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Supplementary Information for

AuCo nanoparticles: magnetisation, ordering, and morphology trends predicted by DFT

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This document contains supplementary information in the form of tables and figures for a complete insight into the performed calculations of the structural, energetic, and magnetic properties of core-shell, $L1_0$ ordered, and disordered gold-cobalt alloy nanoparticles.

Contents

Computational details

AuCo NP composition

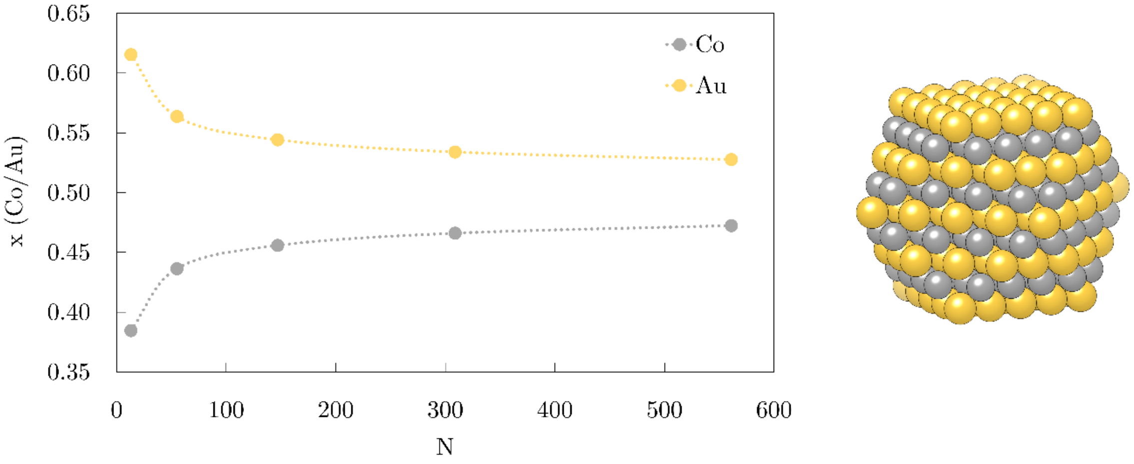

Figure S1 Concentrations of Co and Au in the investigated AuCo bimetallic NPs of different magic sizes according to the composition of the $L1_0$ ordered cuboctahedron as shown on the right.

AuCo NP energetics

For comparison of the energetics of nanoalloys of the same composition but different morphologies, the difference in their configurational energies, $E(\mathrm{A}_m\mathrm{B}_n)$, can give a good indication of the energetic favourability of certain ordering and/or geometry. Another indicator is the excess energy, $E_{\mathrm{exc}}(\mathrm{A}_m\mathrm{B}_n)$, representing an energy difference between the energy of a specific configuration of NP and the energy of the constituent atoms when separated at large distances, as introduced by Cleveland and Landman[64]:

$$E_{\mathrm{exc}}(\mathrm{A}_m\mathrm{B}_n) = E(\mathrm{A}_m\mathrm{B}_n) - (m\varepsilon_{\mathrm{b}}^{\mathrm{A}} + n\varepsilon_{\mathrm{b}}^{\mathrm{B}})$$

where $\varepsilon_{\mathrm{b}}^{\mathrm{A}}$ and $\varepsilon_{\mathrm{b}}^{\mathrm{B}}$ are the bulk cohesive energies of A and B metallic species. The excess energy, hence, represents the excess in the energy of the NP with respect to m/n A/B atoms in the bulk solid, similar to the definition of surface energies. It could consequently be expected that the excess energy scales with the number of surface atoms of the NP ($N^{2/3}$ for larger diameters), although, depending on the shape, there may be some volumetric contributions to the excess energy due to strain or nanoalloy mixing arrangements. However, this can be a fairly biased parameter since metals with large cohesive energies tend to contribute to the higher values of excess energies. Therefore, it is preferable to quantify the propensity of the two elements to mix (or segregate) within the given morphology through the mixing energy, $E_{\mathrm{mix}}(\mathrm{A}_m\mathrm{B}_n)$, which was introduced by Jellinek and Krissinel[65] as:

$$E_{\mathrm{mix}}(\mathrm{A}_m\mathrm{B}_n) = E(\mathrm{A}_m\mathrm{B}_n) - \left(m\frac{E(\mathrm{A}_N)}{m+n} + n\frac{E(\mathrm{B}_N)}{m+n}\right)$$

such that the appropriate fraction of the configurational energy of reference monometallic NPs with the same number of atoms is subtracted from the configurational energy of the bimetallic NP instead of the bulk cohesive energies. Such definition gives zero energies for pure monometallic NPs and diminishes any bias of the cohesive energies. More negative $E_{\mathrm{mix}}(\mathrm{A}_m\mathrm{B}_n)$ indicates a more favourable morphology. This parameter can also be used for comparison of the mixing stability within nanoalloys of different compositions. The global mixing coefficient, $M(\mathrm{A}_m\mathrm{B}_n)$, can be defined as the percentage of the mixing energy in the total configurational energy of the NP:

$$M(\mathrm{A}_m\mathrm{B}_n) = \frac{E_{\mathrm{mix}}(\mathrm{A}_m\mathrm{B}_n)}{E(\mathrm{A}_m\mathrm{B}_n)} \times 100\%.$$

The evaluation of excess or mixing energy requires only total configuration energies of monometallic and bimetallic systems which can be obtained within potential models, DFT, or other *ab initio* methods.

The average binding energy of bimetallic nanoparticles, E_b, is given by:

$$E_b = \frac{1}{m+n}\left[E(\mathrm{A}_m\mathrm{B}_n) - (mE(\mathrm{A}_1) + nE(\mathrm{B}_1))\right]$$

where $E(\mathrm{A}_1)$ and $E(\mathrm{B}_1)$ are the energies of single atoms of the two constituent species.

Electronic properties

Disordered AuCo NPs DOS

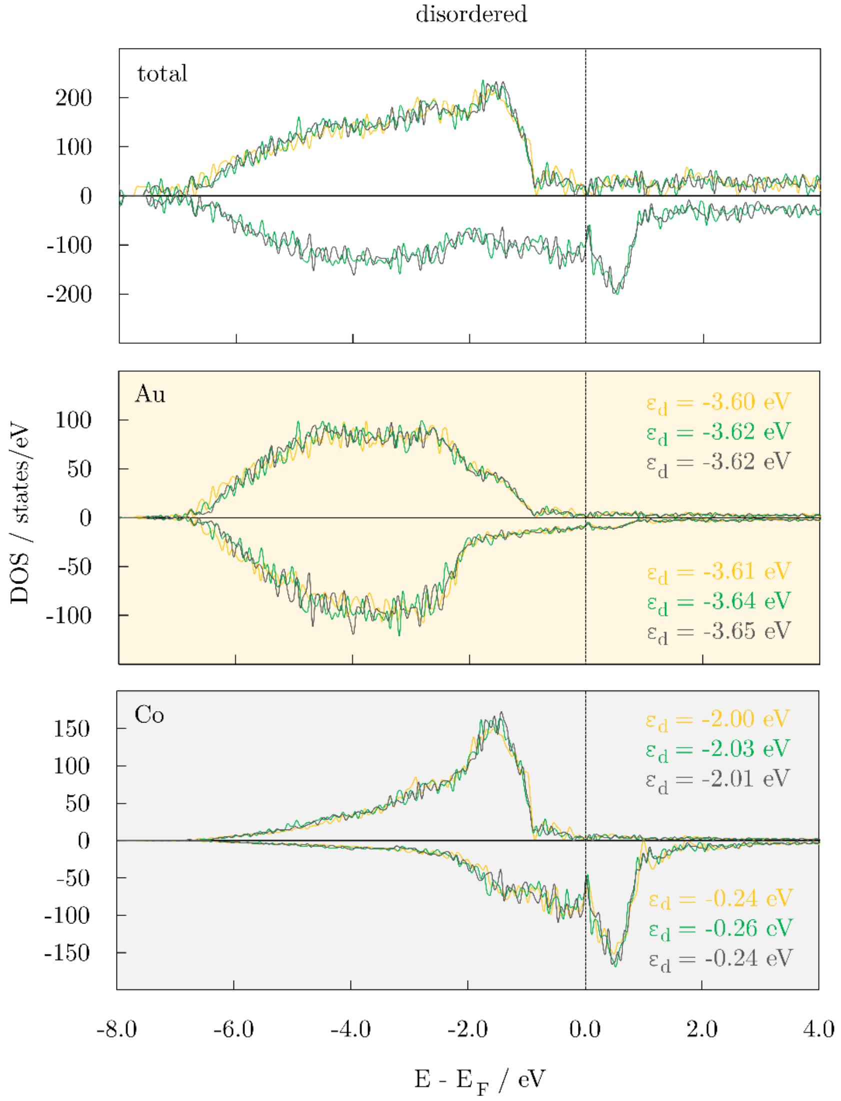

Figure S2 Total, 5d Au-projected, and 3d Co-projected densities of state, DOS, of 147-atom disordered cuboctahedron (grey), decahedron (green), and icosahedron (yellow) AuCo NPs. Both majority- and minority-spin states are shown. d-band energy centres are given for Au 5d and Co 3d states in corresponding colours.

Atom-resolved Bader charge

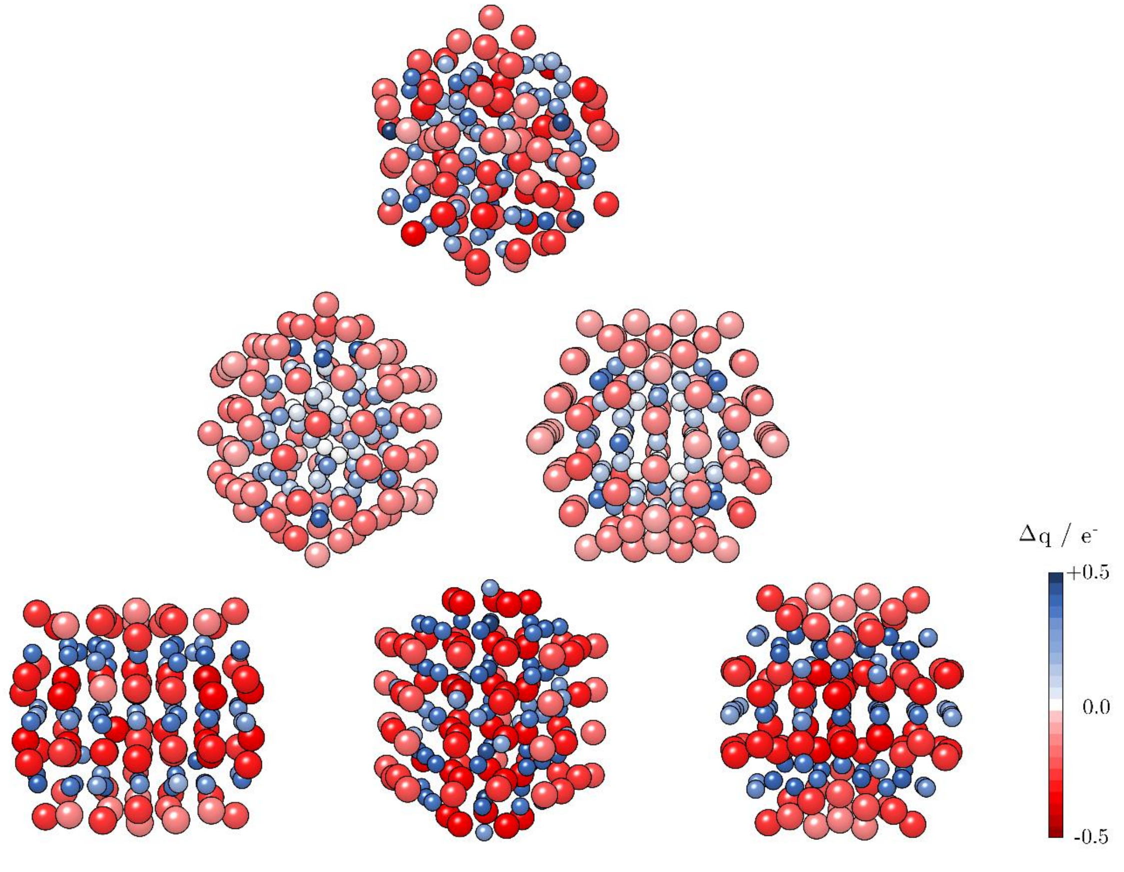

Figure S3 Atom-resolved Bader charge for 147-atom AuCo NPs: disordered decahedron (top panel), core-shell decahedron and icosahedron (middle panel) and $L1_0$ cuboctahedron, decahedron, and icosahedron (bottom panel). Blue and red shades indicate electron accumulation and depletion, respectively; a scale is provided on the bottom right. Larger spheres represent Au atoms and smaller spheres represent Co atoms.

Magnetic properties

Staggered anitoferromagnetic structure – $L1_0$ AuCo cuboctahedron

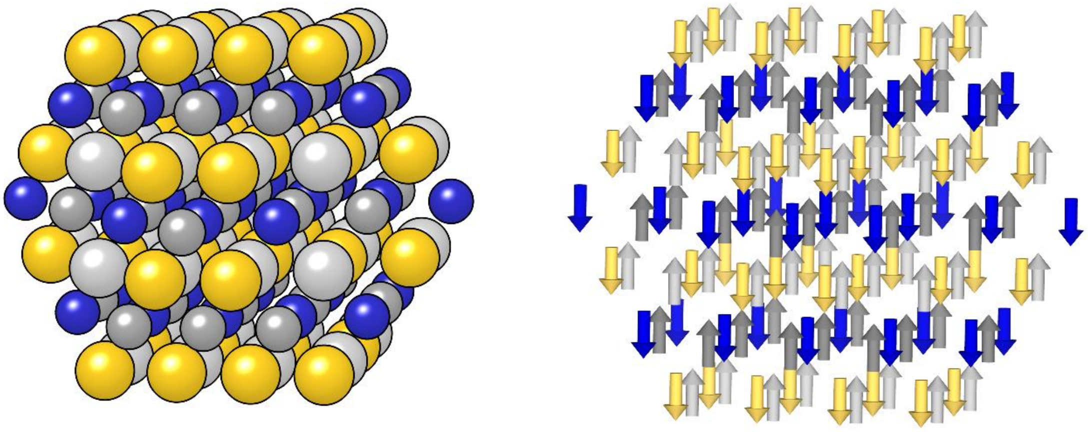

Figure S4 Schematic representation of the staggered antiferromagnetic structure of the 147-atom $L1_0$ ordered AuCo cuboctahedron. Larger spheres (in yellow and light grey) represent Au atoms and smaller spheres (in blue and dark grey) represent Co atoms.

Atom-resolved orbital anisotropy – monometallic Co NPs

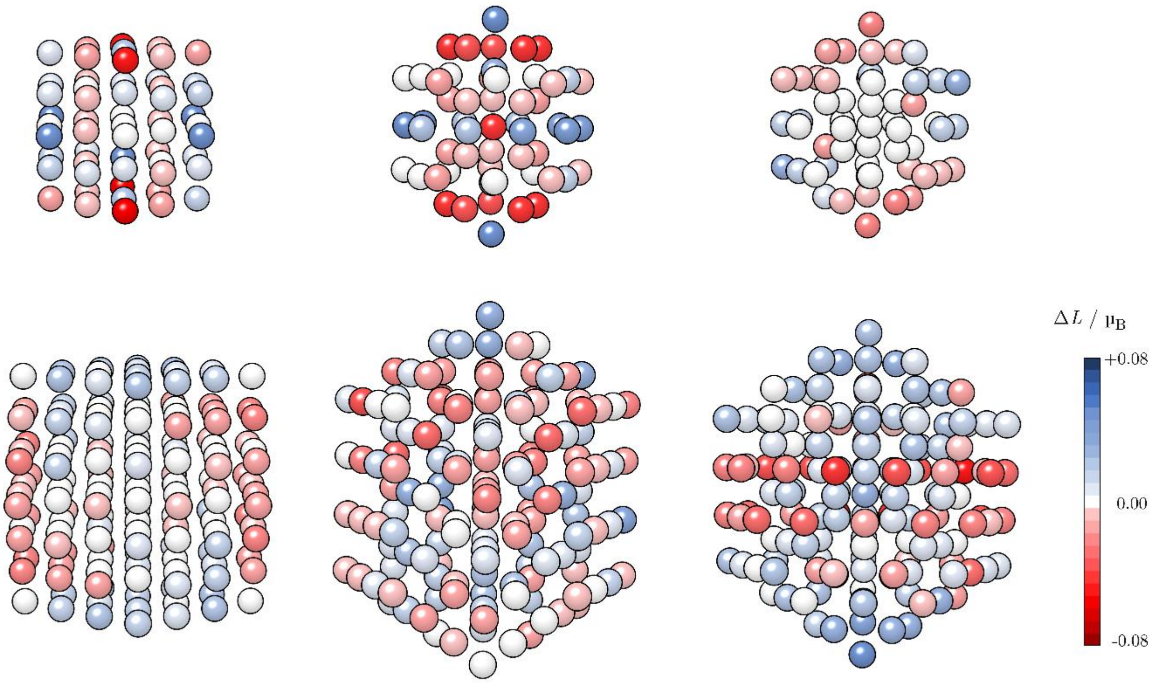

Figure S5 Atom-resolved local anisotropies for 55- and 147-atom monometallic Co NPs: cuboctahedron (left), Ino decahedron (middle), and icosahedron (right). Blue and red shades indicate positive and negative differences in the easy and hard magnetisation direction of orbital moments, respectively; a scale is provided on the bottom right.