

**Supplementary material for**  
**Morphology and symmetry driven by lattice accommodation in**  
**polycrystalline bcc-fcc core-shell metallic nanoparticles**

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- I. Lattice accommodation and residual misfits at the bcc-fcc interfaces**
- II. Patterns of all possible bcc(core)@fcc(shell) NP morphologies with an 18 faces core (truncated rhombic dodecahedron)**
- III. Examples of dissymmetric NPs with a cube-shaped core and with a truncated cube-shaped core**

**I. Lattice accommodation and residual misfits at the bcc-fcc interfaces**

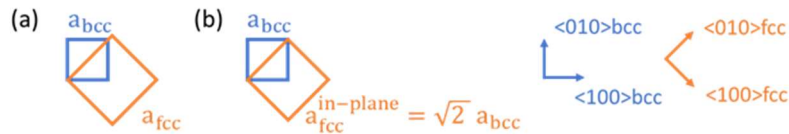
Here the bcc metal is considered as a 2D substrate for the epitaxial growth of the fcc metal. The lattice parameters are respectively  $a_{\text{bcc}}$  and  $a_{\text{fcc}}$ .

**a) At the {001}bcc/{001}fcc interface (Bain epitaxial relationship)**

Fig. S1(a) shows the superimposition of the two basal {001} cells for the relaxed crystals. The misfit is:

$$f = \frac{a_{\text{fcc}} - \sqrt{2} a_{\text{bcc}}}{\sqrt{2} a_{\text{bcc}}}$$

In coherent epitaxy (Fig. S2(b)), the fcc crystal adopts the in-plane parameter  $a_{\text{fcc}}^{\text{in-plane}} = \sqrt{2} a_{\text{bcc}}$



**Fig. S1.** Superimposition of the two basal {001} cells. (a) Relaxed bcc and fcc crystals; (b) coherent epitaxy.

This results in a compressive bi-axial stress of the fcc crystal. The in-plane and out-of-plane components of the elastic strain are, respectively,

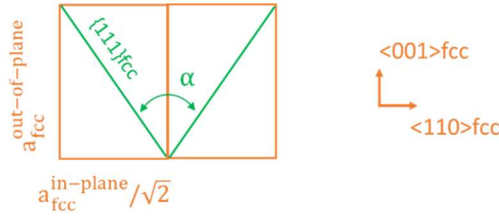
$$\varepsilon_{fcc}^{\text{in-plane}} = \frac{\sqrt{2} a_{bcc} - a_{fcc}}{a_{fcc}} \quad \text{and} \quad \varepsilon_{fcc}^{\text{out-of-plane}} = -\frac{2C_{12}}{C_{11}} \varepsilon_{fcc}^{\text{in-plane}}$$

where  $C_{11}$  and  $C_{12}$  are the elastic constants of the fcc metal. The out-of-plane parameter  $a_{fcc}^{\text{out-of-plane}}$  is related to the strain by:

$$a_{fcc}^{\text{out-of-plane}} = (1 + \varepsilon_{fcc}^{\text{out-of-plane}}) a_{fcc}$$

The angle  $\alpha$  between two different  $\{111\}$  fcc planes can be calculated (Fig. S2) as:

$$\tan\left(\frac{\alpha}{2}\right) = \frac{a_{fcc}^{\text{in-plane}}}{\sqrt{2} a_{fcc}^{\text{out-of-plane}}}$$



**Fig. S2.** Two families of  $\{111\}$  fcc planes seen in projection along a  $\langle 110 \rangle_{fcc}$  direction.

$a_{bcc}$ (nm)	$a_{fcc}$ (nm)	f	$\varepsilon_{fcc}^{\text{in-plane}}$	$a_{fcc}^{\text{in-plane}}$ (nm)	$\varepsilon_{fcc}^{\text{out-of-plane}}$	$a_{fcc}^{\text{out-of-plane}}$ (nm)
0.28665	0.40784	0.61 %	-0.60 %	0.40538	1.02 %	0.4120

**Table S-I.** Numerical values for Au on Fe. (Au elastic constants at 300 K:  $C_{11}=192$  GPa and  $C_{12}=163$  GPa, from J.R. Neighbours and G.A. Alers, Phys. Rev. 111, 707 (1958). Lattice parameters from H. Okamoto, T. Massalski, L. Swartzendruber and P. Beck. 1984, Bulletin of Alloy Phase Diagrams 5, 592 (1984).)

It comes from Table S-I that  $\alpha = 69.66^\circ$  in the strained fcc crystal versus  $70.53^\circ$  in the relaxed one (or its complement  $110.36^\circ$  versus  $109.47^\circ$ ).

### b) At the $\{110\}_{bcc}/\{111\}_{fcc}$ interface (Nishiyama-Wassermann epitaxial relationship)

In the  $\langle 001 \rangle_{bcc} // \langle 110 \rangle_{fcc}$  direction: see section a). The fcc lattice is slightly stressed in compression in the  $\langle 110 \rangle_{fcc}$  direction (with -0.60% in-plane strain).

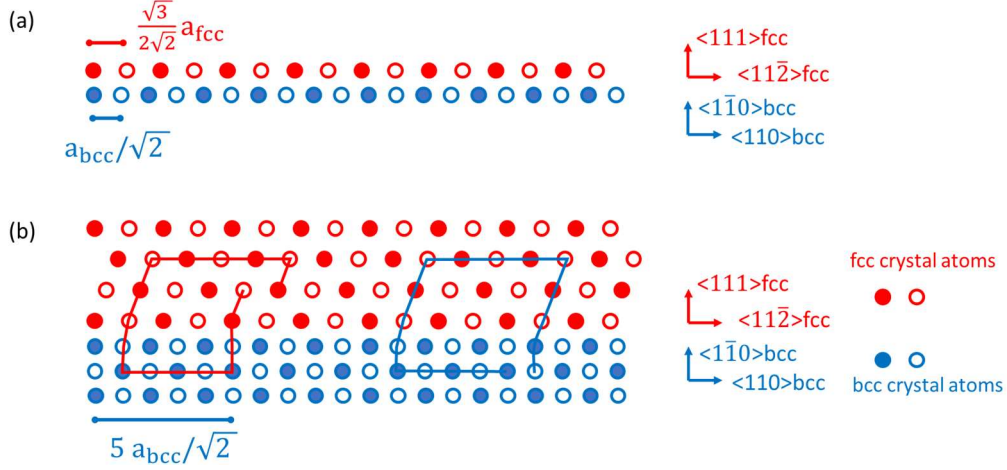
In the  $\langle 110 \rangle_{bcc} // \langle 11\bar{2} \rangle_{fcc}$  direction, the misfit f is 23% and is accommodated by a coincidence network of 4 fcc atoms for 5 bcc atoms (Fig. S3). There is a residual misfit  $f_{\text{residual}}$  (Table S-II). The fcc lattice is slightly stressed in tension in the  $\langle 11\bar{2} \rangle_{fcc}$  direction (with 1.42% in-plane strain) (Table S-II).

The coincidence network corresponds to a dislocation every 4 fcc and 5 bcc atomic columns. The dislocation line is along the  $\langle 001 \rangle_{bcc} // \langle 110 \rangle_{fcc}$  direction. The Burgers vector is (Fig. S3(b)):

$\vec{b} = a_{\text{fcc}}/2 \langle 01\bar{1} \rangle$  in the fcc lattice. The 23% misfit accommodation is insured by the edge component  $a_{\text{fcc}}/4 \langle 11\bar{2} \rangle$ . The screw component is  $a_{\text{fcc}}/4 \langle \bar{1}10 \rangle$ .

$\vec{b} = a_{\text{bcc}}/2 \langle 111 \rangle$  in the bcc lattice (edge component  $a_{\text{bcc}}/2 \langle 110 \rangle$  and screw component  $a_{\text{bcc}}/2 \langle 001 \rangle$ .)

Two successive dislocations have opposite screw components that annihilate each other, so that the dislocation network has overall an edge character.



**Fig. S3.** (a) Projection along  $\langle \bar{1}10 \rangle_{\text{fcc}}$  and  $\langle 001 \rangle_{\text{bcc}}$  directions of relaxed lattices with a 23% misfit along the  $\langle 110 \rangle_{\text{bcc}} // \langle 11\bar{2} \rangle_{\text{fcc}}$  directions. (b) Thanks to a slight tensile stress of the fcc lattice in the  $\langle 11\bar{2} \rangle_{\text{fcc}}$  direction, the coincidence network accommodates the misfit by a dislocation every 4 fcc and 5 bcc atomic planes. The atoms represented by full or empty symbols are not in the same  $\{\bar{1}10\}_{\text{fcc}}$  or  $\{001\}_{\text{bcc}}$  plane.

$a_{\text{bcc}} \sqrt{2}/2$ (nm)	$a_{\text{fcc}} \sqrt{6}/4$ (nm)	f	$5(a_{\text{bcc}} \sqrt{2}/2)$ (nm)	$4(a_{\text{fcc}} \sqrt{6}/4)$ (nm)	$f_{\text{residual}}$
0.20269	0.24975	23%	1.01346	0.9990	-1.42%

**Table S-II.** Numerical values for Au on Fe.

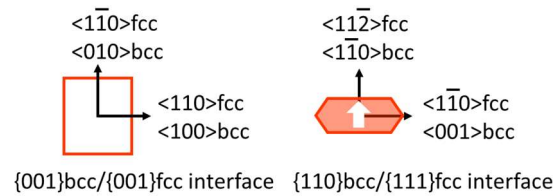
## II. Patterns of all possible bcc(core)@fcc(shell) NP morphologies with an 18 faces core (truncated rhombic dodecahedron)

Figure S4 displays the patterns of the different possible morphologies of the nanoparticles (NPs) with a truncated rhombic dodecahedron core, and their symmetry group (exhaustive except for groups  $m$  and  $l$ ). Some patterns can be grouped as follow:

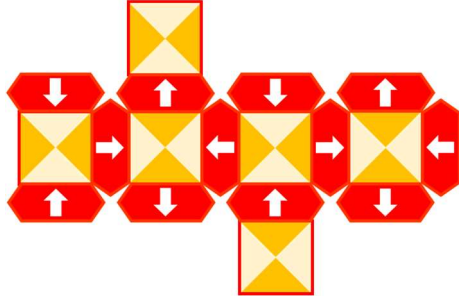
- Chirality: The patterns in the groups 3, 4, 2, and  $l$  are chiral. Enantiomorph patterns are labelled in Fig. S4 with the same letter and a different number (for instance a1, a2). (Two enantiomorph patterns differ only by the sense of rotation of the arrow sequence around the fold axis.)
- The two patterns of each pair (b1, c1), (b1, c2), (b2, c1) and (b2, c2) of group 3 are identical “by half”, and chiral “by half”.

- (c) If two different patterns a and b derive from each other by complete inversion of the arrows, they are noted  $b=\text{inv}[a]$ . This occurs in groups 3 ( $a_1/a_2$ ),  $4/m$  ( $a/b$ ),  $mm2$  ( $a/b$ ;  $c/d$ ), 2 ( $a_1/b_1$ ;  $a_2/b_2$ ),  $m$  (one example  $a/b$ ) and  $I$  (two examples  $a_1/b_1$ ,  $a_2/b_2$ ). In all other cases, the pattern is similar to its own inverse ( $a=\text{inv}[a]$ ).

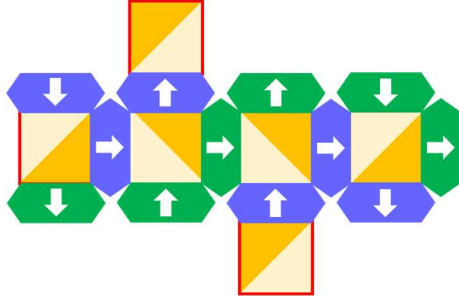
**Fig. S4.** Patterns of all possible  $\text{bcc}(\text{core})@\text{fcc}(\text{shell})$  NP morphologies with a 18 faces core (rhombic dodecahedron core truncated by  $\{001\}$  bcc faces), exhaustive except for groups  $m$  and  $I$ . The arrows symbolize the fcc variant distribution on the  $\{110\}$  bcc faces, that determines the NP symmetry. The same color for the hexagonal basis of  $\langle 111 \rangle$  fcc oriented grains means that they are in symmetrical position between them. The light or dark yellow shades symbolize the morphology of the  $\langle 001 \rangle$  fcc oriented grains (the nearest boundary is a  $\{111\}$  fcc twin or  $\{111\}$  fcc low angle grain boundary, respectively). The Hermann-Mauguin notation of the NP symmetry groups refers to the crystallographic directions of the bcc core (Schoenflies notation in parenthesis).



$m\bar{3} (T_h)$



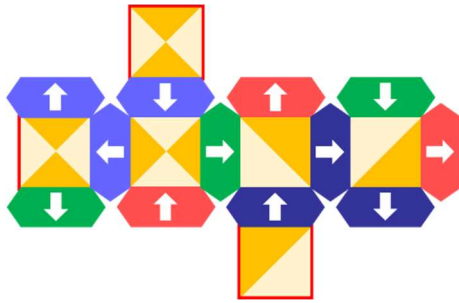
$\bar{3} (S_6)$



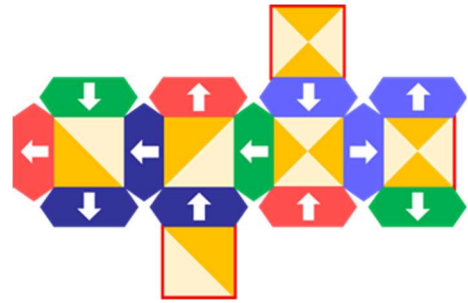
$3 (C_3)$

a1=inv[a2]

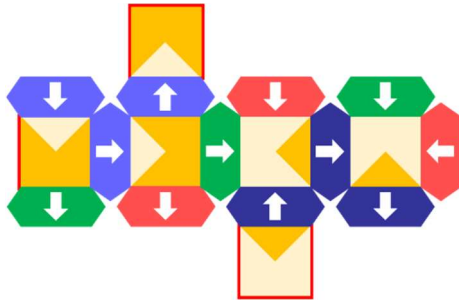
a2=inv[a1]



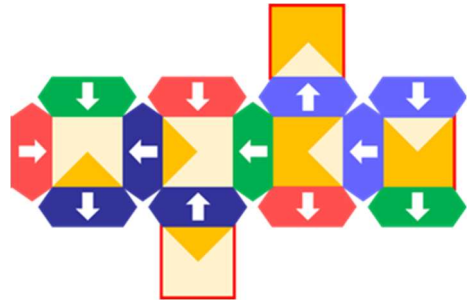
b1



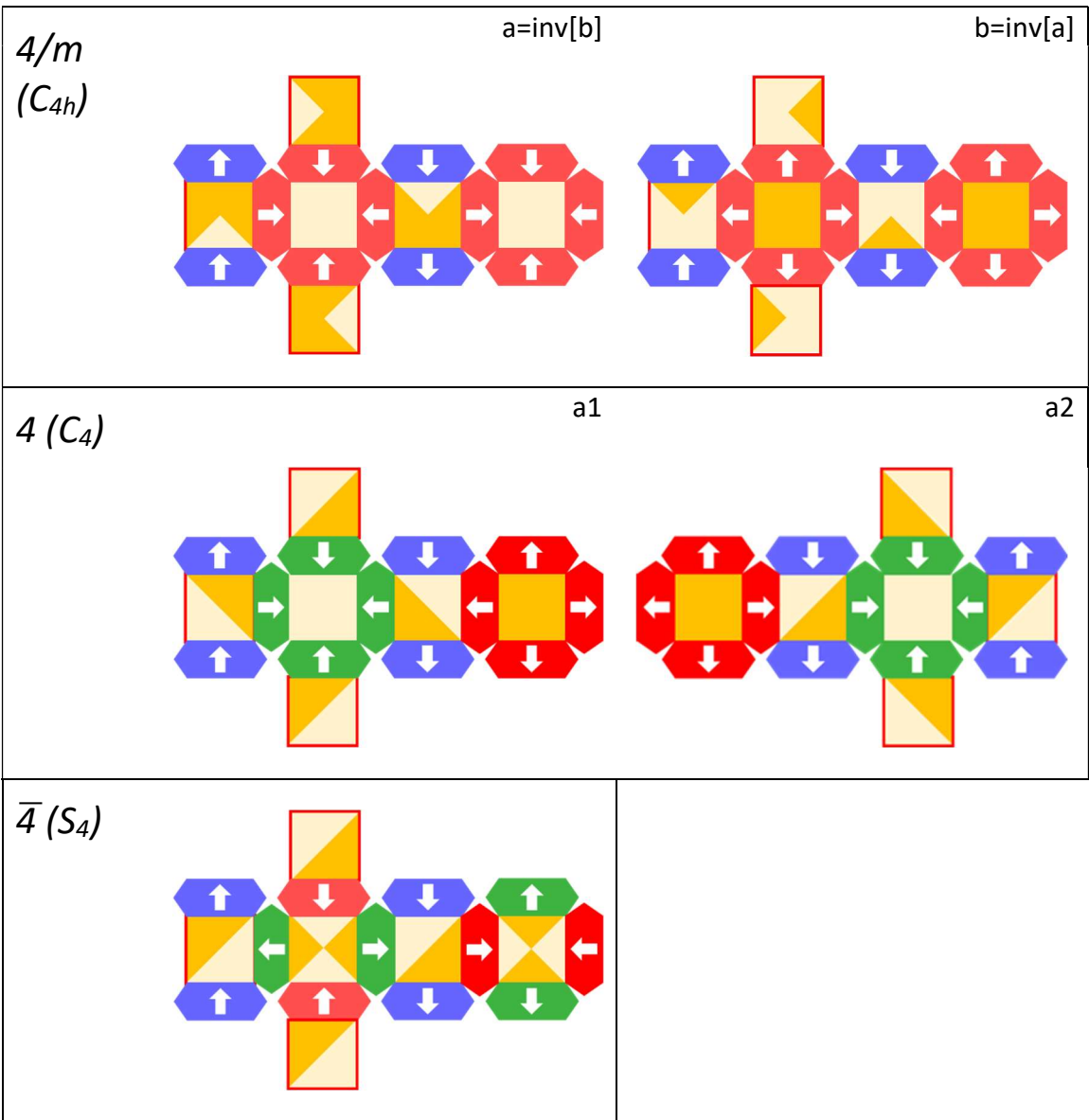
b2



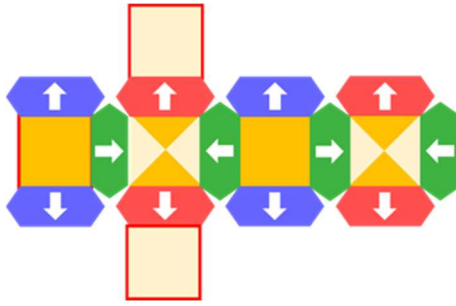
c1



c2



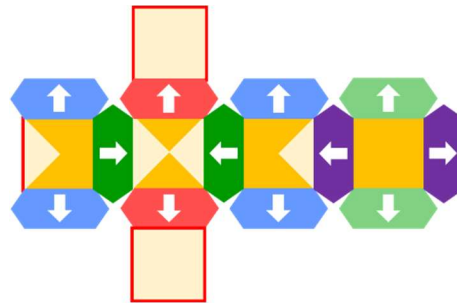
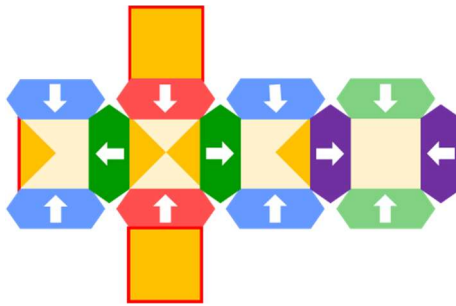
*mmm*  
( $D_{2h}$ )



*mm2*  
( $C_{2v}$ )

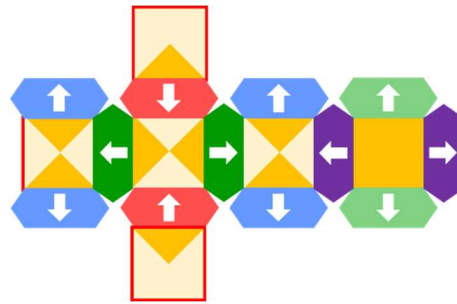
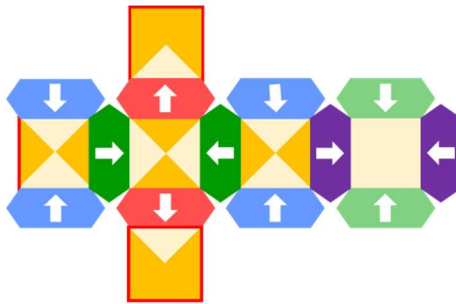
a=inv[b]

b=inv[a]



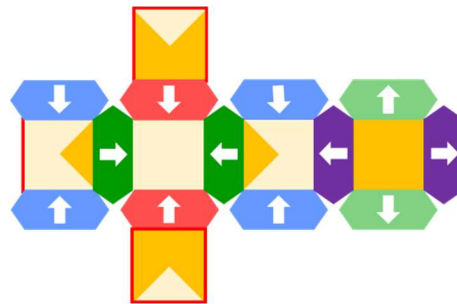
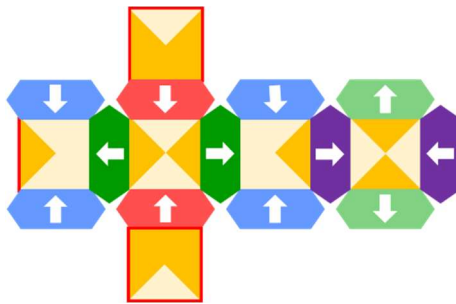
c=inv[d]

d=inv[c]

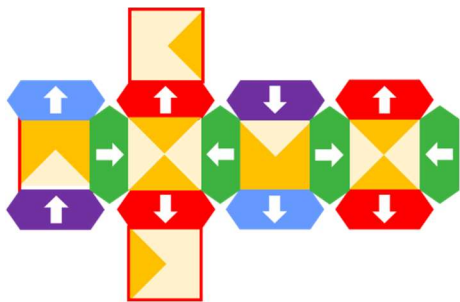


e

f



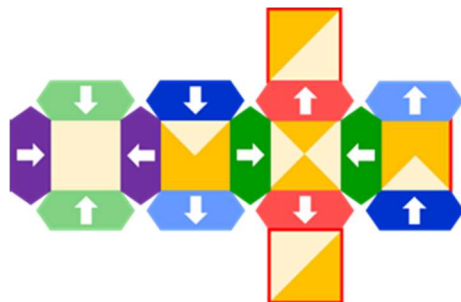
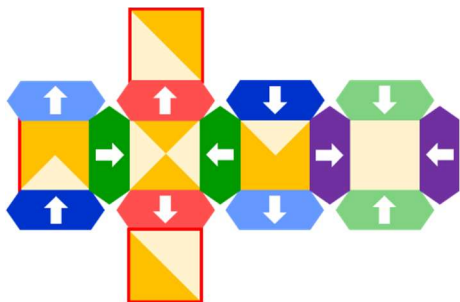
$2/m$   
( $C_{2h}$ )



$2 (C_2)$

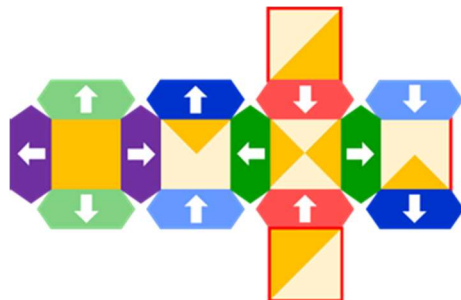
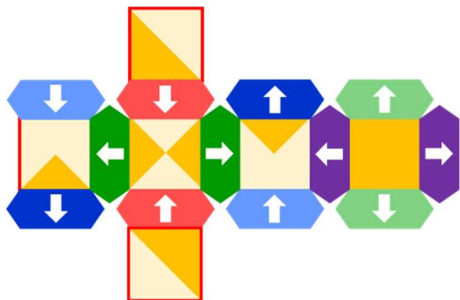
$a_1 = \text{inv}[b_1]$

$a_2 = \text{inv}[b_2]$



$b_1 = \text{inv}[a_1]$

$b_2 = \text{inv}[a_2]$

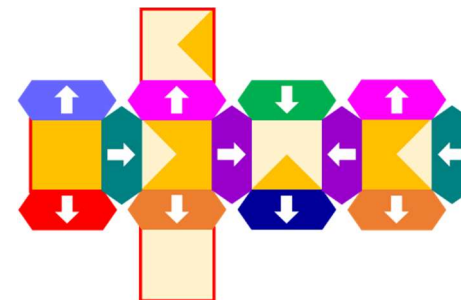
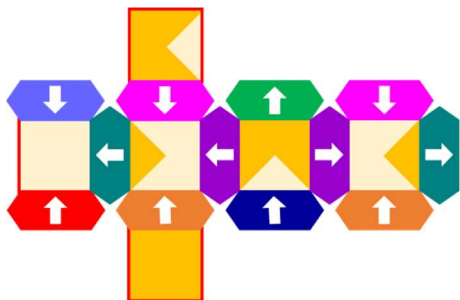


$m (C_s)$

$a = \text{inv}[b]$

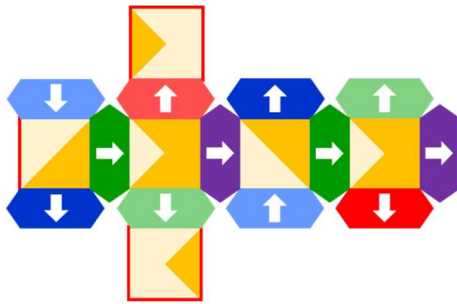
$b = \text{inv}[a]$

non-  
exhaustive





$\bar{1}(C_i)$

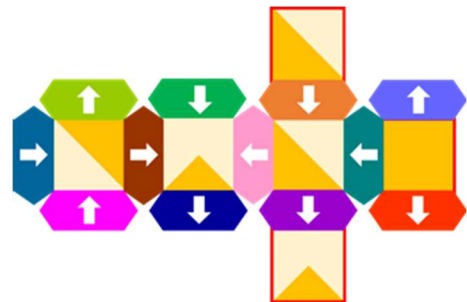
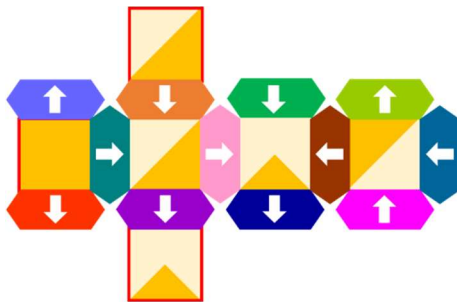


$1(C_1)$

non-exhaustive

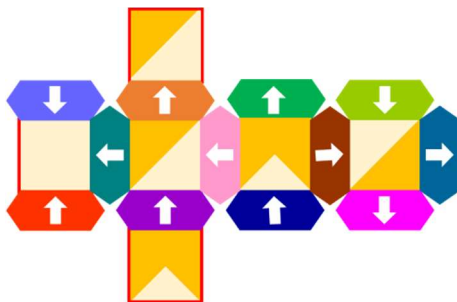
$a_1 = \text{inv}[b_1]$

$a_2 = \text{inv}[b_2]$



$b_1 = \text{inv}[a_1]$

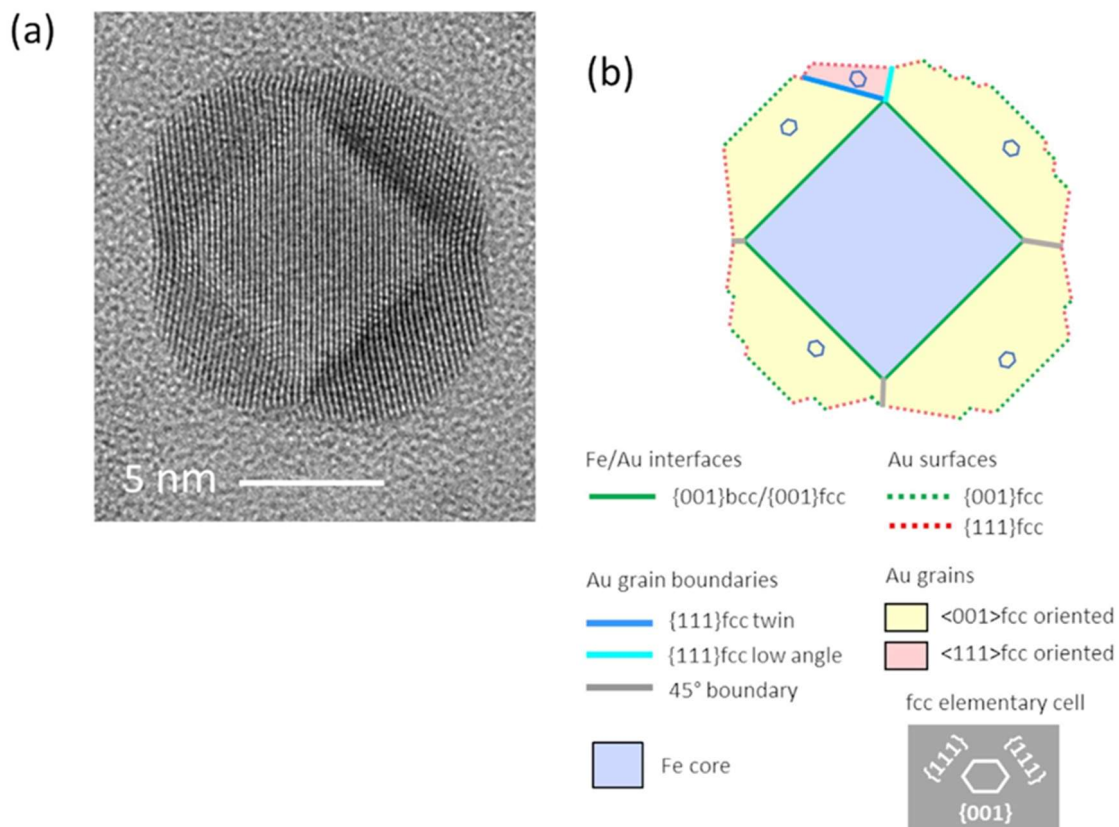
$b_2 = \text{inv}[a_2]$



### III. Examples of dissymmetric NPs with a cube-shaped core and with a truncated cube-shaped core

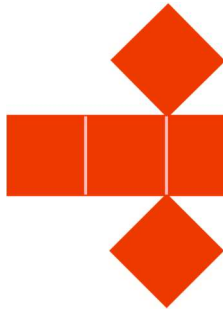
#### a) Experimental case of non-cubic shells with cube-shaped cores

Experimentally, we sometimes observe Fe@Au NPs with square core section, that fail to fully restore a cubic symmetry (Fig. S5). The case of a single truncation of the core also illustrates the 3D morphology and symmetry of such NPs, by considering that the truncation, basis of the  $\langle 111 \rangle$ fcc oriented grain, is reduced to a cube edge (Fig. S6 adapted from the Fig. 13(d-e)). The shell morphology can then be understood as having kept the memory of a  $\langle 111 \rangle$ fcc oriented grain formerly grown on a  $\{110\}$ bcc face now disappeared.

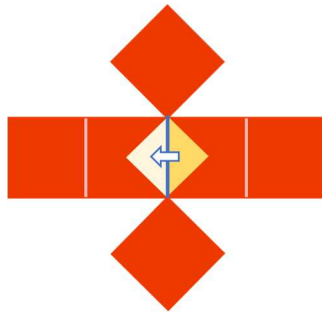


**Fig. S5.** (a) High resolution TEM micrograph of a Fe@Au NP observed close to a  $\langle 001 \rangle$ bcc zone axis. (The NP core is not perfectly oriented along the  $\langle 001 \rangle$ bcc zone axis, so that one family of  $\{110\}$ bcc planes is much better observed than the other.) (b) Crystallographic analysis of the NP. The NP displays a square core section and a non-fully cubic symmetry for the shell. The  $\langle 001 \rangle$ fcc oriented pyramids are separated quasi-symmetrically by the so called  $45^\circ$  boundaries, except at top, where a twin is clearly visible.

(a) Core pattern  
(Group  $m\bar{3}m$ )



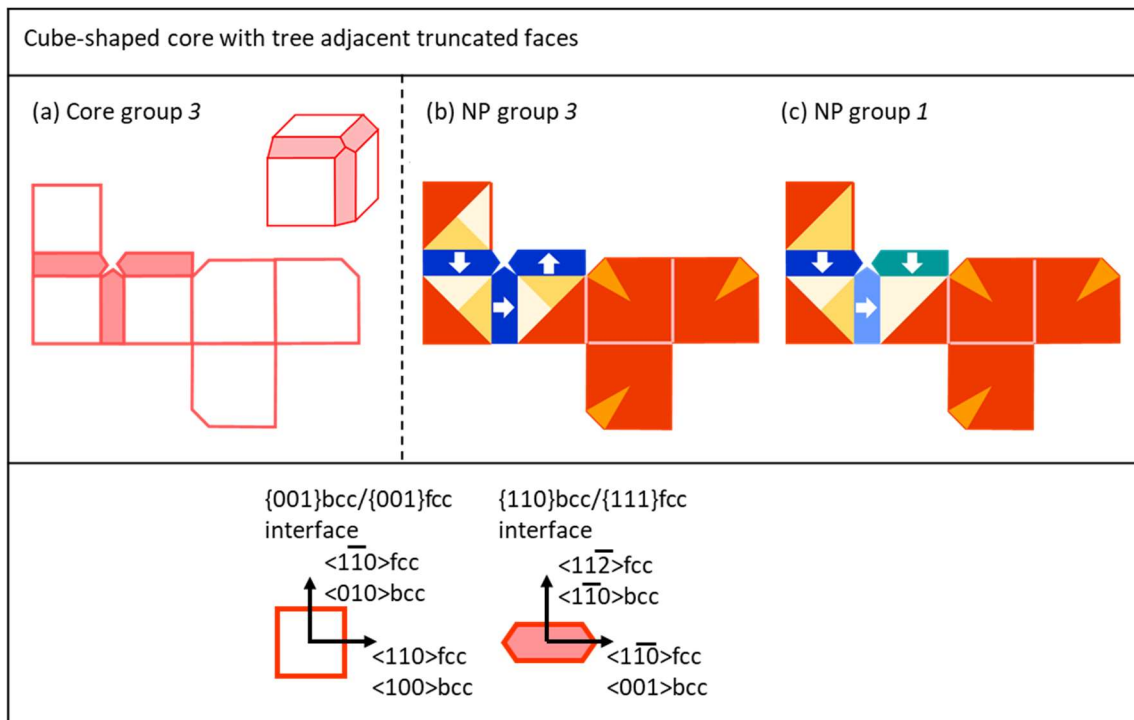
(b) NP pattern (Group  $m$ )



**Fig. S6.** Pattern of a cube-shaped core (a) and of a NP (b) developing a non-cubic shell (group  $m$ ). The arrow symbolizes the variant of a  $\langle 111 \rangle_{\text{fcc}}$  oriented grain whose base is reduced to a cube edge (blue line). Light and medium yellow shades indicate that the boundaries between the  $\langle 111 \rangle_{\text{fcc}}$  oriented grain and the  $\langle 001 \rangle_{\text{fcc}}$  oriented neighbors will be a twin and a LAGB boundary, respectively.

### b) Multiple truncations from a cube-shaped core

Fig. S7 displays an example of multiple truncations of same extension from a cube-shaped core. Three truncated faces joining at a cube corner lower the core symmetry to the group 3 (Fig. S7(a)). Either this symmetry subsists for the NP (Fig. S7(b)) or it is lowered to group 1 (Fig. S7(c)), depending on the variants growing on the three truncated faces. While there are 2 different kinds of  $\{001\}_{\text{bcc}}$  faces on the core (squares and pentagons) (Fig. S7(a)), the number of different morphologies of  $\langle 001 \rangle_{\text{fcc}}$  oriented grain is 2 and 4, in Fig. S7(b) and Fig. S7(c), respectively.



**Fig. S7.** Core and NP patterns with a cube-shaped core with three adjacent truncations. The core belongs to the group 3 (a), and the NP either to the group 3 (b) or 1 (c). The arrows symbolize the variants of  $\langle 111 \rangle_{\text{fcc}}$  oriented grains growing on  $\{110\}_{\text{bcc}}$  truncated faces. The same color for the basis of the  $\langle 111 \rangle_{\text{fcc}}$  oriented grains means that they are symmetrical to each other. Light, medium or dark yellow shades indicate that the nearest neighbor of a  $\langle 001 \rangle_{\text{fcc}}$  oriented grain will be a  $\langle 111 \rangle_{\text{fcc}}$  oriented grain separated by a twin, a LAGB boundary or the third type of boundary, respectively, and chestnut color indicates that the neighbor is another  $\langle 001 \rangle_{\text{fcc}}$  oriented grain.