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# The Band Structure, Heat of Formation, and Atomic Interactions in Titanium Monophosphide

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The Linear Muffin Tin Orbital (LMTO) method has been used to calculate the band structure and the heat of formation of titanium monophosphide. The phosphide is found to be metallic with a low state density at the Fermi level. The most important bonding interactions take place between the titanium *d* and the phosphorus *p* orbitals forming $\sigma$ and $\pi$ bonds. The valence electron density around the titanium atoms is higher in the directions of the $d_\gamma$ orbitals facing the nearest phosphorus atoms than in the directions of the $d_\varepsilon$ orbitals which largely point in the direction of the nearest titanium atoms. However, a peak in the state density just below the Fermi level and an increased electron density between the nearest titanium atoms indicate a certain amount of metal–metal interactions. The equilibrium average atomic sphere radius 1.533 Å calculated from the overall minimum in the total valence energy compares excellently with the value 1.547 Å derived from the experimental cell volume. The computed heat of formation is −249 kJ/mole which can be compared with the experimental value of −265 kJ/mole. © 1990 Academic Press, Inc.

## 1. Introduction

In the series of 3*d* monophosphides ScP, TiP, and VP the crystal structures change from the sodium chloride for ScP to the nickel arsenide structure for VP via the TiP structure which can be regarded as a stacking of alternating blocks of the sodium chloride and the nickel arsenide structures. The series is suitable for a study of the electronic conditions which favor the sodium chloride and nickel arsenide structures with respect to each other. The study is performed by self-consistent band and total energy calculations *ab initio* by the LMTO (Linear Muffin Tin Orbital) method (*1*). The calculations for the scandium monophosphide have been performed previously (*2, 3*) and this paper reports the results of calculations for the TiP structure.

## 2. The Crystal Structure of TiP

The crystallographic parameters for the TiP structure are summarized in Table I as reported by Snell (*4*). The structure is reported to be nonstoichiometric at high temperatures (*5*).

The metal atoms are octahedrally surrounded (slightly distorted octahedra) by

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TABLE I

CRYSTAL STRUCTURE DATA AND INTERATOMIC DISTANCES FOR TiP AS REPORTED BY SNELL (*4*)

Space group: $P6_3/mmc$
$a = 3.499$ Å; $c = 11.700$ Å
4 Ti atoms in 4(*f*) with $z = 0.1170$
2P atoms in 2(*a*) (P1)
2P atoms in 2(*d*) (P2)

Interatomic distances:

| | | | |
|---|---|---|---|
| Ti–3P1 | 2.440Å | P1–6Ti | 2.440 Å |
| –3P2 | 2.550 Å | –6P1 | 3.499 Å |
| –1Ti | 3.112 Å | –6P2 | 3.555 Å |
| –3Ti | 3.402 Å | | |
| –6Ti | 3.499 Å | P2–6Ti | 2.550 Å |
| | | –6P2 | 3.499 Å |
| | | –6P1 | 3.555 Å |

the nonmetal atoms (Fig. 1) as in the sodium chloride and the nickel arsenide structures. Outside of the octahedron there are metal neighbors, but because of the stacking sequence BBCCBBCC . . . for the metal atoms there are only 10 metal neighbors in the TiP structure in contrast to the 12 metal neighbors found in the sodium chloride and in the ideal nickel arsenide structures. One of the metal neighbors is particularly close because it resides in the same type of layer either above or beneath the central metal atom. Of the 9 remaining metal neighbors there are 6 atoms within the layer and these have the largest metal–metal distances.

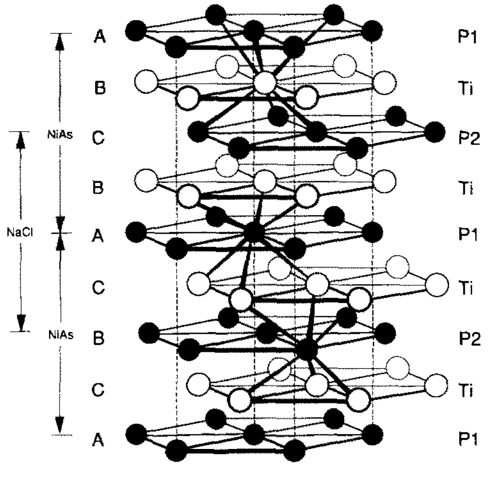

FIG. 1. The crystal structure of TiP showing the octahedra around the Ti and P1 atoms and the trigonal prisms around the P2 atoms.

Because of the stacking sequence in blocks of sodium chloride and nickel arsenide structures the nonmetal atoms are surrounded alternately by metal octahedra as in the sodium chloride structure and by trigonal prisms of metal atoms as in the nickel arsenide structure. In contrast to the single crystallographic position for the metal atoms there are thus two different phosphorus sites which have slightly different properties.

## 3. The Total and Partial Densities and Numbers of States

The LMTO computer programs used for the band structure calculations were those developed by Skriver (*6*). Details about the calculations are given in the Appendix.

The total and the partial densities of states (DOS) and the corresponding integrated quantities (numbers of states, NOS) are shown in Figs. 2–4. The partial quantities for the two phosphorus sites differ very little so the curves for the phosphorus atoms have been chosen as the arithmetic mean of the two sites. The energy scale has been adjusted so that the Fermi level is at zero energy.

The Fermi level is located just above a minimum in the total density of states and at this point the state density is primarily composed of titanium *d* states (Fig. 3c). The total state density at the Fermi level (8.2 electrons/Rydberg/formula unit) is twice as large as for the scandium monophosphide (*2*) (4.0 electrons/Rydberg/formula unit) and indicates a more metallic

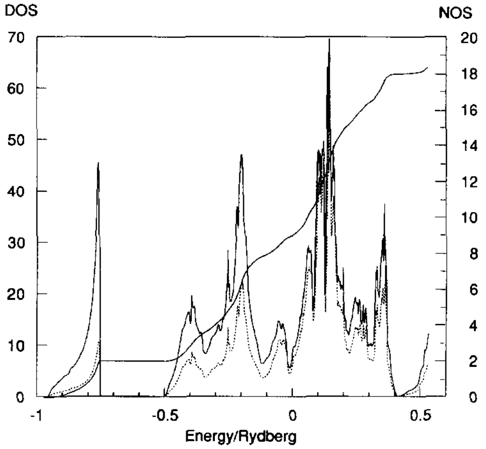

FIG. 2. The total density of states (DOS) and the number of states (NOS) for TiP and the partial state density for titanium (dotted curve). The calculations were performed with the experimental parameters in Table I and a radius ratio $r_{Ti}/r_P$ between the atomic spheres of 1.07. The state density is given in units of states/Rydberg per formula unit and the number of states is given per formula unit. The Fermi level is set at zero energy.

behavior in TiP than in ScP, the latter having only a weak metallic behavior. These results are in agreement with the XPS measurements made by Myers, Franzen, and Anderegg (*7*).

### *The Phosphorus State Density*

The phosphorus valence electrons form two distinct bands separated by a band gap (Fig. 4); one *s* band in the energy range −0.95 to −0.75 Ry and one *p* band in the range −0.50 to +0.40 Ry. The latter band is also overlapped by a low state density of the phosphorus *d* electrons. The integrated number of electrons at the Fermi level are approximately 1.5, 3.1, and 0.3 for the *s*, *p*, and *d* orbitals, respectively. Because of the well-separated *s* and *p* bands of the phosphorus atoms and the atoms being almost neutral these occupation numbers are very close to those calculated for black phosphorus (*8*).

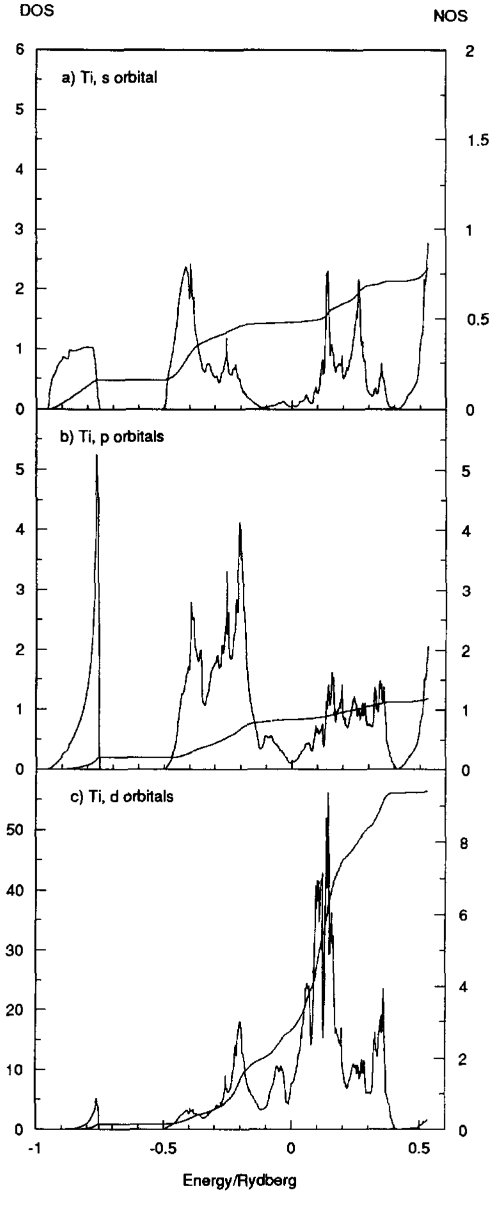

FIG. 3. The partial densities of states (DOS) and numbers of states (NOS) for the titanium atoms in the TiP structure.

### *The Titanium State Density in the Energy Range −0.95 to −0.12 Ry*

In the energy range −0.95 to −0.12 Ry the general features of the titanium state

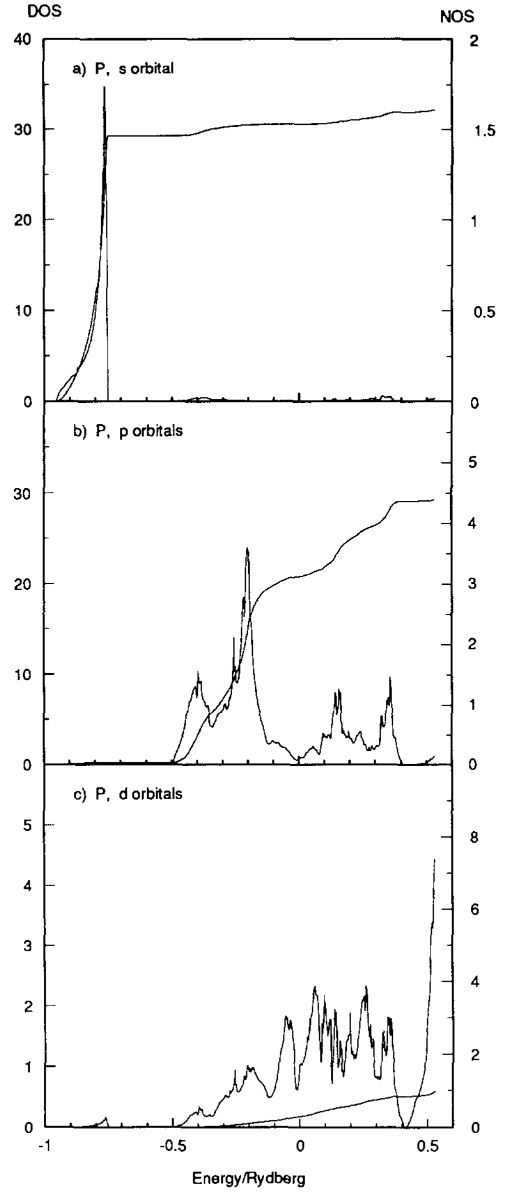

FIG. 4. The partial densities of states (DOS) and numbers of states (NOS) for the phosphorus atoms in the TiP structure. The curves represent the arithmetic mean for the two sites because the difference between the two sites is very small.

density resemble those of the phosphorus atoms and the gap of the total state density can be recognized in the partial densities for both kinds of atoms although the decomposition into various partial orbital densities differ (Figs. 3 and 4). It can also be noted that the titanium partial state density is in general higher in the energy range of the phosphorus $p$ band than at the phosphorus $s$ band. This holds in particular for the titanium $d$ states. These conditions signify the close interaction between the titanium and the phosphorus electrons and the formation of titanium–phosphorus bonds, mainly of $p$–$d$ character.

Further information about the bonding situation around the titanium atoms can be obtained by resolving the partial titanium $d$ state density into $d_\gamma$ and $d_\varepsilon$ orbitals with respect to local coordinates with the $d_\gamma$ orbitals pointing in the direction of the nearest phosphorus atoms (Fig. 5). Most of the $d_\varepsilon$ orbitals then point in the directions of the nearest titanium atoms. The integrated number of $d_\gamma$ electrons up to $-0.12$ Ry is 0.85 and the corresponding value for the $d_\varepsilon$ orbitals is 1.10. Since there are two $d_\gamma$ and three $d_\varepsilon$ orbitals the occupation numbers are 0.43 and 0.37 electrons per orbital, respectively. Hence there is a preference in this energy range for the $d$ electrons to form $\sigma$ bonds (overlap between Ti $d_\gamma$ and phosphorus $p$ orbitals) and to a smaller extent to form $\pi$ bonds with the phosphorus neighbors (overlap between Ti $d_\varepsilon$ and phosphorus $p$ orbitals) and to form metal–metal $\sigma$ bonds (overlap between Ti $d_\varepsilon$ orbitals).

### *The Titanium State Density in the Energy Range −0.12 to 0 Ry*

The total density of states in the energy range $-0.12$ Ry to the Fermi level consists of one single peak which mainly comprises a peak in the partial $d$ density of the titanium atoms. In contrast to the situation for the energy region $(-0.95, -0.12)$, the titanium density in the present energy range just below the Fermi energy is *not* followed by a similar peak in the partial phosphorus state density. This condition and the fact that there are as much as 0.8 titanium and only 0.3 phosphorus electrons in the present energy range show that the interaction between the titanium and the phosphorus atoms are weak in this energy range. The peak consisting of almost pure titanium *d* bands instead indicates an interaction between the central titanium atom and the surrounding titanium atoms. Moreover, the titanium *d* electrons in this energy region can be divided into 0.30 $d_\gamma$ and 0.49 $d_\varepsilon$ electrons. Since the $d_\varepsilon$ orbitals point in the directions of the nearest metal atoms and thereby give better orbital overlap than the $d_\gamma$ orbitals, their predominance shows that the density of states just below the Fermi energy mainly originates from metal–metal bonding.

The number of electrons involved in the orbitals between the two titanium atoms with the short separation distance of 3.11 Å can be obtained by decomposing the *d* orbitals using a coordinate system with the crystallographic *a* axis as the *x* axis and the *c* axis as the *z* axis. The titanium $d_{z^2}$ orbital then points in the direction of the closest titanium atom. This figure is 0.17 electrons which is slightly larger than for the orbitals pointing in the other directions (0.15 electrons) so this condition also indicates a metal–metal interaction. Myers *et al.* (*7*) found an increased metal–metal interaction in TiP in comparison with ScP in their XPS measurements and this condition supports the formation of Ti–Ti bonds in TiP.

### *Occupation Numbers for Orbitals*

In the calculations on the scandium monophosphide (*3*) it was found that the sodium chloride structure had a higher occupancy number for the metal *d* orbitals than in the less stable NiAs structure. This effect was caused by a preference of the metal *d* electrons in the NaCl structure to occupy the $d_\gamma$ orbitals and to form $\sigma$ bonds to the phosphorus atoms. For TiP the TiP structure is more stable than the sodium chloride and the nickel arsenide structures. It is therefore of interest to see if a lattice compression will lead to a higher *d* occupation number for the titanium atoms (possibly favoring the sodium chloride structure) or not (favoring the nickel arsenide structure). The major change in the occupation

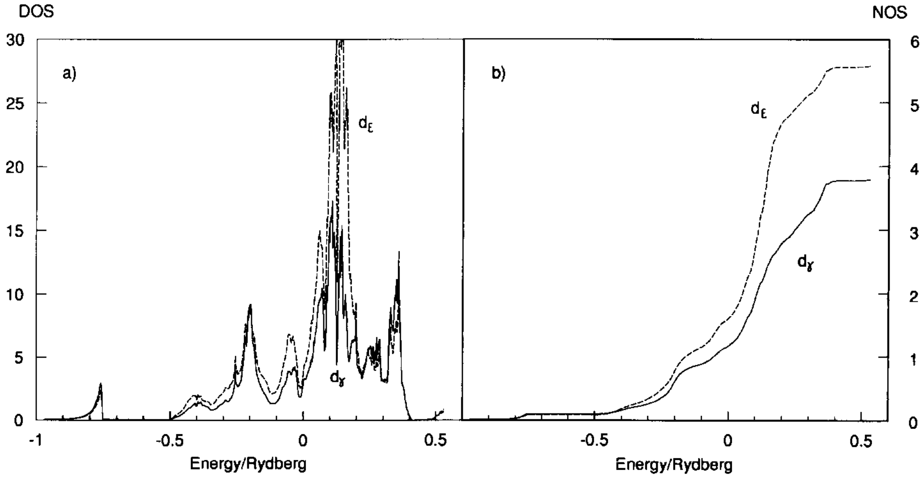

FIG. 5. The partial densities of states (DOS) (a) and numbers of states (NOS) (b) for the titanium $d_\gamma$ and $d_\varepsilon$ orbitals. The decomposition of the *d* orbitals has been made for local coordinates matching the octahedral surroundings of the titanium atoms.

numbers for the various orbital types on such a compression of the cell volume at a fixed value of the radius ratio is a transfer of phosphorus *p* electrons to titanium *d* electrons. A compression of the structure therefore seems to stabilize the sodium chloride structure (Figs. 6a and 6c) although it is not possible to decide from the present calculations whether this effect is sufficiently large to make the sodium chloride structure the most stable form within experimentally obtainable pressures.

The actual values of the occupation numbers at a fixed value of the cell volume are of course dependent on the radius ratio $r_{Ti}/r_P$ of the atomic spheres (Figs. 6b and 6d). An increase in the size of the titanium sphere leads to higher occupation numbers for the titanium atom and to the corresponding reduction in the occupation numbers for the phosphorus atom. Therefore also the ionicities associated with the atoms are dependent on the radius ratio. The changes in these quantities however do not correspond to any real changes in the compound since the values of the radii are just a way of dividing the space occupied by the atoms on to separate atoms and their associated potential spheres. The values of ionicities and occupation numbers must there-

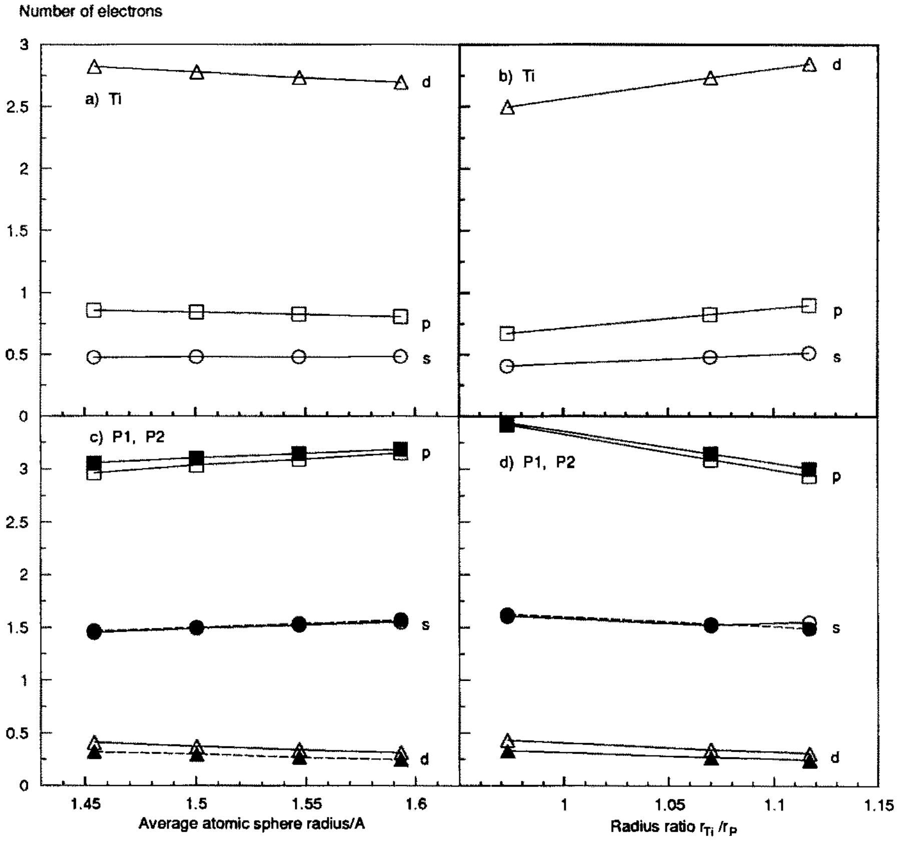

FIG. 6. The occupation numbers for the *s*, *p*, and *d* orbitals as a function of the average atomic sphere radius and the atomic sphere ratio $r_{Ti}/r_P$ in the TiP structure. The dashed lines represent the P2 atoms. (a) and (c) are drawn at a fixed value of 1.07 for the radius ratio $r_{Ti}/r_P$ and (b) and (d) are drawn at an average atomic sphere radius of 1.5470 Å.

fore be used with caution when compared with results obtained with other computational methods.

## 4. The Total Energy and the Heat of Formation

The computer programs by Skriver (*6*) have been modified in order to calculate the total energy according to the formalism of Gunnarsson *et al.* (*9*). In their formation the total valence energy can be written as a sum of four parts:

$$E_v = E_{\text{kin}} + E_A + E_B + E_{\text{Mad}}. \quad (1)$$

The first term is the one-particle energy and the second and third terms together form the electrostatic energy corrected for exchange and correlation. The last term is the Madelung energy. In the following, we first discuss the total energy and thereafter we consider the various contributions to the valency energy in some detail.

The total valence energy for a uniform lattice compression was evaluated using a Murnaghan (*10*) expression and it is shown as a function of the average atomic sphere radius in Fig. 7. In order to obtain a good result for the heat of formation a minimum in the total valence energy as a function the radius ratio $r_{\text{Ti}}/r_{\text{P}}$ of the atomic sphere radii must be determined. Therefore the radius ratio was verified in the range 0.97–1.12 and the minimum in the total energy was found at a radius ratio of 1.07. The variation in the valence energy in this range was 0.050 and 0.020 Ry in the range $1.02 \leq r_{\text{Ti}}/r_{\text{p}} \leq 1.12$. The value 1.07 for the ratio at the minimum was subsequently fixed for the calculations in which the cell volume was varied.

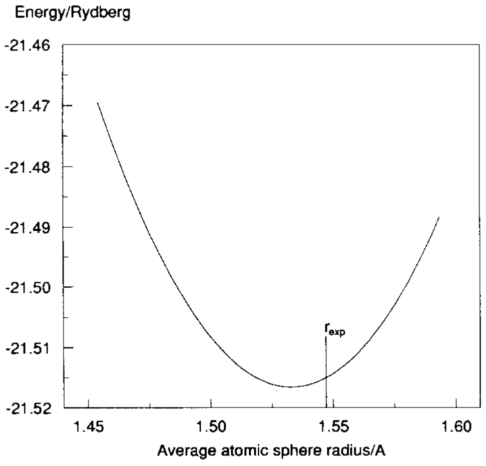

FIG. 7. The total valence energy of TiP per formula unit as a function of the average atomic sphere radius.

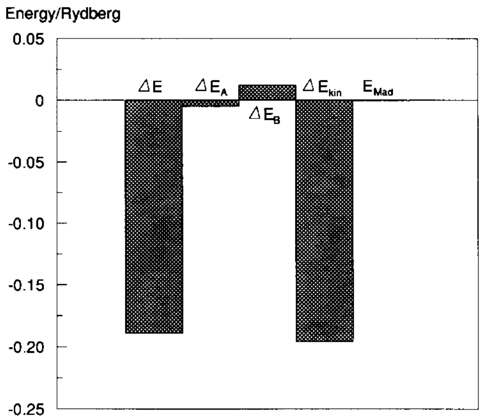

FIG. 8. The difference between the total energy of the compound at the energy minimum and the total energies of the pure constituent elements and its decomposition into separate terms.

The minimum in total valence energy is at −21.517 Ry at an average atomic sphere radius of 1.533 Å. From similar calculations for titanium metal and black phosphorus the difference in total energy between the compound and the elements was calculated to be −0.190 Ry. This value corresponds to a heat of formation of −249 kJ/mole and can be compared with the experimental value of −265 kJ/mole (*11*).

The difference in total energy between the compound at its energy minimum and the elements has been separated into its various consituents in Fig. 8. It is the kinetic energy term, i.e., the sum of the one-

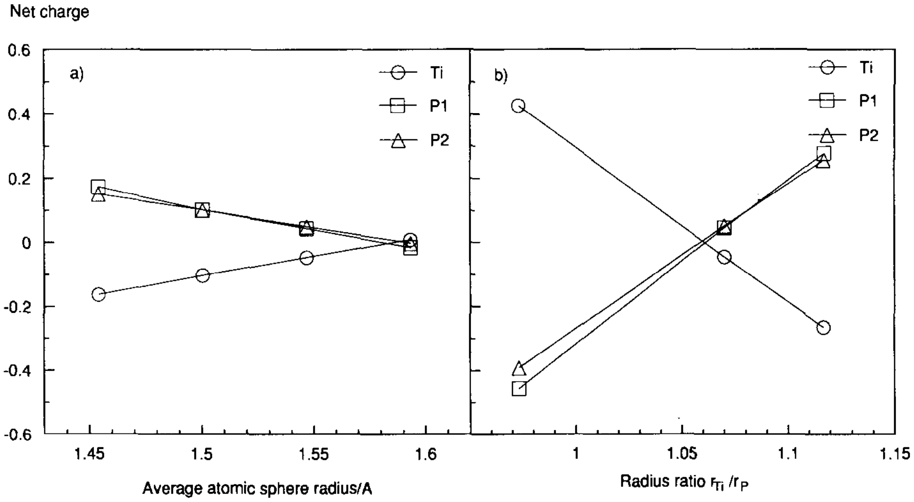

FIG. 9. The net charge (electrons) within the atomic spheres of titanium and phosphorus (ionicity) as functions of the average atomic sphere radius and the radius ratio $r_{Ti}/r_P$.

particle energies, which completely dominates the energy difference. However, the total energy of the phosphide is a delicate balance between primarily the strongly varying terms $E_{kin}$ and $E_A$ and at other values of the average atomic sphere radius the relative sizes between these terms are different. If the difference in energy is divided into contributions from the two kinds of atoms the difference can be described as a net effect of a decrease of the partial energy of the titanium atoms and an increase of the partial energy for the phosphorus atoms.

The Madelung energy is very small, the largest absolute value being only 4.4 mRy. This is caused by the small net charges (ionicities) within the atomic spheres (Fig. 9).

## 5. The Cell Unit Size and Bulk Modulus

As mentioned previously the minimum in total valence energy occurs at an average atomic sphere radius of 1.533 Å. The average atomic sphere radius calculated from the experimental cell volume is 1.547 Å which differs only 0.9% from the theoretical value. The agreement is thus excellent.

The calculated value of the bulk modulus at the energy minimum using the Murnaghan expression is 289 GPa which is substantially larger than that for pure titanium metal (105.1 GPa) (*12*).

## 6. Summary

Titanium monophosphide is calculated to be metallic but with a rather low state density at the Fermi level. Nevertheless the state density is twice as high as for the scandium monophosphide. In contrast to the scandium monophosphide the density of states and the occupation numbers for particular orbitals indicate a certain measure of metal–metal interactions. These results are in agreement with XPS measurements. However, the most important bonding interactions are the formation of $\sigma$ and $\pi$ bonds between the titanium *d* orbitals and the phosphorus *p* orbitals. The valence

TABLE II

POTENTIAL PARAMETERS FOR TITANIUM IN TITANIUM MONOPHOSPHIDE

| Orbital | $E_v$ | $\omega(-)$ | $s\Phi^2$ | $\Phi(-)/\Phi(+)$ | $\sqrt{\langle\dot{\Phi}^2\rangle}$ |
|---|---|---|---|---|---|
| $s$ | 0.1489 | 0.3869 | 0.3194 | 0.8779 | 0.2090 |
| $p$ | 0.2749 | 1.1221 | 0.3046 | 0.7371 | 0.1918 |
| $d$ | 0.4526 | 0.3061 | 0.0474 | 0.1746 | 0.9350 |

*Note.* The atomic radius is 1.597 Å. The notation is that of Skriver and the energy unit is Rydberg.

TABLE IV

POTENTIAL PARAMETERS FOR THE PHOSPHORUS IN THE TRIGONAL PRISMATIC POSITION (P2) IN TITANIUM MONOPHOSPHIDE

| Orbital | $E_v$ | $\omega(-)$ | $s\Phi^2$ | $\Phi(-)/\Phi(+)$ | $\sqrt{\langle\dot{\Phi}^2\rangle}$ |
|---|---|---|---|---|---|
| $s$ | −0.1115 | −0.2117 | 0.1829 | 0.7589 | 0.0000 |
| $p$ | 0.4029 | 0.1029 | 0.1576 | 0.4887 | 0.4295 |
| $d$ | 0.4864 | 1.3535 | 0.2082 | 0.4976 | 0.2213 |

*Note.* The atomic radius is 1.493 Å.

electron density around the titanium atoms is higher in the directions of the $d_\gamma$ orbitals facing the nearest phosphorus atoms than in the directions of $d_\varepsilon$ orbitals which largely point in the direction of the nearest titanium atoms.

There is a good agreement between calculated and experimental heats of formation and the result regarding the cell unit size is excellent.

## Appendix

### *Computational Details*

The calculations were carried out for 112 $k$-points in $\frac{1}{24}$ of the Brillouin zone and orbitals of $s$, $p$, and $d$ character were considered. The combined correction terms for the atomic sphere approximation (ASA) were included.

TABLE III

POTENTIAL PARAMETERS FOR THE PHOSPHORUS IN THE OCTAHEDRAL POSITION (P1) IN TITANIUM MONOPHOSPHIDE

| Orbital | $E_v$ | $\omega(-)$ | $s\Phi^2$ | $\Phi(-)/\Phi(+)$ | $\sqrt{\langle\dot{\Phi}^2\rangle}$ |
|---|---|---|---|---|---|
| $s$ | −0.1136 | −0.2099 | 0.1824 | 0.7589 | 0.0000 |
| $p$ | 0.3988 | 0.1069 | 0.1574 | 0.4894 | 0.4293 |
| $d$ | 0.5048 | 1.3305 | 0.2066 | 0.4946 | 0.2238 |

*Note.* The atomic radius is 1.493 Å.

The self-consistency was carried out to less than 1 mRy in total valence energy, and to less than 0.001 electron/Å in the radial charge density. The change in the electronic pressure from the last cycle to the previous was less than 1 kbar.

The experimental cell volume corresponds to an average atomic sphere radius of 1.5470 Å and in the figures which show various quantities as functions of the atomic sphere radius ratio $r_{Ti}/r_P$ this average size has been used. In figures which show quantities as functions of the average atomic sphere radius the radius ratio has been fixed at 1.07.

## Acknowledgments

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