed to find in our samples of $TaCoTe_2$ any crystals of the orthorhombic phase. A recent report[17] on Ta_2Te_3, prepared with the transport technique, revealed (i) the presence of "*a systematic twinning of all crystals, with the intensities of the individuals varying within 5–100% relative to each other*" and (ii) a twinning mechanism similar to that discussed for our samples in the following section. Consequently, this behavior is not uncommon within layered tellurides.

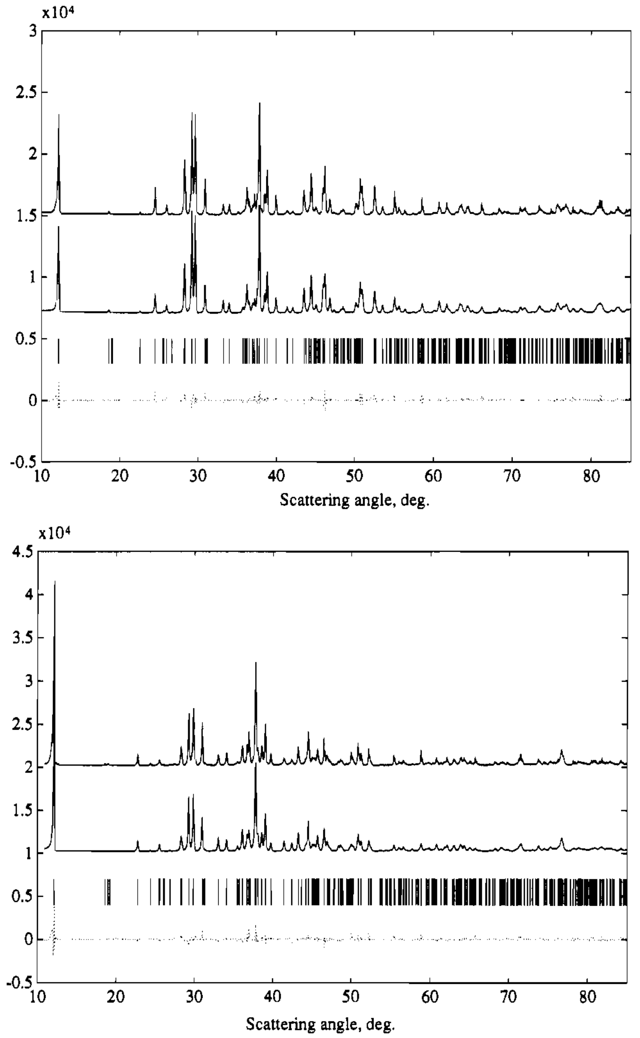


Figure 1. Observed (top), calculated, and difference (bottom) XRPD patterns for $NbCoTe_2$ (a, top) and $TaCoTe_2$ (b, bottom).

---

(15) The matrix transforming the monoclinic cell into the orthorhombic one is [2,0,1; 0,0,−1; 0,1,0].

(16) Giacovazzo, C. In *Fundamentals of Crystallography*; Giacovazzo, C. Ed.; IUCr-Oxford University Press: Oxford, U.K., 1992; pp 83–87.

(17) Conrad, M.; Harbrecht, B. *J. Alloys Compounds* **1992**, *187*, 181.

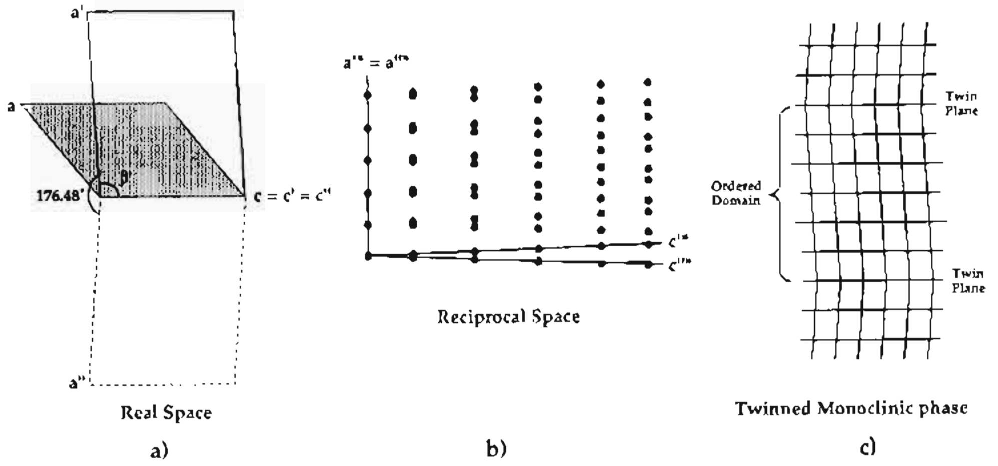


Figure 2. (a) Geometrical relation between the $P2_1/c$ (shaded) and $B2_1/c$ cells (two orientations; see text). (b) Schematic drawing of the reciprocal lattice of the (pseudoorthorhombic) twinned crystals. (c) Stacking of ($B2_1/c$) cells along [100], with twin faults. For clarity, all monoclinic angles are exaggerated.

The twinning mechanism observed in $TaCoTe_2$ has a simple geometrical interpretation if the primitive $P2_1/c$ lattice is transformed into a (*quasi*-orthorhombic) *B*-centered monoclinic supercell. Under this transformation (**a**' = 2**a** + **c**, **b**' = **b**, **c**' = **c**) the space group becomes $B2_1/c$ with $\beta' = 91.75°$. On taking the **b**'**c**' plane (100) as the *twin* plane, two adjacent *misaligned* but *identical* monoclinic cells can be drawn, as reported in Figure 2a. The two cells are characterized by the **a**',**c**' and **a**'',**c**'' vectors, respectively, with **a**'**a**'' = 360° – 2β' = 176.50°. In the reciprocal space, the slight misalignment of **a**' and **a**'' generates two independent **c**'* and **c**''* vectors (see Figure 2b); therefore, diffraction maxima with nonzero *l* values appear as more or less distinct double spots. This is particularly evident for the (00*l*) reflections: an ω–θ plot for the 004 reflection of a pseudosingle crystal of $TaCoTe_2$ is given in the supplementary material.

If the two **c**'* and **c**''* vectors are superimposed (and the β' angle taken at *exactly* 90°), and a mirror plane perpendicular to **c** is added to the $B2_1/c$ space group, an orthorhombic space group, namely *Bbcm*, can be generated. Under proper axes permutation, this cell can be transformed into *Cmca*, the space group reported for the already published orthorhombic phase of $NbCoTe_2$.[4a,c] The stereochemical interpretation of this twinning will be described later; it should be noted, however, that both twinning and stacking of the telluride layers occur normal to the [100] direction (in the $B2_1/c$ formulation).

Structure Description. The XRPD analysis has indicated an interesting structure for $NbCoTe_2$: the crystal structure previously proposed does not represent the structure of the bulk material, synthesized at the same temperature. This latter belongs to a lower symmetry monoclinic space group $P2_1/c$ rather than the orthorhombic *Cmca*.[4a,c] A closer look at the two structures shows, however, that despite the difference in their space groups, the two structures have much in common. The ideal sequence of orthorhombic blocks building the crystals is somewhat affected in the twinned monoclinic phases, where domains, related by the twin planes, can be envisaged (see Figure 2c). Both structures belong to a layered type with the metal network "sandwiched" between the capping Te atoms, as shown in Figure 3. The interlayer Te–Te contacts are long (>3.7 Å) and weak, similar to many other Nb/Ta telluride compounds studied.[3–7] The metal–metal bonding interactions are almost identical in the two structures, as well as the Co–Te interatomic distances.

The most significant change comes from the Nb-to-Te coordination. The $Nb_2Co_2(\mu_4\text{-}Te)_{4/2}(\mu_4\text{-}Te)_{6/3}$ cluster, as taken from Huang's formulation,[4b] is now located about an inversion center, rather than a $2/m$ position as in *Cmca*. As a consequence, some of the internuclear distances, which are identical in the orthorhombic phase, become crystallographically distinct. The major difference, observed in *both* monoclinic Nb and Ta compounds, is the bending of the Te2 atom toward one Nb(Ta) atom, making the two Nb(Ta)–Te2 distances quite different (3.01, 3.44 and 2.97, 3.48 Å for the Nb and Ta compounds, respectively; 2 × 3.23 Å in the Nb orthorhombic phase; see Figure 4). Accordingly, the clusters should be rephrased as $M_2Co_2(\mu_4\text{-}Te)_{4/2}(\mu_5\text{-}Te)_{6/3}$ (M = Nb, Ta). The coordination of the Te atoms about each Nb(Ta) atom, formerly described as a 4 + 2 distorted octahedron, is therefore better described as a 4 + 1 environment, of approximate square pyramidal shape. Such a Nb(Ta) coordination is quite unusual and, to our knowledge, has been observed only in Ta_2Te_3[17] but never in the ternary solid-state Nb(Ta) chalcogenide compounds. Correspondingly, the M_2Co_2 (M = Nb, Ta) and Co_2Te_2 rhombi, sharing a common hinge, are now at about 82°, rather than *exactly* 90°, as in the orthorhombic phase. It should be emphasized that the afore-

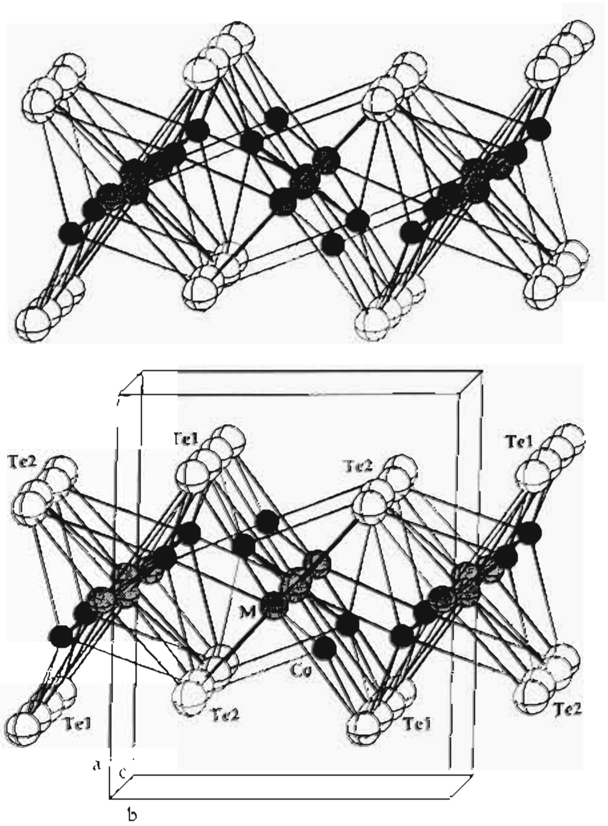
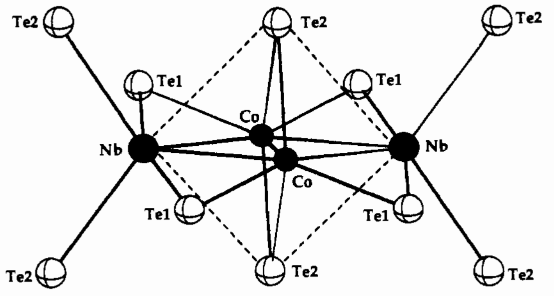
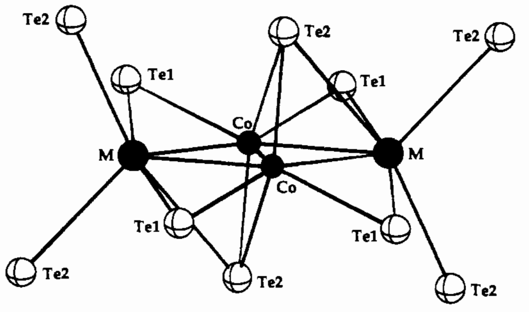


Figure 3. Perspective view of the layered $TaCoTe_2$ compound. The solid circles are Co atoms, the dotted circles Ta, and the cross-hatched circles Te.



$Nb_2Co_2(\mu_4\text{-}Te)_{4/2}(\mu_4\text{-}Te)_{6/3}$



$M_2Co_2(\mu_4\text{-}Te)_{4/2}(\mu_5\text{-}Te)_{6/3}$ M=Ta, Nb

Figure 4. $MCoTe_2$ cluster in the orthorhombic (M = Nb) (top) and monoclinic (M = Nb, Ta) (bottom) phases. The dashed lines between Nb and Te(2) address the long Nb–Te bonds, 3.23 Å.

mentioned bending represents the *chemical* clue for the existence of the monoclinic phases. In fact, starting from the orthorhombic phase, the bending of the Te2 atom toward one Nb atom determines a phase transition of displacive type, which lowers the crystal symmetry down to monoclinic. The equally probable bending toward the second Nb atom of each cluster would create an identical, but differently oriented, layer. Therefore, the stacking of adjacent layers having opposite bending directions is causing the observed twinning.[18] Note that equal probability of this bending does not imply a random sequence of the two types of layers (A, B), which would produce a disordered structure (*e.g.* ...ABAABABBAB...), *i.e. microtwins*; rather, the different energetics at the interfaces between layers (AA or AB) cause the formation of conglomerated crystallites, containing large ordered domains (...AAAAABBBBB...), i.e. *macrotwins*.

The few other differences observed in the distances reported in Table IV are consistent in the two monoclinic compounds and differ only slightly from those of the orthorhombic phase. Nevertheless, on passing from the Nb to the Ta derivatives, we observed a systematic decrease of the M–Co and M–M interactions (M = Nb, Ta); this is accompanied by an anisotropization of the Co environment, which shows, in the Ta compound, longer Co–Te and shorter Co–Co distances, the latter being the shortest metal–metal bond observed among all the investigated telluride compounds of this class. Care, however, should be taken into account in evaluating the correct Co–Co distance in the title compounds, as the cobalt atoms represent here the lightest atoms, *i.e.* those with the least scattering power for X-rays.

So far all six MTe_2 derivatives of groups 8–10 transition-metal elements Fe, Co, and Ni of the $MM'Te_2$ type have been synthesized and studied (see Table I).[3i,4–7] They crystallize in four different space groups, *Cmca* ($NbCoTe_2$),[4a,c] *Pman* ($NbFeTe_2$, $TaFeTe_2$),[4–5,19] *Pma*2 ($NbNiTe_2$, $TaNiTe_2$),[6,7] and $P2_1/c$ [$NbCoTe_2$, $TaCoTe_2$ (this work)]. All are layered types with weak interlayer interactions through long Te–Te contacts. The metal atoms form a strong covalent bonded network extended throughout the layer.[3i] The Te atoms close-packings in all six structures are distorted from those in MTe_2[20] to accommodate the metal atoms. The Nb (Ta) in the parent MTe_2 structure has a distorted octahedral coordination to six Te atoms. This remains true in the *Cmca*, *Pmna*, and *Pma*2 structures but changes to a square-pyramidal coordination in the $P2_1/c$ structures. These compounds, as well as other $M_xM'Te_{2x}$ type structures, can also be prepared by direct mixing of MTe_2 with appropriate amounts of M′.[3i] Upon the addition of Fe, Co, or Ni to MS_2, however, an intercalation product is yielded.[21] These third atoms enter the positions between the two adjacent MS_2 layers, and the parent structure remains unchanged. Electronic band calculations[22] have been performed on members of this family, for example $NbFeTe_2$ and Nb_3SiTe_6. Our preliminary results[3i] suggest that highly covalent bonds are formed among all three participating atoms in these structures. During the M′ *intra*layer insertion process into Nb (Ta) ditelluride, strong stabilizing covalent bonding interactions between the Nb (Ta) and M′ orbitals occur. At variance, such interactions are absent in the *inter*calation process with the corresponding disulfides.

Conclusions

Two group 5 ternary telluride compounds, $NbCoTe_2$ and $TaCoTe_2$, have been prepared via solid-state reactions and their structures determined by X-ray powder diffraction methods. Both compounds have layer structures, similar to those found for all six known $MM'Te_2$ compounds[4–7] (M = Nb, Ta; M′ = Fe, Co, Ni), which consist of identical $M_2M'_2$ clusters encapsulated in a (distorted) hcp packing of Te atoms, as shown in Figure 3, but with the stacking sequence of the layers generating different space groups. The XRPD analysis has revealed the structural differences in the bulk material and the single crystal whose structure was solved previously. Owing to the simultaneous sampling of reciprocal lattice nodes having the same *d* values, XRPD has also been shown to be superior to standard four-circle diffractometry in dealing with TQLS twinned structures, as long as the moderate complexity of the crystal structure allows a successful Rietveld refinement of a chemically meaningful model.

The distorted square-pyramidal coordinations of Nb and Ta to the Te atoms are quite unusual. To our knowledge, this is the second example in which Nb and Ta atoms are heavily deviated from the normal (distorted) octahedral or trigonal prismatic coordination to the anions in their known chalcogenide compounds.

Acknowledgment. J.L., S.L.M., and F.M. are grateful to the Research Corp. for its generous support through the Schering-Plough Award and the Bristol-Myers Squibb Co. Award. Thanks also go to Rutgers University for the Henry Rutgers Research Fellowship, the Research Council Grant, and the matching fund to the Schering-Plough Award. The courtesy of Dr. Paolo Cairati, who helped in the XRPD experimental work, is acknowledged. N.M., D.M.P., and A.S. wish to thank the Italian CNR (Consiglio Nazionale delle Ricerche, Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate") for funding.

Supplementary Material Available: A detailed list of crystallographic parameters (Table S1), a full list of bond distances and angles (Tables S2 and S3), and an ω–θ plot for the 004 reflection of a twinned $TaCoTe_2$ crystal (Figure S1) (5 pages). Ordering information is given on any current masthead page.

---

(18) This, however, does not imply the true existence of such a phase transition, whose thermodynamic aspects are beyond the scope of the present study.

(19) The refined stoichiometry for $TaFeTe_2$ is $Ta_{0.77}Fe_{0.90}Te_2$; see ref 5.

(20) Brown, B. E. *Acta Crystallogr.* **1966**, *20*, 264.

(21) Van der Berg, J. M.; Cossee, P. *Inorg. Chim. Acta* **1968**, *2*, 143. Van Laar, B.; Rietveld, H. M.; Ijdo, D. J. W. *J. Solid State Chem.* **1971**, *3*, 154.

(22) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872. Hoffmann, R.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1978**, *100*, 6093. Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London* **1979**, *A366*, 23.