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The Ternary Titanium Transition Metal Bismuthides Ti_4TBi_2 with T = Cr, Mn, Fe, Co, and Ni

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The title compounds were prepared by reaction of the elemental components and with the exception of the isotypic chromium compound their tetragonal V_4SiSb_2-type crystal structures ($I4/mcm$, $Z = 4$) were determined and refined from single-crystal X-ray data. Ti_4CrBi_2: $a = 1051.6(1)$, $c = 506.7(1)$ pm; Ti_4MnBi_2: $a = 1049.1(1)$, $c = 497.8(1)$ pm, $R = 0.031$ for 176 structure factors; Ti_4FeBi_2: $a = 1048.6(1)$, $c = 493.3(1)$ pm, $R = 0.013$ (274 F values); Ti_4CoBi_2: $a = 1050.6(2)$, $c = 488.2(1)$ pm, $R = 0.038$ (472 F values); Ti_4NiBi_2: $a = 1055.4(1)$, $c = 481.4(1)$ pm, $R = 0.020$ (373 F values), and 14 variable parameters each. The compounds are isotypic with V_4SiSb_2, a structure which is isopointal with U_6Mn and closely related to the structures of W_5Si_3 and TlTe. All atoms have high coordination numbers. Unusual features of the structure are channels formed solely by the bismuth atoms and linear chains of the heavier transition metal ions with bond distances varying between 253.3 (Cr–Cr) and 240.7 pm (Ni–Ni). The electrical conductivities of Ti_4TBi_2 (T = Fe, Co, Ni)—determined with a four-probe technique for sintered polycrystalline samples between 4 K and room temperature—indicate metallic behavior. The magnetic susceptibilities of the five compounds were determined with a SQUID magnetometer. Ti_4CrBi_2, Ti_4FeBi_2, and Ti_4NiBi_2 are Pauli paramagnetic. The magnetic susceptibilities of Ti_4MnBi_2 and Ti_4CoBi_2 are strongly temperature dependent. The evaluation of these data according to a modified Curie–Weiss law suggests that both compounds contain one unpaired electron per formula unit. A brief discussion of chemical bonding in these compounds leads to the conclusion that considerable Ti–Ti bonding must be present in these bismuthides, in spite of the fact that the shortest Ti–Ti bonds are as long as 299 pm.

INTRODUCTION

Apparently the ternary systems of titanium, zirconium, and hafnium with the late transition metals and bismuth have not been investigated. In contrast, at least a few ternary bismuthides are known with the lanthanoids (Ln) and the late transition metals. The compounds Ln_5CuBi_3 crystallize with the Hf_5CuSn_3 structure (1), sometimes also designated as Ti_5Ga_4-type or "filled" Mn_5Si_3-type structure; the bismuthides of the series LnTBi (T = Ni, Pd, Pt) are isotypic with MgAgAs (ordered fluorite structure) (2, 3); EuCuBi has a structure derived from the hexagonal Ni_2In type (4); YPd_2Bi has a filled MgAgAs (ordered BiF_3, $MnCu_2Al$, Heusler) type structure (5); and finally the compounds of the series $LnNi_{2-x}Bi_2$ have a defect $CaBe_2Ge_2$-type structure (6). In searching for similar or isotypic compounds, where the rare earth metal components are substituted by titanium, we encountered the compounds reported here, which surprisingly were found to be isotypic with a new structure only recently established for the antimonide V_4SiSb_2 (7). The late transition metal atoms of the presently reported compounds occupy the positions of the main group element silicon in V_4SiSb_2, and they form similar short T–T bonds as the silicon atoms in the antimonide.

SAMPLE PREPARATION

Starting materials were small pieces of titanium and bismuth (both from Ventron, 99.9%), and powders of chromium (Riedel-de-Haën, > 99%), manganese (Heraeus, 99.95%), iron and cobalt (both Merck, > 99.9%), and nickel (Merck, "reinst"). The compounds were obtained by arc melting of cold-pressed pellets (~ 0.4 g) prepared from the elemental components with an excess of 10 wt% bismuth to compensate for its evaporation during the arc melting under argon. The ternary compounds were already present in the quenched ingots, however, we usually annealed the samples for 1 week at 800 °C in evacuated, sealed silica tubes. Nearly homogeneous samples were also obtained by sintering the cold-pressed pellets for 1 week at 800°C.

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PROPERTIES AND LATTICE CONSTANTS

The compact samples of the ternary bismuthides were shiny with a light-gray color. They are easily crushed and ground to dark-gray powders, which are stable in air for long periods of time, in contrast to binary titanium bismuthides, which are pyrophoric (8). Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope were in good agreement with the ideal composition and did not reveal any impurity elements heavier than sodium.

The compounds were identified by their Guinier powder patterns, recorded with Cu$K\alpha_1$ radiation. The lattice constants (Table 1) were obtained by least-squares fits of these data using α quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard.

ELECTRICAL CONDUCTIVITY

The electrical conductivites of polycrystalline samples of the three compounds Ti_4FeBi_2, Ti_4CoBi_2, and Ti_4NiBi_2, prepared by sintering cold-pressed pellets of the ideal composition, were determined by a four-probe technique (9). Porous polycrystalline samples of irregular shape with about 0.3 mm as the largest dimension were contacted with four copper filaments using a silver epoxy cement. This set-up was sealed in beeswax and slowly cooled to liquid helium temperature together with a contacting thermocouple. For all three compounds several samples were contacted and measured this way. They were essentially all in agreement with each other. Typical conductivity plots are shown in Fig. 1. It can be seen that the electrical resistivities of the three bismuthides increase with increasing temperature, as is typical for metallic conductors. Due to the difficulty in estimating the size of the contacting areas the absolute values measured for these samples are accurate only by a factor of two. Furthermore, the porosity of these samples was not taken into account. Therefore, the specific resistivities as plotted in Fig. 1 are almost certainly too high. The relative values, however, are much more reliable. The decreases of the electrical resistivities between room temperature and 4 K varied between a factor of 1.5 for Ti_4FeBi_2

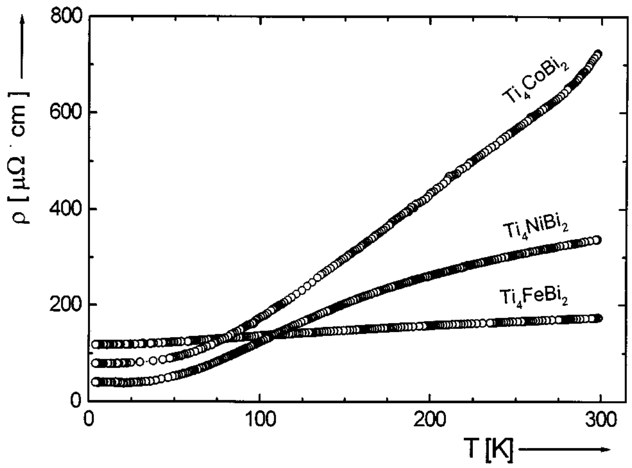

FIG. 1. Electrical resistivities of sintered, porous samples of Ti_4FeBi_2, Ti_4CoBi_2, and Ti_4NiBi_2 as a function of temperature.

TABLE 1
Crystal Data for the Compounds Ti_4TBi_2 (T = Cr–Ni)[a]

Compound	Ti_4CrBi_2	Ti_4MnBi_2	Ti_4FeBi_2	Ti_4CoBi_2	Ti_4NiBi_2
Structure type	V_4SiSb_2	V_4SiSb_2	V_4SiSb_2	V_4SiSb_2	V_4SiSb_2
Space group	$I4/mcm$	$I4/mcm$	$I4/mcm$	$I4/mcm$	$I4/mcm$
Lattice constants from Guinier powder data					
a (pm)	1051.6(1)	1049.1(1)	1048.6(1)	1050.6(2)	1055.4(1)
c (pm)	506.7(1)	497.8(1)	493.3(1)	488.2(1)	481.4(1)
V (nm^3)	0.5603	0.5479	0.5424	0.5389	0.5362
Formula units/cell	$Z = 4$	$Z = 4$	$Z = 4$	$Z = 4$	$Z = 4$
Formula mass	661.6	664.5	665.4	668.5	668.3
Calculated density (g/cm^3)[b]	7.84	8.05	8.15	8.24	8.28
Crystal dimensions (μm^3)		$50 \times 20 \times 15$	$22 \times 28 \times 33$	$60 \times 40 \times 10$	$60 \times 20 \times 10$
$\theta/2\theta$ Scans up to		$2\theta = 70°$	$2\theta = 95°$	$2\theta = 95°$	$2\theta = 70°$
Range in h, k, l		$\pm16, \pm16, 0 \leq l \leq 8$	$\pm17, \pm17, -8 \leq l \leq 4$	$\pm20, \pm20, \leqslant 0 \leqslant l \leqslant 9$	$\pm19, \pm19 \leqslant 0 \leq l \leq 8$
Total number of reflections		2668	5480	4788	3793
Highest/lowest transmission		1.83	1.28	3.28	1.19
Unique reflections		379	537	673	526
Inner residual		$R_i = 0.074$	$R_i = 0.030$	$R_i = 0.039$	$R_i = 0.023$
Reflections with $I > 3\sigma(I)$		176	274	471	373
Number of variables		14	14	14	14
Highest residual electron density (e/Å^3)		2.22	0.65	1.49	0.74
Conventional residual		$R = 0.031$	$R = 0.013$	$R = 0.038$	$R = 0.020$
Weighted residual		$R_w = 0.030$	$R_w = 0.015$	$R_w = 0.046$	$R_w = 0.028$

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

[b] Assuming the ideal formula.

and 9.2 for Ti_4CoBi_2. The absolute values of the resistivities at room temperature for the porous samples are higher than those of elemental titanium or bismuth (10) by a factor of about 10 and 5, respectively.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The magnetic susceptibilities of polycrystalline samples (40 mg) of the five compounds were measured with a SQUID magnetometer in the temperature range between 2 and 300 K with magnetic flux densities up to 5.5 T. All samples contained minor amounts of ferromagnetic impurities (not visible on the Guinier powder diagrams) as revealed by the field dependence of the magnetic susceptibilities. Therefore, the magnetic susceptibilities as obtained by extrapolation to infinite magnetic flux densities were determined for Ti_4FeBi_2 and Ti_4CoBi_2. The magnetic susceptibilities of the other samples measured at 3 and 5 T were practically the same, and therefore the susceptibilities and the inverse susceptibilities, respectively, as obtained at 5 T (Figs. 2 and 3), were used for the evaluations.

The magnetic susceptibilities of the compounds Ti_4CrBi_2, Ti_4FeBi_2, and Ti_4NiBi_2 are nearly temperature independent above 50 K, as is typically observed for Pauli paramagnets. The real values of the susceptibilites may be somewhat lower because of the contamination of the samples, as already mentioned. This can especially be assumed for the sample of Ti_4FeBi_2. The upturns of the magnetic susceptibilities below 50 K can be ascribed to paramagnetic impurities or surface states.

In contrast, the magnetic susceptibilities of Ti_4MnBi_2 and Ti_4CoBi_2 are strongly temperature dependent. It can be seen (Fig. 3), that Ti_4MnBi_2 shows Curie–Weiss behavior. Ti_4CoBi_2 exhibits some deviation from the Curie–Weiss law, which we ascribe to impurities. Samples of Ti_4CoBi_2 with higher impurity contents (visible on Guinier diagrams) showed even larger deviations from the Curie–Weiss law. The magnetic susceptibilities of Ti_4MnBi_2 and Ti_4CoBi_2, measured above 50 K, were evaluated with the modified Curie–Weiss law $\chi = \chi_0 + C/(T - \Theta)$. The negative Weiss constants ($\Theta = -28 \pm 4$ K for Ti_4MnBi_2 and $\Theta = -120 \pm 40$ K for Ti_4CoBi_2) suggest antiferromagnetic order. No indications for such order were observed from the magnetic data recorded above 2 K for Ti_4MnBi_2. In contrast, the reciprocal susceptibility curve for Ti_4CoBi_2 shows a slight minimum (inset of Fig. 3) indicating antiferromagnetic order at the Néel temperature $T_N = 3.5 \pm 0.5$ K. As mentioned above, this sample contained some ferromagnetic impurity and the susceptibility values, obtained by extrapolation to infinite magnetic field strengths, should be considered with some caution. The magnetic moments were calculated from the relation $\mu_{exp} = (8 \times C)^{1/2}$ μ_B. They amount to $\mu_{exp} = 1.7 \pm 0.2$ μ_B for Ti_4MnBi_2 per formula unit and $\mu_{exp} = 1.6 \pm 0.3$ μ_B/fu for Ti_4CoBi_2. This suggests that these compounds have one unpaired electron per formula unit, since their magnetic moments are close to the theoretical moment of $\mu_{eff} = 1.73$ μ_B for the spin-only value.

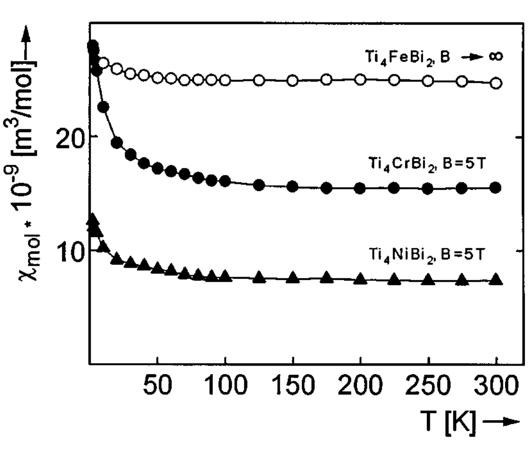

FIG. 2. Magnetic susceptibilities of the Pauli paramagnets Ti_4CrBi_2, Ti_4FeBi_2, and Ti_4NiBi_2 as measured with high magnetic flux densities.

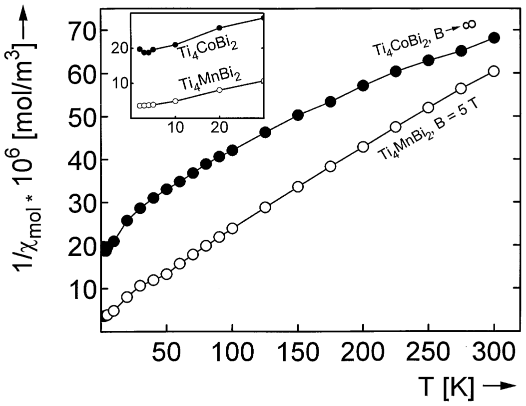

FIG. 3. Temperature dependence of the reciprocal magnetic susceptibilities of the compounds Ti_4MnBi_2 and Ti_4CoBi_2. The inset shows the reciprocal susceptibility behavior at low temperatures.

SINGLE-CRYSTAL DIFFRACTOMETRY

Single crystals for the structure determination were isolated from the crushed samples and examined by the Laue technique to establish their suitability for the data collection. For this purpose an Enraf–Nonius CAD4 diffractometer was used with graphite-monochromated Mo$K\alpha$ radiation, a scintillation counter, a pulse-height discriminator, and background counts on both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were applied from psi scans.

The structure of Ti_4FeBi_2 was determined first. The Laue symmetry $4/mmm$ and the systematic extinctions suggested the space groups *I*4*cm*, *I*$\bar{4}$*c*2, and *I*4/*mcm*. Of these the group with the highest symmetry, *I*4/*mcm* (No. 140) was found to be correct during the structure refinements. The positions of the iron and bismuth atoms were deduced from a Patterson synthesis, and the titanium atoms were located by a difference Fourier synthesis. The structure was refined by a full-matrix least-squares program (11) using atomic scattering factors (12) corrected for anomalous dispersion (13). The weighting scheme accounted for the counting statistics, and a factor correcting for secondary extinction was optimized as a least-squares parameter. All atoms were refined with ellipsoidal displacement parameters. To check for deviations from the ideal composition, the occupancy factors were allowed to vary together with the displacement parameters during one series of least-squares cycles, while the scale factor was held constant. No serious deviations from the ideal occupancies were observed and therefore in the final cycles the ideal occupancies were assumed.

The structures of Ti_4MnBi_2, Ti_4CoBi_2, and Ti_4NiBi_2 were also determined from single-crystal diffractometer data and refined entirely analogous to the structure of Ti_4FeBi_2. The positional parameters were standardized using the program STRUCTURE TIDY (14). The crystal data and the resulting atomic parameters as well as the interatomic distances are summarized in the Tables 1–3. The anisotropic displacement parameters and the structure factor tables are available from the authors (15).

TABLE 2
Atomic Parameters of Ti_4MnBi_2, Ti_4FeBi_2, Ti_4CoBi_2, and Ti_4NiBi_2[a]

Atom	*I*4/*mcm*	Occupancy	*x*	*y*	*z*	*B*
Ti_4MnBi_2						
Ti	16*k*	0.950(7)	0.0827(3)	0.1973(3)	0	0.50(5)
Mn	4*a*	1.01(1)	0	0	$\frac{1}{4}$	0.44(5)
Bi	8*h*	0.999(2)	0.1390(1)	$\frac{1}{2}+x$	0	0.471(1)
Ti_4FeBi_2						
Ti	16*k*	0.988(3)	0.0822(1)	0.19640(9)	0	0.56(1)
Fe	4*a*	0.993(5)	0	0	$\frac{1}{4}$	0.73(2)
Bi	8*h*	1.006(1)	0.13933(2)	$\frac{1}{2}+x$	0	0.565(2)
Ti_4CoBi_2						
Ti	16*k*	0.991(6)	0.0820(1)	0.1966(1)	0	0.46(2)
Co	4*a*	0.949(7)	0	0	$\frac{1}{4}$	0.42(2)
Bi	8*h*	1.010(2)	0.13955(3)	$\frac{1}{2}+x$	0	0.472(3)
Ti_4NiBi_2						
Ti	16*k*	1.007(4)	0.0828(1)	0.1992(1)	0	0.55(2)
Ni	4*a*	0.960(5)	0	0	$\frac{1}{4}$	0.48(2)
Bi	8*h*	1.008(1)	0.1400(1)	$\frac{1}{2}+x$	0	0.475(3)

[a] The occupancy parameters were obtained in separate refinement cycles. In the final cycles the ideal occupancy parameters were used. The last column contains the equivalent isotropic *B* values (in units of 10^4 pm^2).

TABLE 3
Interatomic Distances in the Structures of Ti_4TBi_2 (T = Mn, Fe, Co, Ni)[a]

		Ti_4MnBi_2	Ti_4FeBi_2	Ti_4CoBi_2	Ti_4NiBi_2
Ti:	1Bi	289.1(4)	289.2(1)	289.4(1)	290.0(1)
	1Bi	298.3(4)	298.1(1)	298.7(1)	299.2(1)
	2Bi	308.1(2)	306.8(1)	304.7(1)	300.6(1)
	2T	256.6(3)	255.0(1)	254.9(1)	257.5(1)
	2Ti	301.4(3)	299.2(1)	297.6(1)	296.8(1)
	2Ti	303.4(3)	300.9(1)	298.7(1)	297.4(1)
	2Ti	317.4(5)	315.7(1)	316.5(2)	321.9(2)
	1Ti	326.4(5)	328.4(1)	329.0(2)	325.5(2)
T:	2T	248.9(1)	246.7(1)	244.1(1)	240.7(1)
	8Ti	256.6(3)	255.1(1)	254.9(1)	257.5(1)
Bi:	2Ti	289.1(4)	289.2(1)	289.4(1)	290.0(1)
	2Ti	298.3(4)	298.1(1)	298.7(1)	299.2(1)
	4Ti	308.1(2)	306.8(1)	304.7(1)	300.6(1)
	4Bi	383.4(1)	382.4(1)	381.5(1)	381.1(1)

[a] All distances shorter than 400 pm are listed.

DISCUSSION

The five compounds Ti_4TBi_2 (T = Cr–Ni) are reported here for the first time. They crystallize with a structure type established only recently for V_4SiSb_2 (7). In the present work we have first determined the structure of the iron compound (Fig. 4), and for that reason we will mostly discuss the structure of these compounds by referring to Ti_4FeBi_2. This structure is related to several others. We compare them in Table 4 and in Fig. 5. The same atomic positions as those found for Ti_4FeBi_2 and V_4SiSb_2 are

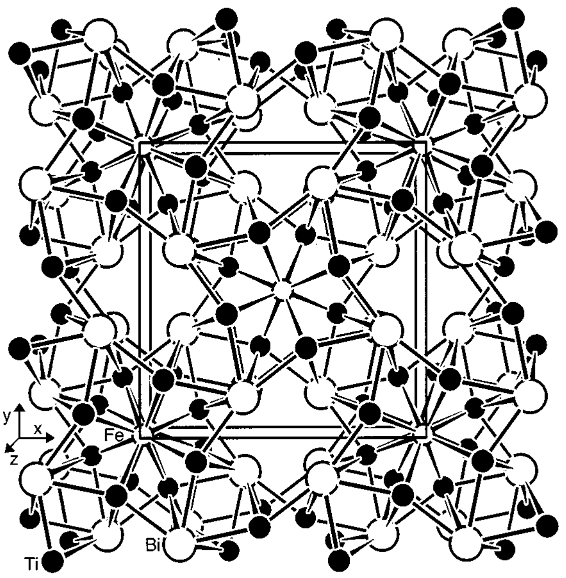

FIG. 4. The structure of the tetragonal compound Ti_4FeBi_2.

TABLE 4
Positional Parameters of Five Closely Related Structures Crystallizing in the Space Group *I*4/*mcm*[a]

Compound	16*k*	8*h*	4*a*	4*b*/4*d*	Ref.
Ti_4FeBi_2	Ti 08/20/00	Bi 14/64/00	Fe 00/00/25	—	This work
V_4SiSb_2	V 09/21/00	Sb 14/64/0	Si 00/00/25	—	7
U_6Mn	U1 10/21/00	U2 09/59/00	Mn 00/00/25	—	16
W_5Si_3	W2 07/22/00	Si2 17/67/00	Si1 00/00/25	W1 00/50/25	17
TlTe	Tl 08/23/00	Te3 16/66/00	Te1 00/00/25	Te2 00/50/25	18
T1Te	Tl 08/23/00	Te3 17/67/00	Te1 00/00/25	Te2 00/50/00	19

[a] All structures were normalized by the program STRUCTURE TIDY (14). The positions *x*/*y*/*z* of corresponding atoms are listed in hundredths. The Te2 atoms of TlTe were originally assumed (18) to occupy the position 4*b*; they were subsequently located at the position 4*d* (19).

occupied in the binary intermetallic compound U_6Mn (16). The structure of the latter compound, however, has somewhat different atomic parameters and this results in a different coordination for the U2 atoms in the position 8*h*. The U2 atoms have the coordination number 13 and 8 U1 and 5 U2 neighbors at distances covering the range between 273 and 339 ppm. The U2 atoms of U_6Mn correspond to the Bi atoms of Ti_4FeBi_2. In contrast to the U2 atoms of U_6Mn, the Bi atoms of Ti_4FeBi_2 have the coordination numbers 8 and 12: they are surrounded by 8 Ti atoms and in addition by 4 Bi atoms with the rather long Ti–Bi distances of 382 pm. For compounds with structures having nearly the same atomic positions, but different coordination polyhedra, Parthé and Gelato have proposed the term *isopointal* (14), while the term *isotypic* should be reversed for compounds with corresponding coordinations. Thus, Ti_4FeBi_2 and V_4SiSb_2 are isotypic, whereas Ti_4FeBi_2 and U_6Mn may be called isopointal.

It can be seen from Fig. 4, that the structure of Ti_4FeBi_2 contains channels formed by the bismuth atoms. These channels are filled by the W1 atoms in the structure of W_5Si_3 (17). However, the atomic environment of these W1 atoms is somewhat different from the environment formed by the channels in Ti_4FeBi_2, because of slightly different positional parameters, as can be seen from Fig. 5. A closely related structure was reported for TlTe by Bukhardt and Schubert (18), who described this structure as a substitution variant of the W_5Si_3 type. Later it was shown (19) that the tungsten atoms in the "channels" (formed by the bismuth atoms in Ti_4FeBi_2) are located in the position 4*d* and not in 4*b*, as previously assumed.

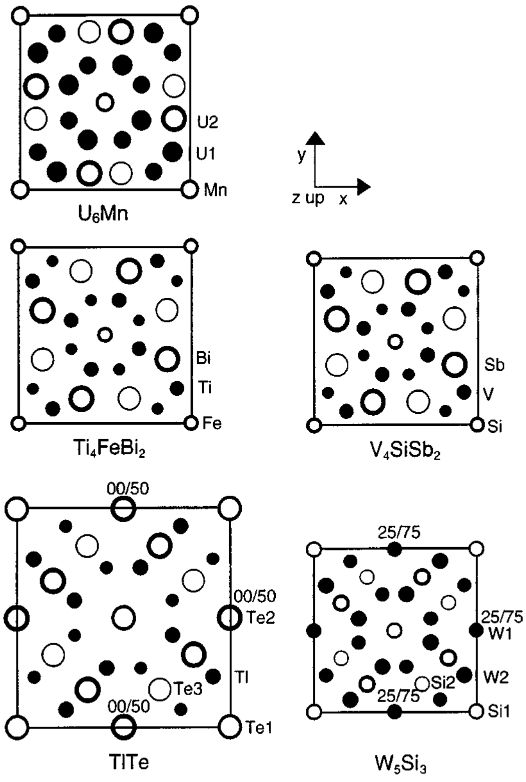

FIG. 5. Atomic positions in five closely related structures with the space group *I*4/*mcm*.

The structure of Ti_4FeBi_2 is relatively simple with only one atomic site for each atomic species. All atoms have somewhat unusual coordinations. The titanium atoms have four bismuth neighbors, all of them located at one side of the coordination shell (Fig. 6) at distances varying between 289.2 and 306.8 pm. At the other side of their coordination shell the titanium atoms have two iron neighbors at the rather short distance of 255.1 pm. Considering the sum of the metallic radii (20) for the coordination number 12 for titanium ($r = 146.2$ pm) and iron ($r = 127.4$ pm) of 273.6 pm, the Ti–Fe interactions are certainly strongly bonding. We will see later that the iron atoms have an anionic character in this compound. The coordination shell of the titanium atom is completed by seven titanium atoms at distances ranging from 299.2 to 328.4 pm, all greater than the average Ti–Ti distance of 292 pm in the hexagonal modification of the element (21). Therefore, at first sight, the titanium atoms do not seem to be strongly bonded to each other. However, because of the high titanium content of the compound, considerable titanium–titanium bonding will need to be assumed, as is discussed further below.

The iron atoms are situated in a square-antiprism of titanium atoms. In addition, they have two iron neighbors, which are capping the square faces formed by titanium atoms. The Fe–Fe distances of 246.6 pm are rather short

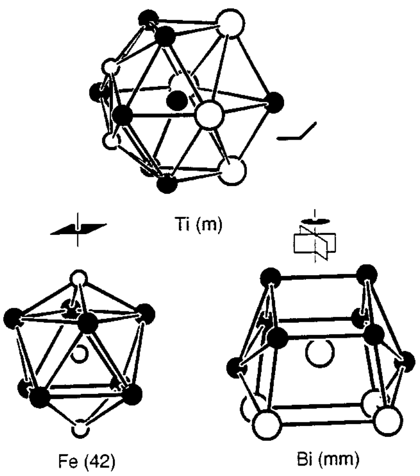

FIG. 6. Coordination polyhedra in the structure of Ti_4FeBi_2. The polyhedra contain all neighbors as listed in Table 3. Thus, not all of the atoms shown in the polyhedra are bonded to the central atoms. The site symmetries of the central atoms are indicated.

and these interactions are certainly strongly bonding. In the compound V_4SiSb_2 (7) the corresponding Si–Si distances have a length of 235.4 pm, which is practically the same as the two-electron bond distance of 235.2 pm in the diamond modification of elemental silicon (21).

The bismuth atoms have eight titanium neighbors, all on one side of their coordination shell. At the other side they are surrounded by four bismuth atoms at a distance of 382.4 pm. This distance is surprisingly large, considering the fact that the three short Bi–Bi distances in the α-modification of elemental bismuth are 307.2 pm, and the shortest interlayer distance of α-bismuth—in simplistic descriptions of this structure sometimes referred to as the van der Waals distance—amounts to only 352.9 pm (21). We therefore cannot ascribe much bonding character to the Bi–Bi interactions in Ti_4FeBi_2, and we assume that the channels formed by the bismuth atoms in this structure (Fig. 4) are filled with nonbonding electrons of the bismuth atoms. In view of the following discussion we emphasize that these channels are not filled by light atoms like oxygen or nitrogen. The highest residual electron densities shown in the difference Fourier analyses of the four structure refinements are all less than 2.5 electrons per Å^3 (Table 1), much less than the densities of 15–20 e/Å^3, expected for such impurity atoms. The much lighter hydrogen atoms can also be ruled out, since these compounds are readily prepared by arc melting. Any hydrogen atoms would evaporate at these high temperatures.

At first sight chemical bonding in Ti_4FeBi_2 is difficult to rationalize. The titanium atoms as the most electropositive components of the compound could be expected to have their valence electrons involved in bonding toward the iron and bismuth atoms. On the other hand, since the bismuth atoms are the most electronegative components, and since they do not form any Bi–Bi bonds, these atoms can be assigned the oxidation number −3, assuming the octet rule to be valid. These assignments would result in the formula $(Ti^{4+})_4Fe^{10-}(Bi^{3-})_2$, where the superscripts represent oxidation numbers (formal charges). The formula is in agreement with the absence of any iron–bismuth interactions, and at first sight it might suggest that the iron atoms attain 18 electrons, the inert gas configuration. However, this formula does not at all allow to rationalize the strong iron–iron bonds. Thus, we must assume that the titanium atoms retain some of their valence electrons. They may lower their energy by forming Ti–Ti bonds, in spite of the rather long Ti–Ti distances of between 299.2 and 328.4 pm, as discussed above.

A realistic description of chemical bonding in the five compounds must account for the fact that the interatomic distances change only little in going from Ti_4MnBi_2 to Ti_4NiBi_2. There are strong T–T bonds with the bond distances decreasing from 253.3 pm for the Cr–Cr distance in Ti_4CrBi_2 (as calculated from the lattice constant c) to 240.7 pm for the Ni–Ni distance in Ti_4NiBi_2. This decrease is not much greater than the decrease of the metallic radii for the coordination number 12 from $2r(Cr) = 256.4$ pm to $2r(Ni) = 249.2$ pm (20) or the decrease of the two-electron bond distance of 235.2 to 230.8 pm calculated from the single-bond metallic radii for chromium and nickel given by Pauling (22). If we assume a "rigid band" model and if we do not want to exceed an electron count of 18 for the T atoms, we can write the formula of these compounds with oxidation numbers as $(Ti^{3+})_4T^{6-}(Bi^{3-})_2$. This leaves one electron for each titanium atom to be engaged in Ti–Ti bonding, and the nickel atoms obtain the inert gas shell of 18 electrons: 10 from their position in the P.S., 6 from the (formal) charge, and 2 from the neighboring nickel atoms (for simplicity assuming two-electron Ni–Ni bonds). With a rigid band model the cobalt, iron, manganese, and chromium atoms then obtain 17, 16, 15, and 14 electrons, respectively. This allows to rationalize the magnetism of the cobalt and the manganese compounds with the uneven numbers of 17 and 15 electrons, respectively.

In concluding, we emphasize that this account of chemical bonding is certainly quite coarse. We have aimed at integer numbers of electrons for each atom, which is not a requirement for the band structure of an extended solid. We also note that the occupancy parameters of the cobalt and nickel atoms with 0.949(7) and 0.960(5) deviate from the full occupancy. These deviations amount to about 8 standard deviations. Assuming that these deviations are real, this indicates that the highest occupied states involving atomic orbitals of the cobalt and nickel atoms are antibonding, as was discussed in more detail for the $ThCr_2Si_2$ type structure of $CaCu_{1.75}P_2$(23).

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