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The Metallic Polyphosphide Ti_2NiP_5

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The new phosphide Ti_2NiP_5 was prepared by reaction of a titanium–nickel alloy with red phosphorus in a tin flux. It has orthorhombic symmetry, space group *Pnma*, and the lattice constants a = 1111.0 (6) pm, b = 333.4 (2) pm, c = 1242.4 (6) pm; Z = 4. The structure was determined from single-crystal X-ray data and refined to a residual of R = 0.033 for 795 structure factors and 50 variable parameters. The two different kinds of Ti atoms have seven and eight P neighbors, respectively. The Ni atoms have square-pyramidal phosphorus coordination. The five different P atoms have greatly varying coordinations. One extreme case is a P atom that has only metal neighbors (4Ti + 2Ni). The other extreme is a P atom with three close P neighbors at the typical two-electron-bond distances of about 220 ppm and one additional Ni neighbor, thus forming a (distorted) tetrahedron. In aiming for integer oxidation numbers and in counting intermediate P–P interactions (of between 240 and 256 pm) as one-electron bonds one arrives at the formula $(Ti^{4+})_2Ni^0P^0P^-(P^{2-})_2P^{3-}$. The compound may be considered as intermediate between the high-coordination phosphides with high metal content and the low-coordination polyphosphides. Accordingly Ti_2NiP_5 is a metallic conductor and Pauli paramagnetic.

Introduction

The crystal structures of the transition-metal phosphides can be divided into two groups depending on coordination numbers.[1,2] The phosphides with high metal content, especially those of the early transition metals, have high coordination numbers. They are metallic conductors. The phosphides with high phosphorus content have low coordination numbers, e.g., octahedral for Ti, a square for Ni, and tetrahedral coordination for the phosphorus atoms. Their electrical conductivity and magnetic behavior can be rationalized on the basis of classical two-electron bonds. The compound reported here has a structure intermediate between the two extremes with high and low coordination.

Sample Preparation

The preparation of polyphosphides by direct reaction of the elemental components is difficult. At high temperatures (e.g., 800 °C) the polyphosphides are not stable due to their high phosphorus vapor pressure. At lower temperatures the reaction rates are too slow. Frequently good results are obtained by using the tin flux technique.[3] By starting with powders of the elements, even this technique was not suited to prepare Ti_2NiP_5. We have obtained this new polyphosphide with good yield only by starting with powders of a titanium–nickel alloy.

Starting materials were powders of titanium and nickel (both 99.9%), red phosphorus (Hoechst, "ultrapure"), and tin (Merck, "rein"). The titanium–nickel alloy was prepared by arc-melting of cold-pressed pellets with the atomic ratio Ti:Ni = 1:1. The alloy was then ground to a fine powder and reacted with red phosphorus and tin in the ratio Ti:Ni:P:Sn = 1:1:20:25 in evacuated sealed silica tubes (tube volume 5 cm^3, P content 0.5 g). The tubes were annealed at 450 °C for 1 day to react the phosphorus with the tin and then for 1 month at 650 °C. After quenching in air, the sample was placed in 3 N hydrochloric acid, which dissolved the matrix of tin phosphides. The resulting product consisted of needle-shaped Ti_2NiP_5 crystals forming polycrystalline aggregates and small equidimensional single crystals of NiP_3 that could be separated from the Ti_2NiP_5 aggregates mechanically under a microscope. An energy-dispersive X-ray analysis of the Ti_2NiP_5 crystals did not reveal any impurities such as silicon or tin.

Properties

The crystals of Ti_2NiP_5 are black with metallic luster. They are stable in air and not visibly attacked by nonoxidizing acids.

Electrical conductivity measurements of a needle-shaped single-crystal of Ti_2NiP_5 (dimensions 25 × 25 × 2000 μm^3) were made with a four-probe setup. A constant alternating current was maintained through the whole length of the needle, and the voltage difference was measured at two additional contacts within the needle. The copper filaments of the probe were glued to the crystal by a well-conducting silver epoxy cement. The electrical resistance of Ti_2NiP_5 decreases with temperature (Figure 1) as is typical for a metallic conductor. A specific resistivity of $\rho = 280 \pm 100$ $\mu\Omega\cdot cm$ was obtained at room temperature. When compared to the specific resistivities of silver (ρ = 1.5 $\mu\Omega\cdot cm$) or iron (ρ = 8.6 $\mu\Omega\cdot cm$), Ti_2NiP_5 is a rather poor metallic conductor. The structure determination of Ti_2NiP_5 showed no great anisotropies in the near-neighbor coordinations. Thus we do not expect a strong directionality of the electrical conductivity.

Magnetic susceptibility measurements of selected, crushed Ti_2NiP_5 crystals with a SQUID magnetometer between 5 and 300 K indicate Pauli paramagnetism. The magnetic susceptibility is approximately constant between 100 and 300 K (Figure 2). The susceptibility increase below 80 K is probably due to an unknown paramagnetic impurity. This paramagnetic upturn was even more pronounced in the susceptibility curve of another sample. The average of the measured susceptibility between 200 and 300 K is $\chi_{mol} = 3.4 \times 10^{-9}$ m^3/mol. For an approximate diamagnetic correction we assumed the atomic susceptibilities (in units of 10^{-12} m^3/mol) of −60 for Ti^{4+} and −200 for Ni^0 extrapolated from values given by Klemm[4] and the value of −200 for phosphorus in polyphosphides obtained by Haraldsen.[5] With the thus calculated diamagnetic correction of $\chi = -1.3 \times 10^{-9}$ m^3/mol a value of $\chi = 4.7 \times 10^{-9}$ m^3/mol is obtained for the Pauli paramagnetism of the conduction electrons. This value is probably somewhat too high because of the paramagnetic impurity mentioned above.

Crystal Structure

Single crystals of Ti_2NiP_5 were investigated with a Weissenberg camera. They showed orthorhombic symmetry. The lattice constants of a = 1111.0 (6) pm, b = 333.4 (2) pm, c = 1242.4 (6) pm, and V = 0.4602 nm^3 were obtained by least-squares refinement of the Guinier pow-

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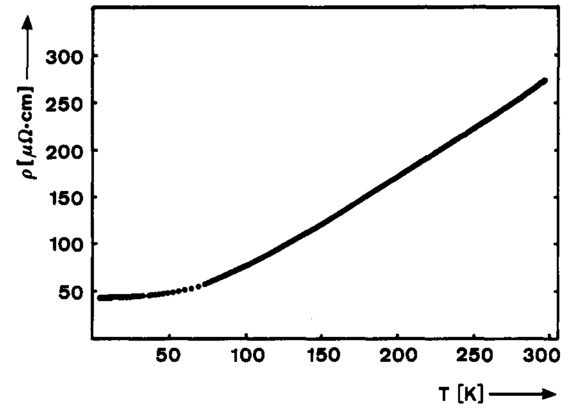

Figure 1. Specific resistivity of Ti_2NiP_5 as a function of temperature.

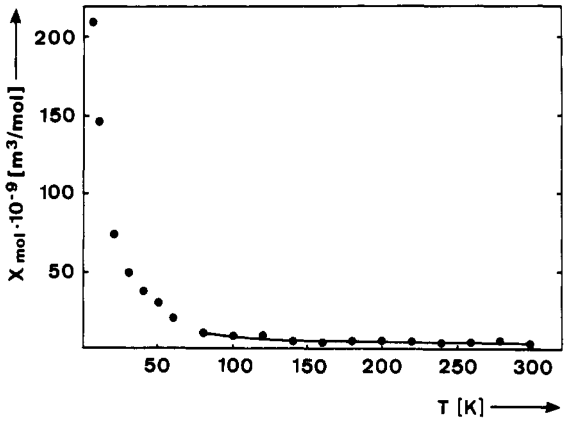

Figure 2. Molar susceptibility of Ti_2NiP_5. The upturn at low temperature is probably caused by a small amount of a paramagnetic impurity.

der data (Table I) using α-quartz (a = 491.30 pm, c = 540.46 pm) as the standard. The systematic extinctions ($hk0$ observed only with $h = 2n$, and $0kl$ only with $k + l = 2n$) led to the space groups $Pc2_1n$ and $Pnma$, of which the centrosymmetric group $Pnma$ (No. 62) was found to be correct during the structure refinements.

Intensity data for the structure determination were recorded from a crystal of dimensions 20 × 20 × 150 μm³ on a four-circle diffractometer with graphite-monochromated Mo Kα radiation, a scintillation counter, and a pulse-height discriminator. All reflections within one-half of the reciprocal sphere were collected with $\theta/2\theta$ scans up to 2θ = 70°. The background was determined at both ends of each scan. An absorption correction was made on the basis of ψ scan data. The ratio of the highest to the lowest transmission was 1.12. In addition an absorption correction was made assuming spherical crystal shape. A total of 4597 reflections was measured. After data averaging (R_i = 0.037) 1239 reflections remained, of which 795 had structure factors greater than 3 times their standard deviations.

The structure was solved by direct methods,[6] which resulted in the positions of the metal atoms. The phosphorus atoms were located on difference Fourier syntheses. A full-matrix least-squares program supplied by the Enraf-Nonius company was used to refine the structure. The atomic scattering factors[7] were corrected for anomalous dispersion.[8] A parameter accounting for secondary extinction was refined and applied to the calculated structure factors. Weights were assigned according to the counting statistics. A refinement of the occupancy parameters together with the thermal parameters gave no indication for partial occupancy (The largest deviations from the ideal occupancies were found for the P(1) and P(5) atoms with occupancies of 99.2% and 101.9%, both with standard deviations of 0.6%). In the final least-squares cycles the ideal occupancies were assumed. The conventional residuals are R = 0.033 and R_w = 0.034. The atomic parameters and interatomic distances are given in Tables II and III. Listings of the anisotropic thermal parameters and the structure factors are available as supplementary material (see the paragraph at the end of the paper).

Table I. Guinier Powder Pattern of Ti_2NiP_5[a]

$h\ k\ l$	Q_c	Q_o	I_c	I_o
1 0 1	146		6	
0 0 2	259	260	16	w
1 0 2	340		5	
2 0 1	389	392	13	w
2 0 3	907		4	
0 1 1	964	965	29	s
1 1 1	1045		3	
1 0 4	1118	1117	14	w
2 1 0	1224	1222	22	s
4 0 0	1296	1307	31	C[b]
3 0 3	1312		16	
2 0 4	1361	1360	85	vs
2 1 2	1483	1480	26	m
4 0 2	1555	1564	13	w
1 1 3	1564		8	
3 1 1	1694	1690	46	s
2 1 3	1807	1809	12	w
2 0 5	1944		6	
1 1 4	2017	2020	15	w
4 1 0	2196	2192	82	vs
2 1 4	2260	2259	100	vs
4 1 1	2261		40	
5 0 2	2285		5	
3 0 5	2349	2350	10	vw
1 0 6	2413		7	
4 1 2	2455	2451	19	m
0 1 5	2519		6	
1 1 5	2600	2608	50	s
3 1 4	2665	2668	14	w
5 1 1	2990		5	
3 0 6	3061	3061	8	m
5 0 4	3062		24	
4 1 4	3232		6	
3 1 5	3248	3250	15	C[b]
1 0 7	3256		12	
2 0 7	3499		3	
6 0 3	3500	3501	9	s
5 1 3	3508		26	
2 1 6	3556		13	
0 2 0	3599	3600	54	vs
5 0 5	3645		3	

[a] The diagram was recorded with Cu Kα_1 radiation. The Q values are defined by $Q = 100/d^2$ [nm⁻²]. For the intensity calculations the positional parameters of the refined structure were used. Very weak reflections with $I_c < 3$ were omitted. Observed intensities I_o are abbreviated as follows: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] Coincidence NiP_3.

Discussion

Ti_2NiP_5 crystallizes with a new structure type. All atoms are situated on mirror planes at $y = {}^1/_4$ and $y = {}^3/_4$ (Figure 3). The coordination polyhedra of the metal atoms (Figure 4) show some similarities with the coordination polyhedra found in the corresponding binary phosphides. The

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Table II. Atomic Parameters of Ti_2NiP_5[a]

atom	*Pnma*	*x*	*y*	*z*	B^b
Ti(1)	4c	0.09713 (9)	0.25	0.23407 (8)	0.35 (1)
Ti(2)	4c	0.34343 (9)	0.25	0.40157 (8)	0.32 (1)
Ni	4c	0.34560 (8)	0.25	0.17256 (6)	0.41 (1)
P(1)	4c	0.0666 (1)	0.25	0.0355 (1)	0.43 (2)
P(2)	4c	0.0723 (1)	0.25	0.7708 (1)	0.40 (2)
P(3)	4c	0.2817 (1)	0.25	0.6125 (1)	0.46 (2)
P(4)	4c	0.3242 (1)	0.25	0.8741 (1)	0.41 (2)
P(5)	4c	0.4377 (1)	0.25	0.0178 (1)	0.43 (2)

[a] Standard deviations in the least significant digit are given in parentheses. The program STRUCTURE TIDY[9] was used to standardize the positional parameters. [b] The last column contains the equivalent isotropic *B* values (×100 in units of nm^2) of the anisotropic thermal parameters.

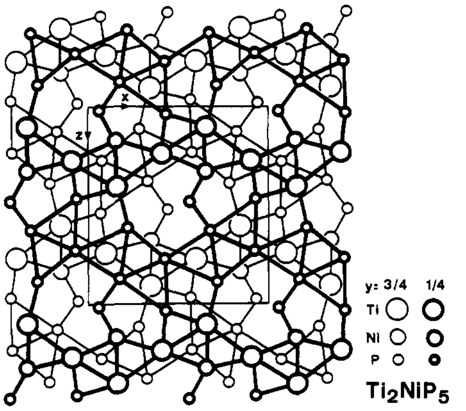

Figure 3. Projection of the Ti_2NiP_5 structure along the *b* axis. Atoms at $y = {}^3/_4$ and ${}^1/_4$ are connected by thin and thick lines, respectively. These lines do not necessarily imply chemical bonds.

greatest similarities for the coordination polyhedra of the metal atoms occur with the structures of TiP_2[10] and NiP.[11] In this respect the compound might be formulated as $2TiP_2 \cdot NiP$. In spite of some differences, this comparison is much better than the formulation $2TiP \cdot NiP_3$, where both metal atoms have octahedral phosphorus coordinations.[12,13]

In TiP_2 the titanium atoms have nine phosphorus neighbors: a trigonal prism with three additional phosphorus atoms outside the rectangular faces of the prism. In NiP the nickel atoms are coordinated to five phosphorus atoms forming a (distorted) square pyramid. The two kinds of titanium atoms in Ti_2NiP_5 also have trigonal prismatic phosphorus coordinations, however only with one (Ti(1)) and two (Ti(2)) additional phosphorus atoms outside the rectangular faces of the prisms. Thus, the coordination numbers of the titanium atoms vs phosphorus are 7 and 8, which are practically not reflected by the average Ti–P distances of 255.6 and 256.1 pm for the Ti(1) and Ti(2) atoms, respectively. This, however, should not be considered as an inconsistency, since the Ti–P bond lengths cover the range from 249 to 271 pm and thus should not be averaged with the same weight. Furthermore, in addition to these phosphorus neighbors the titanium atoms have metal neighbors at distances, which might still be considered as weakly bonding (Ti(1)–Ni: 286.4 and 302.6 pm; Ti(2)–Ni 284.5 pm). These metal neighbors are always positioned at the same mirror plane as the central metal atoms; they are thus outside the rectangular faces of the trigonal phosphorus prisms.

Table III. Interatomic Distances (pm) in Ti_2NiP_5[a]

atom	atom	dist	atom	atom	dist
Ti(1)	1P(1)	249.1 (3)	P(1)	2P(1)	239.7 (2)
	2P(2)	251.5 (2)		1Ti(1)	249.1 (3)
	2P(4)	256.3 (2)		2P(3)	255.7 (3)
	2P(3)	262.1 (2)		2Ti(2)	255.9 (2)
	1Ni	286.4 (2)		1Ti(2)	260.0 (3)
	1Ni	302.6 (2)			
	1Ti(2)	328.4 (2)	P(2)	2Ni	225.8 (2)
				2Ti(2)	250.9 (2)
Ti(2)	2P(2)	250.9 (2)		2Ti(1)	251.5 (2)
	2P(4)	252.2 (2)			
	2P(1)	255.9 (2)	P(3)	2Ni	231.0 (2)
	1P(1)	260.0 (3)		2P(1)	255.7 (3)
	1P(3)	270.9 (3)		2Ti(1)	262.1 (2)
	1Ni	284.5 (2)		1Ti(2)	270.9 (3)
	1Ti(1)	328.4 (2)			
			P(4)	1P(5)	218.6 (3)
Ni	1P(5)	217.8 (3)		2Ti(2)	252.2 (2)
	2P(2)	225.8 (2)		2Ti(1)	256.3 (2)
	2P(3)	231.0 (2)			
	Ti(2)	284.5 (2)	P(5)	1Ni	217.8 (3)
	Ti(1)	286.4 (2)		1P(4)	218.6 (3)
	Ti(1)	302.6 (2)		2P(5)	221.1 (2)

[a] Each atom has two identical neighbors at a distance of 333.4 pm, the length of the *b* axis. All distances shorter than 333.4 pm (Ti–Ti, Ti–Ni, Ti–P, Ni–Ni, Ni–P) and 300 pm (P–P) are listed. Standard deviations, computed from those of the lattice constants and the positional parameters, are given in the position of the least significant digit.

The nickel atoms have five phosphorus neighbors in (distorted) square-pyramidal coordination. The average Ni–P distance is 226.3 pm. This compares to the average distance of 228.9 pm in NiP. Again, this should not be considered an inconsistency, since the Ni atoms in Ti_2NiP_5 have three additional Ti atoms as neighbors at the rather long distances of 284.5, 286.4, and 302.6 pm, while the two additional Ni neighbors of the Ni atoms in NiP are at the much shorter (even when we account for the smaller atomic radius of nickel) distances of 253 pm. Nevertheless, even the Ti–Ni distances of about 285 and 303 pm might be considered as bonding. An indication for this is the fact that the central Ni atoms are rather close (34 pm) to the square face of the phosphorus pyramid, and the two Ti atoms at about 285 pm occupy the space on the other side of the square.

The phosphorus atoms in Ti_2NiP_5 occupy five different sites and show great differences in their coordination. One extreme is the coordination of the P(2) atoms, which consists of four Ti and two Ni atoms in trigonal prismatic arrangement, as is frequently observed in phosphides with high metal content, e.g., in $ScFe_4P_2$[14] and $HoCo_3P_2$.[15] The other extreme is the P(5) atom, which has three P neighbors, one at 218.6 and two at 221.1 pm. These are close to the typical two-electron-bond distance of about 222 ± 3 pm found in many polyphosphides.[16,17] The fourth neighbor of the P(5) atom is a Ni atom, which together with the three P neighbors forms a distorted tetrahedron. The P(5) atom may therefore be considered as forming four two-electron bonds ("sp^3 hybrid"). The coordination shells of the remaining three phosphorus sites are between these two extremes. The P(4) atoms have one close P(5) neighbor and four Ti neighbors (Figure 4). Together the P(4) and P(5) atoms form a one-dimensionally infinite polyanion consisting of a zigzag chain of P(5) atoms with

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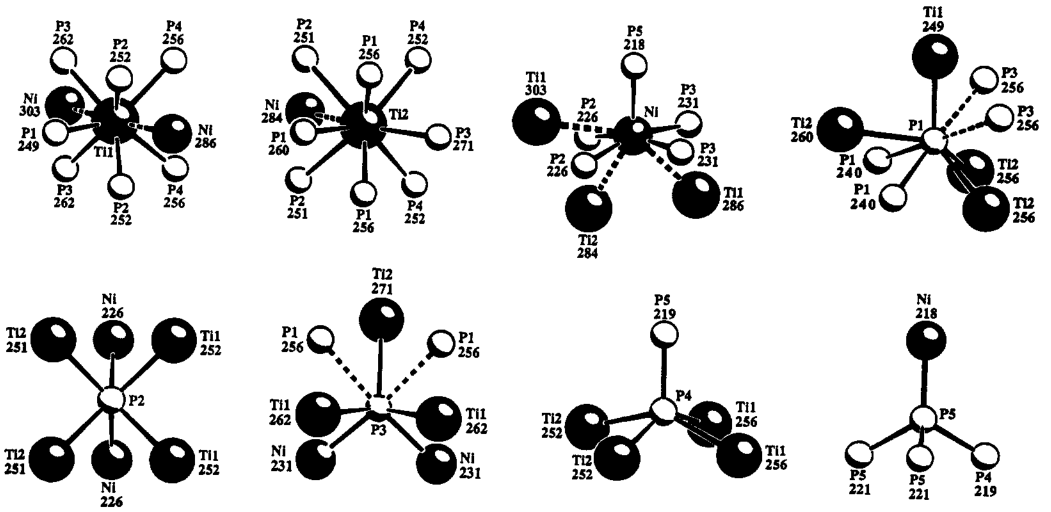

Figure 4. Atom coordination in Ti_2NiP_5. Interatomic distances are indicated in picometers.

one P(4) atom branching off from each P(5) atom. The P(1)–P(1) and P(1)–P(3) bonds of 239.7 and 255.7 pm are longer than two-electron bonds, but certainly still bonding. The total coordination shells of the P(1) and P(3) atoms are actually very close to the near-neighbor coordinations of the two phosphorus sites in TiP_2.[10] The great variety of near-neighbor coordinations of the phosphorus atoms is at variance with Pauling's fifth rule.[18] It is an indication of the covalent character of the metal–phosphorus bonds. In an oxide or fluoride such a variety has never been observed.

In aiming for integer oxidation numbers and in counting the intermediate P–P interactions of between 240 to 256 pm as one-electron bonds, we arrive at a formula $(Ti^{4+})_2Ni^0P(1)^-P(2)^{3-}P(3)^{2-}P(5)^0$, which is consistent with the fact that the compound is essentially nonmagnetic. We remind the reader how we count electrons to arrive at such a formula. One assumes that the octet rule is valid for all phosphorus atoms. The P–P bonds are then broken homolytically. In this way the P(5) atom, which forms three two-electron P–P bonds, obtains the oxidation number 0, while the P(2) atom, which has no phosphorus neighbor, obtains the oxidation number 3–. The other phosphorus atoms obtain intermediate oxidation numbers consistent with the number of phosphorus neighbors and the lengths of the P–P bonds. The oxidation numbers of the metal atoms are assigned such that they balance the formal charge. In agreement with the high electropositivity of the titanium atoms and considering the magnetic properties of the compound it makes sense to assigne the oxidation number 4+ to the titanium atoms. The nickel atoms then necessarily obtain the oxidation number 0. Obviously integer oxidation numbers are an oversimplification.

In polyphosphides with higher phosphorus content, e.g. Re_6P_{13} and Re_2P_5[3], the metallic or semiconducting character can be rationalized by the concept of the two-electron bond (Mooser–Pearson rule[19]). Even though some two-electron bonds occur in Ti_2NiP_5, most atoms in this compound have coordination numbers so high that the bonding cannot be rationalized by this simple concept. The high coordinations suggest broad bands and are typical for compounds with high metal content. The metallic conductivity of Ti_2NiP_5 therefore is not surprising. Nevertheless the spins of all valence electrons are practically compensated for as indicated by the Pauli paramagnetism.

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Registry No. Ti, 7440-32-6; Ni, 7440-02-0; P, 7723-14-0; Ti_2NiP_5, 132338-94-4.

Supplementary Material Available: Listing of anisotropic thermal parameters (1 page); listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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