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Technetium Arsenide Tc_2As_3: A Compound with a Superstructure of Mo_2As_3 Attributed to Differences in Metal–Metal Bonding*

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The new compound Tc_2As_3 crystallizes in the triclinic space group $P\bar{1}$ with the lattice constants a = 6.574(1) Å, b = 6.632(1) Å, c = 8.023(2) Å, α = 95.69(1)°, β = 102.03(1)°, γ = 104.31(2)°, V = 327.3(2) Å^3, and Z = 4 formula units per cell. The structure was determined from single-crystal X-ray data and refined to a residual of R = 0.053 for 3104 F values and 42 variable parameters. It is closely related to the monoclinic structure of Mo_2As_3 from which it can be derived by distortion and by doubling of one translation period. Chemical bonding, especially the differences in metal–metal bonding of Mo_2As_3 and Tc_2As_3 are discussed.

Introduction

Recently the binary system technetium–phosphorus was investigated for the first time (*1*). Six technetium phosphides were identified of which Tc_3P (*1*), TcP_3 (*2*), and TcP_4 (*1*) could be characterized by single-crystal structure determinations. In the course of that work a few technetium arsenide samples were prepared (*3*). Our crystals and Guinier powder patterns originate from that investigation. To our knowledge the only technetium arsenide mentioned in the literature is Tc_3As_7 which was reported to crystallize with the cubic Ir_3Ge_7 (Ru_3Sn_7)-type structure (*4*). We have only the results of three samples annealed at 950°C with starting compositions in the atomic ratios Tc : As = 1 : 2, 1 : 3, and 1 : 9. The first sample has an X-ray powder pattern of a new phase, the other two samples gave a pattern identified as that of Tc_2As_3 plus lines of excess arsenic. Thus our investigation was not comprehensive enough to corroborate the literature results.

Experimental and Lattice Constants

Crystals of Tc_2As_3 used for the structure determination were picked from a sample with the starting composition Tc : As = 1 : 3. It had been prepared by reaction of technetium powder (^{99}Tc, Oak Ridge National Laboratory, nominal purity 99.8%) and arsenic (>99.5% purified by fractional sublimation) in an evacuated and sealed silica tube which contained a small amount of iodine to enhance crystal growth. The sam-

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TABLE I

Evaluation of a Guinier Powder Pattern of Tc_2As_3[a]

Subcell *h k l*	*h k l*	Q_o	Q_c	I_o	I_c
0 0 1	0 0 1	—	167	—	4
2 0–1	0 1 0	—	248	—	4
—	1 0–1	—	327	—	3
2 0 0	0 1–1	350	350	m	53
2 0–2	0 1 1	479	480	vw	16
2 0 1	0 1–2	786	786	w	26
4 0–1	0 2–1	1031	1031	vw	15
1 1–1	2–1–1	1044	1044	w	16
2 0–3	0 1 2		1044		13
1 1–1	2 0 0		1047		17
1 1 1	2 0–2	1311	1310	vvw	13
1 1 1	2–1 1	—	1318	—	11
4 0 0	0 2–2	1402	1401	m	57
1 1–2	2–1–2*	1407	1407	w	61
1 1–2	2 0 1*	1414	1415	w	62
3 1–1	2 1–1	—	1476	—	23
3 1–1	2–2 0	1477	1479	w	24
0 0 3	0 0 3	1501	1500	w	54
—	1 2 0	—	1536	—	5
3 1–2	2–2–1	1574	1573	vs	100
3 1–2	2 1 0		1576		96
4 0–4	0 2 2	—	1919	—	7
2 0–4	0 1 3	1941	1942	m	83
3 1–3	2–2–2	2006	2001	w	26
3 1–3	2 1 1		2009		25
—	1 0 3	—	2064	—	6
1 1–3	2–1–3	2104	2103	m	47
4 0 1	0 2–3		2105		52
1 1–3	2 0 2	2117	2117	m	44
—	1–3 1	—	2150	—	3
—	3–1 0	—	2183	—	8
—	3 0–1	—	2219	—	5
6 0–3	0 3 0	2236	2236	m	58
3 1 1	2 1–3*	2276	2276	w	30
3 1 1	2–2 2*	2290	2291	w	29
—	1 2–3	—	2345	—	3
5 1–2	2 2–1	2438	2437	s	82
5 1–2	2–3 0		2441		84
6 0–1	0 3–2	2515	2514	m	45
5 1–1	2 2–2	—	2606	—	4
5 1–1	2–3 1	—	2615	—	3
0 0 4	0 0 4	2666	2666	vw	47
3 1–4	2–2–3	2770	2762	m	15
3 1–4	2 1 2		2775		14
—	3 0–3	—	2947	—	3
6 0 0	0 3–3	3152	3153	vw	19
2 0–5	0 1 4	—	3173	—	9
3 1 2	2 1–4*	3176	3176	w	75
3 1 2	2–2 3*	3197	3196	w	73

TABLE I—*Continued*

Subcell *h k l*	*h k l*	Q_o	Q_c	I_o	I_c
6 0–5	0 3 2	3290	3291	w	34
—	3–2 2	—	3520	—	5
0 2 0	4–1–1	3702	3702	w	84
3 1–5	2–2–4	—	3856	—	9
3 1–5	2 1 3	—	3875	—	8
8 0–3	0 4–1	—	3883	—	3
7 1–3	2 3–1	—	3896	—	3
7 1–3	2–4 0	—	3899	—	3
5 1–5	2–3–3	—	3917	—	10
5 1–5	2 2 2	—	3931	—	9
8 0–4	0 4 0	3975	3975	vw	21
7 1–4	2–4–1	—	4123	—	4
7 1–4	2 3 0	—	4125	—	4
6 0 1	0 3–4	—	4126	—	4
4 0–6	0 2 4	—	4177	—	12
6 0–6	0 3 3	—	4318	—	8

[a] The pattern was recorded with Cu$K\alpha_1$ radiation. The indices of the monoclinic subcell in the standard *C*2/*m* setting ($a \sim 12.85$ Å, $b \sim 3.287$ Å, $c \sim 9.32$ Å, $\beta \sim 123.8°$) are listed in the first column. Observed splitted reflections are marked with an asterisk. Because of the large number of unobserved very weak reflections only reflections with calculated intensities (5) greater than $I_c = 2$ are listed.

ple was annealed for two weeks at 950°C and subsequently quenched.

Tc_2As_3 crystals were investigated in a precession camera. They showed triclinic symmetry. The structure refinement resulted in the centrosymmetric group $P\bar{1}$. Lattice constants were refined from a carefully indexed Guinier powder pattern (Table I) where overlapping reflections were assigned zero weight in the least-squares refinement. The resulting lattice constants are: $a = 6.574(1)$ Å, $b = 6.632(1)$ Å, $c = 8.023(2)$ Å, $\alpha = 95.69(1)°$, $\beta = 102.03(1)°$, $\gamma = 104.31(2)°$, $V = 327.3(2)$ Å^3.

The pattern can also be indexed on the basis of a C-centered monoclinic cell corresponding to the Mo_2As_3-type structure. That monoclinic cell has been given in three different settings in the literature (*6, 7*). These cells and their relationship to the tri-

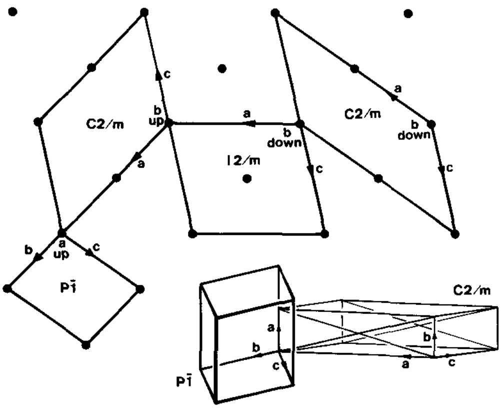

FIG. 1. Relation of the monoclinic centered Mo_2As_3-type subcell to the triclinic $P\bar{1}$ cell of Tc_2As_3. In the upper left-hand corner the standard $C2/m$ setting for the cell of Mo_2As_3 is outlined. This is the cell given by Taylor *et al.* (*6*). The structure has been determined and described by Jensen *et al.* (*7*) in the $C2/m$ cell shown in the upper right-hand corner. These authors have also given lattice constants for the alternate $I2/m$ setting. In the lower right-hand corner the relation of the standard $C2/m$ cell of Mo_2As_3 to the $P\bar{1}$ cell of Tc_2As_3 is shown in a view almost perpendicular to the pseudo $2/m$ axis.

clinic cell of Tc_2As_3 are shown in Fig. 1. The doubled *b* axis of the monoclinic cell corresponds to the *a* axis of the triclinic cell. The powder pattern of Tc_2As_3 does not contain any of the very weak superstructure reflections due to this doubling. However, the triclinic distortion can clearly be seen from the resolved line splitting of three pairs of reflections. These are marked with asterisks in Table I. Thus the triclinic cell obtained in the single-crystal study is representative for the whole sample.

Structure Determination

Single-crystal X-ray data were recorded in an automated four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The scans were taken along θ with background counts at both ends of each scan. The variable scan rate was optimized by a fast prescan for each reflection. A total of 10670 reflections was measured in the whole reciprocal space up to $2\theta = 90°$. The crystal was about equidimensional with diameters varying between 0.06 and 0.08 mm. An empirical absorption correction was made on the basis of ψ scan data. The ratio of the highest to lowest transmission was 1.62. After averaging equivalent reflections and omitting those with structure factors, less than four standard deviations 3114 F values were obtained for the structure determination.

Because the exact composition of the compound was not known, we plotted average atomic volumes versus composition for several binary systems of manganese, technetium, and rhenium with phosphorus and arsenic. From these plots it was possible to narrow the cell content down to only three possibilities: "Tc_6As_{13}," "Tc_8As_{12}," and "$Tc_{10}As_{11}$." The formulas with an odd number of As atoms seemed very improbable to us because they required the As atoms to occupy centrosymmetric positions in the more likely space group $P\bar{1}$,[1] and the expected coordination of the As atoms was incompatible with a centrosymmetric site. Thus the most likely formula was "Tc_8P_{12}," i.e., Tc_2As_3 with $Z = 4$ formula units per cell, a calculated density of $\rho_c = 8.59$ g · cm^{-3} and a linear absorption coefficient of $\mu_{MoK\alpha} = 383$ cm^{-1}.

The structure was then determined by direct methods and subsequent difference Fourier methods. The refinement was carried out by full matrix least-squares calculations employing atomic scattering factors (*9*) corrected for anomalous dispersion (*10*). Weights were assigned according to counting statistics. An isotropic secondary extinction parameter was also refined and applied to the F_c values. The 10 strongest reflections for which this correction was insufficient were excluded from the final

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[1] The noncentrosymmetric group $P1$ is very rare for typical solid-state compounds (*8*).

TABLE II

ATOM PARAMETERS OF Tc_2As_3[a]

	x	y	z	B (Å^2)
Tc(1)	0.91439(10)	0.12485(10)	0.62598(8)	0.121(7)
Tc(2)	0.46559(10)	0.13475(10)	0.63453(8)	0.120(7)
Tc(3)	0.62816(10)	0.57273(10)	0.86623(8)	0.123(7)
Tc(4)	0.08892(10)	0.57575(10)	0.85861(8)	0.134(7)
As(1)	0.54274(14)	0.20064(14)	0.96148(11)	0.181(9)
As(2)	0.03250(14)	0.18744(14)	0.95013(11)	0.161(9)
As(3)	0.62869(14)	0.84500(14)	0.68028(11)	0.143(9)
As(4)	0.13992(14)	0.86792(13)	0.68559(11)	0.160(9)
As(5)	0.76438(13)	0.43386(13)	0.61569(11)	0.135(9)
As(6)	0.26369(15)	0.41081(14)	0.64958(12)	0.229(9)

[a] All atoms are in the general position of the centrosymmetric space group $P\bar{1}$. Standard deviations in the least significant digits are given in parentheses.

least-squares cycles. The final residual value is $R = 0.053$ for 3104 structure factors and 42 variable parameters. A refinement which allowed ellipsoidal thermal parameters lowered the R value ($R = 0.047$ for 92 variables) in our judgement essentially only because of correlations with absorption effects. In the listed refinement results (Table II), the thermal parameters are probably somewhat too low because of insufficient absorption correction. Interatomic distances are given in Table III. A listing of observed and calculated structure factors can be obtained from the authors.

Discussion

The pnictides (especially the phosphides and arsenides, to a lesser extent the antimonides, but not the bismutides) of the transition metals (T) can be divided into two groups depending on coordination numbers. In the compounds with low coordination numbers the pnictogen atoms are mostly tetrahedrally coordinated to metal and pnictogen atoms, while the metal atoms have linear twofold (Au_2P_3), tetrahedral (Cu_2P_7, Ag_3P_{11}), square planar (PdP_2), or octahedral (most other compounds of this category) coordination. These are the compounds with high pnictogen content especially of the late transition metals (*11*). The compounds with high metal content have higher coordination numbers as is typical for intermetallic compounds. The physical properties (especially electrical conductivity and magnetism) of the compounds with low coordination numbers can be rationalized on the basis of classical two-electron bonds. This is not true for the compounds with high coordination numbers, although most of them are metallic conductors.

The transition from high to low coordination is gradual. For instance for the composition TX_2 (X = P or As) the compounds with T being an element of the Fe, Co, or Ni group have low coordination, i.e., tetrahedral coordination of the X atoms. In MoP_2 and isotypic β-WP_2 one P atom is tetrahedrally coordinated and the other has square pyramidal coordination (*12*). In CrP_2, α-WP_2, $CrAs_2$, $MoAs_2$, and WAs_2, all with $OsGe_2$-type structure (*13*), there is also one tetrahedral and one square pyramidal pnictogen atom, however, several second nearest neighbors, which are only 10 to 15% further away, increase the coordination numbers. Such higher coordination numbers occur also for the dipnictides of the vanadium and titanium group metals.

So far no dipnictides of Mn, Tc, or Re are known. Of the well-characterized compounds with a metal/pnictogen ratio smaller than one, Re_3P_4 (*14, 15*) can be classified as a high-coordination compound with two crystallographically independent pentacoordinated P atoms. The other compounds with a composition close to Tc_2As_3 are Re_6P_{13} (*16, 17*), Re_2P_5 (*18*), and Re_3As_7 (*19–22*). These compounds have tetrahedral coordination for the P atoms and can be rationalized on the basis of classical two-electron bonds.[2]

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[2] At first sight the diamagnetism reported for Re_3As_7 (*4, 19, 21*) seems to be at variance with this statement. In counting two electrons for each short Re–Re, Re–

TABLE III

INTERATOMIC DISTANCES (Å) IN Tc_2As_3 AS COMPARED TO THE CORRESPONDING DISTANCES IN Mo_2As_3[a]

Tc(1):	As(3)	2.437	Tc(2):	As(4)	2.553	Mo(1):	As(2)	2.509
	As(4)	2.457		As(3)	2.497		As(2)	2.545
	As(5)	2.485		As(6)	2.520		As(3)	2.553
	As(2)	2.515		As(1)	2.537		As(1)	2.578
	As(4)	2.539		As(3)	2.444		As(2)	2.509
	As(6)	2.550		As(5)	2.464		As(3)	2.553
	Tc(2)	2.925		Tc(1)	2.925		Mo(1)	2.942
	Tc(2)	2.982*		Tc(1)	2.982*		Mo(1)	3.235
	Tc(1)	3.050*		Tc(2)	2.846		Mo(1)	2.942
	Tc(4)	3.170		Tc(3)	3.099*		Mo(2)	3.257
	Tc(2)	3.594*		Tc(1)	3.594*		Mo(1)	3.235
Tc(3):	As(3)	2.453*	Tc(4):	As(4)	2.490	Mo(2):	As(2)	2.581
	As(2)	2.468		As(1)	2.548		As(1)	2.527
	As(5)	2.546		As(6)	2.528		As(3)	2.575
	As(1)	2.550		As(2)	2.472		As(1)	2.527
	As(6)	2.557		As(5)	2.479		As(3)	2.575
	As(1)	2.619		As(2)	2.706		As(1)	2.608
	Tc(4)	2.988		Tc(3)	2.988		Mo(2)	2.955
	Tc(4)	3.037*		Tc(3)	3.037*		Mo(2)	3.235
	Tc(3)	3.081*		Tc(4)	2.915		Mo(2)	2.955
	Tc(2)	3.099*		Tc(1)	3.170		Mo(1)	3.257
	Tc(4)	3.538*		Tc(3)	3.538*		Mo(2)	3.235
As(1):	Tc(2)	2.537	As(2):	Tc(1)	2.515	As(1):	Mo(1)	2.578
	Tc(4)	2.548		Tc(3)	2.468		Mo(2)	2.527
	Tc(3)	2.550		Tc(4)	2.472		Mo(2)	2.527
	Tc(3)	2.619		Tc(4)	2.706		Mo(2)	2.608
	As(1)	2.741*		As(2)	2.649*		As(1)	2.976
As(3):	Tc(1)	2.437	As(4):	Tc(2)	2.553	As(2):	Mo(1)	2.509
	Tc(2)	2.444		Tc(1)	2.539		Mo(1)	2.509
	Tc(3)	2.453*		Tc(4)	2.490		Mo(2)	2.581
	Tc(2)	2.497		Tc(1)	2.457		Mo(1)	2.545
As(5):	Tc(2)	2.464	As(6):	Tc(1)	2.550	As(3):	Mo(1)	2.553
	Tc(4)	2.479		Tc(3)	2.557		Mo(2)	2.575
	Tc(1)	2.485		Tc(2)	2.520		Mo(1)	2.553
	Tc(3)	2.546		Tc(4)	2.528		Mo(2)	2.575
	As(6)	2.447		As(5)	2.447		As(3)	2.445

[a] Standard deviations are all 0.001 Å. All Tc–Tc and Tc–As distances less than 3.7 Å and all As–As distances less than 3.1 Å are listed. Distances in Tc_2As_3 which differ by more than 0.1 Å from the corresponding one in Mo_2As_3 are marked with an asterisk.

The structural characteristics of Tc_2As_3 are close to those of Re_3P_4. Only the As(3) and As(4) atoms have (distorted) tetrahedral coordination. The As(5) and As(6) atoms have (slightly distorted) square pyramidal coordination. The As(1) and As(2) atoms may also be considered as square pyramidal, although two of their neighbors are at larger distances than the other three. Each of the four nonequivalent Tc atoms has six As neighbors forming a considerably distorted octahedron. In addition each

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As, and As–As interaction one electron per formula unit remains unaccounted for. This electron is probably responsible for the metallic conductivity (*21*) of this compound. It must be assumed that the weak Pauli paramagnetism caused by this electron is overcompensated by the core diamagnetism.

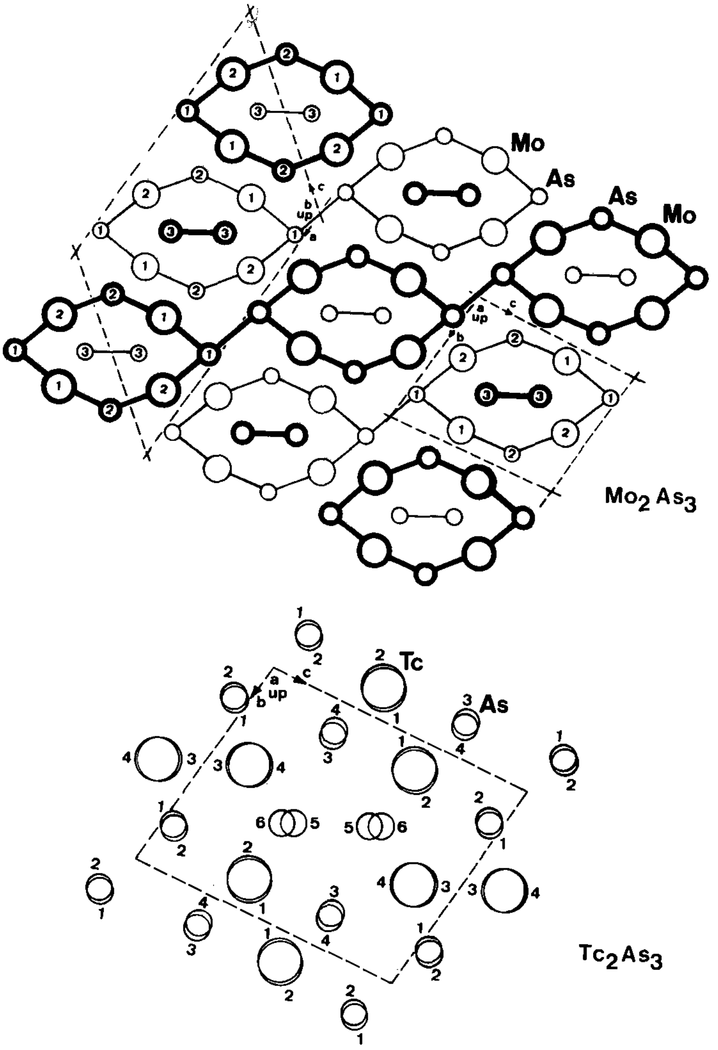

FIG. 2. Projections of the structures of Mo_2As_3 and Tc_2As_3. The numbers correspond to the atom designations. In the upper part of the figure atoms connected by thick lines and atoms connected by thin lines are separated from each other by half a translation period of the projection direction. The standard setting of the conventional C-centered cell is outlined in the left part; on the right side the primitive cell of Mo_2As_3 is shown. In the Tc_2As_3 structure this cell is doubled in the projection direction. As can be seen from the enlarged projection of this structure in the lower part of the figure, the distortions are not very great when viewed along this projection direction.

Tc atom has four Tc neighbors at distances ranging between 2.846 and 3.170 Å. These distances are rather large at first sight, however, the distortions of the $TcAs_6$ octahedra clearly indicate the Tc–Tc bonding character. They are also close to the shortest *T*–*T* bonding distances in the aforementioned compounds Re_6P_{13} (2.76 to 2.94 Å), Re_2P_5 (2.85 to 2.96 Å), Re_3As_7 (2.78 Å), TcP_3 (3.09 Å), and isotypic $ReP_3(2)$ (3.12 Å) where the *T*–*T* bonding character is in agreement with the physical properties. Nevertheless the

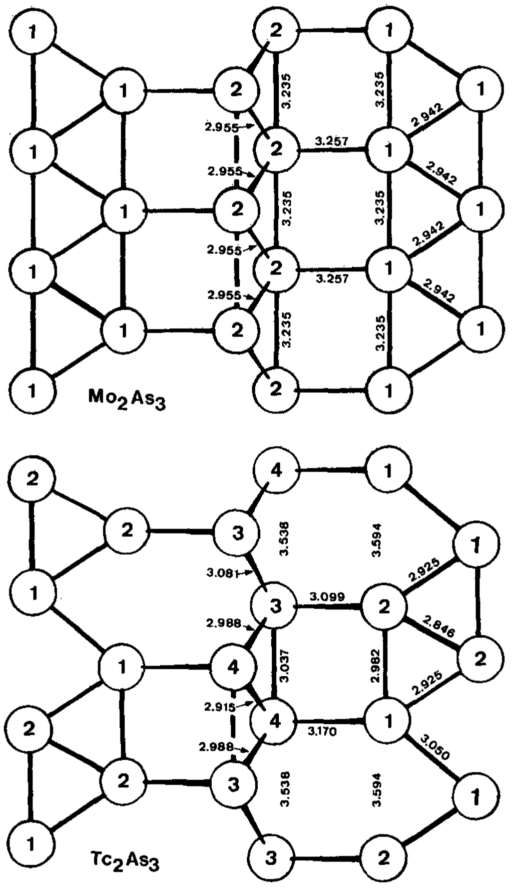

FIG. 3. Metal–metal bonding in Mo_2As_3 and Tc_2As_3. For both structures corresponding sections of the two dimensionally infinite sheets with metal–metal bonds are shown. For clarity the considerably distorted octahedral As coordinations of the metal atoms are not shown. Almost all metal–metal bonds occur across common edges of the TAs_6 octahedra. The only exceptions are the horizontal bonds of 3.257 Å in the Mo_2As_3 structure and the corresponding bonds in Tc_2As_3. These bonds are formed across common faces of the octahedra. The distances are in Å units. The designations of the metal atoms are indicated by large numbers.

structure of Tc_2As_3 cannot be fully rationalized on the basis of two-electron bonds, because the Tc atoms have a total of 10 near neighbors and they have only 9 atomic orbitals available to participate in the formation of the bonding system (violation of the 18-electron rule). In the overall account, there are 17 near-neighbor interactions per formula unit which would require 34 valence electrons for the saturation of two-electron bonds, but there are only 29 valence electrons available. Thus, although most near-neighbor interactions will come close to two-electron bonds, some bonds (notably the Tc–As bonds of 2.62 and 2.71 Å and the As–As bonds of 2.65 and 2.74 Å) will have a bond order of less than one. The structure may thus be considered as transitional from the low-coordination structures with two-electron bonds to the high-coordination structures typical for intermetallic phases.

The most striking structural property of Tc_2As_3 is its relation to the Mo_2As_3-type structure. Figure 2 shows corresponding projections of the two structures along the short translation period of Mo_2As_3. It can be seen that the distortions in Tc_2As_3 are only minor if viewed along this direction. A view perpendicular to this direction, however, shows much greater distortions. They occur mainly for the Tc atoms while the As positions in Tc_2As_3 remain close to the positions of the As atoms in Mo_2As_3. A comparison of the T–T distances in Mo_2As_3 and Tc_2As_3 shows (Fig. 3) that each Mo atom in Mo_2As_3 has five Mo neighbors at distances ranging between 2.942 and 3.235 Å. In going from the Mo_2As_3 to the Tc_2As_3 structure one of the five *T* neighbors of each *T* atom is moving to greater distances (from 3.235 Å to 3.538 and 3.594 Å, respectively) while the other four *T*—*T* interactions are shortened on average (from an average of 3.097 Å in Mo_2As_3 to an average of 3.020 Å in Tc_2As_3).[3] This we take as an indication that all five short Mo–Mo interactions in Mo_2As_3 are bonding and that the additional

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[3] In judging this difference one should, however, also consider that the Mo atoms are slightly larger than the Tc atoms. This can be seen from the average *T*–As bond lengths which are 2.553 Å in Mo_2As_3 and 2.517 Å in Tc_2As_3.

valence electron per metal atom in Tc_2As_3 is going into an orbital which is antibonding with respect to the fifth *T*–*T* interaction. Thus the metal atoms can relax in their distorted TAs_6 octahedra to form shorter bonds to the four remaining *T* neighbors. (It is impossible for a TAs_6 octahedron to distort in such a way as to allow five additional *T*–*T* bonds with optimal bond distances; if one of the five *T* neighbors is lost, a better overlap of *T* atomic orbitals and shorter bond distances to the remaining four *T* neighbors can be achieved.)

The diamagnetism of Mo_2As_3 has tempted Kjekshus *et al.* (*7*) to apply the general (8-N) rule (a formalism to count electrons in two-electron bonds)[4] to this compound. For this purpose the Mo–Mo bonds of about 2.9 Å had to be considered as bonding while the Mo–Mo bonds of about 3.2 Å had to be counted as nonbonding. Our discussion in comparison with Tc_2As_3 has shown that two-electron bonds cannot account fully for both structures, but nevertheless most near-neighbor interactions will come close to such bonds. We also expect diamagnetism for Tc_2As_3 and metallic or semimetallic (zero band gap semiconductor) behavior for both compounds.

A question which remains unresolved is the participation of one 3*d* orbital of the As(5) and As(6) atoms in Tc_2As_3 and of the corresponding As(3) atom in Mo_2As_3. The bonding distances of these pentacordinated As atoms to the *T* atoms are on average only 0.03 Å larger than the bond distances of the tetrahedrally coordinated As(3) and As(4) atoms of Tc_2As_3 and the corresponding As(2) atom of Mo_2As_3. The smallness of this difference may be taken as an indication that indeed one 3*d* orbital participates in the bonding. In that case the (8-N) rule would not be applicable in the first place because the As atoms would exceed the electron octett, whereas the classical concept of the two-electron bond would not need to be given up for that reason.

The metal–metal bonding in the Mo_2As_3 structure and its distorted version Tc_2As_3 somewhat resembles the situation of the d^4 marcasite and the distorted d^5 arsenopyrite structure. Metal–metal bonding in these compounds has been discussed extensively in the literature (*25*, *26*). As is known for the arsenopyrite compounds $CoAs_2$ and $CoSb_2$ (*27*) we expect a displacive phase transition of Tc_2As_3 upon heating which should result in a high-temperature modification of Tc_2As_3 with Mo_2As_3-type structure.

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References

1. R. Rühl, W. Jeitschko, and K. Schwochau, *J. Solid State Chem.* **44**, 134 (1982).
2. R. Rühl and W. Jeitschko, *Acta Crystallogr. Sect. B* **38**, 2784 (1982).
3. R. Rühl, dissertation, Univ. Giessen (1982).
4. F. Hulliger, *Nature* (*London*) **209**, 500 (1966).
5. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
6. J. B. Taylor, L. D. Calvert, and M. R. Hunt, *Canad. J. Chem.* **43**, 3045 (1965).
7. P. Jensen, A. Kjekshus, and T. Skansen, *Acta Chem. Scand.* **20**, 1003 (1966).
8. A. D. Mighell and H. M. Ondik, *J. Phys. Chem. Ref. Data* **6**, 675 (1977).
9. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
10. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
11. W. Jeitschko, U. Flörke, M. H. Möller, and R. Rühl, *Ann. Chim.* (*Paris*) **7**, 525 (1982).

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[4] This remark is not intended to downgrade the great progress which was made in the understanding of electrical and magnetic properties by using this rule to predict such properties from structural data (*23*, *24*).

12. R. Rühl and W. Jeitschko, *Monatsh. Chem.* **114,** 817 (1983).

13. W. Jeitschko and P. C. Donohue, *Acta Crystallogr. Sect. B* **29,** 783 (1973).

14. S. Rundqvist, *Acta Chem. Scand.* **20,** 2075 (1966).

15. R. Rühl, U. Flörke, and W. Jeitschko, *J. Solid State Chem.* **53,** 55 (1983).

16. R. Guérin, M. Potel, and M. Sergent, *Mater. Res. Bull.* **14,** 1335 (1979).

17. R. Rühl and W. Jeitschko, *Z. Anorg. Allg. Chem.* **466,** 171 (1980).

18. R. Rühl and W. Jeitschko, *Inorg. Chem.* **21,** 1886 (1982).

19. S. Weglowski, *Rocz. Chem.* **39,** 779 (1965).

20. M. Klein and H. G. v. Schnering, *J. Less-Common Met.* **11,** 298 (1966).

21. P. Jensen, A. Kjekshus, and T. Skansen, *J. Less-Common Met.* **17,** 455 (1969).

22. S. Furuseth and A. Kjekshus, *Acta Chem. Scand.* **20,** 245 (1966).

23. E. Mooser and W. B. Pearson, *Prog. Semicond.* **5,** 103 (1960).

24. F. Hulliger, *Struct. Bonding* **4,** 83 (1968).

25. S. D. Wijeyesekera and R. Hoffmann, *Inorg. Chem.* **22,** 3287 (1983).

26. W. Jeitschko, U. Flörke, and U. D. Scholz, *J. Solid State Chem.* **52,** 320 (1984).

27. A. Kjekshus and T. Rakke, *Acta Chem. Scand. A* **31,** 517 (1977).