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Size Dependence of Cubic to Trigonal Structural Distortion in Silver Micro- and Nanocrystals under High Pressure

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Silver micro- and nanocrystals with sizes of ~2–3.5 μm and ~50–100 nm were uniaxially compressed under nonhydrostatic pressures (strong deviatoric stress) up to ~30 GPa at room temperature in a symmetric diamond-anvil cell and studied *in situ* using angle-dispersive synchrotron X-ray diffraction. A cubic to trigonal structural distortion along a 3-fold rotational axis was discovered by careful and comprehensive analysis of the apparent lattice parameter and full width at half maximum, which are strongly dependent upon the Miller index and crystal size.

In the past fifteen years, much attention has been paid to the high pressure behavior of nanomaterials, especially the pressure-induced structural transformations in semiconductor nanocrystals.¹⁻¹⁰ In contrast, there are few reports on structural transformations and distortions in noble metals under high pressure due to their close-packed structures. It is generally accepted that sub-millimeter crystals of silver ($\sim 149\ \mu\text{m}$) and palladium ($\sim 250\ \mu\text{m}$) are stable in the face-centered cubic (fcc) structure at room temperature up to at least 91.8 GPa and 77.4 GPa, respectively.^{11, 12} Recently Alivisatos and coworkers reported that Ag nanoparticles ($\sim 5\text{--}10\ \text{nm}$) undergo a structural transformation under *hydrostatic* pressures up to $\sim 10\ \text{GPa}$.^{13, 14} Gu *et al.* studied $\sim 10\ \text{nm}$ commercially available Ag nanoparticles under *quasihydrostatic* pressures up to $\sim 30\ \text{GPa}$ and no phase transformations were observed.¹⁵ We observed a cubic to tetragonal phase transformation in $\sim 10\ \text{nm}$ Pd nanocubes under *nonhydrostatic* pressures (strong deviatoric stress) up to $\sim 25\ \text{GPa}$.¹⁶ These results motivated us to study the high pressure behavior of Ag and Pd crystals with submicro- and micro-scale dimensions, which fall between the classic sub-millimeter and nanometer size. Herein, we report a cubic to trigonal structural distortion in Ag crystals with sizes of $\sim 2\text{--}3.5\ \mu\text{m}$ and $\sim 50\text{--}100\ \text{nm}$, respectively, under *nonhydrostatic* pressures up to $\sim 30\ \text{GPa}$. This discovery provides new insights into the crystal structure of noble metals under high pressure.

Two samples of conventional, irregularly-structured Ag crystals were purchased from Aldrich and used in our comparative study. They have reported average sizes and purities of $2\text{--}3.5\ \mu\text{m}$ and 99.9+% and $<100\ \text{nm}$ and 99.5%, respectively and are referred to as micro- and nano-Ag powders from hereon. Figure 1 shows representative scanning and transmission electron micrographs (SEM and TEM, respectively) of the Ag samples. These samples were uniaxially compressed under *nonhydrostatic* pressures up to $\sim 30\ \text{GPa}$ in a symmetric diamond-anvil cell (DAC) and studied *in situ* using angle-dispersive synchrotron X-ray diffraction. Two ruby grains, located in the center and at the edge of the samples, respectively, were used for pressure calibration and radial pressure gradient estimation.¹⁷ Detailed experimental procedures are similar to our previous report.¹⁶

Figure 2 shows X-ray diffraction patterns, up to ~30 GPa, for the micro- and nano-Ag powders. From first analysis, it appeared that no phase transformations or distortions occurred because no splits, disappearances, or appearances of the diffraction peaks were observed. But when the d -spacing of the (200) peak was carefully compared with that of the (111) peak, it became apparent that some sort of distortion was induced at high pressures. For convenience, we introduce the concept of apparent lattice parameter (ALP), a_{hkl} .¹⁸ Here, $a_{hkl}(P)$ can be derived from an individual hkl Bragg reflection (e.g., $hkl = 111$ or 200) at a given pressure, P , in GPa by the equation $a_{hkl}(P) = d_{hkl}(P) * (h^2 + k^2 + l^2)^{1/2}$ for the cubic crystal system. It was found that $a_{hkl}(P)$ was strongly dependent upon the Miller index and crystal size.

The apparent lattice parameters a_{200} and a_{111} and their ratio a_{200}/a_{111} for the nano-Ag powder are shown in Figure 3a and Figure 3b, respectively. It is well-known that a_{hkl} of Ag with the idealized fcc structure is not dependent upon the Miller index; however, according to Figure 3, it becomes apparent that $a_{hkl}(P)$ in the nano-Ag is actually strongly dependent upon the Miller index when $P > 1.9$ GPa. In general, a_{200} was always larger than the corresponding a_{111} and the higher the pressure, the larger the relative difference (within the pressure range of 0 to 11.2 GPa). Specifically, the relative difference at ambient pressure was less than 0.03% but increased to 0.37% at a pressure of 11.2 GPa. Beyond 11.2 GPa, this difference decreased slightly and then became relatively constant at ~ 0.31% between 19.9 and 32.0 GPa, which is one order of magnitude larger than the 0.03% at ambient pressure.

Based on the results for the nano-Ag powder, we decided to do similar analyses for the micro-Ag powder. The a_{200}/a_{111} ratio as a function of pressure for the micro-Ag powder is shown in Figure 3b, which is compared to the results obtained from the nano-Ag powder. By comparing the two curves, we can conclude that the a_{200}/a_{111} ratio *under high pressure* is dependent upon the crystal size, with the ratio increasing with decreasing crystal size.

These results suggest that some kind of phase distortion is occurring in the micro- and nano-Ag samples under high pressure. It is well-known that fcc metals have three 4-fold rotational axes and

four 3-fold rotational axes. If slight structural deformation in an fcc metal occurs along a 4-fold rotational axis under applied pressure, a cubic to tetragonal phase distortion can be induced, as has been observed in ~10 nm Pd nanocubes at ~25 GPa.¹⁶ Similarly, if the deformation occurs along a 3-fold rotation axis, a cubic to trigonal distortion may be induced. Figure 4 shows simulated X-ray diffraction patterns for trigonal (a slightly distorted-fcc) Ag with different degrees of distortion, defined as D .¹⁹ For convenience, the a value was fixed as a_0 . When D is greater than or equal to 0.5%, splits in the diffraction peaks are observed. It should be noted that the observation of peak splits is also strongly dependent upon the full width at half maximum (FWHM) and crystal orientation, among other crystallographic parameters. By careful and comprehensive analysis of our current high pressure X-ray diffraction data, we proposed that despite no observable peak splits, a cubic to trigonal structural distortion along a 3-fold rotational axis accounts for the change of a_{200}/a_{111} . The lattice parameter of the Ag nano powder at 27.3 GPa can be indexed as $a = 2.753(1) \text{ \AA}$, $c = 6.710(2) \text{ \AA}$, and $c/a = 2.437(2) \approx \sqrt{6} \times (1 - 0.5\%)$. We selected this data point as a reference because it located in the asymptotic region of Figure 3a. It should be noted that we did not observe peak splitting/shoulder peak even when $D \approx 0.5\%$ (Figure 2b, $P = 27.3 \text{ GPa}$). This may be attributed to the peak merging associated with the peak broadening, which is usually caused by strong deviatoric stress in the sample under *nonhydrostatic* pressures.

The FWHM for both the (200) and (111) reflections (W_{200} and W_{111} , respectively) as a function of pressure for the nano-Ag powder and the ratio W_{200}/W_{111} for the nano-Ag and micro-Ag powder are shown in Figure 5a and Figure 5b, respectively. At ambient pressure, W_{200} and W_{111} are essentially the same. Yet, with increasing pressure, both W_{200} and W_{111} increase while their slopes differ, which is characterized by W_{200}/W_{111} . W_{200}/W_{111} is obviously larger at high pressure, indicating the high micro-stress anisotropy in the sample. This result suggests that more micro-stress accumulates along the [200] direction in slightly distorted-fcc Ag under high pressure, which is consistent with the lower compressibility along [200] ($a_{200}/a_{111} > 1$). From Figure 5b and 3b, one can see that the curve

characteristics of W_{200}/W_{111} as a function of pressure is very similar to that of a_{200}/a_{111} , which reflects the relationship between micro-stress anisotropy and compressibility anisotropy. In turn, the micro-stress and compressibility anisotropies can account for the phase distortion according to the analysis of the FWHM and ALP.

It is obvious that the W_{200}/W_{111} ratio was always larger than that at ambient pressure for the two samples. By comparing the curve from nano-Ag sample with that from micro-Ag powder, we may also conclude that the W_{200}/W_{111} ratio *under high pressure* is dependent upon the particle size and that the smaller the size, the larger the ratio. This relationship between W_{200}/W_{111} and particle size is very similar to that between a_{200}/a_{111} ratio and particle size, which indicates that our experiments are self-consistent. *Under high pressure*, the W_{200}/W_{111} ratios in the micro-Ag sample and nano-Ag samples are ~ 1.15 and ~ 1.40 , respectively; thus, the degree of micro-stress anisotropy in the micro sample may be lower than that in the nano samples, which makes it more challenge to realize the phase distortion in the micro sample. It should be pointed out that the W_{200}/W_{111} ratio at ambient conditions is dependent upon the samples. For the micro-Ag and nano-Ag samples discussed here, W_{200}/W_{111} at ambient pressure was 1.02 and 1.04, respectively. We believe the difference is associated with crystal size and micro-stress, among other crystallographic parameters. However, for the two samples, W_{200}/W_{111} *under high pressure* is larger than one, indicating a higher micro-stress along [200], which is consistent with a lower compressibility along [200] ($a_{200}/a_{111} > 1$).

Based on our preliminary X-ray diffraction experiments on noble metal micro- and nanocrystals under high pressure in DAC, we conclude that phase distortions under *nonhydrostatic* pressure are mainly dominated by micro-stress anisotropy in nanocrystals and by relaxation of periodic lattice in microcrystals, respectively. In other words, microcrystals of noble metals have periodic lattice and micro-stress anisotropy can be greatly reduced by lattice relaxation, making it a great challenge to realize their phase distortions. However, nanocrystals, have few unit cells and micro-stress anisotropy cannot be reduced effectively, which makes it possible to observe their phase distortions. We believe

that there should be plenty of opportunities in the high-pressure research field of metal nanocrystals. More experimental and theoretical studies are needed to discover and understand a number of new nonclassical phenomena in this system, which are not dominated by lattice relaxation.

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Figures and Captions

Figure 1. Representative electron micrographs of the Ag samples studied: (a) a SEM image of the micro-Ag powder, and (b) a TEM image of the nano-Ag powder.

Figure 2. X-ray diffraction patterns as a function of pressure (up to ~30 GPa) for (a) micro-Ag powder, and (b) nano-Ag powder.

Figure 3. (a) Apparent lattice parameters a_{200} and a_{111} for nano-Ag powder as a function of pressure up to ~30 GPa. (b) The a_{200}/a_{111} ratio for the micro-Ag powder and nano-Ag powder, as a function of pressure up to ~30 GPa.

Figure 4. Simulated X-ray diffraction patterns for trigonal (a slightly distorted-fcc) silver with different degrees of distortion, D , and $a_0 = 2.8894 \text{ Å}$, $c_0 = 7.0775 \text{ Å}$, and $c_0/a_0 \approx \sqrt{6}$.

Figure 5. (a) Full width at half maximum W_{200} and W_{111} for nano-Ag powder as a function of pressure up to ~ 30 GPa. (b) The W_{200}/W_{111} ratio for the micro-Ag powder and nano-Ag powder, as a function of pressure up to ~ 30 GPa.

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