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Short-Range Structures of Amorphous and Liquid Iron and $Pd_{0.8}$–$Si_{0.2}$ Alloy*

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Synopsis

A comparison has been made on the short-range structures of iron and $Pd_{0.8}$-$Si_{0.2}$ alloy between the amorphous and the liquid states. It is suggested that the short-range structure of amorphous Fe film has higher degree of ordering in comparison to liquid Fe. The atomic configuration in the nearest neighbour in amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy is close to that in Pd_3Si crystal and is not completely reproduced by the Percus-Yevick Hard Sphere model with high packing fraction corresponding to instantaneous freezing of the liquid structure.

I. Introduction

It has been known that the films of amorphous metals stable at relatively high temperatures can be formed on the substrate cooled by liquid helium, when some amounts of impurity gases such as oxygen are adsorbed in the film during the deposition. Though the rapid quenching from the melt is also used to realize the amorphous state of metals, non-volatile light elements such as B, C, Si and P must be mixed into molten metals before quenching in this method. In both cases some light elements, which can form covalent chemical bonds with metallic atoms, must be added into metals during the preparation of amorphous metals, whether amorphous metals are deposited from the gaseous state or solidified from the liquid state.

Davies and Hull,[1] and Scott and Maddin[24] have reported at the MIT conference that no differences were found by means of diffraction experiments in the structures of the amorphous samples prepared by these two methods. A comparison of the structure of metals between the amorphous and the liquid state is still an interesting problem to attract attention, and some results and discussions are presented on this problem.

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* The **1656th** report of the Research Institute for Iron, Steel and Other Metals.

(1) H.A. Davies and J.B. Hull, D-10 presentation in Second International Conference on Rapidly Quenched Metals, Nov. 17–19, 1975, MIT, Cambridge, Massachusetts.

(2) M.G. Scott and R. Maddin, C-4 presentation in Second International Conference on Rapidly Quenched Metals, Nov. 17–19, 1975, MIT, Cambridge, Massachusetts.

II. Short-range structures of amorphous and liquid iron

The observed interference functions $S(Q)$ of amorphous Fe film[3] and liquid Fe[4] are shown in Fig. 1. The oscillation of $S(Q)$ found for amorphous Fe film has a larger amplitude and persists until higher scattering vector $Q(=4\pi \sin\theta/\lambda$, 2θ; scattering angle and λ; wavelength of radiation used) compared with that for liquid Fe. A marked feature of $S(Q)$ for amorphous Fe film is that the 2nd peak splits into two subpeaks, i.e. a bigger one followed by a smaller one.

Fig. 2 shows the pair distribution functions g(r) for the amorphous Fe film[3] and the liquid Fe[4], which are the Fourier transforms of $S(Q)$ in Fig. 1. For the amorphous Fe film the splitting the 2nd peak into two subpeaks is again found in $g(r)$, and the peaks become sharper and shift a little toward the origin compared with those of the liquid Fe.

The Percus-Yevick Hard Sphere (PYHS) model reproduces well the behaviour of $S(Q)$ for liquid noble and transition metals, when the packing fraction $\eta(=4\pi/3\cdot(\sigma/2)^3\rho$, σ; hard sphere diameter and ρ; average atomic number density) is chosen as about 0.45[5]. The short-range structures of amorphous metals, on the other hand, are described fairy well in terms of the Dense Random Packing (DRP) model originated by Bernal[6] in which the packing fraction η is approximately 0.63.

When η is increased from 0.45 to 0.60 in the PYHS model, as shown in Fig. 3, the 1st peak in $g(r/\sigma)$ becomes sharper, and the peaks of higher order obtain stronger oscillation and broader width and shift toward smaller value of r/σ. These behaviours correspond qualitatively to the observed changes in $g(r)$ of both

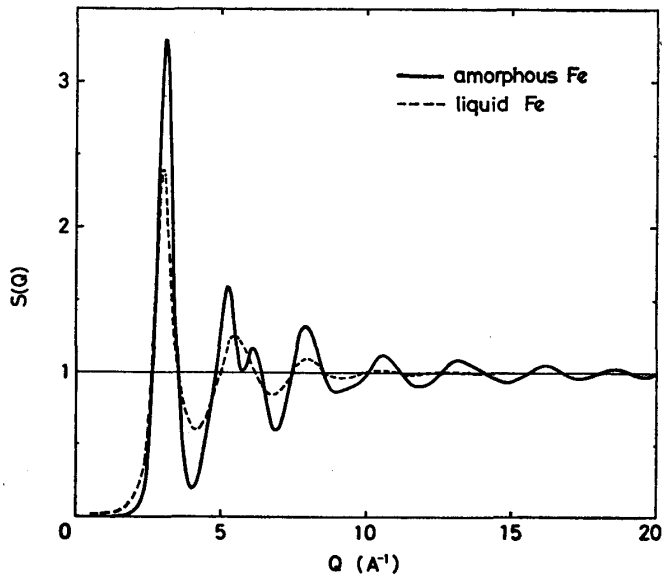

Fig. 1. Interference functions of amorphous Fe film[3] and liquid Fe[4].

(3) T. Ichikawa, phys. stat. sol. (a), **19** (1973), 707.
(4) Y. Waseda and M. Ohtani, phys. stat. sol. (b), **62** (1974), 535.
(5) N.W. Ashcroft and J. Lekner, Phys. Rev., **145** (1966), 83.
(6) J.D. Bernal, Proc. Roy. Soc., **A280** (1964), 299.

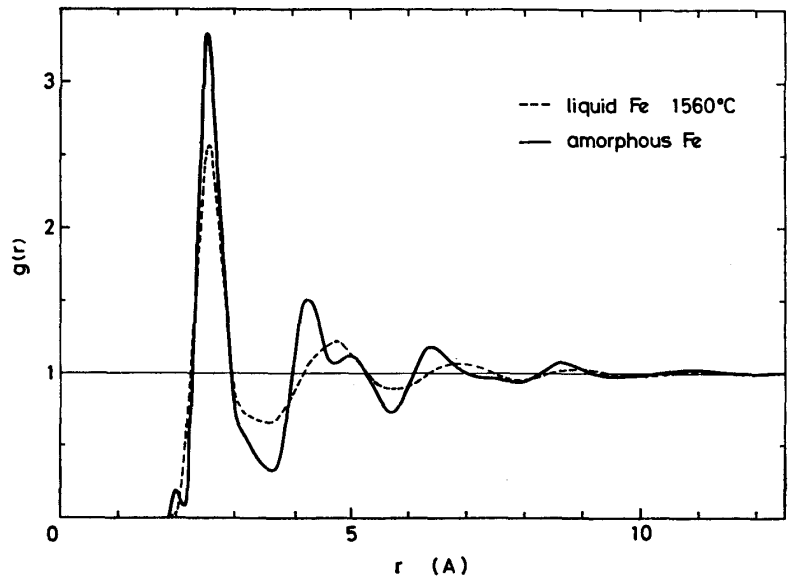

Fig. 2. Pair distribution functions of amorphous Fe film[3] and liquid Fe[4].

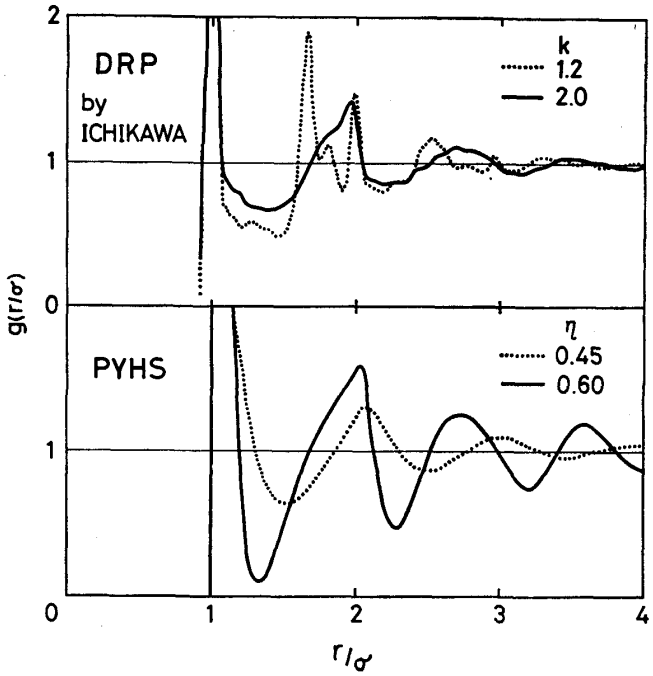

Fig. 3. Pair distribution functions in terms of Ichikawa's Dense Random Packing model and Percus-Yevick Hard Sphere model.

the amorphous and the liquid state in Fig. 2 except for the splitting of the 2nd peak. Ichikawa[7] and Sadoc et al.[8] have verified that the DRP model consisting of nearly regular tetrahedra (k=1.2 in Ichikawa's model shown in Fig. 3) can result in the splitting which corresponds to the observed splitting of the 2nd peak in both of $S(Q)$ and g(r). The behaviour of $g(r/\sigma)$ in the PYHS model with η=0.6

(7) T. Ichikawa, phys. stat. sol. (a), **29** (1975), 293.
(8) J.F. Sadoc, J. Dixmier and A. Guinier, J. Non-Cryst. Solids, **12** (1973), 46.

is quite similar with that of Bennett's DRP model[9] which is constructed from assemblies of distorted tetrahedra (k=2.0 in Ichikawa's model shown in Fig. 3).

The atomic configuration in the amorphous Fe film is suggested to be different from the structure for instantaneous freezing of liquid Fe. This means that the amorphous Fe film has much higher degree of ordering in its short-range structure than the liquid Fe. The oxygen adsorption may result in the fact that the amorphous Fe film prefers to form nearly regular tetrahedra as an elementary atomic configuration.

III. High resolution radial distribution functions of amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy

The interference functions $S(Q)$ of amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy[10] were observed over a wide range of Q up to as high as 30 A^{-1} by means of time-of-flight neutron diffraction using pulsed neutrons produced by an electron linear accelerator[11]. These results are shown in Fig. 4 together with conventional X-ray diffraction results measured by Waseda and Masumoto[12]. The $S(Q)$ of the amorphous alloy observed by neutron diffraction has an oscillation persistent up

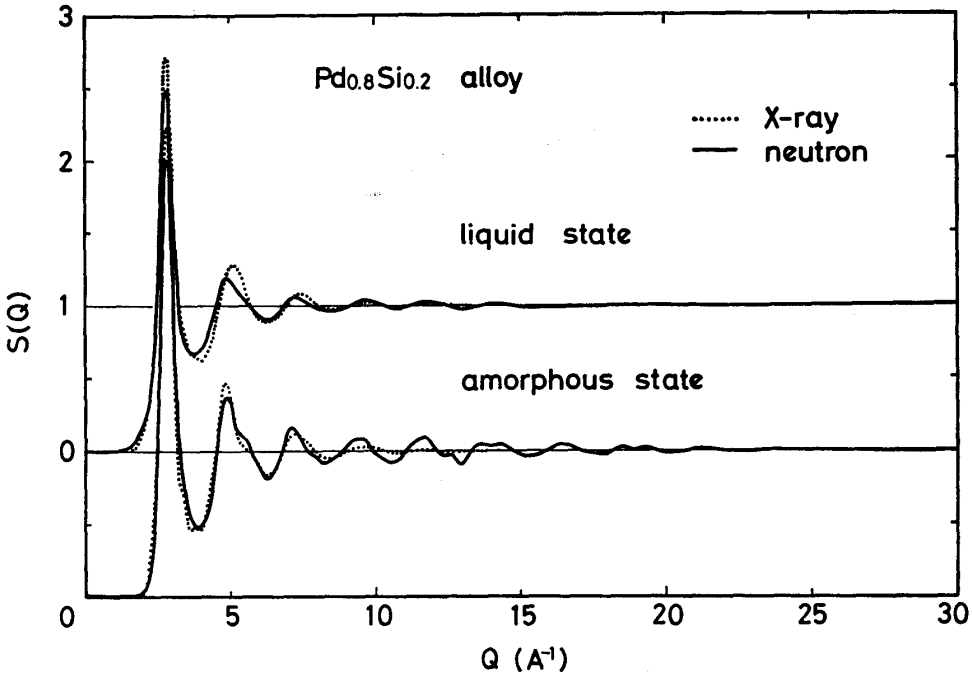

Fig. 4. Interference functions of amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy.

(9) C.H. Bennett, J. Appl. Phys., **43** (1972), 2727.

(10) K. Suzuki, T. Fukunaga, M. Misawa and T. Masumoto, Mater. Sci. Eng., **23** (1976), 215 (Proc. 2nd Intern. Conf. on Rapidly Quenched Metals, (Section II), MIT, Cambridge, Mass., 1975).

(11) M. Misawa, K. Kai, K. Suzuki and S. Takeuchi, Res. Report Lab. Nucl. Sci., Tohoku Univ., **5** (2) (1972), 73.

(12) Y. Waseda and T. Masumoto, phys. stat. sol. (a), **31** (1975), 477.

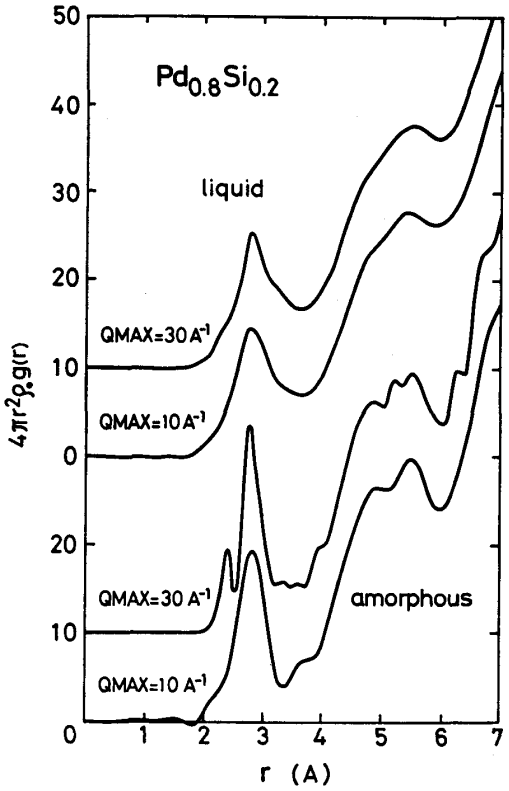

Fig. 5. Radial distribution functions of amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy.

to a value of Q close to 25 A^{-1}, while the $S(Q)$ by X-ray diffraction loses quickly the oscillation beyond a relatively small Q value. Therefore, the neutron diffraction using epithermal neutrons is a quite powerful experiment to observe clearly the short-range structures of amorphous materials containing a high degree of atomic ordering among nearest neighbours[13].

Shoulders or fine subpeaks are found in the peaks of higher order as well as in the 2nd peak in the $S(Q)$ of the amorphous alloy. In the $S(Q)$ of the liquid alloy the peaks are quite smooth and broad, and their positions correspond exactly to those of the amorphous alloy. The oscillation of $S(Q)$ vanishes so rapidly with increasing Q within the range of Q less than 17 A^{-1}.

Fig. 5 shows the radial distribution functions (RDF) of the amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloys which are the Fourier transforms of $S(Q)$. In the numerical integration truncation was made at low and high values of Q. Most of the conventional observations for the RDF correspond to the result obtained by truncating Fourier transformation at Q_{max}=10 A^{-1}. The resolution of $g(r)$ is progressively improved as truncation is made at higher Q_{max}, and the 1st peak of the RDF of the amorphous alloy distinctly splits into two subpeaks at 2.42 A and 2.81 A for Q_{max}=30 A^{-1}.

Because of large thermal fluctuation of atoms in the liquid state no splitting

(13) K. Suzuki, Buturi, **30** (1975), 610 (in Japanese).

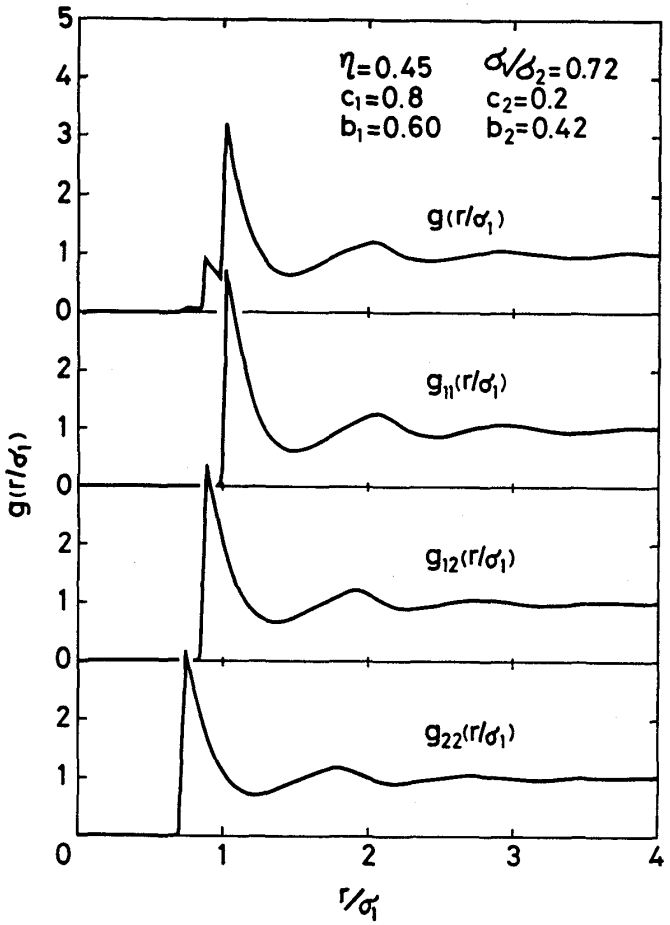

Fig. 6. Comparison between RDF of amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy and Pd-Pd, Pd-Si, Si-Si correlations in Pd_3Si crystalline compound.

of peaks can be found in the RDF of the liquid alloy even in the case of Q_{max}=30 A^{-1}. However, the RDF for Q_{max}=30 A^{-1} of the liquid alloy in Fig. 5 indicates that a shallow hump appears at the position corresponding to that of the 1st subpeak (2.42 A) in the RDF of the amorphous alloy and a small tail is extended toward lower side of the 1st peak.

These features in the RDF for liquid $Pd_{0.8}$-$Si_{0.2}$ alloy are qualitatively reproduced in terms of the Percus- Yevick Hard Sphere model for binary system[14] with the packing fraction η=0.45 as shown in Fig. 6. If the amorphous state of $Pd_{0.8}$-$Si_{0.2}$ alloy had an atomic configuration that would be obtained by freezing instantaneously the liquid state, the RDF of the amorphous state should be described by the PYHS model by increasing η from 0.45 to 0.68. Fig. 7 shows that the 1st peak in the $g(r/\sigma)$ of the PYHS model splits into three subpeaks corresponding to Si-Si, Pd-Si and Pd-Pd nearest neighbour correlations and the shallow hump does not appear on lower side of the 2nd peak. This means that the behaviour of the nearest neighbour Si-Si correlation in amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy is entirely different from that in the liquid state.

(14) N.W. Ashcroft and C. Langreth, Phys. Rev., **156** (1967), 685.

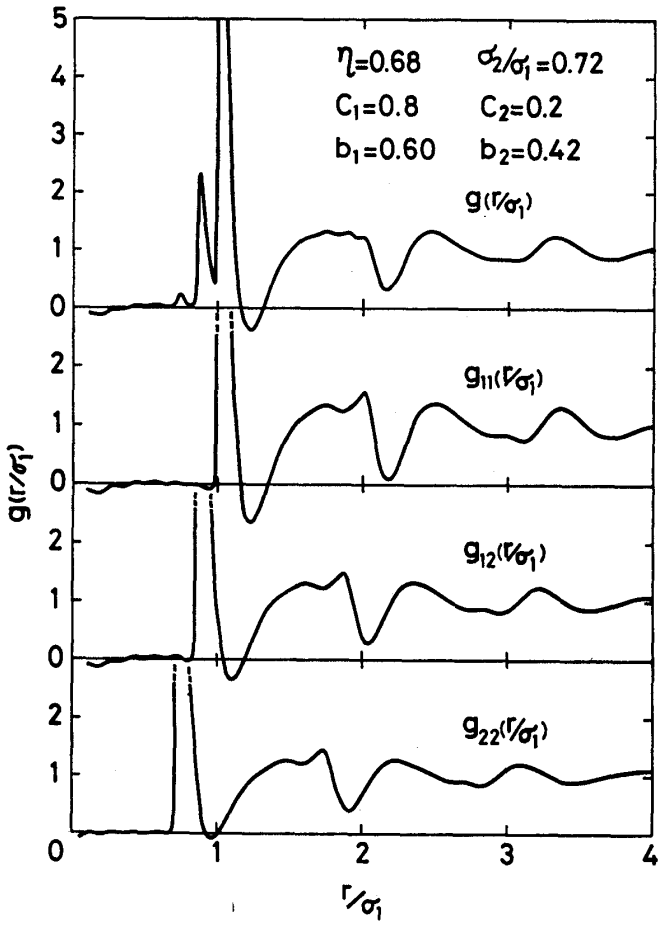

Fig. 7. Pair distribution functions for liquid $Pd_{0.8}$-$Si_{0.2}$ alloy calculated in terms of PYHS model. 1 means Pd atom, 2 menas Si atom, σ is hard sphere diameter, c is concentration and b is coherent neutron scattering amplitude.

Fig. 8 shows a comparision between the crystal structure of Pd_3Si compound (orthorhombic)[15] and the observed RDF of amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy. The nearest neighbour Pd-Pd and Pd-Si spacings contained in Pd_3Si crystalline structure are very close to the position of two subpeaks split from the 1st peak in $Pd_{0.8}$-$Si_{0.2}$ amorphous alloy. As shown in Table 1, the coordination numbers for the nearest neighbour Pd-Pd and Pd-Si correlations are also closely related between amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy and Pd_3Si crystalline compound. The nearest neighbour Si-Si spacing in Pd_3Si crystalline structure is not found in the range less than 3.68 A. This fact indicates that Si atoms never occupy the adjacent lattice sites in the close contact in Pd_3Si crystalline compound. A small hump appearing at near 4 A in the observed RDF may suggest that the close contact of Si atoms is prohibited in amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy as like in Pd_3Si crystalline structure as pointed out by Sadoc and Dixmier[16] in an amorphous Co-P alloy.

(15) B. Aronson and Anna Nylund, Acta Chem. Scand., **14** (1960), 1011.

(16) J.F. Sadoc and J. Dixmier, D-3 presentation in Second International Conference on Rapidly Quenched Metals, Nov. 17–19, 1975, MIT, Cambridge, Massachusetts.

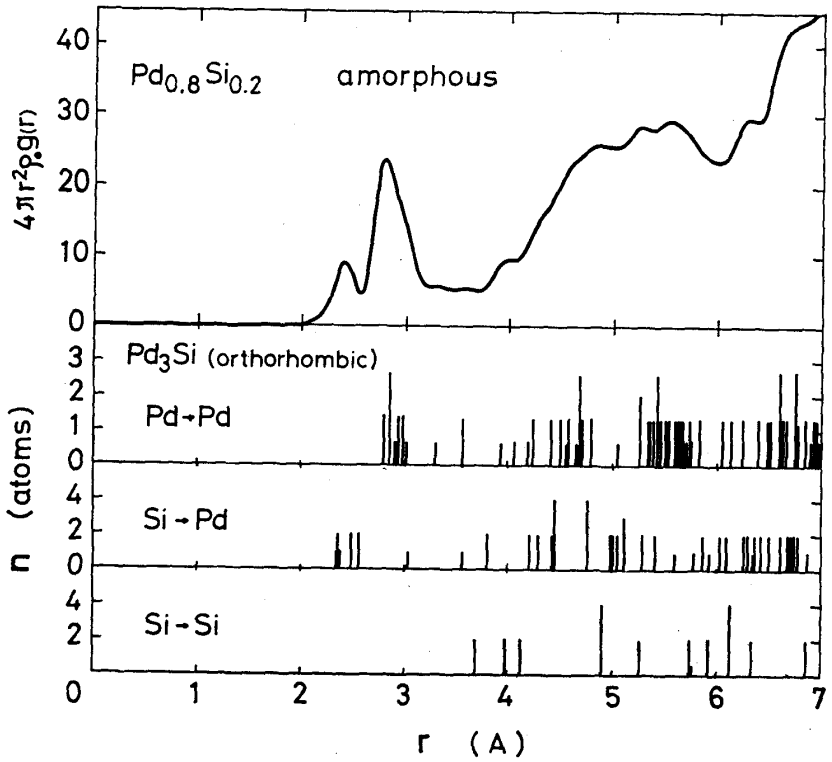

Fig. 8. Pair distribution functions for amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy calculated in terms of PYHS model. Meanings of notations are same with those in Fig. 7. $\eta=0.68$ is referred from G.S. Cargill III, Solid State Physics Vol. 30 (Academic Press, 1975).

Table 1. Bond lengths and coordination numbers of Pd-Si and Pd-Pd correlations in $Pd_{0.8}$-$Si_{0.2}$ amorphous alloy and Pd_3Si crystalline compound

	$Pd_{0.8}$-$Si_{0.2}$ amorphous alloy		Pd_3Si crystalline compound	
	Bond length	Coordination number	Bond. length	Coordination number
Pd-Si	2.42A	1.8*	2.44A	2*
Pd-Pd	2.81A	10.4	2.9~3.0A	10~11

*; average number of Si atoms around a Pd atom

IV. Pd-Pd and Pd-Si correlations in amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy

The observed $S(Q)$ of a A-B binary system is expressed by the three partial interference function $S_{AA}(Q)$, $S_{AB}(Q)$ and $S_{BB}(Q)$ for A-A, A-B and B-B correlation in the system as follows,

$$S(Q)=(1/\langle b\rangle^2)\{w_{AA}S_{AA}(Q)+w_{AB}S_{AB}(Q)+w_{BB}S_{BB}(Q)\},$$

$$w_{AA}=c_A{}^2b_A{}^2,\quad w_{AB}=2c_Ac_Bb_Ab_B,\quad w_{BB}=c_B{}^2b_B{}^2 \text{ and } \langle b\rangle=c_Ab_A+c_Bb_B,$$

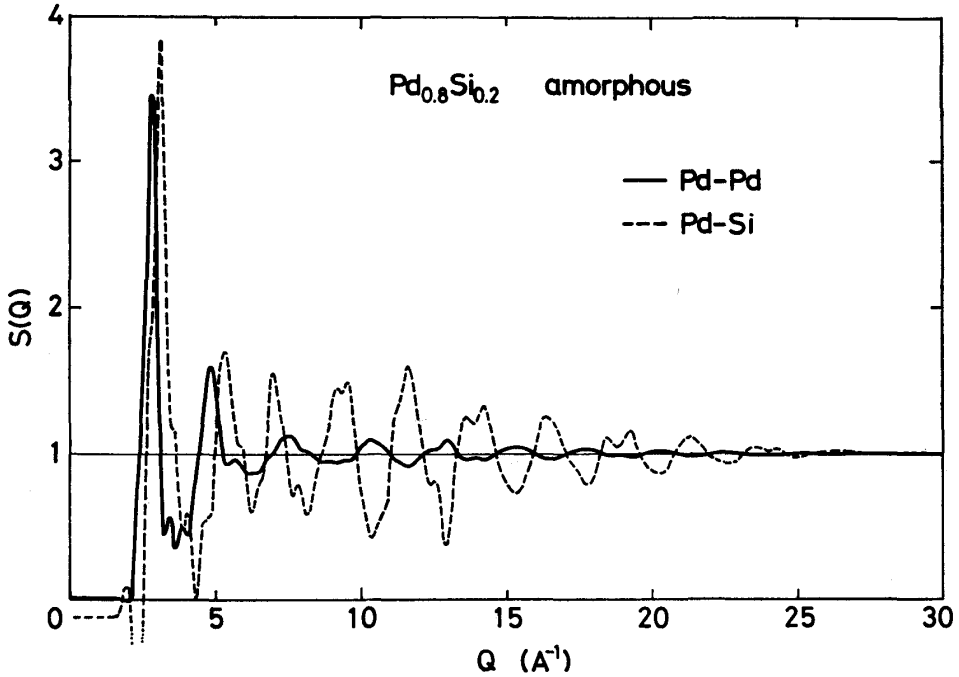

Fig. 9. Partial interference functions for Pd-Pd and Pd-Si correlations in amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy.

Table 2. Relative contributions of three partial correlations to total correlation in $Pd_{0.8}$-$Si_{0.2}$ alloy by X-ray and neutron diffraction

	w_{PdPd}	w_{PdSi}	w_{SiSi}
X-ray	0.864	0.131	0.005
Neutron	0.724	0.254	0.022

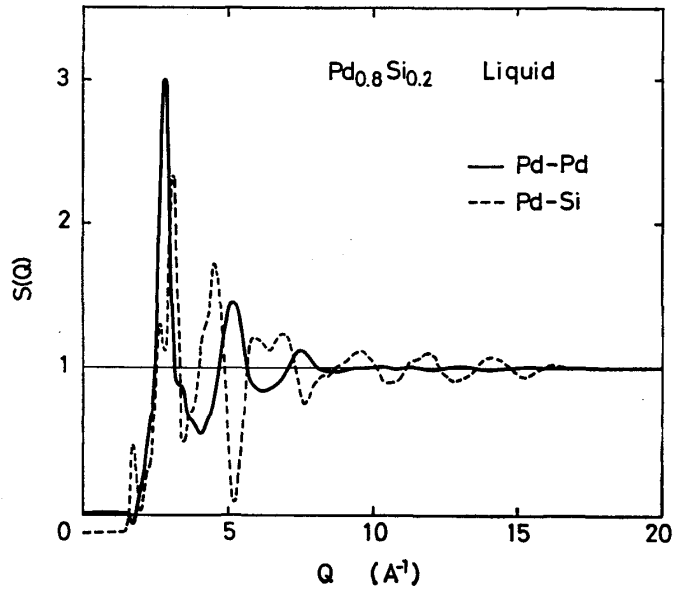

Fig. 10. Partial interference functions for Pd-Pd and Pd-Si correlations in liquid $Pd_{0.8}$-$Si_{0.2}$ alloy.

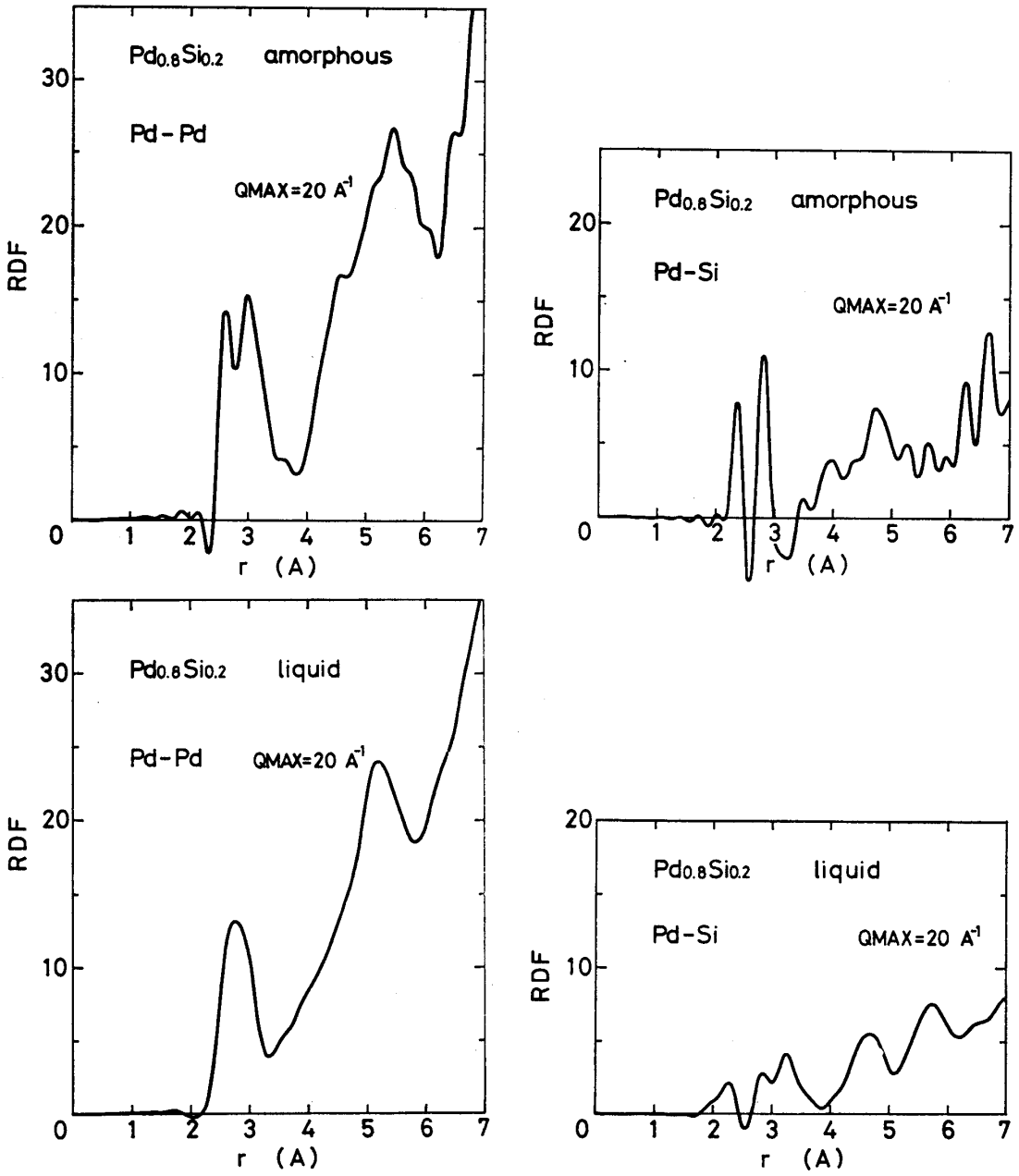

Fig. 11. Partial distribution functions for Pd-Pd and Pd-Si correlations in amorphous and liquid $Pd_{0.8}$-$Si_{0.2}$ alloy.

where c_A(or c_B) is the compositional fraction of element A(or B) and b_A(or b_B) is the scattering amplitude of element A(or B). Values of w_{AA}, w_{AB} and w_{BB} for $Pd_{0.8}$-$Si_{0.2}$ alloy are summarized in Table 2 for both cases of X-ray and neutron diffraction experiment.

Even in neutron diffraction experiment the value of w_{SiSi} is still too small for the Si-Si correlation to be observed experimentally like in X-ray diffraction experiment. In addition, the Si-Si correlation in the amorphous alloy seems to vanish, namely $S_{SiSi}(Q)=1$, like uncorrelated atoms in the gaseous state, because Si

atoms can not be in the close contact with one another. Hence, $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$ can be calculated from the above equation by combining the observed $S(Q)$ of neutron and X-ray diffraction shown in Fig. 4.

Figs. 9 and 10 show that $S_{PdPd}(Q)$ in the amorphous and liquid states behave like those of pure liquid metals, and their oscillations fall down rapidly. In fact, $S_{PdPd}(Q)$ are essentially similar to the $S(Q)$ observed by X-ray diffraction in the ranges of Q less than 15 A^{-1}. In contrast, $S_{PdSi}(Q)$ in the amorphous state shows that the oscillation is not damped even in the range of Q as high as 20 A^{-1}. This fact comes from the occurrence of a strong chemical bond between Pd and Si atoms. Such a behaviour of $S_{PdSi}(Q)$ actually corresponds to that of the $S(Q)$ observed in high Q region by neutron diffraction.

The partial RDF of the amorphous and liquid state Fourier transformed from $S_{PdPd}(Q)$ and $S_{PdSi}(Q)$ with Q_{max}=20 A^{-1} are shown in Fig. 11. It is understood from Figs. 5, 6 and 11 that the 1st subpeak of the total RDF of the amorphous alloy corresponds to the Pd-Si correlation of which separation is very close to those in Pd_3Si crystalline compound, and the 2nd subpeak of the total RDF mainly corresponds to the mixture of Pd-Pd and Pd-Si correlations, where one to two Pd atoms are substituted by Si atoms, with a bond length corresponding to the Pd-Pd separation in Pd_3Si crystalline compound. Such behaviours of partial short-range structure are observed also in liquid $Pd_{0.8}$-$Si_{0.2}$ alloy. This fact suggests that the essential features of short-range structures of amorphous $Pd_{0.8}$-$Si_{0.2}$ alloy are already prepared in the liquid state but the Si-Si correlation is brought about so that Si atoms are not in the close contact during quenching from the melt.