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# Polyhedral Metal Nanoparticles with Cubic Lattice: Theory of Structural Properties

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## Abstract

We examine the structure of compact metal nanoparticles (NPs) forming polyhedral sections of the ideal cubic lattice, face centered (fcc), body centered (bcc), and simple (sc), cubic, which are confined by facets characterized by densest, second, and third densest {*hkl*} monolayers of the lattice. Together with the constraint that the NPs exhibit the same point symmetry as the ideal cubic lattice, i.e. $O_h$, different types of generic NPs serve for the definition of general compact polyhedral cubic NPs. Their structural properties, such as shape, size, and surface facets, are discussed in analytical detail with visualization of characteristic examples. This illustrates the complexity of seemingly simple nanoparticles in a quantitative account. The geometric relationships of the model particles can also be used to estimate shapes and sizes of real compact metal nanoparticles observed by experiment.

# I. Introduction

Nanoparticles of many sizes, shapes, and composition have become the target of a large number of recent experimental and theoretical studies. This is due to their exciting physical and chemical properties [1, 2] which deviate from those of corresponding bulk material. Here we mention only important applications in medicine [3] or in catalytic chemistry where metal nanoparticles have become ubiquitious [4, 5].

Physical and chemical properties of real metal nanoparticles (NP) observed by experiment are intimately connected with their size and shape since the individual NP atoms are exposed to different local environments. Atoms close to the particle surface experience fewer neighbors compared to those inside the particle bulk which influences their interatomic binding and, hence, their physical behavior. The variation of atom environments in finite particles depends strongly on the particle size since the relative number of surface atoms compared with those of the particle bulk becomes smaller with increasing size. This suggests that deviations from a crystalline bulk structure with its equivalent atom centers arranged in three-dimensional periodicity become less important as the particle size increases.

In many cases, structural properties of metal NPs with only a few atoms do not reflect those of corresponding bulk crystals and there are no general guidelines as to interatomic distances or angles or as to symmetry. This is illustrated by theoretical studies on silver NPs up to $Ag_{12}$ [6] where equilibrium structures are found to deviate substantially from those of local sections of the face-centered cubic crystal describing bulk silver. Further, very small NPs offer different stable isomers with varying shape and structure [6]. Larger compact metal NPs can also exhibit symmetry properties which are not compatible with those of bulk crystals. As examples, many alkaline earth and transition metal (Nickel, Cobalt) NPs in gas phase with up to 5000 atoms [7, 8] are believed to form compact particles with icosahedral symmetry $I_h$ including 5-fold rotational axes which cannot appear in perfect bulk crystals. Their structure can be described by the concept of polyhedral atom shell filling which yields preferred NP sizes connected with so-called magic numbers of atoms [8, 9].

Many larger metal NPs have been shown by experiment to exhibit internal cubic $O_h$ symmetry which can be associated with compact sections of cubic bulk crystal structures, both face- and body-centered cubic, or can be approximated accordingly [10]. Examples are Aluminum and Indium NPs between 1000 and 10000 atoms [7]. They are suggested to form compact polyhedral particles of internal face-centered cubic structure where confining facets are described by sections of densest (low Miller index) monolayers referring to different {*hkl*} families. Amongst these, cuboctahedral shapes enclosed by both triangular {111} and square {100} facets, have been discussed [7]. The corresponding NPs represent a reasonable approximation to spherical NPs since the atoms at the different facet surfaces do not vary too much in their distance from the NP center. Also other high-symmetry structures representing compact sections of face-centered cubic bulk crystals have been proposed as possible structures of compact metal NPs in the literature where we mention only octahedral NPs [7, 8]. Finally, metal NPs of $O_h$ symmetry described by sections of body-centered cubic bulk crystals have been reported [7, 11]. Here theoretical structure studies can help to describe and classify ideal compact cubic nanoparticles which allows to identify structural properties of real metal nanoparticles observed in experiment.

In this work, extending a previous theoretical analysis [12], we examine theoretical nanoparticles forming polyhedral sections of the ideal cubic lattice, face centered (fcc) and body centered (bcc) cubic which can be considered models of real metal particles. In addition simple (sc), cubic nanoparticles are included for completeness. These particles are assumed to be confined by facets describing finite sections of densest, second, and third densest monolayers described by Miller indexed {*hkl*} families, {100}, {110}, and {111}. Together with the constraint that the NPs exhibit the same point symmetry as the ideal cubic lattice, i.e. $O_h$, there are different types of generic NPs which serve for the definition of general polyhedral NPs as examples of finite crystallographic objects. Their structural properties , such as shape, size, and surface facets, are discussed in detail with visualization of characteristic examples. This illustrates the complexity the seemingly simple model nanoparticles in a quantitative account. The different examples can also be used as a repository for structures of compact NPs with internal cubic lattice.

All analytical results of this work have been obtained by extended calculus based on number theory and verified by mathematical proofs of induction, not discussed in detail, as well as by extended visualization using the Balsac software developed by the author [13]. The paper is grouped in three sections dealing with the three types of cubic lattices separately where the sections are structured identically and presented in parts with very similar phrasing to enable easy comparison. Further structural details can also be found in the Supplement.

# II. Formalism and Discussion

In the following we discuss structural properties of highly symmetric nanoparticles with atom arrangements reflecting local sections of the simple (sc), body centered (bcc), and face centered (fcc) cubic bulk. Thus, atom positions inside the nanoparticle are given by

$$\underline{R} = n_1 \underline{R}_1 + n_2 \underline{R}_2 + n_3 \underline{R}_3 + \underline{o} \qquad \text{(A.1)}$$

where $\underline{R}_1$, $\underline{R}_2$, $\underline{R}_3$ are lattice vectors of the corresponding crystal lattice and $n_1$, $n_2$, $n_3$ are integer multiples describing the bulk periodicity. Further, vector $\underline{o}$ denotes the lattice origin describing a high symmetric site ($O_h$ symmetry) of the cubic lattice where $\underline{o}$ is assumed to form the origin of a Cartesian coordinate system, i.e. $\underline{o} = (0, 0, 0)$. In the following, we treat discuss nanoparticles reflecting the three different cubic lattice structures separately.

## A. Face Centered Cubic (fcc) Nanoparticles

The face centered cubic (fcc) lattice can be defined as a non-primitive simple cubic lattice by lattice vectors $\underline{R}_1$, $\underline{R}_2$, $\underline{R}_3$ in Cartesian coordinates together with four lattice basis vectors $\underline{r}_1$ to $\underline{r}_4$ according to

$$\underline{R}_1 = a_o\,(1, 0, 0)\,, \qquad \underline{R}_2 = a_o\,(0, 1, 0)\,, \qquad \underline{R}_3 = a_o\,(0, 0, 1) \qquad \text{(A.1a)}$$

$$\underline{r}_1 = a_o\,(0, 0, 0)\,, \quad \underline{r}_2 = a_o/2\,(0, 1, 1)\,, \quad \underline{r}_3 = a_o/2\,(1, 0, 1)\,, \quad \underline{r}_3 = a_o/2\,(1, 1, 0) \qquad \text{(A.1b)}$$

where $a_o$ is the lattice constant. The three densest monolayer families $\{hkl\}$ of the fcc lattice are described by six {100} netplanes (square mesh), twelve {110} (rectangular mesh), and eight {111} netplanes (hexagonal mesh, highest atom density) where distances between adjacent parallel netplanes are given by

$$d_{\{100\}} = a_o/2\,, \qquad d_{\{110\}} = a_o/(2\surd 2)\,, \qquad d_{\{111\}} = a_o/\surd 3 \qquad \text{(A.2)}$$

The point symmetry of the fcc lattice is characterized by $O_h$ with high symmetry centers at all atom sites and at the void centers of each elementary cell.

Compact face centered cubic nanoparticles (NPs) are confined by finite sections of monolayers (facets) whose structure is described by different netplanes ($hkl$). If they exhibit central $O_h$ symmetry and show an ($hkl$) oriented facet they must also include all other symmetry related facets characterized by orientations of the complete $\{hkl\}$ family. Thus, surfaces of general fcc NPs of $O_h$ symmetry are described by facets whose orientation can be defined by those of different $\{hkl\}$ families (denoted $\{hkl\}$ facets in the following). As an example, we mention the {111} family with its eight netplane orientations (±1 ±1 ±1). These facets are confined by edges which can be described by families of Miller index directions <*hkl*> (denoted <*hkl*> edges in the following). In addition, NP corners can be characterized by directions <*hkl*> pointing from the NP center to the corresponding corner (denoted <*hkl*> corners in the following). Further, according to the symmetry of the fcc host lattice possible NP centers can only be atom sites or $O_h$ symmetry void sites of the lattice. Thus, we distinguish between atom centered and void centered fcc NPs denoted **ac** and **vc** in the following.

Assuming an fcc NP to be confined by facets of the three cubic netplane families, {100}, {110}, and {111}, its size and shape can be described by three integer parameters, *N*, *M*, *K* (polyhedral NP parameters), which refer to the distances $D_{\{100\}}$, $D_{\{110\}}$, $D_{\{111\}}$ (NP diameters) between parallel monolayer facets of a given netplane family expressed by multiples of corresponding netplane distances where

$$D_{\{100\}} = 2N\, d_{\{100\}}\ , \qquad D_{\{110\}} = 2M\, d_{\{110\}}\ , \qquad D_{\{111\}} = K\, d_{\{111\}} \qquad \text{(A.3)}$$

with $d_{\{hkl\}}$ according to (A.2), Thus, in the most general case fcc NPs can be denoted **fcc(*N, M, K*)**. If a facet type does not appear in the NP the corresponding parameter value *N*, *M*, or *K* is replaced by a minus sign. As an example, an fcc NP with only {100} and {111} facets is denoted fcc(*N*, -, *K*). These notations will be used in the following. Further, auxiliary parameters ***g***, ***h***, ***h’*** with

$$g = 0 \quad \text{(ac; } K \text{ even)}\ , \qquad = 1 \quad \text{(vc; } K \text{ odd)} \qquad \text{(A.4)}$$

$$h = 0 \quad (N + K \text{ even})\ , \qquad = 1 \quad (N + K \text{ odd}) \qquad \text{(A.5)}$$

$$h' = 0 \quad (M + K \text{ even})\ , \qquad = 1 \quad (M + K \text{ odd}) \qquad \text{(A.6)}$$

will be used throughout Sec. A.

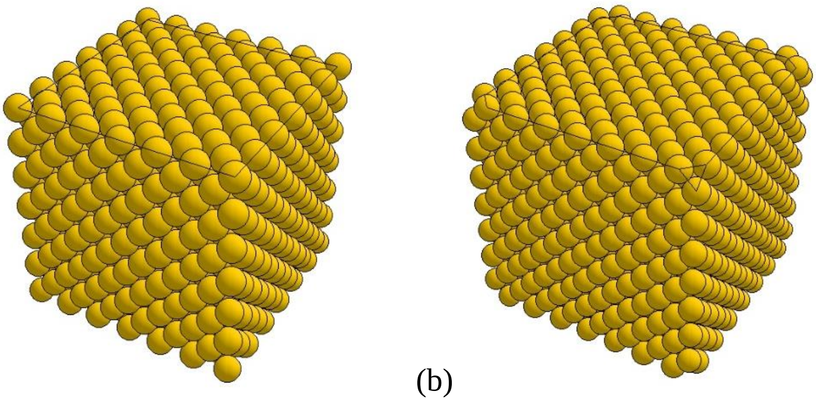
## A.1. Generic fcc Nanoparticles, fcc(*N*, -, -), (-, *M*, -), and (-, -, *K*) NPs

Generic fcc nanoparticles (NPs) of $O_h$ symmetry are confined by facets with orientations of only one netplane family {*hkl*}. Here we focus on {100}, {110}, and {111} facets derived from the densest monolayers of the fcc lattice which offer the flattest NP facets. This allows to distinguish between different generic NP types.

**(a)** **Generic cubic** fcc NPs, denoted **fcc(*N*, -, -)** (the notation is explained above), are confined by all six {100} monolayers with distances $D_{\{100\}} = 2N\, d_{\{100\}}$ between parallel monolayers. This yields six {100} facets as well as possibly eight {111} facets, see Fig. A.1.

The **{100} facets** for ac, $N$ even or vc, $N$ odd are square shaped with <100> edges of length $N\,a_o$ while for ac, $N$ odd or vc, $N$ even they are octagonal (capped square) with alternating edges, four <100> of length $(N - 1)\,a_o$ and four <110> of length $a_o/\sqrt{2}$.

The **{111} facets** appear only for ac, $N$ odd or vc, $N$ even and are triangular shaped with three <110> edges of length $a_o/\sqrt{2}$.



(a) (b)

**Figure A.1.** Atom ball models of atom centered generic cubic NPs, (a) fcc(6, -, -,) and (b) fcc(7, -, -,). The black lines sketch the square and octagonal {100} facets as well as the triangular {111} facet.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, -)}$, (outer polyhedral shell), are given with (A.5) by

$$N_{vol}(N, -, -) = [(2N + 1)^3 + 1]/2 - h \qquad \text{(A.7)}$$

$$N_{facet}(N, -, -) = 12N^2 + 2\,(1 - h) \qquad \text{(A.8)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given with (A.5) by

$$s_{<100>}(N, -, -) = N\, d_{\{100\}} \qquad \text{(A.9a)}$$

$$s_{<110>}(N, -, -) = 2N\, d_{\{110\}} \qquad \text{(A.9b)}$$

$$s_{<111>}(N, -, -) = (3N - h)/2\, d_{\{111\}} \qquad \text{(A.9c)}$$

with $d_{\{hkl\}}$ according to (A.2). These quantities will be used in Secs. A.2.

**(b)** **Generic rhombohedral** fcc NPs, denoted **fcc(-, *M*, -)**, are confined by all twelve {110} monolayers with distances $D_{\{110\}} = 2M\, d_{\{110\}}$ between parallel monolayers. This yields twelve {110} facets as well as possibly six smaller {100} and eight {111} facets, see Figs. A.2, A.3. Corresponding edge parameters $n$, $m$, $k$ depending on $M$ are given in Table A.1 where $M$ is represented by $M = 4p + x$ with $p$, $x$ integer.

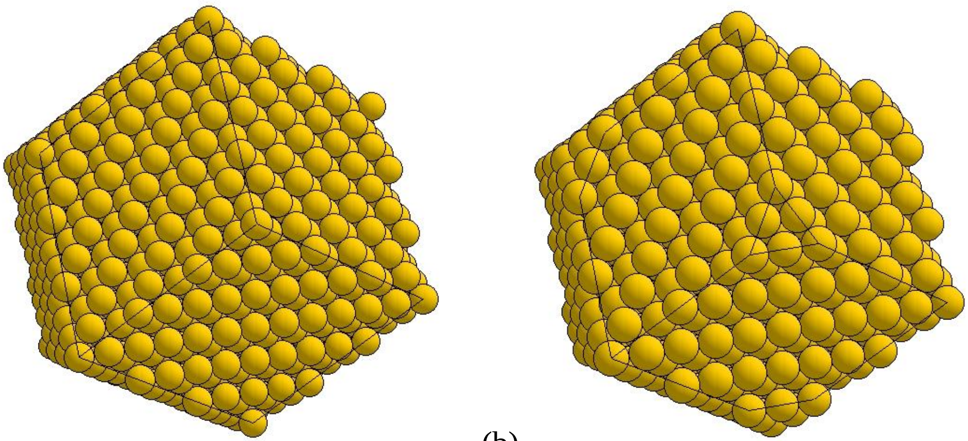
The **{100} facets** appear only for ac, $M$ odd or vc, $M$ even and are square shaped with four <100> edges of length $n\ a_o$.

The **{110} facets** are rhombic, hexagonal, or octagonal shaped with two <100> edges of length $n\ a_o$, two <110> edges of length $m\ a_o/\sqrt{2}$, and four <111> edges of length $k\ \sqrt{3}a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $m\ a_o/\sqrt{2}$.

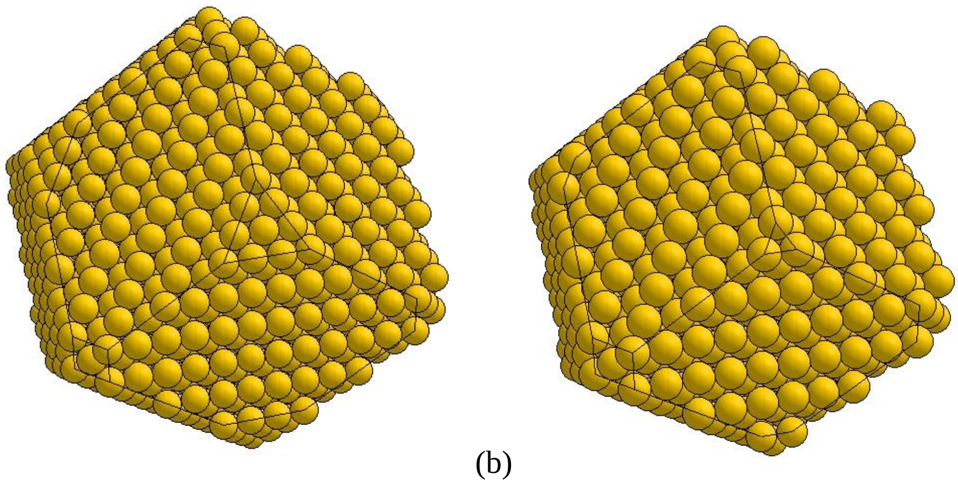
| Centering | $M = 4p$ | $M = 4p + 1$ | $M = 4p + 2$ | $M = 4p + 3$ |
|---|---|---|---|---|
| ac | $n = 0$<br>$m = 0$<br>$k = M/4$ | $n = 1$<br>$m = 3$<br>$k = (M - 5)/4$ | $n = 0$<br>$m = 2$<br>$k = (M - 2)/4$ | $n = 1$<br>$m = 1$<br>$k = (M - 3)/4$ |
| vc | $n = 1$<br>$m = 2$<br>$k = (M - 4)/4$ | $n = 0$<br>$m = 1$<br>$k = (M - 1)/4$ | $n = 1$<br>$m = 0$<br>$k = (M - 2)/4$ | $n = 0$<br>$m = 3$<br>$k = (M - 3)/4$ |

**Table A.1.** Edge parameters $n$, $m$, $k$ of {100}, and {110} and {111} facets of fcc(-, $M$, -) NPs, see text. Values $n = m = 0$ result in rhombic, $n = 0$, $m \neq 0$ or $n \neq 0$, $m = 0$ in hexagonal, and $n \neq 0$, m $\neq 0$ in octagonal facets.



(a) (b)

**Figure A.2.** Atom ball models of atom centered generic rhombohedral NPs for $M$ even, (a) fcc(-, 12, -) and (b) fcc(-, 10, -). The black lines sketch the (capped) rhombic {110} and triangular {111} facets.



(a) (b)

**Figure A.3.** Atom ball models of atom centered generic rhombohedral NPs for *M* odd, (a) fcc(-, 13, -) and (b) fcc(-, 11, -). The black lines sketch the (capped) rhombic {110} and triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, M, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, M, -)}$, (outer polyhedral shell) are given by

$$N_{vol}(-, M, -) = (2\,M^3 + 3\,M^2 + 2\,M + b)/2 \qquad \text{(A.10)}$$

$$N_{facet}(-, M, -) = 3\,M^2 + c \qquad \text{(A.11)}$$

with

| Centering | $M = 4p$ | $M = 4p + 1$ | $M = 4p + 2$ | $M = 4p + 3$ |
|---|---|---|---|---|
| ac | $b = 2$<br>$c = 2$ | $b = -5$<br>$c = 11$ | $b = 6$<br>$c = 6$ | $b = -1$<br>$c = 3$ |
| vc | $b = 0$<br>$c = 6$ | $b = 5$<br>$c = 3$ | $b = -4$<br>$c = 2$ | $b = 1$<br>$c = 11$ |

**Table A.2.** Constants *b*, *c* used for number of NP atoms of fcc(-, *M*, -) NPs, see text.

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given by

$$s_{<100>}(-, M, -) = M\,d_{\{100\}} \quad \text{(ac, } M \text{ even; vc, } M \text{ odd)} \qquad \text{(A.12a)}$$

$$= (M - h')\,d_{\{100\}} \quad \text{(ac, } M \text{ odd; vc, } M \text{ even)} \qquad \text{(A.12b)}$$

$$s_{<110>}(-, M, -) = M\,d_{\{110\}} \qquad \text{(A.12c)}$$

$$s_{<111>}(-, M, -) = 3M/4\,d_{\{111\}} \quad \text{(ac, } M = 4p\text{; vc, } M = 4p + 2) \qquad \text{(A.12d)}$$

$$= (3M - 3)/4\,d_{\{111\}} \quad \text{(ac, } M = 4p + 1\text{; vc, } M = 4p + 3) \qquad \text{(A.12e)}$$

$$= (3M - 2)/4\,d_{\{111\}} \quad \text{(ac, } M = 4p + 2\text{; vc, } M = 4p) \qquad \text{(A.12f)}$$

$$= (3M - 1)/4\,d_{\{111\}} \quad \text{(ac, } M = 4p + 3\text{; vc, } M = 4p + 1) \qquad \text{(A.12g)}$$

with $d_{\{hkl\}}$ according to (A.2). These quantities will be used in Secs. A.2.

**(c)** **Generic octahedral** fcc NPs, denoted **fcc(-, -, *K*)**, are confined by all eight {111} monolayers with distances $D_{\{111\}} = K\, d_{\{111\}}$ between parallel monolayers. This yields eight {111} facets, see Fig. A.4 where ac (*K* even) and vc (*K* odd) NPs are structurally identical. All **{111} facets** are triangular shaped with three <110> edges of length $K\, a_o/\sqrt{2}$.

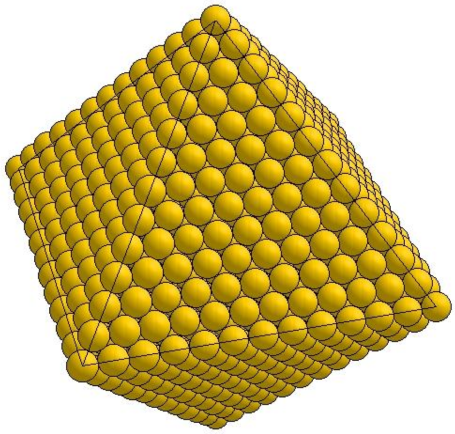


**Figure A.4.** Atom ball model of an atom centered generic octahedral NP, fcc(-, -, 12). The black lines sketch the triangular {111} facet shapes.

The total number of NP atoms, $\boldsymbol{N_{vol}}$**(-, -, *K*)**, and the number of facet atoms, $\boldsymbol{N_{facet}}$**(-, -, *K*)**, (outer polyhedral shell), are given by

$$N_{vol}(\text{-}, \text{-}, K) = (K + 1)\,[2\,(K + 1)^2 + 1]/3 \quad \text{(A.13)}$$

$$N_{facet}(\text{-}, \text{-}, K) = 4\,K^2 + 2 \quad \text{(A.14)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given by

$$s_{<100>}(\text{-}, \text{-}, K) = K\, d_{\{100\}} \quad \text{(A.15a)}$$

$$s_{<110>}(\text{-}, \text{-}, K) = K\, d_{\{110\}} \quad \text{(A.15b)}$$

$$s_{<111>}(\text{-}, \text{-}, K) = K/2\, d_{\{111\}} \quad \text{(A.15c)}$$

with $d_{\{hkl\}}$ according to (A.2). These quantities will be used in Secs. A.2.

Table A.3 collects types, constraints, and shapes of all generic fcc NPs.

| Generic type | Constraints | Facets | Corners |
|---|---|---|---|
| Cubic<br>fcc(*N*, -, -) | ac, *N* even,<br>vc, *N* odd | {100} 6<br>{110} 0<br>{111} 0 | <100> 0<br><110> 0<br><111> 8 |
| | ac, *N* odd,<br>vc, *N* even | {100} 6<br>{110} 0<br>{111} 8 | <100> 0<br><110> 0<br><111> $8^{\&}$ |
| Rhombohedral<br>fcc(-, *M*, -) | ac, $M = 4p$ | {100} 0<br>{110} 12<br>{111} 0 | <100> 6<br><110> 0<br><111> 8 |
| | ac, $M = 4p + 1$<br>$M = 4p + 3$<br>vc, $M = 4p$ | {100} 6<br>{110} 12<br>{111} 8 | <100> $6^{\&}$<br><110> 0<br><111> $8^{\&}$ |
| | ac, $M = 4p + 2$<br>vc, $M = 4p + 1$<br>$M = 4p + 3$ | {100} 0<br>{110} 12<br>{111} 8 | <100> 6<br><110> 0<br><111> $8^{\&}$ |
| | vc, $M = 4p + 2$ | {100} 6<br>{110} 12<br>{111} 0 | <100> $6^{\&}$<br><110> 0<br><111> 8 |
| Octahedral<br>fcc(-, -, *K*) | ac, *K* even | {100} 0<br>{110} 0<br>{111} 8 | <100> 6<br><110> 0<br><111> 0 |
| | vc, *K* odd | {100} $6^{+}$<br>{110} $12^{+}$<br>{111} 8 | <100> $6^{\&}$<br><110> 0<br><111> 0 |

**Table A.3.** Types and notations of all generic fcc NPs where “ac“ denotes atom centered and “vc“ void centered NPs. Further, the superscript label “&” denotes corner quadruplets about <100> and corner triplets about <111>.

## A.2. Non-generic fcc Nanoparticles

Non-generic fcc nanoparticles of $O_h$ symmetry can be either atom or void centered and show facets with orientations of several {*hkl*} netplane families. This can be considered as combining confinements of the corresponding generic NPs discussed in Sec. A.1 with suitable polyhedral parameters *N*, *M*, *K* sharing their symmetry center (atom or void). Here we discuss non-generic fcc NPs which combine constraints of up to three generic NPs, cubic fcc(*N*, -, -), rhombohedral fcc(-, *M*, -), and octahedral fcc(-, -, *K*). These allow {100}, {110}, as well as {111} facets and will be denoted **fcc(*N, M, K*)** in the following. Clearly, the corresponding polyhedral parameters *N*, *M*, *K* depend on each other and determine the overall NP shape. In particular, if a participating generic NP encloses another participant it will not contribute to the overall NP shape and the respective {*hkl*} facets will not appear at the surface of the non-generic NP. In the following, we consider the three types of non-generic NPs which combine constraints due to two generic NPs (Secs. A.2.1-3) before we discuss the most general case of fcc(*N*, *M*, *K*) NPs in Sec. A.2.4.

### A.2.1 Combining (100) and (110) Facets, fcc(*N*, *M*, -) NPs

Non-generic **cubo-rhombic** NPs, denoted **fcc(*N, M,* -)**, are confined by facets referring to the two generic NPs, fcc(*N*, -, -) (cubic) and fcc(-, *M*, -) (rhombohedral). Thus, they can show {100} as well as {110} facets (apart from {111} microfacets) depending on the polyhedral parameters *N*, *M*. Clearly, both generic NPs must exhibit the same centering, atom centered (ac) or void (vc) centered, to result in a non-generic fcc NP of $O_h$ symmetry. If the edges of the cubic NP fcc(*N*, -, -) lie inside the rhombohedral NP fcc(-, *M*, -) the resulting combination fcc(*N*, *M*, -) will be generic cubic which can be expressed formally by

$$s_{<110>}(N, -, -) \leq s_{<110>}(-, M, -) \qquad \text{(A.16)}$$

leading, according to (A.9), (A.12), to

$$2N \leq M \qquad \text{(A.17)}$$

for both ac and vc NPs. On the other hand, if the corners of the rhombohedral NP fcc(-, *M*, -) lie inside the cubic NP fcc(*N*, -, -) the resulting combination fcc(*N*, *M*, -) will be generic rhombohedral which can be expressed formally by

$$s_{<100>}(-, M, -) \leq s_{<100>}(N, -, -) \qquad \text{(A.18)}$$

leading, according to (A.9), (A.12) with (A.6), to

$$N \geq (M - h') \qquad \text{(A.19)}$$

Thus, the two generic NPs intersect and define a true non-generic NP fcc(*N*, *M*, -) offering both {100} and {110} facets only for polyhedral parameters *N*, *M* where with (A.6)

$$N + h' < M < 2N \qquad \text{(A.20)}$$

while fcc(*N*, *M*, -) is generic cubic for larger *M* according to (A.17) and generic rhombohedral for smaller *M* according to (A.19). This suggests that generic cubic and rhombohedral fcc NPs can be considered as special cases of non-generic NPs fcc(*N*, *M*, -) where with (A.6)

$$\text{fcc}(N, -, -) = \text{fcc}(N, M = 2N, -) \qquad \text{(cubic)} \qquad \text{(A.21a)}$$

$$\text{fcc}(-, M, -) = \text{fcc}(N = M - h', M, -) \qquad \text{(rhombohedral)} \qquad \text{(A.21b)}$$

Parameters $N$, $M$ provide additional information about geometric properties of the NPs describing the shape and all facet edges. In the most general case, cubo-rhombic fcc($N$, $M$, -) NPs exhibit six {100} facets, twelve {110} facets, and eight smaller {111} facets, see Figs. A.5, A.6. Corresponding edge parameters $n$, $m$, $k$ depending on $N$, $M$ are given in Table A.4 where $M$ is represented by $M = 4p + x$ with $p$, $x$ integer.

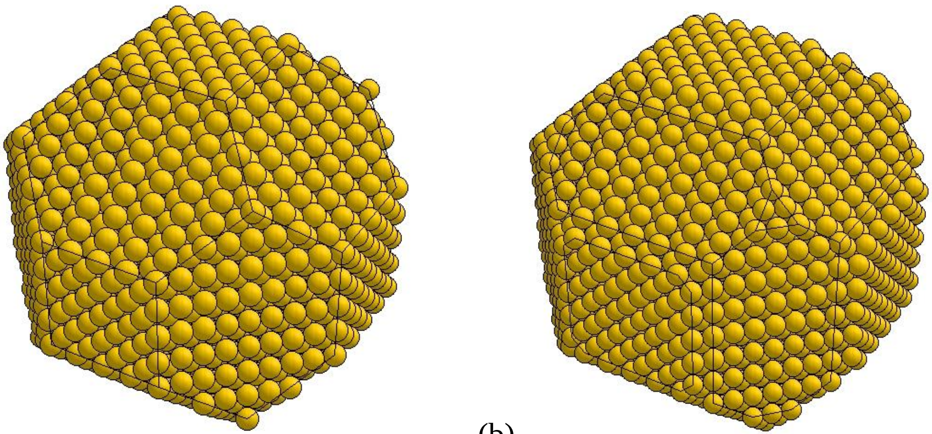
The **{100} facets** for ac, $N$ even or vc, $N$ odd are square shaped with four <100> edges of length $n\ a_o$ while for ac, $N$ odd or vc, $N$ even they are octagonal (capped square) with alternating edges, four <100> of length $(n - 2)\ a_o$ and four <110> of length $a_o/\sqrt{2}$.

The **{110} facets** are octagonal (hexagonal) shaped with two <100> edges of length $n\ a_o$, two <110> edges of length $m\ a_o/\sqrt{2}$, and four <111> edges of length $k\ \sqrt{3}a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $m\ a_o/\sqrt{2}$.

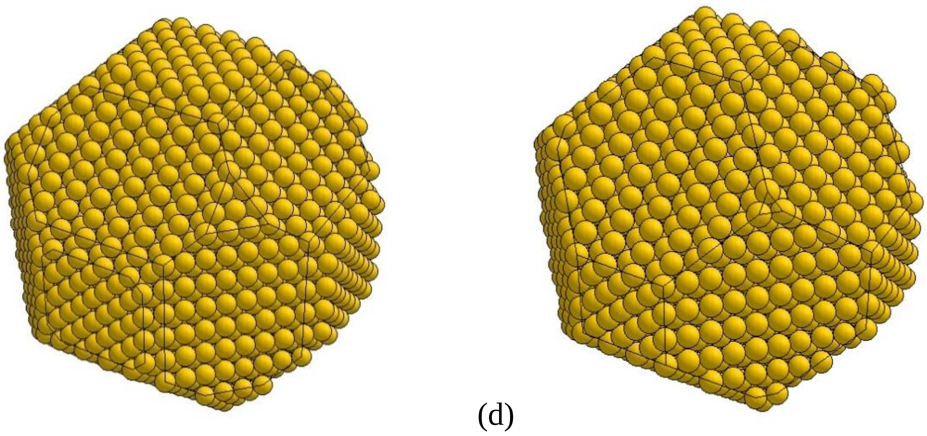
| Centering | $M = 4p$ | $M = 4p + 1$ | $M = 4p + 2$ | $M = 4p + 3$ |
|---|---|---|---|---|
| ac<br>$N$ even | $n = M - N$<br>$m = 0$<br>$k = (2N - M)/4$ | $n = M - N$<br>$m = 3$<br>$k = (2N - M - 3)/4$ | $n = M - N$<br>$m = 2$<br>$k = (2N - M - 2)/4$ | $n = M - N$<br>$m = 1$<br>$k = (2N - M - 1)/4$ |
| ac<br>$N$ odd | $n = M - N + 1$<br>+ ext<br>$m = 0$<br>$k = (2N - M - 2)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 3$<br>$k = (2N - M - 5)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 2$<br>$k = (2N - M - 4)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 1$<br>$k = (2N - M - 3)/4$ |
| vc<br>$N$ odd | $n = M - N$<br>$m = 2$<br>$k = (2N - M - 2)/4$ | $n = M - N$<br>$m = 1$<br>$k = (2N - M - 1)/4$ | $n = M - N$<br>$m = 0$<br>$k = (2N - M)/4$ | $n = M - N$<br>$m = 3$<br>$k = (2N - M - 3)/4$ |
| vc<br>$N$ even | $n = M - N + 1$<br>+ ext<br>$m = 2$<br>$k = (2N - M - 4)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 1$<br>$k = (2N - M - 3)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 0$<br>$k = (2N - M - 2)/4$ | $n = M - N + 1$<br>+ ext<br>$m = 3$<br>$k = (2N - M - 5)/4$ |

**Table A.4.** Edge parameters $n$, $m$, $k$ of {100}, and {110} and {111} facets of fcc($N$, $M$, -) NPs, see text. Values $m = 0$ result in hexagonal rather than octagonal facets. Further, "+ ext" indicates that each {110} facet is extended by two atom rows of length $(M - N - 1)\ a_o$ along <100>.



(a) (b)

**Figure A.5.** Atom ball models of atom centered cubo-rhombic NPs for *M* even, (a) fcc(12, 16, -) and (b) fcc(13, 18, -). The black lines sketch the (capped) square {100}, (capped) hexagonal {110} and triangular {111} facets.



(b) (d)

**Figure A.6.** Atom ball models of atom centered cubo-rhombic NPs, for *M* odd, (b) fcc(13, 17, -) and (d) fcc(12, 15, -). The black lines sketch the (capped) square {100}, (capped) hexagonal {110} and triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, -)}$, (outer polyhedral shell) are given with (A.10), (A.11) by

$$N_{vol}(N, M, -) = N_{vol}(-, M, -) - (M - N)\,[4\,(M - N)^2 - 1] - a \qquad \text{(A.22)}$$

$a = 0$    ($N + M$ even)
$= 3$    ($N + M$ odd: ac, $M$ even; vc, $M$ odd)
$= -3$    ($N + M$ odd: ac, $M$ odd; vc, $M$ even)

$$N_{facet}(N, M, -) = N_{facet}(-, M, -) - c \qquad \text{(A.23)}$$

$c = 0$    (ac, $N$ even; vc, $N$ odd) ,    $= 6$    (ac, $N$ odd; vc, $N$ even)

The present discussion allows a classification of fcc($N$, $M$, -) NPs for all combinations of polyhedral parameters $N$, $M$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table A.5 illustrates all possible NP types.

| Constraints | NP types | fcc Isomorphs |
|---|---|---|
| $M \geq 2N$ | Generic cubic | ($N$, -, -) = ($N$, $M$ = 2$N$, -) |
| $N \leq M \leq 2N$ | Cubo-rhombic | ($N$, $M$, -) |
| $M \leq N$ | Generic rhombohedral | (-, $M$, -) = ($N$ = $M$ - $h'$, $M$, -) |

**Table A.5.** Constraints and types including isomorphs of atom (ac) and void centered (vc) fcc($N$, $M$, -) NPs with (A.6).

### A.2.2 Combining (100) and (111) Facets, fcc(*N*, -, *K*) NPs

Non-generic **cubo-octahedral** NPs, denoted **fcc(*N*, -, *K*)**, are confined by facets referring to the two generic NPs, fcc($N$, -, -) (cubic) and fcc(-, -, $K$) (octahedral). Thus, they can show {100} as well as {111} facets depending on the polyhedral parameters $N$, $K$. Clearly, both generic NPs must exhibit the same centering, atom centered (ac, $K$ even) or void centered (vc, $K$ odd), to yield a non-generic fcc NP of $O_h$ symmetry. If the (capped) corners of the cubic NP fcc($N$, -, -) lie inside the octahedral NP fcc(-, -, $K$) the resulting combination fcc($N$, -, $K$) will be generic cubic which can be expressed formally by

$$s_{<111>}(N, -, -) \leq s_{<111>}(-, -, K) \quad \text{(A.24)}$$

leading, according to (A.9), (A.15) with (A.5) to

$$3N \leq K + h \quad \text{(A.25)}$$

for ac and vc NPs. On the other hand, if the corners of the octahedral NP fcc(-, -, $K$) lie inside the cubic NP fcc($N$, -, -) the resulting combination fcc($N$, -, $K$) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(N, -, -) \quad \text{(A.26)}$$

leading, according to (A.9), (A.15), to

$$N \geq K \quad \text{(A.27)}$$

Thus, the two generic NPs intersect and define a true non-generic NP fcc($N$, -, $K$) offering both {100} and {111} facets only for polyhedral parameters $N$, $K$ where with (A.5)

$$N < K < 3N - h \qquad \text{(A.28)}$$

while fcc($N$, -, $K$) is generic cubic for larger $K$ according to (A.25) and generic octahedral for smaller $K$ according to (A.27). This suggests that generic cubic and octahedral fcc NPs can be considered as special cases of non-generic NPs fcc($N$, -, $K$) where with (A.5)

$$\text{fcc}(N, -, -) = \text{fcc}(N, -, K = 3N - h) \qquad \text{(cubic)} \qquad \text{(A.29a)}$$

$$\text{fcc}(-, -, K) = \text{fcc}(N = K, -, K) \qquad \text{(octahedral)} \qquad \text{(A.29b)}$$

Further, amongst the true intersecting cubo-octahedral NPs according to (A.28) we can distinguish between so-called **truncated octahedral** NPs where $K < 2N$ and **truncated cubic** NPs for $K > 2N$ as will be discussed in the following.

Parameters $N$, $K$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, cubo-octahedral NPs fcc($N$, -, $K$), both ac and vc, exhibit six {100} and eight {111} facets, see Figs. A.7, A.8.

**Truncated octhedral** NPs ($K < 2N$), Fig. A.7a, can be characterized by their facets as follows.

The **{100} facets** are square shaped with four <110> edges of length $(K - N)\ a_o/\sqrt{2}$.

The **{111} facets** are hexagonal shaped with <110> edges of alternating lengths $(K - N)\ a_o/\sqrt{2}$ and $(2N - K)\ a_o/\sqrt{2}$.

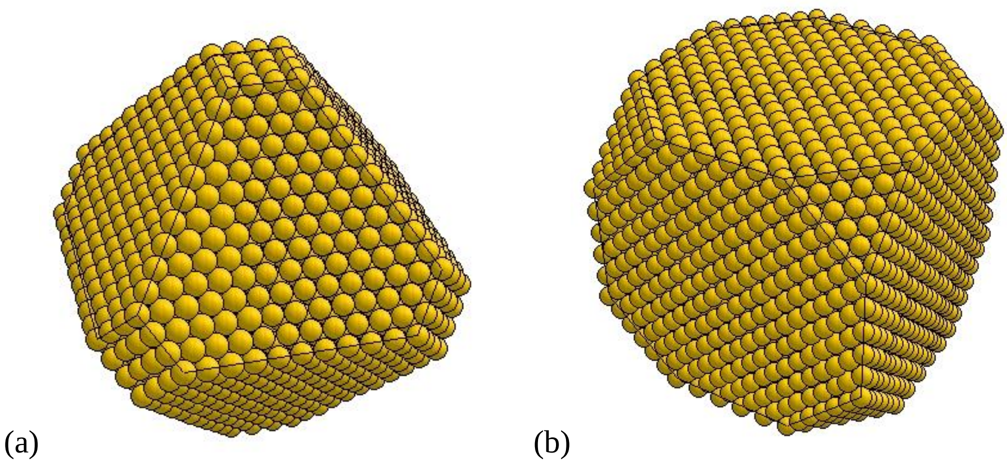


**Figure A.7.** Atom ball models of cubo-octahedral NPs, (a) ac fcc(13, -, 16) (truncated octahedral) and (b) vc fcc(11, -, 27) (truncated cubic) . The black lines sketch the square/octagonal {100} and the hexagonal/triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (A.13), (A.14) by

$$N_{vol}(N, -, K) = N_{vol}(-, -, K) - H\,(H + 1)\,(2H + 1)\,, \qquad H = K - N \qquad \text{(A.30)}$$

$$N_{facet}(N, -, K) = N_{facet}(-, -, K) - 6\,(K - N)^2 \qquad \text{(A.31)}$$

**Truncated cubic** NPs ($K > 2N$), Fig. A.7b, can be characterized by their facets as follows.

The **{100} facets** are octagonal shaped with alternating edges, four <100> of length ($K$ - 2$N$) $a_o$ and four <110> of length (3$N$ - $K$) $a_o/\sqrt{2}$, respectively.

The **{111} facets** are triangular shaped with <110> edges of length (3$N$ - $K$) $a_o/\sqrt{2}$.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, for ac and vc NPs and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (A.7), (A.8), (A.5) by

$$N_{vol}(N, -, K) = N_{vol}(N, -, -) - H\,(H + 2)\,(2H - 1)/3 + h \qquad H = 3N - K \qquad \text{(A.32)}$$

$$N_{facet}(N, -, K) = N_{facet}(N, -, -) - 2H^2 + 2h \qquad \text{(A.33)}$$

There are fcc NPs which can be assigned to both truncated cubic and truncated octahedral type, the **generic cuboctahedral** fcc($N$, -, $K$) NPs, defined by $K$ = 2$N$. These NPs exist only as atom centered variants since $K$ must be even. They exhibit six {100} and eight {111} facets, see Fig. A.8. All **{100} facets** are square shaped with four <110> edges of length $N\,a_o/\sqrt{2}$ while all **{111} facets** are triangular with three <110> edges of length $N\,a_o/\sqrt{2}$ shared with those of the {100} facets.

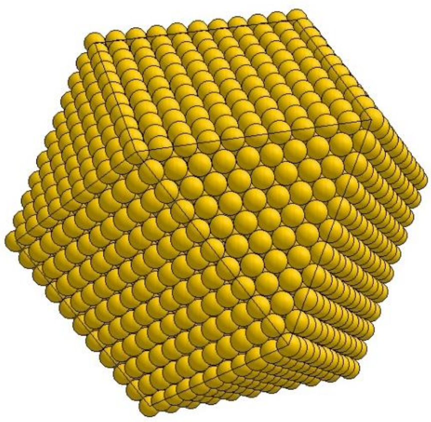


**Figure A.8.** Atom ball model of an atom centered generic cuboctahedral fcc(10, -, 20). The black lines sketch the triangular {111} and octagonal/square {100}facet shapes.

The present discussion allows a classification of fcc($N$, -, $K$) NPs for all combinations of polyhedral parameters $N$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table A.6 illustrates all possible NP types.

| Constraints | NP types | fcc Isomorphs |
|---|---|---|
| $K \geq 3N - h$ | Generic cubic | ($N$, -, -) =<br>($N$ , -, $K = 3N - h$) |
| $2N \leq K \leq 3N - h$ | Cubo-octahedral truncated cubic | ($N$, -, $K$) |
| $K = 2N$ | Cuboctahedral | ($N$, -, $K = 2N$) ,<br>($N = K/2$, -, $K$) |
| $N \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) |
| $K \leq N$ | Generic octahedral | (-, -, $K$) =<br>($N = K$, -, $K$) |

**Table A.6.** Constraints and types including isomorphs of atom ($K$ even) and void centered ($K$ odd) fcc($N$, -, $K$) NPs.

## A.2.3 Combining (110) and (111) Facets, fcc(-, *M*, *K*) NPs

Non-generic **rhombo-octahedral** NPs, denoted **fcc(-, *M*, *K*)**, are confined by facets referring to the two generic NPs, fcc(-, $M$, -) (rhombohedral) and fcc(-, -, $K$) (octahedral). Thus, they can show {110} as well as {111} facets (apart from small {100} facets) depending on the polyhedral parameters $M$, $K$. Clearly, both generic NPs must exhibit the same centering, atom centered (ac, $K$ even) or void centered (vc, $K$ odd), to yield a non-generic fcc NP of $O_h$ symmetry. If the corners of the rhombohedral NP fcc(-, $M$, -) lie inside the octahedral NP fcc(-, -, $K$) the resulting combination fcc(-, $M$, $K$) will be generic rhombohedral which can be expressed formally by

$$s_{<111>}(-, M, -) \leq s_{<111>}(-, -, K) \qquad \text{(A.34)}$$

leading, according to (A.12), (A.15), to

$$3M \leq 2K \qquad (\text{ac}, M = 4p; \text{vc}, M = 4p + 2) \qquad \text{(A.35a)}$$

$$3M \leq 2K + 3 \qquad (\text{ac}, M = 4p + 1; \text{vc}, M = 4p + 3) \qquad \text{(A.35b)}$$

$$3M \leq 2K + 2 \qquad (\text{ac}, M = 4p + 2; \text{vc}, M = 4p) \qquad \text{(A.35c)}$$

$$3M \leq 2K + 1 \qquad (\text{ac}, M = 4p + 3; \text{vc}, M = 4p + 1) \qquad \text{(A.35d)}$$

On the other hand, if the corners of the octahedral NP fcc(-, -, *K*) lie inside the rhombohedral NP fcc(-, *M*, -) the resulting combination fcc(-, *M*, *K*) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(-, M, -) \qquad \text{(A.36)}$$

leading, according to (A.12), (A.15), (A.6) to

$$K \leq M - h' \qquad \text{(A.37)}$$

Thus, the two generic NPs intersect and define a true non-generic NP fcc(-, *M*, *K*) offering both {110} and {111} facets only for polyhedral parameters *M*, *K* where with (A.4)

$$2M - 2g \;<\; 2K \;<\; M - 2g \qquad (M = 4p) \qquad \text{(A.38a)}$$

$$2M - 2(1 - g) \;<\; 2K \;<\; 3M - 1 - 2(1 - g) \qquad (M = 4p + 1) \qquad \text{(A.38b)}$$

$$2M - 2g \;<\; 2K \;<\; 3M - 2(1 - g) \qquad (M = 4p + 2) \qquad \text{(A.38c)}$$

$$2M - 2(1 - g) \;<\; 2K \;<\; 3M - 1 - 2g \qquad (M = 4p + 3) \qquad \text{(A.38d)}$$

while fcc(-, *M*, *K*) is generic rhombohedral for larger *K* according to (A.35) and generic octahedral for smaller *K* according to (A.37). This suggests that generic rhombohedral and octahedral fcc NPs can be considered as special cases of non-generic NPs fcc(-, *M*, *K*) where with (A.4)

$$\text{fcc}(-, M, -) = \text{fcc}(-, M, 3M/2) \qquad (\text{rhombohedral, } M = 4p + 2g) \qquad \text{(A.39a)}$$

$$= \text{fcc}(-, M, (3M - 3)/2) \qquad (M = 4p + 1 + 2g) \qquad \text{(A.39b)}$$

$$= \text{fcc}(-, M, (3M - 2)/2) \qquad (M = 4p + 2 - 2g) \qquad \text{(A.39c)}$$

$$= \text{fcc}(-, M, (3M - 1)/2) \qquad (M = 4p + 3 - 2g) \qquad \text{(A.39d)}$$

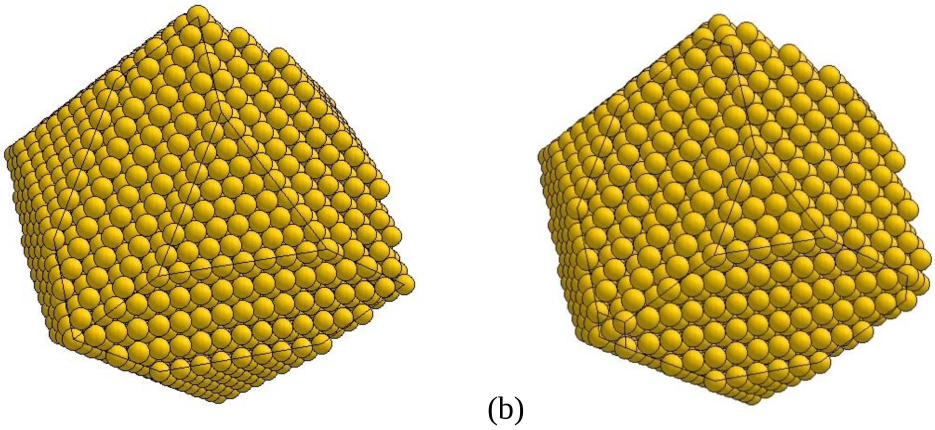
$$\text{fcc}(-, -, K) = \text{fcc}(-, K, K) \qquad (\text{octahedral}) \qquad \text{(A.40)}$$

Parameters *M*, *K* provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, rhombo-octahedral NPs fcc(-, *M*, *K*) exhibit twelve {110}, eight {111} facets, and six possible {100} facets, see Figs. A.9, A.10.

The **{100} facets** appear only for ac, *M* odd or vc, *M* even and are square shaped with <100> edges of length $a_o$.

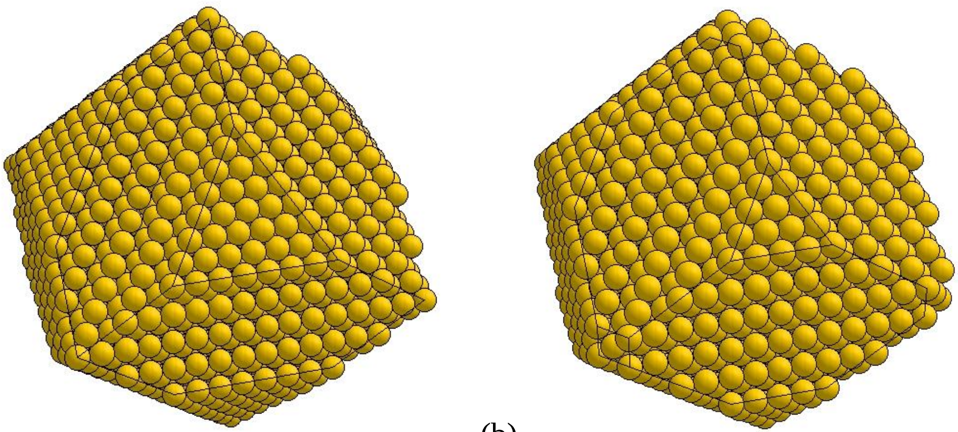
The **{110} facets** for ac, *M* even or vc, *M* odd are hexagonal (capped rhombic) shaped with four <111> edges of length $(K - M)/2\ \sqrt{3}a_o$ and two <110> edges of $(3M - 2K)\ a_o/\sqrt{2}$.
For ac, *M* odd or vc, *M* even the facets are octagonal shaped with four <111> edges of length $(K - M - 1)/2\ \sqrt{3}a_o$ and two <110> edges of $(3M - 2K)\ a_o/\sqrt{2}$.

The **{111} facets** are triangular shaped with three <110> edges of length $(3M - 2K)\ a_o/\sqrt{2}$.



(a) (b)

**Figure A.9.** Atom ball models of atom centered rhombo-octahedral NPs, (a) fcc( -, 16, 20) and (b) fcc( -, 15, 20). The black lines sketch the hexagonal/octagonal{110,}triangular {111}, and small square {100} facets.



(a) (b)

**Figure A.10.** Atom ball models of void centered rhombo-octahedral NPs, (a) fcc( -, 15, 19) and (b) fcc( -, 14, 19). The black lines sketch the hexagonal/octagonal{110,}triangular {111}, and small square {100} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, M, K)}$, (outer polyhedral shell) are given with (A.6) by

$$N_{vol}(-, M, K) = (2\,M^3 + 3\,M^2 + 2\,M)/2 - H\,(2\,H^2 - 3\,H - 8)/6 + 1 - 3h' \qquad \text{(A.41)}$$

$$N_{facet}(-, M, K) = 3\,M^2 + H^2 + 2 \qquad H = 3M - 2K \qquad \text{(A.42)}$$

The present discussion allows a classification of fcc(-, $M$, $K$) NPs for all combinations of polyhedral parameters $M$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table A.7 illustrates all possible NP types where parameter $K_a$ inside the table is defined by

$K_a(N, M)$ = $3M/2$ (ac, $M = 4p$; vc, $M = 4p + 2$) (A.43a)

= $(3M - 3)/2$ (ac, $M = 4p + 1$; vc, $M = 4p + 3$) (A.43b)

= $(3M - 2)/2$ (ac, $M = 4p + 2$; vc, $M = 4p$) (A.43c)

= $(3M - 1)/2$ (ac, $M = 4p + 3$; vc, $M = 4p + 1$) (A.43d)

and will be used later on.

| Constraints | NP types | fcc Isomorphs |
|---|---|---|
| $K \geq K_a$ | Generic rhombohedral | (-, $M$, -) =<br>(-, $M$, $K = K_a$) |
| $M \leq K \leq K_a$ | Rhombo-octahedral | (-, $M$, $K$) |
| $K \leq M$ | Generic octahedral | (-, -, $K$) =<br>(-, $M = K$, $K$) |

**Table A.7.** Constraints and types including isomorphs of atom centered (ac, $K$ even) and void centered (vc, $K$ odd) fcc(-, $M$, $K$) NPs.

## A.2.4 Combining (100), (110), and (111) Facets, fcc($N$, $M$, $K$) NPs

Non-generic **cubo-rhombo-octahedral** NPs, denoted **fcc(*N*, *M*, *K*)**, are confined by facets referring to all three generic NPs, fcc($N$, -, -) (cubic), fcc(-, $M$, -) (rhombohedral), and fcc(-, -, $K$) (octahedral). Thus, they can show {100}, {110}, and {111} facets depending on the polyhedral parameters $N$, $M$, $K$. Clearly, the three generic NPs must exhibit the same centering, atom centered (ac, $K$ even) or void centered (vc, $K$ odd), to yield a non-generic fcc NP of $O_h$ symmetry. A general discussion of these NPs requires a number of different scenarios using results of for generic and non-generic NPs with one or two types of facets, Secs. A.1, A.2.1-3, as will be detailed in the following.

First, we consider the general notation for generic fcc NPs discussed in Sec. A.1. Cubic NPs fcc($N$, -, -) are surrounded by rhombohedral NPs fcc(-, $M$, -) if $M \geq 2N$ according to (A.17) and by octahedral NPs fcc(-, -, $K$) if $N$, $K$ satisfy relations (A.25). This allows a notation fcc($N$, $M$, $K$) where

fcc($N$, -, -) = fcc($N$, $M = 2N$, $K = 3N - h$) (A.44)

Further, rhombohedral NPs fcc(-, $M$, -) are surrounded by cubic NPs fcc($N$, -, -) if $M$, $N$ satisfy relations (A.19) and by octahedral NPs fcc(-, -, $K$) if $M$, $K$ satisfy relations (A.35). This allows a notation fcc($N$, $M$, $K$) where with (A.43), (A.4)

fcc(-, $M$, -) = fcc($N = M - g$, $M$, $K_a$) (A.45)

In addition , the octahedral NPs fcc(-, -, $K$) are surrounded by cubic NPs fcc($N$, -, -) if $N \geq K$ according to (A.27) and by rhombohedral NPs fcc(-, $M$, -) if $M \geq K$ according to (A.37). This allows a notation fcc($N$, $M$, $K$) where

$$\mathrm{fcc}(-, -, K) = \mathrm{fcc}(N = K, M = K, K) \tag{A.46}$$

General notations for non-generic fcc NPs discussed in Secs. A.2.1-3 are obtained by analogous arguments. According to Sec. A.2.1, true cubo-rhombic NPs fcc($N$, $M$, -) with both {100} and {110} facets are subject to $N\ (+\ 1) \leq M \leq 2N$ according to (A.20). They are surrounded by octahedral NPs fcc(-, -, $K$) if $K \geq K_a$ with $K_a$ defined by (A.43). This allows a general notation fcc($N$, $M$, $K$) where

$$\mathrm{fcc}(N, M, -) = \mathrm{fcc}(N, M, K = K_a) \tag{A.47}$$

According to Sec. A.2.2, true cubo-octahedral NPs fcc($N$, -, $K$) with both {100} and {111} facets are subject to $N \leq K \leq 3N\ (-\ 1)$ according to (A.28). They are surrounded by rhombohedral NPs fcc(-, $M$, -) if $M \geq M_a$ with

$$M_a(N, K) = \min(K, 2N) \tag{A.48}$$

This allows a general notation fcc($N$, $M$, $K$) where

$$\mathrm{fcc}(N, -, K) = \mathrm{fcc}(N, M = M_a, K) \tag{A.49}$$

According to Sec. A.2.3, true rhombo-octahedral NPs fcc(-, $M$, $K$) with both {110} and {111} facets are subject to $M \leq K \leq 3M/2$ etc., see (A.38). They are surrounded by cubic NPs fcc($N$, -, -) if $N \geq N_a$ with

$$N_a(M, K) = M - h' \tag{A.50}$$

This allows a general notation fcc($N$, $M$, $K$) where

$$\mathrm{fcc}(-, M, K) = \mathrm{fcc}(N = N_a, M, K) \tag{A.51}$$

In the most general case of a true fcc($N$, $M$, $K$) NP with {100}, {110}, and {111} facets we start from a true cubo-rhombic NP, fcc($N$, $M$, -), with its constraints $N \leq M \leq 2N$ (ac, $M$ even; vc, $M$ odd) or $N + 1 \leq M \leq 2N$ (ac, $M$ odd; vc, $M$ even) and add constraints of a generic octahedral NP, fcc(-, -, $K$), where according to the discussion above $K$ values are below $K_a$. This allows to distinguish four different ranges of parameter $K$, defined by separating values $K_a \geq K_b \geq K_c$, with $K_a$ given by (A.43) and

$K_b(N, M) = 2M - N - h$ (A.52)

$K_c(N, M) = M - h'$ (A.53)

which result in different NP shapes starting from the initial cubo-rhombic NP fcc($N$, $M$, $K_a$) as illustrated for the ac NP fcc(20, 26, 38) in Fig. A.11.

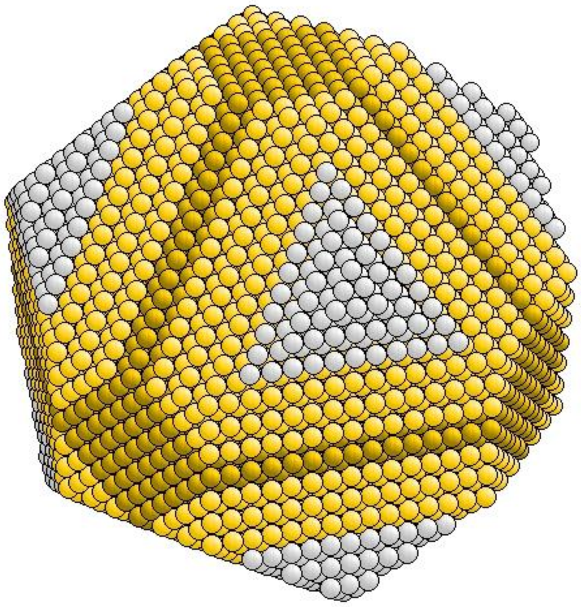


**Figure A.11.** Atom ball model of an atom centered cubo-rhombic NP, fcc(20, 26, 38) ($K = K_a$, all atom balls), with its cubo-rhombo-octahedral NP components, fcc(20, 26, 32) ($K = K_b$), and fcc(20, 26, 26) ($K = K_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $K$ ranges at $K = K_c$ (inner vs. lower central ) and at $K = K_b$, (lower vs. upper central), respectively, see text.

**Outer *K* range** of fcc($N$, $M$, $K$) where with (A.43)

$K \geq K_a$ (A.54)

For these $K$ values the NP becomes cubo-rhombohedral and does exhibits only small triangular {111} facets of 1, 3, 6, or 10 atoms depending on $M$, see Sec. A.2.1. It is isomorphic with fcc($N$, $M$, $K_a$) as discussed above and in Sec. A.2.1.

**Upper central *K* range** of fcc($N$, $M$, $K$) where with (A.43), (A.52)

$K_b \leq K \leq K_a$ (A.55)

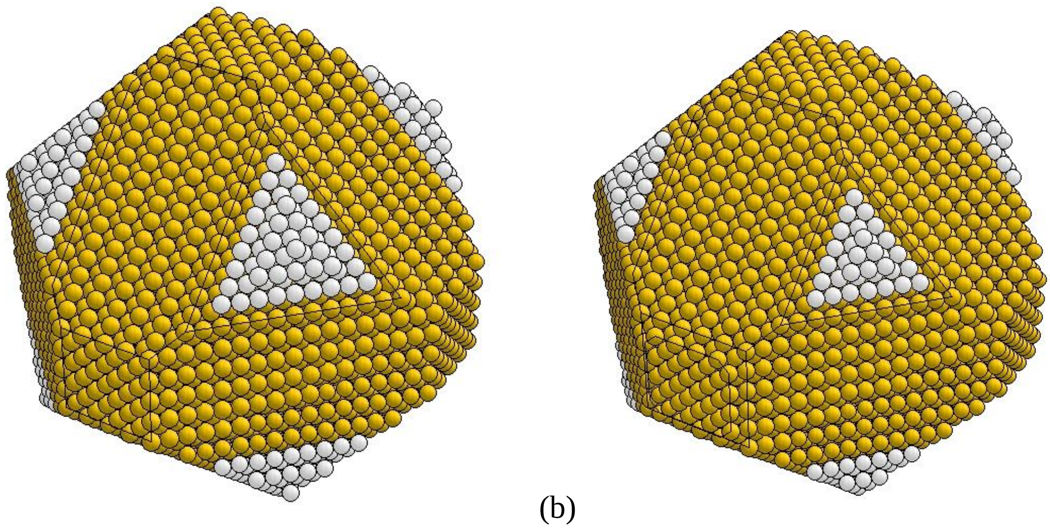
For these $K$ values the initial fcc($N$, $M$, $K_a$) NP is capped at its <111> corners forming eight larger {111} facets of equilateral triangular shape. Altogether, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. A.12.

The **{100} facets** for $N + K$ even are square shaped with four <100> edges of length $(M - N)\, a_o$. For $N + K$ odd the facets are octagonal shaped with alternating edges, four <100> of length $(M - N - 1)\, a_o$ and four <110> of length $a_o/\sqrt{2}$.

The **{110} facets** are octagonal or rectangular ($K = K_b$) shaped with two <110>edges of length $(3M - 2K)\, a_o/\sqrt{2}$, two <100> edges of $(M - N + h)\, a_o$, and four <111> edges of $(K + N - 2M - h)/2\ \sqrt{3} a_o$ with (A.5).

The **{111} facets** are triangular shaped with three <110> edges of length $(3M - 2K)\, a_o/\sqrt{2}$.

The NP structures are illustrated in Fig. A.12 for the ac NP fcc(20, 24, 30) ($K_a = 36$, $K_b = 28$) and the vc NP fcc(20, 24, 31) ($K_a = 36$, $K_b = 27$), both shown by yellow atom balls where white atom balls above the {111} facets are added to yield the corresponding cubo-rhombic fcc($N$, $M$, $K_a$) NP.



(a) (b)

**Figure A.12.** Atom ball model of cubo-rhombo-octahedral NPs, (a) atom centered fcc(20, 24, 30) and (b) void centered fcc(20, 24, 31). The NPs are shown by yellow balls with white atom balls added for completion, see text. The black lines sketch the square/octaonal {100}, octagonal{110}, and triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (A.22), (A.23) by

$$N_{vol}(N, M, K) \quad = N_{vol}(N, M, -) - (2\, H^3 - 3\, H^2 + 8\, H)/6 + b \qquad \text{(A.56)}$$

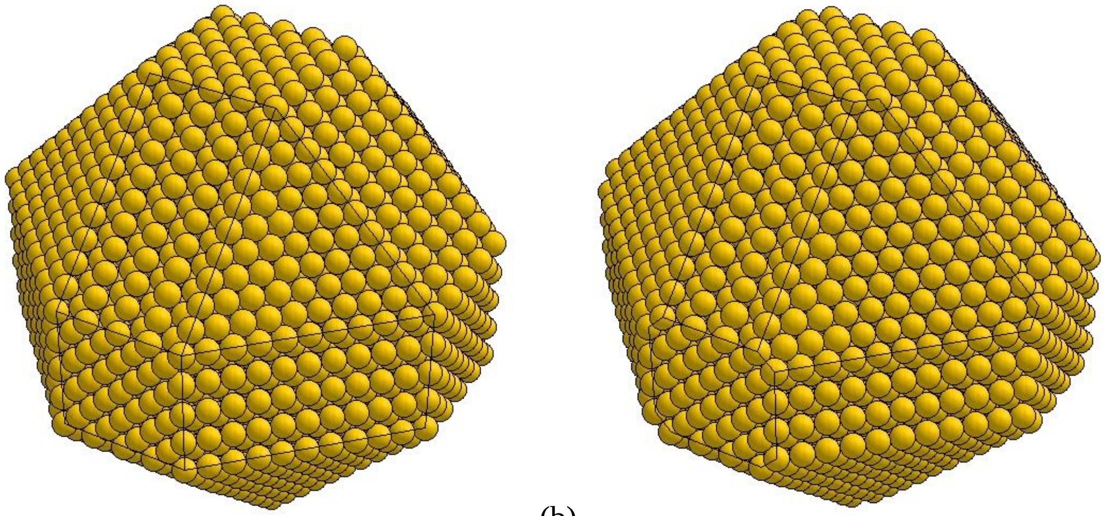
$$N_{facet}(N, M, K) \quad = N_{facet}(N, M, -) + H^2 - c \qquad H = 3M - 2K \qquad \text{(A.57)}$$

with

| Centering | $M = 4p$ | $M = 4p + 1$ | $M = 4p + 2$ | $M = 4p + 3$ |
|---|---|---|---|---|
| ac, $K$ even | $b = 0$<br>$c = 0$ | $b = -3$<br>$c = 9$ | $b = 12$<br>$c = 4$ | $b = 9$<br>$c = 1$ |
| vc, $K$ odd | $b = 12$<br>$c = 4$ | $b = 9$<br>$c = 1$ | $b = 0$<br>$c = 0$ | $b = -3$<br>$c = 9$ |

**Table A.8.** Constants $b$, $c$ used for number of NP atoms of fcc($N$, $M$, $K$) NPs, see text.

For $K = K_b$, the fcc($N$, $M$, $K$) NP assumes a particular shape. Its six **{100} facets** are square/octahedral shaped with alternating edges, four <100> of length $(M - N - h)\ a_o$ and four <110> of length $h\ a_o/\sqrt{2}$. Its twelve **{110} facets** are rectangular shaped with two <110> edges of length $(2N - M)\ a_o/\sqrt{2}$ and two <100> edges of $(M - N - h)\ a_o$. Finally, its eight **{111} facets** are triangular/hexagonal shaped with alternating edges, three <110> of length $(2N - M)\ a_o/\sqrt{2}$ and three <110> of length $h\ a_o/\sqrt{2}$. In all cases, $h$ is given by (A.5). The NP structures are illustrated in Fig. A.13 for (a) fcc(14, 18, 22) ($K_b = 22$) and (b) fcc(14, 18, 21) ($K_b = 21$).



(a) (b)

**Figure A.13.** Atom ball model of cubo-rhombo-octahedral NPs, (a) atom centered fcc(14, 18, 22), (b) void centered fcc(14, 18, 21). The black lines sketch the square {100}, rectangular {110}, and triangular {111} facets.

**Lower central *K* range** of fcc($N$, $M$, $K$) where with (A.52), (A.53)

$$K_c \leq K \leq K_b \quad \text{(A.58)}$$

For these $K$ values the capping of the initial fcc($N$, $M$, $K_b$) along the <111> directions is continued to yield eight hexagonal {111} facets. As before, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. A.14.

The **{100} facets** are octagonal shaped with alternating edges, four <100> of length $(K - M)\, a_o$ and four <110> of length $(K_b - K)\, a_o/\sqrt{2}$.

The **{110} facets** are rectangular shaped with two <110> edges of length $(2N - M)\, a_o/\sqrt{2}$ and two <100> edges of length $(K - M)\, a_o$.

The **{111} facets** are hexagonal shaped with <110> edges of alternating lengths $(K_b - K)\, a_o/\sqrt{2}$ and $(2N - M)\, a_o/\sqrt{2}$.

This is illustrated in Fig. A.14 for the vc NP fcc(15, 21, 23) ($K_b = 27$, $K_c = 21$) where white atom balls above the {111} facets are added to fcc($N$, $M$, $K$) to yield the corresponding fcc($N$, $M$, $K_b$) NP.

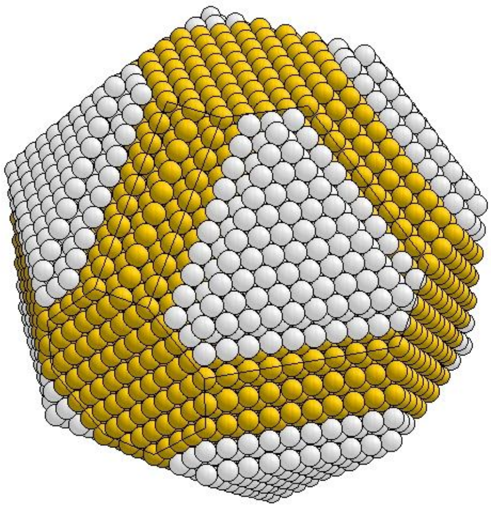


**Figure A.14.** Atom ball model of a void centered cubo-rhombo-octahedral NP, fcc(15, 21, 23) shown by yellow balls with white atom balls completing the NP, see text. The black lines sketch the octagonal {100}, rectangular{110}, and hexagonal/triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (A.56), (A.57), (A.5) by

$$N_{vol}(N, M, K) = N_{vol}(N, M, K_b) - 2/3\, H\, \{(H+2)\,(2\,H + 12\,G - 1 + 6h)/2 + 3\,G\,(G - 5 + 4h)\} \quad \text{(A.59)}$$

$$N_{facet}(N, M, K) = N_{facet}(N, M, K_b) + 2H\,(2G - H - 2h) \quad \text{(A.60)}$$

$H = K_b - K$ ,     $G = 2N - M$

**Inner *K* range** of fcc($N$, $M$, $K$) where with (A.53)

$$K \leq K_c \tag{A.61}$$

For these $K$ values the NP becomes cubo-octahedral and does not exhibit any {110} facets. It is isomorphic with fcc($N$, $M_a$, $K$) as discussed above and in Sec. A.2.2.

The present discussion allows a classification of fcc($N$, $M$, $K$) NPs for all combinations of polyhedral parameters $N$, $M$, $K$. This includes NPs where one or two parameters define the structure already uniquely. Table A.9 illustrates all possible NP types.

| Constraints 1 | Constraints 2 | NP types | fcc Isomorphs |
|---|---|---|---|
| $M \geq 2N$ | $K \geq 3N$ | Generic cubic | $(N, -, -) =$<br>$(N, 2N, 3N)$ |
| | $2N \leq K \leq 3N$ | Cubo-octahedral truncated cubic | $(N, -, K) =$<br>$(N, 2N, K)$ |
| | $K = 2N$ ($K$ even) | Cuboctahedral | $(N, -, K) =$<br>$(N, 2N, 2N)$ |
| | $N \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | $(N, -, K) =$<br>$(N, K, K)$ |
| | $K \leq N$ | Octahedral | $(-, -, K) =$<br>$(K, K, K)$ |
| $N + h' \leq M \leq 2N$<br>$M_u = N + h'$ | $K \geq K_a$ | Cubo-rhombohedral | $(N, M, -) =$<br>$(N, M, K_a)$ |
| | $K_b \leq K \leq K_a$ | Cubo-rhombo-oct. upper central | $(N, M, K)$ |
| | $K_c \leq K \leq K_b$ | Cubo-rhombo-oct. lower central | $(N, M, K)$ |
| | $N \leq K \leq K_c$ | Cubo-octahedral truncated octahedral | $(N, -, K) =$<br>$(N, K, K)$ |
| | $K \leq N$ | Octahedral | $(-, -, K) =$<br>$(K, K, K)$ |
| $M \leq N + h'$ | $K \geq K_a$ | Generic rhombohedral | $(-, M, -) =$<br>$(N_a, M, K_a)$ |
| | $M - h' \leq K \leq K_a$ | Octo-rhombohedral | $(-, M, K) =$<br>$(N_a, M, K)$ |
| | $K \leq M - h'$ | Generic octahedral | $(-, -, K) =$<br>$(N_a, M_a, K)$ |

**Table A.9.** Constraints and types including isomorphs of fcc($N$, $M$, $K$) NPs, (a) atom centered ($K$ even) and (b) void centered ($K$ odd). Polyhedral parameters $N_a$, $M_a$, $K_a$ are defined above.

Altogether, true cubo-rhombo-octahedral NPs, fcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities

$$N + h' \leq M \leq 2N\,, \qquad K_c \leq K \leq K_a \tag{A.62}$$

with (A.43), (A.53).

## B. Body Centered Cubic (bcc) Nanoparticles

The body centered cubic (bcc) lattice can be defined as a non-primitive simple cubic lattice by lattice vectors $\underline{R}_1$, $\underline{R}_2$, $\underline{R}_3$ in Cartesian coordinates together with two lattice basis vectors $\underline{r}_1$, $\underline{r}_2$ according to

$$\underline{R}_1 = a_o\,(1, 0, 0)\,, \qquad \underline{R}_2 = a_o\,(0, 1, 0)\,, \qquad \underline{R}_3 = a_o\,(0, 0, 1) \qquad \text{(B.1a)}$$

$$\underline{r}_1 = a_o\,(0, 0, 0)\,, \qquad \underline{r}_2 = a_o/2\,(1, 1, 1) \qquad \text{(B.1b)}$$

in Cartesian coordinates where $a_o$ is the lattice constant. The three densest monolayer families {*hkl*} of the bcc lattice are described by six {100} netplanes (square mesh), twelve {110} (centered rectangular mesh, highest atom density), and eight {111} netplanes (hexagonal mesh) where distances between adjacent parallel netplanes are given by

$$d_{\{100\}} = a_o/2\,, \qquad d_{\{110\}} = a_o/\sqrt{2}\,, \qquad d_{\{111\}} = a_o/(2\sqrt{3}) \qquad \text{(B.2)}$$

The point symmetry of the bcc lattice is characterized by $O_h$ with high symmetry centers at all atom sites.

Compact body centered cubic nanoparticles (NPs) are confined by finite sections of monolayers (facets) whose structure is described by different netplanes (*hkl*). If they exhibit central $O_h$ symmetry and show an (*hkl*) oriented facet they must also include all other symmetry related facets characterized by orientations of the complete {*hkl*} family. Thus, general bcc NPs of $O_h$ symmetry are described by facets whose orientation can be defined by those of different {*hkl*} families (denoted {*hkl*} facets in the following). As an example, we mention the {110} family with its twelve netplane orientations (±1 ±1 0), (±1 0 ±1), (0 ±1 ±1). These facets are confined by edges which can be described by families of Miller index directions <*hkl*> (denoted <*hkl*> edges in the following). In addition, NP corners can be characterized by directions <*hkl*> pointing from the NP center to the corresponding corner (denoted {*hkl*} corners in the following). Further, according to the symmetry of the bcc host lattice possible NP centers can only be atom sites of the lattice, the NPs are always atom centered.

Assuming a bcc NP to be confined by facets of the three cubic netplane families, {100}, {110}, and {111}, its size and shape can be described by three integer type structure parameters, *N*, *M*, *K* (polyhedral NP parameters), which refer to the distances $D_{\{100\}}$, $D_{\{110\}}$, $D_{\{111\}}$ (NP diameters) between parallel monolayer facets of a given netplane family expressed by multiples of corresponding netplane distances where

$$D_{\{100\}} = 2N\,d_{\{100\}}\,, \qquad D_{\{110\}} = 2M\,d_{\{110\}}\,, \qquad D_{\{111\}} = 2K\,d_{\{111\}} \qquad \text{(B.3)}$$

with $d_{\{hkl\}}$ according to (B.2), Thus, in the most general case bcc NPs can be denoted **bcc(*N*, *M*, *K*)**. If a facet type does not appear in the NP the corresponding parameter value *N*, *M*, or *K* is replaced by a minus sign. As an example, a bcc NP with only {100} and {110} facets is denoted bcc(*N*, *M*, -). These notations will be used in the following. Further, auxiliary parameters ***g***, ***h*** with

$$g = 0 \quad (K \text{ even}) , \qquad = 1 \quad (K \text{ odd}) \tag{B.4}$$

$$h = 0 \quad (N + K \text{ even}) , \qquad = 1 \quad (N + K \text{ odd}) \tag{B.5}$$

will be used throughout Sec. B.

## B.1. Generic bcc Nanoparticles, bcc(*N*, -, -), (-, *M*, -), and (-, -, *K*) NPs

Generic bcc nanoparticles (NPs) of $O_h$ symmetry are confined by facets with orientations of only one {*hkl*} netplane family. Here we focus on {100}, {110}, and {111} facets derived from the densest monolayers of the bcc lattice which offer the flattest NP facets. This allows to distinguish between three different generic NP types

**(a)** **Generic cubic** bcc NPs, denoted **bcc(*N*, -, -)** (the notation is explained above), are confined by all six {100} monolayers with distances $D_{\{100\}} = 2N\, d_{\{100\}}$ between parallel monolayers. This yields six {100} facets, see Fig. B.1. The **{100} facets** are square shaped with <100> edges of length $N\, a_o$.

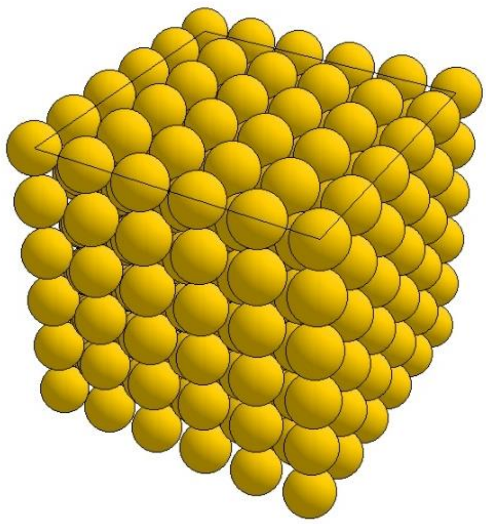


**Figure B.1.** Atom ball model of a generic cubic bcc NP, bcc(5, -, -). The black lines sketch the square {100} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, -)}$, (outer polyhedral shell), are given by

$$N_{vol}(N, -, -) = (N + 1)^3 + N^3 \quad \text{(B.6)}$$

$$N_{facet}(N, -, -) = 6N^2 + 2 \quad \text{(B.7)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given by

$$s_{<100>}(N, -, -) = N\, d_{\{100\}} \quad \text{(B.8a)}$$

$$s_{<110>}(N, -, -) = N\, d_{\{110\}} \quad \text{(B.8b)}$$

$$s_{<111>}(N, -, -) = 3N\, d_{\{111\}} \quad \text{(B.8c)}$$

with $d_{\{hkl\}}$ according to (B.2). These quantities will be used in Secs. B.2.

**(b)** **Generic rhombohedral** bcc NPs, denoted **bcc(-, *M*, -)**, are confined by all twelve {110} monolayers with distances $D_{\{110\}} = 2M\, d_{\{110\}}$ between parallel monolayers. This yields twelve {110} facets, see Fig. B.2.

The **{110} facets** are rhombic shaped with <111> edges of length $M/2\ \sqrt{3}a_o$. Thus, the NPs can be described as rhombic dodecahedra reminding of the shape of Wigner-Seitz cells of the face centered cubic (fcc) crystal lattice [14].

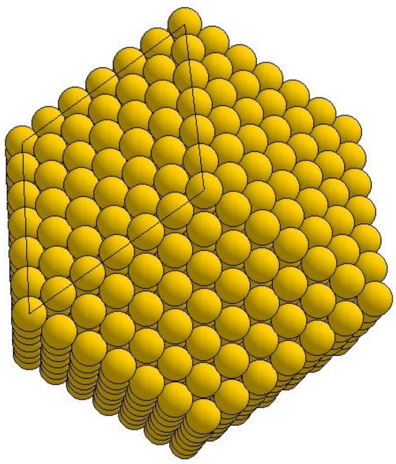


**Figure B.2.** Atom ball model of a generic cubic bcc(-, 6, -) NP. The black lines sketch the rhombic {110}facet shapes.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, M, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, M, -)}$, (outer polyhedral shell), are given by

$$N_{vol}(-, M, -) = (2M + 1)\,[(2M + 1)^2 + 1]/2 \quad \text{(B.9)}$$

$$N_{facet}(-, M, -) = 12M^2 + 2 \quad \text{(B.10)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s}_{<hkl>}$, is given by

$s_{<100>}(-, M, -) = 2M\, d_{\{100\}}$ (B.11a)

$s_{<110>}(-, M, -) = M\, d_{\{110\}}$ (B.11b)

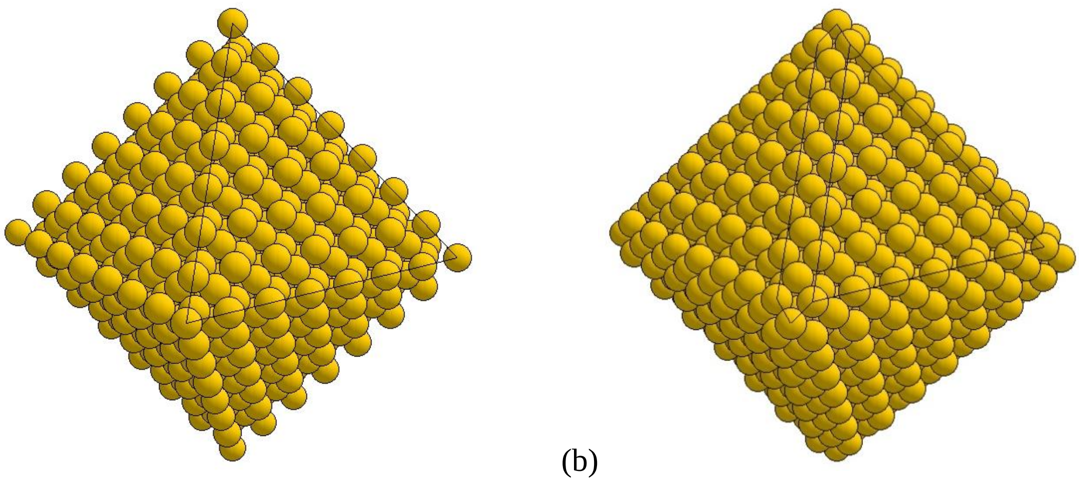
$s_{<111>}(-, M, -) = 3M\, d_{\{111\}}$ (B.11c)

with $d_{\{hkl\}}$ according to (B.2). These quantities will be used in Secs. B.2.

**(c)** **Generic octahedral** bcc NPs, denoted **bcc(-, -, *K*)**, are confined by all eight {111} monolayers with distances $D_{\{111\}} = 2K\, d_{\{111\}}$ between parallel monolayers. This yields eight {111} facets as well as possibly twelve {110} facets, see Fig. B.3.

The **{111} facets** are triangular shaped with three <110> edges of length $K\, a_o/\sqrt{2}$ for $K$ even and of length $(K - 3)\, a_o/\sqrt{2}$ for $K$ odd.

The **{110} facets** appear only for $K$ odd and are hexagonal shaped with two <110> edges of length $(K - 3)\, a_o/\sqrt{2}$ and four <111> edges of length $1/2\, \sqrt{3} a_o$.



(a) (b)

**Figure B.3.** Atom ball models of generic octahedral bcc NPs, (a) bcc(-, -, 14) and (b) bcc(-, -, 15). The black lines sketch the triangular {111} and the stripped {110} facet shapes.

The total number of NP atoms, $\boldsymbol{N_{vol}}$**(-, -, *K*)**, and the number of facet atoms, $\boldsymbol{N_{facet}}$**(-, -, *K*)**, (outer polyhedral shell), are given with (B.4) by

$N_{vol}(-, -, K) = \{(K+1)\, [(K+1)^2 + 1] + K^3 + 4 - 9g\}/6$ (B.12)

$N_{facet}(-, -, K) = K^2 + 2 - 3g$ (B.13)

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s}_{<hkl>}$, is given with (B.4) by

$$s_{<100>}(\text{-}, \text{-}, K) = (K - g)\ d_{\{100\}} \quad \text{(B.14a)}$$

$$s_{<110>}(\text{-}, \text{-}, K) = (K - g)/2\ d_{\{110\}} \quad \text{(B.14b)}$$

$$s_{<111>}(\text{-}, \text{-}, K) = K\ d_{\{111\}} \quad \text{(B.14c)}$$

with $d_{\{hkl\}}$ according to (B.2). These quantities will be used in Secs. B.2.

Table B.1 collects types, constraints, and shapes of all generic bcc NPs.

| Generic type | Constraints | Facets | Corners |
|---|---|---|---|
| Cubic<br>bcc(*N*, -, -) | | {100} 6<br>{110} 0<br>{111} 0 | <100> 0<br><110> 0<br><111> 8 |
| Rhombohedral<br>bcc(-, *M*, -) | | {100} 0<br>{110} 12<br>{111} 0 | <100> 6<br><110> 0<br><111> 8 |
| Octahedral<br>bcc(-, -, *K*) | *K* even | {100} 0<br>{110} 0<br>{111} 8 | <100> 6<br><110> 0<br><111> 0 |
| | *K* odd | {100} 0<br>{110} 12<br>{111} 8 | <100> 6<br><110> 0<br><111> 0 |

**Table B.1.** Types and notations of all generic bcc NPs.

## B.2. Non-generic bcc Nanoparticles

Non-generic bcc nanoparticles of $O_h$ symmetry are always atom centered and show facets with orientations of several {*hkl*} netplane families. This can be considered as combining confinements of the corresponding generic NPs discussed in Sec. B.1 with suitable polyhedral parameters *N*, *M*, *K* sharing their symmetry center. Here we discuss non-generic bcc NPs which combine constraints of up to three generic NPs, cubic bcc(*N*, -, -), rhombohedral bcc(-, *M*, -), and octahedral bcc(-, -, *K*). These allow {100}, {110}, as well as {111} facets and will be denoted **bcc(*N*, *M*, *K*)** in the following. Clearly, the corresponding polyhedral parameters *N*, *M*, *K* depend on each other and determine the overall NP shape. In particular, if a participating generic NP encloses another participant it will not contribute to the overall NP shape and the respective {*hkl*} facets will not appear at the surface of the non-generic NP. In the following, we consider the three types of non-generic NPs which combine constraints due to two generic NPs (Secs. B.2.1-3) before we discuss the most general case of bcc($N$, $M$, $K$) NPs in Sec. B.2.4.

### B.2.1 Combining (100) and (110) Facets, bcc(*N*, *M*, -) NPs

Non-generic **cubo-rhombic** NPs, denoted **bcc(*N*, *M*, -)**, are confined by facets referring to the two generic NPs, bcc($N$, -, -) (cubic) and bcc(-, $M$, -) (rhombohedral). Thus, they can show {100} as well as {110} facets depending on relations between the polyhedral parameters $N$, $M$. If the edges of the cubic NP bcc($N$, -, -) lie inside the rhombohedral NP bcc(-, $M$, -) the resulting combination bcc($N$, $M$, -) will be generic cubic which can be expressed formally by

$$s_{<110>}(N, -, -) \leq s_{<110>}(-, M, -) \qquad \text{(B.15)}$$

leading, according to (B.8), (B.11), to

$$N \leq M \qquad \text{(B.16)}$$

On the other hand, if the corners of the rhombohedral NP bcc(-, $M$, -) lie inside the cubic NP bcc($N$, -, -) the resulting combination bcc($N$, $M$, -) will be generic rhombohedral which can be expressed formally by

$$s_{<100>}(-, M, -) \leq s_{<100>}(N, -, -) \qquad \text{(B.17)}$$

leading, according to (B.8), (B.11), to

$$N \geq 2M \qquad \text{(B.18)}$$

Thus, the two generic NPs intersect and define a true non-generic NP bcc($N$, $M$, -) offering both {100} and {110} facets only for polyhedral parameters $N$, $M$ with

$$M < N < 2M \qquad \text{(B.19)}$$

while bcc($N$, $M$, -) is generic cubic for smaller $N$ according to (B.16) and generic rhombohedral for larger $N$ according to (B.18). This suggests that generic cubic and rhombohedral bcc NPs can be considered as special cases of non-generic NPs bcc($N$, $M$, -) where

$$\text{bcc}(N, -, -) = \text{bcc}(N, M = N, -) \qquad \text{(cubic)} \qquad \text{(B.20a)}$$

$$\text{bcc}(-, M, -) = \text{bcc}(N = 2M, M, -) \qquad \text{(rhombohedral)} \qquad \text{(B.20b)}$$

Parameters $N$, $M$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, cubo-rhombic NPs bcc($N$, $M$, -) exhibit six {100} facets and twelve {110} facets, see Fig. B.4.

The **{100} facets** are square shaped with four <100> edges of length $(2M - N)\, a_o$.

The **{110} facets** are hexagonal shaped with four <111> edges of length $(N - M)/2\ \sqrt{3}a_o$ and two <100> edges of length $(2M - N)\ a_o$.

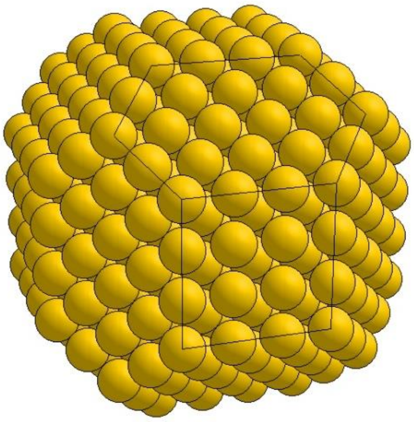


**Figure B.4.** Atom ball model of the cubo-rhombic NP bcc(7, 5, -). The black lines sketch the square {100} and hexagonal {110} facet shapes.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, -)}$, (outer polyhedral shell) are given with (B.9), (B.10) by

$$N_{vol}(N, M, -) \quad = N_{vol}(-, M, -) - H\,(H + 1)\,(2H + 1)\,, \qquad H = 2M - N \tag{B.21}$$

$$N_{facet}(N, M, -) = N_{facet}(-, M, -) - 6\,(2M - N)^2 \tag{B.22}$$

The present discussion allows a classification of bcc($N$, $M$, -) NPs for all combinations of polyhedral parameters $N$, $M$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table B.2 illustrates all possible NP types.

| Constraints | NP types | bcc Isomorphs |
|---|---|---|
| $N \geq 2M$ | Generic rhombohedral | (-, $M$, -) =<br>($N$ = 2$M$, $M$, -) |
| $M \leq N \leq 2M$ | Cubo-rhombic | ($N$, $M$, -) |
| $N \leq M$ | Generic cubic | ($N$, -, -) =<br>($N$, $M$ = $N$, -) |

**Table B.2.** Constraints and types including isomorphs of cubo-rhombic bcc($N$, $M$, -) NPs. All NPs are atom centered.

### B.2.2 Combining (100) and (111) Facets, bcc(*N*, -, *K*) NPs

Non-generic **cubo-octahedral** NPs, denoted **bcc(*N*, -, *K*)**, are confined by facets referring to the two generic NPs, bcc(*N*, -, -) (cubic) and bcc(-, -, *K*) (octahedral). Thus, they can show {100} as well as {111} facets (apart from {110} microstrips) depending on the polyhedral parameters *N*, *K*. Clearly, both generic NPs must be atom centered to yield a non-generic sc NP of $O_h$ symmetry. If the corners of the cubic NP bcc(*N*, -, -) lie inside the octahedral NP bcc(-, -, *K*) the resulting combination bcc(*N*, -, *K*) will be generic cubic which can be expressed formally by

$$s_{<111>}(N, -, -) \leq s_{<111>}(-, -, K) \tag{B.23}$$

leading, according to (B.8), (B.14), to

$$3N \leq K \tag{B.24}$$

On the other hand, if the corners of the octahedral NP bcc(-, -, *K*) lie inside the cubic NP bcc(*N*, -, -) the resulting combination bcc(*N*, -, *K*) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(N, -, -) \tag{B.25}$$

leading, according to (B.8), (B.14), to

$$N \geq K - g \tag{B.26}$$

Thus, the two generic NPs intersect and define a true non-generic NP bcc(*N*, -, *K*) offering both {100} and {111} facets only for polyhedral parameters *N*, *K* with

$$N + g < K < 3N \tag{B.27}$$

while bcc(*N*, -, *K*) is generic cubic for larger *K* according to (B.24) and generic octahedral for smaller *K* according to (B.26). This suggests that generic cubic and octahedral bcc NPs can be considered as special cases of non-generic NPs bcc(*N*, -, *K*) where

$$\text{bcc}(N, -, -) = \text{bcc}(N, -, K = 3N) \quad \text{(cubic)} \tag{B.28a}$$

$$\text{bcc}(-, -, K) = \text{bcc}(N = K - g, -, K) \quad \text{(octahedral)} \tag{B.28b}$$

Further, amongst the true intersecting cubo-octahedral NPs according to (B.27) we can distinguish between so-called **truncated octahedral** NPs where $K < 2N$ and **truncated cubic** NPs for $K > 2N$ as will be discussed in the following.

Parameters *N*, *K* provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, cubo-octahedral NPs bcc(*N*, -, *K*) exhibit six {100}, twelve {110}, and eight {111} facets, see Figs. B.5, B.6, B.7.

**Truncated octhedral** NPs ($K < 2N$), Figs. B.5, B.6, can be characterized by their facets as follows.

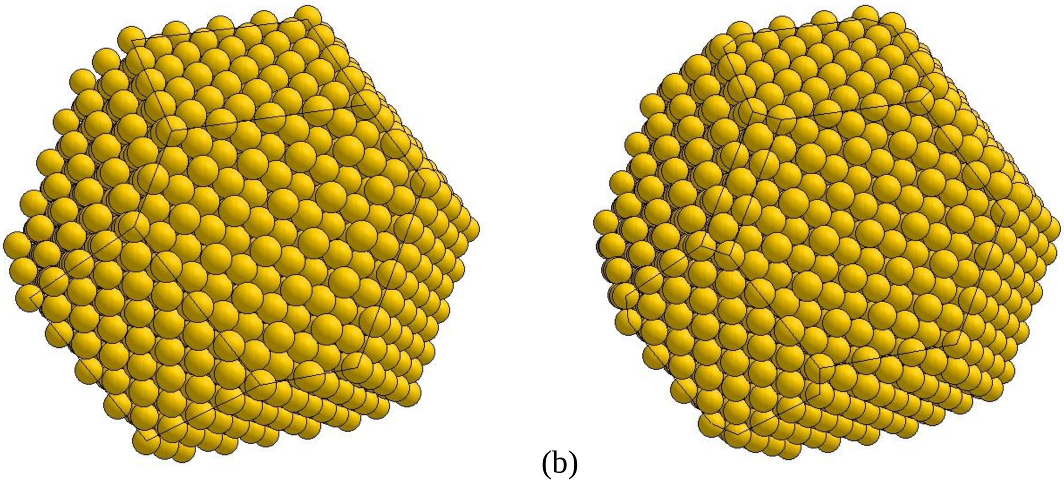
The **{100} facets** for $N$ even are square shaped with four <110> edges of length $(K - N)/2\ \sqrt{2}a_o$ (with $K$ even) or $(K - N - 1)/2\ \sqrt{2}a_o$ (with $K$ odd). For $N$ odd the facets are octagonal (capped square) shaped with alternating edges, four <100> of length $a_o$ and four <110> of length $(K - N - 3)/2\ \sqrt{2}a_o$ (with $K$ even) or $(K - N - 2)/2\ \sqrt{2}a_o$ (with $K$ odd).

The **{111} facets** are hexagonal shaped with three <110> edges of alternating lengths $(K - N + b)/2\ \sqrt{2}a_o$ and $(2N - K + c)/2\ \sqrt{2}a_o$ where constants $b$, $c$ are given in the following table.

| | | $b$ | $c$ |
|---|---|---|---|
| $N$ even | $K$ even | 0 | 0 |
| | $K$ odd | -1 | -1 |
| $N$ odd | $K$ even | 1 | -2 |
| | $K$ odd | -2 | 1 |

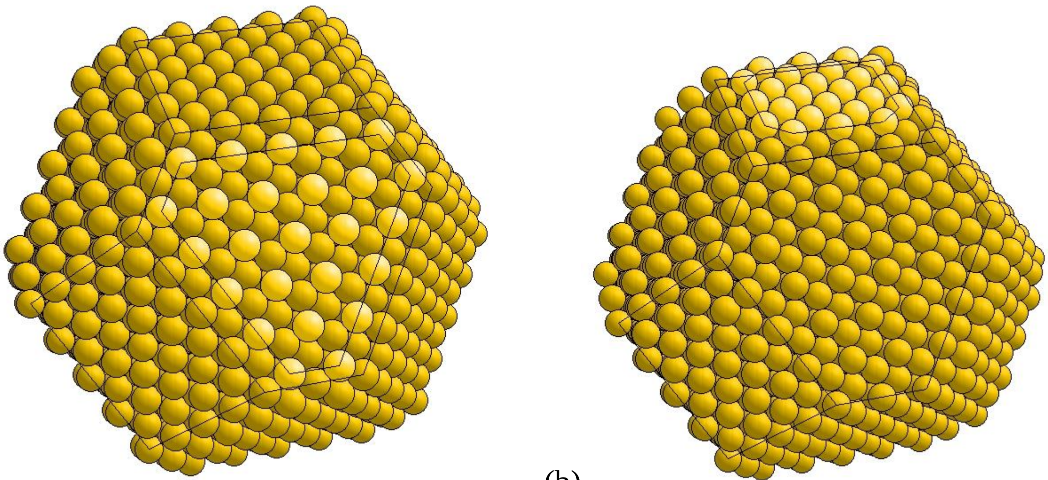
**Table B.3.** Constants $b$, $c$ used for edge lengths of {111} facets of bcc($N$, -, $K$) NPs, see text.

The **{110} facets** appear only for $K$ odd and are for $N$ even hexagonal shaped with two <110> edges of lengths $(2N - K - 1)/2\ \sqrt{2}a_o$ and four <111> edges of length $1/2\ \sqrt{3}a_o$. For $N$ odd the facets are rectangular shaped with two <110> edges of lengths $(2N - K + 1)/2\ \sqrt{2}a_o$ and two <100> edges of length $a_o$.



(a) (b)

**Figure B.5.** Atom ball models of cubo-octahedral bcc NPs of truncated octahedral type, (a) bcc(12, -, 20) and (b) bcc(13, -, 21). The black lines sketch the square / octagonal {100}, the hexagonal {111} facets, and connecting {110} facets, see text.



(a) (b)

**Figure B.6.** Atom ball models of cubo-octahedral bcc NPs of truncated octahedral type, (a) bcc(12, -, 21) and (b) bcc(13, -, 20). The black lines sketch the square / octagonal {100} and the hexagonal {111} facets. The light color balls indicate one (a) {111} and (b) {100}facet, see text.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (B.12), (B.13), (B.4), (B.5) by

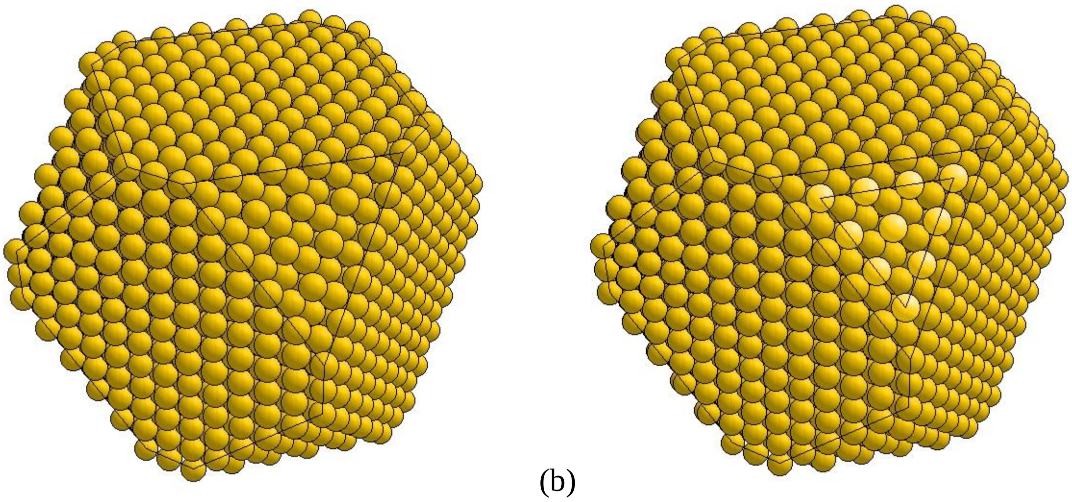
$$N_{vol}(N, -, K) = N_{vol}(-, -, K) - H\,(H^2 - 1) - 3h\,(H + 1 - 2g)\,, \qquad H = K - N \tag{B.29}$$

$$N_{facet}(N, -, K) = N_{facet}(-, -, K) + 6h\,(2g - 1) \tag{B.30}$$

**Truncated cubic** NPs ($K > 2N$), Fig. B.7, can be characterized by their facets as follows.

The **{100} facets** are octagonal shaped with alternating edges, four <110> of length $(3N - K + h)/2\ \sqrt{2}a_o$ and four <100> of length $(K - 2N - h)\ a_o$ with (B.5).

The **{111} facets** are triangular shaped with three <110> edges of length $(3N - K)/2\ \sqrt{2}a_o$ (if $N + K$ even) or of length $(3N - K - 3)/2\ \sqrt{2}a_o$ (if $N + K$ odd).



(a) (b)

**Figure B.7.** Atom ball models of cubo-octahedral bcc NPs of truncated cubic type, (a) bcc(12, -, 26) and (b) bcc(12, -, 27). black lines sketch the octagonal {100} and the triangular {111} facets. The light color balls indicate one {111} facet, see text.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (B.6), (B.7), (B.5) by

$$N_{vol}(N, -, K) = N_{vol}(N, -, -) - (H + 1)\ (H^2 + 2H + 9h)/3\ , \qquad H = 3N - K \qquad \text{(B.31)}$$

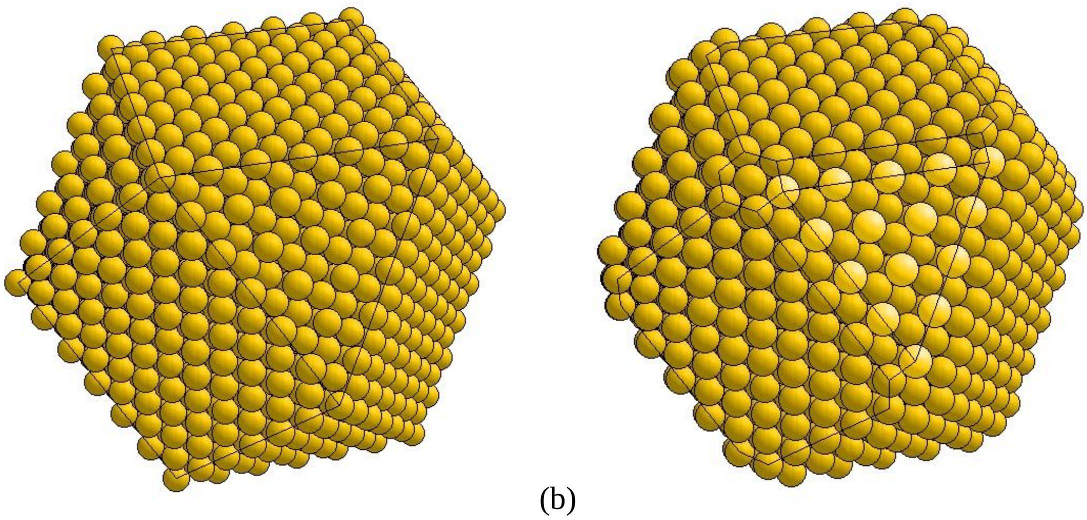
$$N_{facet}(N, -, K) = N_{facet}(N, -, -) - 2\ (K - 3N)^2 - 6h \qquad \text{(B.32)}$$

There are bcc NPs which can be assigned to both truncated cubic and truncated octahedral type, the **generic cuboctahedral** bcc($N$, -, $K$) NPs, defined by $K = 2N$. These NPs exhibit six {100}, eight {111}, and twelve possible {110} facets, see Fig. B.8.

**The {100} facets** are square shaped with four <110> edges of length $N/2\ \sqrt{2}a_o$ if $N$ even while for $N$ odd the facets are octagonal (capped square) shaped with alternating edges, four <110> of length $(N - 3)/2\ \sqrt{2}a_o$ and four <100> of length $a_o$.

**The {110} facets** appear only for $N$ odd and are hexagonal shaped with two <100> edges of length $a_o$ and four <111> edges of length $1/2\ \sqrt{3}a_o$.

**The {111} facets** are triangular shaped with <110> edges of length $N/2\ \sqrt{2}a_o$ if $N$ even and of length $(N - 3)/2\ \sqrt{2}a_o$ if $N$ odd.



(a) (b)

**Figure B.8.** Atom ball models of cuboctahedral bcc NPs, (a) bcc(12, -, 24) and (b) bcc(11, -, 22). black lines sketch the square / octagonal {100}and triangular {111} facets with connecting hexagonal {110} facets and {112} strips. The light color balls indicate one {111} facet, see text.

The present discussion allows a classification of bcc($N$, -, $K$) NPs for all combinations of polyhedral parameters $N$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table B.4 illustrates all possible NP types.

| Constraints | NP types | bcc Isomorphs |
| --- | --- | --- |
| $K \geq 3N$ | Generic cubic | ($N$, -, -) =<br>($N$ , -, $K$ = 3$N$) |
| $2N \leq K \leq 3N$ | Cubo-octahedral truncated cubic | ($N$, -, $K$) |
| $K = 2N$ | Cuboctahedral | ($N$, -, $K$ = 2$N$) ,<br>($N$ = $K$/2, -, 2$K$) |
| $N \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) |
| $K \leq N$<br><br>$N_u = K$, $K$ even<br>$= K - 1$ $K$ odd | Generic octahedral | (-, -, $K$) =<br>($N = N_u$, -, $K$) |

**Table B.4.** Constraints and types including isomorphs of bcc($N$, -, $K$) NPs.

### B.2.3 Combining (110) and (111) Facets, bcc(-, *M*, *K*) NPs

Non-generic **rhombo-octahedral** NPs, denoted **bcc(-, *M*, *K*)**, are confined by facets referring to the two generic NPs, bcc(-, $M$, -) (rhombohedral) and bcc(-, -, $K$) (octahedral). Thus, they can show {110} as well as {111} facets depending on the polyhedral parameters $M$, $K$. Clearly, both generic NPs must be atom centered to yield a non-generic sc NP of $O_h$ symmetry. If the corners of the rhombohedral NP bcc(-, $M$, -) lie inside the octahedral NP bcc(-, -, $K$) the resulting combination bcc(-, $M$, $K$) will be generic rhombohedral which can be expressed formally by

$$s_{<111>}(-, M, -) \leq s_{<111>}(-, -, K) \quad \text{(B.33)}$$

leading, according to (B.11), (B.14), to

$$3M \leq K \quad \text{(B.34)}$$

On the other hand, if the corners of the octahedral NP bcc(-, -, $K$) lie inside the rhombohedral NP bcc(-, $M$, -) the resulting combination bcc(-, $M$, $K$) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(-, M, -) \quad \text{(B.35)}$$

leading, according to (B.11), (B.14), to

$$2M \geq K - g \quad \text{(B.36)}$$

Thus, the two generic NPs intersect and define a true non-generic NP bcc(-, $M$, $K$) offering both {110} and {111} facets only for polyhedral parameters $M$, $K$ with

$2M + g < K < 3M$ (B.37)

while bcc(-, $M$, $K$) is generic rhombohedral for larger $K$ according to (B.34) and generic octahedral for smaller $K$ according to (B.36). This suggests that generic rhombohedral and octahedral bcc NPs can be considered as special cases of non-generic NPs bcc(-, $M$, $K$) where

bcc(-, $M$, -) = bcc(-, $M$, 3$M$) (rhombohedral) (B.38a)

bcc(-, -, $K$) = bcc(-, $K$/2, $K$) (octahedral, $K$ even) (B.38b)

bcc(-, -, $K$) = bcc(-, ($K$ - 1)/2, $K$) (octahedral, $K$ odd) (B.38c)

Parameters $M$, $K$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, rhombo-octahedral NPs bcc(-, $M$, $K$) exhibit twelve {110} and eight {111} facets, see Fig. B.9.

The **{110} facets** are hexagonal shaped with four <111> edges of length $(K - 2M)/2\ \sqrt{3} a_o$ and two <110> edges of length $(3M - K)\ \sqrt{2} a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $(3M - K)\ \sqrt{2} a_o$.

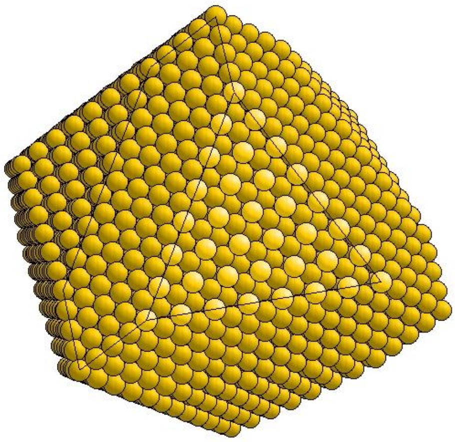


**Figure B.9.** Atom ball models of the rhombo-octahedral NP bcc( -, 11, 26). The black lines sketch the hexagonal {110}and triangular {111} facets. One {111} facet is emphasized by atom balls of light color.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, M, K)}$, (outer polyhedral shell) are given with (B.9), (B.10) by

$N_{vol}(-, M, K) = N_{vol}(-, M, -) - 4H (H + 1) (H + 2)/3$ , $H = 3M - K$ (B.39)

$N_{facet}(-, M, K) = N_{facet}(-, M, -) - 8 (3M - K)^2$ (B.40)

The present discussion allows a classification of bcc(-, $M$, $K$) NPs for all combinations of polyhedral parameters $M$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table B.5 illustrates all possible NP types.

| Constraints | NP types | bcc Isomorphs |
|---|---|---|
| $K \geq 3M$ | Generic rhombohedral | (-, $M$, -) =<br>(-, $M$, $K = 3M$) |
| $2M \leq K \leq 3M$ | Rhombo-octahedral | (-, $M$, $K$) |
| $K \leq 2M$<br><br>$M_u$= K/2    $K$ even<br>= $(K - 1)/2$    $K$ odd | Generic octahedral | (-, -, $K$) =<br>(-, $M = M_u$, $K$) |

**Table B.5.** Constraints and types including isomorphs of bcc(-, $M$, $K$) NPs.

### B.2.4 Combining (100), (110), and (111) Facets, bcc(*N*, *M*, *K*) NPs

Non-generic **cubo-rhombo-octahedral** NPs, denoted **bcc(*N*, *M*, *K*)**, are confined by facets referring to all three generic NPs, bcc($N$, -, -) (cubic), bcc(-, $M$, -) (rhombohedral), and bcc(-, -, $K$) (octahedral). Thus, they can show {100}, {110}, and {111} facets depending on the polyhedral parameters $N$, $M$, $K$. Clearly, bcc($N$, $M$, $K$) NPs must contain an atom at their center to yield a non-generic bcc NP of $O_h$ symmetry. A general discussion of these NPs requires a number of different scenarios using results of for generic and non-generic NPs with one or two types of facets, Secs. B. 1, B.2.1-3, as will be detailed in the following.

First, we consider the general notation for generic bcc NPs discussed in Sec. B.1. Cubic NPs bcc($N$, -, -) are surrounded by rhombohedral NPs bcc(-, $M$, -) if $M \geq N$ according to (B.16) and by octahedral NPs bcc(-, -, $K$) if $K \geq 3N$ according to (B.24). This allows a notation bcc($N$, $M$, $K$) where

$$\text{bcc}(N, -, -) = \text{bcc}(N, M = N, K = 3N) \qquad \text{(B.41)}$$

Further, rhombohedral NPs bcc(-, $M$, -) are surrounded by cubic NPs bcc($N$, -, -) if $N \geq 2M$ according to (B.18) and by octahedral NPs bcc(-, -, $K$) if $K \geq 3M$ according to (B.34). This allows a notation bcc($N$, $M$, $K$) where

$$\text{bcc}(-, M, -) = \text{bcc}(N = 2M, M, K = 3M) \qquad \text{(B.42)}$$

In addition , the octahedral NPs bcc(-, -, $K$) are surrounded by cubic NPs bcc($N$, -, -) if $N$, $K$ satisfy relations (B.26) and by rhombohedral NPs bcc(-, $M$, -) if $M$, $K$ satisfy relations (B.36). This allows a notation bcc($N$, $M$, $K$) where

$$\text{bcc}(-, -, K) = \text{bcc}(N = K - g, M = (K - g)/2, K) \quad \text{(B.43)}$$

General notations for non-generic bcc NPs discussed in Secs. B.2.1-3 are obtained by analogous arguments. According to Sec. B.2.1, true cubo-rhombic NPs bcc($N$, $M$, -) with both {100} and {110} facets are subject to $M \leq N \leq 2M$ according to (B.19). They are surrounded by octahedral NPs bcc(-, -, $K$) if $K \geq K_a$ with

$$K_a(N, M) = \min(3N, 3M) = 3M \quad \text{(B.44)}$$

This allows a general notation bcc($N$, $M$, $K$) where

$$\text{bcc}(N, M, -) = \text{bcc}(N, M, K = K_a) \quad \text{(B.45)}$$

According to Sec. B.2.2, true cubo-octahedral NPs bcc($N$, -, $K$) with both {100} and {111} facets are subject to $N\ (+\ 1) \leq K \leq 3N$ ($K$ even) according to (B.27). They are surrounded by rhombohedral NPs bcc(-, $M$, -) if $M \geq M_a$ with

$$M_a(N, K) = \min((K - g)/2, N) \quad \text{(B.46)}$$

This allows a general notation bcc($N$, $M$, $K$) where

$$\text{bcc}(N, -, K) = \text{bcc}(N, M = M_a, K) \quad \text{(B.47)}$$

According to Sec. B.2.3, true rhombo-octahedral NPs bcc(-, $M$, $K$) with both {110} and {111} facets are subject to $2M\ (+\ 1) \leq K \leq 3M$ according to (B.37). They are surrounded by cubic NPs bcc($N$, -, -) if $N \geq N_a$ with

$$N_a(M, K) = \min(2M, K) = 2M \quad \text{(B.48)}$$

This allows a general notation bcc($N$, $M$, $K$) where

$$\text{bcc}(-, M, K) = \text{bcc}(N = N_a, M, K) \quad \text{(B.49)}$$

In the most general case of a true bcc($N$, $M$, $K$) NP with {100}, {110}, and {111} facets we start from a true cubo-rhombic NP, bcc($N$, $M$, -), with its constraints $M \leq N \leq 2M$ and add constraints of a generic octahedral NP, bcc(-, -, $K$), where according to the discussion above $K$ values are below $K_a$. This allows to distinguish four different ranges of parameter $K$, defined by separating values $K_a \geq K_b \geq K_c$, with $K_a$ given by (B.44) and

$K_b(N, M) = 4M - N$ (B.50)

$K_c(N, M) = 2M$ (N even) (B.51a)

$= 2M + 1$ (N odd) (B.51b)

which result in different NP shapes starting from the initial cubo-rhombic NP bcc($N$, $M$, $K_a$) as illustrated for bcc(18, 12, 36) in Fig. B.10.

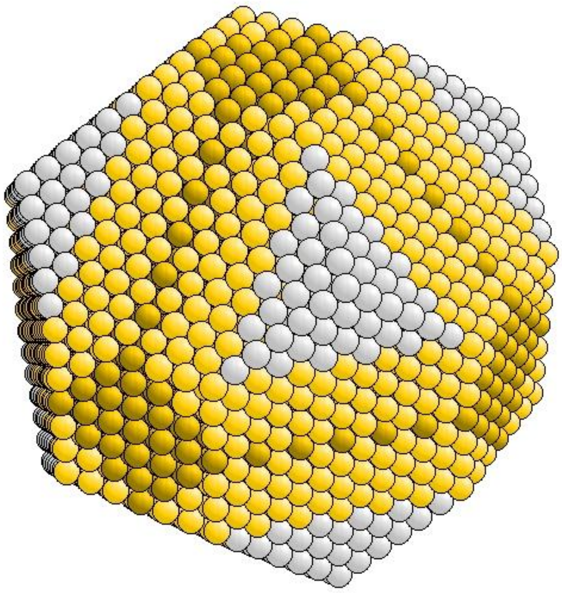


**Figure B.10.** Atom ball model of a cubo-rhombic NP, bcc(18, 12, 36) ($K = K_a$, all atom balls), with its cubo-rhombo-octahedral NP components, bcc(18, 12, 30) ($K = K_b$), and bcc(18, 12, 24) ($K = K_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $K$ ranges at $K = K_c$ (inner vs. lower central ) and at $K = K_b$, (lower vs. upper central), respectively, see text.

**Outer *K* range** of bcc($N$, $M$, $K$) where with (B.44)

$K \geq K_a$ (B.52)

For these $K$ values the NP becomes cubo-rhombohedral and does not exhibit any {111} facets (except for microfacets with three atoms). It is isomorphic with bcc($N$, $M$, $K_a$) as discussed above and in Sec. B.2.1.

**Upper central *K* range** of bcc($N$, $M$, $K$) where with (B.50), (B.51)

$K_b \leq K \leq K_a$ (B.53)

For these $K$ values the initial bcc($N$, $M$, $K_a$) NP is capped at its <111> corners forming eight additional {111} facets of equilateral triangular shape. Altogether, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. B.11.

The **{100} facets** are square shaped with four <100> edges of length (2$M$ - $N$) $a_o$.

The **{110} facets** are octagonal or rectangular ($K = K_b$) shaped with two <110> edges of length (3$M$ - $K$) $\sqrt{2}a_o$, two <100> of length (2$M$ - $N$) $a_o$, and two <111> of length ($K$ + N - 4M)/2 $\sqrt{3}a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length (3$M$ - $K$) $\sqrt{2}a_o$.

The NP structure is illustrated in Fig. B.11 for the NP bcc(18, 10, 26) ($K_a$ = 30, $K_b$ = 22, yellow atom balls) where white balls above the {111} facets are added to yield the corresponding cubo-rhombic bcc($N$, $M$, $K_a$) NP.

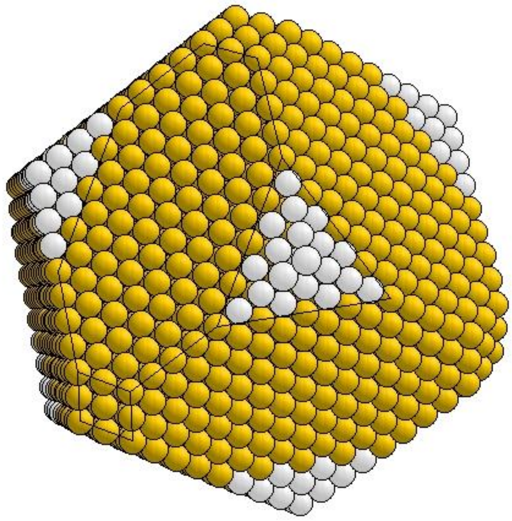


**Figure B.11.** Atom ball model of a cubo-rhombo-octahedral bcc NP, bcc(18, 10, 26), shown by yellow balls with white atom balls completing the NP, see text. The black lines sketch the square {100}, octagonal{110}, and triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (B.21), (B.22) by

$$N_{vol}(N, M, K) = N_{vol}(N, M, -) - 4H (H + 1) (H + 2)/3 , \quad H = 3M - K \qquad \text{(B.54)}$$

$$N_{facet}(N, M, K) = N_{facet}(N, M, -) - 8 H^2 \qquad \text{(B.55)}$$

For $K = K_b$, the bcc($N$, $M$, $K$) NP assumes a particular shape where its twelve **{110} facets** are rectangular with two edges of length ($N$ - $M$) $\sqrt{2}a_o$ and of (2$M$ - $N$) $a_o$ while the **{100}** and **{111} facets** are square and triangular shaped as described before. This is illustrated in Fig. B.12 for the NP bcc(12, 8, 20) ($K_b$ = 20).

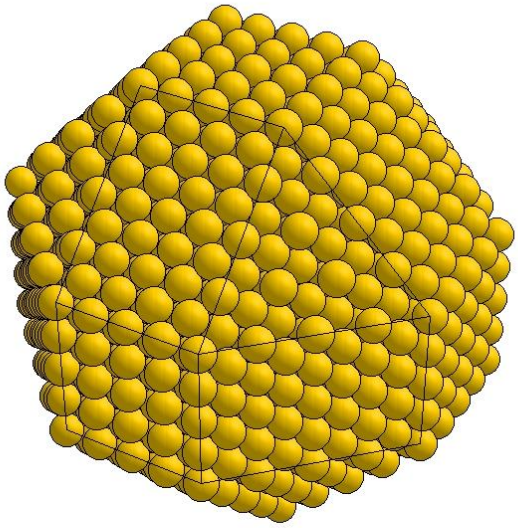


**Figure B.12.** Atom ball model of a cubo-rhombo-octahedral bcc NP, void centered bcc(12, 8, 20). The black lines sketch the square {100}, rectangular {110}, and triangular {111} facets.

**Lower central *K* range** of bcc($N$, $M$, $K$) where with (B.51)

$$K_c \leq K \leq K_b \tag{B.56}$$

For these $K$ values the capping of the initial bcc($N$, $M$, $K_b$) along the <111> directions is continued to yield eight hexagonal {111} facets. As before, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. B.13.

The **{100} facets** are octagonal shaped with alternating edges, four <100> of length ($K$ - 2$M$) $a_o$ and four <110> of length (4$M$ - $N$ - $K$)/2 $\sqrt{2}a_o$.

The **{110} facets** are rectangular shaped with two <110> edges of length ($N$ - $M$) $\sqrt{2}a_o$ and two <100> edges of length ($K$ - 2$M$) $a_o$.

The **{111} facets** are hexagonal shaped with <110> edges of alternating lengths (4$M$ - $N$ - $K$)/2 $\sqrt{2}a_o$ and ($N$ - $M$) $\sqrt{2}a_o$.

The NP structure is illustrated in Fig. B.13 for the NP bcc(18, 12, 26) ($K_b$ = 30, $K_c$ = 24) where white atom balls above the {111} facets are added to bcc($N$, $M$, $K$) to yield the corresponding bcc($N$, $M$, $K_b$) NP.

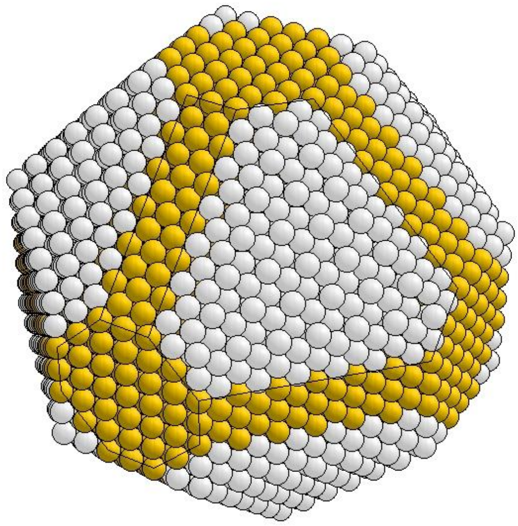


**Figure B.13.** Atom ball model of a cubo-rhombo-octahedral bcc NP, atom centered bcc(18, 12, 26) shown by yellow balls with white atom balls completing the NP, see text. The black lines sketch the octagonal {100}, rectangular{110}, and hexagonal/triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (B.54), (B.55), (B.5) by

$$N_{vol}(N, M, K) = N_{vol}(N, M, K_b) - \\ - H\,\{(H + 2)\,(H + 12G + 1)/3 + 4\,G^2 + 3h\} - 3h \qquad \text{(B.57)}$$

$$N_{facet}(N, M, K) = N_{facet}(N, M, K_b) - 2H\,(H + 8G) - 6h \qquad \text{(B.58)}$$

$$H = 4M - N - K\,, \quad G = N - M$$

**Inner *K* range** of bcc($N$, $M$, $K$) where with (B.51)

$$K \leq K_c \qquad \text{(B.59)}$$

For these $K$ values the NP becomes cubo-octahedral and does not exhibit {110} facets (except for possible microstrips). It is isomorphic with bcc($N$, $M_a$, $K$) as discussed above and in Sec. B.2.2.

The present discussion allows a classification of bcc($N$, $M$, $K$) NPs for all combinations of polyhedral parameters $N$, $M$, $K$. This includes NPs where one or two parameters define the structure already uniquely. Table B.6 illustrates all possible NP types.

| Constraints 1 | Constraints 2 | NP types | bcc Isomorphs |
|---|---|---|---|
| $N \geq 2M$ | $K \geq 3M$ | Generic rhombohedral | (-, $M$, -) = ($N_a$, $M$, $K_a$) |
| | $2M + g \leq K \leq 3M$ | Rhombo-octahedral | (-, $M$, $K$) = ($N_a$, $M$, $K$) |
| | $K \leq 2M + g$ | Generic octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |
| $M \leq N \leq 2M$ | $K \geq 3M$ | Cubo-rhombohedral | ($N$, $M$, -) = ($N$, $M$, $K_a$) |
| | $4M - N \leq K \leq 3M$ | Cubo-rhombo-oct. upper central | ($N$, $M$, $K$) |
| | $2M \leq K \leq 4M - N$ | Cubo-rhombo-oct. lower central | ($N$, $M$, $K$) |
| | $N + g \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K \leq N + g$ | Generic octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |
| $N \leq M$ | $K \geq 3N$ | Generic cubic | ($N$, -, -) = ($N$, $M_a$, $K_a$) |
| | $2N \leq K \leq 3N$ | Cubo-octahedral truncated cubic | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K = 2N$     $K$ even | Cuboctahedral | ($N$, $M_a$, $K$) |
| | $N + g \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K \leq N + g$ | Octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |

**Table B.6.** Constraints and types including isomorphs of bcc($N$, $M$, $K$) NPs. Polyhedral parameters $N_a$, $M_a$, $K_a$ are defined above.

Altogether, true cubo-rhombo-octahedral NPs, bcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities

$$M \leq N \leq 2M, \qquad 2M \leq K \leq 3M \tag{B.60}$$

## C. Simple Cubic (sc) Nanoparticles

The simple cubic (sc) lattice is defined by lattice vectors $\underline{R}_1$, $\underline{R}_2$, $\underline{R}_3$ according to

$$\underline{R}_1 = a_o\,(1, 0, 0)\ , \qquad \underline{R}_2 = a_o\,(0, 1, 0)\ , \qquad \underline{R}_3 = a_o\,(0, 0, 1) \qquad \text{(C.2)}$$

in Cartesian coordinates where $a_o$ is the lattice constant. The three densest monolayer families {*hkl*} of the sc lattice are described by six {100} netplanes (square mesh, highest atom density), twelve {110} (rectangular mesh), and eight {111} netplanes (hexagonal mesh) where distances between adjacent parallel netplanes are given by

$$d_{\{100\}} = a_o\ , \qquad d_{\{110\}} = a_o/\sqrt{2}\ , \qquad d_{\{111\}} = a_o/\sqrt{3} \qquad \text{(C.3)}$$

The point symmetry of the sc lattice is characterized by $O_h$ with high symmetry centers at all atom sites and at the void centers of each elementary cell.

Compact simple cubic nanoparticles (NPs) are confined by finite sections of monolayers (facets) whose structure is described by different netplanes (*hkl*). If they exhibit central $O_h$ symmetry and show an (*hkl*) oriented facet they must also include all other symmetry related facets characterized by orientations of the complete {*hkl*} family. Thus, surfaces of general sc NPs of $O_h$ symmetry are described by facets whose orientation can be defined by those of different {*hkl*} families (denoted {*hkl*} facets in the following). As an example, we mention the {100} family with its six netplane orientations (±1 0 0), (0 ±1 0), (0 0 ±1). These facets are confined by edges which can be described by families of Miller index directions <*hkl*> (denoted <*hkl*> edges in the following). In addition, NP corners can be characterized by directions <*hkl*> pointing from the NP center to the corresponding corner (denoted <*hkl*> corners in the following). Further, according to the symmetry of the sc host lattice possible NP centers can only be atom sites or $O_h$ symmetry void sites of the lattice. Thus, we distinguish between atom centered and void centered sc NPs denoted **ac** and **vc** in the following.

Assuming an sc NP to be confined by facets of the three cubic netplane families, {100}, {110}, and {111}, its size and shape can be described by three integer type structure parameters, *N*, *M*, *K* (polyhedral NP parameters), which refer to the distances $D_{\{100\}}$, $D_{\{110\}}$, $D_{\{111\}}$ (NP diameters) between parallel monolayer facets of a given netplane family expressed by multiples of corresponding netplane distances where

$$D_{\{100\}} = N\, d_{\{100\}}\ , \qquad D_{\{110\}} = 2M\, d_{\{110\}}\ , \qquad D_{\{111\}} = K\, d_{\{111\}} \qquad \text{(C.4)}$$

with $d_{\{hkl\}}$ according to (C.3), Thus, in the most general case sc NPs can be denoted **sc(*N*, *M*, *K*)**. If a facet type does not appear in the NP the corresponding parameter value *N*, *M*, or *K* is replaced by a minus sign. As an example, an sc NP with only {100} and {111} facets is denoted sc(*N*, -, *K*). These notations will be used in the following. Further, auxiliary parameters ***g***, ***h*** with

$$g = 0 \quad (\text{ac; } N, K \text{ even}) , \quad = 1 \quad (\text{vc; } N, K \text{ odd}) \tag{C.5}$$

$$h = 0 \quad (M + N \text{ even; } M + K \text{ even}) , \quad = 1 \quad (M + N \text{ odd; } M + K \text{ odd}) \tag{C.6}$$

will be used throughout Sec. C.

## C.1. Generic sc Nanoparticles, sc(*N*, -, -), (-, *M*, -), and (-, -, *K*) NPs

Generic sc nanoparticles (NPs) of $O_h$ symmetry are confined by facets with orientations of only one {*hkl*} netplane family. Here we focus on {100}, {110}, and {111} facets derived from the densest monolayers of the sc lattice which offer the flattest NP facets. This allows to distinguish between three different generic NP types

**(a)** **Generic cubic** sc NPs, denoted **sc(*N*, -, -)** (the notation is explained above), are confined by all six {100} monolayers with distances $D_{\{100\}} = N\, d_{\{100\}}$ between parallel monolayers. This yields six {100} facets, see Fig. C.1. The **{100} facets** for both ac (*N* even) and vc (*N* odd) are square shaped with <100> edges of length $N\, a_o$.

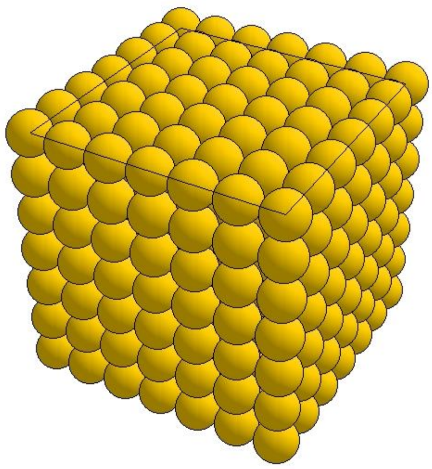


**Figure C.1.** Atom ball model of a generic atom centered NP, sc(6, -, -). The black lines sketch the square {100} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, -)}$, (outer polyhedral shell), are given by

$$N_{vol}(N, -, -) = (N + 1)^3 \qquad \text{(C.7)}$$

$$N_{facet}(N, -, -) = 6N^2 + 2 \qquad \text{(C.8)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, for <*hkl*> = <100>, <110>, and <111>, is given by

$$s_{<100>}(N, -, -) = N/2\ d_{\{100\}} \qquad \text{(C.9a)}$$

$$s_{<110>}(N, -, -) = N\ d_{\{110\}} \qquad \text{(C.9b)}$$

$$s_{<111>}(N, -, -) = 3N/2\ d_{\{111\}} \qquad \text{(C.9c)}$$

with $d_{\{hkl\}}$ according to (C.3). These quantities will be used in Secs. C.2.

**(b)** **Generic rhombohedral** sc NPs, denoted **sc(-, *M*, -)** are confined by all twelve {110} monolayers with distances $D_{\{110\}} = 2M\ d_{\{110\}}$ between parallel monolayers. This yields twelve {110} facets as well as possibly six smaller {100} and eight {111} facets, see Fig. C.2, C..3. Corresponding edge parameters *n*, *m*, *k* depending on *M* are given in Table C.1.

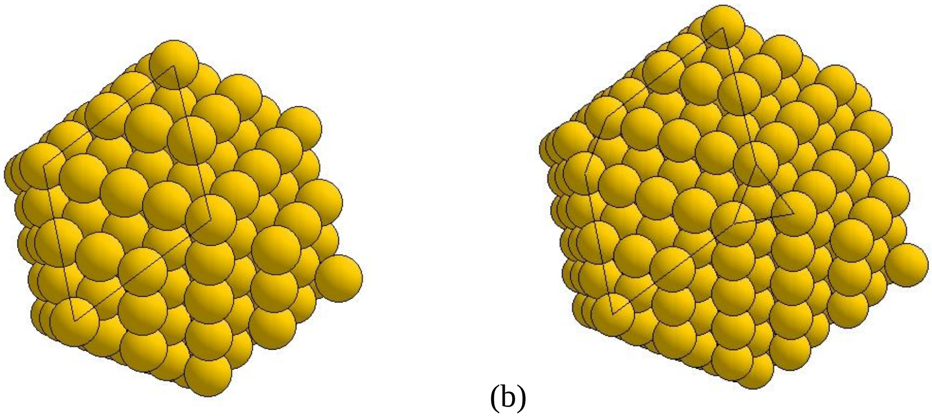
The **{100} facets** appear only for void NPs and are square shaped with four <100> edges of length $a_o$.

The **{110} facets** are rhombic, hexagonal, or octagonal shaped with two <100> edges of length $n\ a_o$, two <110> edges of length $m\ a_o/\sqrt{2}$, and four <111> edges of length $k\ \sqrt{3}a_o$. For ac NPs with *M* even the NPs can be described as rhombic dodecahedra reminding of the shape of Wigner-Seitz cells of the face centered cubic (fcc) crystal lattice [14].

The **{111} facets** appear only for ac, *M* odd or vc, *M* even and are triangular shaped with three <110> edges of length $m\ a_o/\sqrt{2}$.

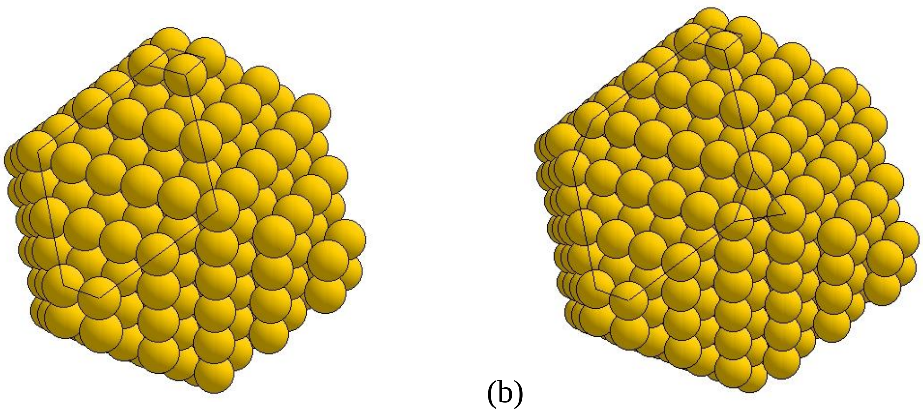
| Centering | *M* even | *M* odd |
|---|---|---|
| ac | $n = 0$<br>$m = 0$<br>$k = M/2$ | $n = 0$<br>$m = 2$<br>$k = (M - 1)/2$ |
| vc | $n = 1$<br>$m = 2$<br>$k = (M - 2)/2$ | $n = 1$<br>$m = 0$<br>$k = (M - 1)/2$ |

**Table C.1.** Edge parameters $n$, $m$, $k$ of {100}, and {110} and {111} facets of sc(-, $M$, -) NPs, see text. Values $n = m = 0$ result in rhombic, $n = 0$, $m \neq 0$ or $n \neq 0$, $m = 0$ in hexagonal, and $n \neq 0$, m $\neq$ 0 in octagonal facets.



(a) (b)

**Figure C.2.** Atom ball models of generic rhombohedral atom centered NPs, (a) sc(-, 4, -) and (b) sc(-, 5, -). The black lines sketch the (capped) rhombic {110} and triangular {111} microfacets.



(a) (b)

**Figure C.3.** Atom ball models of generic rhombohedral void centered NPs, (a) sc(-, 5, -) and (b) vc (-, 6, -). The black lines sketch the capped rhombic {110}, the square {100}, and the triangular {111} microfacets.

The total number of NP atoms, $\boldsymbol{N_{vol}}$**(-, *M*, -)**, and the number of facet atoms, $\boldsymbol{N_{facet}}$**(-, *M*, -)**, (outer polyhedral shell), are given with (C.6) by

$$N_{vol}(-, M, -) = M\,(2M^2 + 3M + 2) + 1 - h \qquad \text{(C.10)}$$

$$N_{facet}(-, M, -) = 6M^2 + 2(1 - h) \qquad \text{(C.11)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given with (C.5), (C.6) by

$$s_{<100>}(-, M, -) = (2M - g)/2\ d_{\{100\}} \qquad \text{(C.12a)}$$

$$s_{<110>}(-, M, -) = M\ d_{\{110\}} \qquad \text{(C.12b)}$$

$$s_{<111>}(-, M, -) = (3M - h)/2\ d_{\{111\}} \qquad \text{(C.12c)}$$

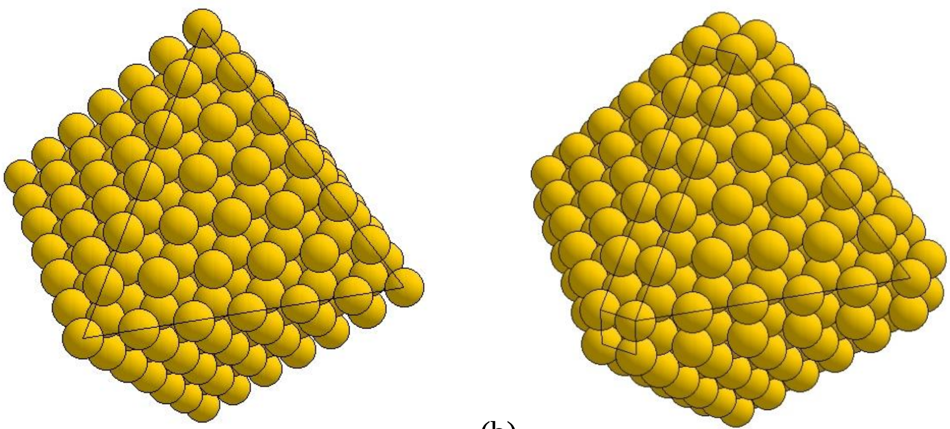
with $d_{\{hkl\}}$ according to (C.3). These quantities will be used in Secs. C.2.

**(c)** **Generic octahedral** sc NPs, denoted **sc(-, -, *K*)**, are confined by all eight {111} monolayers with distances $D_{\{111\}} = K\ d_{\{111\}}$ between parallel monolayers. This yields eight {111} facets as well as possibly six smaller {100} and twelve {110} facets, see Fig. C.4.

The **{100} facets** appear only for vc, *K* odd NPs and are square shaped with four <100> edges of length $a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $K\ a_o/\sqrt{2}$ for ac, *K* even and of length $(K - 3)\ a_o/\sqrt{2}$ for vc *K* odd.

The **{110} facets** appear only for vc, *K* odd NPs and are rectangular shaped with two <100> edges of length $a_o$ and two <110> edges of length $(K - 3)\ a_o/\sqrt{2}$.



(a) (b)

**Figure C.4.** Atom ball models of generic octahedral NPs, (a) atom centered sc(-, -, 12) and (b) void centered sc(-, -, 13). The black lines in sketch the triangular {111}, the stripped {110}, and the square {100} microfacets.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, -, K)}$, (outer polyhedral shell), are given with (C.5) by

$$N_{vol}(-, -, K) = (K+1)\,[(K+1)^2 + 5 - 9g]/6 \qquad \text{(C.13)}$$

$$N_{facet}(-, -, K) = K^2 + 2 - 3g \qquad \text{(C.14)}$$

The largest distance from the NP center to its surface along <*hkl*> directions, $\boldsymbol{s_{<hkl>}}$, is given with (C.5) by

$$s_{<100>}(-, -, K) = (K - 2g)/2\; d_{\{100\}} \qquad \text{(C.15a)}$$

$$s_{<110>}(-, -, K) = (K - g)/2\; d_{\{110\}} \qquad \text{(C.15b)}$$

$$s_{<111>}(-, -, K) = K/2\; d_{\{111\}} \qquad \text{(C.15c)}$$

with $d_{\{hkl\}}$ according to (C.3). These quantities will be used in Secs. C.2.

Table C.2 collects types, constraints, and shapes of all generic sc NPs.

| Generic type | Constraints | Facets | Corners |
|---|---|---|---|
| Cubic<br>sc(*N*, -, -) | ac, *N* even,<br>vc, *N* odd | {100} 6<br>{110} 0<br>{111} 0 | <100> 0<br><110> 0<br><111> 8 |
| Rhombohedral ac<br>sc(-, *M*, -) | *M* even | {100} 0<br>{110} 12<br>{111} 0 | <100> 6<br><110> 0<br><111> 8 |
| | *M* odd | {100} 0<br>{110} 12<br>{111} 8 | <100> 6<br><110> 0<br><111> 8 & |
| Rhombohedral vc<br>sc(-, *M*, -) | *M* even | {100} 6<br>{110} 12<br>{111} 8 | <100> 6 &<br><110> 0<br><111> 8 & |
| | *M* odd | {100} 6<br>{110} 12<br>{111} 0 | <100> 6 &<br><110> 0<br><111> 8 |
| Octahedral<br>sc(-, -, *K*) | ac, *K* even | {100} 0<br>{110} 0<br>{111} 8 | <100> 6<br><110> 0<br><111> 0 |
| | vc, *K* odd | {100} 6<br>{110} 12<br>{111} 8 | <100> 6 &<br><110> 0<br><111> 0 |

**Table C.2.** Types and notations of all generic sc NPs where “ac“ denotes atom centered and “vc“ void centered NPs. Further, the superscript label “&” denotes corner quadruplets about <100> and corner triplets about <111>.

## C.2. Non-generic sc Nanoparticles

Non-generic sc nanoparticles of $O_h$ symmetry can be either atom or void centered and show facets with orientations of several {*hkl*} netplane families. This can be considered as combining confinements of the corresponding generic NPs discussed in Sec. C.1 with suitable polyhedral parameters *N*, *M*, *K* sharing their symmetry center (atom or void). Here we discuss non-generic sc NPs which combine constraints of up to three generic NPs, cubic sc(*N*, -, -), rhombohedral sc(-, *M*, -), and octahedral sc(-, -, *K*). These allow {100}, {110}, as well as {111} facets and will be denoted **sc(*N, M, K*)** in the following. Clearly, the corresponding polyhedral parameters *N*, *M*, *K* depend on each other and determine the overall NP shape. In particular, if a participating generic NP encloses another participant it will not contribute to the overall NP shape and the respective {*hkl*} facets will not appear at the surface of the non-generic NP. In the following, we consider the three types of non-generic NPs which combine constraints due to two generic NPs (Secs. C.2.1-3) before we discuss the most general case of sc(*N*, *M*, *K*) NPs in Sec. C.2.4.

### C.2.1 Combining {100} and {110} Facets, sc(*N*, *M*, -) NPs

Non-generic **cubo-rhombic** NPs, denoted **sc(*N, M,* -)**, are confined by facets referring to the two generic NPs, sc(*N*, -, -) (cubic) and sc(-, *M*, -) (rhombohedral). Thus, they can show {100} as well as {110} facets (apart from {111} microfacets) depending on the polyhedral parameters *N*, *M*. Clearly, both generic NPs must exhibit the same centering, atom centered (ac, *N* even) or void centered (vc, *N* odd), to yield a non-generic sc NP of $O_h$ symmetry. If the edges of the cubic NP sc(*N*, -, -) lie inside the rhombohedral NP sc(-, *M*, -) the resulting combination sc(*N*, *M*, -) will be generic cubic which can be expressed formally by

$$s_{<110>}(N, -, -) \leq s_{<110>}(-, M, -) \qquad \text{(C.16)}$$

leading, according to (C.9), (C.12), to

$$N \leq M \qquad \text{(C.17)}$$

for both ac and vc NPs. On the other hand, if the corners of the rhombohedral NP sc(-, *M*, -) lie inside the cubic NP sc(*N*, -, -) the resulting combination sc(*N*, *M*, -) will be generic rhombohedral which can be expressed formally by

$$s_{<100>}(-, M, -) \leq s_{<100>}(N, -, -) \qquad \text{(C.18)}$$

leading, according to (C.9), (C.12) with (C.5) to

$$N \geq 2M - g \qquad \text{(C.19)}$$

Thus, the two generic NPs intersect and define a true non-generic NP sc($N$, $M$, -) offering both {100} and {110} facets only for polyhedral parameters $N$, $M$ where with (C.5)

$$M < N < 2M - g \qquad \text{(ac, } N \text{ even)} \qquad \text{(C.20)}$$

while sc($N$, $M$, -) is generic cubic for smaller $N$ according to (C.17) and generic rhombohedral for larger $N$ according to (C.19). This suggests that generic cubic and rhombohedral sc NPs can be considered as special cases of non-generic NPs
sc($N$, $M$, -) where with (C.5)

$$\text{sc}(N, -, -) = \text{sc}(N, M = N, -) \qquad \text{(cubic)} \qquad \text{(C.21a)}$$

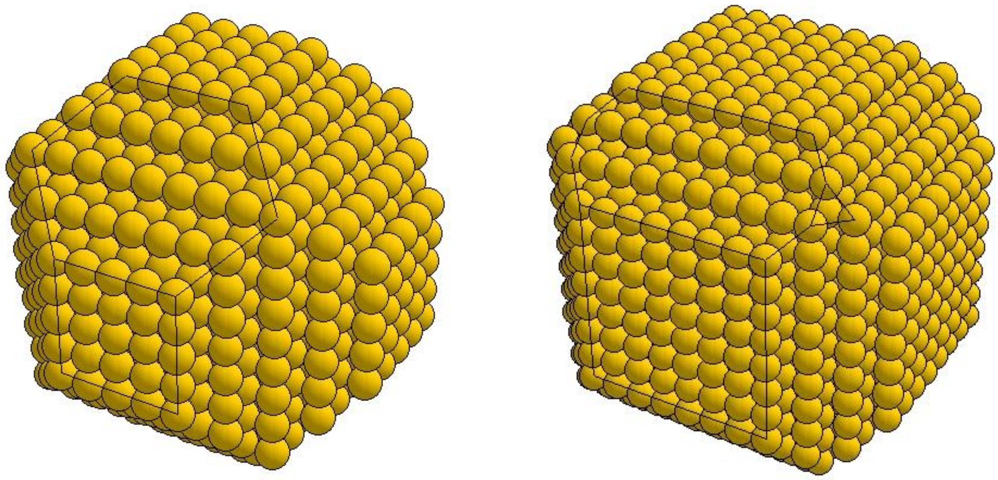
$$\text{sc}(-, M, -) = \text{sc}(N = 2M - g, M, -) \qquad \text{(rhombohedral)} \qquad \text{(C.21b)}$$

Parameters $N$, $M$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, cubo-rhombic NPs
sc($N$, $M$, -) exhibit six {100} facets, twelve {110} facets, and eight smaller {111} facets,
see Fig. C.5.

The **{100} facets** are square shaped with four <100> edges of length $(2M - N)\ a_o$.

The **{110} facets** for $(N + M)$ even are hexagonal shaped with four <111> edges of length $(N - M)/2\ \sqrt{3}a_o$ and two <100> edges of length $(2M - N)\ a_o$ . For $(N + M)$ odd, the facets are octagonal (capped hexagonal) with four <111> edges of length $(N - M - 1)/2\ \sqrt{3}a_o$, two <100> edges of length $(2M - N)\ a_o$, and two <110> edges of length $\sqrt{2}a_o$.

The **{111} facets** appear only for $(N + M)$ odd and are triangular shaped with three <110> edges of length $\sqrt{2}a_o$.



(a) (b)

**Figure C.5.** Atom ball models of cubo-rhombic NPs, (a) atom centered sc(12, 8, -) and (b) void centered sc(13, 10, -). The black lines sketch the square {100}, (capped) hexagonal {110} and triangular {111} microfacets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, -)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, -)}$, (outer polyhedral shell) are given with (C.10), (C.11) by

$$N_{vol}(N, M, -) = N_{vol}(-, M, -) - H\,(H^2 - 1)\,, \qquad H = 2M - N \qquad \text{(C.22)}$$

$$N_{facet}(N, M, -) = N_{facet}(-, M, -) \qquad \text{(C.23)}$$

The present discussion allows a classification of sc($N$, $M$, -) NPs for all combinations of polyhedral parameters $N$, $M$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table C.3 illustrates all possible NP types.

**(a) Atom centered** (ac) sc($N$, $M$, -), $N$ even

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $N \geq 2M$ | Generic rhombohedral | (-, $M$, -) = ($N$ = 2$M$, $M$, -) |
| $M \leq N \leq 2M$ | Cubo-rhombic | ($N$, $M$, -) |
| $N \leq M$ | Generic cubic | ($N$, -, -) = ($N$, $M$ = $N$, -) |

**(b) Void centered** (vc) sc($N$, $M$, -), $N$ odd

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $N \geq 2M - 1$ | Generic rhombohedral | (-, $M$, -) = ($N = 2M - 1$, $M$, -) |
| $M \leq N \leq 2M - 1$ | Cubo-rhombic | ($N$, $M$, -) |
| $N \leq M$ | Generic cubic | ($N$, -, -) = ($N$, $M = N$, -) |

**Table C.3.** Constraints and types including isomorphs of (a) atom and (b) void centered sc($N$, $M$, -) NPs.

### C.2.2 Combining {100} and {111} Facets, sc(*N*, -, *K*) NPs

Non-generic **cubo-octahedral** NPs, denoted **sc(*N*, -, *K*)**, are confined by facets referring to the two generic NPs, sc($N$, -, -) (cubic) and sc(-, -, $K$) (octahedral). Thus, they can show {100} as well as {111} facets (apart from {110} microstrips) depending on the polyhedral parameters $N$, $K$. Clearly, both generic NPs must exhibit the same centering, atom centered (ac, both $N$, $K$ even) or void centered (vc, both $N$, $K$ odd), to yield a non-generic sc NP of $O_h$ symmetry. If the corners of the cubic NP sc($N$, -, -) lie inside the octahedral NP sc(-, -, $K$) the resulting combination sc($N$, -, $K$) will be generic cubic which can be expressed formally by

$$s_{<111>}(N, -, -) \leq s_{<111>}(-, -, K) \qquad \text{(C.24)}$$

leading, according to (C.9), (C.15), to

$$3N \leq K \qquad \text{(C.25)}$$

for both ac and vc NPs. On the other hand, if the corners of the octahedral NP sc(-, -, $K$) lie inside the cubic NP sc($N$, -, -) the resulting combination sc($N$, -, $K$) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(N, -, -) \qquad \text{(C.26)}$$

leading, according to (C.9), (C.15) and with (C.5) to

$$N \geq K - 2g \qquad \text{(C.27)}$$

Thus, the two generic NPs intersect and define a true non-generic NP sc($N$, -, $K$) offering both {100} and {111} facets only for polyhedral parameters $N$, $K$ where with (C.5)

$$N + 2g < K < 3N \qquad \text{(ac, } N, K \text{ even)} \qquad \text{(C.28)}$$

while sc($N$, -, $K$) is generic cubic for larger $K$ according to (C.25) and generic octahedral for smaller $K$ according to (C.27). This suggests that generic cubic and octahedral sc NPs can be considered as special cases of non-generic NPs sc($N$, -, $K$) where with (C.5)

sc($N$, -, -) = sc($N$, -, $K$ = 3$N$)    (cubic)    (C.29a)

sc(-, -, $K$) = sc($N$ = $K$ - 2$g$, -, $K$)    (octahedral)    (C.29b)

Further, amongst the true intersecting cubo-octahedral NPs according to (C.28) we can distinguish between so-called **truncated octahedral** NPs where $K < 2N$ and **truncated cubic** NPs for $K > 2N$ as will be discussed in the following.

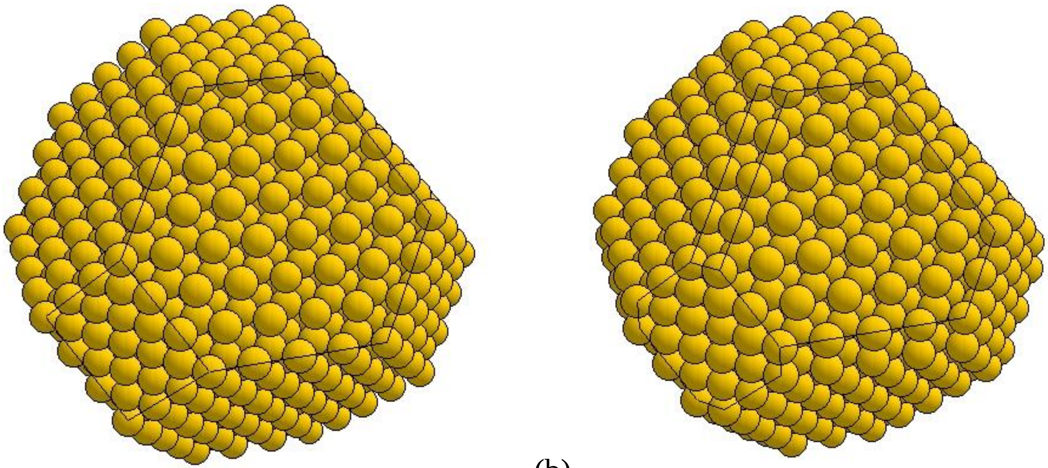
Parameters $N$, $M$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, cubo-octahedral NPs sc($N$, -, $K$) exhibit six {100}, twelve {110}, and eight {111} facets, see Figs. C.6, C.7.

**Truncated octhedral** NPs ($K < 2N$), Fig. C.6, can be characterized by their facets as follows.

The **{100} facets** for $N$, $K$ even are square shaped with four <110> edges of length ($K$ - $N$)/2 $\sqrt{2}a_o$. For $N$, $K$ odd the facets are octagonal (capped square) shaped with alternating edges, four <110> of length ($K$ - $N$ - 2)/2 $\sqrt{2}a_o$ and four <100> of length $a_o$.

The **{110} facets** appear only for $N$, $K$ odd and are rectangular shaped with two <110> edges of length (2$N$ - $K$ + 1)/2 $\sqrt{2}a_o$ and two <100> edges of length $a_o$.

The **{111} facets** are hexagonal shaped with alternating <110> edges of lengths ($K$ - $N$)/2 $\sqrt{2}a_o$ and (2$N$ - $K$)/2 $\sqrt{2}a_o$ for $N$, $K$ even while for $N$, $K$ odd the alternating edges are of lengths ($K$ - $N$ - 2)/2 $\sqrt{2}a_o$ and (2$N$ - $K$ + 1)/2 $\sqrt{2}a_o$.



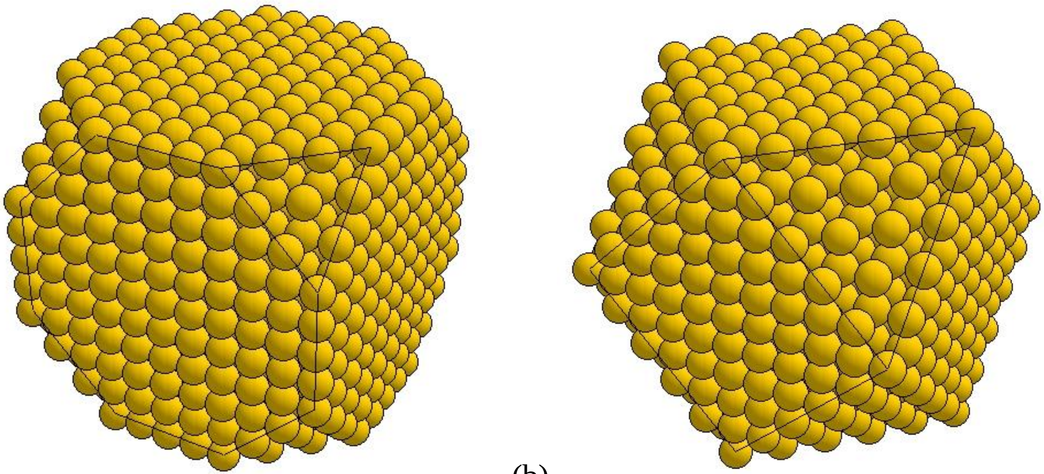
(a) (b)

**Figure C.6.** Atom ball models of cubo-octahedral NPs of truncated octahedral type, (a) atom centered sc(14, -, 20) and (b) void centered sc(13, -, 19). The black lines sketch the square {100}, the stripped {110}, and the hexagonal {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (C.13), (C.14), (C.5) by

$$N_{vol}(N, -, K) = N_{vol}(-, -, K) - H\,(H^2 + 2 - 6g)/2\,, \qquad H = K - N \qquad \text{(C.30)}$$

$$N_{facet}(N, -, K) = N_{facet}(-, -, K) \qquad \text{(C.31)}$$



(a) (b)

**Figure C.7.** Atom ball models of atom centered NPs, (a) cubo-octahedral sc(10, -, 24) (truncated cubic ) and (b) generic cuboctahedral sc(10, -, 20). The black lines sketch the octagonal/square {100}, triangular {111} facets.

**Truncated cubic** NPs ($K > 2N$), Fig. 7, can be characterized by their facets as follows.

The **{100} facets** are octagonal shaped with alternating edges, four <100> of length $(K - 2N)\, a_o$ and four <110> of length $(3N - K)/2\ \sqrt{2}a_o$.

The **{111} facets** are triangular shaped with <110> edges of length $(3N - K)/2\ \sqrt{2}a_o$.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, -, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, -, K)}$, (outer polyhedral shell) are given with (C.7), (C.8) by

$$N_{vol}(N, -, K) \quad = N_{vol}(N, -, -) - H\,(H + 2)\,(H + 4)/6 \qquad \text{(C.32)}$$

$$N_{facet}(N, -, K) \quad = N_{facet}(N, -, -) - 2H^2\,, \qquad H = 3N - K \qquad \text{(C.33)}$$

There are sc NPs which can be assigned to both truncated cubic and truncated octahedral type, the **generic cuboctahedral** sc($N$, -, $K$) NPs, defined by $K = 2N$. These NPs exist only as atom centered variants since both $N$ and $K$ must be even. They exhibit six {100} and eight {111} facets, see Fig. C.7b. All **{100} facets** are square shaped with four <110> edges of length $N/2\ \sqrt{2}a_o$ while all **{111} facets** are triangular shaped with three<110> edges of length $N/2\ \sqrt{2}a_o$ shared with those of the {100} facets.

The present discussion allows a classification of sc($N$, -, $K$) NPs for all combinations of polyhedral parameters $N$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table C.4 illustrates all possible NP types.

**(a) Atom centered** (ac) sc($N$, -, $K$), $N$, $K$ even

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $K \geq 3N$ | Generic cubic | ($N$, -, -) =<br>($N$ , -, $K = 3N$) |
| $2N \leq K \leq 3N$ | Cubo-octahedral<br>truncated cubic | ($N$, -, $K$) |
| $K = 2N$ | Cuboctahedral | ($N$, -, $K = 2N$) ,<br>($N = K/2$, -, $K$) |
| $N \leq K \leq 2N$ | Cubo-octahedral<br>truncated octahedral | ($N$, -, $K$) |
| $K \leq N$ | Generic octahedral | (-, -, $K$) =<br>($N = K$, -, $K$) |

**(b) Void centered** (vc) sc($N$, -, $K$), $N$, $K$ odd

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $K \geq 3N$ | Generic cubic | ($N$, -, -) = <br> ($N$ , -, $K$ = 3$N$) |
| $2N + 1 \leq K \leq 3N$ | Cubo-octahedral truncated cubic | ($N$, -, $K$) |
| $N + 2 \leq K \leq 2N - 1$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) |
| $K \leq N + 2$ | Generic octahedral | (-, -, $K$) = <br> ($N = K - 2$, -, $K$) |

**Table C.4.** Constraints and types including isomorphs of (a) atom and (b) void centered sc($N$, -, $K$) NPs.

### C.2.3 Combining {110} and {111} Facets, sc(-, *M*, *K*) NPs

Non-generic **rhombo-octahedral** NPs, denoted **sc(-, *M*, *K*)**, are confined by facets referring to the two generic NPs, sc(-, $M$, -) (rhombohedral) and sc(-, -, $K$) (octahedral). Thus, they can show {110} as well as {111} facets (apart from {100} microfacets) depending on the polyhedral parameters $M$, $K$. Clearly, both generic NPs must exhibit the same centering, atom centered (ac, $K$ even) or void centered (vc, $K$ odd), to yield a non-generic sc NP of $O_h$ symmetry. If the corners of the rhombohedral NP sc(-, $M$, -) lie inside the octahedral NP sc(-, -, $K$) the resulting combination sc(-, $M$, $K$) will be generic rhombohedral which can be expressed formally by

$$s_{<111>}(-, M, -) \leq s_{<111>}(-, -, K) \qquad \text{(C.34)}$$

leading, according to (C.12), (C.15) and with (C.6), to

$$3M \leq K + h \qquad \text{(C.35)}$$

On the other hand, if the corners of the octahedral NP sc(-, -, $K$) lie inside the rhombohedral NP sc(-, $M$, -) the resulting combination sc(-, $M$, $K$) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, K) \leq s_{<100>}(-, M, -) \qquad \text{(C.36)}$$

leading, according to (C.12), (C.15) and with (C.5) to

$$2M \geq K - g \qquad \text{(C.37)}$$

Thus, the two generic NPs intersect and define a true non-generic NP sc(-, $M$, $K$) offering both {110} and {111} facets only for polyhedral parameters $M$, $K$ where with (C.5), (C.6)

$$2M + g < K < 3M - h \qquad \text{(C.38)}$$

while sc(-, $M$, $K$) is generic rhombohedral for larger $K$ according to (C.35) and generic octahedral for smaller $K$ according to (C.37). This suggests that generic rhombohedral and octahedral sc NPs can be considered as special cases of non-generic NPs sc(-, $M$, $K$) where with (C.5), (C.6)

sc(-, $M$, -) = sc(-, $M$, $K = 3M - h$) (rhombohedral) (C.39a)

sc(-, -, $K$) = sc(-, $M = (K - g)/2$, $K$) (octahedral) (C.39b)

Parameters $M$, $K$ provide additional information about geometric properties of the NPs describing their shapes and all facet edges. In the most general case, rhombo-octahedral NPs sc(-, $M$, $K$) exhibit twelve {110} and eight {111} facets with six possible {100} microfacets, see Fig. C.8.

The **{100} facets** appear only for $N$, $K$ odd and are square shaped with <100> edges of length $a_o$.

The **{110} facets** for $N$, $K$ even are hexagonal shaped with four <111> edges of length $(K - 2M)/2\ \sqrt{3}a_o$ and two <110> edges of length $(3M - K)\ \sqrt{2}a_o$. For $N$, $K$ odd the facets are octagonal shaped with four <111> edges of length $(K - 2M - 1)/2\ \sqrt{3}a_o$, two <100> edges of length $a_o$, and two <110> edges of length $(3M - K)\ \sqrt{2}a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $(3M - K)\ \sqrt{2}a_o$.

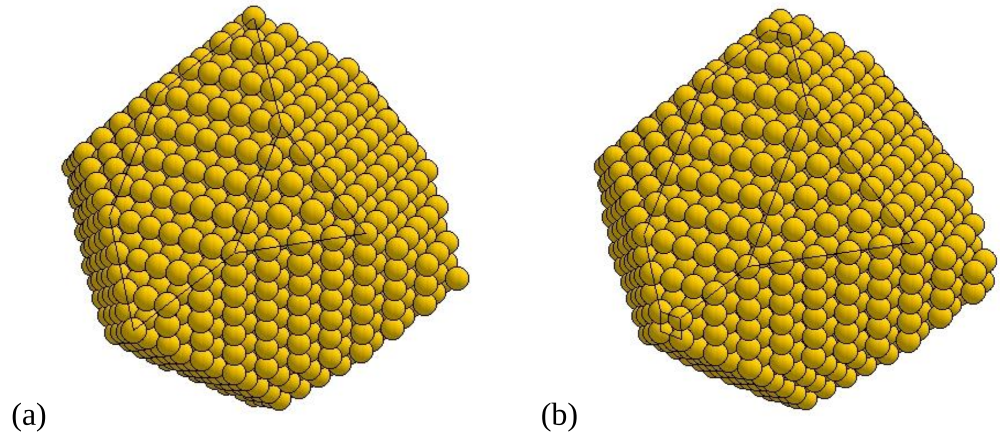



**Figure C.8.** Atom ball models of rhombo-octahedral NPs, (a) atom centered sc( -, 10, 26) and (b) void centered sc( -, 10, 25). The black lines sketch the hexagonal/octagonal{110}and triangular {111} facets with square {100} microfacets.

The total number of NP atoms, $\boldsymbol{N_{vol}(-, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(-, M, K)}$, (outer polyhedral shell) are given with (C.10), (C.11), (C.6) by

$$N_{vol}(-, M, K) = N_{vol}(-, M, -) - H\,(H + 2)\,(2H - 1)/3 + h\,, \qquad H = 3M - K \qquad \text{(C.40)}$$

$$N_{facet}(-, M, K) = N_{facet}(-, M, -) - 2H^2 + 2h \qquad \text{(C.41)}$$

The present discussion allows a classification of sc(-, $M$, $K$) NPs for all combinations of polyhedral parameters $M$, $K$. This includes generic NPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic NP. Table C.5 illustrates all possible NP types.

**(a) Atom centered** (ac) sc(-, $M$, $K$), $K$ even

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $K \geq 3M - h$ | Generic rhombohedral | (-, $M$, -) =<br>(-, $M$, $K = 3M - h$) |
| $2M \leq K \leq 3M - h$ | Rhombo-octahedral | (-, $M$, $K$) |
| $K \leq 2M$ | Generic octahedral | (-, -, $K$) =<br>(-, $M = K/2$, $K$) |

**(b) Void centered** (vc) sc(-, $M$, $K$), $K$ odd

| Constraints | NP types | sc Isomorphs |
|---|---|---|
| $K \geq 3M - h$ | Generic rhombohedral | (-, $M$, -) =<br>(-, $M$, $K = 3M - h$) |
| $2M + 1 \leq K \leq 3M - h$ | Rhombo-octahedral | (-, $M$, $K$) |
| $K \leq 2M + 1$ | Generic octahedral | (-, -, $K$) =<br>(-, $M = (K - 1)/2$, $K$) |

**Table C.5.** Constraints and types including isomorphs of (a) atom and (b) void centered sc(-, $M$, $K$) NPs.

### C.2.4 Combining {100}, {110}, and {111} Facets, sc($N$, $M$, $K$) NPs

Non-generic **cubo-rhombo-octahedral** NPs, denoted **sc(*N*, *M*, *K*)**, are confined by facets referring to all three generic NPs, sc($N$, -, -) (cubic), sc(-, $M$, -) (rhombohedral), and sc(-, -, $K$) (octahedral). Thus, they can show {100}, {110}, and {111} facets depending on the polyhedral parameters $N$, $M$, $K$. Clearly, the three generic NPs must exhibit the same centering, atom centered (ac, both $N$, $K$ even) or void centered (vc, both $N$, $K$ odd), to yield a non-generic sc NP of $O_h$ symmetry. A general discussion of these NPs requires a number of different scenarios using results of for generic and non-generic NPs , Secs. C.1, C.2.1-3, respectively, as will be detailed in the following.

First, we consider the general notation for generic sc NPs discussed in Sec. C.1. Cubic NPs sc($N$, -, -) are surrounded by rhombohedral NPs sc(-, $M$, -) if $M \geq N$ according to (C.17) and by octahedral NPs sc(-, -, $K$) if $K \geq 3N$ according to (C.25). This allows a notation sc($N$, $M$, $K$) where

$$\mathrm{sc}(N, -, -) = \mathrm{sc}(N, M = N, K = 3N) \qquad \text{(C.42)}$$

Further, rhombohedral NPs sc(-, $M$, -) are surrounded by cubic NPs sc($N$, -, -) if $N$, $M$ satisfy relations (C.19) and by octahedral NPs sc(-, -, $K$) if $M$, $K$ satisfy relations (C.35). This allows a notation sc($N$, $M$, $K$) where with (C.5), (C.6)

$$\mathrm{sc}(-, M, -) \;\; = \mathrm{sc}(N = 2M - g, M, K = 3M - h) \qquad \text{(C.43)}$$

In addition , the octahedral NPs sc(-, -, $K$) are surrounded by cubic NPs sc($N$, -, -) if if $N$, $K$ satisfy relations (C.27) and by rhombohedral NPs sc(-, $M$, -) if $M$, $K$ satisfy relations (C.37). This allows a notation sc($N$, $M$, $K$) where with (C.5)

$$\mathrm{sc}(-, -, K) \;\; = \mathrm{sc}(N = K - 2g, M = (K - g)/2, K) \qquad \text{(C.44)}$$

General notations for non-generic sc NPs discussed in Secs. C.2.1-3 are obtained by analogous arguments. According to Sec. C.2.1, true cubo-rhombic NPs sc($N$, $M$, -) with both {100} and {110} facets are subject to $M \leq N \leq 2M$ (- 1) according to (C.20). They are surrounded by octahedral NPs sc(-, -, $K$) if $K \geq K_a$ where with (C.6)

$$K_a(N, M) \;\; = \min(3N, 3M - h) = 3M - h \qquad \text{(C.45)}$$

This allows a general notation sc($N$, $M$, $K$) where

$$\mathrm{sc}(N, M, -) = \mathrm{sc}(N, M, K = K_a) \qquad \text{(C.46)}$$

According to Sec. C.2.2, true cubo-octahedral NPs sc($N$, -, $K$) with both {100} and {111} facets are subject to $N$ (+ 2) $\leq K \leq 3N$ according to (C.28). They are surrounded by rhombohedral NPs sc(-, $M$, -) if $M \geq M_a$ were with (C.5)

$$M_a(N, K) \;\;\; = \min((K - g)/2, N) \qquad \text{(C.47)}$$

This allows a general notation sc($N$, $M$, $K$) where

$$\mathrm{sc}(N, -, K) = \mathrm{sc}(N, M = M_a, K) \qquad \text{(C.48)}$$

According to Sec. C.2.3, true rhombo-octahedral NPs sc(-, $M$, $K$) with both {110} and {111} facets are subject to $2M$ (+ 1) $\leq K \leq 3M$ (- 1) according to (C.38). They are surrounded by cubic NPs sc($N$, -, -) if $N \geq N_a$ were with (C.5)

$N_a(M, K) \quad = \min(2M - g, K - 2g)$ (C.49)

This allows a general notation sc($N$, $M$, $K$) where

sc(-, $M$, $K$) = sc($N = N_a$, $M$, $K$) (C.50)

In the most general case of a true sc($N$, $M$, $K$) NP with {100}, {110}, and {111} facets we start from a true cubo-rhombic NP, sc($N$, $M$, -), with its constraints $M \leq N \leq 2M$ and add constraints of a generic octahedral NP, sc(-, -, $K$), where according to the discussion above $K$ values are below $K_a$. This allows to distinguish four different ranges of parameter $K$, defined by separating values $K_a \geq K_b \geq K_c$, with $K_a$ given by (C.45) and

$K_b(N, M) = 4M - N$ (C.51)

$K_c(N, M) = 2M$ (C.52)

which result in different NP shapes starting from the initial cubo-rhombic NP sc($N$, $M$, $K_a$) as illustrated for the ac NP sc(20, 14, 42) in Fig. C.9.

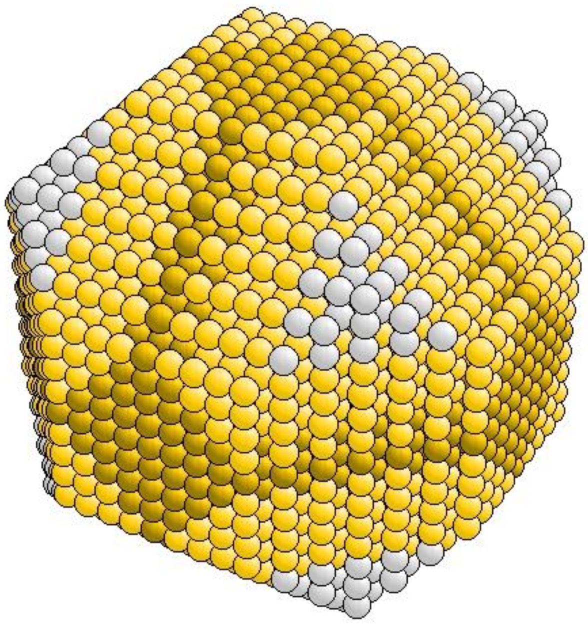


**Figure C.9.** Atom ball model of an atom centered cubo-rhombic NP, sc(20, 14, 42) ($K = K_a$, all atom balls), with its cubo-rhombo-octahedral NP components, sc(20, 14, 36) ($K = K_b$), and sc(20, 14, 28) ($K = K_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $K$ ranges at $K = K_c$ (inner vs. lower central ) and at $K = K_b$, (lower vs. upper central), respectively, see text.

**Outer *K* range** of sc(*N*, *M*, *K*) where with (C.45)

$$K \geq K_a \quad (C.53)$$

For these *K* values the NP becomes cubo-rhombohedral and does not exhibit any {111} facets (except for microfacets with three atoms). It is isomorphic with sc($N$, $M$, $K_a$) as discussed above and in Sec. C.2.1.

**Upper central *K* range** of sc(*N*, *M*, *K*) where with (C.45), (C.51)

$$K_b \leq K \leq K_a \quad (C.54)$$

For these *K* values the initial sc($N$, $M$, $K_a$) NP is capped at its <111> corners forming eight additional {111} facets of equilateral triangular shape. Altogether, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. C.10.

The **{100} facets** are square shaped with four <100> edges of length $(2M - N)\, a_o$.

The **{110} facets** are octagonal or rectangular ($K = K_b$) shaped with two <110> edges of length $(3M - K)\, \sqrt{2}a_o$, two <100> edges of $(2M - N)\, a_o$, and four <111> edges of $(K + N - 4M)/2\, \sqrt{3}a_o$.

The **{111} facets** are triangular shaped with three <110> edges of length $(3M - K)\, \sqrt{2}a_o$.

The NP structure is illustrated in Fig. C.10 for the ac NP sc(24, 14, 36) ($K_a = 42$, $K_b = 32$, yellow atom balls) where white balls above the {111} facets are added to yield the corresponding cubo-rhombic sc($N$, $M$, $K_a$) NP.

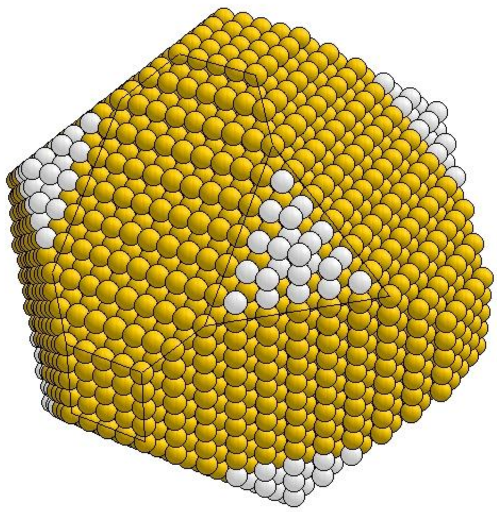


**Figure C.10.** Atom ball model of an atom centered cubo-rhombo-octahedral NP, sc(24, 14, 36), shown by yellow balls with white atom balls completing the NP, see text. The black lines sketch the square {100}, octagonal{110}, and triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (C.22), (C.23), (C.6) by

$$N_{vol}(N, M, K) \quad = N_{vol}(N, M, -) - H\,(H + 2)\,(2H - 1)/3 + h \qquad \text{(C.55)}$$

$$N_{facet}(N, M, K) \quad = N_{facet}(N, M, -) - 2H^2 + 2h\ , \qquad H = 3M - K \qquad \text{(C.56)}$$

For $K = K_b$, the sc($N$, $M$, $K$) NP assumes a particular shape where its twelve **{110} facets** are rectangular with two edges of length $(N - M)\ \sqrt{2}a_o$ and of $(2M - N)\ a_o$ while the **{100}** and **{111} facets** are square and triangular shaped as described before. This is illustrated in Fig. C.11 for the vc NP sc(15, 9, 21) ($K_b$ = 21).

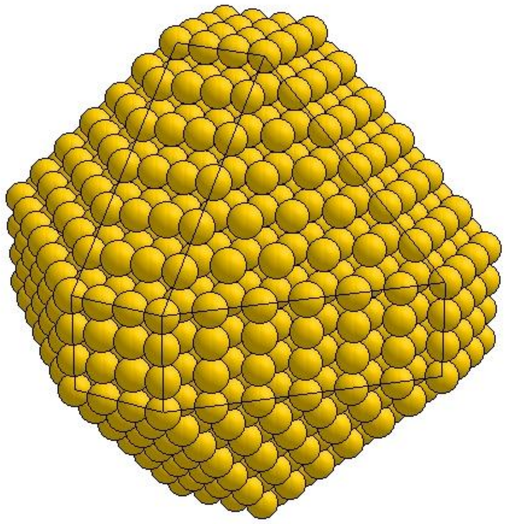


**Figure C.11.** Atom ball model of a void centered cubo-rhombo-octahedral NP, sc(15, 9, 21). The black lines sketch the square {100}, rectangular {110}, and triangular {111} facets.

**Lower central *K* range** of sc($N$, $M$, $K$) where with (C.51), (C.52)

$$K_c \leq K \leq K_b \qquad \text{(C.57)}$$

For these $K$ values the capping of the initial sc($N$, $M$, $K_b$) along the <111> directions is continued to yield eight hexagonal {111} facets. As before, these NPs exhibit six {100} facets, twelve {110} facets, and eight {111} facets, see Fig. C.12.

The **{100} facets** are octagonal shaped with alternating edges, four <100> of length $(K - 2M)\ a_o$ and four <110> of length $(4M - N - K)/2\ \sqrt{2}a_o$.

The **{110} facets** are rectangular shaped with two <110> edges of length $(N - M)\ \sqrt{2}a_o$ and two <100> edges of length $(K - 2M)\ a_o$.

The **{111} facets** are hexagonal shaped with <110> edges of alternating lengths $(4M - N - K)/2\ \sqrt{2}a_o$ and $(N - M)\ \sqrt{2}a_o$.

The NP structure is illustrated in Fig. C.12 for the NP sc(22, 14, 30) ($K_b$ = 34, $K_c$ = 28) where white atom balls above the {111} facets are added to sc($N$, $M$, $K$) to yield the corresponding sc($N$, $M$, $K_b$) NP.

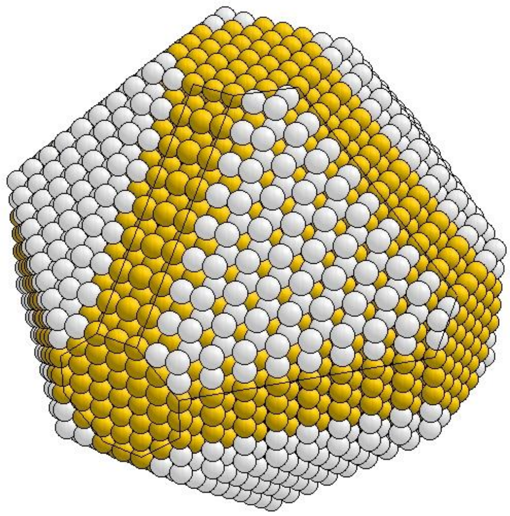


**Figure C.12.** Atom ball model of an atom centered cubo-rhombo-octahedral NP, sc(22, 14, 30) shown by yellow balls with white atom balls completing the NP, see text. The black lines sketch the octagonal {100}, rectangular{110}, and hexagonal/triangular {111} facets.

The total number of NP atoms, $\boldsymbol{N_{vol}(N, M, K)}$, and the number of facet atoms, $\boldsymbol{N_{facet}(N, M, K)}$, (outer polyhedral shell) are given with (C.55), (C.56), (C.6) by

$$N_{vol}(N, M, K) \quad = N_{vol}(N, M, K_b) - H\,[G\,(G + 2) - 2/3\,(H^2 - 4)]/2 \qquad \text{(C.58)}$$

$$N_{facet}(N, M, K) \quad = N_{facet}(N, M, -) - 2(N - M)^2 - 2G\,H + 2h \qquad \text{(C.59)}$$

$$H = 4M - N - K\,, \qquad G = 2M + N - K$$

**Inner *K* range** of sc($N$, $M$, $K$) where with (C.52)

$$K \le K_c \qquad \text{(C.60)}$$

For these $K$ values the NP becomes cubo-octahedral and does not exhibit {110} facets (except for possible microstrips). It is isomorphic with sc($N$, $M_a$, $K$) as discussed above and in Sec. C.2.2.

The present discussion allows a classification of sc($N$, $M$, $K$) NPs for all combinations of polyhedral parameters $N$, $M$, $K$. This includes NPs where one or two parameters define the structure already uniquely. Table C.6 illustrates all possible NP types.

| Constraints 1 | Constraints 2 | NP types | sc Isomorphs |
|---|---|---|---|
| $N \geq 2M$ | $K \geq 3M$ | Generic rhombohedral | (-, $M$, -) = ($N_a$, $M$, $K_a$) |
| | $2M \leq K \leq 3M$ | Rhombo-octahedral | (-, $M$, $K$) = ($N_a$, $M$, $K$) |
| | $K \leq 2M$ | Generic octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |
| $M \leq N \leq 2M$ | $K \geq 3M$ | Cubo-rhombohedral | ($N$, $M$, -) = ($N$, $M$, $K_a$) |
| | $4M - N \leq K \leq 3M$ | Cubo-rhombo-oct. upper central | ($N$, $M$, $K$) |
| | $2M \leq K \leq 4M - N$ | Cubo-rhombo-oct. lower central | ($N$, $M$, $K$) |
| | $N + 2g \leq K \leq 2M$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K \leq N + 2g$ | Generic octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |
| $N \leq M$ | $K \geq 3N$ | Generic cubic | ($N$, -, -) = ($N$, $M_a$, $K_a$) |
| | $2N \leq K \leq 3N$ | Cubo-octahedral truncated cubic | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K = 2N$ (ac) | Cuboctahedral | ($N$, $M_a$, $K$) |
| | $N + 2g \leq K \leq 2N$ | Cubo-octahedral truncated octahedral | ($N$, -, $K$) = ($N$, $M_a$, $K$) |
| | $K \leq N + 2g$ | Generic octahedral | (-, -, $K$) = ($N_a$, $M_a$, $K$) |

**Table C.6.** Constraints and types including isomorphs of sc($N$, $M$, $K$) NPs for atom centered (ac, $N$, $K$ even) and void centered (vc, $N$, $K$ odd) with (C.5). Polyhedral parameters $N_a$, $M_a$, $K_a$ are defined above.

Altogether, true cubo-rhombo-octahedral NPs, sc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities

$$M \leq N \leq 2M\,, \qquad 2M \leq K \leq 3M \tag{C.61}$$

## III. Conclusion

The present work gives a full theoretical account of the shape and structure of nanoparticles (NPs) forming compact polyhedral sections of the ideal cubic lattice where simple, body centered, and face centered variants are considered. We focus on particles of $O_h$ symmetry which are confined by facets of densest, second, and third densest monolayers of the lattice reflecting Miller index families {100}, {110}, and {111}. The structure evaluation identifies different types of generic NPs which serve for the definition of general polyhedral NPs. These can be classified according to three integer valued polyhedral parameters $N$, $M$, $K$ which are connected with particle diameters along corresponding facet normal directions reflecting $\{hkl\}$ monolayer families of the underlying lattice. Detailed structural properties of the general polyhedral NPs, such as shape, size, and surfaces, are discussed in analytical and numerical detail with visualization of characteristic examples. This illustrates the complexity of seemingly simple nanoparticles in a quantitative account.

Clearly, the present results deal only with ideal cubic NPs and cannot account for all possible structures of the most general metal nanoparticles observed, for example, by electron microscopy [15]. Realistic NPs may exhibit very different shapes, including less compact particles, and symmetry, including local structural disorder and deviations from (or incompatibility with) the crystal lattice structure in their inner core. This can only be examined in case-by-case studies where exact quantitative data are difficult to obtain. However, the present results can be used to estimate typical particle sizes and shapes of metal NPs as well as for a repository of possible structures of compact NPs with internal cubic lattice.

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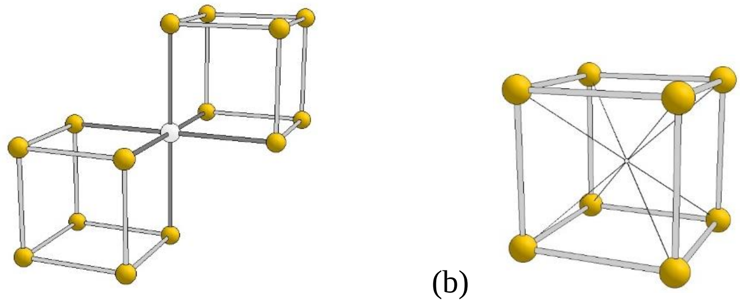
# V. Supplementary Information

Here we give additional information and further analytic relationships of structure properties relevant to cubic (sc, bcc, and fcc) nanoparticles discussed in the previous sections.

## S.1. Symmetry Centers

The cubic NPs, sc(*N*, *M*, *K*), bcc(*N*, *M*, *K*), and fcc(*N*, *M*, *K*) of $O_h$ symmetry contain atoms or high symmetry voids at their center depending on the lattice type and on parameters *N*, *M*, *K*.

The **simple cubic** lattice offers two different centers of $O_h$ symmetry, an atom site and a high symmetry void site as shown in Fig. S.1. This discriminates between two symmetry types of sc(*N*, *M*, *K*) NPs, those about an atom center and those about a high symmetry void.



(a) (b)

**Figure S.1.** $O_h$ symmetry centers of the simple cubic lattice, (a) atom site, (b) high symmetry void site. The symmetry centers are emphasized by white color and connected with their nearest neighbor atoms.

This discriminates between two types of octahedral and cubic sc[*N*, *M*, *K*) NPs, about an atom center and about a high symmetry void, depending on the parities (even, odd, any) of parameters *N*, *M*, *K* as spelled out in table S.1.

| NP center type | *N* | *M* | *K* |
|---|---|---|---|
| atom | even | any | even |
| void | odd | any | odd |

**Table S.1.** Parity of *N*, *M*, *K* for atom and void centered sc[*N*, *M*, *K*) NPs, see text.

The **body centered cubic** lattice offers only one center of $O_h$ symmetry which coincides with an atom site as shown in Fig. S.2. This allows for one symmetry type of bcc(*N*, *M*, *K*) NPs, about an atom center, independent of the parities of parameters *N*, *M*, *K*.

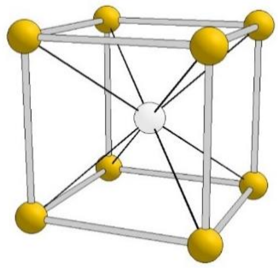
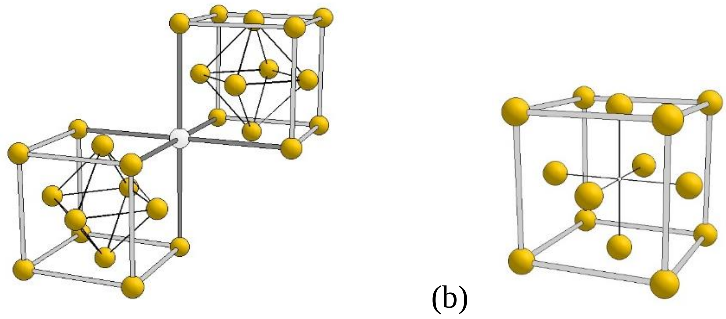


**Figure S.2.** $O_h$ symmetry center of the body centered cubic lattice at atom site. The center is emphasized by white color and connected with its nearest neighbor atoms.

The **face centered cubic** lattice offers two different centers of $O_h$ symmetry, an atom site and a high symmetry void as shown in Fig. S.3.



(a) (b)

**Figure S.3.** $O_h$ symmetry centers of the face centered cubic lattice, (a) atom site, (b) high symmetry void site. The centers are emphasized by white color and connected with their nearest neighbor atoms (void site) and next nearest neighbors (atom site), respectively.

This discriminates between two symmetry types of octahedral and cubic fcc(*N*, *M*, *K*) NPs, about an atom center and about a high symmetry void, depending on the parities (even, odd, any) of parameters *N*, *M*, *K* as spelled out in table S.2.

| NP center type | *N* | *M* | *K* |
|---|---|---|---|
| atom | any | any | even |
| void | any | any | odd |

**Table S.2.** Parity of *N*, *M*, *K* for atom and void centered fcc[*N*, *M*, *K*) NPs, see text.

## S.2. Alternative Descriptions of Cubic (*N*, *M*, *K*) Nanoparticles

### S.2.1 Face Centered Cubic NPs

There are two strategies to describe a general fcc($N$, $M$, $K$) NP which differ from that discussed in Sec. A.2.4. They start from either a true cubo-octahedral NP, fcc($N$, -, $K$), or from true rhombo-octahedral NP, fcc(-, $M$, $K$). Both strategies yield the same fcc($N$, $M$, $K$) NP description as given in Sec. A.2.4 and will be mentioned only briefly in the following.

Starting from a true cubo-octahedral NP, fcc($N$, -, $K$), with its constraints $N \leq K \leq 3N$ ($N + K$ even) or $N \leq K \leq 3N - 1$ ($N + K$ odd) and adding constraints of a generic rhombohedral NP, fcc(-, $M$, -), to yield the cubo-rhombo-octahedral NP fcc($N$, $M$, $K$) requires, according to the discussion above, $M$ values below $M_a$ where

$$M_a(N, K) = \min(K, 2N) \quad \text{(S.1)}$$

with truncated octahedral and truncated cubic fcc($N$, -, $K$) NPs defined by ($K \leq 2N$) and ($K \geq 2N$), respectively. In this scenario we can distinguish four different ranges of parameter $M$, defined by separating values $M_a \geq M_b \geq M_c$, with (S.1), (A.4) and

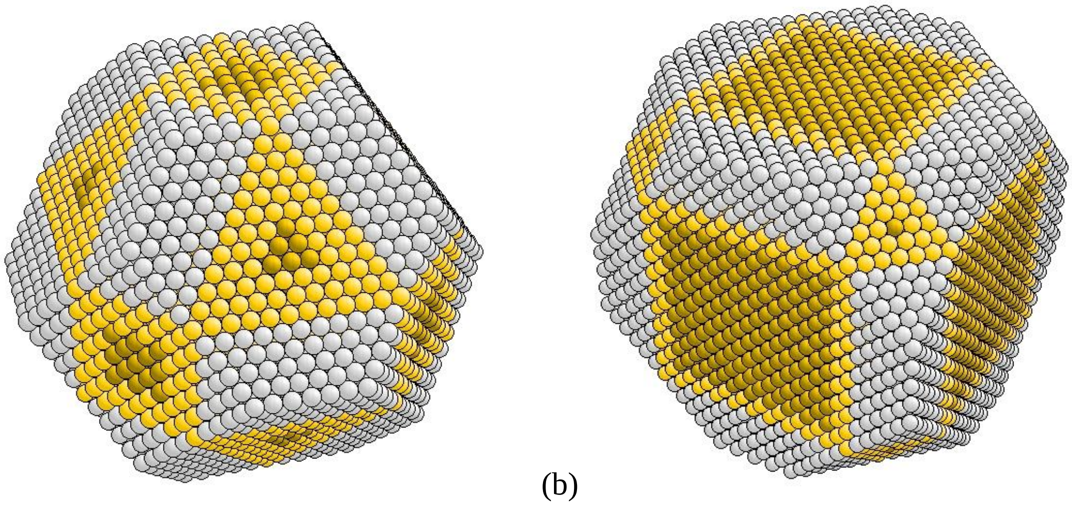
$$M_b(N, K) = (N + K)/2 \quad \text{(S.2)}$$

$$M_c(N, K) = 2K/3 \qquad = (2K + 3)/3 \qquad K = 6p + 3g \quad \text{(S.3a)}$$

$$= (2K + 2)/3 \qquad K = 6p + 2 + 3g \quad \text{(S.3b)}$$

$$= (2K + 1)/3 \qquad K = 6p + 4 - 3g \quad \text{(S.3c)}$$

(where $M_b(N, K)$, $M_c(N, K)$ may be fractional) which result in different NP shapes starting from the initial cubo-octahedral NP fcc($N$, $M_a$, $K$) as illustrated for fcc(16, 26, 26) (ac, truncated octahedral) in Fig. S.8a and for fcc(16, 32, 36) (ac, truncated cubic) in Fig. S.8b.



(a) (b)

**Figure S.8.** Atom ball models of atom centered cubo-octahedral NPs, (a) fcc(16, 26, 26) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, fcc(16, 21, 26) ($M = M_b$), and fcc(16, 18, 26) ($M = M_c$); (b) fcc(16, 32, 36) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, fcc(16, 26, 36) ($M = M_b$), and fcc(16, 24, 36) ($M = M_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $M$ ranges at $M = M_c$ (inner vs. lower central ) and at $M = M_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *M* range**, $M \geq M_a$, (all atom balls in Fig. S.8) where the fcc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph fcc($N$, $M_a$, $K$), an **upper**, $M_b \leq M \leq M_a$, (white atom balls in Fig. S.8) and **lower central *M* range**, $M_c \leq M \leq M_b$, (light yellow atom balls in Fig. S.8) where the fcc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *M* range**, $M \leq M_c$, (dark yellow atom balls in Fig. S.8) where the fcc($N$, $M$, $K$) NP becomes cubo-rhombohedral with the isomorph fcc($N$, $M$, $K_a$) or rhombo-octahedral with the isomorph fcc($N_a$, $M$, $K$). Altogether, true cubo-rhombo-octahedral NPs, fcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (A.62).

Starting from a true rhombo-octahedral NP, fcc(-, $M$, $K$), with its constraints $M \leq K \leq 3M/2$, etc., see (A.38). and adding constraints of a generic cubic NP, fcc($N$, -, -), to yield the cubo-rhombo-octahedral NP fcc($N$, $M$, $K$) requires, according to the discussion above, $N$ values below $N_a$. where with (A.6)

$$N_a(M, K) \quad = M - h' \qquad (M + K \text{ even}) \qquad \text{(S.4)}$$

In this scenario we can distinguish four different ranges of parameter $N$, defined by separating values $N_a \geq N_b \geq N_c$, with (S.4) and

$$N_b(M, K) = 2M - K \qquad \text{(S.5)}$$

$$N_c(M, K) = M/2 \qquad (M \text{ even}) \qquad \text{(S.6a)}$$

$$= (M - 1)/2 \qquad (M \text{ odd}) \qquad \text{(S.6b)}$$

which result in different NP shapes starting from the initial rhombo-octahedral NP fcc($N_a$, $M$, $K$) as illustrated for fcc(24, 24, 32) in Fig. S.9.

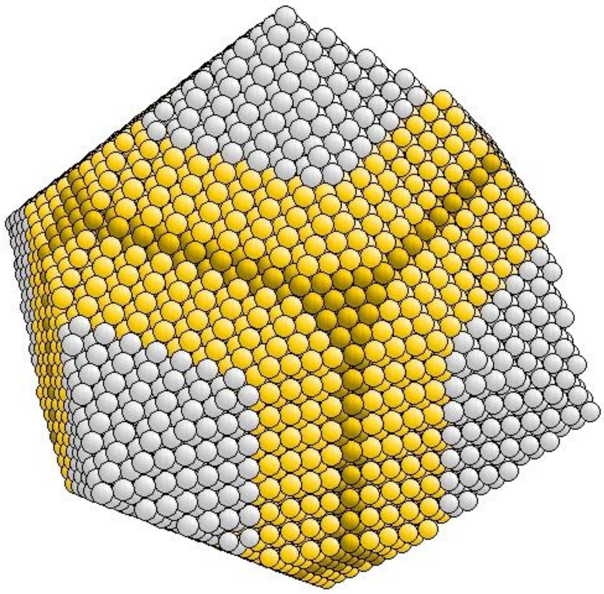


**Figure S.9.** Atom ball model of an atom centered rhombo-octahedral NP, fcc(24, 24, 32) ($N = N_a$, all atom balls), with its cubo-rhombo-octahedral NP components, fcc(16, 24, 32) ($N = N_b$), and fcc(12, 24, 32) ($N = N_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $N$ ranges at $N = N_c$ (inner vs. lower central ) and at $N = N_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *N* range**, $N \geq N_a$, (all atom balls in Fig. S.9) where the fcc($N$, $M$, $K$) NP becomes rhombo-octahedral with the isomorph fcc($N_a$, $M$, $K$), an **upper**, $N_b \leq N \leq N_a$, (white atom balls in Fig. S.9) and **lower central *N* range**, $N_c \leq N \leq N_b$, (light yellow atom balls in Fig. S.9) where the fcc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *N* range**, $N \leq N_c$, (dark yellow atom balls in Fig. S.8) where the fcc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph fcc($N$, $M_a$, $K$). Altogether, true cubo-rhombo-octahedral NPs, fcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (A.62).

### S.2.2 Body Centered Cubic NPs

There are two strategies to describe a general bcc($N$, $M$, $K$) NP which differ from that discussed in Sec. B.2.4. They start from either a true cubo-octahedral NP, bcc($N$, -, $K$), or from true rhombo-octahedral NP, bcc(-, $M$, $K$). Both strategies yield the same bcc($N$, $M$, $K$) NP description as given in Sec. B.2.4 and will be mentioned only briefly in the following.

Starting from a true cubo-octahedral NP, bcc($N$, -, $K$), with its constraints $N \leq K \leq 3N$ ($K$ even) or $N + 1 \leq K \leq 3N$ ($K$ odd) and adding constraints of a generic rhombohedral NP, bcc(-, $M$, -), to yield the cubo-rhombo-octahedral NP bcc($N$, $M$, $K$) requires, according to the discussion above, $M$ values below $M_a$. Here we distinguish between truncated octahedral bcc($N$, -, $K$) NPs where $K \leq 2N$ and truncated cubic NPs with $K \geq 2N$ where

$$M_a(N, K) \quad = K/2 \qquad (K \leq 2N,\ K \text{ even}) \qquad \text{(S.7a)}$$

$$= (K - 1)/2 \qquad (K \leq 2N + 1,\ K \text{ odd}) \qquad \text{(S.7b)}$$

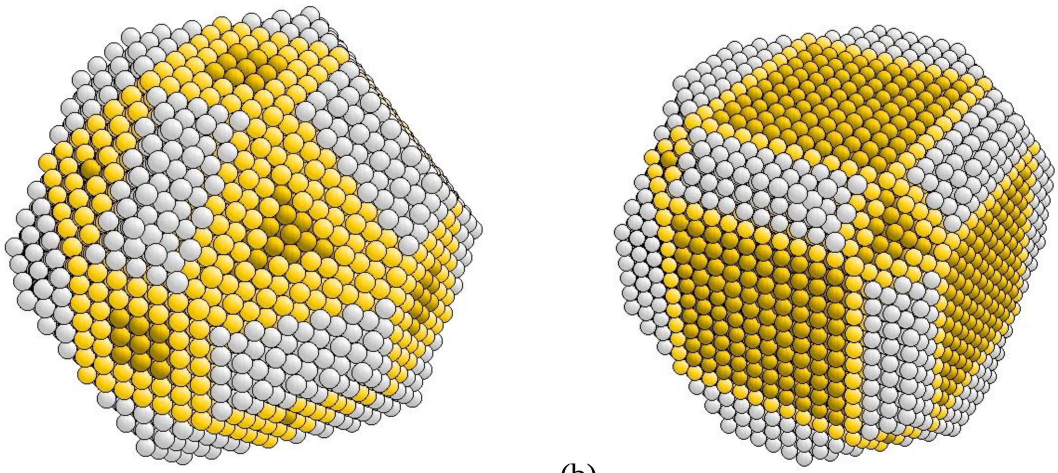
$$= N \qquad (K \geq 2N) \qquad \text{(S.7c)}$$

In this scenario we can distinguish four different ranges of parameter $M$, defined by separating values $M_a \geq M_b \geq M_c$, with (S.7) and

$$M_b(N, K) = (N + K)/4 \qquad \text{(S.8)}$$

$$M_c(N, K) = K/3 \qquad \text{(S.9)}$$

(where $M_b(N, K)$, $M_c(N, K)$ may be fractional) which result in different NP shapes starting from the initial cubo-octahedral NP bcc($N$, $M_a$, $K$) as illustrated for bcc(18, 15, 30) (truncated octahedral) in Fig. S.6a and for bcc(17, 17, 39) (truncated cubic) in Fig. S.6b.



(a) (b)

**Figure S.6.** Atom ball models of cubo-octahedral NPs, (a) bcc(18, 15, 30) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, bcc(18, 12, 30) ($M = M_b$), and bcc(18, 10, 30) ($M = M_c$); (b) bcc(17, 17, 39) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, bcc(17, 14, 39) ($M = M_b$), and bcc(17, 13, 39) ($M = M_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $M$ ranges at $M = M_c$ (inner vs. lower central ) and at $M = M_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *M* range**, $M \geq M_a$, (all atom balls in Fig. S.6) where the bcc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph bcc($N$, $M_a$, $K$), an **upper**, $M_b \leq M \leq M_a$, (white atom balls in Fig. S.6) and **lower central *M* range**, $M_c \leq M \leq M_b$, (light yellow atom balls in Fig. S.6) where the bcc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *M* range**, $M \leq M_c$, (dark yellow atom balls in Fig. S.6) where the bcc($N$, $M$, $K$) NP becomes cubo-rhombohedral with the isomorph bcc($N$, $M$, $K_a$) or rhombo-octahedral with the isomorph bcc($N_a$, $M$, $K$). Altogether, true cubo-rhombo-octahedral NPs, bcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (B.60).

Starting from a true rhombo-octahedral NP, bcc(-, $M$, $K$), with its constraints $2M \leq K \leq 3M$ and adding constraints of a generic cubic NP, bcc($N$, -, -), to yield the cubo-rhombo-octahedral NP bcc($N$, $M$, $K$) requires, according to the discussion above, $N$ values below $N_a$. where

$$N_a(M, K) \quad = 2M \qquad \text{(S.10)}$$

In this scenario we can distinguish four different ranges of parameter $N$, defined by separating values $N_a \geq N_b \geq N_c$, with (S.10) and

$N_b(M, K) = 4M - K$ (S.11)

$N_c(M, K) = M$ (S.12)

which result in different NP shapes starting from the initial rhombo-octahedral NP bcc($N_a$, $M$, $K$) as illustrated for bcc(26, 13, 33) in Fig. S.7.

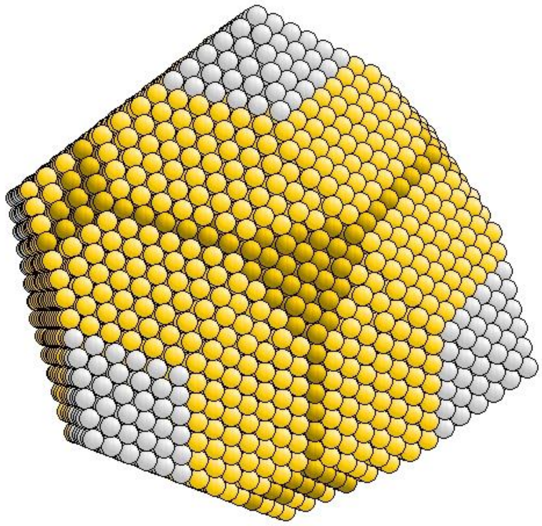


**Figure S.7.** Atom ball model of a rhombo-octahedral NP, bcc(26, 13, 33) ($N = N_a$, all atom balls), with its cubo-rhombo-octahedral NP components, bcc(20, 13, 33) ($N = N_b$), and bcc(13, 13, 33) ($N = N_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $N$ ranges at $N = N_c$ (inner vs. lower central ) and at $N = N_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *N* range**, $N \geq N_a$, (all atom balls in Fig. S.7) where the bcc($N$, $M$, $K$) NP becomes rhombo-octahedral with the isomorph bcc($N_a$, $M$, $K$), an **upper**, $N_b \leq N \leq N_a$, (white atom balls in Fig. S.7) and **lower central *N* range**, $N_c \leq N \leq N_b$, (light yellow atom balls in Fig. S.7) where the bcc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *N* range**, $N \leq N_c$, (dark yellow atom balls in Fig. S.7) where the bcc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph bcc($N$, $M_a$, $K$). Altogether, true cubo-rhombo-octahedral NPs, bcc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (B.60).

### S.2.3 Simple Cubic NPs

There are two strategies to describe a general sc($N$, $M$, $K$) NP which differ from that discussed in Sec. C.2.4. They start from either a true cubo-octahedral NP, sc($N$, -, $K$), or from true rhombo-octahedral NP, sc(-, $M$, $K$). Both strategies yield the same sc($N$, $M$, $K$) NP description as given in Sec. C.2.4 and will be mentioned only briefly in the following.

Starting from a true cubo-octahedral NP, sc($N$, -, $K$), with its constraints $N \leq K \leq 3N$ (ac) or $N + 2 \leq K \leq 3N$ (vc) and adding constraints of a generic rhombohedral NP, sc(-, $M$, -), to yield the cubo-rhombo-octahedral NP sc($N$, $M$, $K$) requires, according to the discussion above, $M$ values below $M_a$ where with (C.5)

$$M_a(N, K) = (K - g)/2 \qquad (K \leq 2N) \qquad \text{(S.13a)}$$

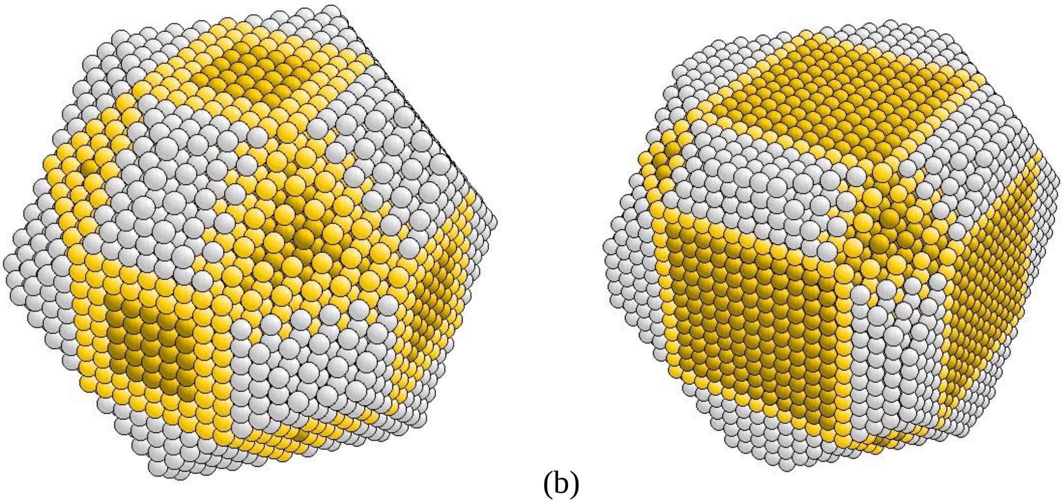
$$= N \qquad (K \geq 2N) \qquad \text{(S.13b)}$$

with truncated octahedral and truncated cubic sc($N$, -, $K$) NPs defined by ($K \leq 2N$) and ($K \geq 2N$), respectively. In this scenario we can distinguish four different ranges of parameter $M$, defined by separating values $M_a \geq M_b \geq M_c$, with (S.13) and

$$M_b(N, K) = (N + K)/4 \qquad \text{(S.14)}$$

$$M_c(N, K) = K/3 \qquad \text{(S.15)}$$

(where $M_b(N, K)$, $M_c(N, K)$ may be fractional) which result in different NP shapes starting from the initial cubo-octahedral NP sc($N$, $M_a$, $K$) as illustrated for sc(20, 18, 36) (truncated octahedral) in Fig. S.4a and for sc(20, 20, 44) (truncated cubic) in Fig. S.4b.



(a) (b)

**Figure S.4.** Atom ball models of atom centered cubo-octahedral NPs, (a) truncated octahedral sc(20, 18, 36) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, sc(20, 14, 36) ($M = M_b$), and sc(20, 12, 36) ($M = M_c$); (b) truncated cubic sc(20, 20, 44) ($M = M_a$, all atom balls), with its cubo-rhombo-octahedral NP components, sc(20, 16, 44) ($M = M_b$), and sc(20, 15, 44) ($M = M_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $M$ ranges at $M = M_c$ (inner vs. lower central ) and at $M = M_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *M* range**, $M \geq M_a$, (all atom balls in Fig. S.4) where the sc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph sc($N$, $M_a$, $K$), an **upper**, $M_b \leq M \leq M_a$, (white atom balls in Fig. S.4) and **lower central *M* range**, $M_c \leq M \leq M_b$, (light yellow atom balls in Fig. S.4) where the sc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *M* range**, $M \leq M_c$, (dark yellow atom balls in Fig. S.4) where the sc($N$, $M$, $K$) NP becomes cubo-rhombohedral with the isomorph sc($N$, $M$, $K_a$) or rhombo-octahedral with the isomorph sc($N_a$, $M$, $K$). Altogether, true cubo-rhombo-octahedral NPs, sc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (C.61).

Starting from a true rhombo-octahedral NP, sc(-, $M$, $K$), with its constraints $2M \leq K \leq 3M$ and adding constraints of a generic cubic NP, sc($N$, -, -), to yield the cubo-rhombo-octahedral NP sc($N$, $M$, $K$) requires, according to the discussion above, $N$ values below $N_a$. where with (C.5)

$$N_a(M, K) \quad = 2M - g \qquad \text{(S.16)}$$

In this scenario we can distinguish four different ranges of parameter $N$, defined by separating values $N_a \geq N_b \geq N_c$, with (S.16) and

$N_b(M, K) = 4M - K$ (S.17)

$N_c(M, K) = M$ (S.18)

which result in different NP shapes starting from the initial rhombo-octahedral NP sc($N_a$, $M$, $K$) as illustrated for sc(28, 14, 34) in Fig. S.5.

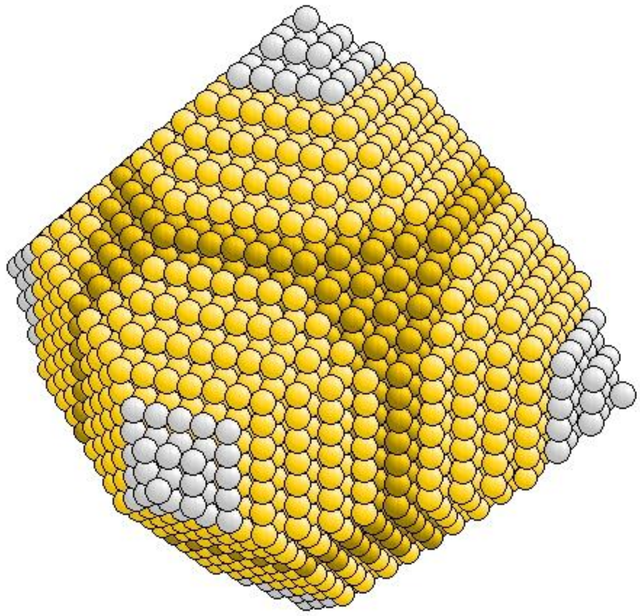


**Figure S.5.** Atom ball model of an atom centered rhombo-octahedral NP, sc(28, 14, 34) ($N = N_a$, all atom balls), with its cubo-rhombo-octahedral NP components, sc(22, 14, 34) ($N = N_b$), and sc(14, 14, 34) ($N = N_c$). The boundaries between dark, light yellow, and white balls reflect the separations of the different $N$ ranges at $N = N_c$ (inner vs. lower central ) and at $N = N_b$, (lower vs. upper central), respectively, see text.

Analogous to the discussion above, we discriminate between an **outer *N* range**, $N \geq N_a$, (all atom balls in Fig. S.5) where the sc($N$, $M$, $K$) NP becomes rhombo-octahedral with the isomorph sc($N_a$, $M$, $K$), an **upper**, $N_b \leq N \leq N_a$, (white atom balls in Fig. S.5) and **lower central *N* range**, $N_c \leq N \leq N_b$, (light yellow atom balls in Fig. S.5) where the sc($N$, $M$, $K$) NP becomes truly cubo-rhombo-octahedral, and an **inner *N* range**, $N \leq N_c$, (dark yellow atom balls in Fig. S.4) where the sc($N$, $M$, $K$) NP becomes cubo-octahedral with the isomorph sc($N$, $M_a$, $K$). Altogether, true cubo-rhombo-octahedral NPs, sc($N$, $M$, $K$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities given in (C.61).

## S.3. Cubic Macroparticles

Compact particles with cubic lattices and of $O_h$ symmetry, discussed in Secs. A - C, are uniquely described by polyhedral NP parameters *N*, *M*, *K* referring to distances $D_{\{100\}}$, $D_{\{110\}}$, $D_{\{111\}}$ (NP diameters) between parallel monolayer facets of given netplane families. This description becomes particularly simple if *N*, *M*, *K* assume very large values and can be approximated by real rather than integer quantities. As a consequence, {*hkl*} monolayer planes can still be defined by their normal directions in Cartesian coordinates but their distribution becomes continuous rather than discrete. Further, {*hkl*} facets confining the macroparticles (MP) are not restricted to discrete variations but may vary continuously as long as the overall $O_h$ symmetry is conserved. Thus, assuming a confinement by facets of the three cubic netplane families, {100}, {110}, and {111} NP diameters of these macroparticles can be written as

$$D_{\{100\}} = A\ , \quad D_{\{110\}} = B/\surd 2\ , \quad D_{\{111\}} = C/\surd 3 \qquad \text{(D.1)}$$

with *A*, *B*, *C* real valued. And in the most general case the particles can be denoted **cb(*A, B, C*)**. If a facet type does not appear in the MP the corresponding parameter value *A*, *B*, or *C* is replaced by a minus sign. As an example, a cubic MP with only {100} and {110} facets is denoted cb(*A*, *B*, -). These notations will be used in the following discussion.

### S.3.1. Generic Cubic Macroparticles , cb(*A*, -, -), (-, *B*, -), (-, -, *C*)

Generic cubic macroparticles (MPs) of $O_h$ symmetry are confined by facets with orientations of only one {*hkl*} netplane family. Here we focus on {100}, {110}, and {111} facets derived from the densest monolayers of the cubic lattice. This allows to distinguish between three different generic MP types

**(a)** **Generic cubic** MPs, denoted **cb(*A*, -, -)** (the notation is explained above), are confined by all six {100} monolayers with distances $D_{\{100\}} = A$ between parallel monolayers. This yields six square shaped {100} facets with <100> edges of length *A* and eight polyhedral <111> atom corners, see Fig. D.1.

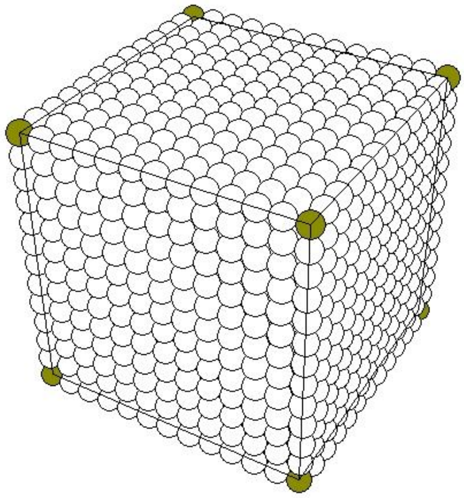


**Figure D.1.** Generic cubic MP filled with atom balls of an sc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MP.

The largest distance from the MP center to its surface along <*hkl*> directions, $\boldsymbol{s}_{<hkl>}$, is given by

$$s_{<100>}(A, \text{-}, \text{-}) = A/2 \quad \text{(D.2a)}$$

$$s_{<110>}(A, \text{-}, \text{-}) = \sqrt{2}\, A/2 \quad \text{(D.2b)}$$

$$s_{<111>}(A, \text{-}, \text{-}) = \sqrt{3}\, A/2 \quad \text{(D.2c)}$$

These quantities will be used in Secs. S.3.2.

**(b)** **Generic rhombohedral** MPs, denoted **cb(-, *B*, -)**, are confined by all twelve {110} monolayers with distances $D_{\{110\}} = B/\sqrt{2}$ between parallel monolayers. This yields twelve complete rhombic {110} facets with <111> edges of length $\sqrt{3}\, B/4$, see Fig. D.2. As a result, these MPs include atoms at six <100> and eight <111> corners and can be described as rhombic dodecahedra reminding of the shape of Wigner-Seitz cells of the face centered cubic (fcc) crystal lattice [14].

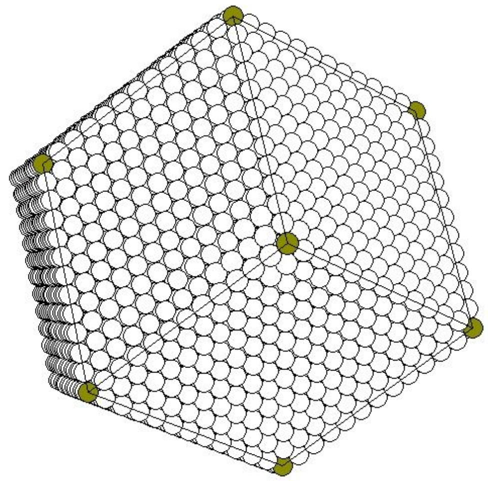


**Figure D.2.** Generic rhombohedral MP filled with atom balls of a bcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MP.

The largest distance from the MP center to its surface along <*hkl*> directions, $s_{<hkl>}$, is given by

$s_{<100>}(-, B, -) \;= B/2$ (D.3a)

$s_{<110>}(-, B, -) \;= \sqrt{2}\, B/4$ (D.3b)

$s_{<111>}(-, B, -) \;= \sqrt{3}\, B/4$ (D.3c)

These quantities will be used in Secs. S.3.2.

**(c)** **Generic octahedral** MPs, denoted **cb(-, -, *K*)**, are confined by all eight {111} monolayers with distances $D_{\{111\}} = C/\sqrt{3}$ between parallel monolayers. This yields eight {111} facets forming equilateral triangles with <110> edges of length $\sqrt{2}\, C/2$ and six polyhedral <100> atom corners , see Fig. D.3.

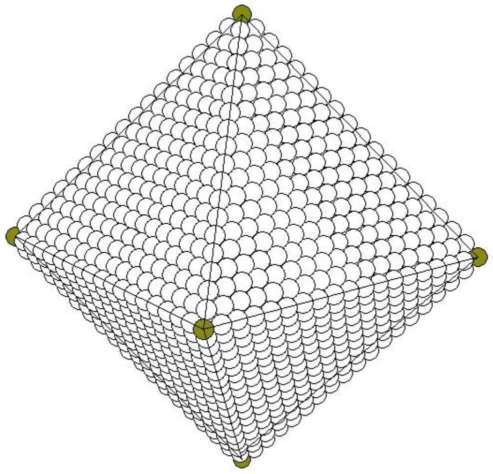


**Figure D.3.** Generic octahedral MP filled with atom balls of an fcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MP.

The largest distance from the MP center to its surface along <*hkl*> directions, $s_{<hkl>}$, is given by

$$s_{<100>}(-, -, C) \quad = C/2 \tag{D.4a}$$

$$s_{<110>}(-, -, C) \quad = \sqrt{2}\, C/4 \tag{D.4b}$$

$$s_{<111>}(-, -, C) \quad = \sqrt{3}\, C/6 \tag{D.4c}$$

These quantities will be used in Secs. S.3.2.

Table D.1 collects types and shapes of all generic cb MPs.

| Generic type | Facets | Corners |
|---|---|---|
| Cubic<br>cb(*N*, -, -) | {100} 6<br>{110} 0<br>{111} 0 | <100> 0<br><110> 0<br><111> 8 |
| Rhombohedral<br>cb(-, *M*, -) | {100} 0<br>{110} 12<br>{111} 0 | <100> 6<br><110> 0<br><111> 8 |
| Octahedral<br>cb(-, -, *K*) | {100} 0<br>{110} 0<br>{111} 8 | <100> 6<br><110> 0<br><111> 0 |

**Table D.1.** Types and notations of all generic cb MPs.

## S.3.2. Non-generic Cubic Macroparticles

Non-generic cubic nanoparticles of $O_h$ symmetry show facets with orientations of several {*hkl*} netplane families. This can be considered as combining confinements of the corresponding generic MPs discussed in Sec. S.3.1 with suitable polyhedral parameters *A*, *B*, *C* sharing their symmetry center. Here we discuss non-generic MPs which combine constraints of up to three generic MPs, cubic cb(*A*, -, -), rhombohedral cb(-, *B*, -), and octahedral cb(-, -, *C*). These allow {100}, {110}, as well as {111} facets and will be denoted **cb(*A*, *B*, *C*)** in the following. Clearly, the corresponding polyhedral parameters *A*, *B*, *C* depend on each other and determine the overall MP shape. In particular, if a participating generic MP encloses another participant it will not contribute to the overall MP shape and the respective {*hkl*} facets will not appear at the surface of the non-generic MP. In the following, we consider the three types of non-generic MPs which combine constraints due to two generic MPs (Secs. S.3.2.1-3) before we discuss the most general case of cb(*A*, *B*, *C*) MPs in Sec. S.3.2.4.

### S.3.2.1. Truncated cb(*A*, *B*, -) Macroparticles

Non-generic **cubo-rhombic** MPs, denoted **cb(*A*, *B*, -)**, are confined by facets referring to the two generic MPs, cb(*A*, -, -) (cubic) and cb(-, *B*, -) (rhombohedral). Thus, they can show {100} as well as {110} facets depending on relations between the polyhedral parameters *A*, *B*. If the edges of the cubic MP cb(*A*, -, -) lie inside the rhombohedral MP cb(-, *B*, -) the resulting combination cb(*A*, *B*, -) will be generic cubic which can be expressed formally by

$$s_{<110>}(A, -, -) \leq s_{<110>}(-, B, -) \qquad \text{(D.5)}$$

leading, according to (D.2), (D.3), to

$$B \geq 2A \qquad \text{(D.6)}$$

On the other hand, if the corners of the rhombohedral MP cb(-, *B*, -) lie inside the cubic MP cb(*A*, -, -) the resulting combination cb(*A*, *B*, -) will be generic rhombohedral which can be expressed formally by

$$s_{<100>}(-, B, -) \leq s_{<100>}(A, -, -) \qquad \text{(D.7)}$$

leading, according to (D.2), (D.3), to

$$B \leq A \qquad \text{(D.8)}$$

Thus, the two generic MPs intersect and define a true non-generic MP cb(*A*, *B*, -) offering both {100} and {110} facets only for polyhedral parameters *N*, *M* with

$$A < B < 2A \qquad \text{(D.9)}$$

while cb($A$, $B$, -) is generic cubic for $B \geq 2A$ and generic rhombohedral for $B \leq A$. This suggests that generic cubic and rhombohedral MPs can be considered as special cases of non-generic MPs cb($N$, $M$, -) where

cb($A$, -, -) = cb($A$, $B = 2A$, -) (cubic) (D.10a)

cb(-, $B$, -) = cb($A = B$, $B$, -) (rhombohedral) (D.10b)

Parameters $A$, $B$ provide additional information about geometric properties of the MPs describing their shapes and all facet edges. In the most general case, cubo-rhombic MPs cb($A$, $B$, -) exhibit six {100} facets of square shape with <100> edges of length ($B$ - $A$) and all twelve {110} facets, see Fig. D.4. The {110} facets are shaped as hexagons defined by four <111> edges of length $\sqrt{3}/4$ (2$A$ - $B$) and two <100> edges of length ($B$ - $A$) where triplets of adjoining <111> edges form a <111> corner.

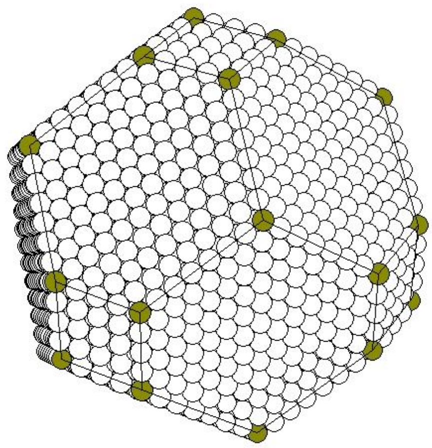


**Figure D.4.** Cubo-rhombic MP filled with atom balls of a bcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MP.

The present discussion allows a classification of cb($A$, $B$, -) MPs for all combinations of polyhedral parameters $A$, $B$. This includes generic MPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic MP. Table D.2 illustrates all possible MP types.

| Constraints | MP types | Isomorphs |
|---|---|---|
| $B \geq 2A$ | Generic cubic | ($A$, -, -) = ($A$, $B$ = 2$A$, -) |
| $A \leq B \leq 2A$ | Cubo-rhombic | ($A$, $B$, -) |
| $B \leq A$ | Generic rhombohedral | (-, $B$, -) = ($A$ = $B$, $B$, -) |

**Table D.2.** Constraints and types including isomorphs of cubo-rhombic cb($A$, $B$, -) MPs.

## S.3.2.2. Truncated cb(*A*, -, *C*) Macroparticles

Non-generic **cubo-octahedral** MPs, denoted **cb(*A*, -, *C*)**, are confined by facets referring to the two generic MPs, cb($A$, -, -) (cubic) and cb(-, -, $C$) (octahedral). Thus, they can show {100} as well as {111} facets depending on the polyhedral parameters $A$, $C$. If the corners of the cubic MP cb($A$, -, -) lie inside the octahedral MP cb(-, -, $C$) the resulting combination cb($A$, -, $C$) will be generic cubic which can be expressed formally by

$$s_{<111>}(A, -, -) \leq s_{<111>}(-, -, C) \qquad \text{(D.11)}$$

leading, according to (D.2), (D.4), to

$$C \geq 3A \qquad \text{(D.12)}$$

On the other hand, if the corners of the octahedral MP cb(-, -, $C$) lie inside the cubic MP cb($A$, -, -) the resulting combination cb($A$, -, $C$) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, C) \leq s_{<100>}(A, -, -) \qquad \text{(D.13)}$$

leading, according to (D.2), (D.4), to

$$C \leq A \qquad \text{(D.14)}$$

Thus, the two generic MPs intersect and define a true non-generic MP cb($A$, -, $C$) offering both {100} and {111} facets only for polyhedral parameters $A$, $C$ with

$$A < C < 3A \qquad \text{(D.15)}$$

while cb($A$, -, $C$) is generic cubic for $C \geq 3A$ and generic octahedral for $C \leq A$. This suggests that generic cubic and octahedral cb MPs can be considered as special cases of non-generic MPs cb($A$, -, $C$) where

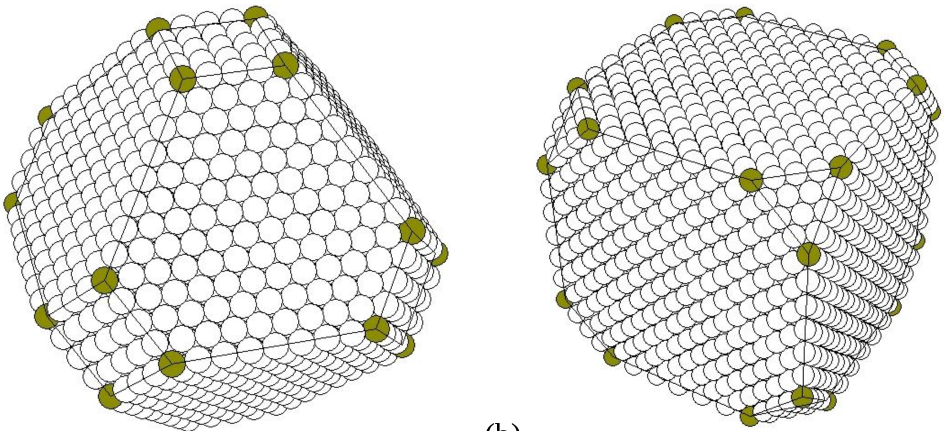
$$\text{cb}(A, -, -) = \text{cb}(A, -, C = 3A) \quad \text{(cubic)} \qquad \text{(D.16a)}$$

$$\text{cb}(-, -, C) = \text{cb}(A = C, -, C) \quad \text{(octahedral)} \qquad \text{(D.16b)}$$

Further, amongst the true intersecting cubo-octahedral MPs according to (D.15) we can distinguish between so-called **truncated octahedral** MPs where $C < 2A$ and **truncated cubic** MPs for $C > 2A$ with **cuboctahedral** MPs for $C = 2A$ separating between the two types as will be discussed in the following.

Parameters $A$, $C$ provide additional information about geometric properties of the MPs describing their shapes and all facet edges. In the most general case, cubo-octahedral MPs cb($A$, -, $C$) include six {100} and eight {111} facets.

**Truncated octhedral** MPs cb($A$, -, $C$) ($C < 2A$) exhibit {100} facets of square shape with <110> edges of length $\sqrt{2}\ (C - A)/2$, see Fig. D.5a. The {111} facets are of hexagonal shape with <110> edges of alternating lengths $\sqrt{2}\ (C - A)/2$ and $\sqrt{2}\ (2A - C)/2$.



(a) (b)

**Figure D.5.** Cubo-octahedral MPs filled with atom balls of an fcc lattice, (a) truncated octahedral, (b) truncated cubic type. The corners are emphasized by dark color and the black lines are meant to outline the MPs.

**Truncated cubic** MPs cb($A$, -, $C$) ($C > 2A$) exhibit {100} facets of square shape with <110> edges of length $\sqrt{2}\ (C - A)/2$, see Fig. D.5b. The {111} facets are of triangular shape with <110> edges of length $\sqrt{2}\ (3A - C)/2$.

**Cuboctahedral** MPs cb($A$, -, $C = 2A$) exhibit {100} facets of square shape with <110> edges of length $A/\sqrt{2}$, see Fig. D.6. The {111} facets form equilateral triangles with <110> edges of length $A/\sqrt{2}$ shared with those of the {100} facets.

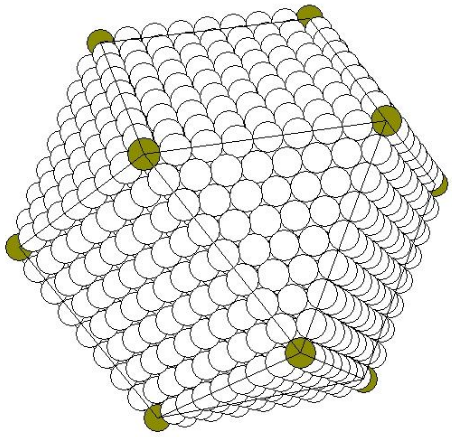


**Figure D.6.** Cuboctahedral MP filled with atom balls of an fcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MPs.

The present discussion allows a classification of cb(*A*, -, *C*) MPs for all combinations of polyhedral parameters *A*, *C*. This includes generic MPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic MP. Table D.3 illustrates all possible MP types.

| Constraints | MP types | Isomorphs |
|---|---|---|
| $C \geq 3A$ | Generic cubic | (*A*, -, -) = (*A* , -, *C* = 3*A*) |
| $2A \leq C \leq 3A$ | Cubo-octahedral truncated cubic | (*A*, -, *C*) |
| $C = 2A$ | Cuboctahedral | (*A*, -, *C* = 2*A*) , (*A* = *C*/2, -, *C*) |
| $A \leq C \leq 2A$ | Cubo-octahedral truncated octahedral | (*A*, -, *C*) |
| $C \leq A$ | Generic octahedral | (-, -, *C*) = (*A* = *C*, -, *C*) |

**Table D.3.** Constraints and types including isomorphs of cb(*A*, -, *C*) MPs.

## S.3.2.3. Truncated cb(-, *B*, *C*) Macroparticles

Non-generic **rhombo-octahedral** MPs, denoted **cb(-, *B*, *C*)**, are confined by facets referring to the two generic MPs, cb(-, *B*, -) (rhombohedral) and cb(-, -, *C*) (octahedral). Thus, they can show {110} as well as {111} facets depending on the polyhedral parameters *B*, *C*. If the corners of the rhombohedral MP cb(-, *B*, -) lie inside the octahedral MP cb(-, -, *C*) the resulting combination cb(-, *B*, *C*) will be generic rhombohedral which can be expressed formally by

$$s_{<111>}(-, B, -) \leq s_{<111>}(-, -, C) \qquad \text{(D.17)}$$

leading, according to (D.3), (D.4), to

$$C \geq 3/2\ B \qquad \text{(D.18)}$$

On the other hand, if the corners of the octahedral MP cb(-, -, *C*) lie inside the rhombohedral MP cb(-, *B*, -) the resulting combination cb(-, *B*, *C*) will be generic octahedral which can be expressed formally by

$$s_{<100>}(-, -, C) \leq s_{<100>}(-, B, -) \qquad \text{(D.19)}$$

leading, according to (D.3), (D.4), to

$$C \leq B \qquad \text{(D.20)}$$

Thus, the two generic MPs intersect and define a true non-generic MP cb(-, *B*, *C*) offering both {110} and {111} facets only for polyhedral parameters *B*, *C* with

$$B < C < 3/2\ B \qquad \text{(D.21)}$$

while cb(-, *B*, *C*) is generic rhombohedral for $C \geq 3/2$ and generic octahedral for $C \leq B$. This suggests that generic rhombohedral and octahedral cb MPs can be considered as special cases of non-generic MPs cb(-, *B*, *C*) where

$$\text{cb}(-, B, -) = \text{cb}(-, B, C = 3/2\ B) \qquad \text{(rhombohedral)} \qquad \text{(D.22a)}$$

$$\text{cb}(-, -, C) = \text{cb}(-, B = C, C) \qquad \text{(octahedral)} \qquad \text{(D.22b)}$$

Parameters *B*, *C* provide additional information about geometric properties of the MPs describing their shapes and all facet edges. In the most general case, rhombo-octahedral MPs cb(-, *B*, *C*) exhibit twelve {110} and eight {111} facets, see Fig. D.7. The MPs, show {110} facets of hexagonal shape with four <111> edges of length $(C - B)/2\ \sqrt{3}$ and two <110> edges of $(3/2\ B - C)\ \sqrt{2}$. The <110> edges confine also the triangular {111} facets.

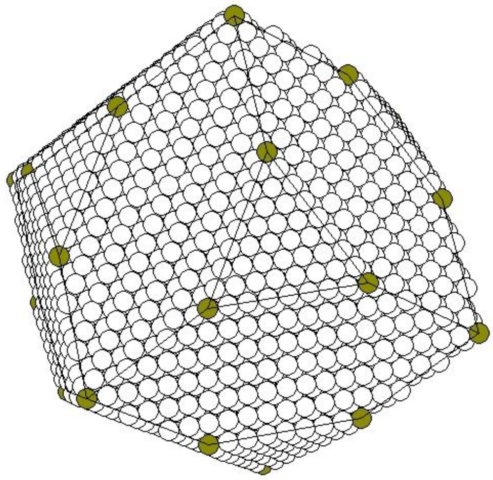


**Figure D.7.** Rhombo-octahedral MP filled with atom balls of an fcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the MP.

The present discussion allows a classification of cb(-, *B*, *C*) MPs for all combinations of polyhedral parameters *B*, *C*. This includes generic MPs where one parameter defines the structure already uniquely while the other can be chosen arbitrarily above a minimum value specifying the isomorphic MP. Table D.4 illustrates all possible MP types.

| Constraints | MP types | Isomorphs |
|---|---|---|
| $C \geq 3/2\ B$ | Generic rhombohedral | (-, *B*, -) =<br>(-, *B*, *C* = 3/2 *B*) |
| $B \leq C \leq 3/2\ B$ | Rhombo-octahedral | (-, *B*, *C*) |
| $C \leq B$ | Generic octahedral | (-, -, *C*) =<br>(-, *B* = *C*, *C*) |

**Table D.4.** Constraints and types including isomorphs of cb(-, *B*, *C*) MPs.

## S.3.2.4. Truncated cb(*A*, *B*, *C*) Macroparticles

Non-generic **cubo-rhombo-octahedral** MPs, denoted **cb(*A*, *B*, *C*)**, are confined by facets referring to all three generic MPs, cb(*A*, -, -) (cubic), cb(-, *B*, -) (rhombohedral), and cb(-, -, *C*) (octahedral). Thus, they can show {100}, {110}, and {111} facets depending on the polyhedral parameters *A*, *B*, *C*. A general discussion of these MPs requires a number of different scenarios using results of for generic and non-generic MPs with one or two types of facets, Secs. S.3.1, S.3.2.1-3, as will be detailed in the following.

First, we consider the general notation for generic cb MPs discussed in Sec. S.3.1. Cubic MPs cb($A$, -, -) are surrounded by rhombohedral MPs cb(-, $B$, -) if $B \geq 2A$ and by octahedral MPs cb(-, -, $K$) if $C \geq 3A$. This allows a notation cb($A$, $B$, $C$) where

$$\text{cb}(A, -, -) = \text{cb}(A, B = 2A, C = 3A) \tag{D.23}$$

Further, rhombohedral MPs cb(-, $B$, -) are surrounded by cubic MPs cb($A$, -, -) if $A \geq B$ and by octahedral MPs cb(-, -, $C$) if $C \geq 3/2\ B$. This allows a notation cb($A$, $B$, $C$) where

$$\text{cb}(-, B, -) \quad = \text{cb}(A = B, B, C = 3/2\ B) \tag{D.24}$$

In addition , the octahedral MPs cb(-, -, $C$) are surrounded by cubic MPs cb($A$, -, -) if $A \geq C$ and by rhombohedral MPs cb(-, $B$, -) if $B \geq C$. This allows a notation cb($A$, $B$, $C$) where

$$\text{cb}(-, -, C) \quad = \text{cb}(A = C, B = C, C) \tag{D.25}$$

General notations for non-generic cb MPs discussed in Secs. S.3.2.1-3 are obtained by analogous arguments.

According to Sec. S.3.2.1, true cubo-rhombic MPs cb($A$, $B$, -) with both {100} and {110} facets are subject to $A \leq B \leq 2A$. They are surrounded by octahedral MPs cb(-, -, $C$) if $C \geq C_a$ with

$$C_a(A, B) \quad = \min(3A, 3/2\ B) = 3/2\ B \tag{D.26}$$

This allows a general notation cb($A$, $B$, $C$) where

$$\text{cb}(A, B, -) = \text{cb}(A, B, C = C_a) \tag{D.27}$$

According to Sec. S.3.2.2, true cubo-octahedral MPs cb($A$, -, $C$) with both {100} and {111} facets are subject to $A \leq C \leq 3A$. They are surrounded by rhombohedral MPs cb(-, $B$, -) if $B \geq B_a$ with

$$B_a(A, C) \quad = \min(2A, C) \tag{D.28a}$$

$$= 2A \qquad \text{(truncated cubic)} \tag{D.28b}$$

$$= C \qquad \text{(truncated octahedral)} \tag{D.28c}$$

This allows a general notation cb($A$, $B$, $C$) where

$$\text{cb}(A, -, C) = \text{cb}(A, B = B_a, C) \tag{D.29}$$

According to Sec. S.3.2.3, true rhombo-octahedral MPs cb(-, $B$, $C$) with both {110} and {111} facets are subject to $B \leq C \leq 3/2\ B$. They are surrounded by cubic MPs cb($A$, -, -) if $A \geq A_a$ with

$$A_a(B, C) \quad = \min(B, C) = B \tag{D.30}$$

This allows a general notation cb($A$, $B$, $C$) where

$$\text{cb}(\text{-}, B, C) = \text{cb}(A = A_a, B, C) \qquad \text{(D.31)}$$

In the most general case of a true cb($A$, $B$, $C$) MP with {100}, {110}, and {111} facets we start from a true cubo-rhombic MP, cb($A$, $B$, -), with its constraints $A \le B \le 2A$ and add constraints of a generic octahedral MP, cb(-, -, $C$), where according to the discussion above $C$ values are below $C_a$. This allows to distinguish four different ranges of parameter $C$, defined by separating values $C_a \ge C_b \ge C_c$, with $C_a$ given by (D.26) and

$$C_b(A, B) \;\; = 2B - A \qquad \text{(D.32)}$$

$$C_c(A, B) \;\; = B \qquad \text{(D.33)}$$

which result in different MP shapes starting from the initial cubo-rhombic MP cb($A$, $B$, $C_a$) as illustrated in Fig. D.8.

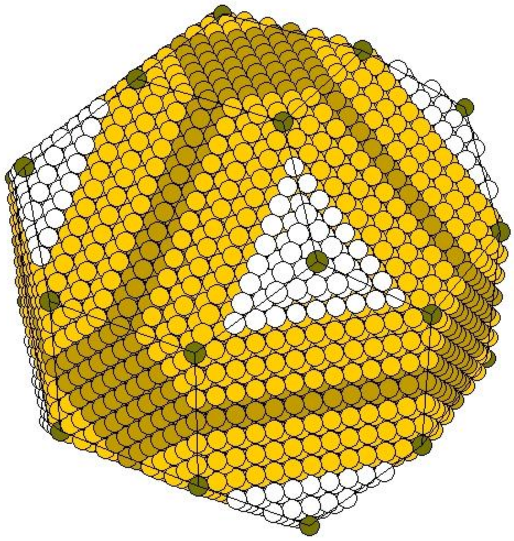


**Figure D.8.** Cubo-rhombic MP cb(A, B, $C_a$) filled with atom balls of an fcc lattice (all atom balls) with its cubo-rhombo-octahedral MP components cb(A, B, $C_b$) (dark and light yellow), and cb(A, B, $C_c$) (dark yellow). The corners are emphasized by dark color and the black lines are meant to outline the boundaries of the MP.

**Outer *C* range** of cb($A$, $B$, $C$) where with (D.26)

$$C \ge C_a \qquad \text{(D.34)}$$

For these $C$ values the MP becomes cubo-rhombohedral and does not exhibit any {111} facets. It is isomorphic with cb($A$, $B$, -) = cb($A$, $B$, $C_a$) as discussed above and in Sec. S.3.2.1.

**Upper central *C* range** of cb(*A*, *B*, *C*) where with (D.26), (D.32)

$$C_b \leq C \leq C_a \qquad \text{(D.35)}$$

For these *C* values the initial cb(*A*, *B*, $C_a$) MP is capped at its <111> corners forming eight additional {111} facets of equilateral triangular shape with edges of length (3*B* - 2*C*)/√2. This creates, in addition to the {111} facets, twelve {110} facets of octagonal/rectangular shape with two edges of length (3*B* - 2*C*)/√2, two edges of (*B* - *A*), and two of ($C - C_b$)/2 √3. Further, the cb(*A*, *B*, *C*) MP exhibits six {100} facets of square shape with edge lengths of (*B* - *A*). This is illustrated in Fig. D.9 for the MP filled by yellow atom balls where white balls above the {111} facets are added to yield the corresponding cubo-rhombic cb(*A*, *B*, $C_a$) MP.

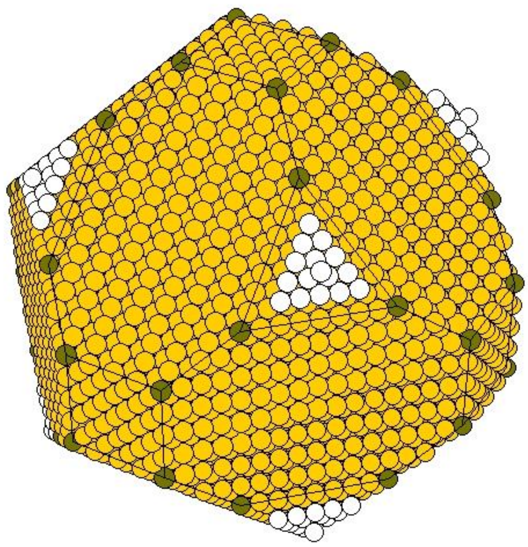


**Figure D.9.** Cubo-rhombo-octahedral MP cb(*A*, *B*, *C*) for $C_b < C < C_a$ filled with atom balls of an fcc lattice (yellow balls) with white balls completing the MP to cubo-rhombic, see text. The corners are emphasized by dark color and the black lines are meant to outline the boundaries of the MP.

For $C = C_b$, the cb(*A*, *B*, *C*) MP assumes a particular shape, see Fig. D.10. Its eight **{111} facets** are equilateral triangular with edge lengths of (2*A* - *B*)/√2 and its twelve **{110} facets** are rectangular with two edges of length (2*A* - *B*)/√2 and of (B - *A*). In addition, there are six **{100} facets** of square shape with edge lengths of (B - *A*). This is illustrated in Fig. D.10 for the MP cb(14, 20, 26) ($C_b$ = 26).

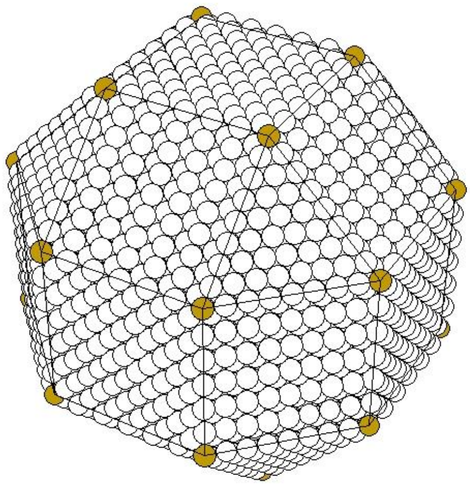


**Figure D.10.** Cubo-rhombo-octahedral MP cb($A$, $B$, $C_b$) filled with atom balls of an fcc lattice. The corners are emphasized by dark color and the black lines are meant to outline the boundaries of the MP.

**Lower central *C* range** of cb($A$, $B$, $C$) where with (D.32), (D.33)

$$C_c \leq C \leq C_b \qquad \text{(D.36)}$$

For these $C$ values the capping of the initial cb($A$, $B$, $C_b$) along the <111> directions is continued to yield eight hexagonal {111} facets with <110> edges of alternating lengths $(C_b - C)/\sqrt{2}$ and $(2A - B)/\sqrt{2}$. Further, there are twelve rectangular {110} facets of length $(2A - B)/\sqrt{2}$ and width $(C - B)$. Finally, the MP exhibits six octagonal {100} facets with alternating edges, four <100> of length $(C - B)$ and four <110> of length $(C_b - C)/\sqrt{2}$. This is illustrated in Fig. D.11 for the MP filled by yellow atom balls where white balls above the {111} facets are added to yield the corresponding cb($A$, $B$, $C_b$) MP.

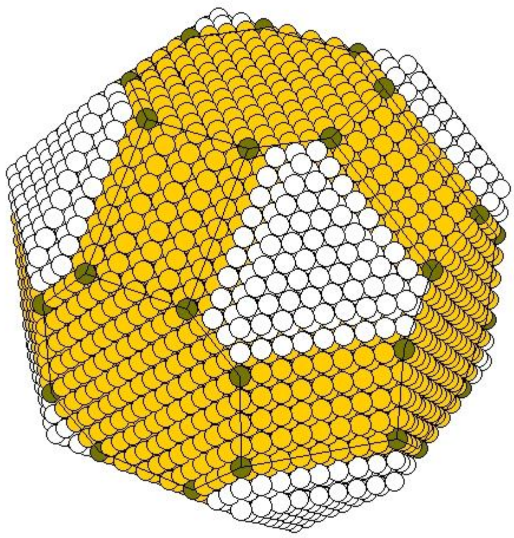


**Figure D.11.** Cubo-rhombo-octahedral MP cb(*A*, *B*, *C*) for $C_c < C < C_b$ filled with atom balls of an fcc lattice (yellow balls) with white balls completing the MP to cb(*A*, *B*, $C_b$), see text. The corners are emphasized by dark color and the black lines are meant to outline the boundaries of the MP.

**Inner *C* range** of cb(*A*, *B*, *C*) where with (D.33)

$$C \leq C_c \tag{D.37}$$

For these *C* values the MP becomes cubo-octahedral and does not exhibit any {110} facets. It is isomorphic with cb(*A*, -, *C*) = cb(*A*, $B_a$, *C*) as discussed above and in Sec. S.3.2.2.

The present discussion allows a classification of cb(*A*, *B*, *C*) MPs for all combinations of polyhedral parameters *A*, *B*, *C*. This includes MPs where one or two parameters define the structure already uniquely. Table D.5 illustrates all possible MP types.

| Constraints 1 | Constraints 2 | MP types | Isomorphs |
|---|---|---|---|
| $B \geq 2A$ | $C \geq 3A$ | Generic cubic | $(A, -, -) = (A, B_a, C_a)$ |
| | $2A \leq C \leq 3A$ | Cubo-octahedral truncated cubic | $(A, -, C) = (A, B_a, C)$ |
| | $C = 2A$ | Cuboctahedral | $(A, B_a, C)$ |
| | $A \leq C \leq 2A$ | Cubo-octahedral truncated octahedral | $(A, -, C) = (A, B_a, C)$ |
| | $C \leq A$ | Generic octahedral | $(-, -, K) = (N_a, M_a, K)$ |
| $A \leq B \leq 2A$ | $C \geq C_a$<br>$C_a = 3/2\ B$ | Cubo-rhombohedral | $(A, B, -) = (A, B, C_a)$ |
| | $C_b \leq C \leq C_a$<br>$C_b = 2B - A$ | Cubo-rhombo-oct. upper central | $(A, B, C)$ |
| | $C_c \leq C \leq C_b$<br>$C_c = B$ | Cubo-rhombo-oct. lower central | $(A, B, C)$ |
| | $A \leq C \leq C_c$ | Cubo-octahedral truncated octahedral | $(A, -, C) = (A, B_a, C)$ |
| | $C \leq A$ | Generic octahedral | $(-, -, C) = (A_a, B_a, C)$ |
| $B \leq A$ | $C \geq 3/2\ B$ | Generic rhombohedral | $(-, B, -) = (A_a, B, C_a)$ |
| | $B \leq C \leq 3/2\ B$ | Rhombo-octahedral | $(-, B, C) = (A_a, B, C)$ |
| | $C \leq B$ | Generic octahedral | $(-, -, C) = (A_a, B_a, C)$ |

**Table D.5.** Constraints and types including isomorphs of cb($A$, $B$, $C$) MPs. Polyhedral parameters $C_a$, $C_b$, $C_c$ are defined above.

Altogether, true cubo-rhombo-octahedral MPs, cb($A$, $B$, $C$) with {100}, {110}, and {111} facets can exist only if the polyhedral parameters $N$, $M$, $K$ fulfill the two inequalities

$$A \leq B \leq 2A\ , \qquad\qquad B \leq C \leq 3/2\ B \qquad\qquad (D.38)$$