Fast and slow dynamics in $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts as seen by neutron scattering

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We present experimental results on the fast β and slow α relaxational dynamics observed through incoherent quasielastic neutron scattering from $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts. The density correlation function, measured over a range of temperatures, shows a clear two-step relaxation process. The critical or crossover temperature, T_c , evaluated from the asymptotic scaling function of the mode-coupling theory was found to be at 620 ± 5 K. The correlation decay is not exponential, being extended over a far wider time range. In addition, the stretched exponent β_q was found to be independent of temperature and momentum transfer (q). The self-diffusivity is an order lower compared with that observed in simple metallic liquids at their melting temperature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2827486]

I. INTRODUCTION

When cooled or quenched on laboratory time scales, few alloy melts form glass. Liquid alloys such as $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ or $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ vitrify when cooled at rates less than 0.1 K s^{-1} .^{1,2} On the other hand, many binary or ternary melts require cooling rates of 10^6 K s^{-1} or more to become a glass.³ Understanding the atomic dynamics leading to vitrification of materials is an important challenge in condensed matter physics.⁴ Mode-coupling theory (MCT),⁵ for the liquid-to-glass transition gives a consistent description of the dynamics within the liquids that lead to vitrification. The theory predicts collective atomic transport and a two-step relaxation process in the glass-forming viscous liquids. Inelastic neutron scattering in a dense, hard-sphere like metallic glass-forming $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ melts shows that collective atomic motion extends up to temperatures as high as 1800 K and that self-diffusion is controlled by the packing density.⁶

$\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ is a newcomer to the glass-forming metallic family and can easily be die cast in rods with diameters up to 5 mm.⁷ It has an exceptionally low glass transition temperature, T_g , and is reported to have a fragility index of $m=31$.⁷ Most of the alloys melt at high temperatures, where it is difficult to distinguish between phonons and a fast β process. $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ alloy melts at comparatively low temperatures and is expected to clearly show a β -relaxation process. The reported fragility index indicates that it should be a strong glass former, but, in general, metallic glasses that show low-temperature T_g are very fragile.⁸ Moreover, the critical casting thickness of the alloy is only 5 mm, much smaller than that of good metallic glass-forming alloys. Because of these reported contradictory properties and low li-

quidus temperature, making it suitable for studying the β -relaxation process, we have investigated microscopic dynamics in the $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melt through quasielastic neutron scattering (QNS).

II. MEASURING $S(q, \omega)$ AND $\Phi(q, t)$

$\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ alloy was prepared by arc melting of high-purity (99.9%) elements under an argon atmosphere. The glass transition T_g (420 K), crystallization T_x (472 K), and liquidus temperatures T_{liq} (730 K) were measured using differential scanning calorimetry (DSC) with a heating rate of 40 K s^{-1} and were in good agreement [Fig. 1(b)] with reported values.⁷

The arc melted alloy ingots were powdered in an inert atmosphere and filled in a thin-walled Al_2O_3 container by remelting 2–3 times in a high-vacuum (1×10^{-8} mbar) furnace. The Al_2O_3 container imparts a hollow cylindrical shape to the sample with 30 mm height, 22 mm diameter, and 1.2 mm thickness. The alumina is not only transparent to neutrons at $\lambda=5.4 \text{ Å}$, but also chemically inert with $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts at high temperatures. The small sample thickness helps to reduce multiple scattering and with this sample geometry only 6%–8% of the incoming neutrons will be scattered.

The inelastic neutron-scattering experiments were carried out using a crystal monochromatized time-of-flight spectrometer FOCUS at the Paul Scherrer Institute, Villigen, Switzerland. For a 5.4 Å neutron wavelength and $10^\circ < 2\theta < 130^\circ$ scattering angle, the accessible wavenumber range at zero energy transfer for the experimental setup was $0.4 - 2.1 \text{ Å}^{-1}$, providing an energy resolution of $\approx 130 \text{ μeV}$ (full width at half maximum). Regarding the contribution to the scattered signals, the elements in the alloys are predominantly coherent scatterers, but the structure factor maximum (q_0) for all these alloy melts are well above the q range accessible by the experimental setup. Thus, the scattered signals in our experiments are dominated by the incoherent contributions from Ni and Cu atoms. The resulting scattering

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FIG. 1. (Color online) (a) The self-correlation function $\Phi(q,t)$ of $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts obtained on the neutron time-of-flight spectrometer FOCUS. $\Phi(q,t)$ shows a fast β -relaxation process and the solid lines are from fits using a MCT β -scaling law [Eq. (1)] with $\lambda=0.77$. (b) The characteristic temperatures of the melt-spun ribbon from the DSC scan with a heating rate of 40 K/min.

law represents the mean dynamics of Cu and Ni atoms in the melt. The samples were measured at room temperature to obtain the instrumental energy resolution function. The alloy melts were measured close to the liquidus temperature, 803 K and at six additional temperatures with a step interval of 30 K. The data were collected over a duration of 4–5 h at each temperature. The empty sample container was also measured at each temperature, and for the normalization of scattered signals, measurements were made of a vanadium sample with a similar geometry.

The raw data reduction and analysis of the spectra were undertaken using the Frida-1 code.⁹ The scattering law, $S(q,\omega)$, was determined by normalizing the raw data to a vanadium standard, correcting for self-absorption and container scattering, interpolating to constant q , and symmetrized with respect to energy with the detailed balance factor. Fourier deconvolution of $S(q,\omega)$ and normalization to 1 for $t=0$ gives the self-correlation function $\Phi(q,t)$.

III. β -SCALING ANALYSIS

According to mode-coupling theory, the structural relaxation or α process is preceded by a cage rattling of atoms. This is visible in the density correlation function as an additional shoulder following the short-time vibrational relaxation and as an antecedent to the long-time diffusional relaxation, whose time scale is of the order of a picosecond. Asymptotically, the time correlation function of the dynamical variable in this regime is expected to follow

$$\Phi_q(t) = f_q + h_q g_\lambda(t/t_\sigma), \quad (1)$$

where the time dependent term $g_\lambda(t/t_\sigma)$ is completely determined by a single unique exponent parameter λ . Here, f_q is the Debye–Waller factor, h_q is the amplitude of β relaxation, and t_σ is the crossover time. The theory predicts the temperature variation of t_σ and h_q with the asymptotic scaling functions to be

FIG. 2. (Color online) (a) The temperature dependence of the amplitude $\langle h_q \rangle$ and time scale t_σ of the β -relaxation process according to the Eq. (2). Both lines are extrapolated consistently to get the mode-coupling crossover temperature, T_c at 620 ± 5 K. (b) The amplitude of the β process as a function of q .

$$h_q \propto (T - T_c)^{1/2},$$

$$t_\sigma \propto (T - T_c)^{(-1/2a)}, \quad (2)$$

where the exponent a is determined by λ . The values of a , h_q , and γ as a function of λ were obtained from Ref. 10.

Figure 1(a) displays the density correlation function of the liquid $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ at $q=1.83 \text{ \AA}^{-1}$ in a semilogarithmic representation, which clearly shows a two-step relaxation process. Between 0 and 0.2 ps, phonons lead to a rapid decay of atomic correlations. As the time increases, $\Phi(q,t)$ shows nearly a constant value or a plateau for f_q . On approaching this plateau, before $\Phi(q,t)$ decays toward zero, a fast relaxation is clearly visible. Since the vibrational part of the spectrum [represented by the first data point in $\Phi(q,t)$] is well separated from the relaxational parts, this gives us an advantage in investigating the picosecond dynamics in the vicinity of f_q , the fast β -relaxation process.

The two-step decay can be fitted with a MCT β -scaling law [Eq. (1)] in the range from 0.2 to 10 ps. The fitting of the data was undertaken using a two-step scheme, starting with an arbitrary value for the line shape parameter λ , fitted to individual curves. From this fitting, average values were estimated for the scaling factors. After fixing a q independent mean t_σ , the fit gives a temperature and q independent T_c , which was found to be 0.77 ± 0.05 . This result is in agreement with the value of λ calculated for a mixture of hard spheres, $\lambda=0.766$.¹¹ The rest of the analysis was undertaken with λ fixed to a value of 0.77. The Debye–Waller factor f_q , obtained from the fitting, varies only weakly with temperature, but the temperature dependence of the amplitude h_q and the crossover time t_σ strongly indicate the slowing down of the relaxational dynamics upon cooling.

Figure 2(a) displays the temperature variation of h_q and t_σ for the fast β relaxation in liquid $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$, given according to Eq. (2). The temperature dependence of h_q and t_σ is in accordance with the MCT predictions with an exponent $a=0.295$, based on $\lambda=0.77$. When h_q and t_σ are ex-

FIG. 3. (Color online) (a): The dynamic structure factor of $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melt at 983 K for $q=1.13 \text{ \AA}^{-1}$. The solid line is the fit from a Fourier-transformed Kohlrausch stretched exponential function and the dotted line is a simple Lorentzian fit. The spectrum measured at 300 K is the instrumental energy resolution. (b) The $(1/T)$ dependence of the average self-diffusivity of Cu and Ni in $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts. The solid line is the τ scaling law fitted to the measured diffusivities with $\gamma=2.7$ and $T_c=620 \text{ K}$.

trapolated for the experimentally inaccessible metastable liquid below T_{liq} , a consistent value for the microscopic glass transition temperature, $T_c=620 \pm 5 \text{ K}$, is obtained. In the fluid regime, the T_c derived from idealized mode-coupling theory does not show its universal character, i.e., $T_c=1.2T_g$ (the heating rate dependence of T_g will have a small effect on the earlier approximation), rather it shows $T_c \approx 1.5T_g$.

The factorial property of the β -relaxation process in the time interval 0.1 ps to t_σ is well satisfied, i.e., $[\Phi(q, t) - f_q]/h_q$ is independent of q . This factorial property will only occur if the line shape parameter λ and the crossover time t_σ of the β correlator are both independent of the wavenumber. The q dependence of the amplitude h_q is shown for 803 K in Fig. 2(b). h_q is found to be independent of q ; similar observations have been reported for $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ (Ref. 6) melts and also in nonmetallic glass formers.^{12,13}

IV. α RELAXATION AND SELF-DIFFUSION

Figure 3(a) shows the dynamic structure factor or the scattering law $S(q, \omega)$ of $\text{Pd}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{P}_{10}$ melts at 300 and 983 K for a q value of $1.13 \text{ \AA}^{-1}$. At 983 K, the spectrum shows broadening, a sign of atomic self-diffusion in the liquid. The spectral shape of $S(q, \omega)$ at 983 K is not well described by a single Lorentzian function [dashed line in Fig. 3(a)]. As in other glass-forming systems, we observed a non-Debye relaxation on microscopic scales. An appropriate representation of the relaxation is the stretched exponential or Kohlrausch stretched exponential function (KWW), $b_q + f_q \exp[(-t/\tau_q)^{\beta_q}]$; the constant b_q accounts for the background, f_q is the Debye–Waller factor and β_q is the stretching exponent. The solid line in Fig. 3(a) is the Fourier-transformed KWW function fitted to the measured $S(q, \omega)$ at 983 K. The function was convolved with the instrumental energy resolution function when fitting the data. A smooth

instrumental energy resolution function was obtained from a fit of the sum of a Gaussian and a constant to the scattering law measured at 300 K.

The data points were initially fitted using an arbitrary value for τ_q and β_q . Over the assessable q range, β_q is found to vary around a value of 0.66 ± 0.04 . Further analysis was carried out by fixing the β_q value to a constant, 0.66. This fitting procedure shows that data measured at different temperatures can be best described by a temperature and a q independent stretching exponent $\beta_q=0.66$. The value of β_q observed in this multicomponent metallic glass-forming liquid is similar to that found in molecular systems.¹⁴

In contrast, the β_q value observed in many glass-forming liquids exhibits temperature dependence. Most of the nonmetallic glass formers show this dependence. In many cases it increases with increasing temperature. In more fragile glass-forming liquids, β_q is found to be more pronounced. For example, van der Waals liquids such as orthoterphenyl show $\beta_q=0.5$ (Ref. 13) and has a fragility index of $m=81$.¹⁴ Glycerol, a hydrogen bond forming with $m=51$,¹⁵ shows $\beta_q=0.6$,¹⁶ in neutron-scattering experiments. The strong stretching observed from the neutron scattering in $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts differs from the general expectations for β_q and the fragility index (m) derived from the DSC measurements.⁷ Unfortunately, there are no viscosity measurements reported for $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts to compare with the obtained value for m .

The resulting mean relaxation time obtained from the iterative fitting procedure described earlier is

$$\langle \tau_q \rangle = \tau_q \beta_q^{-1} \Gamma(\beta_q^{-1}) \quad (3)$$

and is proportional to $1/q^2$ as expected in the hydrodynamic limit for $q \ll q_0$.¹⁷ This enables us to determine the average self-diffusivity

$$D = \frac{1}{q^2 \langle \tau_q \rangle}. \quad (4)$$

Since Cu and Ni atoms possess an incoherent cross section, the derived D will be the average for Cu and Ni. Within the window of neutron scattering, $\tau_q \propto q^2$, there was no deviation away from this behavior (possibly toward $\tau_q \propto q^{2/\beta}$), as is observed in several polymers from neutron scattering and dielectric spectroscopy.^{18,19} Figure 3(b) shows the self-diffusivity of CuNi derived with a q range of $0.3\text{--}1.6 \text{ \AA}^{-1}$.

The self-diffusion obtained at 803 K, 15 K above the liquidus temperature, is $1.4 \pm 0.06 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This is comparatively larger than the better metallic glass-forming $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ ($D=3 \pm 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$),⁶ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, and $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ at their liquidus temperatures.^{20,25} Since $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ is a better glass former than $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$, the larger atomic self-diffusivity close to the liquidus temperature reflects the poorer glass-forming ability of the $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ alloy melt. On the other hand, it is approximately an order smaller than monoatomic simple metallic melts, such as liquid Ni close to the melting temperature,^{21,22} or the self-diffusion in liquid Sn measured under microgravity conditions $D=2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.²³ The diffusion scenario is completely different from that in the network glass former, such as in Na_2O

2SiO_2 , $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, or $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ melts, where smaller atoms diffuse faster through the channels formed by the SiO_2 networks.^{24,25}

Even though the D measured is not over a very large temperature range, the temperature dependence of the self-diffusivity indicates a non-Arrhenius behavior [Fig. 3(b)]. This is similar to what is found in multicomponent glass-forming melts from inelastic neutron scattering and tracer diffusion measurements.^{26,20,21} The temperature dependence of the self-diffusivity is well described by a τ scaling law of MCT, $D \propto [(T - T_c)/T_c]^\gamma$. The solid line is the τ scaling law fitted to the measured diffusion with $T_c = 620$ K and $\gamma = 2.7$. Present QNS study clearly indicates that the smaller the diffusivity close to the liquidus temperature, the larger the glass-forming ability of a metallic melt.

V. CONCLUSIONS

In summary, quasielastic neutron scattering from $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melts show a fast β -relaxation process. A mode-coupling analysis indicates that the critical temperature T_c for the dynamical crossover is at 620 ± 5 K. The stretching of the self-correlation indicates that it is a highly fragile liquid and the β_q value observed is comparable to that found in many molecular glass formers. The self-diffusivity close to liquidus temperature is an order of magnitude less than for simple metallic liquids at their melting temperatures, but comparatively larger than that of good metallic glass formers. This enhanced diffusivity must be the reason for the reduced glass-forming ability of the $\text{Pr}_{60}\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{10}$ melt as compared with other, better metallic glass formers.

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- ¹J. Schroers, W. L. Johnson, and R. Busch, Appl. Phys. Lett. **77**, 1158 (2000).
- ²Y. J. Kim, R. Busch, W. L. Johnson, A. J. Rulison, and W. K. Rhim, Appl. Phys. Lett. **68**, 1057 (1996).
- ³W. H. Wang, C. Dong, and C. H. Shek, Mater. Sci. Eng., R. **44**, 45 (2004).
- ⁴F. Faupel, W. Frank, M.-P. Macht, H. Mehrer, V. Naundorf, H. R. Schober, S. K. Sharma, and H. Teichler, Rev. Mod. Phys. **75**, 237 (2003).
- ⁵W. Götzke, Rep. Prog. Phys. **55**, 241 (1992).
- ⁶A. Meyer, Phys. Rev. B **86**, 011918 (2002).
- ⁷Z. F. Zhao, Z. Zhang, P. Wen, M. X. Pan, D. Q. Zhao, W. H. Wang, and W. L. Wang, Appl. Phys. Lett. **82**, 4699 (2003).
- ⁸C. A. Angell, J. Non-Cryst. Solids **73**, 1 (1985).
- ⁹<http://sourceforge.net/projects/frida>.
- ¹⁰W. Götzke, J. Phys.: Condens. Matter **2**, 8485 (1990).
- ¹¹M. Fuchs, I. Hofacker, and A. Latz, Phys. Rev. A **45**, 898 (1992).
- ¹²A. Tölle, H. Schober, J. Wuttke, and F. Fujara, Phys. Rev. E **56**, 809 (1997).
- ¹³A. Tölle, Rep. Prog. Phys. **64**, 1473 (2001).
- ¹⁴R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
- ¹⁵L.-M. Wang, V. Velikov, and C. A. Angell, J. Chem. Phys. **117**, 10184 (2002).
- ¹⁶J. Wuttke, I. Chang, O. G. Randl, F. Fujara, and W. Petry, Phys. Rev. B **54**, 5364 (1996).
- ¹⁷J. P. Boon and S. Yip, *Molecular Hydrodynamic* (McGraw-Hill, New York, 1980).
- ¹⁸J. Colmenero, A. Alegria, and A. Arbe, Phys. Rev. Lett. **69**, 478 (1992).
- ¹⁹A. Arbe, J. Colmenero, M. Monkenbusch, and D. Richter, Phys. Lett. **81**, 590 (1998).
- ²⁰A. Meyer, W. Petry, M. Koza, and M.-P. Macht, Appl. Phys. Lett. **83**, 3894 (2003).
- ²¹S. M. Chathoth, A. Meyer, M. M. Koza, and F. Juranyi, Appl. Phys. Lett. **85**, 4881 (2004).
- ²²S. K. Das, J. Horbach, M. M. Koza, S. M. Chathoth, and A. Meyer, Appl. Phys. Lett. **86**, 011918 (2005).
- ²³G. Frohberg, K.-H. Kraatz, and H. Wever, Mater. Sci. Forum **15–18**, 529 (1987).
- ²⁴F. Kargl, A. Meyer, M. M. Koza, and H. Schober, Phys. Rev. B **74**, 014304 (2006).
- ²⁵A. Meyer, J. Horbach, W. Kob, F. Kargl, and H. Schober, Phys. Rev. Lett. **93**, 027801 (2004).
- ²⁶V. Zöllmer, K. Rätzke, F. Faupel, and A. Meyer, Phys. Rev. Lett. **90**, 195502 (2003).