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# Local Structure around Pd Atoms in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ Excellent Glass-Former Studied by Anomalous X-ray Scattering

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In order to study local structure around the Pd atoms in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent metallic glass-former, an anomalous X-ray scattering (AXS) experiment was performed at energies close to the Pd K absorption edge at the beamline BM02 of the European Synchrotron Radiation Facility. The differential structure factor, $\Delta_{Pd}S(Q)$, was obtained with a good statistical quality, which demonstrates that a pre-shoulder at about $20\,nm^{-1}$, indicating the existence of an intermediate-range order, originates from the Pd-Pd atomic correlation. The first peak in the differential pair correlation function, $\Delta_{Pd}g(r)$, shows a longer inter-atomic length around the Pd atoms than the average value. The local structure around the Pd atoms is discussed in detail by comparing to the previous experiments of AXS and electronic structure.
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## 1. Introduction

Bulk metallic glasses of Pd-Ni-Cu-P alloys, discovered by Nishiyama and Inoue,[1)] have been intensively investigated due to their good glass-forming abilities (GFA). They have optimized the concentration dependence of the critical-cooling-rate (CCR), and found that $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ has at present the lowest CCR of 0.067 K/s among metallic glasses and can form a massive bulk glass with a diameter of more than 40 mm by simple water-quenching.[2)]

Although several thermodynamic and mechanical properties have been investigated in detail in the Pd-Ni-Cu-P glassy alloys,[2)] only a few basic attempts have been made from the viewpoints of their structural and electronic properties, to understand why it has such an excellent GFA. In order to clarify the role of electronic structure in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ glass by comparing the $Pd_{40}Ni_{40}P_{20}$ reference glass, having a worse CCR of about 1.6 K/s,[3)] several electronic spectroscopic measurements were performed using synchrotron radiation, and partial density of states (DOS) of Pd 4d, Ni 3d, and Cu 3d electrons were estimated.[4)] It was found that the Pd 4d partial DOS largely decreases near the Fermi energy, which is consistent with the conductivity data,[5,6)] and its feature seems to become localized by replacing the Ni atoms with the Cu atoms, while that of the Ni partial DOS remains almost unchanged. Therefore, these electronic data demonstrate that these results are closely related to the excellent GFA of the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glass through a selective formation of Pd-P covalent bonds although supporting experiments or theoretical calculations on the partial DOS of P 2p have not yet been performed.

For the atomic structure, an anomalous X-ray scattering (AXS) experiment was performed by Park *et al.*[7)] at the beamline BL7C of the Photon Factory at KEK for the similar alloys of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ bulk metallic glass and the $Pd_{40}Ni_{40}P_{20}$ reference glass at energies close to the Ni and Cu K absorption edges. From the features of the differential data, they concluded that the effect of elemental substitution with Cu for Ni in the Pd-Ni-Cu-P alloy induces a particular atomic association related to Cu, which is an important factor for exhibiting its excellent GFA. Although the electronic study revealed that the Pd atoms play an important role for the stability of the glassy state, the local structure around the Pd atoms could not be examined due to the limited energy range of an older generation synchrotron facility. In this paper, the authors report AXS results close to the Pd K absorption edge, and discuss the local structure around the Pd atoms in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent glass-former.

## 2. Experimental Procedure

The AXS technique utilizes an anomalous change of an atomic form-factor of a specific element near an absorption edge of the element. Near the absorption edge of the constituent element, the energy dependent anomalous terms change prominently. If two X-ray scattering experiments are carried out at energies far from and very close to the absorption edge of *i*-th element, a differential structure factor, $\Delta_i S(Q)$, can be obtained by the difference of the scattering intensities, which highly enhances the contribution of the *i*-th element-related partial structures, $S_{ij}(Q)$, and suppresses the other partials.

The AXS experiments were carried out at the beamline

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Table 1 The large contributions of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{Pd}S(Q)$ and $S(Q)$ in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloys at the first maximum around 29 $nm^{-1}$ in $S(Q)$.

| $S(Q)$ | | $\Delta_{Pd}S(Q)$ | |
|---|---|---|---|
| Pd-Pd | 0.38 | Pd-Pd | 0.56 |
| Pd-Cu | 0.31 | Pd-Cu | 0.29 |
| Pd-P | 0.10 | Pd-P | 0.08 |
| Pd-Ni | 0.07 | Pd-Ni | 0.07 |
| Cu-Cu | 0.06 | | |

BM02 of the European Synchrotron Radiation Facility (ESRF). For obtaining the $\Delta_{Pd}S(Q)$, two scattering measurements were performed at energies 30 eV and 200 eV below the Pd K absorption edge (24.350 keV) using a standard $\omega$-$2\theta$ diffractometer installed at the beamline. The experimental setup, in particular on the new detecting system, is in detail given elsewhere.[8] Following the procedure given in Ref. 9), $\Delta_{Pd}S(Q)$ was calculated from the scattering data. The large contributions of $S_{ij}(Q)$ (more than 0.05) to the $\Delta_{Pd}S(Q)$ and $S(Q)$ in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy at the first maximum around 29 $nm^{-1}$ in $S(Q)$ are tabulated in Table 1. The values change slightly with $Q$. The large difference between the $\Delta_{Pd}S(Q)$ and $S(Q)$ is seen in mainly $S_{PdPd}(Q)$, and the others change very small.

## 3. Results

The open and closed circles in Fig. 1 show the $\Delta_{Pd}S(Q)$ and $S(Q)$ spectra in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy, $S(Q)$ being measured at 24.150 keV, 200 eV below the Pd K edge. Also given by the dotted curve is the $S(Q)$ of $Pd_{40}Ni_{40}P_{20}$ reference alloy. Because of the good statistic quality, an excellent quality of the $\Delta_{Pd}S(Q)$ data were able to be obtained although the contrast of the spectra between two energies far from and very close to the Pd K edge is only several % of $S(Q)$. Due to the high energy of incident X-rays, the spectra were obtained in a wide $Q$ range from 8 to 180 $nm^{-1}$.

These three spectra look similar to each other, but small differences are found by a detailed observation of the spectra. The oscillation in $\Delta_{Pd}S(Q)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy beyond the third peak around 70 $nm^{-1}$ shifts towards the low $Q$ side compared to $S(Q)$, corresponding to the larger first-nearest-neighbor distance around the Pd atoms than the average, which will be shown later. The shoulder beyond the second peak in $S(Q)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy seems to be clearer than that of $Pd_{40}Ni_{40}P_{20}$ reference alloy, which slightly comes into prominence in $\Delta_{Pd}S(Q)$.

To observe the spectra near the first maxima in detail, the enlarged figure is given in Fig. 2. The marks are the same as in Fig. 1. The first peak positions in $S(Q)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy and $Pd_{40}Ni_{40}P_{20}$ reference alloy are 28.8 and 29.1 $nm^{-1}$, respectively. On the other hand, that in $\Delta_{Pd}S(Q)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy is 28.4 $nm^{-1}$, which is slightly smaller than that in $S(Q)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy. The most interesting result in this figure is that a pre-shoulder is observed at about 20 $nm^{-1}$ in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy, indicating the existence of an intermediate-range order, but not in the $Pd_{40}Ni_{40}P_{20}$ reference alloy. This result was not reported in the previous AXS paper[7] and other papers. It should be noted that this pre-shoulder becomes much clearer in $\Delta_{Pd}S(Q)$. Due to the contributions of $S_{ij}(Q)$ to these spectra as shown in Table 1, it is easily concluded that the pre-shoulder originates from the Pd-Pd atomic correlation

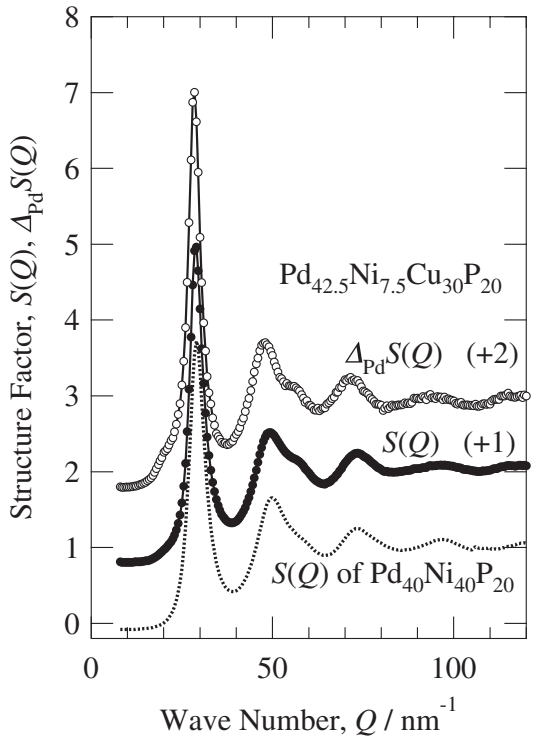


Fig. 1 The $\Delta_{Pd}S(Q)$ and $S(Q)$ spectra in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy are shown by open and closed circles, respectively. Also given by the dotted curve is the $S(Q)$ of $Pd_{40}Ni_{40}P_{20}$ reference alloy.

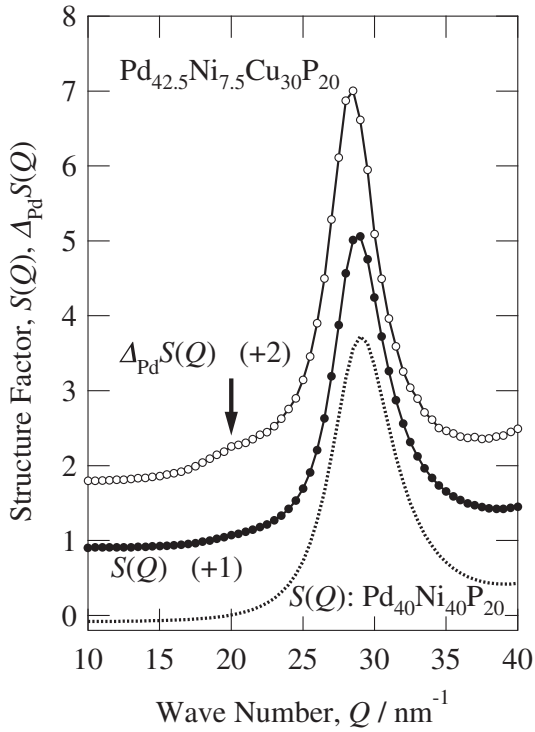


Fig. 2 The $\Delta_{Pd}S(Q)$ and $S(Q)$ spectra given in an enlarged scale near the first maximum around 29 $nm^{-1}$.

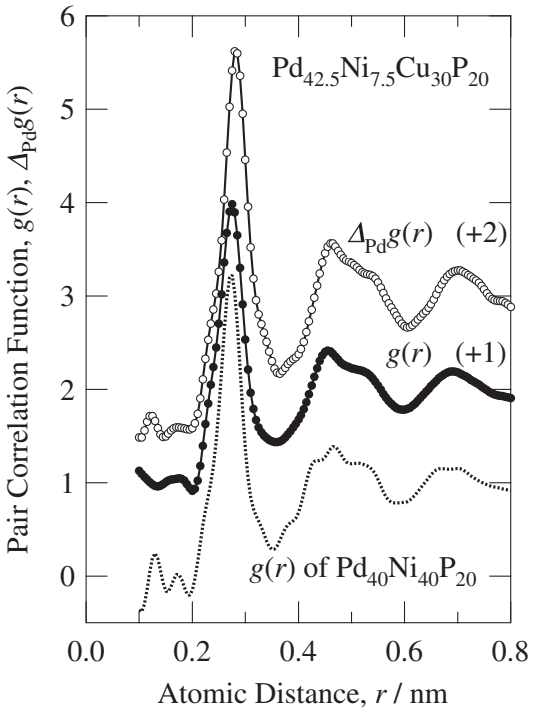


Fig. 3 The $\Delta_{Pd}g(r)$ and $g(r)$ spectra in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy are shown by open and closed circles, respectively. Also given by the dotted curve is the $g(r)$ of $Pd_{40}Ni_{40}P_{20}$ reference alloy.

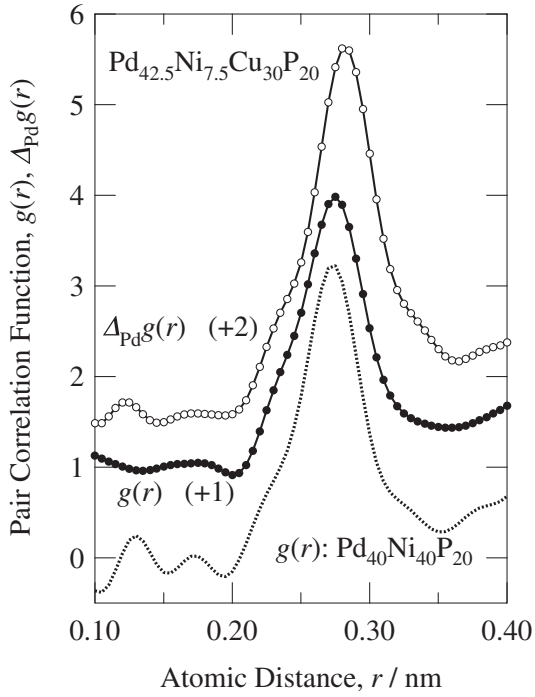


Fig. 4 The $\Delta_{Pd}g(r)$ and $g(r)$ spectra given in an enlarged scale near the first maximum around 0.28 nm.

induced by replacing the Ni atoms with Cu atoms in this metallic glass.

## 4. Discussion

From the $\Delta_{Pd}S(Q)$ and $S(Q)$ spectra in these alloys, the differential and ordinary pair-correlation functions, $\Delta_{Pd}g(r)$ and $g(r)$, are respectively obtained by a standard Fourier-transform, which are given in Fig. 3. The marks are the same as in Figs. 1 and 2. Due to the wide $Q$ range measurable, the truncation errors are relatively small below 0.2 nm without any special handling of the data analysis. The result of $\Delta_{Pd}g(r)$ for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ oscillates much larger than $g(r)$, *i.e.*, the $\Delta_{Pd}g(r)$ values below 0.2 nm show large minus, which may be due to the error that the magnitude of the real part of anomalous atomic form-factor, $f'$, of Pd atoms close to the Pd K absorption edge for this alloy would be larger than the theoretical value[10] used for this analysis. To evaluate the coordination number from $\Delta_{Pd}g(r)$, the correction of $f'$ is very important, and thus an X-ray absorption experiment to calculate $f'$ is now in progress.

Figure 4 shows $\Delta_{Pd}g(r)$ and $g(r)$ on an enlarged scale near the first maximum. The marks are the same as in Figs. 1–3. The first peak positions of $g(r)$ in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy and $Pd_{40}Ni_{40}P_{20}$ reference alloy are respectively 0.275 and 0.273 nm, similar to each other. On the other hand, that in $\Delta_{Pd}g(r)$ of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy locates at 0.282 nm, indicating a longer inter-atomic length around the Pd atoms than the average value. This value is consistent with the estimation by Park *et al.*,[7] 0.280 nm, for an interatomic distance between Pd-M (M: Pd, Ni, and Cu) in the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy based on the topological short-range order (TSRO) model using polyhedra clusters (a trigonal prism capped with three half octahedra and a transformed tetragonal dodecahedron), which are expected to exist in metallic glasses.

A shoulder is seen at the lower $r$ value of about 0.230 nm of the first maximum in $g(r)$, which was considered as M-P correlations in the TSRO model, but was not directly observed in the previous AXS results. This finding demonstrates the advantage of high-energy AXS measurements. Due to the wide $Q$ range up to 180 $nm^{-1}$ used for the Fourier analysis, the first peak can be well separated into the long M-M and short M-P contributions, while the previous AXS measured in the limited $Q$ range up to 80 or 100 $nm^{-1}$, and thus the first peak looks a broad single peak.[7] The shoulder in the present measurement locates about 0.23 nm, which does not originate from truncation ripples as mentioned above. The truncation ripples can be easily estimated in the $r$ range of 0.23-nm shoulder, and almost negligible compared to the large shoulder in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$. This value of inter-atomic length is much shorter than the results of TSRO model, 0.248 nm for the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ glass and 0.241 nm for the $Pd_{40}Ni_{40}P_{20}$ glass. This difference may originate from the fact that the M-P correlates much stronger than expected from the model, and the clusters would be highly distorted from the model cluster. The recent study of the electronic structure[4] demonstrates that the Pd atoms selectively form the covalent bonds with the P atoms, and the distortion may happen in the Pd-P bonds. However, the present AXS result cannot conclude it because the contrast of the Pd-P contribution between the $\Delta_{Pd}g(r)$ and $g(r)$ is very small as given in Table 1.

Finally, we discuss the intermediate-range order (IRO) in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent glass-former. As seen in Fig. 2, a pre-shoulder is observed in the $S(Q)$ and $\Delta_{Pd}S(Q)$,

originating the Pd-Pd interatomic correlation. It was believed for the long time that the pre-shoulder at $Q_p \sim 20\,nm^{-1}$ reflects the existence of an IRO with a correlation length of $r \sim 2\pi/Q_p \sim 0.31$ nm in real space. Since it is not a sharp peak, the Pd-Pd correlation has a large distribution of the correlation length. Several models were proposed to explain the correlation of this length, such as clusters, layer structures, and voids. In fact, a small shoulder around 0.33 nm is visible in the $\Delta_{Pd}g(r)$ spectrum. Moreover, since there is no structure in the $g(r)$, it is plausible that this shoulder originates from the Pd-Pd correlation. If this shoulder really exists and the Pd-Pd correlation is made of Pd-P-Pd connections, the bond angle can be calculated to be 85°–92°, almost the right angle, which is plausible to form in the TSRO model using polyhedra clusters. It should be, however, noted that since the truncation error would appear in the same $r$ region as the small 0.33-nm shoulder in the $\Delta_{Pd}g(r)$ spectrum, the existence of the Pd-P-Pd connections with the right bond angle cannot be concluded at present for the model of the IRO in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent glass-former.

## 5. Conclusion

In order to study local structure around the Pd atoms in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ excellent metallic glass-former, an AXS experiment was performed at energies close to the Pd K absorption edge at the beamline BM02 of the ESRF. The $\Delta_{Pd}S(Q)$ spectrum was obtained with a good statistical quality, which demonstrates that a pre-shoulder at about $20\,nm^{-1}$, indicating the existence of an IRO, originates from the Pd-Pd atomic correlation. The first peak in the $\Delta_{Pd}g(r)$ shows a longer inter-atomic length around the Pd atoms than the average value. The local structure around the Pd atoms is discussed in detail by comparing to the previous experiments of AXS and electronic structure.

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