Lattice relaxation in icosahedra of binary alloys: Segregation vs. intrinsic effects

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The physical properties of nanoparticles differ largely from those of their bulk counterparts due to the enhanced surface-to-volume ratio at small sizes. Due to a variety of different particle morphologies, different types of surfaces are present. In this report we use aberration-corrected electron microscopy to study directly the lattice structure of multiply twinned FePt, CuAu and Au nanoparticles. These icosahedral particles are comprised of twenty twinned tetrahedra resulting in only (111) surfaces. Using state-of-the-art aberration-corrected microscopy delocalization-free imaging allows for a direct measurement of atom positions and lattice constants even at the surface layers. It is found that for a wide range of particle sizes binary nanoparticles show an expansion of the lattice in the surface layers [1-3]. In FePt nanoparticles with $L1_0$ structure the segregation of Pt atoms toward the particle surface was shown theoretically using Monte Carlo simulations [4]. Here, due to the ordering, Pt segregation was mainly observed for non-stoichiometric nanoparticles with an excess of platinum. Interestingly the Pt excess tends to segregate toward the (001) rather than on the (111) facets, although surface energies would imply the opposite scenario [5].

FePt, CuAu and Au nanoparticles were prepared by inert gas condensation in order to obtain ligand-free particles [6]. The particles are deposited on carbon-coated copper grids, and their atomic structure is investigated by means of aberration-corrected HRTEM using a FEI Titan^3 80-300 microscope equipped with an image C_S corrector. In Fig 1a.an icosahedral CuAu nanoparticle is shown along the 2-fold symmetry axis. In this orientation, it is possible to measure the (111) lattice spacing in four tedrahedral sub-units. Fig 1b shows the measured lattice parameter for the four top-most inter-layer spacings as indicated by the yellow lines in Fig. 1a. Such measurements are carried out for a large number of particles and a statistical analysis was performed. The measurements show that FePt and CuAu icosahedral particles have an average lattice expansion of 10 % that even exceeds their bulk lattice constants. To analyze the effect of twinning-related strain onto this lattice relaxation, Au icosahedra are also examined. An exemplary HRTEM image of an Au icosahedron along its 2-fold symmetry axis is shown in Fig. 2 together with the measured lattice parameter for a single tetrahedron. Even for elementary Au icosahedra, on average a lattice expansion of 5% is found. It is ascribed to the intrinsic strain that is inherent to the multiple twinning in these particles. This finding is in accordance with the results of theoretical studies on the structural relaxation of icosahedral Argon clusters [7].

In order to gain insight in the origin of the observed lattice expansion at the surfaces of metallic nanoparticles, molecular dynamics (MD) simulations are performed. The resulting structures are then used as input structures for subsequent HRTEM contrast simulations and the calculated images are analyzed in the same way as the experimental ones. This comparison of the experimental images with the MD-relaxed structures clearly shows that mainly two effects contribute to the lattice expansion in twinned nanoparticles. On the one hand, an intrinsic effect of strain release in the particle leads to a lattice expansion towards the surface. On the other hand, segregation of Au in CuAu and of Pt in FePt nanoparticles towards the surface leads to an additional lattice expansion. Our studies thus reveal that both, surface segregation and intrinsic strain effects need to be taken into account in order to fully understand the large near-surface lattice expansion in multiply twinned nanoparticles of binary alloys.

References

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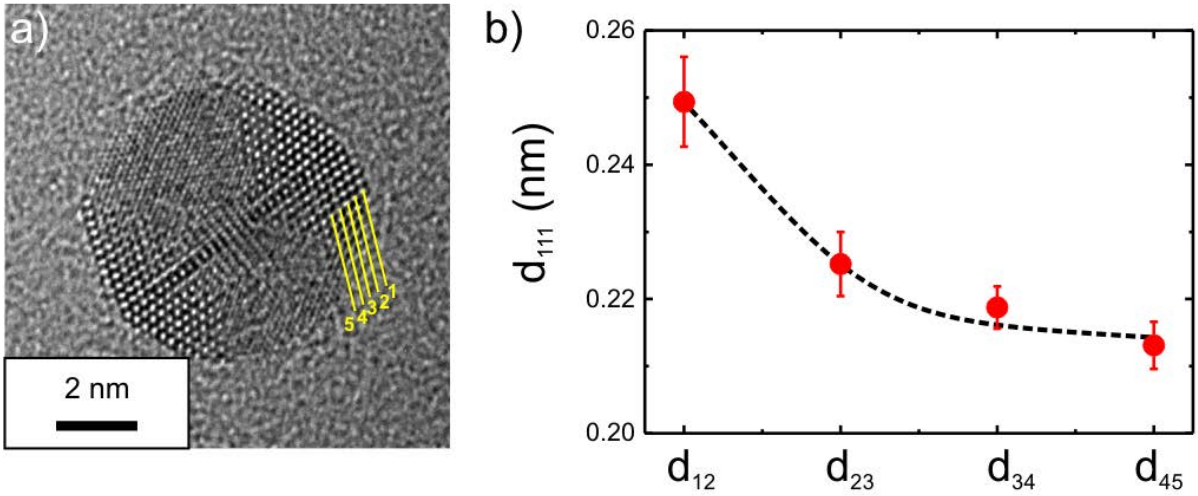

Figure 1. *Exemplary HRTEM image of an icosahedral CuAu nanoparticle (a) and the measured lattice dilation towards the surface (b).*

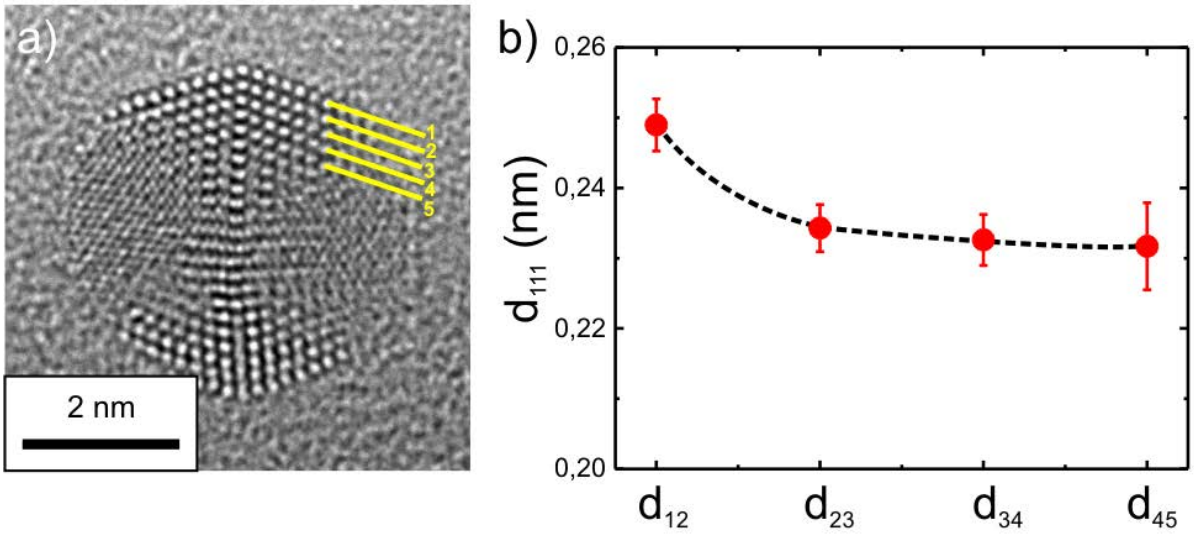

Figure 2. *Exemplary HRTEM image of an icosahedral Au nanoparticle (a) and the measured lattice relaxation towards the surface (b).*