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Ambient Pressure Synthesis, Properties, and Structure Refinements of VP_4 and CoP_2

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The previously reported compounds VP_4 and CoP_2, prepared at high pressure, were synthesized in well-crystallized form at ambient pressure by reaction of the elemental components in the presence of iodine. Their structures were refined from single-crystal X-ray diffractometer data to conventional residuals of $R = 0.033$ for VP_4 (CrP_4 type structure, 11 variables, 815 F values) and $R = 0.019$ for CoP_2 (arsenopyrite structure, 14 variables, 932 F values). VP_4 is paramagnetic and a metallic conductor. CoP_2 is a diamagnetic semiconductor with an activation energy of 0.34 eV. Chemical bonding and potential displacive phase transitions of these compounds are discussed.

Introduction

The direct synthesis of transition-metal polyphosphides from the elemental components is difficult. At relatively low temperatures (e.g., 800 K) the reactions are very slow. At higher temperatures polyphosphides tend to decompose into lower phosphides and phosphorus vapor. These difficulties can be avoided by using high pressure techniques. Then, however, one is not sure whether the compounds thus prepared are thermodynamically stable at ambient pressure. For instance, CrP_4 was first synthesized at 65 kbar and at 3 kbar (*1*), but later it was also prepared at ambient pressure by reaction of the elemental components in a tin flux or in the presence of iodine (*2*). Similarly the eight-layer modification (*3*) of MnP_4 was first prepared at high pressure (*4*), but later could also be synthesized at ambient pressure (*2*). This is also true for MoP_4 (*1, 5*). Other transition-metal polyphosphides synthesized at high pressure are $VP_{1.75}$ and $NbP_{1.7}$ (*6*), VP_4 (*7*), Nb_2P_5 (*8*), CrP_2 (*9*), WP_4 (*10*), β-FeP_4 (*11, 12*), CoP_2 (*13*), and pyrite-type NiP_2 (*14*). In the course of our studies of ternary systems involving transition-metal phosphides (*15–17*) we have also prepared many samples corresponding to the binary compositions listed above. Of these we were successful in synthesizing VP_4 and CoP_2 at ambient pressure which we report on here.

Synthesis and Crystal Growth

Both compounds were prepared by reac-

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tion of the elemental components in the presence of iodine. Starting materials were powders of vanadium (>99.7%), cobalt (99.9%), and red phosphorus (Merck, "rein") which was purified by boiling in dilute solutions of NaOH (*18*). The components were sealed in silica tubes together with enough iodine to yield a pressure of about 1 to 2 atm at 600°C.

For the preparation of VP_4 the best conditions were as follows: starting composition V : P = 1 : 5, heating to 550°C within 4 hr, annealing at this temperature for 7 days, and cooling to room temperature within 3 days. Before the tubes were opened, the excess P was driven to the cold end. The reaction product consisted of small crystals and microcrystalline VP_4. We have also prepared VP_4 in closed alumina containers. This excludes the possibility of small amounts of Si (from the silica tubes) stabilizing VP_4. With annealing temperatures of 650 or 750°C only VP_2 was obtained. It was not possible to synthesize VP_4 without iodine as mineralizer, although we have not observed chemical transport of VP_4, neither from the hot to the cold end of the tube nor vice versa.

In contrast to this experience with VP_4 we have obtained CoP_2 in pure form only by chemical transport. The powders (starting ratio Co : P = 1 : 2) were annealed at 600 or 700°C for about 5 days. After this treatment the reaction products consisted of CoP (*19*) and CoP_3 (*20*). Only occasionally did we additionally observe small amounts of CoP_2. The products were then placed at the hot end (750°C) of the silica tubes (length: 15 cm; 6 cm^3). After 7 days single-phase CoP_2 was obtained in well-crystallized form at the cold end (650°C) of the tubes. At higher temperatures and in samples with higher P contents we have also transported CoP_3. We have also tried to prepare CoP_2 from a tin flux (starting ratios Co : P : Sn = 1 : 2 : 6). By annealing at temperatures above 600°C we observed only CoP and CoP_3. Annealing at 500 or 550°C resulted in small amounts of CoP_2 in addition to CoP and CoP_3. Very recently CoP_2 was obtained by the tin flux technique also by Lutz *et al.* (*21*). In agreement with our results these authors also report CoP_3 impurities in their samples.

Physical Properties

Electrical conductivities were measured for both compounds between liquid-nitrogen temperature and about 200°C using a two-probe technique. The samples consisted of a microcrystalline cold-pressed pellet of VP_4 and small single crystals of CoP_2, respectively. They were squeezed between tungsten blocks and the potential differences were determined with a compensator. The current–voltage relations were found to be linear for both directions of the currents and the data were reproducible for repeated heating and cooling cycles. Considering the estimates for the contacting areas and the porosity of the VP_4 pellet, absolute values of the specific resistivities were judged to be correct to within a factor of about 3. The results of these measurements are shown in Fig. 1. In agreement with the measurements of the compounds prepared at high pressure, (*7, 13*) VP_4 is a metallic conductor while CoP_2 is semiconducting. The evaluation of the slope at high temperatures according to $\rho = \rho_0 \exp E_a/2kT$ resulted in an activation energy of $E_a = 0.34 \pm 0.03$ eV. This value is much higher than the one found earlier (*13*). The small activation energy of that high-pressure sample probably corresponds to the germanium impurity levels.

The magnetic susceptibility of VP_4 at room temperature was determined with a Faraday balance. VP_4 is paramagnetic with a molar susceptibility (uncorrected for diamagnetism) of $\chi_{mol} = 0.53 \times 10^{-3}$ cm^3/mol. We have also determined the susceptibility of VP_2. It is also paramagnetic, however, with the much smaller value of $\chi = 97$

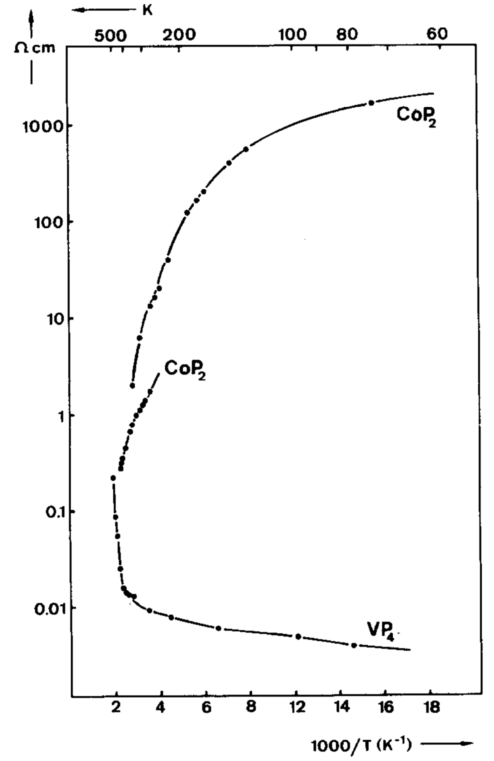

FIG. 1. Specific electrical resistivity of VP_4 and of two different samples of CoP_2 as a function of temperature.

× 10^{-6} cm^3/mol. Thus a small amount of VP_2 which could have been present in our VP_4 sample would not have had a great influence on the magnetism of our VP_4 sample. CoP_2 was found to be diamagnetic (*13*).

Structure Refinements

The lattice constants were determined from Guinier powder diagrams with α-quartz (a = 4.9130, c = 5.4046 Å) as standard. There is good agreement between our data and the data of the compounds prepared at high pressure in the case of VP_4 (Table I). For CoP_2 there is a significant difference which might be due to the small amount of germanium in the sample prepared at high pressure (*13*).

The crystal structures of VP_4 and CoP_2 were refined from single-crystal X-ray diffractometer data collected with an automated four-circle instrument with graphite-monochromatized Mo$K\alpha$ radiation, θ-2θ scans, a scintillation counter, and a pulse-height discriminator. To reduce absorption effects, very small crystals were used with no dimension exceeding 0.1 mm. Totals of 5182 reflections were measured for the VP_4 crystal, 5091 reflections for the CoP_2 crystal, up to 2θ = 90°. Empirical absorption corrections were applied from azimuthal scans. After averaging for equivalent reflections and omitting those with structure factors smaller than three times their standard deviations 815 and 932 structure factors remained for VP_4 and CoP_2, respectively, which were used for the structure refinements.

Starting parameters for the refinements were those of CrP_4 (*1*) and $CoSb_2$ (*22*)

TABLE I

LATTICE CONSTANTS OF VP_4 AND CoP_2[a]

	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)	Reference
VP_4	5.263	10.98	5.871	110.88	317.0	7
VP_4	5.259(4)	10.997(7)	5.879(6)	110.87(7)	317.7(2)	[b]
CoP_2 (Ge)	5.610(2)	5.591(1)	5.643(2)	116.82	157.9	13
CoP_2	5.551(1)	5.549(2)	5.614(1)	114.71(2)	157.09(5)	[b]

[a] Standard deviations in the least significant digits are listed in parentheses.

[b] This work.

which is isotypic with monoclinic arsenopyrite FeAsS (*23*). Atomic scattering factors (*24*) were used, corrected for anomalous dispersion (*25*). The weighting schemes were according to counting statistics. Parameters accounting for isotropic secondary extinction were refined and applied to the F_c values. All atoms were assumed to have isotropic thermal parameters. Refinements with ellipsoidal thermal parameters reflected the insufficiencies of the absorption corrections. Final difference Fourier syntheses resulted in no values higher than 1.9 and 1.2 electrons/Å^3 for VP_4 and CoP_2, respectively. The final conventional residuals are $R = 0.0033$ for VP_4 (11 variables) and $R = 0.019$ for CoP_2 (14 variables). Atomic parameters are summarized in Table II, interatomic distances in Table III. Listings of observed and calculated structure factors can be obtained from the authors.

TABLE III

INTERATOMIC DISTANCES IN VP_4 AND CoP_2[a]

VP_4		CoP_2	
V	P(1) 2.362 (2*x*)	Co	P(1) 2.210
	P(1) 2.436 (2*x*)		P(1) 2.213
	P(2) 2.394 (2*x*)		P(1) 2.220
	V 3.247 (2*x*)		P(2) 2.265
			P(2) 2.281
P(1)	V 2.362		P(2) 2.291
	V 2.436		Co 2.672
	P(1) 2.194		
	P(2) 2.242	P(1)	Co 2.210
			Co 2.213
P(2)	V 2.394		Co 2.220
	P(1) 2.242		P(2) 2.212
	P(2) 2.208		
	P(2) 2.215	P(2)	Co 2.265
			Co 2.281
			Co 2.291
			P(1) 2.212

[a] All metal–metal and metal–phosphorus distances less than 3.3 Å and all phosphorus–phosphorus distances less than 2.8 Å are listed. Standard deviations, computed from the standard deviations of the lattice constants and positional parameters, are all less than 0.003 Å for VP_4 and less than 0.0015 Å for CoP_2.

Discussion

Both VP_4 and CoP_2 are polyphosphides with low-coordination numbers. The metal atoms are octahedrally coordinated by P atoms, and the P atoms are tetrahedrally coordinated by P and metal atoms. Such compounds can be rationalized on the basis of classical two-electron bonds (*26–28*). By counting two electrons for each of the short near-neighbor interactions the vanadium atoms obtain the oxidation number +2 (d^3 system) and the cobalt atoms obtain the oxidation number +4 (d^5 system). As is observed in many other transition metal polyphosphides (*29*) one can assume that the remaining three and five, respectively, electrons of the metal atoms will lower their energy by forming as many metal–metal bonds as is possible by the topology of the structure. This we want to discuss now in more detail.

TABLE II

RESULTS OF THE LEAST-SQUARES REFINEMENTS OF THE STRUCTURES OF VP_4 AND CoP_2[a]

VP_4	*C*2/*c*	*x*	*y*	*z*	*B* (Å^2)
V	4*e*	0	0.06271(6)	¼	0.219(5)
P(1)	8*f*	0.2767(1)	0.09058(6)	0.6780(1)	0.328(7)
P(2)	8*f*	0.2757(1)	0.22344(6)	0.1886(1)	0.308(7)
CoP_2	$P2_1/c$				
Co	4*e*	0.27079(3)	0.00124(5)	0.28585(4)	0.251(2)
P(1)	4*e*	0.33830(7)	0.37213(8)	0.18196(7)	0.328(4)
P(2)	4*e*	0.15899(7)	0.62666(8)	0.36478(7)	0.342(4)

[a] Standard deviations in the least significant digits are given in parentheses.

CoP_2 has arsenopyrite (monoclinic FeAsS or $CoSb_2$ type) structure which is closely related to the marcasite (monoclinic FeS_2 type) structure. Both structures may be considered as made up from parallel strings of edge-sharing TX_6 octahedra (T = transition metal, X = pnicogen or chalcogen) which are further condensed by corner-sharing. The differences can be attributed to the differing T–T interactions. In the d^6 marcasites no T–T bonding is possible because all d orbitals are occupied: The e_g orbitals participate in the six essentially covalent T–X bonds, and the t_{2g} orbitals are filled with six electrons which are nonbonding and in part antibonding with respect to the T–T interactions. Thus the d^6 marcasites have long T–T distances. In CoP_2 and the other d^5 compounds with this structure (*30*) short and long T–T distances alternate along the chain. This leads to a doubling of the translation period in the chain direction and the arsenopyrite structure may thus be considered as a distorted version of the marcasite structure. The short T—T distances may be rationalized as T–T bonds which are formed by the overlap of the singly occupied t_{2g} orbitals of adjacent T atoms. In the d^4 marcasites all T–T distances of the T chain are short. Every T atom may thus be considered as forming T–T bonds to both of the adjacent T neighbors. These two bonds can be rationalized as two σ and two π half-bonds (*4*).

Optimal short T–T bond lengths cannot be achieved in these structures because too large deviations from the ideal bond angles would be required. However, the bonding character of the short T–T interactions can clearly be seen from the deviations from the ideal bond angles (Fig. 2): the ideally tetrahedral Co–P–Co angle of 109° at the bridging P atom is reduced to 74°, and the ideally octahedral P–Co–P angle of 90° is increased to 106° to allow the short Co–Co interactions of 2.67 Å. The diamagnetism and the semiconductivity of CoP_2 are consistent with this simple rationalization of chemical bonding. It is also in agreement with the generalized 8-N rule (*30*).

Chemical bonding in marcasites and arsenopyrites has been discussed extensively (*4, 26, 30–41*) and will not be reviewed here. We should, however, not conceal that not all bonding models agree with T–T bonding for the short T–T interactions in these compounds. In our opinion such models cannot be right in this respect for the following reasons.

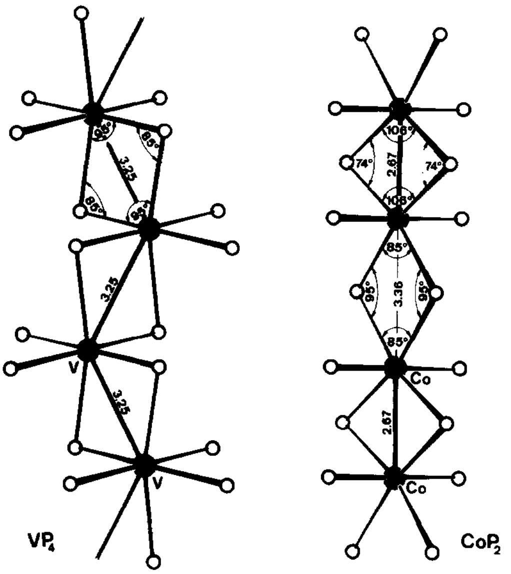

FIG. 2. Metal–metal bonding in the structures of VP_4 and CoP_2. Interatomic distances are in Ångstroms.

There exists now a large amount of structural data on molecular and solid state compounds with metal–metal bonding and there is general agreement that short intermetallic distances are bonding, especially when the coordination polyhedra are distorted in such a way as to permit a close approach of the metal atoms. Particularly in solid state chemistry the preparation conditions (long-time annealing) practically always warrant the formation of the thermodynamically most stable atomic arrangement. If the short T–T interactions in the d^4 marcasites and d^5 arsenopyrites were really antibonding, the structures would not form, because they would be thermodynamically unstable with respect to the pyrite structure. (The pyrite structure offers practically the same near-neighbor coordinations as the marcasite and arsenopyrite structures except that short T–T interactions are avoided because the TX_6 octahedra in pyrite are linked only via corners.) If one or the other experimental evidence seems to contradict bonding T–T interactions in the "compressed" marcasites one should search for explanations which are compatible with T–T bonding. In this context it is gratifying that the "d^0" compressed marcasite compound "$Mo_{2/3}As_2$" was finally recognized as never having existed (*37, 38*).

It is well known that on heating distorted structures tend to transform by a displacive phase transition to the undistorted (not quenchable) form. It can therefore be expected that compounds with arsenopyrite structure will on heating be transformed to the marcasite structure. We have therefore recorded high-temperature Guinier powder photographs of CoP_2 with Fe$K\alpha$ radiation up to temperatures of about 570 K. We did not observe such a transition within this temperature range. Such transitions, however, were observed for the homologous isotypic compounds $CoSb_2$ and $CoAs_2$ at 650 and 870 K, respectively (*42*). The extrapolation for CoP_2 leads to a transition temperature of about 1000 K which comes close to the decomposition temperature. The phase transition of CoP_2 would therefore need to be recorded very fast (e.g., with synchrotron radiation) or in a sample with high phosphorus vapor pressure. In analogy to the well-known metal–insulator transition of VO_2 (*43–45*) this phase transition could also change the character of the electrical conductivity from semiconducting in the arsenopyrite form to metallic in the marcasite form.

VP_4 is isotypic with CrP_4. Due to the larger size of the V atoms the average V–P distance is 0.06 Å greater than the average Cr–P distance. The bonding V–V distance is also 0.06 Å greater than the Cr–Cr distance, and the relevant bond angles (Fig. 2) are practically the same in both compounds. Thus the metal-metal bonding situations in VP_4 and CrP_4 must be very similar even though Cr in CrP_4 has a d^4 system while V in VP_4 has a d^3 system. In CrP_4 it is assumed (*1*) that two electrons of the d^4 system are paired in a nonbonding t_{2g} orbital while the other two electrons form Cr–Cr bonds across the edges of two adjacent CrP_6 octahedra. Since the bonding situations of the metal atoms in VP_4 and CrP_4 are practically the same, again two of the t_{2g} electrons of a V atom in VP_4 can be assumed to form V–V bonds to two adjacent V atoms while the nonbonding t_{2g} orbital will hold only one electron. The paramagnetism of VP_4 observed by us corresponds (after correction for the diamagnetism) to $\mu_{\text{eff}} = 1.2\ \mu_B$ at room temperature. It is considerably greater than the Pauli paramagnetism observed for CrP_4 and reflects the one unpaired electron per formula unit. A more careful investigation of the magnetic properties of VP_4 and CrP_4 is planned for the near future.

The metal–metal bonds in VP_4 (3.247 Å) and CrP_4 (3.183 Å) are considerably greater than the ideal single-bond distances of about 2.6 Å. These deviations from the ideal bond distances can be ascribed to the compromise which is necessary to avoid too large deviations from the ideal octahedral and tetrahedral bond angles as is discussed above for CoP_2. The metallic character of the electrical conductivity of both VP_4 and CrP_4 probably is a consequence of these large bonding metal–metal distances which do not allow a sufficient splitting of the bonding and antibonding bands. Smaller metal–metal distances in VP_4 and CrP_4 would be possible if the metal atoms would form pairs with metal–metal double bonds as it is known for MoO_2 (*46*). As a consequence of such pairing distortions at low temperatures the compounds would probably become semiconducting. Our conductivity measurements of VP_4 do not give any indication for such a transition down to temperatures as low as 77 K.

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