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1 **Nucleation of Dislocations in 3.9 nm Nanocrystals at High Pressure**

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17

18 **Abstract:**

19 As circuitry approaches single nanometer length scales, it has become important to predict the  
20 stability of single nanometer-sized metals. The behavior of metals at larger scales can be predicted  
21 based on the behavior of dislocations, but it is unclear if dislocations can form and be sustained at  
22 single nanometer dimensions. Here, we report the formation of dislocations within individual 3.9  
23 nm Au nanocrystals under nonhydrostatic pressure in a diamond anvil cell. We used a combination

24 of x-ray diffraction, optical absorbance spectroscopy, and molecular dynamics simulation to  
25 characterize the defects that are formed, which were found to be surface-nucleated partial  
26 dislocations. These results indicate that dislocations are still active at single nanometer length  
27 scales and can lead to permanent plasticity.

28

29 **Main text:**

30 Permanent plastic deformation occurs in bulk crystalline metals that are subjected to large strains  
31 at room temperature. This irreversible deformation can be due to the short-range interactions  
32 between dislocations, or the formation of dislocation arrays at grain or twin boundaries. Recently,  
33 reversible deformation from large strains has been observed in sub-10 nm Ag nanocrystals [1] and  
34 3.9 nm Au nanocrystals, [2] in which the nanocrystal rapidly recovers from a flattened state after  
35 load is removed, and reverts to its original faceted shape. The mechanisms behind this behavior  
36 remain unclear, as there is evidence for both diffusion and dislocation mediated plasticity. Rapid  
37 diffusion of atoms at free surfaces and stress-induced diffusion at the nanocrystal-indenter and  
38 nanocrystal-substrate interfaces have been proposed as mechanisms, based on theoretical  
39 considerations and *in situ* transmission electron microscope (TEM) observations [1,3]. Others  
40 have instead observed surface-nucleated dislocations and deformation twinning in sub-10 nm  
41 nanowires, and stacking faults tetrahedra in sub-20 nm nanowires under tension in both  
42 experiments and molecular dynamics (MD) simulations [4–7]. Dislocations and diffusion may  
43 also act cooperatively. *In situ* TEM tension tests on ~20 nm and sub 5 nm Ag nanowires showed  
44 that surface diffusion is enhanced at surface steps created by the passage of dislocations [8,9].  
45 Previous work from our group showed that pseudoelastic shape recovery (diffusion mediated

46 process) in 3.9 nm Au nanocrystals is accompanied by the formation of irreversible defects, but  
47 the nature of the defects could not be determined [2].

48         These observations prompt the questions: Is there a limit to plasticity at small length scales?  
49 What is the smallest crystal in which dislocations can form and lead to irreversible deformation?  
50 This is critical to the processing and mechanical behavior of nanostructured materials such as  
51 nanocrystalline, nanotwinned and nanoporous metals, and the design of stable nano-devices with  
52 single nanometer metallic features [10]. To answer these questions, deformation mechanisms in  
53 very small nanocrystals must be experimentally determined, but this remains challenging. *In situ*  
54 TEM mechanical testing is the leading method to investigate deformation mechanisms at this  
55 length scale, but results may be influenced by heating from the electron beam. In addition, fast  
56 dislocations and dislocations that are invisible at specific imaging conditions cannot be observed.  
57 X-ray diffraction (XRD) is another method to measure elastic strain and defect formation in metals  
58 under mechanical stress. The width and relative intensities of XRD peaks have previously been  
59 used to detect dislocation activity in nanocrystalline Ni under uniaxial tension [11] and  
60 compression in a diamond anvil cell (DAC) [12]. These studies involve the response at grain  
61 boundaries as well as within the grains, so they cannot be directly applied to understand plasticity  
62 in individual nanocrystals. To do this, the structural response of isolated nanocrystals must be  
63 obtained. This presents a challenge for *in situ* XRD because the diffracted intensities from a single  
64 nanocrystal are much too small for detection.

65         Here, we use XRD to detect structural changes in an ensemble of monodisperse 3.9 nm Au  
66 nanocrystals that are compressed under a non-hydrostatic pressure in a DAC. Surfaces of the  
67 nanocrystals are protected by organic ligands, which prevents contact between the nanocrystals.  
68 Structural changes from XRD are corroborated with optical spectroscopy measurements, and MD

69 simulations are used to determine the specific defects that correspond to the ensemble-averaged  
70 behavior from XRD. We show that irreversible deformation due to the formation of surface  
71 nucleated partial dislocations can occur in small metallic nanocrystals. This indicates that  
72 dislocation-mediated plasticity is still active at single nanometer length scales and must be  
73 considered in designing structures at this scale. Theoretical work on homogenous dislocation  
74 nucleation has been studied well for nanoindentation experiments on larger nanocrystals [new  
75 refs]. However, these results prompt for development of theoretical work on heterogenous  
76 dislocation nucleation from nanocrystal surface in compression in DAC.

77 Au nanocrystals were synthesized using the organic phase reduction of chloroauric acid  
78 and capped with dodecanethiol ligands [13]. The nanocrystal size distribution was found to be  
79  $3.9 \pm 0.6$  nm using TEM (see Fig. 1A and see the Supplementary Material [14]). High-resolution  
80 TEM images showed that most of the identified nanocrystals were either icosahedral or decahedral  
81 in shape (Fig. 1B-C). Icosahedral nanocrystals have 20 twin boundaries, and decahedral  
82 nanocrystals have 5 twin boundaries. Ambient pressure XRD showed an FCC crystal structure,  
83 and significantly broader peaks than bulk Au due to the limited coherent scattering volume within  
84 the nanocrystals (see the Supplementary Material [14]). The (111), (220), (311) and (222) XRD  
85 peaks were shifted to higher  $2\theta$  angles by  $\sim 0.1^\circ$  compared to that of the bulk, which corresponds  
86 to a  $\sim 1.8\%$  volumetric compressive strain. The position of the (200) peak was shifted to lower  $2\theta$   
87 angles by  $0.15^\circ$ . Broad shoulders were observed on the (200) and (220) peaks. These features are  
88 indicative of the high twin density in icosahedral and decahedral nanocrystals [22]. In addition,  
89 the (111) peak showed asymmetric broadening due to tensile and compressive stresses at the  
90 surfaces and the interior of the nanocrystals due to surface stresses [30]. The Au nanocrystals  
91 consist of  $\sim 20\%$  surface atoms with most of the surface covered with (111) planes. As a result, the

92 (111) peak shows the most asymmetrical broadening compared to the other peaks. The Debye  
93 scattering equation was used to fit the XRD pattern to determine the structure of the nanocrystals.  
94 In this method, the atomic positions for icosahedral and decahedral nanocrystals were generated  
95 for 1 to 6 nm diameter nanocrystals and used to simulate XRD patterns. A Rietveld-like refinement  
96 procedure was used to fit the experimental data [22,24]. The best fit was obtained by combining  
97 60% icosahedral nanocrystals with a size distribution of  $3.2\pm 0.2$  nm and 40% decahedral  
98 nanocrystals with a size distribution of  $3.8\pm 0.6$  nm (see the Supplementary Material [14]). This  
99 result is in close agreement with the nanocrystal shape and size distribution observed in TEM.

100 High pressure XRD was obtained during DAC compression experiments at the Advanced  
101 Light Source at Lawrence Berkeley National Laboratory (Fig. 2A-B). A non-hydrostatic pressure  
102 was applied to the nanocrystals by loading the nanocrystals as a thick film at the bottom of the  
103 DAC sample chamber, and using toluene as a non-hydrostatic pressure medium [31]. XRD was  
104 collected while the nanocrystals were loaded up to 7.5 GPa and as pressure was released. The  
105 pressure was limited to 7.5 GPa to avoid sintering between the nanocrystals, which has been  
106 observed by our group and others at higher pressures [32–34]. The XRD peak position and width  
107 (full width at half max) were observed to change with increasing and decreasing pressure and  
108 quantified at each pressure (Fig. 2C-D). The relative intensity of the XRD peaks does not change  
109 under pressure, which indicates that the nanocrystals remain randomly oriented.

110 The change in peak position indicates the elastic strain in the nanocrystals. The shift in the  
111 peak position shows that the lattice spacing decreases by  $0.042 \text{ \AA}$  over 7.5 GPa and recovers to  
112  $\sim 0.2\%$  of its original value upon unloading. The (200) peak position gives information about the  
113 extent of twinning in the sample (see Fig. S8 for the qualitative effect of twinning on the XRD  
114 peak). The complete recovery of the (200) peak position indicates that the initial multiply twinned

115 structure (icosahedral/decahedral) is preserved after the pressure cycle. Due to the non-hydrostatic  
116 pressure, the change in lattice spacing is different along the loading axis (axial) and orthogonal to  
117 the loading axis (radial). The geometry of the X-ray setup is such that the measured lattice spacings  
118 correspond to planes that are almost aligned with the loading axis. Therefore, the measured change  
119 in lattice spacing is lower than in the hydrostatic case (see the Supplementary Material [14]). The  
120 difference between radial and axial stress components (termed as  $t$ ) can give us an estimate of  
121 maximum deviatoric and shear stresses in the system. This difference can be calculated by  
122 considering the elastic anisotropy of a polycrystalline, FCC metal. We used lattice strain theory to  
123 get a rough estimate of ' $t$ ' [29,35] (see the Supplementary Material [14]). Using this we estimated  
124 the maximum shear stress of Au nanoparticles to be about 2.3 GPa (see the Supplementary  
125 Material [14]).

126 Fig. 2D shows the change in peak width for the (111), (200) and (220) peaks with a  
127 complete pressure cycle. The (200) peak width showed a significant increase of 16% and the (220)  
128 peak width showed an increase of 23% with increasing pressure and remained at higher values  
129 after unloading. This indicates that irreversible deformation is occurring in the nanocrystals and  
130 remains in the nanocrystals on the time scale of the experimental measurements. The XRD peak  
131 width can be affected by changes in crystallite size, shape and microstrain [36]. It is possible that  
132 crystalline domains within the nanocrystal become elongated under compression and split into  
133 smaller domains, but post-compression TEM images showed that the nanocrystal shape and size  
134 distribution is identical to that of the as-synthesized nanocrystals (see the Supplementary  
135 Material [14]). The (111) peak width is mostly affected by domain size changes and is least  
136 affected by the presence of defects like twinning and stacking faults in the nanocrystal (see the  
137 Supplementary Material [14]). The peak width for (111) peak remained at about 2% of its initial

138 value with pressure cycling. The insignificant change in the (111) peak width also indicates that  
139 domain size does not change under pressure [22,37]. From this analysis, we determine that the  
140 increased peak width after unloading is caused by the formation of crystalline defects such as  
141 dislocations rather than changes in the size and shape of crystalline domains. The observation that  
142 (200) and (220) peak were the most affected and the (111) peak is least affected indicates the  
143 presence of stacking faults, twinning and dislocations (see the Supplementary Material [14]).

144         These XRD results were corroborated by high-pressure optical absorbance spectroscopy.  
145 Au nanocrystals have a plasmonic resonance that is dependent upon nanocrystal size, shape and  
146 microstructure [38]. Previous optical modeling showed that the plasmon peak wavelength is  
147 indicative of nanocrystal shape, while an irreversible decrease in the plasmon peak intensity is  
148 indicative of the formation of crystalline defects [2]. The plasmon peak wavelength of the 3.9 nm  
149 Au nanocrystals increased by ~30 nm when pressure was increased to 7.5 GPa and recovered its  
150 initial value upon unloading (see the Supplementary Material [14]). These optical measurements  
151 showed that the nanocrystals elongate into ellipsoids and then recover their original shape after  
152 unloading. The plasmon peak intensity showed an irreversible decrease after unloading. The  
153 reduced absorbance peak intensity after unloading is correlated to the formation of defects in  
154 nanocrystals through a damping factor [2]. The optical data supports the conclusion that the  
155 irreversible increase in XRD peak width after pressure cycling is due to the formation of crystalline  
156 defects, rather than a change in the size and shape of crystalline domains within the nanocrystals.  
157 UV-vis absorbance provides conclusive information about nanocrystal shape, and XRD provides  
158 conclusive information about defect formation.

159         MD simulations were used to understand the crystalline defects that form within the  
160 nanocrystals, and their interactions with existing twin boundaries and surfaces. Two types of



161 stacking faults (SF) were formed in an icosahedral nanocrystal under pressure (Fig. 3A); SF type  
162 1 refers to a stacking fault parallel to the outer surface of the nanocrystal (or parallel to surface  
163 steps formed during deformation), and SF type 2 is a stacking fault parallel to an internal twin  
164 boundary that intersects with two other twin boundaries. Both types of stacking fault were formed  
165 by the nucleation and propagation of a Shockley partial dislocation with a Burgers vector of  
166  $\frac{1}{6}\langle 112 \rangle a$ . SF type 1 forms when a Shockley partial dislocation with Burgers vector parallel to the  
167 outer surface propagates on a slip plane parallel to the outer surface. This results in a displacement  
168 relative to adjacent grains that is about the magnitude of the Burgers vector (see the Supplementary  
169 Material [14]). When trailing partials are activated on the same plane, the stacking fault is  
170 removed, which results in the formation of a larger displacement. The trailing partial slip in one  
171 grain sometimes triggers stacking fault formation in an adjacent grain. This occurs if the Burgers  
172 vector of the trailing partial dislocation (i.e. the slip direction) is aligned well with the Burgers  
173 vector of a leading partial dislocation (Fig. 3B). SF type 2 is a dislocation that has a Burgers vector  
174 parallel to an interior twin boundary. The passage of SF type 2 is blocked by intersecting twin  
175 boundaries and forms interfacial dislocations with a  $\frac{1}{9}\langle 222 \rangle a$  Burgers vector. This type of stacking  
176 fault has also been observed in penta-twinned silver nanowire with >40 nm diameter [39]. In  
177 contrast to the penta-twinned silver nanowires, the trailing partial does not follow the leading  
178 partial (or, the SF type 2) in the 3.9 nm nanocrystal because the image stress is very large due to  
179 the proximity to the free surface and opposes the motion of the trailing partial. For this reason, SF  
180 type 2 is harder to form, and the plastic deformation of the nanocrystal is dominated by the  
181 successive formation of SF type 1 defects. This is in contrast with work by Sun et al. on Ag  
182 nanocrystals where they reported liquid like deformation via surface diffusion; however, they had  
183 performed very high temperature MD simulations to observe diffusion activity in MD time

184 scale [1]. We conducted room-temperature MD simulations where surface diffusion was limited.  
185 This is in line with experiments where the Au nanocrystal surface was protected by bulky organic  
186 ligands that form Au-SR bonds which prevent diffusion at the nanocrystal surface [40].

187 We attribute the irreversible deformation in the nanocrystals to SF type 1 defects, as  
188 portions of these defects remain in the simulated nanocrystal after unloading (See Fig. 3B). The  
189 stacking fault parallel to the outer surface is energetically meta-stable, because of the finite energy  
190 barrier required to form a partial dislocation to reversely sweep out the stacking fault. In  
191 experimental time scales, some meta-stable stacking faults can be expected to remain. In contrast,  
192 SF type 2 escapes quickly to the free surface during unloading upon the removal of deviatoric  
193 stress, which implies that the plastic deformation by this type of stacking fault is reversible. SF  
194 type 2 forms a partial dislocation loop that is blocked by twin boundaries. This is an unstable  
195 structure that is easily pulled towards the free surface by an image stress [39].

196 The correspondence between the experimental data and MD simulation was evaluated by  
197 generating XRD patterns from the MD simulated structures at different pressures by using the  
198 Debye scattering equation [24] (see Fig. 4A-B). The Debye scattering equation is a Fourier  
199 transform of the interatomic distances in a nanocrystal. Large ripples are observed in the computed  
200 patterns due to the small number of atoms in a finite sized nanocrystal (see Fig. S10). These ripples  
201 become less prominent when diffraction patterns for different sized nanocrystals are combined.  
202 Figure 4 shows the average XRD pattern for 3.5, 3.9, and 4.5 nm icosahedral and 4 nm decahedral  
203 nanocrystals to mimic the experimental nanocrystal size distribution. A small ripple to the left of  
204 (111), and to the right of (200) and (220) can still be observed in Figure 4. While these ripples  
205 could be further smoothed by simulating the same nanocrystal size distribution as in  
206 experiments, this is infeasible due to constraints on computing time. The XRD peaks were fitted

207 using Lorentzian and Gaussian peak profile with a high order polynomial for the background. Due  
208 to the ripple on the (220) peak, the exact (220) peak width cannot be obtained but can still be  
209 analyzed qualitatively. The XRD peak width for the simulated patterns showed a similar trend to  
210 experimental data in that the (111) peak width broadened the least, and the (200) peak broadened  
211 the most under pressure (Fig. 4C-D). The (220) peak width also increased, similarly to experiments  
212 (Fig. S11). The effect of adding stacking faults to the nanocrystal is evident from the significant  
213 increase of peak width for the (200) and (220) peaks. The close agreement of MD simulated XRD  
214 patterns and experimental XRD patterns shows that MD simulations are a true representation of  
215 experiments.

216 In summary, using high-pressure XRD, optical absorbance spectroscopy and MD  
217 simulations we provide the first evidence of plastic deformation in individual 3.9 nm Au  
218 nanocrystals. The plastic deformation governed was by stacking faults formed via surface  
219 nucleated partial dislocations. The formation of surface steps during the passage of sequential  
220 partial dislocations as well as remaining stacking faults led to residual defects in the nanocrystal.  
221 The kinetics of residual defect recovery after unloading the sample will be explored further in  
222 future studies. This work provides a critical advancement in using experimental and simulation  
223 generated XRD as a comprehensive measurement technique to study defect formation in  
224 nanomaterials.

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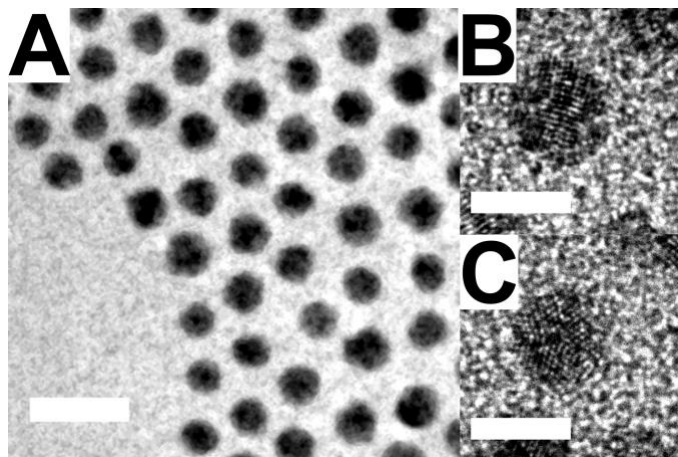
290

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305 **Figures**

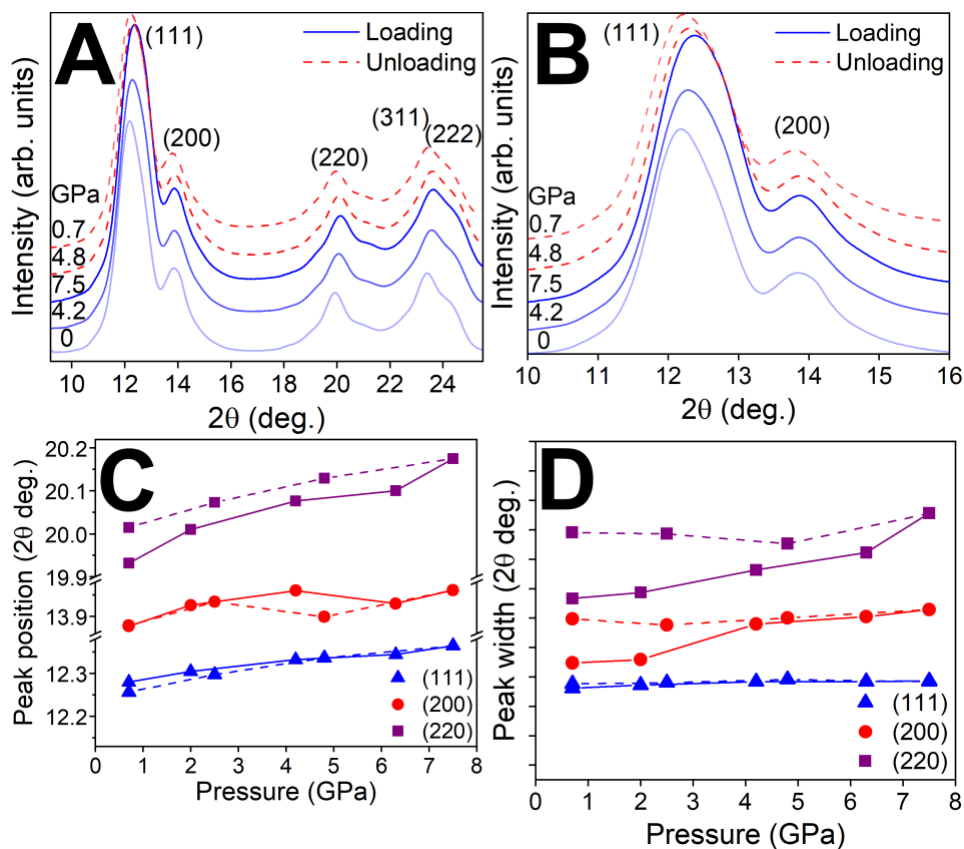


306

307 **Fig. 1. TEM images of nanocrystals.** A) Monodisperse 3.9 nm Au nanocrystals. Scale bar is 10  
308 nm. High-resolution images of B) icosahedral and C) decahedral nanocrystals. Scale bar is 4 nm.

309



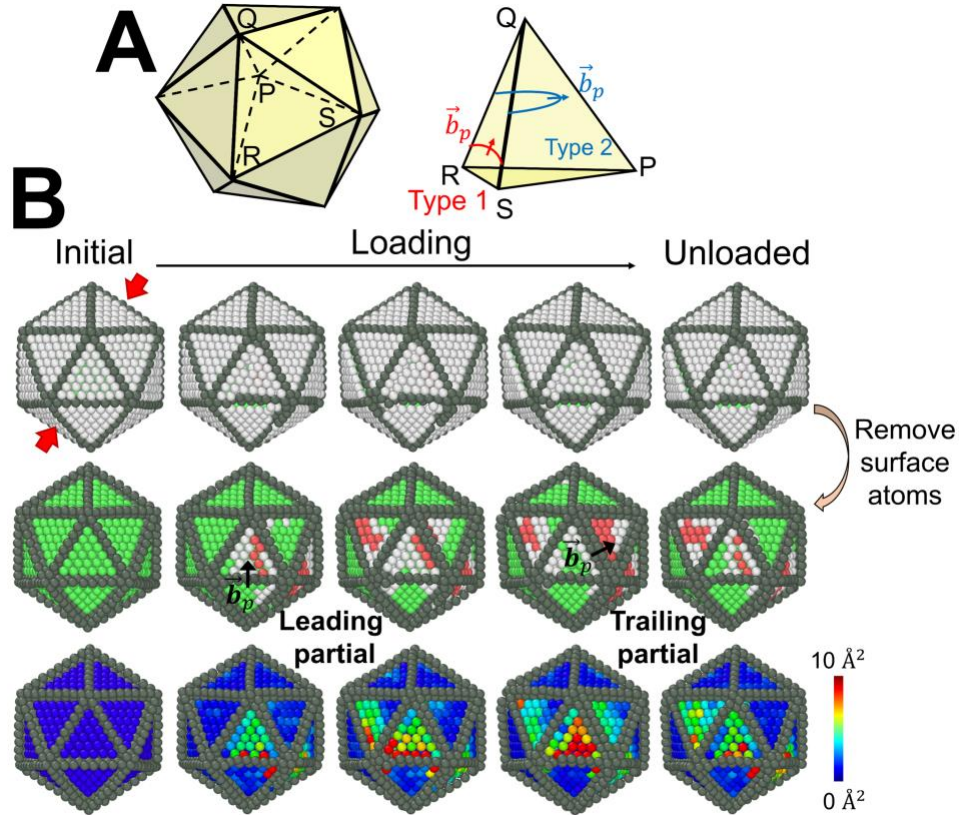


310

311 **Fig. 2. Experimental high-pressure XRD patterns.** A) All diffraction peaks and B) magnified

312 view of (111) and (200) peaks. Change in diffraction peak C) position and D) width (each

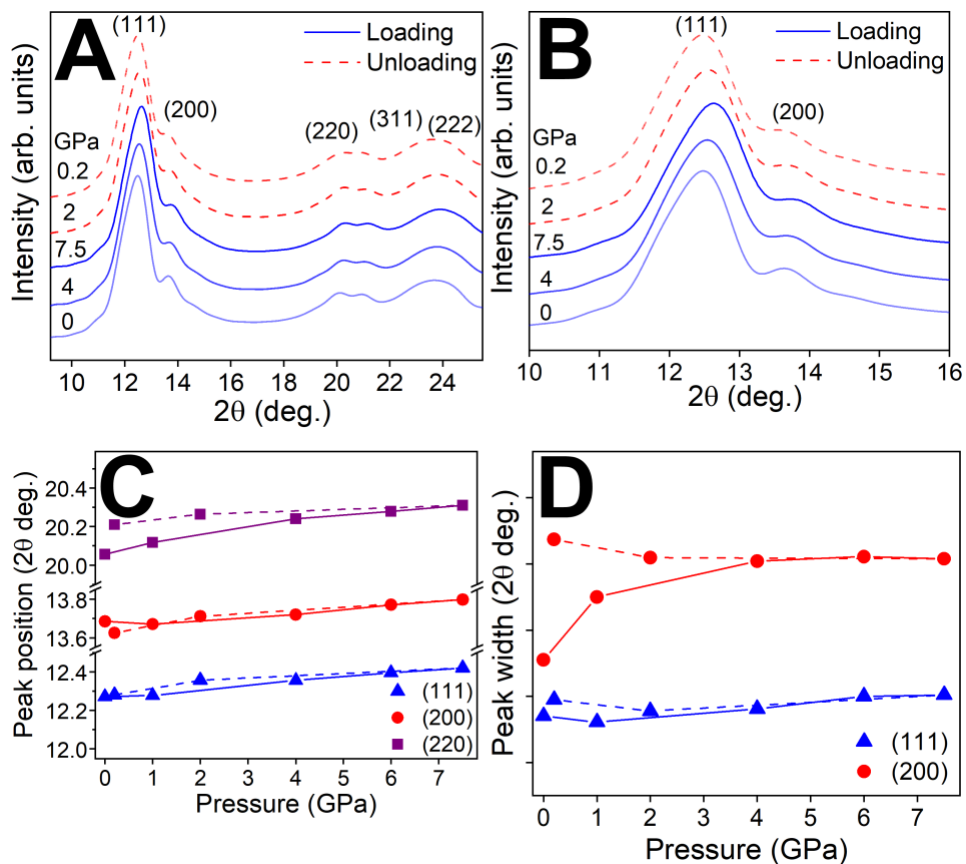
313 division is  $0.1^\circ$ ), upon loading (solid line) and unloading (dashed line).



314

315 **Fig. 3. MD simulation of a 3.9 nm icosahedral nanocrystal.** A) Schematic of nanocrystal  
 316 geometry and slip planes for stacking fault type 1 and type 2. B) Atomic configurations during  
 317 loading and unloading process. Top row shows the surface atoms and the loading direction (red  
 318 arrows). In the next two rows, outermost atoms are omitted to visualize the formation of defects.  
 319 Images in middle row have green atoms for FCC, white atoms for unclassified crystal structure  
 320 (typically near the core of a partial dislocation or at the surface), and red atoms for HCP. Images  
 321 in bottom row are colored according to non-affine squared displacement, in which the slip plane  
 322 swept by a perfect dislocation is identified.

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324

325 **Fig. 4. Simulated high-pressure XRD patterns from MD simulations.** A) All diffraction  
 326 peaks and B) magnified view of (111) and (200) peaks. Change in diffraction peak C) position  
 327 and D) width (each division is  $0.1^\circ$ ), upon loading (solid line) and unloading (dashed line).

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