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Structural Study of an Amorphous Liquid-quenched Ni₈₀-P₂₀ Alloy*

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Synopsis

The structure of amorphous Ni₈₀-P₂₀ alloy obtained by rapid quenching from the liquid state has been studied by X-ray diffraction. After calculating the structure factor by means of the common Fourier analysis, the atomic radial distribution function is obtained from which interatomic distance and coordination number were estimated. Comparing the results with those in the liquid state, it is found that the general feature of the structure in the amorphous state is quite similar to that in the liquid state. A brief comment on the partial structures in this alloy is also made.

I. Introduction

X-ray diffraction studies have been carried out on a number of amorphous alloy systems⁽¹⁻³⁾. The amorphous systems reported are prepared by several methods such as vapour quenching, liquid quenching, electrodeposition and chemical deposition.

The main purpose of this work is to determine the structural informations, structure factor and atomic radial distribution function, of amorphous Ni-P alloy, prepared by liquid quenching method using X-ray diffraction. In addition, a brief comment is made on the atomic distributions in the amorphous state based on the measurements in the liquid state and the structural informations of the electrodeposited amorphous sample previously reported⁽⁴⁾.

II. Experimental procedures

The amorphous alloy samples were prepared by a rapid-quenching centrifugal

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mill device⁽⁵⁾. The samples obtained were about 2 mm in width and about 0.02 mm in thickness. The X-ray scattering measurements of amorphous samples and operating procedures were identical to those described in the previous work^(4,6,7). The observed X-ray intensity was corrected for lost counts, background, absorption and polarization by the common procedures. The density of as quenched sample was measured by hydrostatic weighing with toluene.

III. Analysis of intensity patterns

The analysis of the measured X-ray intensity was made in the same as that described previously^(4,6,7). For convenience, the essential features are given below. If it is assumed that the disordered materials such as amorphous and liquid have a continuous distribution of atoms, the X-ray intensity, $I_{eu}^{coh}(Q)$, coherently scattered from more than one species of atoms can be written as,

$$I_{eu}^{coh}(Q) = \langle f^2 \rangle + \langle f \rangle^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin(Qr)}{Qr} dr, \quad (1)$$

where $\langle f^2 \rangle = \sum c_i f_i^2$, $\langle f \rangle = \sum c_i f_i$, c_i and f_i are the concentration and atomic scattering factor of the i -th kind atom, $\rho(r)$ the radial density function, and ρ_0 the average number density of atoms. As the total structure factor $S(Q)$ is defined by,

$$S(Q) = [I_{eu}^{coh}(Q) - \langle f^2 \rangle + \langle f \rangle^2] / \langle f \rangle^2, \quad (2)$$

the atomic radial distribution function $4\pi r^2 \rho(r)$ can be evaluated as the Fourier transform of $S(Q)$ by the following equation,

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ. \quad (3)$$

The pair distribution function $g(r) = \rho(r) / \rho_0$ is also frequently used to discuss the structure of amorphous solids and liquids.

IV. Results and discussion

The structure factors of amorphous and liquid Ni₈₀-P₂₀ alloy are shown in Fig. 1 together with that of the electrodeposited amorphous Ni₇₄-P₂₆ alloy⁽⁴⁾. The positions of maxima in the curve were determined from the position of apex of the parabola obtained by three points around at the peak maximum and the values are given in Table 1. The structure factor of the liquid-quenched amorphous sample shows a small subsidiary peak on the high angle side of the second peak. This subsidiary peak was also observed in most of metallic amorphous alloys⁽¹⁻³⁾ including the electrodeposited amorphous Ni-P alloys^(4,8,9) whereas this peak is not

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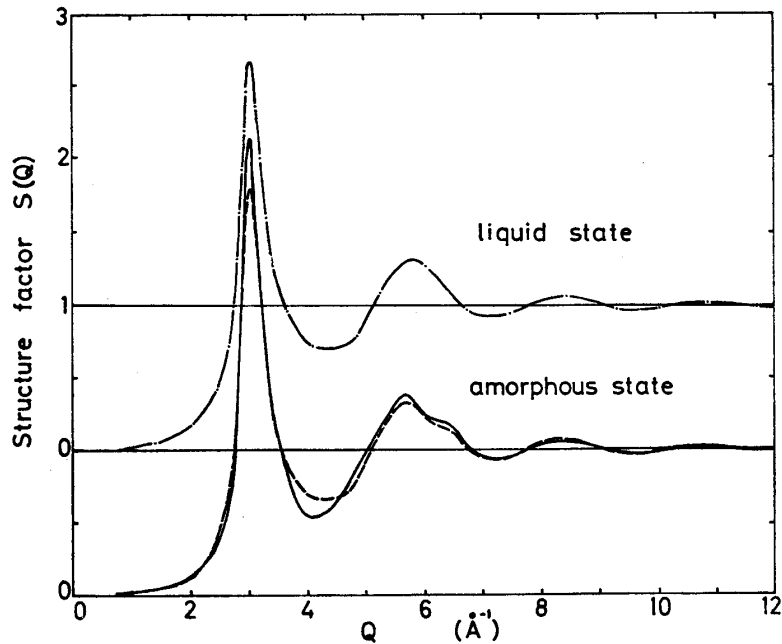


Fig. 1. Structure factor of $\text{Ni}_{80}\text{-P}_{20}$ alloy in the amorphous and liquid states. The dashed line denotes the result of the electrodeposited sample⁽⁴⁾.

specified in the liquid state. Except for a broadening of the peaks observed in the liquid state, the essential features of the structure factor are quite similar between the amorphous state and the liquid state. This feature was also found in the amorphous alloy systems of Cu-Zr⁽⁶⁾, Pd-Si⁽¹⁰⁾ and Fe-P-C⁽⁷⁾. The structure factor of $\text{Ni}_{80}\text{-P}_{20}$ alloy in both amorphous and liquid states do not indicate any well-defined structure such as the double peak observed in the Au-Sn system⁽¹¹⁾ or the small peak below the first peak in the Cu-Mg system⁽¹²⁾. Therefore, one cannot expect any compound-like atomic arrangement in the amorphous and liquid $\text{Ni}_{80}\text{-P}_{20}$ alloys. These results are consistent with the previous discussion that the structure of amorphous metals is considered to be liquid-like of dense random packing⁽¹⁻³⁾.

One of the authors (Y.W.) and Suzuki⁽¹³⁾ showed that the ratio, Q_2/Q_1 , of the position of the first peak (Q_1) to that of the second peak (Q_2) is very useful parameter to present the structure of liquid metals. This ratio is constant (≈ 1.86) for most of liquid metals, and shows a good agreement with the value calculated by the hard sphere model⁽¹⁴⁾. As shown in Table 1, the ratio (Q_2/Q_1) of the amorphous state is smaller than that observed in the liquid state. In order to clarify this point, the results of various amorphous metals are also listed in Table 1. It is seen that the

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Table 1. Summary of the structural informations of amorphous metals by X-ray diffraction

	Q_1 (Å ⁻¹)	Q_2 (Å ⁻¹)	sub. (Å ⁻¹)	Q_2/Q_1	r_1 (Å)	r'_2 (Å)	r_2 (Å)	r'_2/r_1	r_2/r_1	n_1 (atoms)	ref.
liquid buenching											
Au ₇₀ -Si ₃₀	(2.60)	(4.75)	—	(1.85)	(2.85)	(4.95)	(5.80)	(1.74)	(2.04)		(1)
Pd ₈₀ -Si ₂₀	2.82	4.85	5.65	1.72	2.81	4.69	5.29	1.67	1.88	11.8	(2)
liquid	2.83	5.12	—	1.83	2.76	—	5.14	—	1.86	11.3	
Cu ₅₇ -Zr ₄₃	2.76	4.87	5.70	1.76	2.79	4.73	5.28	1.70	1.89	11.6	(3)
liquid	2.77	5.10	—	1.84	2.78	—	5.20	—	1.87	11.2	
Fe ₈₀ -P ₁₃ -C ₇	3.03	5.22	6.05	1.72	2.58	4.28	4.96	1.66	1.92	11.7	(4)
liquid	2.98	5.39	—	1.81	2.58	—	4.81	—	1.86	11.4	
Fe ₃₂ -Pd ₄₈ -P ₂₀	2.85	4.80	(5.90)	1.70	2.80	4.66	5.35	1.66	1.91	13.2	(5)
Fe ₄₄ -Pd ₃₆ -P ₂₀	2.89	4.88	(5.90)	1.69	2.76	4.65	5.25	1.68	1.90	14.6	
Ni ₃₂ -Pd ₅₅ -P ₁₅	2.89	4.90	(5.90)	1.70	2.78	4.60	5.30	1.65	1.91	12.7	
Ni ₅₃ -Pd ₂₇ -P ₂₀	2.96	5.07	(5.90)	1.71	2.70	4.51	5.13	1.67	1.90	13.3	(6)
Mn ₇₅ -P ₁₅ -C ₁₀	3.00	5.17	5.90	1.72	2.63	4.47	5.07	1.70	1.93	12.2	
Fe ₇₈ -Si ₁₀ -B ₁₂	3.06	5.27	6.10	1.72	2.58	4.36	4.94	1.69	1.91	12.1	(7)
Co ₇₈ -Si ₁₀ -B ₁₂	3.11	5.33	6.15	1.71	2.53	4.22	4.78	1.67	1.89	11.6	
Ni ₇₈ -Si ₁₀ -B ₁₂	3.13	5.40	6.30	1.73	2.55	4.24	4.83	1.66	1.89	11.8	present work
Ni ₇₈ -P ₂₀	3.10	5.35	6.10	1.73	2.55	3.23	4.76	1.66	1.87	13.5	
liquid	3.10	5.64	—	1.82	2.53	—	4.68	—	1.85	13.1	
vapour quenching											
Ag ₅₅ -Cu ₄₅	2.83	4.88	(5.70)	1.75	2.83	4.95	—	1.75	—	13.0	(8)
Cu ₃₅ -Mg ₆₅	2.97	5.08	(5.90)	1.70	2.56	4.28	—	1.67	—	13.5	
electrrdeposition											
Ni ₇₄ -P ₂₆	3.10	5.37	6.10	1.73	2.55	4.21	4.77	1.65	1.87	13.3	(9)
Ni ₈₁ -P ₁₉	3.14	5.48	(6.10)	1.75	2.52	4.24	4.86	1.68	1.93	13.0	(10)
Co ₇₈ -P ₂₂	3.07	5.34	(6.05)	1.74							(11)
Co ₈₅ -P ₁₅	(3.10)	(5.46)	(6.20)	(1.76)	(2.54)	(4.27)	(4.83)	(1.68)	(1.90)		(12)

The values in parentheses denote the ones estimated from the original figures by the present authors.

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above citation holds in these metals. This is one of the characteristics in the structure of disordered atomic distributions, both amorphous and liquid states.

Fig. 2 is the pair distribution functions $g(r) = \rho(r)/\rho_0$ calculated from equation

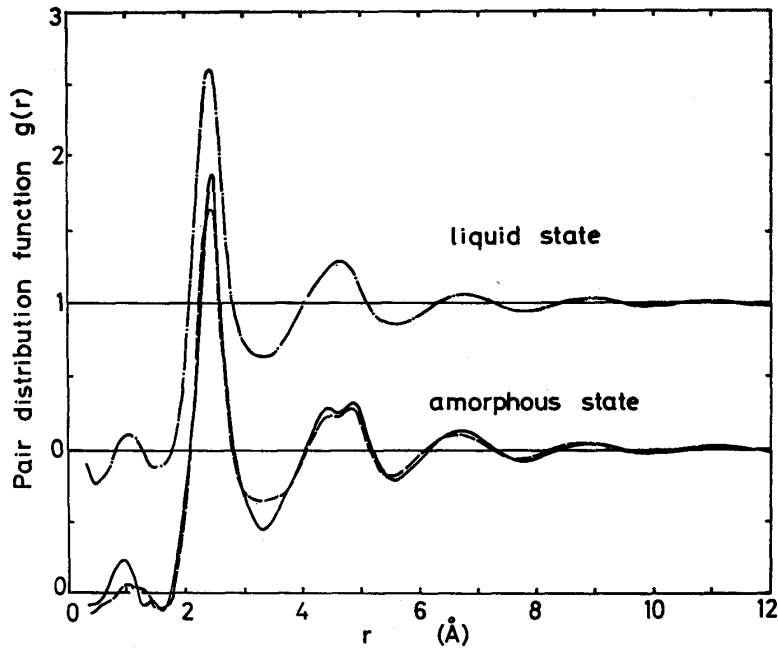


Fig. 2. Pair distribution function of $\text{Ni}_{80}\text{-P}_{20}$ alloy in the amorphous and liquid states. The dashed line denotes the result of the electrodeposited sample⁽⁴⁾.

(3) with the measured density. As shown in the figure, all curves of $g(r)$ oscillate about unity and the spurious ripple is considerably reduced in a region of small r . This is consistent with the fact that the atoms do not come closer inside the atomic diameter due to the repulsive part in the pair potential.

The interatomic distances were determined from the curve of $4\pi r^2[\rho(r) - \rho_0]$. The area under the first peak in the atomic radial distribution function was used to estimate the coordination number n_1 of the nearest neighbour atoms. Since there is no definite method of evaluating the coordination number, the values obtained by the following equation are given in Table 1,

$$n_1 = \int_{r_0}^{r_m} 4\pi r^2 \rho(r) dr, \quad (4)$$

where r_0 and r_m are the radial distances of the edge of the left-hand side and the first minimum on the right-hand side of the first peak in $4\pi r^2 \rho(r)$ curve. The error in the coordination number is less than ± 0.5 .

The first peak at 2.55 Å is followed by the second peak and its subsidiary peak, at 4.23 Å (r_2') and 4.76 Å (r_2). The subsidiary peak of the second peak in the structure factor may be related to the split double peak observed in the pair distribution function $g(r)$. As shown in Fig. 2, the split double peak disappears in the liquid state. The ratio r_2'/r_1 1.66 is close to the mean value (1.68) of the c/a ratio in close-packed hexagonal structure, i.e., $c/a=1.63$, and the ratio of the third atomic shell radius to the nearest neighbour distance in fcc structure, i.e., $\sqrt{3}=1.73$. On the other hand, the ratio $r_2/r_1=(1.87)$ is almost equal to the value (1.86)

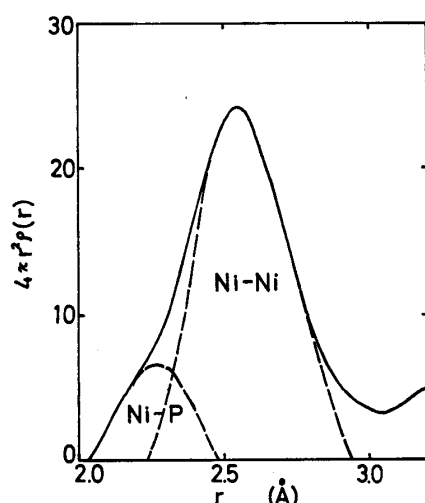


Fig. 3. Atomic radial distribution function of amorphous Ni₈₀-P₂₀ alloy near the first peak.

observed for the liquid state. From these results we suggest that the atomic arrangements in amorphous Ni-P alloy are both liquid-like and crystalline-like. It is easily found from the following result that the crystalline-like feature seems to be of a Ni₃P type structure. Fig. 3 is the atomic radial distribution function near the first peak experimentally obtained, and the near neighbour correlation in amorphous Ni₈₀-P₂₀ alloy is interpreted as the superposition of the correlations of Ni-Ni and Ni-P pairs. As shown in Table 1, the number of nearest neighbours within a distance of $r_m = 3.05$ Å is about 13.5 in amorphous Ni₈₀-P₂₀ alloy and is close to 14 in crystalline Ni₃P⁽¹⁵⁾. This situation is also reported in the amorphous systems of Co-P⁽¹⁶⁾ and Fe-P⁽¹⁷⁾. At first sight, this result implies that amorphous Ni₈₀-P₂₀ alloy is composed of small crystallites with Ni₃P structure. If this definite configuration of atoms exists, the features such as those observed in amorphous Ag₄₈-Cu₅₂ alloy⁽¹⁸⁾ should be found. Namely the peak maxima of nearest neighbours in the pair distribution function are very sharp and almost completely resolved, whereas the oscillations of $g(r)$ decay rapidly and the pair distribution function shows no structurally significant deviation from the asymptotic value of $g(r) = 1$ in the larger distance. This type configurations correspond to that the local nearest neighbour correlation such as A₃B is considerable distinct, but the complete loss of correlation in these units in a long range region larger than about a few times the nearest neighbour distance. However, these behaviours are not distinctly observed in Fig. 2. On the other hand, the tetrahedral unit is one of the fundamental arrangements in the topological disordered structure of the dense random packing model⁽¹⁾. From these result we suggest

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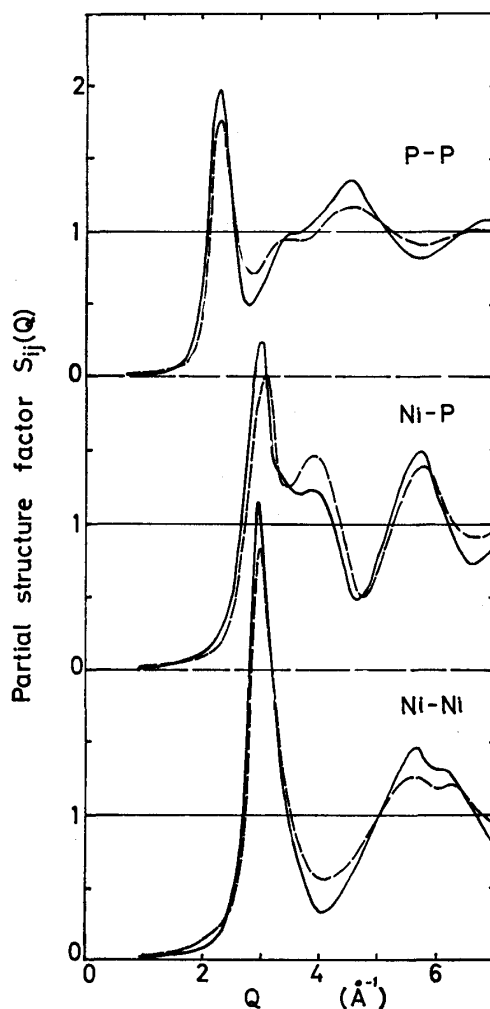


Fig. 4. Partial structure factors for Ni-Ni, P-P and Ni-P pairs in amorphous $\text{Ni}_{80}\text{-P}_{20}$ alloy. The dashed line denotes the result of the electrodeposited sample⁽⁴⁾.

that the atomic distributions in the amorphous Ni-P alloy consist mainly of the disorderly distributed Ni atoms like those in the dense random packing model based on the tetrahedral units with P atoms, and also deformed crystalline-like configurations of atoms partly contribute to the short range order in this amorphous alloy. Here the authors believe that these crystalline-like configurations of atoms are not exactly the same as the arrangements in the crystalline state as already discussed by Cargill and Cochrane⁽¹⁶⁾.

The above discussion is also supported by the information of the partial atomic distributions obtained by the X-ray anomalous scattering technique⁽¹⁹⁾, which has been applied for some disordered binary alloys^(4,20). A brief comment is also given on the previous work of electrodeposited amorphous Ni-P alloys⁽⁴⁾. Figs. 4 and 5 show the partial structure factors $S_{ij}(Q)$ and the partial pair distribution functions $g_{ij}(r)$, respectively. With respect to the position and amplitude, the

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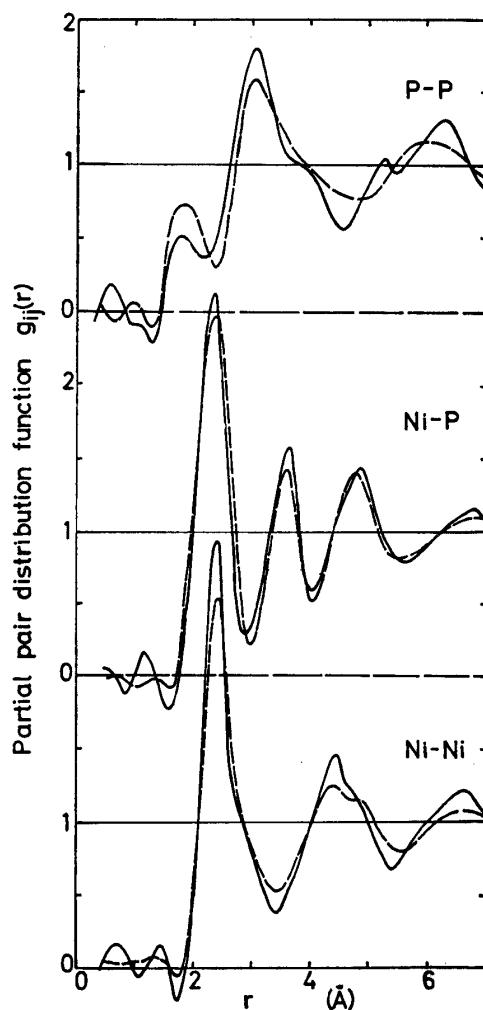


Fig. 5. Partial pair distribution functions for Ni-Ni, P-P and Ni-P pairs in amorphous Ni₈₀-P₂₀ alloy. The dashed line denotes the result of the electrodeposited sample ⁽⁴⁾.

results obtained in this work are in reasonable agreement with those previously obtained⁽⁴⁾. However, the peak at 1.9 Å in the partial pair distribution function of P-P pairs is smaller than that previously reported, and the new peak appears at about 5.2 Å in this work. Since the analysis by means of X-ray anomalous scattering technique is restricted within only up to $Q=7.0\text{Å}^{-1}$, the spurious ripples in $g_{ij}(r)$ caused by the termination of $S_{ij}(Q)$ cannot be removed even though quite accurate data of $S_{ij}(Q)$ are used. However, it is relatively easy to trace the positions where the spurious ripples appear significantly. According to Finback⁽²¹⁾ and Sugawara⁽²²⁾, they appear at $\Delta r \approx \pm 5\pi/2Q_{\max}$ or $\pm 9\pi/2Q_{\max}$ from the principal peak position (r_p), where Q_{\max} is the upper limit of Q experimentally observed. In the present case of the P-P pair distribution ($Q_{\max}=7.0\text{Å}^{-1}$, $r_p=3.12\text{Å}$), the spurious ripples due to the termination effect appear at 1.1, 2.0, 4.2 and 5.1 Å. By this reason the peak at 1.9 Å in the partial pair distribution function of P-P

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pairs observed in both previous and present results seems to be a spurious one as well as those about 1.0 and 5.2 Å, though the corresponding spurious peak at 4.2 Å is not distinctly observed in Fig. 2. Consequently, it is probably reasonable to say that the peak of the P-P pair distribution at 3.12 Å is the significant one and P atoms never be at the first nearest neighbour position in amorphous Ni₈₀-P₂₀ alloy. This is consistent with the discussion that the fundamental configuration of atoms in the short range order of amorphous Ni-P alloy is similar to that of Ni₃P type, (see Table 2), and is also confirmed in amorphous Co-P alloys⁽²³⁾. On the other hand, the distances of Ni-Ni and Ni-P pairs are 2.47 Å and 2.35 Å, respectively. In addition it is important to notice that the first peak in the partial pair distribution function of Ni-Ni pairs is asymmetric where the left-hand side of the first peak is steeper than that of the right-hand side. This may correspond to the situation that the repulsive core part of the pair potential for Ni-Ni pairs is more vertical than the attractive part. The partial structure factor of Ni-P pairs shows a subsidiary peak on the higher angle side of the first peak which is not reproduced by the dense random packing model. As to the information on Ni-Ni and Ni-P pairs obtained in this work there is no significant difference from the previous results⁽⁴⁾.

As shown in Figs. 1 and 2, good overall agreements are found in the structural informations of amorphous Ni-P alloy between the liquid quenched sample and the electrodeposited one, though there are differences in detail. There is a good agreement with respect to parameters, Q_2/Q_1 , r_2'/r_1 and r_2/r_1 among various amorphous metals obtained by different sample preparations listed in Table 1. Thus, the structural difference in amorphous metals due to the methods of sample preparation may not be significant, though no definite answer to this problem is available at present.

Table 2. Comparison between the correlation of atoms in the near neighbours

	Origin atom	Ni		P	
		$r(\text{Å})$	n (atoms)	$r(\text{Å})$	n (atoms)
Amorphous Ni-P alloys	Ni	2.55	10.7	2.35	2.2
	P	2.35	8.5	3.30	3.6
Crystalline Ni ₃ P ⁽¹⁵⁾	Ni	2.68	10	2.28	3
	P	2.28	9	3.44	4

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