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Reentrant glass transition leading to ultrastable metallic glass --Manuscript Draft--

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Corresponding Author:	Z. P. Lu University of Science and Technology Beijing Beijing, China
First Author:	Qing Du
Order of Authors:	Qing Du
	Xiongjun Liu
	Huiyang Fan
	Qiaoshi Zeng
	Yuan Wu
	Hui Wang
	Debaditya Chatterjee
	Yang Ren
	Yubin Ke
	Paul Voyles
	Z. P. Lu
	Evan Ma
Abstract:	Polyamorphs are often observed in amorphous matters, and a representative example is the reentrant glass transition in colloid systems. For metallic amorphous alloys, however, the cases reported so far are limited to metallic glasses (MGs) that undergo electronic transitions under gigapascal applied pressure, or the presence of two liquids at the same composition. Here we report the first observation of a reentrant glass transition in MGs. This unusual reentrant glass transition transforms an MG from its as- quenched state (Glass I) to an ultrastable state (Glass II), mediated by the supercooled liquid of Glass I. Specifically, upon heating to above its glass transition temperature under ambient pressure, Glass I first transitions into its supercooled liquid, which then transforms into a new Glass II, accompanied by an exothermic peak in calorimetric scan, together with a precipitous drop in volume, electrical resistance and specific heat, as well as clear evidence of local structural ordering on the short-to-medium-range scale revealed via in-situ synchrotron X-ray scattering. Atomistic simulations indicate enhanced ordering of locally favored motifs to establish correlations in the medium range that resemble those in equilibrium crystalline compounds. The resulting lower-energy Glass II has its own glass transition temperature higher than that of Glass I by as much as 50 degrees. This route thus delivers a thermodynamically and kinetically ultrastable MG that can be easily retained to ambient conditions.
Suggested Reviewers:	Mo Li mo.li@mse.gatech.edu Prof. Yang is a well-recognized expert in the research on atomic structure and phase transition of metallic glasses, and has published numerous high-profile papers about metallic glasses. Wei Hua Wang whw@iphy.ac.cn

	Prof. Wang is widely recognized for his work on formation, microstructure, and physical properties of bulk metallic glasses under high pressure and microgravity, and has published numerous high-profile papers about metallic glasses in Nature, Science, PNAS, Phys. Rev. Lett. Adv. Mater., Acta Mater., etc. We have cited his work as Refs. 19, 34 and 53 in the manuscript.
	Xun-Li Wang xlwang@cityu.edu.hk Prof. Wang is an elected Fellow of the American Physical Society (APS), American Association for the Advancement of Science (AAAS). His current research interests include structure and dynamics in metallic glass in Nature Materials, Nature Communications, etc. We have cited his work on the phase transition in metallic glasses as Refs. 29 and 52 in the manuscript.
	Eun Soo Park espark@snu.ac.kr Prof. Park is a well-known expert in studying polymorphic transformation, phase separation, deformation mechanism and structure characterization of metallic glasses.
Opposed Reviewers:	
Response to Reviewers:	Comment 1-Reply: We would like to thank the reviewer for his/her carefully analyzing our experimental data. Obviously, many factors can cause the difference in the intensity between the SAXS and SANS data as the reviewer mentioned. We just name a few aspects here: (1) The constituent elements in the glasses show different scattering cross section under neutron and x-ray. The SAXS intensity reflects the fluctuation of electron density in samples, whilst the SANS intensity stems from the heterogeneity of atom nuclei distribution. (2) The incident photon flux in SAXS is usually several orders higher than neutron flux in SANS. More importantly, it should be noted that we only used the relative change in the intensity of both SAXS and SANS results to probe the structural change during ordering inside the sample, and as a matter of fact, the absolute values of both SAXS and SANS are not important. To avoid possible misunderstanding, the intensity of both SAXS and SANS data are modified in arbitrary unit. Speaking of the slight intensity fluctuation at q≈0.4 Å-1 for both Glass I and Glass II, we checked our original SANS data and found that this tiny fluctuation actually came from the background, which includes three layers of Kapton film. As shown in Fig. R1, there is a small drop of intensity at q≈0.4 Å-1 in the SANS curve of background (black one in Fig. R1), which result in the tiny intensity fluctuation after background subtraction. We want to emphasize that no obvious difference in the SANS curves
	between the as-cast Glass I (red curve in Fig. R1) and the ordered Glass II (blue curve in Fig. R1), evidently confirming that the slight intensity fluctuation at q≈0.4 Å-1 is attributed to the background rather than the sample itself. Comment 2-Reply: It seems that the reviewer didnot read the paper carefully. In the paper that reviewer mentioned, the nano-sacle crystal nuclei (≥3 nm) give rise to not only significant intensity changes in V(k) data between the amorphous and the tiny crystallized PCRAM samples, but also additional peaks in the V(k) curve (as indicated by arrows in Fig. R2). In our case, no appearance of extra peaks and even no appreciable change of peak intensity in the V(k) curve between the Glass I and Glass II was observed (we only saw peak narrowing). In addition, we also iterated many times that our FEM results combined with other experimental data by many state-of-the-art techniques provide compelling evidences to rule out the nano-crystallization but to support the reentrant glass transition. Comment 3-Reply: We are most delighted for the kind appreciation of our work.



UNIVERSITY OF SCIENCE & TECHNOLOGY BEIJING

Prof. Z. P. Lu 30 Xueyuan Road, Haidian District Beijing, China 100083 Phone: 86-10-62334577

August 28, 2019

Dr. Yang Lu Associate Editor Materials Today

<u>RE: Manuscript (MATTOD 2019 214 R2) entitled</u> 'Reentrant glass transition leading to ultrastable metallic glass' by Du et al.

Dear Dr. Lu,

Thank you very much for your efforts on handling our manuscript (MATTOD_2019_214_R2). We are pleased to see that that Reviewers 3 has fully supported our rebuttal and recommended the manuscript to publish in Materials Today. Based on the new comments raised by Reviewer 1, however, we start to believe that he/she has strong bias on work. This reviewer has been confusing the concept of crystalline-like (short-to-medium-range) orders and nano-crystals in metallic glasses. In our manuscript and the last response letter, we clearly demonstrated that there is an atomic ordering process at the medium-range scale (typically 0.5-2 nm as defined by the Nature paper [Nature 354 (1991) 445–452]) accompanied with the reentrant glass transition. More importantly, various state-of-the-art structural characterization techniques available at the moment were exploited to clarify the nano-crystallization issue. The fact is that all our experimental data provide compelling evidence to support the claim that the reentrant glass transition is associated with a structural ordering process but not reached the nano-crystallization stage yet. Unfortunately, these robust experimental evidences were not recognized by this Reviewer 1. This reviewer nitpicks about our data, and as stated in our detailed response, his/her comments are actually untenable and not necessarily to be incorporated in the revision.

For your justification, nevertheless, we have still provided detailed explanations in response to the comments in Response Letter. Meanwhile, we have revised the manuscript to further emphasize our key findings, and a summary of point-by-point responses to the reviewers' comments is enclosed. For your convenience, all revisions in the revised manuscript have been highlighted in red color.

We look forward to hearing your favorable decision in due course.

Kind regards,

The Author Team

Point-by-point responses to editor and referees

Referee #1 (Remarks to the Author):

Comment 1: In this revised manuscript, the authors conducted small-angle neutron scattering (SANS) measurements with the Q range up to 0.6 Å⁻¹ for samples. When I compare the data in Fig. 1b in the revised manuscript with Fig. R1, together with Fig. R2, a few points confuse me: (1) At $q \approx 0.011$ Å⁻¹ and 0.02 Å⁻¹, scattering intensities from SAXS are about 2000 and 400 (untis?), respectively, which are much larger than those from SANS to be about 40 and 12 (units?), respectively, why? (2) When one carefully examines the SANS data, it seems that at $q \approx 0.4$ Å⁻¹, the SANS intensity is higher than those at $q \approx 0.1$ Å⁻¹ and 0.6 Å⁻¹, which indicates a density fluctuation on a scale of about 1.5-1.6 nm. This is the exact point, suggesting the formation of 1-2 nm-sized poorly crystallized component

Reply:

We would like to thank the reviewer for his/her carefully analyzing our experimental data. Obviously, many factors can cause the difference in the intensity between the SAXS and SANS data as the reviewer mentioned. We just name a few aspects here: (1) The constituent elements in the glasses show different scattering cross section under neutron and x-ray. The SAXS intensity reflects the fluctuation of electron density in samples, whilst the SANS intensity stems from the heterogeneity of atom nuclei distribution. (2) The incident photon flux in SAXS is usually several orders higher than neutron flux in SANS. More importantly, it should be noted that we only used the relative change in the intensity of both SAXS and SANS results to probe the structural change during ordering inside the sample, and as a matter of fact, the absolute values of both SAXS and SANS are not important. To avoid possible misunderstanding, the intensity of both SAXS and SANS data are modified in arbitrary unit.

Speaking of the slight intensity fluctuation at $q \approx 0.4$ Å⁻¹ for both Glass I and Glass II, we checked our original SANS data and found that this tiny fluctuation actually came from the background, which includes three layers of Kapton film. As shown in Fig. R1, there is a small drop of intensity at $q \approx 0.4$ Å⁻¹ in the SANS curve of background (black one in Fig. R1), which result in the tiny intensity fluctuation after background subtraction. We want to emphasize that no obvious difference in the SANS curves between the as-cast Glass I (red curve in Fig. R1) and the ordered Glass II (blue curve in Fig. R1), evidently confirming that the slight intensity fluctuation at $q \approx 0.4$ Å⁻¹ is attributed to the background rather than the sample itself.



Fig. R1. SANS data of the background, as-cast Glass I, and ordered Glass II from q=0.01 to 0.6 Å⁻¹. The inset enlarges the data from q=0.-1 to 0.6 Å⁻¹.

Comment 2: Concerning FEM results of GST sample in Fig. R2, when one carefully reads the paper (APL 104 (2014) 071907), the authors clearly state that (1) more than 3 nm crystal nuclei exist in the melt-quenched in PCRAM sample, and (2) the larger the crystal nuclei, the higher the Variance. Therefore, the conclusion for the formation of 1-2 nm-sized poorly crystallized component is still supported. It can be concluded that no evidences for the reentrant glass transition were obtained in this work.

Reply:

It seems that the reviewer didnot read the paper carefully. In the paper that reviewer mentioned, the nano-sacle crystal nuclei (\geq 3 nm) give rise to not only significant intensity changes in V(k) data between the amorphous and the tiny crystallized PCRAM samples, but also additional peaks in the V(k) curve (as indicated by arrows in Fig. R2). In our case, no appearance of extra peaks and even no appreciable change of peak intensity in the V(k) curve between the Glass I and Glass II was observed (we only saw peak narrowing). In addition, we also iterated many times that our FEM results combined with other experimental data by many state-of-the-art techniques provide compelling evidences to rule out the nano-crystallization but to support the reentrant glass transition.



Fig. R2. Fluctuation microscopy V(k) data between the melt-quenched GST (with nanoscale nuclei) and as-deposited sample. The variance from the melt-quenched sample is much higher than that of the as-deposited one due to the nanoscale nuclei in the amorphous matrix. [Appl. Phys. Lett. 104 (2014) 071907]. The red arrows indicate the additional peaks in the sample with nano scale crystal nuclei.

Referee #3 (Remarks to the Author):

Comment 1: The previous reviewer raised some important question and the authors addressed them very well in their rebuttal letter. The present reviewer is happy to recommend its publication now.

Reply:

We are most delighted for the kind appreciation of our work.























Reentrant glass transition leading to ultrastable metallic glass

Qing Du,¹Xiongjun Liu,^{1,*} Huiyang Fan,¹ Qiaoshi Zeng,^{2,3} Yuan Wu,¹ Hui Wang,¹ Debaditya Chatterjee,⁴ Yang Ren,⁵ Yubin Ke⁶, Paul M. Voyles,⁴ Zhaoping Lu,^{1,*} Evan Ma⁷

¹ Beijing Advanced Innovation Center for Materials Genome Engineering, State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, People's Republic of China.

²Center for High Pressure Science and Technology Advanced Research, Pudong, Shanghai 201203, People's Republic of China.

³School of Materials Science and Engineering, Southeast University, Nanjing 211189, People's Republic of China.

⁴Department of Materials Science and Engineering, University of Wisconsin-Madison, WI 53706 USA

⁵X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

⁶China Spallation Neutron Source, Dongguan, Guangdong 523000, People's Republic of China. ⁷Department of Materials Science and Engineering, Johns Hopkins University, MD 21218, USA.

*Corresponding author: Correspondence and requests for materials should be addressed to X.J. Liu (email: <u>xiliu@ustb.edu.cn</u>) or Z.P. Lu (email: <u>luzp@ustb.edu.cn</u>).

Polyamorphs are often observed in amorphous matters, and a representative example is the reentrant glass transition in colloid systems. For metallic amorphous alloys, however, the cases reported so far are limited to metallic glasses (MGs) that undergo electronic transitions under gigapascal applied pressure, or the presence of two liquids at the same composition. Here we report the first observation of a reentrant glass transition in MGs. This unusual reentrant glass transition transforms an MG from its as-quenched state (Glass I) to an ultrastable state (Glass II), mediated by the supercooled liquid of Glass I. Specifically, upon heating to above its glass transition temperature under ambient pressure, Glass I first transitions into its supercooled liquid, which then transforms into a new Glass II, accompanied by an exothermic peak in calorimetric scan, together with a precipitous drop in volume, electrical resistance and specific heat, as well as clear evidence of local structural ordering on the short-to-medium-range scale revealed via in-situ synchrotron X-ray scattering. Atomistic simulations indicate enhanced ordering of locally favored motifs to establish correlations in the medium range that resemble those in equilibrium crystalline compounds. The resulting lowerenergy Glass II has its own glass transition temperature higher than that of Glass I by as much as 50 degrees. This route thus delivers a thermodynamically and kinetically ultrastable MG that can be easily retained to ambient conditions.

Keywords: Reentrant Glass Transition; Ultrastable Metallic Glass; Atomic Structure; In-situ Synchrotron X-Ray Scattering; Atomistic Simulation

1 INTRODUCTION

Amorphous matters at a given chemical composition can exist in distinct states. One example is pressure-induced polyamorphism, for example in amorphous ice [1-3], colloidal clay [4], amorphous silicon [5, 6], oxide glasses [7], and chalcogenide glasses [8], where the amorphous structure transforms from an open local coordination environment to a more densely packed structure. The polyamorphic transition is characterized by the coexistence of two different glass states in equilibrium. Another example is reentrant glass transition, as observed in colloid systems [9-14], where a repulsive glass changes into an attractive one with enhanced bonding, mediated by an intermediate liquid in between the two glass states.

In the wide panorama of glassy systems, metallic glasses, especially bulk metallic glasses (BMGs) are an interesting class of materials to investigate the materials physics of glasses due to their densely packed structures [15, 16] arising from non-directional metallic bonds and multiple constituents with different atomic sizes. BMGs have also been emerging as a new class of structural and functional metallic materials due to their unusual structural features and unique properties [17-22]. Pressure-induced polyamorphic transitions were observed to occur in a few rare-earth-based and Ca-Al MGs [23-28], where the changes in electronic structure induced by pressure are believed to be responsible. Unfortunately, the transitions not only need gigapascal-level high pressure, but also are immediately reversed when the pressure is withdrawn. As for reentrant phase transitions, recently a second supercooled liquid (SCL) [29] was reported upon heating the (PdNi)_{82.5}P_{17.5} MG alloy, but the reversible transition between the two SCLs cannot retain a new MG to ambient conditions. Reentrant glass transition has not been observed so far for MG-forming systems.

Here we report the first observation of a reentrant glass transition in MGs, upon

heating of a Pd42.5Ni42.5P15 MG under ambient pressure. Specifically, upon heating the as-cast MG (Glass I) above its glass transition temperature (T_{g1}), the supercooled liquid (SCL I) has adequate atomic mobility to mediate structural ordering in short-to-medium range. This sets off a unique thermally-induced transition into a more ordered Glass II that is thermodynamically and kinetically more stable. Its lower enthalpy and much higher T_{g2} in fact qualify the new glass as "ultrastable", akin to those prepared using slow vapor deposition at elevated substrate temperatures [30-34]. Upon further heating, Glass II exhibits a new glass transition temperature, T_{g2} , before entering its own supercooled region (SCL II). The transition pathway of this alloy, Glass I \rightarrow SCL I \rightarrow Glass II \rightarrow SCL II, demonstrates that reentrant glass transition can indeed happen in MG-forming systems, along with reentrant supercooled liquid. Importantly, this finding opens a new route to a hidden amorphous state inaccessible during the fast cooling of the original cast MG, without having to go through the vapor phase [32-34]. An ultrastable MG with new structural order and properties can then be easily retained to room temperature.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

2.1 Sample preparation

Alloys were prepared by arc melting the mixtures of pure Pd and the Ni-P prealloy in an argon atmosphere. Alloy ingots were fluxed with B_2O_3 at 1273 K for 4 h. Glassy ribbons with a cross-section of $0.05 \times 8 \text{ mm}^2$ were produced via a single copper roller melt-spinning in an argon atmosphere.

2.2 Structure characterization

The annealed samples were firstly heated above T_{L-G} temperature (601K) at 10 K/min in the differential scanning calorimetry (DSC) and then cooled to room

temperature. Both the as-cast and annealed samples were examined by X-ray diffraction (XRD) using Cu Kα radiation (MXP21VAHF) and transmission electron microscopy (TEM, Tecnai F30, operating at 300 kV) techniques. The TEM samples were prepared by twin-jet electropolishing to avoid crystallization.

Small angle X-ray scattering (SAXS) experiments were performed on specimens with a thickness of 15 µm at beamline BL16B1 of Shanghai Synchrotron Radiation Facility. Small angle neutron scattering (SANS) experiments were performed on the SANS instrument at China Spallation Neutron Source (CSNS) [35]. The 3D atom probe tomography (APT) characterization was performed in a CAMECA Instruments LEAP 5000 XR local electrode atom probe. The data were collected for region more than 500 nanometers in length. The APT tip specimens for the as-cast and annealed samples were prepared using a focused ion beam (ZEISS AURIGA). Image Visualization and Analysis Software IVAS 3.6.12 was used for three-dimensional reconstructions and composition analyses. Fluctuation electron microscopy (FEM) experiments were performed on electropolished TEM samples in an FEI Titan STEM with a probe Cs aberration corrector at 200 kV using a 2 nm diameter probe beam defined by a 10 µm diameter condenser aperture at a probe current of 3.36 pA. Nanodiffraction patterns were collected on a Gatan US 1000 CCD camera at the end of a Gatan Imaging Filter 865 using zero-loss energy filtering with a 10 eV wide slit and a 6 s exposure time. A Gatan annular dark- field detector mounted on the 2.5 mm GIF entrance aperture was used to collect STEM images simultaneously with the nanodiffraction patterns. For each sample, nanodiffraction patterns were collected from a 10×10 grid of positions covering a 30×30 nm² area of the sample. Variance data from five different areas of each sample were averaged together and reported with one standard deviation of the mean error bars.

Structure evolution of the as-cast ribbons as a function of temperature was monitored using a high-energy monochromatic x-ray beam at the Beamline 11-ID-C at Advanced Photon Source (APS), Argonne National Laboratory (ANL). X-ray wavelength was set to $\lambda = 0.11798$ Å (photon energy ~105 keV). Samples were placed in a computer-controlled Linkam THMS 600 hot stage with high temperature accuracy and stability of 0.01 K. Flowing Ar atmosphere in the hot stage was used to prevent sample oxidation. Heating and cooling rates were set at 10 K/min. The diffracted photons were collected up to a maximum wave vector momentum transfer $q = 30 \text{ nm}^{-1}$ $(q = 4\pi \sin\theta/\lambda)$ using a Perkin Elmer two-dimensional detector (Perkin Elmer amorphous silicon detector, 2048×2048 pixels, each pixel having effective size of 200 μ m × 200 μ m) calibrated using CeO₂ powder as standard materials. Each image was collected for 1.5 s and accumulated for 10 times. The two-dimensional diffraction images were integrated into one dimensional pattern I(q) with Fit2D software package. Structure factors [S(q)] and reduced pair distribution functions [G(r)] at different temperatures were then derived from I(q) using the program package PDFgetX2 and PDFgetX3 [36-39]. The position of first-sharp diffraction peak (FSDP) and the full width at the half maximum (FWHM) of each S(q) were obtained by fitting the data with Gaussian function.

To prepare the samples to be used in EXAFS analysis, the ribbons was mechanically polished down to $\sim 20 \,\mu\text{m}$ in thickness. Pd K-edge and Ni K-edge EXAFS spectra for both samples at room temperature were measured in the transmission mode at the Beamline 20-BMB, APS, ANL. Ion chambers filled with N₂-Ar/He gas mixture were used as the intensity monitors. Ni and Pd standard films were placed at the downstream end of the beam path as references to calibrate the x-ray energy for each EXAFS spectra. Experimental data were analyzed by using Athena and Artemis

software package [40].

2.3 Thermal analyses, resistivity measurement and mechanical properties

DSC analyses were conducted using differential scanning calorimeter (Netzsch DSC404F1 and DSC214 Polyma). The instruments were calibrated with standard materials, i.e., indium and zinc. The Glass II sample used in DSC scan was obtained from the as-cast MG annealed at 610 K for 30 min followed by cooling to room temperature at the rate of 500 K/min. Temperature modulated DSC (TMDSC) measurements were carried out in a TA DSC 2910 under continuous heating rates of 2 K/min up to 700 K. A temperature amplitude of 1 K and a cycle time of 40 s were used. For the cyclic DSC scans, the specimen was first heated to 633 K at 10 K/min followed by cooling at 100 K/min to 293 K, then heated to 633 K followed by cooling at 100 K/min to 293 K. Ribbons with a dimension of about 15 mm × 0.05 mm were prepared for electrical resistivity measurements using a standard four-probe technique with a heating rate of 10 K/min. Mechanical properties were assessed by continuous stiffness measurement using a MTS DCM (Nano Indenter II) nanoindentation system at a constant strain rate of 0.05 s^{-1} to a depth of 1000 nm.

2.4 Reverse Monte Carlo modeling and structural analysis

Reverse Monte Carlo (RMC) modelling started with the same random packed cubic cell containing 5,000 atoms. Number densities derived from the experimentally measured density based on the Archimedes method were used: $\rho = 0.0791$ atom/Å³ for the as-cast sample and 0.0796 atom/Å³ for the one after reentrant glass transition. The experimental input data consist of the total structure factor S(q) and EXAFS $\chi(k)$ signals on the Pd and Ni K-edges. All the simulations were performed using the RMC Profile software package [41].

Voronoi tessellation method [42] was adopted to analyze the local atomic structures. Top 10 kinds of polyhedra for each centered atom were listed. Bond-angle distribution (BAD) function $f(\theta)$ [43] was calculated based on cutoff distances determined from the first minimum of calculated partial PDF curves. BADs of Ni₂P and Ni₃P crystals were also calculated for comparison. Cluster analyses [44] were conducted to investigate the connectivity of typical Ni₂P-like and Ni₃P-like Voronoi polyhedra. For the cluster-cluster common neighbour analysis, we followed the approach of Sheng et al. [45]. All the structural analysis data were average values from 20 RMC configurations.

3 RESULTS

3.1 Unusual heat release signal in the supercooled liquid region

The as-cast Pd_{42.5}Ni_{42.5}P₁₅ MG is a monolithic amorphous phase, as confirmed by the high-resolution transmission electron microscopy (HRTEM) image and the corresponding selected area electron diffraction (SAED) pattern in **Fig. 1(a)**, which show no identifiable crystal symmetry. SAXS and APT on the as-cast sample demonstrate that it does not exhibit chemical phase separation. The SAXS [**Fig. 1(b**)] and SANS (Supplementary Fig. S1) curves are very smooth with no detectable interference peak over the entire q range, suggesting that there is no obvious chemical composition segregation at the length scale over 1 nm. The three-dimensional reconstruction APT picture and corresponding concentration profile (**Fig. 2**) clearly show a uniform distribution of all the constituent elements in the sample, consistent with the SAXS observation. It is thus conclusive that the as-cast Pd_{42.5}Ni_{42.5}P₁₅ alloy is a single-phase MG with no phase separation in terms of compositional partitioning.

DSC measurements on this glass exhibit an unusual feature [Fig. 1(c)]: a striking

exothermic peak at temperature T_{L-G} (601 K) appeared after T_{g1} [561 K for this as-cast glass, see the inset in Fig. 1(c)] and before the crystallization peak (onset $T_x = 660$ K). The heat release integrated from the exothermic peak amounts to an enthalpy reduction of 1.1 kJ/mol. A similar exothermic feature was observed before by Chen in Pd-Ni-P glassy alloys [46], and it was believed to be a consequence of crystallization at that time. However, for the sample heated to 615 K (past T_{L-G}) and then cooled to room temperature, our results in Fig. 1 show that this DSC feature cannot arise from crystallization or phase separation. HRTEM [Fig. 1(d)], which probes very short length scales at a limited field of view, shows no evidence of crystallization, and the composition remained homogeneous and identical to the as-cast Glass I [see APT results in Fig. 2]. SAXS [Fig. 1(b)] and SANS (Supplementary Fig. S1), which probe a macroscopic sample volume, shows that the annealed sample is almost identical to the as-cast sample, further confirming the chemical homogeneity and no occurrence of crystallization, and the post-annealed structure is also amorphous by the wide-angle Xray synchrotron diffraction (Fig. 5 and discussion below). Systematic electron nanodiffraction [Figs. 3(a)-(d)] probes intermediate length scales and field of view between these two techniques with exquisite sensitivity to nanocrystals. Crystalline nanodiffraction patterns are characterized by strong Friedel pairs of spots, especially in the weaker second diffraction ring [Fig. 3(a) and 3(c)]. Amorphous nanodiffraction patterns have only lower intensity speckles without obvious Friedel pairs. 500 such nanodiffraction patterns sampling an area of 4500 nm² were acquired for each sample, then categorized by hand into crystalline and non-crystalline. The area density of crystals was 0.2% in the as-cast glass (1 pattern out of 500) and 3% in the annealed glass (15 patterns out of 500) in samples measured to be 20 nm thick. If we assume an upper bound on the nanocrystal diameter of ~2 nm (so that they remain invisible in standard TEM imaging) the volume fraction of crystals is 0.02 ± 0.02 % in the as-cast glass and 0.30 ± 0.08 % in the annealed glass. Thus, with this most sensitive measure, there is some crystallinity in the as-cast glass, as there is in every cast metallic glass, and there is some measurable increase in crystallinity with annealing. However, the calculated enthalpy release by an additional 0.28% crystallinity is only 0.014 kJ/mol, which means the change in crystal volume fraction is too small to account for the heat release (1.1 kJ/mol) in DSC or the differences in structure reported below.

We therefore conclude that the supercooled liquid that exists above the glass transition at 561 K transforms into another amorphous state with lower enthalpy around temperature T_{L-G} . The transformation is accompanied by a precipitous drop in electrical resistance (Supplementary **Fig. S2**) and an obvious increase in mass density (see below). Both the hardness and Young's modulus for Glass II, as measured by nanoindentation tests, increased by ~35% and 22% with respect to those for Glass I. These clearly signify that a new MG has emerged around T_{L-G} : the amorphous structure in the as-cast Glass I, upon adequate thermal agitation in its supercooled liquid region above T_{g1} , is able to transform into a new amorphous state, which can be retained to room temperature as Glass II of the same composition.

Fig. 4(a) shows temperature modulated DSC (TMDSC) measurements of the glass transition of Glass II at temperature $T_{g2} = 612$ K. This transition is masked in the conventional DSC data in **Fig. 1(c)** by the tail of the exothermic peak at T_{L-G} . The reversibility of the transition at T_{g2} was confirmed by cyclic DSC experiments on Glass II [**Fig. 4(c)**]. The presence of T_{g2} , a second glass transition temperature that is about 50 K above T_{g1} , indicates that the product of the exothermic event is no longer the preceding supercooled liquid of Glass I, but Glass II.

3.2 Structural evolution underlying the Glass I to Glass II transition

To investigate the underlying structural evolution, *in-situ* heating synchrotron XRD measurements were carried out. Figure 5(a) shows a set of XRD patterns during *in-situ* heating of the as-cast Pd_{42,5}Ni_{42,5}P₁₅ MG from 300 to 672 K at a constant rate of 10 K/min. Dramatic changes as a function of temperature in the XRD patterns separate them into three groups: (i) from 300 to 600 K [blue in Fig. 5(a)], (ii) from 600 to 660 K [green in Fig. 5(a)], and (iii) above 660 K [red in Fig. 5(a)]. Figure 5(b) shows representative structure factor S(q) curves selected from these three groups. The differences in the S(q) are discernable in the temperature range from 300 to 560 K, but become obvious between 560 and 613 K. In particular, the FWHM of the first peak in S(q) decreases remarkably, by as much as 37% from 0.43 Å⁻¹ (560 K) to 0.27 Å⁻¹ (613 K). The narrowed first peak in S(q) indicates that a more ordered atomic structure developed when the sample was heated to 613 K. There is nevertheless no sign of any crystalline phase in the synchrotron high-energy XRD curve of the sample heated up to 613 K [green curve in Fig. 5(b)]. Crystallization was observed only after the sample was heated up to 672 K, when sharp crystalline peaks appeared in the structure factor [the red curve in Fig. 5(b)]. These structural characterization results demonstrate that the as-cast Pd_{42.5}Ni_{42.5}P₁₅ MG, when being continuously heated to 613 K, evolves into a more ordered amorphous state.

The quantitative change of peak position q_1 and peak width (i.e., FWHM) of the principle diffraction peak of all S(q) data are shown as a function of temperature in **Fig. 5(c)**. Since $2\pi/q_1$ correlates with the volume density of the glass via a power law function [47, 48], this parameter can be conveniently used to estimate the relative change in density. Below $T_{\text{relax}} = 516 \text{ K}$, $2\pi/q_1$ increases linearly with temperature and the FWHM is almost constant, indicating normal thermal expansion without significant

structural change. Between 516 and 560 K (i.e., T_{g1}), the FWHM decreases slightly due to structural relaxation, which reduces the free volume and atomic stress. This concurrent relaxation and thermal expansion is commonly observed in MGs [49]. When the Glass I is heated into its supercooled liquid region from 560 to 598 K (i.e., SCL I from T_{gl} to just below T_{L-G}), the volume expansion rate (and slope of $2\pi/q_1$) increases, but the FWHM continues to decrease. Above 598 K, $2\pi/q_1$ quickly decreases, meaning that the SCL contracts (densifies). Meanwhile, the FWHM is sharply reduced by as much as ~37% from 598 to 612 K (T_{g2}), implying a striking increase in the degree of ordering within this temperature span. Together with the observation that the sample heated to 613 K remains fully amorphous [also see Fig. 1(d)], the abnormal thermal contraction is caused by a thermally induced supercooled-liquid-to-glass phase transition with an onset temperature of $T_{L-G} = 598$ K. The result is a new amorphous phase, Glass II, which has higher density and more ordered atomic structure than Glass I (the glass from the as-cast state to before the phase transition). It is thus demonstrated that the system undergoes a reentrant glass transition from Glass I to Glass II mediated by the SCL I. The characteristic temperatures T_{g1} , T_{L-G} , and T_{g2} in the *in-situ* heating synchrotron XRD are 560, 598, and 612 K respectively, in good agreement with those obtained from the DSC measurements in Figs. 1(c) and 4(c). Therefore, the peak temperature of the exothermic peak (i.e., T_{L-G}) is considered as the characteristic temperature of this reentrant glass transition.

3.3 Atomic ordering during the reentrant glass transition

To find the length scale of the structural ordering, we conducted pair distribution function (PDF) analyses of the *in-situ* diffraction data. Typical $G(\mathbf{r})$ curves by Fourier transformation of the corresponding $S(\mathbf{q})$ data shown in **Fig. 5(b)** are shown in **Fig. 5(d)**. The difference in $G(\mathbf{r})$ between Glass II (i.e., the curve obtained at 613 K) and

Glass I (i.e., the curve recorded at 560 K) was obtained by subtracting the latter from the former. As shown in **Fig. 5(e)**, the difference between these two states is relatively small within the *r* range below 6 Å, but substantial at $6 \le r \le 20$ Å, indicating that the atomic ordering is enhanced most obviously at the medium-range scale during the reentrant glass transition process. We therefore conclude that Glass II is more structurally ordered than Glass I, primarily at the medium range scale.

Figs. 6 and **7** present fluctuation electron microscopy (FEM) data, extended X-ray absorption fine structure (EXAFS) data, and RMC modeling comparing the structure of the Glass I and Glass II, both quenched to room temperature. FEM uses the normalized variance V(q) of the all non-crystalline electron nanodiffraction patterns [*e.g.* **Figs. 3(b)** and **3(d)**] to probe nanometer-scale structural heterogeneities in glasses [50]. The V(q) data in **Fig. 6** demonstrates a clear difference in medium-range order between the two glasses, indicated by the narrowing of the first peak around q = 2.95 Å⁻¹. Qualitatively, this narrowing corresponds to the reduced disorder in the interatomic spacings making up ordered regions within the glass.

For more detailed insight, we have employed RMC modeling based on X-ray S(q) and Ni and Pd *K*-edge EXAFS data (see the detailed data in Supplementary **Fig. S3**) to derive the 3D atomic configurations for the two glasses. The use of multiple experimental data sets and the atomic number density obtained from the real mass density measurement of the alloys improve the reliability of the RMC models. **Figures 7(a)** and **7(b)** present the typical RMC fitting curves for S(q) and EXFAS data, respectively, for both Glass I and Glass II. Comprehensive structural analyses including Voronoi tessellation, bond-angle distribution, and cluster analysis were conducted on the RMC configurations to detect the structural differences between these two glasses.

The most appreciable difference noticed in Voronoi tessellation analyses (Supplementary Fig. S4) is in the P-centered atomic coordination environment. Specifically, the most populous P-centered coordination polyhedra in Glass I are the clusters with Voronoi index <0, 4, 4, 0> and <0, 4, 4, 2>. Their populations decrease in Glass II, in favor of the tri-capped trigonal prism (TTP) packing with a Voronoi index of <0, 3, 6, 0> [see Supplementary Fig. S4(c)]. This suggests that the structural ordering associated with the reentrant glass transition is essentially the redistribution of P atoms to form more solute-centered locally favored motifs. Accompanying this are substantial changes in the P- and Ni-centered partial PDFs, whilst the Pd-centered ones show no significant change (Supplementary Fig. S5). The first peak intensity increases significantly for the Ni-Ni and Ni-P partial PDFs [Supplementary Figs. S5(d) and S5(e)] but decreases for the P-P partial PDFs [Supplementary Fig. S5(f)]. Bond-angle distribution (BAD) functions also indicate that those involving Ni and P atoms in Glass II exhibit pronounced differences from Glass I (see Supplementary Fig. S6). In Glass II the Ni-Ni-P, P-Ni-P and Ni-P-Ni BADs are enhanced obviously at around 47°, 89°, and 71°, respectively. Interestingly, these characteristic bond angles are those prevailing in Ni₂P and Ni₃P crystalline phases. Also, the P-centered <0, 3, 6, 0> polyhedra (tri-capped trigonal prisms, or TTPs) are the predominant motifs in Ni₂P (~70% of all P-centered polyhedra) and Ni₃P (100% of all P-centered polyhedra) compounds. Therefore, it is the preferential conversion into Ni₂P- and Ni₃P- like clusters that accounts for the ordering process during the phase transition from Glass I to Glass II. These results are consistent with the FEM data, since an increased preference of chemical short-range order around P atoms and an increased preference for crystal-like clusters will both decrease the spread in interatomic distances and create spatially ordered structures, narrowing the peaks in the FEM V(q).

At a longer length scale, **Figure 7(c)** displays the largest supercluster comprised of Ni₂P- and Ni₃P-like polyhedra in Glass I and Glass II. The size of the supercluster increases by >65% from Glass I to Glass II, demonstrating enhanced ordering in the medium range [**Fig. 5(e)**]. Moreover, as seen in the P-P partial PDF shown in Supplementary **Fig. S7**, the P-P correlation in Glass II is much enhanced, in terms of Ni₂P- and Ni₃P-like features. In other words, P atoms, more precisely the P-centered motifs, are striving to form a packing pattern that resembles those in equilibrium Ni(Pd)₂P- and Ni(Pd)₃P- compounds. This ordering is achieved via reorienting and connecting the TTPs into more correlated and denser packing. The more crystal-like characteristics of Glass II, in terms of both short-range and medium-range ordering, may be the reason why it is more stable (of lower enthalpy and high *T_g*) when compared with Glass I.

4 DISCUSSION

Exothermic peaks like the one at T_{L-G} have previously been attributed to (presumably nano) crystallization and to phase separation [51]. The results in Figs. 1-3 rule out both possibilities. The increase in crystalline volume fraction is negligible, and there is no evidence of phase separation at short or long length scales. The synchrotron x-ray diffraction measurements (Fig. 5) and FEM observations (Fig. 6) strongly suggest that the unusual heat release is associated with a structural ordering process at the medium-range scale but not reached the nano-crystallization stage yet.

We propose instead that we have observed a reentrant glass transition following the path illustrated in **Fig. 8**, where the phases observed in the Pd-Ni-P system are illustrated in a map. The high temperature liquid is rapidly quenched by melt spinning into the Glass I state. Upon heating, Glass I transforms to SCL I via a glass transition at T_{g1} . This SCL undergoes exothermic ordering upon heating to around T_{L-G} , to the extent that its viscosity rises so much that it turns into another solid, Glass II. If Glass II is heated to higher temperatures, it undergoes another glass transition at T_{g2} into less-ordered SCL II. If the system is cooled to room temperature from the Glass II state just above T_{L-G} , the Glass II state is preserved to ambient conditions. Glass II can then be reheated through a glass transition at T_{g2} into the SCL II without passing through Glass I at any temperature.

This sequence of transformation belongs to the realm of reentrant glass transition because we observe two different glasses connected by the supercooled liquid, as shown in Fig. 9. When the SCL I is not very well ordered, it connects with Glass I at T_{g1} . When an ordered SCL results from structural ordering, its dynamics slows down so much that it freezes into Glass II. Upon heating the ordered Glass II obtained, its glass transition temperature is much higher than T_{g1} , entering its own supercooled liquid region only after T_{g2} . This finding reveals the diversity of supercooled glass-forming liquids and solid glasses and is vastly different from previous observations at other compositions in this and other MG systems [52-55]. As described by the theory on reentrant glass transition [9-14], there is a supercooled liquid which transforms into a glass state upon both heating and cooling. Fig. 8 illustrates the evolution of enthalpy (or volume) upon cooling and heating of the alloy, i.e., the transition trajectory that was followed in our experiments. This reentrant glass transition is accomplished via supercooled liquid (of Glass I); this intermediate stage serves as a bridge that provided adequate thermal activation to overcome the kinetic barrier between the two amorphous states. The new and deeper energy megabasin where Glass II resides is reached through thermal activation in the supercooled liquid. Upon further heating, Glass II transitions into its own supercooled liquid. Note that the Glass II basin is not reachable during the

preparation of Glass I, because the cooling rate during casting is too high (~1,000 K/s needed to avoid crystallization) to allow adequate sampling of the PEL.

The Glass II reached via the reentrant glass transition is a remarkable material, strongly reminiscent of "ultrastable" glasses previously reached only in physical vapor deposition [30-34]. Compared to Glass I, a typical rapidly-quenched metallic glass, Glass II has both a lower enthalpy (by 1.1 kJ/mol) and a higher T_g (~50 K). It is therefore both more thermodynamically and more kinetically stable, in contrast with previous reports in MGs which have demonstrated enhanced kinetic stability but not enhanced thermodynamic stability [32-34]. The degree of the increased stability is also noteworthy, relative to other ultrastable glasses reported before. Yu et al. demonstrate a fractional change in T_g between the ultrastable and rapidly quenched glass states of ΔT_g / T_g = 1.6% by depositing on a substrate held at 0.78 T_g [32]. By depositing extremely slowly onto a substrate at 0.48 T_g , Luo *et al.* demonstrate $\Delta T_g / T_g = 8.6\%$ [34]. Our value is $\Delta T_g / T_g = 9.0\%$. Glass II also has higher density, consist with increased thermodynamic stability, as measured by X-ray diffraction and confirmed by the increase in Young's modulus. Also, Glass II is not a very thin film but obtained simply by heating a bulk material. All other ultrastable glasses have been synthesized via physical vapor deposition, in which very high surface mobility enables the glass surface to sample different configurations and settle into a low-energy basin in configuration space. In contrast, we obtained an ultrastable glass through a process that involves only condensed matter.

Structure must play a key role in such a transition. Previously, the structural signatures underlying amorphous-to-amorphous transitions have been difficult to identify [23-27]. For pressure-induced transitions in MGs, bond shortening resulting

from the pressure-induced delocalization of *f*-electrons appears to be the origin of the large volume contraction [23, 24, 26]. This mechanism mainly involves the changes in electronic interactions, rather than the changes in atomic configurational ordering [23]. The reports on liquid-liquid transitions in literature surmise that there is an underlying atomic ordering process, but exactly what kind of structural ordering is actually responsible has not been identified, as the transition happens in a high temperature liquid, making the structural characterization difficult [52-55].

Now that we have both Glass I and Glass II available and stable at room temperature and ambient pressure, we are able to gain significant insight into the structural differences between the two states. The initial Pd42.5Ni42.5P15 Glass I has a lower density and lower degree of local ordering and Glass II is a higher-density MG with a higher degree of short-to-medium range ordering. The atomic ordering involved in the reentrant glass transition is schematically outlined in Fig. 10. During heating, solute avoidance is enhanced to favor more (Ni, Pd)-P bonds due to the large negative heat of mixing between (Ni, Pd) and P. This substantially increases the number of the locally favorable motifs, P-centered <0, 3, 6, 0>, consistent with the observation that the fraction of P-P bonds decreases by ~9% in total, while the Ni-P and Pd-P bonds each increase by ~5% after reentrant glass transition (Supplementary TABLE S1). The dissociation of P-P neighbors happens in those P-centered clusters with less-thanoptimal coordination numbers, which is evidenced by the reduction of P-centered <0, 4, 4, 0> polyhedra, for example (Supplementary Fig. S4c). An energy reduction is expected to accompany the increase in locally favored clusters due to more efficient packing around P. Additionally, earlier theoretical investigation suggested that the presence of some degree of covalent bonding between phosphorous and nickel/palladium, attributed to the hybridization of their electronic orbitals, would make the P-centered trigonal prism cluster energetically more stable in the Pd-Ni-P MG [56]. Moreover, the linkage of the clusters by sharing Ni or Pd atoms at their vertices increases the flexibility of the random cluster network, and thus stabilizes the Pd-Ni-P MG by enhancing entropy without increasing internal energy [56]. In light of these, the free energy of the MG is projected to decrease upon enhanced ordering of P-centered TTPs (<0, 3, 6, 0> polyhedra).

The chemically ordered Ni-P and Pd-P polyhedral form connected superclusters that are larger in Glass II than in Glass I. We speculate that if these polyhedral have slow dynamics, analogous to icosahedral in Zr-based glasses [57], the large increase in $T_{\rm g}$ in Glass II vs Glass I is related to the formation of the large supercluster. In this context, the capacity to further order via the action of phosphorous solutes plays a critical role; the solute content was noticed to sensitively influence the phase selection among diverse Pd-Ni-P supercooled liquids and glasses [58]. Our alloy composition is located outside the metastable liquid miscibility gap of Pd-Ni-P glass-forming liquids [58]. When the phosphorous content is moved to inside the gap, other transitions may take effect. Recently, Lan et al. reported a reentrant phenomenon in the Pd_{41,25}Ni_{41,25}P_{17,5} supercooled liquid [29], as shown by the green dotted line in Fig. 9, where an anomalous exothermal peak in DSC was attributed to a reentrant liquid-liquid transition. Heating the sample brings the hidden SCL II to light. And quenching of the high-temperature SCL I restored the atomic structure of the as-cast Glass I, i.e., this reentrant liquid-liquid transition is a reversible event. In contrast, TMDSC results of our alloy in Fig. 4b confirm the irreversibility of the reentrant glass transition, as manifested by the complete disappearance of the exothermic peak upon heating the Glass II quenched directly from the high-temperature supercooled liquid. Thus, as shown by the red dotted line in Fig. 9, when content of phosphorus decreases to 15%,

the order in SCL II rises so much that it instigates Glass II in the SCL II region. The SCL in between these two MGs serves as a bridge and this closes a reentrant glass transition path.

A broad implication of our results is that a reentrant glass transition may be a general feature of MGs which (1) contain non-metallic or metalloid solutes that form strong covalent (-like) bonds with metallic solvents and (2) have a solute concentration that allows dissociation of solute-solute bonds and formation of solute-solvent bonds upon reheating. In this sense, the reentrant glass transition could be a common phase transition in MGs, especially for those alloys bearing metalloid elements. However, further work is needed to establish the general criterion for the reentrant glass transition. Another implication of this work is that the unique reentrant glass transition provides a potential opportunity to engineer heterogeneity in MGs by controlling the extent of transformation, and thus to improve the physical and mechanical properties of MGs via conventional heat treatments [59].

5 CONCLUSIONS

In summary, we have discovered an unusual thermally induced reentrant glass transition in monolithic amorphous Pd-Ni-P upon heating the MG into its supercooled liquid regime, before crystallization. Distinct from previously reported pressure-induced electronic phase transitions [23, 24, 26], the current reentrant glass transition involves an atomic ordering process, from short-range ordering towards extended ordering on the medium-range scale, building upon locally favored motifs and their medium-range correlations that resemble corresponding crystals, through the redistribution of unsatisfied P. Via the supercooled liquid of the as-cast Glass I, a new

amorphous state (either directly Glass II or its supercooled liquid) can be accessed, such that Glass I can be manipulated to convert into a higher-density, lower enthalpy, higher- T_g Glass II with a more ordered atomic structure, via simple thermal treatment followed by cooling at ordinary laboratory rates. As such, the present reentrant glass transition achieves an unconventional ultrastable MG and retains it to ambient conditions. Therefore, our findings not only expand our understanding of the states of amorphous metals, but also provide a new approach to access MG materials with interesting properties by transforming their atomic packing structures. Specifically, corresponding to its ultrastable state deep inside a PEL megabasin, as manifested by its drastically elevated glass transition temperature and atomic order as well as lower enthalpy, the reentrant MG offers a set of properties different from the conventional glass, such as higher density, electrical conductivity, hardness, and elastic modulus.

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Author Contributions:

Z.P.L. and X.J.L. initiated this research project. X.J.L., Z.P.L., Q.S.Z. and E.M. designed the experiments. Q. D. synthesized and characterized the samples, and performed SAXS, DSC and electrical resistance measurements. Q.S.Z. performed insitu synchrotron radiation X-ray experiments. Y.B.K. performed SANS experiments.

Y.W. conducted APT experiments. H.Y.F., X.J.L. and E.M. conducted RMC simulations and structural analyses. X.J.L., Z.P. L., Q.D. and E.M. wrote the paper. D.C and P.M.V performed the FEM experiments, analyzed the data, and interpreted the results. All the authors analyzed the data and contributed to the discussion and interpretation of the results. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Data availability:

The raw data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)]. The processed data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)].

Competing financial interests:

The authors declare no competing financial interests.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the document: Supplementary data.docx

References

- [1] O. Mishima, L. D. Calvert, E. Whalley, An apparently first-order transition between two amorphous phases of ice induced by pressure, Nature 314 (1985) 76-78. https://doi.org/10.1038/314076a0.
- [2] K. Winkel, E. Mayer, T. Loerting, Equilibrated high-density amorphous ice and its first-order transition to the low-density form, J. Phys. Chem. B 115 (2011) 14141-14148. https://doi.org/10.1021/jp203985w.
- [3] O. Mishima, K. Takemura, K. Aoki, Visual observations of the amorphousamorphous transition in H₂O under pressure, Science 254 (1991) 406-408. https://doi.org/10.1126/science.254.5030.406.
- [4] R. Angelini, E. Zaccarelli, F. A. M. Marques, M. Sztucki, A. Fluerasu, G. Ruocco,
 B. Ruzicka, Glass–glass transition during aging of a colloidal clay, Nat. Commun.
 5 (2014) 4049. https://doi.org/10.1038/ncomms5049.
- [5] S. L. Zhang, L. M. Wang, X. Y. Zhang, L. Qi, S. H. Zhang, M. Z. Ma, R. P. Liu, Polymorphism in glassy silicon: Inherited from liquid-liquid phase transition in supercooled liquid, Sci. Rep. 5 (2015) 8590. https://doi.org/10.1038/srep08590.
- [6] T. Morishita, High density amorphous form and polyamorphic transformations of silicon, Phys. Rev. Lett. 93 (2004) 055503.
 https://doi.org/10.1103/PhysRevLett.93.055503.
- [7] D. J. Lacks, First-order amorphous-amorphous transformation in silica, Phys. Rev. Lett. 84 (2000) 4629-4632. https://doi.org/10.1103/PhysRevLett.84.4629.
- [8] S. Sen, S. Gaudio, B. G. Aitken, C. E. Lesher, Observation of a pressure-induced first-order polyamorphic transition in a chalcogenide glass at ambient temperature, Phys. Rev. Lett. 97 (2006) 025504. https://doi.org/10.1103/PhysRevLett.97.025504.

- K. Dawson, G. Foffi, M. Fuchs, W. Gotze, F. Sciortino, M. Sperl, P. Tartaglia, T. Voigtmann, E. Zaccarelli, Higher-order glass-transition singularities in colloidal systems with attractive interactions, Phys. Rev. E Stat. Nonlin. Soft Matter Phys. 63 (2001) 011401. https://doi.org/10.1103/PhysRevE.63.011401.
- [10]K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaïd, P. N. Pusey, A. B. Schofield, M. E. Cates, M. Fuchs, W. C. K. Poon, Multiple glassy states in a simple model system, Science 296 (2002), 104-106. https://doi.org/10.1126/science.1068238.
- [11] M. Puertas, M. Fuchs, M. E. Cates, Comparative simulation study of colloidal gels and glasses. Phys. Rev. Lett. 88 (2002) 098301. https://doi.org/10.1103/PhysRevLett.88.098301.
- [12]G. Foffi, K. A. Dawson, S. V. Buldyrev, F. Sciortino, E. Zaccarelli, P. Tartaglia, Evidence for an unusual dynamical-arrest scenario in short-ranged colloidal systems, Phys. Rev. E Stat. Nonlin. Soft Matter Phys. 65 (2002) 050802. https://doi.org/10.1103/PhysRevE.65.050802.
- [13]S. H. Chen, W. R. Chen, F. Mallamace, The glass-to-glass transition and its end point in a copolymer micellar system, Science 300 (2003) 619. https://doi.org/10.1126/science.1082364.
- [14]K. Atmuri, G. A. Peklaris, S. Kishore, S. R. Bhatia, A re-entrant glass transition in colloidal disks with adsorbing polymer, Soft Matter 8 (2012) 8965-8971. https://doi.org/10.1039/C2SM25311A.
- [15]H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, E. Ma, Atomic packing and short-to-medium-range order in metallic glasses, Nature 439 (2006) 419-425. https://doi.org/10.1038/nature04421
- [16]D. B. Miracle, A structural model for metallic glasses, Nat. Mater. 3 (2004) 697-

702. https://doi.org/10.1038/nmat1219

- [17] W. L. Johnson, Bulk glass-forming metallic alloys: science and technology, MRS Bull. 24 (1999) 42-56. https://doi.org/10.1557/S0883769400053252.
- [18] A. Inoue, A. Takeuchi, Recent development and application products of bulk glassy alloys, Acta Mater. 59 (2011) 2243-2267.
 https://doi.org/10.1016/j.actamat.2010.11.027.
- [19] W. H. Wang, Bulk metallic glasses with functional physical properties, Adv. Mater.21 (2009) 4524-4544. https://doi.org/10.1002/adma.200901053.
- [20] M. W. Chen, A brief overview of bulk metallic glasses, NPG Asia Mater. 3 (2011)82-90. https://doi.org/10.1038/asiamat.2011.30.
- [21]J. C. Ye, J. Lu, C. T. Liu, Q. Wang, Y. Yang, Atomistic free-volume zones and inelastic deformation of metallic glasses, Nat. Mater. 9 (2010) 619-623. https://doi.org/10.1038/nmat2802.
- [22]E. Ma, Tuning order in disorder, Nat. Mater. 14 (2015) 547-552. https://doi.org/10.1038/nmat4300.
- [23]H. W. Sheng, H. Z. Liu, Y. Q. Cheng;, J. Wen, P. L. Lee, W. K. Luo, S. D. Shastri,
 E. Ma, Polyamorphism in a metallic glass, Nat. Mater. 6 (2007) 192-197. https://doi.org/10.1038/nmat1839.
- [24]Q. S. Zeng, Y. Ding, W. L. Mao, W. G. Yang, S. V. Sinogeikin, J. F. Shu, H. -K. Mao and J. Z. Jiang, Origin of pressure-induced polyamorphism in Ce₇₅Al₂₅ metallic glass, Phys. Rev. Lett. 104 (2010) 105702. https://doi.org/10.1103/PhysRevLett.104.105702.
- [25]G. Li, Y. Y. Wang, P. K. Liaw, Y. C. Li, R. P. Liu, Electronic structure inheritance and pressure-induced polyamorphism in Lanthanide-based metallic glasses, Phys. Rev. Lett. 109 (2012) 125501. https://doi.org/10.1103/PhysRevLett.109.125501.

- [26]H. B. Lou, Y. K. Fang, Q. S. Zeng, Y. H. Lu, X. D. Wang, Q. P. Cao, K. Yang, X. H. Yu, L. Zheng, Y. D. Zhao, W. S. Chu, T. D. Hu, Z. Y. Wu, R. Ahuja and J. Z. Jiang, Pressure-induced amorphous-to-amorphous configuration change in Ca-Al metallic glasses, Sci. Rep. 2 (2012) 376. https://doi.org/10.1038/srep00376.
- [27]Q. Luo, G. Garbarino, B. A. Sun, D. W. Fan, Y. Zhang, Z. Wang, Y. J. Sun, J. Jiao, X. D. Li, P. S. Li, N. Mattern, J. Eckert, J. Shen, Hierarchical densification and negative thermal expansion in Ce-based metallic glass under high pressure, Nat. Commun. 6 (2015) 5703. https://doi.org/10.1038/ncomms6703.
- [28]X. R. Liu, S. M. Hong, Evidence for a pressure-induced phase transition of amorphous to amorphous in two lanthanide-based bulk metallic glasses, Appl. Phys. Lett. 90 (2007) 251903. https://doi.org/10.1063/1.2749722.
- [29]S. Lan, Y. Ren, X. Y. Wei, B. Wang, E. P. Gilbert, T. Shibayama, S. Watanabe, M, Ohnuma, X. L. Wang, Hidden amorphous phase and reentrant supercooled liquid in Pd-Ni-P metallic glasses, Nat. Commun. 8 (2017) 14679. https://doi.org/10.1038/ncomms14679
- [30]S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, S. Satija, Organic glasses with exceptional thermodynamic and kinetic stability, Science 315 (2007) 353-356. https://doi.org/10.1126/science.1135795
- [31]S. Singh, M. D. Ediger, Juan J. de Pablo, Ultrastable glasses from in silico vapour deposition, Nat. Mater. 12 (2013) 139-144. https://doi.org/10.1038/nmat3521.
- [32]H. B. Yu, Y. S. Luo, K. Samwer, Ultrastable metallic glass, Adv. Mater. 25 (2013)5904-5908. https://doi.org/10.1002/adma.201302700.
- [33]D. P. B. Aji, H. Akihiko, F. Zhu, P. Liu, K. M. Reddy, S. X. Song, Y. H. Liu, T. Fujita, S. Kohara, M. W. Chen, Ultrastrong and ultrastable metallic glass,

2013arXiv1306.1575 (2013).

- [34] P. Luo, C. R. Cao, F. Zhu, Y. M. Lv, Y. H. Liu, P. Wen, H. Y. Bai, G. Vaughan, M. di Michiel, B. Ruta, W. H. Wang, Ultrastable metallic glasses formed on cold substrates, Nat. Commun. 9 (2018) 1389. https://doi.org/10.1038/s41467-018-03656-4
- [35]Y. B. Ke, C. Y. He, H. B. Zheng, Y. S. Geng, J. Y. Fu, S. K. Zhang, H. T. Hu, S. L. Wang, B. Zhou, F. W. Wang, J. Z. Tao, The time-of-flight Small-Angle Neutron Spectrometer at China Spallation Neutron Source, Neutron News, 29 (2018):2 14-17. https://doi.org/10.1080/10448632.2018.1514197
- [36]T. Egami, S. J. L. Billinge, Underneath he Bragg Peaks: Structural Analysis of Complex Materials, first ed., Pergamon, Oxford, 2003.
- [37]Y. Waseda, The Structure of Non-crystalline Materials: Liquids and Amorphous Solids, McGraw-Hill, New York, 1980.
- [38]X. Qiu, J.W. Thompson, S. J. L. Billinge, PDFgetX2: a GUI-driven program to obtain the pair distribution function from X-ray powder diffraction data, J. Appl. Cryst. 37 (2004) 678. https://doi.org/10.1107/S0021889804011744.
- [39] P. Juhás, T. Davis, C. L. Farrow, S. J. L. Billinge, PDFgetX3: a rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions, J. Appl. Cryst. 46 (2013) 560-566. https://doi.org/10.1107/S0021889813005190
- [40]B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat. 12 (2005) 537–541. https://doi:10.1107/S0909049505012719
- [41]R. L. McGreevy, L. Pusztai, Reverse Monte Carlo Simulation: A New Technique for the Determination of Disordered Structures, Mol. Simulat. 1 (1988) 359-367.

https://doi.org/10.1080/08927028808080958.

- [42] J. L. Finney, Random packings and the structure of simple liquids. I. The geometry of random close packing, P. Roy. Soc. A-Math. Phy. 319 (1970) 479. https://doi.org/10.1098/rspa.1970.0189.
- [43] J. Hafner, Bond-angle distribution functions in metallic glasses, J. Phys. Colloques46 (1985) C9-69. https://doi.org/10.1051/jphyscol:1985908.
- [44]F. Murtagh, P. Contreras, Algorithms for hierarchical clustering: an overview, Wires. Data Min. Know. 2 (2012) 86-97. https://doi.org/10.1002/widm.53.
- [45]H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, E. Ma, Atomic packing and short-to-medium-range order in metallic glasses, Nature 439 (2006) 419-425. https://doi.org/10.1038/nature04421.
- [46]H. S. Chen, Glass temperature, formation and stability of Fe, Co, Ni, Pd and Pt based glasses, Mat. Sci. Eng. 23 (1976) 151-154. https://doi.org/10.1016/0025-5416(76)90185-3.
- [47] D. Ma, A. D. Stoica, X. L. Wang, Power-law scaling and fractal nature of mediumrange order in metallic glasses, Nat. Mater. 8 (2009) 30-34. https://doi.org/10.1038/nmat2340.
- [48]A. R. Yavari, A. L. Moulec, A. Inoue, N. Nishiyama, N. Lupu, E. Matsubara, W. J. Botta, G. Vaughan, M. D. Michiel, A. Kvick. Excess free volume in metallic glasses measured by X-ray diffraction, Acta Mater. 53 (2005) 1611-1619. https://doi.org/10.1016/j.actamat.2004.12.011.
- [49] J. Bednarcik, C. Curfs, M. Sikorski, H. Franz, J. Z. Jiang, Thermal expansion of La-based BMG studied by in situ high-energy X-ray diffraction, J. Alloy Compd. 504 (2010) S155-S158. https://doi.org/10.1016/j.jallcom.2010.02.053.
- [50] M. M. J. Treacy, J. M. Gibson, L. Fan, D. J. Paterson, I. McNulty, Fluctuation

microscopy: a probe of medium range order, Rep. Prog. Phys. 68 (2005) 2899-2944. https://doi.org/10.1088/0034-4885/68/12/R06.

- [51]A. Inoue, S. Chen, T. Masumoto, Zr-Y base amorphous alloys with two glass transitions and two supercooled liquid regionsMat. Sci. Eng. A 179 (1994) 346-350. https://doi.org/10.1016/0921-5093(94)90224-0.
- [52] J. J. Z. Li, W. K. Rhim, C. P. Kim, K. Samwer, W. L. Johnson, Evidence for a liquid–liquid phase transition in metallic fluids observed by electrostatic levitation, Acta Mater. 59 (2011) 2166-2171. https://doi.org/10.1016/j.actamat.2010.12.017.
- [53]S. Wei, F. Yang, J. Bednarcik, I. Kaban, O. Shuleshova, A. Meyer and R. Busch, Liquid–liquid transition in a strong bulk metallic glass-forming liquid, Nat. Commun. 4 (2013) 2083. https://doi.org/10.1038/ncomms3083.
- [54] S. Lan, M. Blodgett, K. F. Kelton, J. L. Ma, J. Fan, X. L. Wang, Structural crossover in a supercooled metallic liquid and the link to a liquid-to-liquid phase transition, Appl. Phys. Lett. 108 (2016) 211907. https://doi.org/10.1063/1.4952724.
- [55] W Xu, M. T. Sandor, Y. Yu, H. B. Ke, H. P. Zhang, M. Z. Li, W. H. Wang, L. Liu,
 Y. Wu, Evidence of liquid–liquid transition in glass-forming La₅₀Al₃₅Ni₁₅ melt above liquidus temperature, Nat. Commun. 6 (2015) 7696. https://doi.org/10.1038/ncomms8696.
- [56]T. Takeuchi, D. Fukamaki, H. Miyazaki, K. Soda, M. Hasegawa, H. Sato, U. Mizutani, T. Ito, S. Kimura, Electronic structure and stability of the Pd-Ni-P bulk metallic glass, Mater. Trans. 48 (2007) 1292-1298. https://doi.org/10.2320/matertrans.MF200617.
- [57]Y. Q. Cheng, H. W. Sheng, E. Ma, Relationship between structure, dynamics, and mechanical properties in metallic glass-forming alloys, Phys. Rev. B 78, 014207 (2008). https://doi.org/10.1103/PhysRevB.78.014207.

- [58] W. Z. Wu, Z. D. Wu, Y. F. Lo, H. W. Kui, Determination of the complete metastable liquid miscibility gap in Pd–Ni–P, J. Non-cryst. Solids. 432 (2016) 420. https://doi.org/10.1016/j.jnoncrysol.2015.10.042.
- [59]J. C. Qiao, Q. Wang, J. M. Pelletier, H. Kato, R. Casalini, D. Crespo, E. Pineda, Y. Yao, Y. Yang, Structural heterogeneities and mechanical behavior of amorphous alloys, Prog. Mater. Sci. 104 (2019) 250-329. https://doi.org/10.1016/j.pmatsci.2019.04.005.

Captions

Figure. 1. (Color online) **Monolithic Pd42.5Ni42.5P15 glass and its unusual exothermic peak in supercooled liquid region.** (a) HRTEM image and the corresponding SEAD pattern for the as-cast MG. (b) SAXS results for the as-cast and annealed MGs. (c) A conventional DSC curve of the as-cast sample at a heating rate of 10 K/min. The onset temperature of glass transition, T_g , and of crystallization, T_x , as well as the peak temperature of the exothermic hump, T_{L-G} , are indicated using arrows. (d) HRTEM image and the corresponding SEAD pattern for the sample heated to 615 K at a heating rate of 10 K/min, and then quenched to room temperature at the cooling rate of 500 K/min, producing a new and more ordered glass (see text).

Figure 2. (Color online) **Three-dimensional reconstruction APT picture (upper panel) and corresponding concentration profile (lower panel) of the as-cast and ordered Pd42.5Ni42.5P15 metallic glasses**, clearly showing that no phase separation with partitioning of chemical composition occurred in the sample before and after the phase transition. The composition analysis indicates that both the as-cast Glass I and the ordered Glass II have an identical composition of Pd42.5Ni42.5P15, with the constituent elements Pd, Ni and P distributed uniformly in the sample.

Figure 3. (Color online) **Representative electron nano-diffraction patterns from amorphous and crystalline volumes in the as cast and annealed samples acquired during FEM characterization.** (a) and (b) show amorphous nano-diffraction patterns from the as-cast and annealed samples, respectively. (c) and (d) show crystalline nanodiffraction patterns from the as- cast and annealed samples, respectively. Crystalline nano-diffraction patterns are characterized by strong Friedel pairs of spots especially in 31 the weaker second diffraction ring. Analysis of several thousand such patterns indicates an upper bound on crystallinity of 0.02 vol. % in the as-cast glass and 0.3% in the annealed glass.

Figure. 4. (Color online) **TMDSC and DSC scans for the Pd**_{42.5}**Ni**_{42.5}**P**₁₅ **MGs.** (a) TMDSC curves of the as-cast sample. The reversing heat flow curve shows two glass transition temperatures, i.e., T_{g1} (560 K) and T_{g2} (608 K). (b) TMDSC curves of the sample which was heated to 613 K and held for 30 min. It is seen that the exothermic peak in (a) corresponding to the reentrant glass transition disappeared (b). The reversing heat flow curve only shows one glass transition temperature, i.e., Tg_2 (b). This indicates that the as-cast glass after annealing at 613 K for 30 min has transformed the alloy into a new amorphous state; the product retained to room temperature is no longer the original Glass I but a new Glass II, which now has a new glass transition temperature T_{g2} around 612 K, well above T_{g1} for Glass I (560 K). (c) Cyclic DSC scans on Glass II. Three cyclic measurements confirm the reversibility of T_{g2} at 612 K. The slight decrease in the T_g compared to that obtained from the conventional DSC scan at a heating rate of 10 K/min is due to the slower linear heating rate used in TMDSC mode (2 K/min).The unit in TMDSC curves is mW/mg.

Figure. 5. (Color online) Atomic structure evolution. (a) Synchrotron XRD curves taken at various temperatures ranging from 300 to 673 K at a constant heating rate of 10 K/min. (b) Selected structure factor S(q) curves at several representative temperatures. (c) $2\pi/q_1$ (upper panel) and the FWHM (lower panel) of the first peak in S(q) as a function of temperature. The error bars give the standard deviation on the mean value. (d) Typical PDF G(r) curves obtained by Fourier transformation of

structure factors shown in Fig. 2b. (e) Difference in G(r), $\Delta G(r,T)=G(r)_T - G(r)_{560K}$, for Glass II (quenched from 613 K), the crystallized state (672 K) and Glass I (300 K). The vertical dashed line is a guide to the eye, as a demarcation to separate and contrast short-versus medium- range scales, for their difference in $\Delta G(r,T)$.

Figure. 6. (Color online) Fluctuation microscopy V(k) data indicating different medium range order in the two glasses. Narrower peaks in the annealed sample suggest a more uniform interatomic spacing at the scale where nanoscale heterogeneities exist.

Figure. 7. (Color online) **Structure of the as-cast vs annealed glasses.** (a) Experimental and RMC modeled structure factors for the as-cast (Glass I) glass and the product of reentrant glass transition (Glass II). (b) Experimental and RMC modeled Pd *K*-edge EXAFS spectrum. (c) Spatial arrangement of the supercluster comprised of Ni₂P- and Ni₃P-like clusters in the as-cast Glass I (left) and the more ordered Glass II (right) drawn from the RMC models.

Figure. 8. (Color online) **Schematic evolution of enthalpy upon cooling and heating of the Pd**_{42.5}**Ni**_{42.5}**P**₁₅ **alloy.** The new and deeper energy megabasin where Glass II resides is reached through thermal activation in the supercooled liquid. Upon reheating, Glass II transitions into its own supercooled liquid.

Figure. 9. (Color online) **Map of reentrant phase transitions in Pd-Ni-P alloys.** The red and green dotted lines mark the phase transition sequence of Pd_{42.5}Ni_{42.5}P₁₅ and Pd_{41.25}Ni_{41.25}P_{17.5}, respectively.

Figure. 10. (Color online) Schematic illustration of the atomic structural ordering underlying the exothermic event involved in the reentrant glass transition. Thermal agitation facilitates the dissociation of P-P bonds and the formation of additional (Ni, Pd)-P bonds, increasing the number of energetically favorable Ni(Pd)₂P- and Ni(Pd)₃P-like clusters, typically characterized by P-centered <0, 3, 6, 0>, Ni-centered <0, 2, 8, 2>, <0, 0, 12, 2> and <0, 1, 10, 3> polyhedra. These connect to form superclusters at the medium-range scale, leading to substantially enhanced order in Glass II (Fig. 2e).

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Data in Brief

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