Dislocation scarcity makes room for grain-boundary mediated deformation in nanocrystalline PdAu alloys

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We utilized synchrotron-based in-situ diffraction and dominant shear deformation to identify, dissect, and quantify the relevant deformation mechanisms in nanocrystalline Pd_{90}Au_{10} in the limiting case of grain sizes at or below 10 nm. We could identify lattice elasticity, shear shuffling operating in the core region of grain boundaries, stress driven grain boundary migration, and dislocation shear along lattice planes to all contribute, however, with significantly different and non-trivial stress-dependent shares to overall deformation. Regarding lattice elasticity, we find that Hookean linear elasticity prevailed up to material failure beyond 1.5 GPa. Shear shuffling propagating strain at/along grain boundaries increases progressively with increasing load to carry about three quarters of the overall strain in the regime of macroplasticity. Stress driven grain boundary migration requires overcoming a threshold stress slightly below the yield stress and contributes a share of ≈ 10 % to overall strain. Appreciable and progressively increasing dislocation activity requires stress values near the failure stress to eventually propagate a ≈ 10 % share to overall strain. Shear shuffling and linear lattice elasticity exclusively operate in the stress-strain regime characterized by a markedly decreasing tangent modulus (microplastic regime). The material response in this regime seems indicative of nonlinear viscous behavior rather than being correlated with work- or strain hardening in conventional fcc metals.

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INTRODUCTION

When substantially reducing the crystallite (grain) size \( D \) of polycrystalline metals into the nanometer regime, they show superior strength and hardness and are so potential candidate materials for a variety of applications. Over the last decade, this has motivated intense research efforts with the aim of gaining insight into the physics of grain size-dependent deformation mechanisms of nanocrystalline (NC) metals. Since the volume fraction of grain boundaries (GB) scales with the reciprocal grain size, the abundance of GBs at the nanometer scale supplies barriers for intergranular slip and the nanometer-sized grains entail a reduced capacity of dislocation generation and interaction even at the upper limit of the nanometer scale of ≈ 100 nm. As a consequence, higher strength, lower activation volume, and higher strain-rate sensitivity have been observed \([1, 2]\). With decreasing the grain size to the lower end of the nanoscale \( D \approx 10 \) nm or below, it is expected that intragranular crystal plasticity becomes gradually or even dominantly replaced by GB-mediated deformation processes.

Simulations and experiments unraveled a variety of modes of plastic deformation related to GBs. So far the following processes have been identified: GB slip and sliding \([3, 4]\), stress-driven GB migration (SDGBM) coupled to shear deformation and grain rotation \([5, 6]\), as well as shear transformation (ST) mediated plasticity \([7, 8]\), usually observed in glasses or colloidal systems \([9]\, but here operating in the confined space related to the core region of GBs. Moreover, GBs and triple junction lines, locations where typically three GBs meet, may act as stress concentrators \([12, 13]\, so effectively reducing the barrier for partial dislocation nucleation and emission. One of the intriguing aspects is that plastic deformation of NC metals requires that this variety of strain carriers interact in a synergistic way to make deformation happen in a compatible manner.

Because of the complex interplay of disparate mechanisms, operating either sequentially or simultaneously, it is still under debate which role they play in responding to the intrinsic stress field and which share to overall strain propagation is carried by them. Finding answers to these issues is a challenge for experiment and theory, as well as computational simulations. The latter have contributed to an atomic-level understanding of how different plasticity mechanisms interact on the nanoscale \([14, 15, 17]\). Clearly, the deformation of NC materials involves a broad spectrum of time and length scales beginning with the atomistic details of local shear in GBs, dislocation nucleation, -motion and -interaction, likewise, slip transfer across GBs to end in crack propagation or shear banding at the system level. Therefore, direct comparison between computer simulations and deformation experiments or advanced microscopy, likewise, atom probe tomography still remains a tough case. Not least since the atomic interaction potentials used in simulation scenarios may not fully cover the genuine nature of the materials. We address the experimental approach here by focusing...
on NC PdAu alloy, and discuss what can be gathered and contributes to a detailed understanding of plasticity.

Regarding the material system, we prepared NC PdAu alloys by inert-gas condensation (IGC) and compaction which allows us to explore grain sizes at or even below 10 nm. IGC-prepared NC materials manifest a model system to the random polycrystal: being statistically isotropic (untextured) and homogeneous, featuring a GB-misorientation distribution bearing great similarity with the Mackenzie-distribution, as well as being characterized by a lognormal grain size distribution (NS-20). Moreover, the PdAu alloy system is a fully miscible solid solution with a high stacking fault energy $\approx 180 \text{mJm}^{-2}$ (10 nm) in the Pd-rich alloys and low stacking fault energy $\approx 50 \text{mJm}^{-2}$ on the Au-rich side. It so enables to investigate an expected increasing propensity for partial dislocation activity when approaching the Au-rich side of the phase diagram.

Concerning mechanical testing, we recently introduced a small-scale-specimen mechanical testing scheme to achieve that extrinsic factors such as sample size, machine stiffness etc. can be deconvoluted from or do not influence the intrinsic material properties. In fact, we could demonstrate that our testing scheme, which enforces specimens to deform under dominant shear and some superimposed pressure, is capable of reproducing stress-strain data that were generated by standardized (DIN) tensile testing of stainless steel (ASTM 304). The type of specimen we use are for obvious reasons termed shear compression specimen (SCS). Lastly, we note that small scale NC Pd$_{90}$Au$_{10}$ SCS can be shear-deformed in a reproducible manner to strain values $\varepsilon > 0.2$. We go on with an outline of what is known about the material system and relevant to this study.

In a recent work Ames et al. [21] demonstrated that NC Pd$_{90}$Au$_{10}$ ($D \leq 10 \text{nm}$) exhibits a pronounced strain-rate dependence prevailing up to ductile failure. This has been interpreted as an indication of probing intrinsic plasticity being intimately related to the nanoscale microstructure. Utilizing the discriminating power of activation parameters to identify active deformation mechanisms, they found the measured activation volume and strain-rate sensitivity of NC Pd$_{90}$Au$_{10}$ ($D \leq 10 \text{nm}$) to be compatible with partial dislocation activity (PDA), STs (the flow defect in metallic glasses) and SDGBM. Obviously, at the low end of the nanoscale additional information is needed to dissect possible deformation mechanisms and reveal their role during deformation. In a follow-up study, Grewer et al. [25] analyzed the activation energy of deformation in NC Pd$_{90}$Au$_{10}$ ($D \leq 10 \text{nm}$) and studied SDGBM in detail to arrive at the conclusion that ST-based shear shuffling operating in GBs dominates the overall deformation behavior. More fundamentally, they found that the activation energy $\Delta G$ exhibits a barrier height scaling $\Delta G \propto \tau^{3/2}$ which bears great similarity with the Johnson-Samwer universal scaling law of yielding in metallic glasses; $\tau$ is a measure of the applied load here. Finally, Skrotzki et al. [20] studied texture formation in NC Pd$_{90}$Au$_{10}$ induced by high-pressure torsion to find absence of any texture formation up to applied strains of $\gamma \approx 1$. Moreover, they observed that twinning and stacking fault formation is basically missing in this strain regime. Consequently, dislocation activity seems to play a minor role at the low end of the nanoscale. The remaining problem is then to discriminate the relevant from the inferior deformation mechanisms, quantify their share to overall deformation and reveal how they interact and compete with each other.

We employ synchrotron-based diffraction measurements to in-situ study the microstructural evolution during deformation of NC Pd$_{90}$Au$_{10}$. In addition, we analyze dark field transmission electron micrographs at different strain values to extract possible changes of the grain size distribution function caused by SDGBM. First, the experimental setup and measurement procedures are introduced. We then discuss how individual XRD peak parameters have been extracted from the in-situ experiment and relate them to microstructural changes as well as associated deformation mechanisms. We will use this information in conjunction with the data from mechanical testing to quantify the relative deformation share of each identified process as a function of applied strain. We also display the shares of mechanisms to overall deformation as a function of applied load to unravel their stress-dependent sequential and/or simultaneous onset and persistence as well as revealing possible synergistic effects associated with their simultaneous presence.
load to the top and bottom faces forces the SCS to shear along the gauge section, oriented 45° relative to the load direction. Since plastic deformation is confined to the gauge section \[23\], the SCS is ideally suited for synchrotron based transmission experiments with the scattering vector probing the in-plane evolution of XRD peak parameters during deformation. To avoid shadowing of the scattering cones by the edges of the gauge slits, we deviate from the SCS design in \[24\] by using a trapezoid slit profile (see Fig. 1) to adapt the geometry of the SCS to the diffraction measurement. The dimensions of the SCS in this study were \(7 \text{ mm} \times 0.95 \text{ mm} \times 0.77 \text{ mm (H} \times \text{W} \times \text{T})\) and the gauge section was thinned to a thickness of 123 \(\mu\text{m}\).

Figure 1 shows the experimental setup at the high energy microdiffraction endstation (HEMD) of beamline ID15A at the European Synchrotron Radiation Facility (ESRF). Mechanical testing was performed by a Kammrath & Weiss tension/compression device which comprises of two load plungers moving symmetrically towards the center, thus keeping the gauge section in fixed position relative to the incoming beam. The lower plunger was replaced by a roll bearing wagon to substantially reduce the friction coefficient of the horizontal sample movement that goes along with the enforced shear deformation \[23\]. The testing device with the installed SCS was mounted on top of a six axis goniometer, which enables exact placement of the sample with respect to the incoming synchrotron beam. The focused beam with a cross section of \(8 \times 20 \mu\text{m}\) was directed to the center of the thin gauge section, thus penetrating approximately 30 billion grains. The diffracted signal was recorded on a 2D-area detector (mar CCD), capable of recording one scan every seven seconds. The detector-sample distance was set to capture the first five Bragg reflections (Debye-Scherrer rings), so enabling a reasonable compromise between recording sufficiently high diffraction orders while still maintaining a good angular resolution. For data analysis the 2D-scans were averaged over 2°-wide polar segments, so producing 180 radial line scans which where then fitted by Split-Pearson-VII functions to obtain peak parameters like \(2\theta\) peak-position, integral intensity and integral peak width. For more details related to data reduction, we refer to the recent work by Lohmiller et al. \[31\].

![FIG. 1. Picture of the measurement setup at beamline ID15A of ESRF with the mechanical testing device mounted on top of a six axis goniometer. The inset shows a magnification of the compression stage with the roll bearing sample holder and a SCS in place. The sketch on the right displays a SCS in front and side view and serves as a reference frame for the polar plots shown throughout this document. In all cases the slit of the SCS is positioned 45° from lower left to upper right and load is applied along the vertical direction (\(\phi = 90°, 270°\)). Furthermore, all graphs showing \(\{hkl\}\)-data will use the same color code as the Debye-Scherrer rings in this sketch. The smaller side view shows the trapezoid slit geometry.](image1)

![FIG. 2. Stress-strain curves of three Pd\(_{90}\)Au\(_{10}\)-SCS deformed at \(\dot{\varepsilon}_a \approx 1.5 \cdot 10^{-3} \text{s}^{-1}\). The * marks the sample that will be analyzed and discussed throughout this document.](image2)
Sample deformation was recorded by a Pixelink CCD-camera using an inline microscope lens for magnification and several light sources to illuminate the sample. The images were processed by digital image correlation (DIC) to extract true sample displacements to establish load-displacement curves. As the gauge section of the SCS deforms under dominant shear and some superimposed pressure, there are no simple formulas to compute stress-strain curves from load-displacement data. Instead, we employed the finite element method (FEM) using ABAQUS, adapted to each individual sample geometry, to first generate load-displacement curves that best approximated the experimental load-displacement curves. Based on these fits, Von Mises equivalent stress-strain curves were then straightforwardly obtained by FEM. More details on SCS-testing are given in [23, 24].

RESULTS & DISCUSSION

Bragg-peak position & lattice strain

First, we look at the 2θ-angles characterizing the different \{hkl\}-Bragg peak positions. Using Bragg’s law, it is straightforward to compute the corresponding lattice spacing \(d_{hkl} = \lambda(2\sin\theta_{hkl})^{-1}\), where \(\theta_{hkl}\) is half of the diffraction angle and \(\lambda=0.178\ \text{Å}\) is the wavelength of the synchrotron radiation. During deformation the lattice spacings are expected to change so that the resulting elastic lattice strain \(\varepsilon_{hkl}\) can be extracted from

\[
\varepsilon_{hkl} = \frac{\Delta d_{hkl}}{d_{hkl,0}} = \frac{\sin \theta_{hkl,0}}{\sin \theta_{hkl}} - 1, \tag{1}
\]

where \(\Delta d_{hkl} = d_{hkl} - d_{hkl,0}\) and the index 0 corresponds to values of the initially undeformed sample. This definition implies positive lattice strain with increasing lattice spacing (tension), while a decrease (compression) leads to negative strain values. A polar plot of absolute values of the \{111\}-lattice strain of a NC Pd\textsubscript{90}Au\textsubscript{10}-SCS is displayed in Figure 3(a) for several selected deformation states. The large maxima along the vertical load direction correspond to negative compressive strains, while the smaller horizontal maxima are positive strains due to lateral tension. As the scattering vector is oriented perpendicular to the diffracting lattice planes, the signal along the load direction corresponds to a stack of horizontally oriented \{111\}-lattice planes and likewise for higher diffraction orders. Interestingly, the maximal strain values are not observed exactly along the load direction (\(\phi = 90^\circ, 270^\circ\)) but at \(\phi = 95^\circ, 275^\circ\) instead. In fact, the whole graph appears to be rotated \(\approx 5^\circ\) counterclockwise, indicating a transformation of the external...
FIG. 4. Applied stress $\sigma_n$ as a function of the absolute value of lattice strain $|\varepsilon_{hkl}|$ along the load direction. Linear fits show that the elastic lattice deformation essentially follows Hooke’s law up to large stresses. Only the most compliant (200)-planes deviate from the straight line indicating nonlinear elastic contributions.

load state, which, as can be verified by FEM, is related to the specific sample geometry (see sketch in Fig. 1).

Clearly, increasing load and hence applied stress correlate with increasing lattice strain, either compressive or tensile. In Fig. 3(b) we show the compressive lattice strain $\varepsilon_{hkl}$ of all five measured Bragg reflections as a function of applied strain $\varepsilon_n$, evaluated along the load direction ($\phi = 90^\circ$, $\phi = 270^\circ$). Due to the elastic anisotropy of PdAu, lattice planes with different Miller indexes experience different magnitudes of lattice strain and, typical for face centered cubic (FCC) metals, the (200)-planes are elastically most compliant. Apart from the different magnitudes, the lattice strain development of all planes follows roughly the shape of the stress-strain curve. This behavior is not unexpected though, since the evolution of lattice strain essentially describes the elastic deformation of the myriad of nanometer-sized crystal lattices. Interestingly, when plotting the applied stress as a function of the absolute value of lattice strain $|\varepsilon_{hkl}|$ along the load direction, as shown in figure 4, a linear correlation between stress and strain is observed. This evidence implies that even at such high stress values ($\sigma_n > 1.5$ GPa) nonlinear elastic behavior is absent but Hooke’s law $\sigma_n = C_{hkl} \varepsilon_{hkl}$, where $C_{hkl}$ is the $(hkl)$-dependent elastic modulus, still applies. The only exception are the most compliant (200)-planes that slightly deviate from the straight line in Fig. 4, suggesting presence of nonlinear elastic contributions. Nevertheless, evaluation of the arithmetic mean of the slopes $C_{hkl}$ of the linear fits gives $\langle C \rangle = 118.6 \pm 0.7$ GPa, which is remarkably close to the 110 GPa high frequency Young’s modulus of Pd$_{90}$Au$_{10}$ measured by ultrasound [32].

We now exploit the evolution of lattice strain to estimate the contribution of crystal elasticity to overall deformation. In particular, we take the arithmetic mean of the five curves in Fig. 3(b) to obtain an average elastic strain $\langle \varepsilon_{hkl} \rangle$ (in load direction) and divide by the corresponding applied strain $\varepsilon_n$ (also measured along the load direction). The resulting contribution of elastic strain to overall deformation $\langle \varepsilon_{hkl} \rangle/\varepsilon_n$ is displayed in the inset of Fig. 3(b). Initially the deformation is fully elastic (100% contribution), but with successively increasing plasticity the elastic deformation share drops rapidly to reach values as low as 5% at the applied maximum strain.

**Integral scattering intensity & texture formation**

Before deformation, all reflections produced uniform Debye-Scherrer rings with evenly distributed intensities which are typical for an untextured (isotropic) polycrystalline material (Fig. 5(a)). Upon loading the measured intensities remain fairly constant initially, however, when strains larger than 10% are reached, a subtle redistribution of scattering intensities is observed (see Fig. 5(b-d)). More specifically, a 6-fold symmetry revealing intensity maxima every 60° is found for the (111)- and (220)-reflections. In case of the (111)-reflection the first intensity maximum is observed at $\phi = 7^\circ$ whereas the first maximum of the (220)-reflection appears at $\phi = 37^\circ$. The intensity of the (200)-reflex, presented in Fig. 5(c), does not show a 6-fold symmetry, but instead exhibits two minima at $\phi = 97^\circ$ and $\phi = 277^\circ$. Overall, the observed subtle intensity changes share characteristic features with the typical rolling texture of coarse grained FCC metals (an example of which can be found in [33]).

Such textures are indicative of lattice rotations and grain-shape changes caused by dislocation activity. The primary slip system of FCC metals is (111)/(110), resulting in shear deformation on (111)-slip planes along ⟨110⟩ directions. As expected, the geometry of the SCS should promote shear along the gauge section thus enforcing (111)-slip planes to orient along the gauge section to accommodate strain in an optimal manner. As the scattering vector is oriented perpendicular to the diffracting lattice planes, a stack of slip planes aligned along the gauge section produces a diffraction signal at polar angles $\phi = 135^\circ$ and $\phi = 315^\circ$, which are in fact observed in Fig. 5(b). Due to the symmetry of the FCC unit cell, additional intensity peaks corresponding to different possible orientations of (111)-planes within the unit cell are also generated and give rise to the observed six-fold symmetry. The fact that we do not find sharp intensity peaks at the discussed polar angles seems reasonable since not all grains will actually reach the optimal orientation, thus contributing to a broadened intensity distribution around the optimal polar angles; inspection of Fig. 5(b) shows that all of the (111)-intensity peaks cover a range of azimuthal angles $\Delta \phi \approx 30^\circ$. 
Overall, our findings provide strong evidence that dominant shear deformation stimulates glide planes to orient along the gauge direction. However, due to the miniature redistribution of integral scattering intensity, even peak-maxima in Fig. 5 barely rise 20% above the initial values, we expect a rather small activity of dislocation glide across these planes. We note that texture formation in conventional coarse grained metals is accompanied by intensity variations covering several orders of magnitude. Nevertheless, we pursue the goal to relate the unambiguous but faint signatures of texture formation to plastic strain generation through dislocation motion. Unfortunately, there is no direct way to extract dislocation densities from the stress-induced evolution of integral \{111\}-scattering intensities.

In a recent work, Skrotzki et al. utilized forward simulations to analyze texture formation in Pd_{90}Au_{10} (D \approx 20 \text{ nm}) that was severely deformed to large plastic strains ($\gamma \gg 1$) by high pressure torsion (HPT). For strains $\gamma \approx 1$, a faint onset of texture evolution could be detected using a lab-diffractometer in reflection geometry. Surprisingly, even at large strains $\gamma > 10$, the integral intensity redistribution was comparatively weak. The experimentally extracted orientation distribution function (ODF) could be best fitted by a simulated ODF that was based on a Taylor polycrystal with a \{111\}\{112\} brass texture. In conjunction with the rather low reported stacking fault densities, determined from Bragg-peak profile analysis, they argue that the emerging texture is produced by pairs of partial dislocations gliding on \{111\}-lattice planes. In their study, they could not resolve the minuscule signatures of intensity redistribution we observe in the in-situ setup at significantly lower strain values $\gamma < 0.2$. Assuming that these minuscule signatures are related to pairs of partial dislocation activity in our 10 nm Pd_{90}Au_{10} samples too, we are go-
FIG. 6. Grain size and aspect ratio distributions of a Pd_{90}Au_{10}-SCS measured by TEM. (a, c) Undeformed sample (b, d) gauge section deformed to 32% applied strain. A log-normal distribution was fitted to the grain diameter histograms to find the median $D_0$ and distribution width $\sigma$. In case of the aspect ratio, the median $\langle \alpha \rangle_0$ and the arithmetic mean $\langle \alpha \rangle_1$ were calculated directly from the histogram. In all cases, $N$ denotes the number of counted grains.

In order to approximate the number of dislocations having traversed a grain during deformation, we look at grain aspect ratios. If a number $n$ of full dislocations (or pairs of partials) traverses a crystallite of diameter $D$, it is sheared by $n \cdot b$, where $b = 0.275 \text{ nm}$ is the length of the Burgers vector and the resulting shear strain is $\gamma \approx nb/D$. As a consequence of dislocation glide, the shape or aspect ratio $\alpha$ of the grain also changes. For the sake of simplicity, let us assume that the initial undeformed grain is a sphere of diameter $D_0$ and aspect ratio $\alpha_0 = 1$, whereas the sheared grain is an ellipsoid of the same volume as the initial sphere. We characterize the elliptical cross section by a long axis $D_1 = D_0 + nb$ and a short axis $D_2 = \sqrt{D_0^2/(D_0 + nb)}$. When the aspect ratio $\alpha_{\text{def}} = D_1/D_2$ of the deformed crystallite is known, it is straightforward to estimate the average number of dislocations $n = (\alpha_{\text{def}}^{2/3} - 1)D_0/b$ having traversed the grain. In the general case of non-spherical grains $\alpha_0 \geq 1$ and $\alpha_{\text{def}} \geq \alpha_0$, we obtain the following equation for $n$:

$$
n = \left[ \left( \frac{\alpha_{\text{def}}}{\alpha_0} \right)^{2/3} - 1 \right] \frac{D_0}{b}. \tag{2}
$$

In order to characterize the aspect ratio evolution that may occur during deformation, we used focused ion beam (FIB) milling to prepare thin lamellae from the undeformed part of a SCS and its gauge section having experienced 32% applied strain. TEM dark field micrographs were taken and analyzed in ImageJ [34] to measure the grain diameters along the short and long axis of the cross-section of individual grains. The so recorded data are
displayed in Fig. 6. The aspect ratio histogram of the undeformed material is shown in Fig. 6(c), and the histogram of the plastically deformed gauge section is presented in Fig. 6(d). Interestingly, there is no distinct difference in the aspect ratio distributions of the undeformed and deformed material. Both histograms have a median of $⟨α⟩_0 = 1.3$ and an arithmetic mean value of $⟨α⟩_1 ≈ 1.35$.

Despite these practically identical results, some small aspect ratio changes may yet exist within the error margin of the measurements. A reasonable error $δD ≈ 0.5 \text{ nm}$ of the TEM grain diameter measurements leads in turn to an uncertainty of roughly 10% for the aspect ratio. Accounting with a 10% variation of aspect ratio for dislocation activity, we can estimate an upper bound for the number of dislocations having traversed a grain. Using $α_{def}/α_0 = 1.1$ and $D_0 = 10.5 \text{ nm}$ in Eq. 2 we obtain $n = 2.5$ or approximately three dislocations per grain at $ε_a = 32\%$. This rather low dislocation count seems to be consistent with the very weak texture observed in the polar plots of Fig 6 at large strain.

One could argue, that we have underestimated the dislocation deformation share by having not considered grain rotation. Principally, a large number of dislocations could have traversed a grain while still maintaining an equiaxed grain shape if the grain is allowed to rotate such that each subsequent dislocation runs through the grain at a different angle and counteracts the build-up of aspect ratio. As there are only four possible orientations of the main {111} glide planes of a FCC material, such a process would require that grains must either rotate by $≈ 90^\circ$ or dislocations need to populate other glide planes. Based on the data presented in this work, we can not rule out any grain rotations. However, a single grain is certainly not allowed to rotate freely in the matrix due to compatibility constraints and, therefore, large angle rotations seem to be highly unlikely. Following Skrotzki et al. [20], the simulation of alternative slip systems incorporating different glide planes or slip directions did not yield textures compatible with the observed XRD intensity patterns. Thus, we feel confident that grain rotations or activity of peculiar slip systems can be neglected. Consequently, the possible shape change that is bounded by the error margin must be related to a very low amount of dislocation activity per grain.

We now estimate the relative dislocation share as a function of the applied strain. The $n ≈ 3$ dislocations per grain correspond to a shear strain of $γ = nb/D_0 = 0.079$ or a plastic strain of $ε_{p,\text{dis}} = γ/√3 = 0.045$ respectively [35]. Therefore, dislocation glide contributes only $ε_{p,\text{dis}}/ε_a = 14\%$ to overall deformation at an applied strain of $ε_a = 32\%$. We now use this result to scale the polynomial fit in Fig. 7 to approximate the evolution of the deformation share of dislocations, which is displayed in the inset of Fig. 7. At an applied strain of $ε_a = 25\%$ the dislocation share of 10% is just about double as high as the elastic share (see Fig. 3b) to overall strain. We note that Bachurin et al. [36] carried out atomistic simulations of uniaxial tensile and compressive loading of NC Pd with a mean grain size of 10 nm. They came to the conclusion that the contribution of extended partial dislocations emitted from the GBs as well as full dislocations and twinning at later stages of deformation to the total strain is insignificant. Summing up over all sorts of dislocation contributions including dislocation embryos, they found a relative share of about 10% dislocation based deformation slightly below 10% total strain. Taking into account that we discussed upper bound values for dislocation activity, we may conclude that in NC metals with a mean structural correlation length of 10 nm dislocations rather serve as carrier of accommodation processes instead of acting as generic flow defect that propagates strain in a dominant manner.

**Integral peak width, TEM & grain size evolution**

In this paragraph we focus on the evolution of the integral peak width of the diffraction reflexes (Debye-Scherrer rings). The two main factors that contribute to the broadening of diffraction peaks of a NC material are the small size of the scattering domains, i.e. small grain size, and the so called microstrain $ε$. The latter arises from small variations in lattice spacings of neighboring grains, which are commonly attributed to strain fields near GBs or lattice distortions caused by stored dislocations [37]. However, virtual diffraction experiments in conjunction with molecular dynamics (MD) based determination of atomic level strains [38] have shown that the XRD microstrain is insensitive to strain fields that decay faster than $r^{-3/2}$, specifically, the exponentially decaying local strains near GBs. Instead, the

![Graph showing relative increase of intensity and dislocation deformation share as a function of applied strain](image-url)
microstrain broadening in NC materials in the limit of small grain sizes is dominated by long range displacement fields that extend throughout the grains and arise from compatibility constraints imposed on the grains to form a space filling tessellation of crystalline objects. In fact, studying room-temperature grain growth in NC Pd ($D_{\text{initial}} \approx 10\,\text{nm}$), Ames et al. [39] have found the XRD microstrain to be inversely proportional to the average grain size $\epsilon \propto 1/\langle D \rangle$, suggesting that microstrain is in fact related to tesselation constraints and therefore is a generic contribution in any polycrystalline material. Due to the $1/\langle D \rangle$-scaling, microstrain becomes particularly pronounced at the nanoscale even in an undeformed, load-free NC structure.

Upon loading, the deduced microstrain also reflects the elastic anisotropy of the material, as grains with their hard axis being oriented parallel to the load direction will experience less compression than grains oriented along an elastically weaker axis. This behavior is readily illustrated by the polar plot in Fig. 8(a), where the integral {111}-peak width is increasing along the load direction with increasing strain up to $\epsilon_a = 15.8\%$. Further deformation to $\epsilon_a = 27.2\%$ leads to a decrease of the integral peak width, revealing a superimposed change of grain size. Effectively, decreasing peak width is inversely proportional to the size of the scattering domains. Thus, the decrease of integral peak width at large strains in Fig. 8(a) can be attributed to an increase of the volume averaged grain size $\langle D \rangle_{\text{vol}}$ and seems to be indicative of stress driven grain boundary migration (SDGBM) as a viable deformation mechanism in NC Pd$_{90}$Au$_{10}$.

To analyze the microstrain and grain size evolution, we make use of the single line method, introduced by de Keijser et al. [40], which allows to extract separate values of...
FIG. 9. (a) Sketch to estimate the shear strain due to SDGBM. (b) Relative deformation share of SDGBM as a function of applied strain. The single square corresponds to the SDGBM share derived from the TEM grain size histograms.

Originally the microstrain is roughly 0.4% along all polar angles. With increasing deformation, the microstrain steeply rises up to 0.8% along the load direction and 0.65% in the lateral tensile direction at $\varepsilon_a = 10.6 \%$. Further deformation does not yield a significant gain of microstrain. This becomes even more apparent in Fig. 8(d) where the evolutions of $\varepsilon_{\text{rms}}$ along the vertical compressive (dotted) and lateral tensile (dashed) direction are presented as a function of the applied strain. Interestingly, the elliptic shape of the microstrain polar plot corresponds well with the overall shape of the lattice strain development shown in Fig. 3(a). The obvious connection between lattice strain $\varepsilon_{hkl}$ and microstrain $\varepsilon_{\text{rms}}$ corroborates the notion that microstrain in NC metals is essentially a measure of long range displacement fields originating from compatibility constraints. We cannot discriminate between possible additional microstrain contributions resulting from stress concentrators at triple junctions and bending of lattice planes both caused by the likely presence of GB-mediated deformation modes [36, 41].

Regarding grain size evolution, we first focus on the circular shape of the polar plot of the initial grain size (black) in Fig. 8(c). It indicates that the undeformed sample is made up of roughly equiaxed grains with a mean diameter of $\langle D \rangle_{\text{vol}} = 10.4 \pm 0.7 \text{ nm}$. This value is in close agreement with the grain size $\langle D \rangle_{\text{IGC}} \approx 9 \pm 3 \text{ nm}$ of the as-prepared NC material, determined immediately after IGC by a Williamson-Hall analysis of XRD patterns recorded by a XPert Pro laboratory diffractometer in Bragg-Brentano focusing geometry, providing the required fixed orientation of the scattering vector. Therefore, we feel confident that the single line method is capable of catching the essential features of relative change of grain size. From the polar plot at $\varepsilon_a = 27.2 \%$, we deduce a grain size of $13.4 \pm 2.7 \text{ nm}$. Obviously, the deconvolution of microstrain and size broadening of pronouncedly stressed SCS goes along with a higher error margin for the grain size values, especially along the vertical load direction. Within the error margin, the polar plot of the deformed state appears still circular implying that evolution of grain elongation or grain shape anisotropy plays, if at all, a minor role. This reasoning agrees with the TEM analysis, where the mean grain size derived from
the median of the size histogram increased from 10.5 nm to 15.5 nm and the observed constant aspect ratio (Fig. 8) also suggests shape preserving grain growth.

In Fig. 8(d), the evolution of $\langle D \rangle_{\text{vol}}$, averaged over all polar angles, is displayed as a function of the applied strain. Remarkably, the grain size remains nearly constant at $\langle D \rangle_{\text{vol}} = 10.4$ nm up to $\varepsilon_a \approx 4\%$. Beyond that point grain growth is triggered and gradually advances with increasing plastic strain to reach a grain size of 13.4 nm at $\varepsilon_a = 27.2\%$. The fact that grain size is still growing, while the microstrain values shown in Fig. 8(d) reach a plateau, is consistent with the decrease of the integral peak width in Fig. 8(a) beyond $\varepsilon_a \approx 15.8\%$. Since all experiments were performed at room temperature (RT) and the microstructure of NC Pd$_{90}$Au$_{10}$ has been verified being stable up to $120^\circ\text{C}$, curvature-driven grain growth can be ruled out. Consequently, the observed grain growth must be solely due to SDGBM. To estimate the contribution of SDGBM to overall strain, we refer to a simple model displayed in Fig. 9(a).

The phenomenon of SDGBM comprises the migration of a GB parallel and perpendicular to an applied shear stress $\tau$. The coupling factor $\beta = v_\parallel / v_\perp$ describes the ratio of migration parallel and perpendicular to the applied stress. In Fig. 9(a), we assume growth of the middle grain in response to the applied shear stress $\tau$ which induces a shear strain $\gamma = \Delta x/3D$. The shear strain can also be expressed as $\gamma = \beta \Delta D/3D$, where $\Delta D$ is the grain growth relative to the initial grain size $D$. Using the $\langle D \rangle_{\text{vol}}$-data in Fig. 8(d), an average coupling factor of $\langle \beta \rangle = 0.3$ and the relation $\varepsilon = \gamma/\sqrt{3}$, it is straightforward to compute the relative contribution $\varepsilon_{\text{SDGBM}}/\varepsilon_a$ of SDGBM as a function of applied strain. The resulting evolution of the SDGBM share is shown in Fig. 9(b) together with the value from the TEM analysis. It should be noted that by letting both GBs move in opposite vertical and horizontal directions, as shown in Fig. 9(a), we estimate an upper bound for the associated shear strain.

CONCLUSIONS

In the previous sections we identified three different strain carrying mechanisms as well as their relative contributions to overall deformation, which are altogether displayed in Fig. 10. In addition to the elastic, dislocation based, and SDGBM strain shares we also show the difference between the sum of these shares and 100% strain contribution. Strikingly, this residual contribution, steeply rising in the early stage of deformation, approaches a strain share of about 75% implying that three quarters of total deformation are yet unaccounted for. Since diffraction methods are particularly sensitive to microstructural changes associated with deviations from perfect crystal lattice order or coherent scattering domain size, it suggests itself that the unaccounted strain contribution must have been propagated by GB-mediated deformation modes; they may give rise to diffuse scattering but its analysis was beyond the scope of this study.

In a recent work [23], we have been led to the same conclusion, however, based on reverse reasoning. By deriving expressions for the effective activation volume and utilizing experimental or theoretical values for the specific activation volumes of the involved deformation mechanisms, we estimated the relative contributions of deformation modes to arrive at a share of GB-mediated deformation of $\approx 80\%$. From the determination of the effective activation energy and its stress dependence, we concluded that GBs mimic shear shuffling or rather shear transformations (STs) as observed in metallic glasses. We notice that in contrast to metallic glasses, where emerging STs will eventually self-organize to form macroscopic shear bands, the topology and connectivity of GBs effectively impede the emergence of shear bands and thus prevent the material from stick-slip behavior or catastrophic failure, which was clearly not observed (Fig. 2). Based on this independent evidence, it seems justified now to maintain that shear transformations emerging in the core region of GBs account for three quarters of total strain in NC Pd$_{90}$Au$_{10}$ at the low end of the nanoscale ($D \lesssim 10$ nm).

In the pertinent literature dealing with nanoplasticity, GB-mediated deformation usually becomes associated with GB sliding. This term has been originally introduced to denote the rigid body translation of abutting crystallites along a shared interface that produces offsets in marker lines at the GBs. The two classical modes of GB sliding comprise Rachinger sliding, which must be accommodated by intragranular dislocation glide and climb, and Lifshitz sliding that is based on stress-
directed diffusion of vacancies and is self-accommodating. These sliding modes occur under creep conditions at elevated temperatures and are characterized by strain-rate sensitivities $> 0.3$ and activation volumes $< 0.1 \text{ b}^3$, respectively, and, according to our previous work \[25\], can be ruled out being active in our material. In a recent computer simulation on NC Ni, Wu et al. \[17\] demonstrated that the occurrence of rigid body translation of grains is related to the system size. When it is not large enough, the proximity of free surfaces reduces the constraint exerted by surrounding grains so favoring easy sliding; the opposite is true for increasing system size. They argue that in realistic NC microstructures GB sliding is kinematically constrained by triple junction lines and quadrupole points, but nevertheless shear deformation at/along GBs can still occur. Our finding of shear strain propagation at/along GBs, obviously not being hampered by network constraints, is in line with this reasoning. It is additionally supported by noticing that the shear modulus of GBs in NC metals is reduced by about 30\% \[22\] compared to the respective bulk value. So implying that GBs have a lower resistance to shear deformation compared to dislocation shear, which is nucleation controlled at the low end of the nanoscale \[30\]. As recommended by our activation parameter analysis \[25\], we prefer to assign the irreversible shear strain accumulated along/ at GBs to STs and omit the term GB sliding to avoid confusion with nomenclature in what follows. We finally notice that the activity of STs in the core region of GBs genuinely allows for translational and rotational degrees of freedom of grains relative to each other and so is not in conflict with the emergence of displacement discontinuities across/along GBs.

In Fig. \[11\] we display the shares of the different mechanisms as a function of applied stress to unravel their simultaneous and/or sequential onset and persistence. For convenience, we also designate the characteristic stress values extracted from yield criteria applied in the stress-strain domain \[24\]: $\sigma_y$ marks the deviation from linear elasticity or the onset of so-called microplasticity and $\sigma_y$ denotes the yield stress, agreeing with the stress value at which the applied strain rate approaches the materials intrinsic plastic strain rate.

The early stage of deformation $\sigma_a < \sigma_m$ reveals a rather steeply decreasing share of lattice strain and a concomitant increasing share of STs. Surprisingly, both curves cross each other at around $\sigma_m$; this behavior has also been observed for other specimens. The residual strain share (green curve) must involve elastic as well as non recoverable inelastic strain contributions originating from the core regions of GBs because GB-elasticity can hardly accommodate a deformation share of 50\%. With a volume fraction of GBs of $\approx 20\%$ at $D = 10 \text{ nm}$ and a 30\% reduction of the Youngs modulus of GBs, a simple rule of mixture argument yields an upper bound for the elastic deformation share of GBs of $\approx 20\%$. We performed no loading unloading tests in the stress regime below $\sigma_m$ to look for residual strain. However, computations simulated unloading that loading a specimen along a perfectly linear stress-strain trajectory does not necessarily imply presence of Hookean elasticity. Bachurin et al. \[43\] demonstrated that unloading a sample in the apparent elastic regime already results in non recoverable inelastic strain which amounts to $0.1 - 0.15\%$ at an applied strain of 1\%. We therefore suggest that even in the early stage of deformation the residual strain share (green curve) manifests elastic as well as non recoverable inelastic strain contributions to make up for a 50\% share at $\sigma_m$.

In the stress regime $\sigma_m < \sigma_a < \sigma_y$ the deformation behavior is dominated by Hookean elasticity of the grain interior and shear shuffling/STs taking place in the core region of GBs. We observe a rather abrupt onset of SDGBM slightly below the yield stress and an extremely sluggish onset of dislocation activity at the yield stress. Ignoring for the sake of argument the negligibly small contributions of SDGBM and dislocations, our finding has two profound implications. First, GB-mediated deformation by STs is capable of propagating plastic strain without assistance/interplay of simultaneously acting accommodation mechanisms also contributing to irreversible deformation. When analyzing the activation energy of shear shuffling, Grewer et al. had to explicitly assume that the activity of STs is not coupled to an accommodation mechanism with an activation energy distinctively deviating from activation of STs. The identified sole activity of STs acting as carrier of inelastic strain in this regime thus a posteriori justifies the presumption made in \[25\]. Secondly, the concept of work or strain hardening that essentially refers to intraplane
dislocation interactions seems not being applicable here. This notion also coincides with the analysis of the strain-rate dependence of stress in [25], where it could be verified that the material response in this regime agrees with nonlinear viscous behavior. We are aware that Dahmen et al. studied, in the realm of mean field theory and renormalization group tools, the stress response of solids via slip avalanches [44]. The verification of the predicted stress and/or frequency dependent scaling laws for average avalanche size and slip-rate power spectra require, however, high-resolution data in the stress-time domain and Fourier analysis, which we will address in a forthcoming paper.

When \( \sigma_n > \sigma_y \) the share of SDGBM runs through a maximum to then decrease whereas dislocation activity gains progressively more influence to develop the largest rate of increase when the maximum stress values, just before failure, are reached. Hookean lattice elasticity tends to assume the minimum share (\( \approx 5\% \)) here and STs carry a strain share of more than 70%. It seems conceivable that SDGBM and dislocation glide may interact in a synergistic manner e.g. through enhanced grain growth and concomitant increasing intracrystalline dislocation activity at local stress concentrations or before failure thereby avoiding early brittle fracture. Overall, the diverse evolution of the respective deformation shares appears as being just a consequence of a complex hierarchical order of onset/nucleation and upholding stresses of different deformation mechanisms, the presence and degree of activity of which depends severely on grain size. E.g. in a recent study of NC Ni with a grain size of 30 nm, a strain share of about 40% could be assigned to dislocation activity [31]. We finally conjecture that the state of the GB core structure, whether in relaxed (low-excess-energy) or un-relaxed (high-excess-energy state) configuration, should also have a decisive effect on the share and onset stresses of the above discussed deformation modes. Furthermore, the stacking fault energy of the PdAu alloy decreases with rising Au concentration [21] [22] and therefore, partial dislocation activity should increase towards Au-rich alloys. Consequently, we expect the alloy composition to at least influence the magnitude of the dislocation share.

**SUMMARY**

In this work, we have utilized in-situ diffraction and post mortem microscopy in conjunction with dominant shear deformation to identify, dissect, and quantify the relevant deformation mechanisms in NC Pd_{90}Au_{10} in the limiting case of \( D \lesssim 10 \) nm. We could identify lattice elasticity, shear shuffling operating in the core region of GBs, stress driven grain boundary migration (SDGBM), and dislocation shear along lattice planes to all contribute, however, with significantly different and non-trivial stress-dependent shares to overall deformation. We avoid the term GB sliding to specify GB-mediated deformation since shear shuffling or shear transformations (STs), which operate as generic flow defect in metallic glasses, could be unambiguously identified in conjunction with an analysis of activation volume and energy in a previous study [25].

It was not required to invoke nonlinear elasticity to adequately describe the material response. In fact, Hookean linear elasticity prevailed up to material failure beyond 1.5 GPa. In the so-called microplastic regime, STs coexist with lattice elasticity in a way that the share of the latter decreased inversely proportional to the progressive increase of STs. Dislocation activity is basically missing here. The fact that STs and linear lattice elasticity more or less exclusively operate in this regime, characterized by a markedly decreasing tangent modulus, suggests to discard the conventional concept of work- or strain hardening since it is based on intraplanar dislocation interactions. Moreover, STs which propagate strain at/along GBs have been found to carry three quarters of the overall strain in the regime of macroplasticity and so are by far the dominant carrier of strain.

The abrupt onset of SDGBM appeared at stress values in the vicinity of the yield stress. Dislocation shear contributed in a very sluggish manner even above yielding. Appreciable and progressively increasing dislocation activity required stress values near the failure stress. Overall, the diverse evolution of the respective deformation shares appears as being just a consequence of a complex hierarchical order of onset/nucleation and upholding stresses of different deformation mechanisms. We expect that the configurational state of the material’s microstructure, whether tested in as-prepared or relaxed state, should have a decisive influence on this hierarchy.

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