

# Structural influence on atomic hopping and electronic states of Pd-based bulk metallic glasses

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(Received 24 June 2004; accepted 21 December 2004; published online 9 February 2005)

Atomic motion and electronic structures of Pd–Ni–Cu–P bulk metallic glasses were investigated using <sup>31</sup>P nuclear magnetic resonance. The hopping rate of P atoms was determined by the stimulated echo technique. Significant hopping was observed in all alloys well below the glass transition temperature. Increasing the Cu content to above 25 at. % increases P hopping significantly, consistent with the previous finding that the openness of the structure increases with Cu content. In contrast, P hopping is not influenced by changes of local electronic states at P sites, induced by the substitution of Ni by Cu. © 2005 American Institute of Physics.  
[DOI: 10.1063/1.1866217]

The discovery of bulk metallic glasses (BMG) has stimulated intensive research on the understanding of the glass forming ability (GFA) of metallic systems.<sup>1,2</sup> Since diffusion is related to factors controlling the GFA such as local topological constraints and packing efficiency,<sup>3,4</sup> the study of diffusion is important for the understanding of GFA and the nature of glass transition.<sup>5</sup> Previously, beryllium diffusion in Zr<sub>41.2</sub>Ti<sub>13.8</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> (Vit1) and Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> (Vit4) BMGs was investigated and two beryllium diffusion mechanisms were identified: one involves single-atom hopping and the other involves the collective motion of groups of atoms.<sup>6,7</sup> It revealed that beryllium hopping is present in both the glassy and supercooled liquid states and the Arrhenius plot of the hopping rate follows a straight line across the glass transition temperature  $T_g$  with no change of the activation energy. This demonstrates that the observed increase in the apparent activation energy of beryllium diffusion near  $T_g$  arises simply from the stronger temperature dependence of the collective motion contribution as compared to that of single-atom hopping.<sup>6,8</sup> Since the same beryllium hopping is observed in the glassy state and in the supercooled liquid above  $T_g$  where structural relaxation is complete, beryllium hopping is believed to be an intrinsic property of the glassy structures of Vit1 and Vit4. The measurement of small constituent atom hopping is sensitive and could provide valuable insights into why certain alloys with certain compositions possess high GFA. The importance of such study is emphasized by the fact that the

presence of constituent small atoms is crucial for the GFA of BMG due to the requirement of packing efficiency and topological constraints.<sup>3,4</sup>

Pd<sub>40</sub>Cu<sub>x</sub>Ni<sub>40-x</sub>P<sub>20</sub> alloys are also excellent glass formers. Shen *et al.* found that the molar volume of bulk Pd<sub>40</sub>Cu<sub>x</sub>Ni<sub>40-x</sub>P<sub>20</sub> glasses increases rapidly when the copper content exceeds  $x=10$  at. %.<sup>9</sup> Such increased openness of the glassy structure could affect the hopping motion of small atoms such as P. Here we present <sup>31</sup>P NMR measurements of P hopping in five Pd–Ni–P and Pd–Cu–Ni–P bulk metallic glasses. A significant hopping rate was observed below  $T_g$  in all the alloys. It was found that increasing the Cu content indeed enhances the P hopping rate. In addition, <sup>31</sup>P NMR was used to characterize the electronic density of states at the Fermi level, providing information on its relationship with phosphorus hopping.

Five BMGs were used in this study: Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> (S1), Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> (S2), Pd<sub>43</sub>Cu<sub>27</sub>Ni<sub>10</sub>P<sub>20</sub> (S3), Pd<sub>47</sub>Cu<sub>25</sub>Ni<sub>9</sub>P<sub>19</sub> (S4), and Pd<sub>41.75</sub>Cu<sub>41.75</sub>P<sub>16.5</sub> (S5). Their synthesis was described previously.<sup>10,11</sup> NMR measurements were conducted with a pulsed spectrometer at a magnetic field of 9.4 T as described elsewhere.<sup>7,12</sup> Figure 1 shows the <sup>31</sup>P NMR spectra of glassy Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> (S1) and glassy Pd<sub>43</sub>Cu<sub>27</sub>Ni<sub>10</sub>P<sub>20</sub> (S3). The <sup>31</sup>P spectra of S2, S4, and S5 are identical to that of glassy Pd<sub>43</sub>Cu<sub>27</sub>Ni<sub>10</sub>P<sub>20</sub>. The spectral linewidth at the full width at half maximum is about 112.5 kHz for glassy Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> and 94.5 kHz for glassy Pd<sub>43</sub>Cu<sub>27</sub>Ni<sub>10</sub>P<sub>20</sub>. It is interesting to note that the <sup>31</sup>P spectrum of glassy Pd<sub>43</sub>Cu<sub>27</sub>Ni<sub>10</sub>P<sub>20</sub> overlaps with that of glassy Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>, if the frequency axis of the latter is scaled by a factor of 1/1.31 (Fig. 1).

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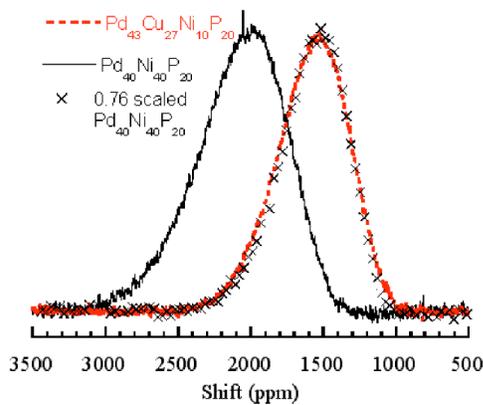


FIG. 1. (Color online) The  $^{31}\text{P}$  spectra (obtained with Hahn echo) of glassy  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  (S1) and  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  (S3) at 9.4 T and 290 K. The shift reference is  $^{31}\text{P}$  in 85%  $\text{H}_3\text{PO}_4$  in  $\text{H}_2\text{O}$ .

The resonance frequency in metals is determined by the Knight shift given by<sup>13</sup>

$$K = \frac{8\pi}{3} \langle |\psi(0)|^2 \rangle_{E_F} V \chi_{\text{Pauli}}, \quad (1)$$

where  $\langle |\psi(0)|^2 \rangle_{E_F}$  is the density of the electron wave function at the nucleus averaged over all states at the Fermi level  $E_F$  and the entire electron wave function  $\langle |\psi(\mathbf{r})|^2 \rangle$  is normalized over the volume  $V$ .  $\chi_{\text{Pauli}}$  is the Pauli paramagnetic susceptibility per unit volume. Assuming noninteracting electrons,  $\chi_{\text{Pauli}}$  is given by  $\chi_{\text{Pauli}} = 2\mu_B^2 g(E_F)$  where  $\mu_B$  is the Bohr magneton and  $g(E_F)$  is the density of states per unit volume at the Fermi level (for a single spin orientation). The observed  $^{31}\text{P}$  spectra in Fig. 1 indicate that  $\langle |\psi(0)|^2 \rangle_{E_F} V g(E_F)$  in glassy  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  (S1) is larger than that in the Cu-containing samples by a factor of 1.31. Since the entire spectrum of S1 overlaps with that of S3 after frequency scaling, the line broadening is most likely due to the Knight shift distribution, predominantly anisotropic Knight shift distribution.<sup>12</sup> Such anisotropic shift distribution originates from the variation of the local structural configuration with respect to the direction of the external magnetic field.

The interaction that gives rise to the Knight shift also determines the nuclear spin-lattice relaxation rate  $1/T_1$  given by<sup>13</sup>

$$\frac{1}{T_1 T} = \frac{64}{9} k_B \pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 [\langle |\psi(0)|^2 \rangle_{E_F} V g(E_F)]^2, \quad (2)$$

where  $\gamma_e = 2\mu_B/\hbar = 1.76 \times 10^{11}$  Hz/T is the electron gyromagnetic ratio,  $\gamma_n = 1.08 \times 10^8$  Hz/T is the  $^{31}\text{P}$  nuclear gyromagnetic ratio, and  $h = 2\pi\hbar$  and  $k_B$  are the Planck and Boltzmann constants, respectively. The  $^{31}\text{P}$   $1/T_1$  was measured by the saturation recovery method. The  $^{31}\text{P}$   $1/T_1$  is almost identical in S2, S3, S4, and S5 but is larger in S1. Figure 2 displays  $1/T_1$  as a function of temperature ( $T$ ).  $1/T_1$  is approximately proportional to  $T$  up to 500 K in all samples, consistent with Eq. (2). The fits give  $1/T_1 T = (1.05 \pm 0.02) \text{ s}^{-1} \text{ K}^{-1}$  for S1 and  $1/T_1 T = (0.70 \pm 0.05) \text{ s}^{-1} \text{ K}^{-1}$  for the other samples. These values, according to Eq. (2), indicate that  $\langle |\psi(0)|^2 \rangle_{E_F} V g(E_F)$  in S1 is larger than that in S2, S3, S4, and S5 by a factor of 1.22, comparable to the 1.31 factor obtained from the Knight shift. The NMR result is consistent with the previous report (Ref. 9), which suggested a change of short-range order in Pd-Cu-

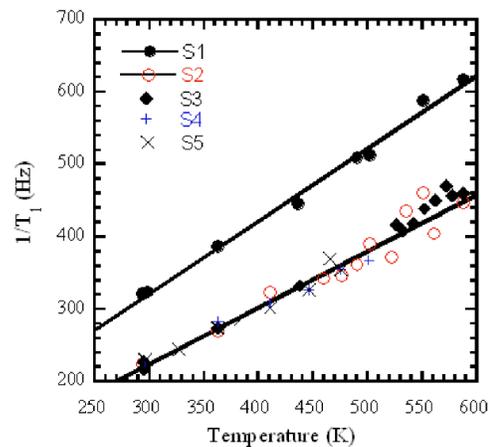


FIG. 2. (Color online) The  $^{31}\text{P}$   $1/T_1$  as a function of temperature for samples S1, S2, S3, S4, and S5. The solid lines are fits of linear temperature dependence of  $1/T_1$ .

Ni-P glasses when the Cu content exceeds 10 at. %.

The  $^{31}\text{P}$  NMR stimulated echo technique,  $90_x^\circ - \tau - 90_y^\circ - t - 90^\circ - \tau' -$ , was used to measure the hopping rate of phosphorus.<sup>14</sup> The typical  $90^\circ$  pulse used was  $1.5 \mu\text{s}$ ,  $\tau = 25 \mu\text{s}$ ,  $t \gg \tau$ , and the signal was detected during the time interval  $\tau'$ . After the third  $90^\circ$  pulse a stimulated echo forms at  $\tau' = \tau$ . Under the condition  $t > T_2$ , where the spin-spin relaxation time  $T_2$  is on the order of  $500 \mu\text{s}$ , the stimulated-echo amplitude is proportional to the ensemble-averaged single-particle correlation function  $f(t) = \langle \sin(\omega\tau) \sin(\omega'\tau') \rangle \exp(-t/T_1)$  where  $\omega$  and  $\omega'$  are proportional to the local magnetic field experienced by a given spin during the time intervals  $\tau$  and  $\tau'$ , respectively. If the local environment of any given spin does not change during the time interval  $t$ ,  $\omega$  and  $\omega'$  will be the same and the correlation function  $f(t)$  will decay only through the spin-lattice relaxation given by the factor  $\exp(-t/T_1)$ . If the probability of atomic hopping over the time interval  $t$  is significant,  $\omega$  experienced by a given spin is likely to change during the time interval  $t$ . This will cause  $\langle \sin(\omega\tau) \sin(\omega'\tau') \rangle$  to decay.<sup>7,14</sup> For a stochastic process with the rate of atom hopping given by  $\Omega$  in an amorphous system,  $\langle \sin(\omega\tau) \sin(\omega'\tau') \rangle$  decays as  $\exp(-\Omega t)$ . Thus,  $f(t)$  is proportional to  $\exp[-(\Omega + 1/T_1)t]$ . We measured the amplitude of the stimulated echo as a function of  $t$ . The decay of the amplitude is exponential. From

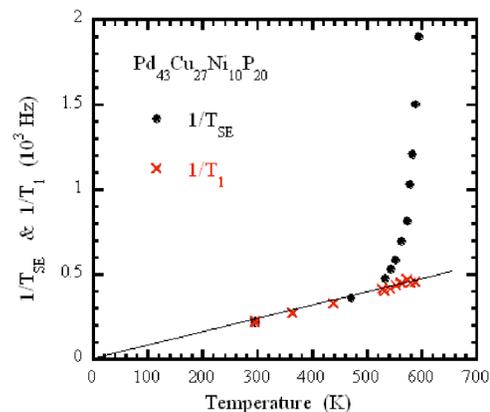


FIG. 3. (Color online) The  $^{31}\text{P}$   $1/T_1$  and  $1/T_{\text{SE}}$  as a function of temperature for sample  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  (S3). The solid line is a fit of the linear temperature dependence of  $1/T_1$ .

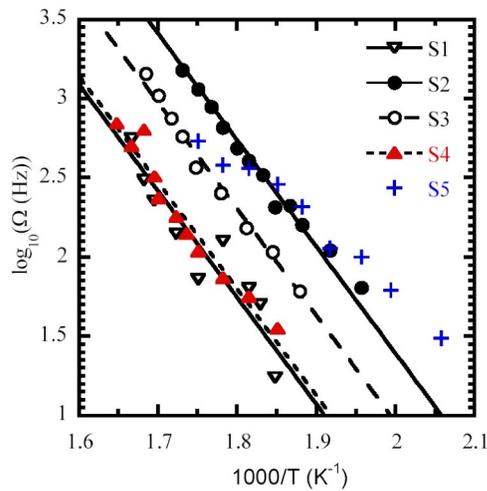


FIG. 4. (Color online) The temperature dependence of atomic jump rates  $\Omega$  in glassy  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  (S1),  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  (S2),  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  (S3),  $\text{Pd}_{47}\text{Cu}_{25}\text{Ni}_9\text{P}_{19}$  (S4), and  $\text{Pd}_{41.75}\text{Cu}_{41.75}\text{P}_{16.5}$  (S5). The straight lines are Arrhenius fits of  $\Omega$ .

this decay  $1/T_{\text{SE}} \equiv \Omega + 1/T_1$  is determined. Since  $1/T_1$  is determined by the saturation recovery method,  $\Omega$  is then determined. Figure 3 shows the measured  $1/T_{\text{SE}}$  and  $1/T_1$  for sample S3. It is clear that  $1/T_{\text{SE}}$  is identical to  $1/T_1$  at low temperatures but increases rapidly above 500 K due to the increase of  $\Omega$ . Annealing at temperature slightly below  $T_g$  (all around 580 K) does not affect the measured hopping rate. Figure 4 is an Arrhenius plot of the measured  $\Omega$  versus  $1000/T$  for the five samples. All  $\Omega$  curves indicate an activated process:  $\Omega(T) = \Omega_0 \exp(-E_a/k_B T)$ . For S1, S2, S3, and S4, the fitted  $E_a$  is  $(1.3 \pm 0.1)$  eV and the respectively fitted prefactor  $\Omega_0$  is about  $7.3 \times 10^{13}$ ,  $7.2 \times 10^{14}$ ,  $2.6 \times 10^{14}$ , and  $8.3 \times 10^{13} \text{ s}^{-1}$ . For S5, the fitting yields  $E_a = (0.8 \pm 0.2)$  eV and  $\Omega_0 = 6.8 \times 10^9 \text{ s}^{-1}$ . The comparison of the results for  $\text{Pd}_{41.75}\text{Cu}_{41.75}\text{P}_{16.5}$  (S5),  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  (S2), and  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  (S1) in Fig. 4, suggests that a substitution of Cu by Ni reduces the P hopping rate. Furthermore, the comparison of the results for  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  (S2),  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  (S3), and  $\text{Pd}_{47}\text{Cu}_{25}\text{Ni}_9\text{P}_{19}$  (S4) in Fig. 4, suggests that a substitution of Cu by Pd also reduces the P hopping rate. These results indicate a significant enhancement of the P hopping when the Cu content exceeds 25 at. %.

Previous studies on a series of metallic glasses  $\text{Pd}_{40}\text{Cu}_x\text{Ni}_{40-x}\text{P}_{20}$  showed that the coordination number around P atoms decreases upon substitution of Ni by Cu.<sup>15</sup> A significant difference was also found in the electronic structure between Pd–Ni–P and Pd–Cu–P.<sup>16,17</sup> Furthermore, a molar volume measurement of glassy  $\text{Pd}_{40}\text{Cu}_x\text{Ni}_{40-x}\text{P}_{20}$  showed<sup>9</sup> that the rate of molar volume increase versus  $x$  is  $0.57 \text{ cm}^3/(\text{mole atoms})$  for  $x < 10$  whereas it is  $0.93 \text{ cm}^3/(\text{mole atoms})$  for  $x \geq 10$ . The molar volume increase versus  $x$  above  $x = 10$  cannot be attributed simply to the size difference between Cu and Ni. This indicates that a structural change occurs when the Ni substitution by Cu reaches  $x = 10$ . This is consistent with the current NMR result which shows that the density of states at the Fermi level is

20%–30% larger in  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  than in S2, S3, S4, and S5 where  $x \geq 25$ . Very little change of the density of states at the Fermi level is observable by NMR above  $x = 25$ . In contrast, the hopping rate measurement shows that changes occur above  $x = 25$  whereas very little change occurs below  $x = 25$ . This suggests that the P hopping is correlated with the openness of the structure (above 25 at. % Cu) whereas the correlation with the electronic structure is weak in current systems. Finally, it is important to note that although the measured single-atom hopping is one order of magnitude slower in  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  (S1) than in  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  (S2) (see Fig. 3), the reported viscosity is similar in S1<sup>18</sup> and S2.<sup>19,20</sup> This shows that single-atom hopping is decoupled from the structural relaxation.

In conclusion, atomic hopping is an intrinsic property of metallic glasses, particularly for small atoms such as P atoms in glassy Pd–Cu–Ni–P and Be atoms in Vit1 and Vit4. The hopping rate of P depends sensitively on the openness of the intrinsic glassy structure of Pd–Ni–Cu–P. However, P hopping is not influenced significantly by changes of local electronic states at P sites induced by the substitution of Ni by Cu. It remains to be seen how such hopping motion in metallic glasses is related to the Johari–Goldstein  $\beta$  relaxation observed in other glassy systems such as polymers.<sup>21</sup>

This work was supported by the US Army Research Office (Grant No. DAAD19-02-1-0225).

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