Superior room-temperature ductility of typically brittle quasicrystals at small sizes

Yu Zou1,†, Pawel Kuczera2, Alla Sologubenko1, Takashi Sumigawa3, Takayuki Kitamura3, Walter Steurer2 & Ralph Spolenak1

The discovery of quasicrystals three decades ago unveiled a class of matter that exhibits long-range order but lacks translational periodicity. Owing to their unique structures, quasicrystals possess many unusual properties. However, a well-known bottleneck that impedes their widespread application is their intrinsic brittleness: plastic deformation has been found to only be possible at high temperatures or under hydrostatic pressures, and their deformation mechanism at low temperatures is still unclear. Here, we report that typically brittle quasicrystals can exhibit remarkable ductility of over 50% strains and high strengths of ~4.5 GPa at room temperature and sub-micrometer scales. In contrast to the generally accepted dominant deformation mechanism in quasicrystals—dislocation climb, our observation suggests that dislocation glide may govern plasticity under high-stress and low-temperature conditions. The ability to plastically deform quasicrystals at room temperature should lead to an improved understanding of their deformation mechanism and application in small-scale devices.

1 Department of Materials, Laboratory for Nanometallurgy, ETH Zurich, Vladimir-Prelog-Weg 5, CH-8093 Zurich, Switzerland. 2 Department of Materials, Laboratory of Crystallography, ETH Zurich, Vladimir-Prelog-Weg 5, CH-8093 Zurich, Switzerland. 3 Department of Mechanical Engineering and Science, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8540, Japan. † Present address: Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA. Correspondence and requests for materials should be addressed to Y.Z. (email: yuzou@mit.edu) or to R.S. (email: ralph.spolenak@mat.ethz.ch).
In materials science, plasticity describes the non-reversible deformation of a solid in response to applied forces and determines the ability of a material to change its shape permanently without breaking. Regular crystalline materials, including most metals and ceramics, are generally plastically deformed through dislocation motion or twinning. The plasticity of amorphous solids, such as metallic glasses, is based on the formation and propagation of shear bands. In quasicrystals, despite their lack of periodicity, plastic deformation can also be achieved by dislocation activities. In contrast to the situation in periodic crystals, every movement of a dislocation in a quasicrystal creates a cloud behind, which is called phason fault. As a consequence, the dislocation motion gets hindered and the material appears brittle. Although a great variety of quasicrystals have been synthesized, and some have even been discovered in nature, and found to be technologically interesting and useful, only few of them can be found in applications so far, mainly limited by their poor ductility and formability at room temperature. Hence, improving the room-temperature ductility of quasicrystals is not only of academic interest but also essential for technological applications. Early studies of the plastic deformation of quasicrystals focused on an easily grown icosahedral quasicrystal, i-Al–Pd–Mn, in the high-temperature regime above ~600 °C (~70% of its melting temperature). These studies demonstrated that the plastic deformation of i-Al–Pd–Mn was dominated by dislocation glide—with the Burgers vector out of the plane of dislocation motion, rather than dislocation glide—with the Burgers vector restricted in the plane of dislocation motion. It is generally believed that dislocation climb is a much easier deformation mode in quasicrystals than dislocation glide. Although there are some hints that the glide motion may be possible in low-temperature conditions as suggested by numerical simulations or under high hydrostatic pressures, the required stress to activate glide is extremely high, on the order of 1/10 of its shear modulus—a stress level generally leading to fracture without showing any ductility. It has been a long-standing question concerning the deformation mechanism in quasicrystals at room temperature. Despite several investigators have sought to explore the plastic deformation of quasicrystals at or near room temperature using indentation or by confining gas or solid pressures, so far there has been no common conclusion: the explanations include shear banding similar to metallic glasses, phase transformation, grain-boundary glide, pure dislocation climb, dislocation climb dominant and crystallization. Therefore, one has to conclude that the plastic deformation of quasicrystals under a wide range of temperatures and pressures has been poorly understood—much in contrast to crystalline and amorphous solids. Two fundamental questions are still open: can steady-state plastic deformation be achieved at room temperature? If so, what is the underlying deformation mechanism?

Unveiling room-temperature plasticity in quasicrystals hence relies on a new method to suppress fracture before plastic yielding in a simple loading experiment. Our strategy is to increase the fracture strength over the yield strength in a quasicrystal by reducing the sample size. Although similar methods have been explored for other brittle materials such as ceramics and metallic glasses, it has, to our knowledge, not previously been reported for quasicrystals—a large family of unusual solids. In this study, we demonstrate a brittle-to-ductile transition in quasicrystals at room temperature due to a sample size reduction—a submicron-sized quasicrystal pillar exhibits superior ductility at room temperature. Furthermore, we suggest that dislocation glide may control the plastic deformation of quasicrystals at room temperature and attempt to shed light on the underlying deformation mechanism in the low-temperature regime.

**Results**

A model to predict brittle-to-ductile transition. To estimate at what size range a typically brittle quasicrystal may become ductile, we compared the different deformation mechanisms as a function of the sample size: dislocation activities, crack propagation and mass transport by diffusion. We identified three deformation regimes: cracking-controlled, dislocatio-controlled (dislocations or shear bands) and diffusion-controlled, as illustrated in Fig. 1. We estimated the critical size, for the brittle-to-ductile transition to be ~500 nm, and the size of the diffusion-controlled zone, to be around 10 nm (see the detailed analysis in Methods section at the end of the article). Our targeted sample size to attain steady-state plasticity thus falls in a range from ~100 to ~500 nm.

**Micro-compression of small-sized quasicrystal pillars.** In our experiments, we compressed single-quasicrystalline i-Al–Pd–Mn pillars with diameters ranging from ~1.8 μm to ~150 nm. We observed a brittle-to-ductile transition with the critical pillar diameter between 510 and 350 nm (Fig. 2a): the 1.8-μm pillar exhibits a catastrophic failure at ~3% compressive strain; the 870- and 510-nm pillars show cracks at about 45° along the loading direction, failing at ~6% strain; when the pillar diameter is below 500 nm, the pillars present significantly improved ductility with compressive strains over 50% and without any cracking. The 400- and 200-nm pillars clearly show...
deformation bands, while the 140-nm pillar reveals the deformation localized at the upper part of the pillar. All the corresponding stress–strain curves exhibit a displacement-burst phenomenon (Fig. 2a), which is generally observed in metals\cite{33,34} and metallic glasses\cite{29,30}. The 140- and 240-nm pillars exhibit earlier plastic yielding than the other pillars, which could be due to localized deformation on the pillar top region or the lateral friction between the indenter tip and the top surface of the pillar.

**Figure 2** | Micro-compression of single-quasicrystalline i-Al–Pd–Mn pillars. Pillar diameters range from ~2 μm to ~150 nm. (a) Typical SEM images of the post-deformed pillars, showing a brittle-to-ductile transition with the critical size between 350 and 510 nm. The corresponding engineering stress–strain curves are presented below. (b) The fracture strain or plastic strain as a function of the pillar diameter, indicating a brittle-to-ductile transition. (c) The fracture strength or yield strength as a function of the pillar diameter. In the brittle regime, the strength increases slightly with decreasing the pillar diameter; in the ductile regime, the strength is almost independent of the sample size.

**Figure 3** | In situ SEM and TEM of i-Al–Pd–Mn pillars during bending tests. (a) SEM snapshots captured during the bending test of a pillar with the diameter of ~300 nm. An initial crack occurs near the pillar base at the bending angle of ~20–30° and eventual fracture happens at the bending angle of ~40°. (b) TEM snapshots during bending tests on a pillar in the diameter of ~100 nm, showing a homogenous deformation without any fracture, and the maximum tensile strain at the pillar centre estimated to be over 50%. Scale bars, 300 nm (a) and 100 nm (b).
Here, the flow stresses after the first displacement bursts were used to give a best estimation of their yield strengths. How the fracture strain or maximum plastic strain changes by decreasing the sample size also demonstrates the brittle-to-ductile transition between 510 and 350 nm (Fig. 2b). When the pillar diameter is smaller than 350 nm, no cracking is observed in our experiments. Regarding the size dependence of strength, the fracture strength increases from $\approx 3.5$ to $\approx 4.5$ GPa with decreasing pillar diameters in the brittle regime, while the yield strength (the flow stress at the first displacement burst) is about 4.5 GPa in the ductile regime (Fig. 2c).

**In situ bending tests of small-sized quasicrystal pillars.** Brittle materials usually show higher ductility in compression than tension. To examine the tensile ductility of the quasicrystal pillars but avoid the complex experimental setup of the tensile test for sub-micrometer-sized samples, we employed micro-bending tests to induce an asymmetrical stress distribution and compare the bending ductility of the pillars in different sizes. The *in situ* scanning electron microscopy (SEM) bending of a 300-nm pillar shows that the deformation localizes near the pillar base by necking. We detected that the crack forms at the bending angle of $\approx 20-30^\circ$, and eventually fails in a catastrophic feature at the bending angle of $\approx 40^\circ$ (Fig. 3a). The *in situ* transmission electron microscopy (TEM) bending of a 100-nm pillar shows in a rather homogenous deformation without any cracking and fracture (Fig. 3b). The longitudinal tensile strain near the pillar centre is estimated to be over 50%. The strain bands’ motion during the tests implies dislocation activity during the deformation (Supplementary Fig. 1).

**TEM characterization and diffraction simulations.** A representative bright-field TEM image reveals the upper part of a deformed pillar along a threefold axis (Fig. 4a). We find a slip line through the pillar and a step at the pillar edge. The loading direction is along a twofold axis and the slip direction is along another twofold axis. The high-resolution TEM image shows the deformation band with a thickness of $\approx 2-5$ nm and strain contrast modulations along the line (periodic dark regions along the band). The rest of the area is nearly defect-free. The inverse Fourier transformation of the regions marked in b, emphasizing the very localized and periodic lattice distortions along the deformation band. The inserted fringes are indicated by arrows. (e) The atomic model of i-Al–Pd–Mn projected along the threefold axis with its calculated diffraction pattern to be compared with the experimental one in a, before the deformation. (f) A schematic view in projection of the model after shear deformation, with the same loading and slip directions as shown in b. (g,h) The local mismatches between the quasi-lattice planes, where the strain is concentrated, and correlating (c) and (d) (the black and orange lines indicate quasi-lattice planes and the circles indicate dislocations). Scale bars, 50 nm (a) and 10 nm (b).
there are strain-contrast modulations with a nearly equal distance of ~2–5 nm and the area surrounding deformation band is nearly defect-free. (Fig. 4b, Supplementary Fig. 2). We do not observe any evidence of melting, crystallization, phase transformation or cracking that was used to explain room-temperature deformation in quasicrystals. Different from the deformation bands formed in i-Al–Pd–Mn under hydrostatic pressures and at deformation morphology with wavy features (see high-resolution SEM images in Supplementary Fig. 3), which is more similar to metallic glasses than to metals. Nevertheless, we show that the quasicrystal plasticity at room temperature is still controlled by dislocation mechanisms.

Although in quasicrystals climb leads to the removal or insertion of so-called ‘worms’ without overlaps or open spaces, this process requires thermal activation. At room temperature, the atomic diffusion in quasicrystals is generally believed to be inhibited. Dislocation glide, however, may be active and even dominate under high-stress and low-temperature conditions, generating a high density of heavily distorted zones in the wake of the dislocation glide. The approach of reducing sample size to enhance the ductility of otherwise brittle quasicrystals may pave way to fundamentally understand the deformation mechanism of quasicrystals at room temperature, possibly at even lower temperatures and for all the other types of quasicrystals.

Towards technological applications, fine-scale quasicrystals are attractive not only due to combining high strength with ductility but also because they offer extraordinary specific strength (strength divided by density or elastic energy density, ~1 MJ kg\(^{-1}\)) among metallic micro/nano-pillars reported to date (Fig. 5), which might be used to store elastic energy. Small dimensional quasicrystals having superior strength and ductility, together with their interesting functional properties, may also enable components that are both structurally and functionally useful in micro- or nano-electromechanical systems. While much work remains to optimize their properties, our observation of superior room-temperature ductility in quasicrystals motivates further fundamental and technological exploration.

### Discussion

The results shown in Figs 2 and 3 confirm that i-Al–Pd–Mn pillars are capable of both excellent ductility (compressive and tensile) and maintaining high strength when the pillar diameter is below about 500 nm. To our knowledge, this result has never been reported for quasicrystals before. The quasicrystal fine-scale pillars exhibit minor size dependence of strength and a deformation morphology with wavy features (see high-resolution SEM images in Supplementary Fig. 3), which is more similar to metallic glasses than to metals. Nevertheless, we show that the quasicrystal plasticity at room temperature is still controlled by dislocation mechanisms.

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### Figure 5 | Strength comparison with other metallic and metallic-glass pillars

Ashby map (designed with CES EduPack 2014) of yield strength versus density, indicating that i-Al–Pd–Mn quasicrystal pillars exhibit, to our knowledge, the highest specific strength or the strength-to-density ratio (CS, single crystalline; NC, nanocrystalline; NL, nanolamellar; MG, metallic glass). The strength levels of i-Al–Pd–Mn quasicrystal pillars are from Fig. 2c. Literature data for pillar strengths: pure metals Au, Al, Ni, Cu, Nb, Ta, Mo and W and Mg, TiAl, nanocrystalline (nc) Cu, Ni, Pt and Rh pillars, NbTaMoW high-entropy alloys, and metallic glasses (for example, Cu- and Zn-based ones).
Methods

Sample preparation and characterization. An initial compact of composition Al_{80}Fe_{10}Co_{10}Mn_{7} was prepared from pure metals (Al 99.9999%, Pd 99.9%, Mn 99.95%). The sample was pre-alloyed in an arc furnace, and subsequently placed in an Al_{2}O_{3} crucible and sealed in a quartz glass ampoule under an Ar atmosphere. The heat treatment consisted of the following steps: heating to 1352 K (above its melting temperature), slow cooling to 1083 K at the rate of 30 K h^{-1}, annealing at 1083 K for 150 h, and slow cooling in water. The composition of the resulting sample was confirmed using energy dispersive X-ray spectroscopy. The X-ray powder diffraction pattern (Supplementary Fig. 4) and TEM diffraction patterns (Supplementary Fig. 5) indicate that the resulting sample is a single-phase icosahedral quasicrystal, which is comparable to that in literature.

The prepared Al-Pd-Mn was thermodynamically stable with an average grain size of around 300 µm and was also highly isotropic. We fabricated single-quasicrystalline pillars, in cylindrical shapes, from a coarse grain in a well-polished Al-Pd-Mn sample using a FIB system (Helios Nanolab 600i, FEI): a coarse milling condition of 30 kV and 80 Pa and a final milling condition of 5 kV and 7 Pa. The diameters of the FIB-milled pillars are in the range of ~150 nm to ~2 µm and the aspect ratios are ~3.0–4.5. A taper of 2–3° was generally observed and the top diameter of the pillar was chosen to calculate stress.

Micro-mechanical testing. We used the nanoindenter (Hysitron Inc., USA) with a diamond flat-tip punch tip (5 µm in diameter, Synton-MDP, Switzerland) to compress the pillars in a displacement control mode and the strain rate of 2 × 10^{-11} s^{-1} by feedback mechanism. At least four pillars for each size were compressed. The deformed pillars were imaged using a high-resolution SEM (Magellan, FEI). For the post-mortem TEM characterization, the deformed pillars were thinned down to a lamella by ion milling, lift-out, thinning and polishing in the FIB system. Their cross-sections were then examined using a TEM (Tecnai F30, FEI). We used the nanoindenter (Hysitron Inc., USA) and the nano-manipulator (Kleindiek, Germany) fitted to a SEM (Hitachi SU 8200) and an indenter holder (Nanofactory Instruments AB, SA2000N) fitted to a TEM (JEOL JEM-2100), respectively, with a displacement rate of ~5 nm s^{-1}.

Prediction of the brittle-to-ductile transition. In a brittle material, the fracture strength, \( \sigma_f \), follows the Griffith’s criterion\(^{28} \), as \( \sigma_f = K_{IC}/(\pi d^{1/2}) \), with \( K_{IC} \) the fracture toughness of the material, \( d \) a geometrical parameter on the order of unit and \( a \) the size of pre-existing cracks or flaws. Statistically, larger samples are more likely to contain larger flaws, or weaker links, and consequently, smaller samples usually exhibit higher fracture strengths than the large ones—the size effect due to the Weibull statistics\(^{38} \). Because the fracture strength, \( \sigma_f \), cannot rise above the yield strength, \( \sigma_y \), below a certain length scale plastic flow may determine the fracture. The intersection between the curves for \( \sigma_f \) and \( \sigma_y \) provides a critical size, \( r_c \), for a brittle-to-ductile transition, as illustrated in Fig. 1a. Assuming that the largest pre-existing cracks or flaws is one order of magnitude smaller than the sample dimension, we can obtain \( r_c \approx 500 \text{ nm} \) for i-Al-Pd-Mn, using \( a \approx 1 \), \( K_{IC} \approx 1.25 \text{ MPa } \cdot \text{m}^{1/2} \) (ref. 39) and the hardness, \( H \approx 8.5 \text{ GPa} \) (ref. 39). However, further reduction of the sample size down to the nanoscale lead to a significant increase of the surface-volume ratio, and surface diffusion may control the plastic flow, resulting in a reduced strength. In a relation similar to the Coble creep\(^{40} \), the diffusion strength, \( r \), control the plastic flow, resulting in a reduced strength. In a relation similar to the Coble creep\(^{40} \), the diffusion strength, \( r \), control the plastic flow, resulting in a reduced strength. In a relation similar to the Coble creep\(^{40} \), the diffusion strength, \( r \), control the plastic flow, resulting in a reduced strength.
37. Griffith, A. A. The phenomena of rupture and flow in solids. Phil. Trans. R. Soc. Lond. A 221, 163–198 (1921).
38. Weibull, W. A statistical distribution function of wide applicability. J. Appl. Mech. 13, 293–297 (1951).
39. Deus, C., Wolf, B. & Paufler, P. On the orientation dependence of crack-like failure formation near indentations on an icosahedral Al–Pd–Mn quasicrystal. Philos. Mag. A 75, 1171–1183 (1997).
40. Coble, R. L. A model for boundary diffusion controlled creep in polycrystalline materials. J. Appl. Phys. 34, 1679–1682 (1963).
41. Luo, J., Wu, F., Huang, J., Wang, J. & Mao, S. Superelongation and atomic chain formation in nanosized metallic glass. Phys. Rev. Lett. 104, 215503 (2010).
42. Tian, L., Li, J., Sun, J., Ma, E. & Shan, Z. W. Visualizing size-dependent deformation mechanism transition in Sn. Sci. Rep. 3, 2113 (2013).
43. Quiney, A. M. & Gratias, D. Unique six-dimensional structural model for Al–Pd–Mn and Al–Cu–Fe icosahedral phases. Phys. Rev. B 74, 214205 (2006).
44. Volpert, C. A. & Lilleodden, E. T. Size effects in the deformation of sub-micron Au columns. Philos. Mag. 86, 5567–5579 (2006).
45. Kunz, A., Pathak, S. & Greer, J. R. Size effects in Al nanopillars: single crystalline vs bicrystalline. Acta Mater. 59, 4416–4424 (2011).
46. Frick, C. P., Clark, B. G., Orso, S., Schneider, A. S. & Arzt, E. Size effect on strength and strain hardening of small-scale [111] nickel compression pillars. Mater. Sci. Eng. A 489, 319–329 (2008).
47. Jennings, A. T., Burek, M. J. & Greer, J. R. Microstructure versus size: mechanical properties of electroplated single crystalline Cu nanopillars. Phys. Rev. Lett. 104, 135503 (2010).
48. Schneider, A. S. et al. Correlation between critical temperature and strength of small-scale bcc pillars. Phys. Rev. Lett. 103, 105501 (2009).
49. Kim, J.-Y., Jung, D. & Greer, J. R. Tensile and compressive behavior of tungsten, molybdenum, tantalum and niobium at the nanoscale. Acta Mater. 58, 2355–2363 (2010).
50. Lilleodden, E. Microcompression study of Mg (0001) single crystal. Scr. Mater. 62, 532–535 (2010).
51. Edalati, K. et al. Ultrahigh strength and high plasticity in TiAl intermetallics with bimodal grain structure and nanotwins. Scr. Mater. 67, 814–817 (2012).
52. Okamoto, N. L., Kashioka, D., Hirato, T. & Inui, H. Specimen- and grain-size dependence of compression deformation behavior in nanocrystalline copper. Int. J. Plast. 56, 173–183 (2014).
53. Rinaldi, A., Peralta, P., Friesen, C. & Sieradzki, K. Sample-size effects in the yield behavior of nanocrystalline nickel. Acta Mater. 56, 511–517 (2008).
54. Jung, D. & Greer, J. R. Size-induced weakening and grain boundary-assisted deformation in 60 nm grained Ni nanopillars. Scr. Mater. 64, 77–80 (2011).
55. Gu, X. W. et al. Size-dependent deformation of nanocrystalline Pt nanopillars. Nano Lett. 12, 6385–6392 (2012).
56. Alshehri, O., Yavuz, M. & Tsui, T. Manifestation of external size reduction effects on the yield point of nanocrystalline zirconium using nanopillars approach. Acta Mater. 61, 40–50 (2013).
57. Zhu, Y., Ma, H. & Spolenak, R. Ultrastable ductile and stable high-entropy alloys at small scales. Nat. Commun. 6, 7748 (2015).
58. Zou, Y., Maiti, S., Steurer, W. & Spolenak, R. Size-dependent plasticity in an Nb25Mo25Ta25W25 refractory high-entropy alloy. Acta Mater. 65, 85–97 (2014).
59. Chen, C.-Q., Pei, Y.-T. & De Hosson, J. T. M. Effects of size on the mechanical response of metallic glasses investigated through in situ TEM bending and compression experiments. Acta Mater. 58, 189–200 (2010).
60. Tsai, A. P., Inoue, A., Yokoyama, Y. & Masumoto, T. Stable icosahedral Al–Pd–Mn and Al–Pd–Re alloys. Mater. Trans. JIM 31, 98–103 (1990).

Acknowledgements
We thank S. Takeuchi (Tokyo University of Science) and K. Edagawa (The University of Tokyo) for their helpful discussion, T. Yukishita and S. Ashida (Kyoto University) for their help in the bending tests, ScopeM (ETH Zurich) for supplying electron microscopy facility and A. Evans for proofreading. Y.Z. acknowledges the financial supports through the Swiss National Science Foundation (SNF Grants: 200021_143633 and P2EZP2_165278) and the JSPS strategic program (GR14103). T.S. and T.K. acknowledge the JSPS Grant (No. 25500012).

Author contributions
Y.Z., W.S. and R.S. created the idea and designed the project; P.K. prepared the bulk sample and did the simulation. Y.Z. carried out the nanomechanical testing; A.S. did the TEM analysis; T.S. and T.K. contributed the design of in situ SEM and TEM experiments. Y.Z. prepared the manuscript. W.S. and R.S. supervised the project. All the authors contributed to the discussion and the interpretation of the data.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications.

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Zou, Y. et al. Superior room-temperature ductility of typically brittle quasicrystals at small sizes. Nat. Commun. 7:12261 doi: 10.1038/ncomms12261 (2016).

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