High-pressure behavior of phosphorus from first principles calculations

A. S. Mikhaylushkin,[1,2] S. I. Simak,[2] B. Johansson,[1,3] and U. Häussermann[4]

[1]*Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden*
[2]*Theory and Modeling, IFM, Linköping University, S-581 83 Linköping, Sweden*
[3]*Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology (KTH),*
SE-10044 Stockholm, Sweden
[4]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA*

High-pressure structural behavior, electronic structure, and vibrational properties of P have been investigated by means of first principles calculations. We perform an *ab initio* search for the P-IV phase by analyzing the phonon dispersions of the simple cubic (sc) structure as a function of pressure. In particular, we use the dynamical instability of the sc structure above the transition into the simple hexagonal structure to extract a possible candidate structure for P-IV. Additionally, in contrast to general expectations, we show that the body-centered cubic (bcc) P-V phase cannot be the end member of the high-pressure structural sequence of P because it becomes dynamically unstable at high compression. We propose that at ultrahigh pressure above 280 GPa, the bcc structure transforms first to the *IM*7 structure and then to the hexagonal close-packed structure.

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The group 15 elements P, As, Sb, and Bi all form layered structures consisting of six-membered rings at ambient conditions and are reported to attain the body-centered cubic (bcc) structure at the highest pressures applied so far.[1,2] In the intermediate pressure region, however, phosphorus and its heavier congeners behave profoundly different from each other. In this region, P first adopts the open-packed simple cubic (sc) structure for a wide range of pressures[3] and then transforms via a not yet characterized intermediate phase into the rarely observed simple hexagonal (sh) structure.[4] For the heavier congeners complex, incommensurately modulated *host-guest* structures[5] emerge as intermediate pressure structures.[6–9]

Despite its apparent simplicity, the high-pressure structural behavior of P is still not fully determined. First of all, the structure of the intermediate phase P-IV between sc-P (P-III) and sh-P (P-V) is unknown. According to the experiment by Akahama *et al.*,[4] the transition sc→P-IV occurs at 107 GPa and P-IV remains stable up to 137 GPa. The diffraction data obtained by Akahama *et al.* were not well resolved in the region between 107 and 137 GPa and, thus, were unsuitable for structure determination. Above 137 GPa, P-IV is succeeded by sh-P, which is stable up to a very high pressure of 262 GPa. At even higher pressures, phosphorus is assumed to adopt the bcc structure (P-VI).[1] However, although reasonable and in line with the heavier group 15 elements, the assignment of the bcc structure for P-VI is not unambiguous. It is based on the observation of only one diffraction line because of overlapping reflections from the coexisting sh phase and the Re gasket.

The experimental findings of Akahama *et al.*[1,4] stimulated several theoretical investigations.[10–13] Akahama *et al.* have argued that the structure of P-IV might be found in a process of a monoclinic distortion along the [110] direction in the sc structure.[4] This possibility has been studied by Ehlers and Christensen while applying the orthorhombic α-Np structure as a structural model for P-IV.[12] However, the amount of distortion and accompanying energy gain was minute and it

was concluded that the structure of P-IV could not be explained by a simple monoclinic distortion of the sc structure. Very recently Ishikawa *et al.* proposed a more reasonable structural model obtained from constant-pressure metadynamics.[13]

In this Brief Report, we undertake an *ab initio* search for P-IV by analyzing the phonon dispersions of the sc structure as a function of pressure. In particular, we use the dynamical instability of the sc structure above the transition into sh-P to extract a possible candidate structure for P-IV. Additionally, and most surprisingly, we show that bcc-P becomes dynamically unstable at very high pressures and, therefore, cannot represent the end member of the high-pressure structural sequence of P.

Total energy calculations were performed in the framework of the frozen core all-electron projector augmented wave method[14] as implemented in the program VASP.[15] P and its heavier congeners As, Sb, and Bi were calculated the same way. The energy cutoff was set to 500 eV. Exchange and correlation effects were treated by the generalized gradient approximation.[16] The integration over the Brillouin zone was done on a grid of special k points determined according to the Monkhorst-Pack scheme.[17] Depending on the structure, we used 500–1500 irreducible k points. For the structural relaxation, the integration was carried out according to the Methfessel-Paxton scheme,[18] while accurate total energy calculations were done with the modified tetrahedron method with Blöchl correction.[19] All necessary convergence tests were performed and total energies were converged to within 0.1 meV/atom. Phonon frequencies were calculated in the framework of the supercell method described in detail in Ref. 20. Forces induced by small atomic displacements were calculated using the VASP program. The technical measures taken to achieve excellent convergence were as follows. We tested the convergence of the phonon free energy and phonon frequencies with respect to both the number of irreducible k points and the supercell size. To maintain the high accuracy as specified above, we adopted $4 \times 4 \times 4$ supercells.
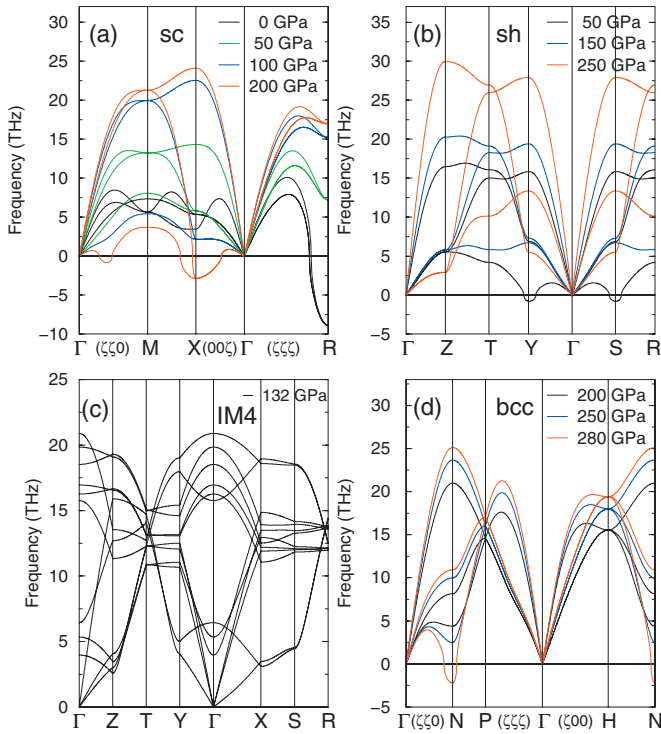
FIG. 1. (Color) Calculated phonon spectra for the (a) sc, (b) sh, (c) $IM4$, and bcc phases of P at different pressures. Note that negative frequency values correspond to imaginary scale as $\sqrt{-\omega^2}$.
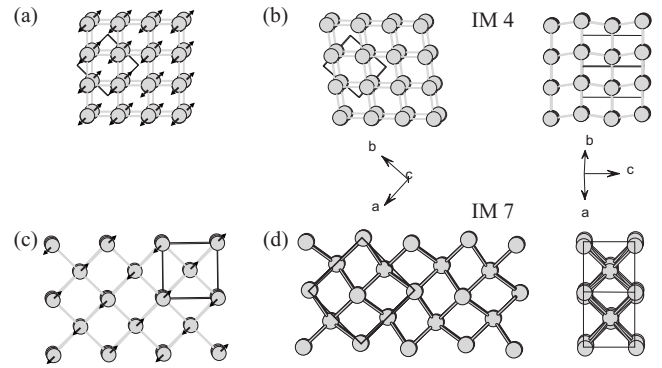

FIG. 2. Atom displacements in the (a) sc and (c) bcc structures leading to the orthorhombic (b) $IM4$ and (d) $IM7$ structures, respectively.

We started the structural search for P-IV by analyzing the phonon dispersions of the sc structure at different volumes [Fig. 1(a)]. At ambient pressure, the dispersion has imaginary frequencies in the longitudinal and both transverse branches at point R. This mirrors the dynamical instability behind the Peierls distortion along the [111] direction. The relaxation of a [111] rhombohedrally distorted sc structure with a doubled unit cell volume (i.e., containing two atoms) will then lead to a pairing of (111) lattice planes in the same (i.e., longitudinal) direction and result in the rhombohedral $A7$ structure. The instability of the sc structure toward this distortion is characteristic for the heavier group 15 (P-Bi) elements with a valence electron configuration s^2p^3.[21]

As shown in Fig. 1, at elevated pressure, the phosphorus sc structure stabilizes and remains stable up to 120 GPa. At higher pressures, the softening of the longitudinal and transverse modes at point X becomes apparent. Additionally, the longitudinal mode is softened along the ΓM [110] direction at about 0.4 of the $|\Gamma M|$ distance. At even higher pressures, the frequencies at X become imaginary, thus manifesting the dynamical instability of the sc structure. The opposite situation is observed for the sh structure [Fig. 1(b)], which is dynamically unstable below 80 GPa. Around this pressure the phonon dispersion displays longitudinal phonon mode instabilities at the points Y and S. An increase of pressure beyond 80 GPa lifts these instabilities. Above 130 GPa, the sh phonon spectrum shows no anomaly. We conclude that our calculated high-pressure behavior of the phonon spectra of the sc and sh phases correlates very well with the structural changes in phosphorus. The phase transition sc→sh takes place between 107 and 137 GPa.[4]

The softening of the longitudinal and transverse normal modes of the sc structure at X indicates a possible distortion along the [001] direction with polarization vectors [100] and [010]. A structural model for P-IV ($IM4$) was obtained as follows. The cell was doubled along the c axis, which is the propagation direction of the unstable transverse modes. Then square layers of atoms were shifted mutually along [110] and $[\bar{1}\bar{1}0]$, which is a linear combination of the polarization vectors [Fig. 2(a)]. This resulted in an orthorhombic arrangement of atoms with $C2mm$ space group symmetry. Initially, this arrangement was described with a C-centered cell of tetragonal metric representing a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the sc structure. Upon relaxation, the cell shape turns orthorhombic and the final structure attained the axis ratios $b/a \approx 1.17(1)$ and $c/a \approx 1.5(0)$ [Fig. 2(b)]. The atoms are located at $2a$ $(x_1,0,0)$, where $x_1 \approx 0.52$, and $2b$ $(x_2,0,0.5)$, where $x_2 \approx 0.67$. In the following, this structure is referred to as $IM4$. Most importantly, the $IM4$ structure is calculated to be dynamically stable in the intermediate pressure region between the sc→sh phase transition [Fig. 1(c)].

According to experiment, the phosphorus sh phase is most likely followed by a bcc phase at around 262 GPa.[1] Several theoretical works seem to confirm such a sh-bcc transition at high pressure. In addition, Ostanin *et al.*[10] also investigated the phonon dispersion of bcc-P and, interestingly, found a softening of the transverse mode (at point N) at a pressure very close to their predicted sh-bcc transition (258 GPa).[10] We confirm this result [Fig. 1(d)]. However, in addition to this, we find that at a slightly higher pressure (around 285 GPa) the frequencies of the transverse mode become imaginary, demonstrating the dynamical instability of the bcc structure. Thus, the bcc-P phase is *only stable over a limited pressure range* and cannot represent the end member of the high-pressure sequence of phosphorus. Similarly for the P-IV structure, we undertake a structural search for the post bcc-P structure on the basis of the instability of the phonon transverse branch $T_{[1\bar{1}0]}(110)$ at point N. The corresponding displacement of neighboring (110) planes in opposite $[1\bar{1}0]$ polarization directions is shown in Fig. 2(c). The resulting atom arrangement ($IM7$) is orthorhombic. The corresponding unit cell is a $\sqrt{2} \times \sqrt{2} \times 1$ supercell of bcc, containing four atoms [Fig. 2(d)].
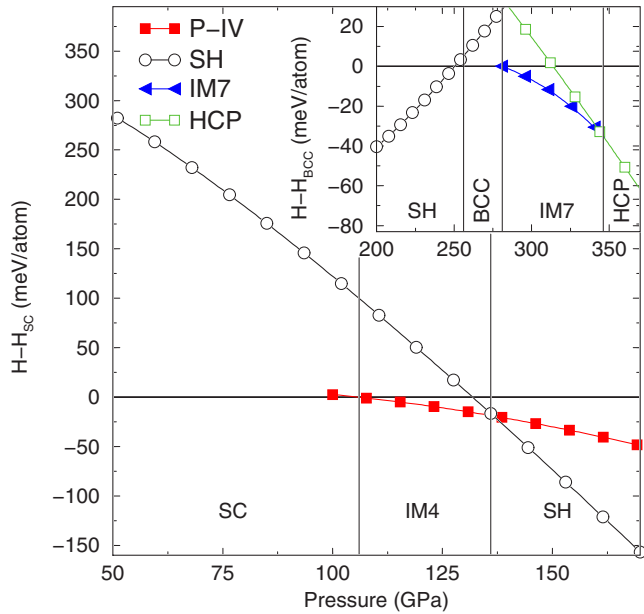
FIG. 3. (Color online) Calculated enthalpy vs pressure for various phases. For lower pressures, the sc structure is taken as a reference; for higher pressures (inset), enthalpies are shown with respect to the bcc structure.

In Fig. 3, we show enthalpy differences relative to the sc structure as a function of pressure. The sc phase is stable up to 106 GPa and then transforms to P-IV with the $IM4$ structure. $IM4$ (P-IV) transforms at 136 GPa to sh-P. The pressure region of stability for the $IM4$ (P-IV) phase matches excellently the experimental data. The most conspicuous feature of the $IM4$ structure [Fig. 2(b)] is the effect of the orthorhombic relaxation of the initial tetragonal cell, which gives the impression of an overall monoclinic distortion. The final atom arrangement appears similar to that of Ishikawa *et al.* obtained from metadynamics simulations. However, a quantitative comparison cannot be made since these authors did not report structural parameters for their model. It is crucial to mention that $IM4$ most likely only approximates the true structure of P-IV. The instability of the longitudinal branch in sc-P along the [110] propagation at around 0.4 of the $|\Gamma M|$ distance suggests the occurrence of a further, possibly incommensurate, modulation. Thus, similar to As, Sb, and Bi, P may also adopt an incommensurately modulated structure at high pressure. However, this structure would be completely different from the host-guest arrangement adopted by the heavier congeners.

At 281 GPa, bcc-P transforms to another intermediate phase for which we propose the $IM7$ structure [cf. Fig. 2(d)]. Finally, at 346 GPa, phosphorus attains the hexagonal close-packed (hcp) structure. The $IM7$ structure can be considered as a true intermediate of the bcc-hcp transformation. The crystallographic relation for this transformation was established by Burgers.[22]

The completely different high-pressure structural behavior of P and its heavier congeners must originate from differences in the electronic structure evolution as group 15 elements become compressed. All group 15 elements display a
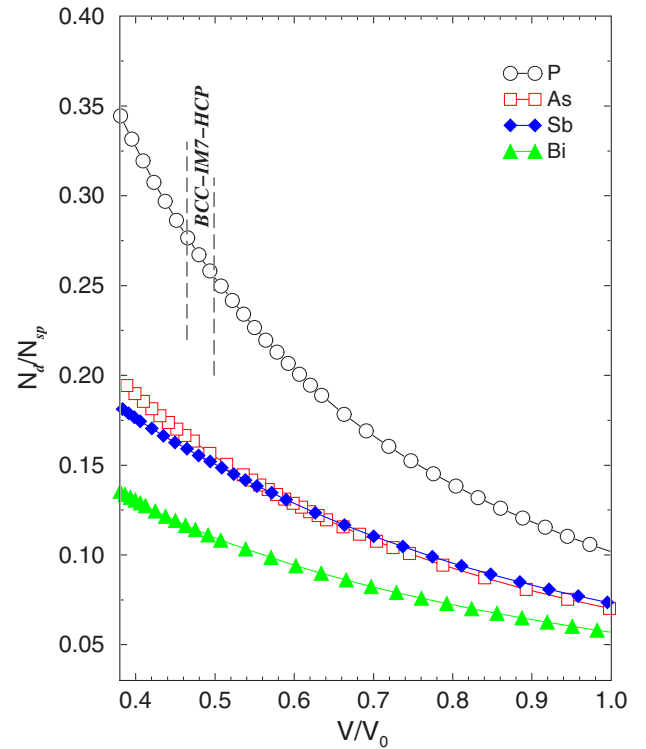

FIG. 4. (Color online) The relations between the d- and sp-occupation numbers (N_d/N_{sp}) for the bcc structure in P, As, Sb, and Bi as functions of compression (V/V_0). The region of the bcc $\rightarrow IM7 \rightarrow$ hcp transition sequence is indicated by the vertical dashed lines.

s^2p^3 ground-state electronic configuration. Under compression, higher lying d bands hybridize with sp bands, and sp electrons transfer partly to d states. In P there are no d electrons in the core and, thus, its $3d$ valence orbitals experience no repulsive core-orthogonality requirement. This ensures an effectively higher sp-d hybridization with the states at and below the Fermi level, compared to the heavier congeners. In Fig. 4, we depict the relation between d- and sp-occupation numbers for bcc P, As, Sb, and Bi as a function of compression (V/V_0).[23] The relative occupancy of d states in P is more pronounced even at ambient conditions ($V = V_0$) and increases essentially under compression, while in As, Sb, and Bi this increase occurs rather slowly. Eventually in the region of the bcc→hcp phase transition in P, the d-state occupancy exceeds 25%. As a consequence, the electronic structure of P at ultrahigh pressure starts to resemble that of the early transition metals from the groups III-IV, where the bcc β phase is stable at high temperature and, upon lowering the temperature, undergoes a martensitic transformation to the hcp α phase. These metals also display an instability of the branch $T_{[1\bar{1}0]}(110)$ at point N in the bcc structure [cf. Fig. 1(b)].[25,26]

In conclusion, our results have reproduced very well recent experimental data on high-pressure structural behavior of elemental phosphorus. We have identified the driving forces and mechanisms of the structural transition from the sc P-III structure into the hitherto undetermined intermediate P-IV phase. A structural model of P-IV, representing a basic structure for a more complex incommensurately modulated

structure, has been suggested. Further, we have shown that, contrary to common wisdom, the bcc P-VI structure does not represent the end member of the high-pressure structural sequence of phosphorus, but instead P transforms via an intermediate phase into the hcp structure. This result is, indeed, surprising because the bcc structure is most favorable from an electrostatic point of view. A transition from the bcc to hcp structure for elements under high pressure is very unusual and is only known for Ba and Fe. While the transition in Fe has a magnetic origin,[27] the transition in Ba is attributed to a peculiarity in the electronic structure which is caused by the $5d$ band just crossing the Fermi level.[28] The stabilization of the hcp over the bcc structure in P at ultrahigh pressure is explained by the significance of the sp-d hybridization due to the increase of the $3d$-band filling.

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