# Electronic Structure and Stability of the Pd-Ni-P Bulk Metallic Glass

Tsunehiro Takeuchi[1,2,3], Daisuke Fukamaki[3], Hidetoshi Miyazaki[4], Kazuo Soda[4],
Masashi Hasegawa[5], Hirokazu Sato[6], Uichiro Mizutani[7],
Takahiro Ito[8] and Shinichi Kimura[8]

[1]*EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan*
[2]*Department of Crystalline Materials Science, Nagoya University, Nagoya 464-8603, Japan*
[3]*Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan*
[4]*Department of Quantum Engineering, Nagoya University, Nagoya 464-8603, Japan*
[5]*Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan*
[6]*Department of Physics, Aichi University of Education, Kariya 448-8542, Japan*
[7]*Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan*
[8]*UVSOR facility, Institute for Molecular Science, Okazaki 444-8686, Japan*

In order to investigate the stabilization mechanism of the Pd-Ni-P bulk metallic glass (BMG), electronic structure of the $(Ni,Pd)_9P$ trigonal clusters with a phosphorus atom in the center and that of the relevant crystals were investigated by use of first principle calculations; discrete variational X$\alpha$ potential (DVX$\alpha$) cluster calculation and full potential linearized augmented planewave (FLAPW) band calculation. Presence of the covalent bonds between phosphorus and nickel/palladium was confirmed in the relevant crystals by observing their density of states, that is characterized by the narrow bandwidth and the eigen values well reproduced by the $(Ni,Pd)_9P$ cluster calculation. We found, as a consequence of the theoretical calculations, that the electronic structure and the number of electrons in the trigonal cluster allow the (Ni,Pd) atoms at the vertices and sides of the clusters to be shared by the neighboring ones, and that the connection-direction and connection-angle of the cluster do not significantly alter the cluster levels nor the internal energy of the cluster. Consequently the network of the cluster has large degree of flexibility with keeping the low internal energy. These characteristics lead to the highly-stable Pd-Ni-P BMG.   [doi:10.2320/matertrans.MF200617]

## 1. Introduction

Bulk metallic glasses (BMGs) have attracted a great deal of interests because of their ability in practical usage, such as mechanical parts of high strength, surface coating materials with high degree of hardness, soft-magnetic materials, etc.[1] In order to design the BMGs suited for each practical usage, stabilization mechanism of the BMG's has to be revealed from microscopic view points; the local atomic arrangements and the electronic structure. Since it is naturally considered that the highly-stable BMGs possess a low free-energy together with a large activation energy for crystallization, the stabilization mechanism of BMG's should be discussed in terms of free-energy and activation energy for crystallization.

One may easily realize that the free-energy of an amorphous solid is reduced when it consists of characteristic clusters of low internal energy and these clusters are connected randomly without altering the internal energy of the clusters. Silica glasses are known to possess such characteristics; $SiO_4$ tetrahedral clusters of low internal energy construct a random network by sharing oxygen atoms at the vertices of the tetrahedron with flexibility in their connection-direction and connection-angle. The low internal energy of the $SiO_4$ clusters are brought about by the $s, p$-electron based covalent bonds. Presence of the relatively large, stable, rigid $SiO_4$ units leads to the large activation energy for crystallization and, therefore, prevents the system from easily crystallizing at a given temperature. Thus, both necessities for the stable amorphous solid are realized in the silica glasses.

We also found, in our resent work,[2,3] that covalent bonds persist in the Zr-based BMGs, and lead to the significant reduction in the internal energy and increase the activation energy for crystallization by producing a large, stable prism clusters. The covalent bonds in the Zr-based BMGs are mainly produced by the hybridization between Zr $d$-orbitals and $s, p, d$-orbitals of the neighboring atoms. The Zr-based BMGs also possess metallic bonds especially around the simple metal and noble metal elements, and that the clusters of the metallic nature, which are considered as the Kasper polyhedra including the well-known icosahedron, play a role to connect the covalent clusters of low internal energy with large degree of freedom in the direction of the inter-cluster-connections. It is strongly argued, therefore, that (a) the presence of the covalent bands in the local atomic arrangements to reduce the internal-energy and (b) the possession of a mechanism to construct the random network of the covalent clusters without altering the low internal-energy of the clusters are observable both in silica glass and Zr-based metallic glasses, and that these two conditions would be the common factors to stabilize the amorphous phase.

In order to further confirm this scenario, we investigate, in this study, the electronic structure of the Pd-Ni-P BMG, that is one of the most famous, stable BMGs obtained in metal-metalloid systems.[4] We employed the relevant crystals to investigate the stability of the Pd-Ni-P BMG in the same way as we did in our previous study on the Zr-based BMGs.[2,3] By making full use of the relevant crystals with the first principle cluster calculation and band calculation, we demonstrate that the local atomic arrangements of the Pd-Ni-P BMG and its relevant crystals are indeed characterized by the covalent bonds, and that large degree of freedom in the inter-cluster-
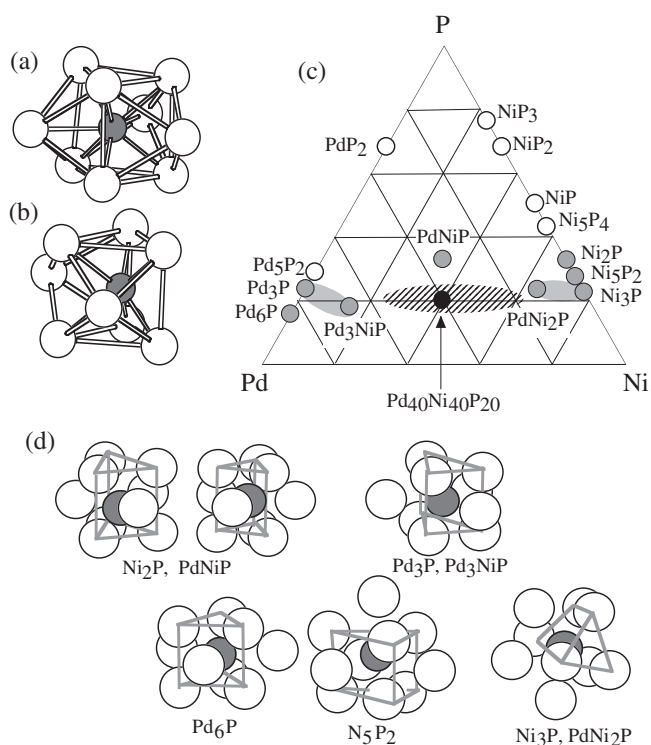
Fig. 1 (a) Trigonal prism cluster and (b) tetragonal dodecahedron cluster exist in the Pd-Ni-Cu-P bulk metallic glass. Ref. 7) (c) Composition diagram in which compositions of the bulk metallic glass (the solid circle and hatched area) are plotted with that of the relevant crystals (the open circles, gray circles, and gray area). The relevant crystals of the gray circles possess the characteristic clusters as those in the bulk metallic glass. Those clusters are shown in (d).

connection enhances entropy without significantly altering the internal energy of the clusters.

## 2. First Principle Calculations

We employed, in this study, the first principle cluster- and band-calculations of the distributed package programs, DVX$\alpha$ and Wien2K, respectively. The former uses the X$\alpha$ potential with the wave functions obtained by linear combination of atomic orbitals, and the latter the generalized gradient approximation (GGA) with the full potential linearized augmented planewave (FLAPW). Details of these calculations were reported elsewhere.[5,6]

Generally speaking, band calculations are not applicable for the amorphous materials because of their lack of the periodicity. We therefore used the FLAPW method to reveal the band structure of the relevant crystals, $Ni_2P$, PdNiP, and $Pd_3P$. The cluster calculation, on the other hand, is applicable even for the amorphous materials provided that the local atomic arrangements were already known. Fortunately, the local atomic arrangements of the BMG have already been investigated by a large number of studies.[7–10] The trigonal prism cluster and the tetragonal dodecahedral cluster,[7] shown in Fig. 1(a) and (b), respectively, were proposed for the structure units constructing the Pd-Ni-Cu-P metallic glass. Notably, these clusters also exist in the relevant crystals, such as PdNiP, $Ni_2P$, $Pd_3P$, $Pd_3NiP$, $Pd_6P$, $Ni_5P_2$, $Ni_3P$, and $PdNi_2P$.

The tetragonal dodecahedral cluster is obtained by slightly deforming the trigonal prism cluster, indicating both cluster's possession of the similar electronic structure and consequently of the similar internal-energy. Therefore we calculated the cluster levels only of the trigonal prism cluster as a structure unit of the BMG and relevant crystals.

## 3. Results

Figure 1(c) shows a composition diagram on which the composition of the most stable BMG, $Pd_{40}Ni_{40}P_{20}$, is plotted together with that of the relevant crystals. Local atomic arrangements about phosphorus atom in these relevant crystals[11,12] are shown in Fig. 1(d). One may easily realize that the phosphorus atoms in the relevant crystals are surrounded by Pd and Ni atoms to form the trigonal prism cluster or tetragonal dodecahedral cluster as well as those reported for the Pd-Ni-P BMGs.[7] It is, therefore, naturally expected that the trigonal prism structure with a phosphorus atom in its body-center has low internal energy and contributes to reduce the free-energy of the relevant crystals and perhaps of the bulk metallic glass.

In the first step, we calculate the density of states of the three relevant crystals, $Ni_2P$, PdNiP, and $Pd_3P$, by using the FLAPW method. The structure reported in the Peason's handbook[11] were used for the calculations. The resulting density of states $N(E)$ is plotted in Figs. 2(a)–(c). Since the relevant crystals have almost the same local atomic arrangements about phosphorus, all relevant crystals show the similar characteristics in $N(E)$ which are described below in detail.

The band at $-15\,\mathrm{eV} < E - E_F < -12\,\mathrm{eV}$ marked as A in Fig. 2 consists mainly of phosphorus $3s$ and $s$ of nickel/palladium at the vertices of the trigonal prism cluster. Here $E_F$ indicates the Fermi level. This A-band has bonding nature, and the corresponding anti-bonding band is located more than $5\,\mathrm{eV}$ above $E_F$. Two groups of bands observed at $-10\,\mathrm{eV} < E - E_F < -5\,\mathrm{eV}$ marked with B and C contain mainly phosphorus $3p$-electrons. In addition to the phosphorus $3p$ electrons, the these bands has $d$-components from palladium/nickel located at the vertices and sides of the trigonal prism cluster. These bands also have bonding nature, and the bands located just above $E_F$ marked as F are assigned as the corresponding anti-bonding bands. The role of hybridization between phosphorus and transition metal elements on stabilization mechanism of the BMG and its relevant crystals will be discussed in more detail after showing the cluster levels later.

These $s$, $p$-dominant bands marked as A~C possess much narrower bandwidth than the free electron like $s$, $p$-bands in the typical metallic phases, such as fcc aluminum shown in Fig. 2(d). This fact indicates that covalency develops in the $s$, $p$-orbitals in the relevant crystals of the Pd-Ni-P BMG as those in the silica glass. The $s$, $p$-dominant bands of the relevant crystals (A~C) are located at lower energy than those in the fcc Al. This feature would be responsible for the development of the covalent bonds rather than the metallic bonds.

One may naturally consider that the covalent nature is brought about by the metalloid element, phosphorus. This
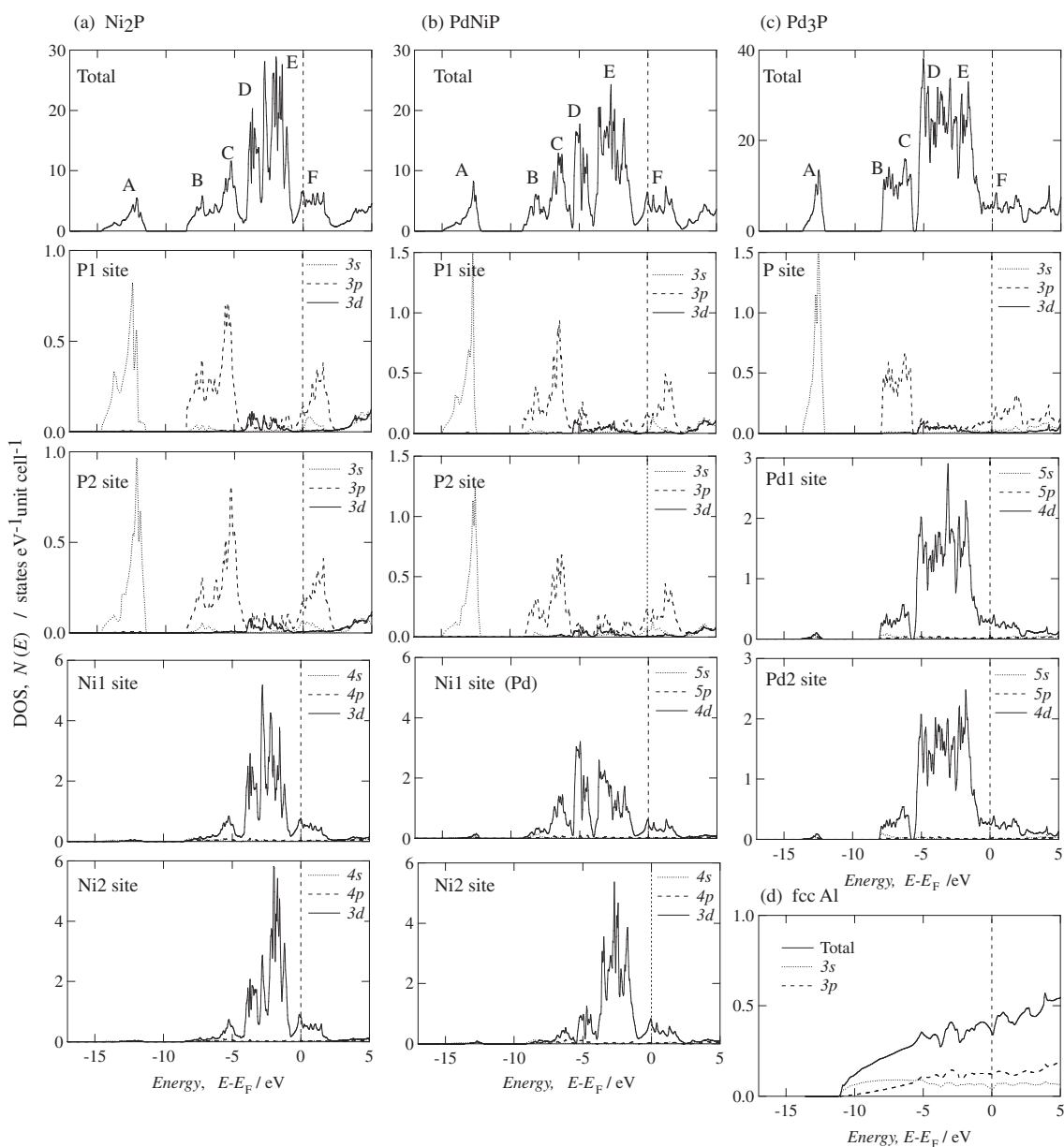
Fig. 2 Electronic density of states of the relevant crystals, (a) Ni$_2$P, (b) PdNiP, and (c) Pd$_3$P calculated by the FLAPW-GGA method (Wien2K). The total density of states is shown together with the partial density of states for each atomic sites, the name of which was reported in Ref. 11). The structure of the PdNiP were obtained by replacing nickel atoms in Ni1 site of the Ni$_2$P with palladium. All phosphorus sites in these three relevant crystals are surrounded by nickel and/or palladium atoms to form a trigonal prism cluster. The density of states of fcc Al, that possesses an electronic structure well accounted for with the nearly free electron approximation, are shown in (d). The density of states of the relevant crystals are commonly characterized by possession of the narrow bands marked as A∼F.

consideration is fully consistent with the presence of the phosphorus atom in the center of the characteristic cluster (the phosphorus centered trigonal prism cluster). Indeed, the bonding bands including the phosphorus *s*, *p*-components stay in the relatively low energy range, and the important role of the phosphorus on the covalent bonds is well confirmed.

The bands mainly consisting of the *d*-components of the transition metal elements exist at $-5.5\,\text{eV} < E - E_\text{F} < 0\,\text{eV}$ as marked with D and E in Fig. 2. These bands contain very small amount of the components form the phosphorus. Nearly 90% *d*-orbitals of the transition elements have nonbonding nature and its contribution to stabilize the cluster is of less importance. It is also easily realized that the energy-width of the *d*-bands becomes wider when palladium is

involved as one of the constituent elements. This palladium-induced widening of the band is caused most likely because the larger extent of *d*-orbitals in palladium than that of nickel leads to the larger transfer integral with the neighbouring atoms.

Fermi level is located in the *p*, *d* anti-bonding bands marked with F in Fig. 2. The metallic electrical conduction in the relevant crystals is caused by these bands. Note here that it is not necessary to consider the metallic cohesive energy for its stabilization mechanism even though a BMG and its relevant crystals have metallic electrical conduction. Indeed, the band structure of the relevant crystals are well accounted for almost solely by the cohesive mechanism of covalent bonds.
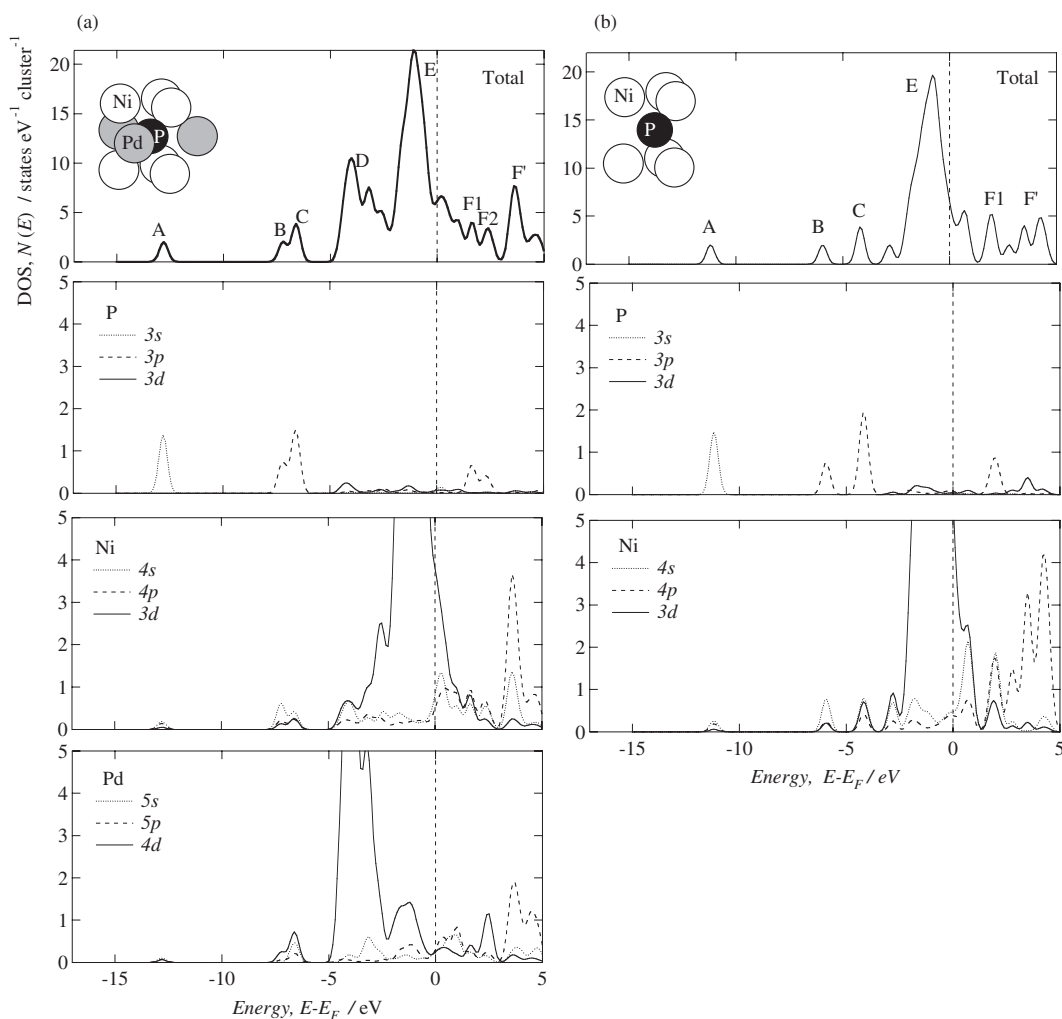
Fig. 3 Electronic density of states for the (a) $Pd_3Ni_6P$ and (b) $Ni_6P$ trigonal prism clusters. The schematic illustration of the cluster is shown in insets. Electronic structure of these clusters shows nearly the same characteristics except for $Ni_6P$'s absence of peaks D and F2, which come from palladium atoms at the sides of the prism cluster.

Figure 3(a) shows the density of states deduced from cluster orbitals calculated by the DVXα method for the $Pd_3Ni_6P$ trigonal cluster found in the PdNiP relevant crystals. To obtain the density of states, each cluster level was broadened by multiplying a gaussian-function of 0.2 eV in width.

The bands obtained by the FLAPW method are qualitatively reproduced by the cluster calculations as marked with A~F in Fig. 3(a). It is, therefore, strongly argued that the electronic structure of the relevant clusters and perhaps that in the corresponding BMGs are determined solely by the local atomic arrangements about the phosphorus atom. One may also realize that each cluster level has slightly different energies from those calculated by the FLAPW method. These differences are mainly caused by the difference in the coulomb potential between the crystalline solid and isolated cluster. Since the coulomb potential in the cluster is different form that in the solid, we do not have to seriously consider the minor difference of the energy levels. We stress here, however, that presence of the bonding-orbitals, which are A~C, is more important for the stability of the local atomic arrangements and their constructing phases.

By using the cluster orbitals, we gain deeper insight into the hybridization of each atomic orbitals. The structure in the $N(\varepsilon)$ marked with B and C in Fig. 3 are made up with three cluster orbitals mainly containing phosphorus $3p$ and palladium/nickel $s$, $p$, $d$. Phosphorus $3p_z$ are more overlapped with $s$, $p$, and $d$ orbitals of the nickel at the vertices of the prism, while the remaining $3p_x$ and $3p_y$ orbitals overlap mainly with $s$, $p$, $d$-orbitals of the palladium atoms at the three sides of the trigonal prism cluster. By observing components of the each cluster levels, we safely assigned that the band-B is made up with $3p_z$ of the phosphorus and $s$, $d$ of the nickel at the vertices, while the band-C with $3p_x/3p_y$ of the phosphorus and $s$, $p$, $d$ of the palladium at the side of the cluster. Both B- and C-bands have bonding nature, and the the corresponding anti-bonding bands are located above $E_F$ as marked with F1 and F2 in Fig. 3(a), respectively.

We also calculated the cluster orbitals with removing the palladium atoms from the sides of trigonal prism cluster to investigate the effect of the hybridization between phosphorus and transition metal elements at the side of the prism. The resulting density of states is shown in Fig. 3(b). Despite the minor differences, the $s$, $p$-dominant cluster-orbitals of bonding nature (A~C) stay essentially the same energy range. Therefore presence or absence of the transition metal
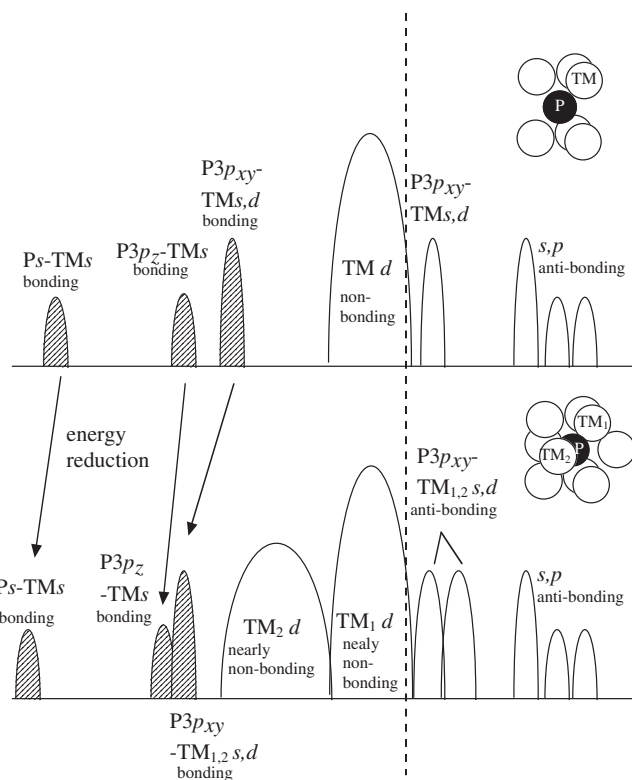
Fig. 4 Schematic illustrations of the electronic structure of the trigonal cluster. Important role of the *s*, *p*-dominant bonding band A∼C and a minor role of the *d*-bands to stabilize the structure are clearly understood. Less important role of the palladium/nickel atoms at the side of the trigonal cluster is also understood by comparing the electronic structures with/without those atoms as schematically illustrated.
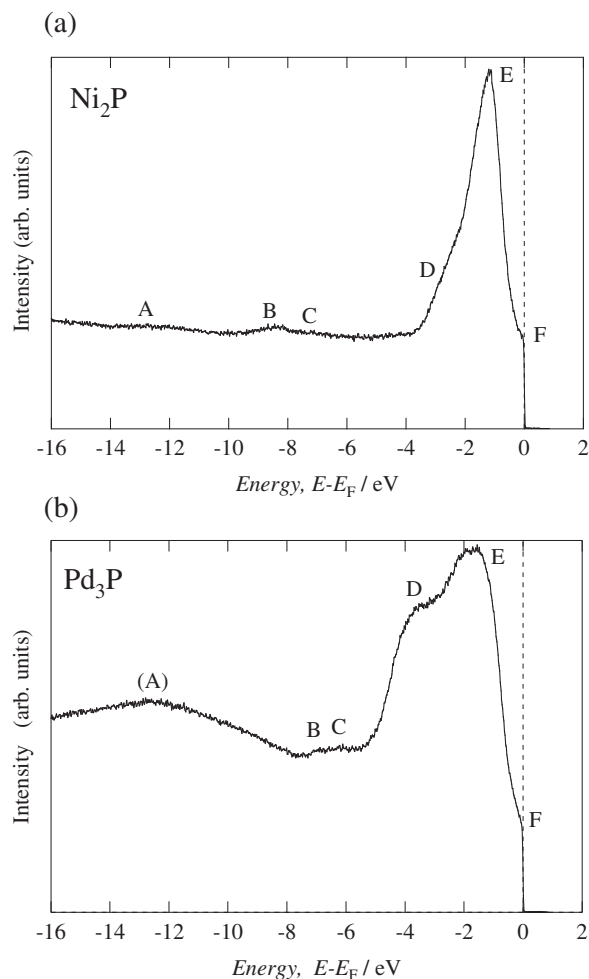


Fig. 5 Photoemission spectra of the (a) $Ni_2P$ and (b) $Pd_3P$ relevant crystals measured with an incident photon energy of 40 eV. The characteristics of electronic structure expected from band-calculation and cluster-calculation are qualitatively reproduced in the spectra. Splitting between D and F becomes larger with Pd atoms because of their large extent of the atomic orbitals. Large spectral weight at (A) of the $Pd_3P$ comes from unidentified extrinsic extrinsic, such as secondary electrons or surface contamination.

elements at the sides of the trigonal prism has less important role in stabilizing the relevant crystals and perhaps to that of the bulk metallic glasses.

Although their presence is not of crucially importance, the transition metal elements at the sides of the cluster still contribute to reduce the internal energy of the cluster. This is confirmed by observing that the energy of the bonding-bands A∼C were slightly increased when the palladium atoms at the sides of the cluster are removed. Simultaneously, one of the nonbonding *d*-bands assigned as D was disappeared together with the $p - d$ anti-bonding bands of F2. We also found, by removing palladium atoms, that the components from the transition metal elements in the band-C is significantly reduced, and the energy difference between the bands C and B becomes larger. It is, therefore, considered that the hybridization between phosphorus *p* and *d* of the transition metal elements pushes the *p*-bands (B and C) towards lower energy with mixing the small amount of *d*-components in the *p*-bands, and creates the corresponding anti-boding bands above the nonbonding *d*-bands. The same role is expected for the *d*-orbitals of the nickel atoms at the vertices. This scenario is well understood from the detailed assignment of the bands schematically drawn in Fig. 4.

In order to confirm the reliability of the present calculations, we measured the photoemission spectra of the relevant crystals, $Ni_2P$ and $Pd_3P$, with an incident energy of $h\nu = 40$ eV at the BL-5U of the synchrotron radiation facility UVSOR in Okazaki, Japan. The resulting photo-

emission spectra are shown in Figs. 5(a) and (b). The detailed structures observed in these photoemission spectra were successfully assigned with the bands A∼F of our present calculation on the relevant crystals and the trigonal prism cluster. The photoemission spectra of the Pd-Ni-P BMG reported by several different groups[13–15] also show similar characteristics. These experimental facts indicate reliability of our present analysis and usefulness of relevant crystals to investigate the stability of the BMG.

## 4. Discussion

By calculating electronic structure of the relevant crystals and the characteristic clusters, we realized that the trigonal prism clusters, $(Pd,Ni)_9P$, would be very stable because of their possession of the *s*, *p*-dominant covalent bonds about the phosphorus atom, and that these trigonal prism clusters behave as structure units in the relevant crystals and perhaps in the corresponding bulk metallic glass. However, even if it has the stable structure units (clusters) possessing extremely
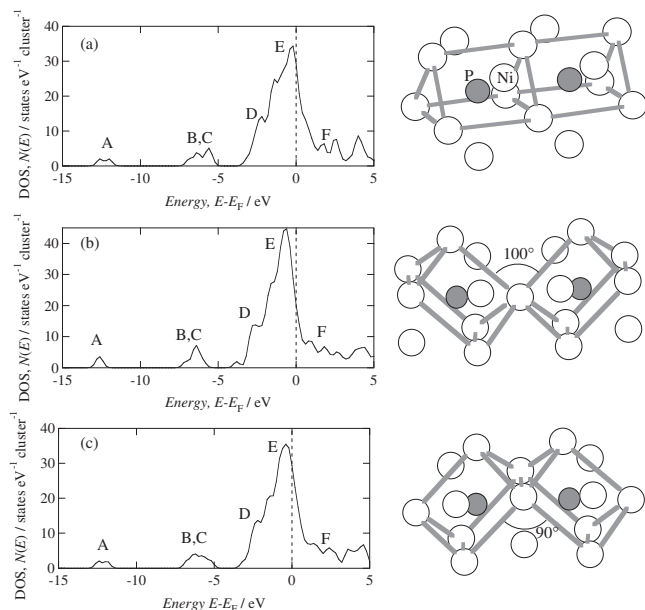
Fig. 6 Density of states of the clusters consisting of two trigonal clusters. Two trigonal prism clusters are connected with (a) face-, (b) edge- and (c) vertex-sharings. Presence of the bands A~F are persisted in the same way as those in a single trigonal cluster.
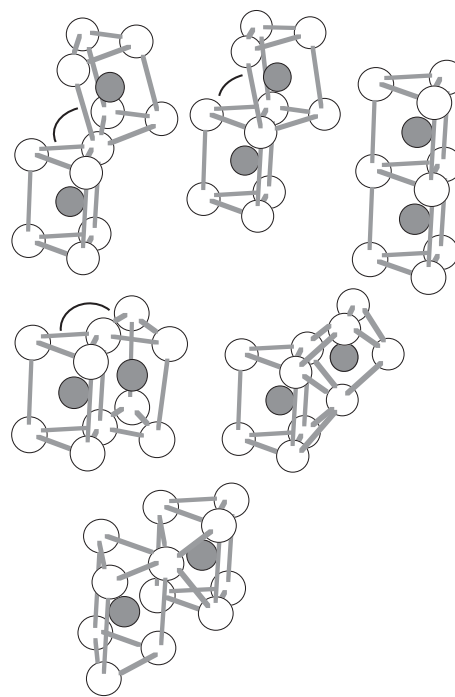


Fig. 7 Schematic illustrations of possible connections of the trigonal prism clusters. Large degree of freedom is easily expected for the inter-cluster-connection.

low internal energy, the metallic glass cannot be stabilized without a specific mechanism leading to a random network of the clusters. It should be realized only when the inter-cluster bonds have flexibility in its angle and direction. Therefore, we discuss whether the phosphorus centered trigonal prism clusters can be connected with a large degree of flexibility in their connection angle and direction.

It is naturally considered that the palladium/nickel atoms in the trigonal prism cluster provide some electrons into the bonding-bands (A~C) because there are four orbitals of bonding nature which is able to contain eight electrons, while the phosphorus atoms has five $s$, $p$-electrons. Three vacancies in the bonding-bands are filled by the 3 electrons from the surrounding 9 palladium/nickel atoms, and therefore each palladium/nickel atom provides 0.33 ($= 3/9$) electrons to the bonding orbitals. Since each palladium/nickel atoms has 10 valence-electrons, remaining 9.67 electrons mainly fill the nonbonding d-bands marked as D and E. Note here that most of the $s$, $p$-components of the palladium/nickel atoms are lifted up into the anti-bonding bands located above $E_F$ and stay unoccupied. Thus the (Pd,Ni)$_9$P cluster is highly stable, because almost no electrons fill the anti-bonding bands while the bonding bands are fully occupied.

When the palladium/nickel atoms at the surface of the trigonal prism clusters are shared, on average, by two neighboring clusters, each palladium/nickel atom turns out to provide 0.67 ($= 3/(9/2)$) electrons to the bonding orbitals. This condition leads to a reduction in the number of electrons in the nonbonding $d$-bands, and consequently to the reduction both of the Fermi level and total energy of the electrons. This energy reduction must cause the condensation of the clusters.

We also realized that the presence of the bonding levels does not significantly altered by the angle nor the direction of the cluster-connection because the orbitals of bonding nature are mainly composed of $s$ and $p$ components of the

phosphorus at the center of the cluster. The $p_x$ and $p_y$ dominant orbitals ($p - d$ bonding orbitals) would be slightly affected by variations in the angle and direction of the inter-cluster connection because of the $p - d$ hybridization, but its effect is considered not to be very serious because we already conformed that the eigen values of the bonding bands have small variation with presence or absence of the palladium/ nickel atoms at the sides of the trigonal prism cluster. (See Figs. 3(a) and (b)).

In order to prove this scenario, we calculated the cluster orbitals of some different inter-cluster-connections. Three different clusters consisting of two prisms and the resulting density of states are shown in Fig. 6. Obviously the electronic structure does not significantly altered by the inter-cluster connection with keeping the bonding-bands (A~C) far below the Fermi level. These characteristics must lead to flexible connections of the clusters as schematically drawn in Fig. 7. Consequently (Pd,Ni)$_9$P clusters are able to construct a random network to form the bulk metallic glass without significantly increasing their internal energy. The enhanced entropy and the small internal energy result in the very low free-energy of the BMG.

We conclude, therefore, that the Pd-Ni-P BMG is stable because of the random cluster network of the rigid, stable, large structure unit (cluster) of covalent nature. As it is already argued in Introduction, this stabilization mechanism is applicable for the Zr-based BMG's and even for the silica glasses, and, therefore, commonly acceptable for highly-stable amorphous solids.

Finally, we comment on the composition of the most stable Pd-Ni-P bulk metallic glass. Since the results obtained by the present analysis on the electronic structure suggest that the (Pd,Ni)$_9$P clusters construct a random network with the

palladium/nickel atoms on the cluster surface being shared by the neighbouring clusters. If all palladium/nickel atoms are shared, on average, by two clusters, the composition of the BMG is predicted to be $(Pd,Ni)_{4.5}P = (Pd,Ni)_{81.8}P_{18.2}$, which has almost the same phosphorus concentration with $Pd_{40}Ni_{40}P_{20}$ where the most stable BMG is observed. Slightly larger phosphorus concentration in the calculated value is compensated, if there exists, on average, one vacancy in the (Pd,Ni) sites of each prism cluster. This condition leads to the composition of BMG as $(Pd,Ni)_4P = (Pd,Ni)_{80}P_{20}$. The assumption of the vacancies sounds reliable partly because the (Pd,Ni) atoms at the sides of the prism cluster have less important role in reducing internal energy of the cluster, and partly because the introduced vacancies naturally lead to increase of the entropy. Since palladium and nickel stay in the same column in the periodic table, substitution of palladium for nickel would not cause a significant variation in the electronic structure nor the internal-energy but in the entropy, which becomes maximum at Pd : Ni = 50 : 50. It is, therefore, concluded that the minimum in the free energy of the Pd-Ni-P should be obtained at $(Pd_{0.5}Ni_{0.5})P_{20} = Pd_{40}$-$Ni_{40}P_{20}$. This composition is indeed good consistency with that of the most stable BMG.

## 5.  Conclusion

By calculating electronic structure of the relevant crystals and that of the $(Ni,Pd)_9P$ trigonal prism clusters with a phosphorus atom in the center, we found that the trigonal prism cluster has covalent nature and highly-stable, and that it persists as a structure unit in the relevant crystals and perhaps in the corresponding bulk metallic glasses. The electronic structure of the trigonal cluster allow the palladium and nickel atoms at the vertices to be shared by the neighboring clusters without seriously altering the eigenval-

ue of the cluster orbitals. This characteristic leads to the large degree of flexibility in the direction and angle of inter-cluster-connections. Consequently the network of the cluster has large degree of flexibility to build a random structure with keeping the low internal energy of the clusters. This mechanism must lead to the highly-stable Pd-Ni-P bulk metallic glasses.

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