THE FORTY-TWO HONDA MEMORIAL LECTURE

Nanostructure of Metallic Amorphous Alloys
—Characterization of Medium-Range Structure and Dynamics by Pulsed Neutron Scattering—†

Kenji Suzuki
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

Atoms in metallic amorphous alloys are preferably combined into a configuration of minimizing the local energy in the short-range structure, while the total energy minimum is realized in the periodic long-range structure of crystalline metals. The topological mechanism of crystal-to-amorphous solid state structure transition is demonstrated as a conversion of octahedral structure units into tetrahedral structure units. However, the short-range structure of metallic amorphous alloys often shows similarity to that of their crystalline counterparts. Survival of the local coordination in metallic amorphous alloys is also confirmed by characterizing the dynamic structure. The low-energy excitation often called the Boson peak in inelastic neutron scattering is observed in an energy range of 1 to 3 meV for metallic amorphous alloys, corresponding to an excess specific heat in addition to the Debye-type harmonic vibration in a temperature range of 10 to 30 K. The medium-range structure of metallic amorphous alloys has a quite unique nature in contrast to the crystalline alloys. In case of metal-metalloid (Pd–Si and Pd–Ge) amorphous alloys it is discussed that the low-energy excitation is correlated to a locally collective atomic motion of hinge-like movement between trigonal prismatic structure units.

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1. Introduction

Depending on the range of the spatial and dynamic hierarchy in the structure of amorphous alloys under investigation, the momentum and energy of incident radiations must be carefully chosen in radiation scattering experiments using photons, electrons and neutrons, because the momentum and energy transferred between the radiations and a target specimen during the scattering process are required to be of the same order of magnitude as the incident radiation used for characterizing the space-time correlation of atoms in the target specimen.

A very wide dynamic range of energy and momentum can be currently surveyed in the neutron scattering experiment using pulsed neutron sources based on accelerators. Therefore, we can obtain the short-range structure, highly resolved in the radial distribution function $g(r)$, by extending the measurement of the structure factor $S(Q)$ up to a very high range of the scattering vector $Q$ beyond $300 \text{ nm}^{-1}$. We have so far demonstrated how powerful the High-$Q$ measurement is for identifying the fine structure not only in oxide glasses but also of amorphous alloys(7), a most interesting but difficult problem inherent in amorphous alloys is the characterization of the medium-range dynamic structure. However, pulsed neutron scattering has been again recognized as a promising technique for finding the medium-range structure and the correlated atomic motion in amorphous solids such as SiO$_2$ and GeSe$_2$ glasses. We have shown that pulsed neutron scattering is quite effective to observe so-called low temperature excitation in metal-metalloid amorphous alloys appearing around an energy range 2–3 meV (30 K), which is often observed as an excess specific heat in addition to the Debye-type harmonic vibration.

In this paper we first demonstrate how clearly total pulsed neutron scattering can detect the structural mutation from a closest-packed fcc crystal to an amorphous state driven by mechanical milling of a Ni–V binary system in the solid state. Secondly, the High-$Q$ measurement using pulsed-neutron scattering shows that Pd–Si and Pd–

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† 1 eV $\approx 1.6 \times 10^{-19}$ J.
Ge amorphous alloys include trigonal prisms as a main fundamental structural unit and the three-dimensional structure of these amorphous alloys is constructed by connecting the trigonal prisms with sharing edges. Thirdly, inelastic pulsed neutron scattering experiment shows that the medium-range low-energy excitation is mainly contributed from a hinge-like motion between the trigonal prisms and very sensitive to the structure relaxation induced by low temperature annealing.

II. Pulsed Neutron Scattering

Neutron scattering is an experiment for measuring the double differential cross-section $d^2\sigma/d\Omega dE$, which is directly related to the spatial arrangement and motion of constituent atoms in a target specimen, as a function of energy- and momentum-transfer during scattering process\(^{(1)}\). In principle, the double differential cross-section for nuclear scattering is contributed from the coherent and incoherent scattering terms, respectively:

$$d^2\sigma/d\Omega dE = d^2\sigma_{coh}/d\Omega dE + d^2\sigma_{incoh}/d\Omega dE.$$ 

The coherent double differential cross-section $d^2\sigma_{coh}/d\Omega dE$ is related to the coherent scattering function $S(Q, E)$ which provides the dynamic correlation between the positions of two different atoms, while the incoherent double differential cross-section $d^2\sigma_{incoh}/d\Omega dE$ gives the incoherent scattering function $S_i(Q, E)$ which describes the dynamic correlation between the positions of the same atom, where $\sigma$ is the total scattering cross-section, $\Omega$ the solid angle, $E$ the energy and $Q$ the magnitude of scattering vector\(^{(1)}\).

Because of the lack of long-range lattice periodicity in an amorphous alloy, the $Q$-$E$ dispersion relation conventionally used to describe the phonon mode in crystals is no longer an appropriate way for representing the atomic vibration in the amorphous alloy. Therefore, the conventional physical quantities available for describing the structure of amorphous alloys are the radial pair correlation function $g(r)$ and the vibrational density of states $G(E)$, which are related to the $S(Q, E)$ and $S_i(Q, E)$ as follows\(^{(2)}\):

\[
d^2\sigma_{coh}/d\Omega dE = N(k'/k)\langle b^2 \rangle S(Q, E) = \frac{1}{2\pi^2} \int dQ [S(Q) - S_i(Q)] G(E) G^*(E)
\]

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<th>Fourier transform $\rightarrow$ $G_i(r, t)$ + $G_o(r, t)$</th>
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<td>Fourier transform $\rightarrow$ $g(r)$</td>
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where $N$ is the number of atoms, $k$ the wave number of incident neutron, $k'$ the wave number of scattered neutron, $b$ the scattering amplitude, $G_i(r, t)$ the self space-time correlation function, $G_o(r, t)$ the distinct space-time correlation function, $r$ the amplitude of position vector, and $t$ the time variable.

However, Carpenter and Pelizzari\(^{(13)}\) have proposed a procedure for extracting explicitly the real-space displacement-displacement correlation in the atomic motions of a specified energy in an amorphous solid from the experimental observation of $S(Q, E)$. The first experimental demonstration for this procedure has been done for SiO$_2$ glass by Carpenter and Price\(^{(8)}\) using the pulsed neutron source IPNS installed at Argonne National Laboratory.

The $g(r)$ is the Fourier transform of the structure factor $S(Q)$ which is theoretically defined by energy-integrating the $S(Q, E)$ over the whole range of energy transfer ($-\infty < E < \infty$) under constant $Q$. The $G(E)$ can be directly obtained from the incoherent scattering function $S_i(Q, E)$. However, this procedure is not easy from the experimental point of view, because the species of atoms having only the incoherent scattering length are quite limited. Therefore, the incoherent approximation\(^{(11)}\) is often employed to result in the generalized vibrational density of states $G(E)$ by averaging $S(Q, E)$ over an extended range of $Q$. Therefore, high energy incident neutrons generated by accelerators are also necessary to approach experimentally the ideal $g(r)$ and $G(E)$ of amorphous alloys\(^{(10)}\).

III. Crystal-to-Amorphous Solid State Structure Transformation

The first approximation for the topological atomic structure of amorphous metals is described in terms of the dense random packing of hard spheres\(^{(14)}\). However, a dense random packing of soft spheres is better fitted to the realistic structure of amorphous metals, because atoms are rather soft in the metallic state. According to the computer simulation for amorphous metals done by Finney and Wallace\(^{(15)}\), polyhedral structure units con-
structing a dense random packing of soft spheres are mostly tetrahedrons. The polyhedral structure units found in a closest-packed crystalline structure such as an fcc lattice are exclusively the tetrahedron and octahedron, which exist in an exact ratio of two-to-one. Therefore, the octahedral structure units have to be transformed into the tetrahedral structure units, if amorphous alloys are directly synthesized in the solid state from the fcc lattice without formation of intermediate crystalline phases.

In the fcc lattice, the second and fifth neighboring atoms surrounding a central atom just occupy the key sites constructing the octahedral structure unit. Therefore, it is expected that the second and fifth peaks in the radial distribution function of the fcc lattice are predominantly lost, while the first, third, fourth and sixth peak are only broadened during the process of the crystal-to-amorphous solid state transformation.

Currently, mechanical milling\(^{16}\) has attracted attention as a promising method for synthesizing amorphous alloys in the solid state at ambient temperature. Figure 1 shows change in the neutron radial distribution function during the solid state formation of Ni\(_4\)V\(_4\) amorphous alloy by mechanical alloying a mixture of elemental Ni and V powders\(^{17x18}\). In fact, we can find that the second and fifth peaks in the radial distribution function of Ni fcc lattice drastically disappear during mechanical alloying with increasing milling time. This experiment successfully utilizes the advantage of neutron diffraction that the coherent scattering cross-section of V nucleus for thermal neutrons is negligibly small compared with that of Ni nucleus. Therefore, we can conclude that the topological mechanism of crystal-to-amorphous solid state structure transformation driven by mechanical milling is based on the mutation of octahedral structure units into tetrahedral structure units.

IV. Polyhedral Structure Unit

The neutron total structure factors \(S(Q)\) of Pd–Ge amorphous alloys\(^{19}\), which were measured by time-of-flight total neutron scattering using the \((\gamma, n)\) pulsed neutron source installed at the Tohoku University 300 MeV electron linac in Sendai\(^{20}\), are shown in terms of the Faber-Ziman formula\(^{21}\) in Fig. 2. There are definitely oscillations in the \(S(Q)\) up to a high \(Q\) region beyond 300 nm\(^{-1}\). In the case of Pd\(_{75}\)Ge\(_{25}\), an amorphous alloy with a stoichiometric composition that corresponds to the Pd\(_3\)Ge crystalline compound, a pre-peak appears clearly at the lower \(Q\) side (17 nm\(^{-1}\)) of the main peak (29 nm\(^{-1}\)) in the \(S(Q)\). This pre-peak is associated with the Ge–Ge correlation in the amorphous alloy.

The truncation of Fourier transform of \(S(Q)\) into \(g(r)\) often provides a great effect on the peak profile of the resulting \(g(r)\) corresponding to the short-range structure\(^{22}\). The first peak of the \(g(r)\) for Pd–Ge amorphous alloys is found to be originally split into two subpeaks, contributed from the Ge–Pd correlation around \(r=0.25\) nm and the Pd–Pd at about \(r=0.28\) nm, when the truncation of the Fourier transform is extended up to a high \(Q\) value beyond 250 nm\(^{-1}\).

The coordination number of Pd atoms around a Ge atom is close to 6 over a whole composition range of Pd–Ge amorphous alloys. This result suggests that the network structure of Pd–Ge amorphous alloys is construct-

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**Fig. 1** Neutron total radial distribution functions RDF for the alloys processed by mechanical alloying reaction 4Ni(fcc) + 6V(bcc)→Ni\(_4\)V\(_4\) (amorphous) as a function of milling time.

**Fig. 2** Neutron total structure factors \(S(Q)\) of Pd–Ge amorphous alloys.
ed by connecting the trigonal prismatic structure units in which 6 Pd atoms are located at each vertex surrounding a central Ge atom as shown in Fig. 3, if the chemical and topological structure units existing in a crystalline counterpart are still preserved in the amorphous state. This model was proposed by Gaskell as the defined local coordination model against the dense random packing model.

Figure 4 indicates that the generalized (neutron-weighted total) vibrational density of states $G(E)$ of Pd$_{59}$Si$_{121}$ amorphous alloy is obviously separated into two bands having a boundary around $E=30$ meV; a low-energy band ($E<30$ meV) for the acoustic mode of Pd–Pd correlation and a high-energy band ($E>30$ meV) for the optic mode of Pd–Si correlation. The $G(E)$ is defined by integrating the $S(Q, E)$ over a range of $Q=50$–100 nm$^{-1}$ (incoherent approximation), which was measured by using the MARI chopper-spectrometer installed at the ISIS spallation pulsed neutron source in Rutherford Appleton Laboratory.

The $Q$-oscillations of $S(Q, E)$ at several characteristic $E$ values for Pd$_{59}$Si$_{121}$ amorphous alloy are shown in Fig. 5. The average period of the $Q$-oscillations in $S(Q, E)$ at a low-energy range $E=8.5$–10.5 meV in the Pd–Pd acoustic vibration band is roughly $\Delta Q=22$ nm$^{-1}$, which is rather close to that of $S(Q)$, due to the Pd–Pd spacing of $r=0.28$ nm. However, with increasing $E$, the amplitude of the $Q$-oscillation in $S(Q, E)$ is drastically damped in a medium-energy range $E=18.0$–22.0 meV, while the period is shortened in a high-energy range $E=33.0$–38.0 meV in the Pd–Si optic vibration band.

It is noteworthy that the Pd–Pd and Pd–Si partial structures can be separated by labeling the vibrational energy of Pd–Pd and Pd–Si bonds in Pd–Si amorphous alloys. We have confirmed that the $Q$-oscillation in the energy range $E=35$–45 meV can be well described in terms of the displacement vector for a symmetric mode (A-mode) of Pd–Si optic vibration in a trigonal prismatic structure unit, as shown by arrows in Fig. 3(a).

V. Medium-Range Low Energy Locally Collective Motion

Besides the Debye-type harmonic motion, the dynamic structure of amorphous solids is characterized by three
different contributions as follows:

1. diffusional relaxation near the glass transition,
2. excess harmonic vibration in a low-energy range $1-4$ meV (20-40 K)
and
3. tunneling in a two-level system at very low temperatures below 1 K.

The contribution (2) mentioned above yields an inelastic neutron scattering peak, which is often called the Boson peak commonly characteristic of amorphous solids\(^{(29)}\), and has often been found as an anomalous excess specific heat and an anomalous temperature dependence of thermal conductivity appearing around the temperature range 10-40 K, corresponding to the energy of 1-4 meV. Currently, this low-energy excess excitation is known to originate from the medium-range motion between fundamental structure units constructing the network structure of amorphous solids such as SiO\(_2\)\(^{(26)}\) and GeS\(_2\) glass\(^{(27)}\).

The scattering functions $S(Q, E)$ for Pd\(_{80}\)Ge\(_{20}\) amorphous alloy and Pd\(_{73}\)Ge\(_{27}\) crystalline alloy, which were measured by inelastic neutron scattering using the LAM-40 inverted-geometry T-O-F spectrometer\(^{(28)}\) installed at the KENS spallation pulsed neutron source in the National Laboratory for High Energy Physics, Tsukuba, are compared around the two positions of $Q=17$ and 26 nm\(^{-1}\) in Fig. 6\(^{(19,29)}\). The value of $Q=17$ nm\(^{-1}\) corresponds to the position of the pre-peak in $S(Q)$ and the position of $Q=26$ nm\(^{-1}\) is closely located near the main peak $Q=28$ nm\(^{-1}\) in $S(Q)$. An excess intensity is obviously observed for the amorphous alloy at $Q=17$ nm\(^{-1}\) within a low-energy range of $E<3$ meV, compared with the crystalline alloy. The same behavior is also found in the $S(Q, E)$ observed at $Q=26$ nm\(^{-1}\), but the excess intensity is extended to a high-energy range of $E>6$ meV.

The phonon term in the specific heat of Pd\(_{80}\)Ge\(_{20}\) amorphous alloy has a significant excess deviated from the Debye model in a temperature range below 30 K, as shown in Fig. 7. This temperature range corresponds well to the energy range of $E<3$ meV, where the excess intensity of inelastic neutron scattering is observed at the $Q$ value of pre-peak.

The pre-peak position of $Q=17$ nm\(^{-1}\) closely corresponds to the atomic spacing of $r=0.4$ nm between Ge atoms occupying the central sites in adjacent trigonal prismatic structure units connected by edge-sharing, as shown in Fig. 3. Therefore, we conclude that the low-energy excitation of $E=1-3$ meV at $Q=17$ nm\(^{-1}\) existing in Pd\(_{80}\)Ge\(_{20}\) amorphous alloy, which contributes to an excess specific heat appearing below 30 K in addition to the Debye model, originates from a hinge-like locally collective motion between trigonal prismatic structure units connected by edge-sharing. The parameters of this locally collective mode were calculated in terms of the soft-potential model proposed by Gil et al.\(^{(30)}\), based on the vibrational density of states measured by inelastic neutron scattering and the experimental specific heat. The application of the soft-potential model shows that there is a mechanism behind the low-energy excitation common between Pd\(_{77}\)Ge\(_{23}\) amorphous alloy and oxide or chalcogenide glasses\(^{(31)}\).

The metal-metal and metal-metalloid correlation in the

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**Fig. 6** Inelastic neutron scattering functions $S(Q, E)$ of Pd\(_{80}\)Ge\(_{20}\) amorphous alloy and Pd\(_{73}\)Ge\(_{27}\) crystalline alloy measured in a low-energy range at pre-peak position ($Q=17$ nm\(^{-1}\)) and just below main peak position ($Q=26$ nm\(^{-1}\)) in $S(Q)$. The energy resolution is shown at elastic scattering position.

**Fig. 7** Specific heats of Pd\(_{80}\)Ge\(_{20}\) amorphous alloy. Open circles: measured points, dashed line: phonon term calculated from vibrational density of states, dash-dotted line: electronic term obtained by a fitting and solid line: sum of phonon and electronic terms.
N_{10}Pd_{46}P_{35} amorphous alloy are separately relaxed at 450 and 550 K, respectively. As shown in Fig. 8, significant decrease in the vibrational density of states by the metal-metal relaxation appears in a low-energy range below 3 meV. The metal-metalloid relaxation results in a great decrease in the vibrational density of states over a high-energy range up to about 6 meV. It is worthy to notice that the low-energy excitation is very sensitive to the structure relaxation of amorphous alloys below the glass transition temperature, although little change in the short-range structure in both the \( g(r) \) and \( S(Q) \) due to the structure relaxation is found.

Luchnikov et al.\(^{16}\) has suggested, based on a computer simulation for the spatial distribution of atomic vibrational modes of Ar amorphous solid, that the low-energy excitation is contributed from the low-density disordered nanometer-scale atomic clusters which are separated by high-density fairly ordered areas. Therefore, the low-energy excitation drastically disappears during the process of structure relaxation.

**VI. Concluding Remarks**

Pulsed-neutron scattering based on accelerator sources are quite powerful to characterize the short- and medium-range static and dynamic structure of amorphous alloys.

The solid state amorphization induced by mechanical milling clearly demonstrated that the topological mechanism of crystal-to-amorphous structure transition is the conversion of octahedral structure units into tetrahedral structure units, which is often followed by the modification of the connectivity between the tetrahedral structure units from vertex-sharing to face- and/or edge-sharing.\(^{17}(18)\). This means that atoms in amorphous alloys are combined into a configuration of minimizing the local energy in the short-range structure, instead of relaxing the total energy minimum of a system.

However, the short-range order of amorphous alloys often shows similarity to that of their crystalline counterparts. The survival of the local coordination in amorphous alloys is also confirmed by the density-of-states. The trigonal prismatic structure units constructing Pd–Si and Pd–Ge alloy glasses can be topologically assigned by observing the \( Q \)-dependence of \( S(Q, E) \) in the selected \( E \) intervals corresponding to the vibration modes of metal-metal and metal-metalloid partial correlation.

The hinge-like movement between the trigonal prismatic structure units connected by edge-sharing causes the low-energy locally collective motion extending within a medium-range distance. Such a medium-range dynamic structure is generally recognized but found only for amorphous solids, being an unique nature in contrast to the crystalline counterparts. The low-energy excitation in amorphous alloys appearing in the energy range of 1 to 3 meV, which is usually observed as an excess specific heat in addition to the Debye-type harmonic vibration, is contributed from the locally collective motion characterized spatially by the medium-range structure fluctuations. The low-energy excitation is also quite sensitive to the structure relaxation below the glass transition temperature.

The experimental results mentioned above for Ni–V, Pd–Si, Pd–Ge and Pd–Ni–P amorphous alloys were observed by pulsed neutron scattering based on accelerators, which is proved to be a powerful tool for characterizing the structure of amorphous alloys, because a very wide dynamic range of energy- and momentum-transfer can be surveyed.

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**REFERENCES**