Origin of the simple modulated structures and the pressure induced superconductivity

H. Nagara¹, K. Mukose², T. Ishikawa³, M. Geshi⁴, and N. Suzuki⁵

¹Grad. School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan, ²Dept. of Electrical Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjyuku-ku, Tokyo 162-8601, Japan, ³Senior Research Fellow Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan, ⁴Organization for the Promotion of Research on Nanoscience and Nanotechnology, Osaka-University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan, ⁵Department of Pure and Applied Physics, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

E-mail: nagara@mp.es.osaka-u.ac.jp

Abstract. We have studied origins of the simple modulations of structures using first-principles calculations for group V, VI, and VII elements which have simple modulated structures. For the approximate structures which are defined by removing the modulations, we calculated phonon frequencies along the direction of the wave vectors of the modulation, and searched for possible phonon modes which may relate with the structural modulations. In phosphorus the Madelung energy works to destabilize the approximate monoclinic structure as well as the simple cubic and simple hexagonal structures, while it works to stabilize the approximate structures in other elements. Observing that the SC phase of phosphorus is stabilized by the band energies, we estimated the superconducting \( T_c \) in the SC phase. The calculated \( T_c \) remains at nearly same values in the SC phase. The electron phonon coupling increases with increasing pressure but the averaged phonon frequency decreases with increasing pressure, which is due to the increasing destabilizing effect of the Madelung energy.

1. Introduction

Simple modulated lattices have been observed in group V, VI, and VII elements. In those elements, iodine (I) of the group VII element was the first one in which simple modulated structure was reported in the sequence of successive phase transitions at high pressures[1]. In bromine (Br), nearly same sequence of structural phase transitions including modulated structure has been reported[2]. In group VI elements also, modulated structures were found in tellurium (Te), selenium (Se), and sulphur (S) under high pressure[3, 4, 5, 6] with another sequence of structural phase transitions including modulated structures. In the theoretical studies of group VI and VII elements, the dips in the phonon dispersion curves have been found in their approximate structures, which suggests the charge density waves (CDW) as the origin of the modulated structures. Lattice modulations driven by CDW suggests strong electron-lattice interaction and the relation between the CDW and the pressure-induced superconductivity in those elements has attracted much interest[7, 8, 9] and the superconductivity in those elements at high pressures has been studied in relation to the CDW[10].

A very simple modulated structure has been found[11], in phosphorus (P) of group V element also. The structure is observed in rather narrow pressure region from 107GPa to 137 GPa.
between simple cubic (SC) and simple hexagonal (SH) structures[7, 12]. Origin of the modulated structure in phosphorus has been studied also from the point of view of CDW[10, 13], but the origin of the modulated structure in this substance seems to be not so clear as the case of the group VI and VII elements.

2. Competing effects of the Madelung and the band energy on the structural stability

At high pressures where the electronic structures become metallic, the role of the electrostatic interaction between ions (Madelung energy) are expected to become more important with increasing pressure. We compared the total energies between the optimized modulated structure and the structure in which the modulation is removed with the unit cell shape and size fixed (we call this the approximate structure). The total energy decomposition into the electrostatic energy, that is Madelung energy ($E_M$), the band energy($E_b$), and the small remaining energy, can show the effects of each energy on the stability of the structures[14].

We studied P of group IV, S, Se, Te of group V, and Br, I of group VII elements, and found that $E_M$ and $E_b$ shows competing effects on the creation of the modulated structure. In the modulated structures above studied only phosphorus shows lowering of $E_M$ in the approximate structures by the creation of the modulation.

3. Phonons in ion-lattices

The ion-lattice is obtained from the real lattice by retaining only Madelung energy as the interaction between atoms. We have further studied the effects of each energy by comparing phonon frequencies of the ion-lattice with frequencies calculated with all energy contributions included.

![Figure 1.](image1.png)

**Figure 1.** Phonon dispersion of the SC ion-lattice along [001] direction. The longitudinal mode frequency becomes ion plasma frequency, $\omega_{PL}$, at $\Gamma$. The dashed lines are dispersion curves calculated by the Thomas-Fermi (TF) model. The difference in the transverse modes between the ion-lattice and the TF model is invisible. The low lying transverse mode frequencies are imaginary as shown by the negative value.

![Figure 2.](image2.png)

**Figure 2.** Phonon frequencies of the SC structure of phosphorus along [001] direction at 15GPa. Calculated phonon modes are stable all over the pressure region of the SC structure. The marks are data points calculated by the use of the codes ABINIT(x) and LMTO(*) respectively. The dashed lines are guides to the eye.
In the approximate structure of above elements, the ion-lattice phonon modes along the direction of the structural modulation are stable in I and Br. In group VI elements S, Se, and Te, the imaginary frequencies in the ion-lattice are only near the Γ-point which do not correspond to the modulation period. [Note that, in other directions, we find unstable modes of the ion-lattice, as is expected.]

In phosphorus, all transverse modes of the approximate monoclinic (MC) ion-lattice ($\gamma = 98^\circ$) along the direction of the structural modulation wave are unstable. The instability of the MC ion-lattice can not be recovered, even when the contributions from all energies are taking account, which is the reason why the modulated structure is realized.

In the SC lattice, the instability of the ion-lattice is blown away by the inclusion of the other energy contributions, which is shown in Figs. 1 and 2.

These observations suggest that main driving force of the modulated structure of phosphorus is the Madelung energy, which we call 'ION-LATTICE driven', and those in the other elements 'CDW driven'. This idea, however, does not answer the question about what should decide the modulation period. The ion-lattice is unstable for any wave vector along the direction of modulation. Probably delicate balance between the $E_M$ and the $E_b$ may decide the modulation period.

Summarizing the effects, we conclude that the roles of the $E_M$ and the $E_b$ contributions in P are in opposite direction to those in the other group VI and VII elements. This suggests the mechanism of the modulated structure in phosphorus is different from the mechanism in the other group VI and VII elements.

4. Superconductivity in phosphorus.

The simple modulated structure of phosphorus appears between SC and SH[15], and the superconductivity has been found in the SC phase below the modulated phase, while in the other group VII and VI elements the superconductivity has been observed at pressures higher than that of the modulated phase.

Table 1. Calculated parameters for the estimation of the superconductivity of phosphorus in SC and SH phase. These results are obtained with phonon modes of the phonon wave number $q$ on 8x8x8 mesh. The pressures are theoretical values obtained at the lattice constants of experimental values. The $\mu^*$ is assumed to be 0.10 or 0.12. Note that the $\lambda$ increases but the $\omega_{log}$ decreases with increasing pressure. The experimental values of $T_c$ in SC exist in the range 6 K to 9.6 K in the pressure range 15GPa to 50GPa and above that pressure the experiment reported rapid fall of $T_c$ with increasing pressure[7]. No observed $T_c$ has been reported in SH.

| Phase | SC Pressure | SH Pressure |
|-------|-------------|-------------|
|       | 15GPa       | 39GPa       | 81GPa       | 135GPa      | 212GPa     |
| $\lambda$ | 0.63 | 0.62 | 0.91 | 0.41 | 0.54 |
| $\omega_{log}$ | 435 K | 399 K | 192 K | 415 K | 168 K |
| $T_c$ ($\mu^* = 0.10$) | 11.9 K | 10.2 K | 11.5 K | 2.0 K | 2.8 K |
| $T_c$ ($\mu^* = 0.12$) | 9.7 K | 8.2 K | 10.2 K | 1.2 K | 2.1 K |

We further report on the role of the Madelung energy in phosphorous in relation to the superconductivity. As is observed in the experiments, the superconducting transition temperature $T_c$ in the modulated phase is suppressed or very low. We also calculated the $T_c$ in the modulated structure and obtained low $T_c$, which will be published elsewhere. The superconductivity, in phosphorus, has not been reported in and above the modulated phase,
while in the other group VI and VII elements superconductivity is found with low \( T_c \) in the modulated phase and \( T_c \) rises at higher pressures after the modulations disappear\[7, 8, 9\]. In the SC phase of phosphorus the band energy sustain the stability of the SC lattice, as is observed above, and the strong electron-lattice coupling may be expected. In fact, the experimentally observed superconducting \( T_c \) in the SC phase of phosphorus is rather high compared with the other group VI and VII elements which have modulated structures.

We theoretically calculated the \( T_c \)’s and obtained values in nearly same range as the experiment\[7\]. We show in Table 1 our calculated \( T_c \) with the parameters used in the estimation of the \( T_c \). Our results of the \( T_c \) in SC show no significant change with increasing pressure and do not show sharp decrease with increasing pressure like the experimental \( T_c \), but the averaged phonon frequency, \( \omega_{\text{log}} \) decreases rapidly with increasing pressure, which suggests the effect of the Madelung energy destabilising the SC lattice.

**Figure 3.** Pressure dependence of the calculated DOS in the SC-phase of phosphorus. The DOS change is slight in the pressure region of SC, as shown in this figure.

**Figure 4.** Pressure dependence of the calculated DOS in the SC-phase of Ca. The DOS increases very much as the pressure approaches the upper boundary of the pressure of SC (108GPa).

Above the modulated phase of phosphorus, the SH phase has been reported by the experiment\[7\]. We made similar calculations in SH. The calculated \( T_c \) in this phase is low
compared with that in the SC phase and shows slight increase with increasing pressure. Similar effect of the $E_M$ as in the SC phase is observed in the SH phase, as is shown in Table 1.

Finally we compare the behavior of the $T_c$ in the SC phase of Calcium (Ca) with that of phosphorus. In Ca the $T_c$ rises rapidly with increasing pressure and reaches to 25 K which is the highest among the elements[16]. In phosphorus the electronic density of states (DOS) at the Fermi-level shows no significant changes as is shown in Fig.3, while the DOS of Ca increases very much as is shown in Fig.4. The big change of the DOS at the Fermi level can be attributed to the sharp increase of $T_c$ in the SC structure of Ca.

References
[1] Takemura K, Sato K, Fujihisa H and Onoda M 2003 Nature 423 971
[2] Kume T, Hiraoa T, Ohya Y, Sasaki S and Shimizu H 2005 Phys. Rev. Lett. 94 065506
[3] Hejny C and McMahon M.I 2003 Phys. Rev. Lett. 99 245502.
[4] McMahon M.I, Hejny C. Lovday S.J, Lundegaad L.F and Hanfland M 2004 Phys. Rev. B 70 054101.
[5] Hejny C, Lundegaad L.F, Falconi S, McMahon M.I and Hanfland M 2005 Phys. Rev. B 71 020101(R)
[6] Degtyareva O, Gregoyanetz E, Somayazulu M, Mao H.K and Hemley R.J 2005 Phys. Rev. B 71 241404
[7] Amaya K, Shimizu K, Eremets M.I, Kobayashi T.C, and Endo S 1998 J. Phys. Condens. Matter 10, 11179.
[8] Karuzawa M, Ishizuka M and EndoS 2002 J. Phys.: Condens. Matter 14 10759
[9] Gregoryantz E, Strutzhin V.V, Hemley R.J, Eremets M.I, Mao H.K and Timofeyev Y.A 2002 Phys. Rev. B 65 064504
[10] Degtyareva O, Magnitskaya M.V, Kohanoff J, Profeta G, Scandolo S, Hanfland M, McMahon M.I and Gregoryantz E 2007 Phys. Rev. Lett. 99 155505
[11] Ishikawa T, Nagara H, Kusakabe K and Suzuki N 2006 Phys. Rev. Lett. bfl 96 095502
[12] Fujihisa H, Akahama Y, Kawamura H, Ohishi Y, Gotoh Y, Yamawaki H, Sakashita M, Takeya S and Honda K 2007 Phys. Rev. Lett. bf 98 175501
[13] Marques M, Ackland G.J, Lundegaad L.F, Falconi S, Hejny C and McMahon M.I 2008 Phys. Rev. B 78 054120
[14] Ishikawa T, Nagara H, Mukose K, Kusakabe K, Miyagi H and Suzuki N 2008 Int. J. High Press. Research 28 459
[15] Akahama Y, Kobayashi M and Kawamura H 1999 Phys. Rev. B 59 8520
[16] Yabuuchi T, Matsuoka T, Nakamoto Y and Shimizu K 2006 J. Phys. Soc. Jpn. 75 83703