Symmetry analysis in the investigation of clusters in complex metallic alloys

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Abstract. In the complex metallic alloys (CMA) it is often found that some parts of the unit cell form well-defined nanoscale building blocks, called clusters, which are characterized by a specific local symmetry and separated from the “matrix” crystal lattice by a partially disordered interface zone. The interior of the cluster is usually a close packed structure, the structure of which is not always exactly known, because of the partial disorder in the outer coordination shells. In many CMA’s the clusters form a high-symmetry superlattice structure, what usually leads to a giant cubic or pseudo cubic unit cell. The present paper shows a possibility to analyze the changes in local symmetry of the clusters (objects decorating the superlattice nodes) during transformations of the global crystal symmetry. The symmetry analysis method applied to tensor objects, attributed to the clusters, provides information about the symmetry relations between the objects located in different nodes as well as the local symmetry of individual objects (local principal axes, local anisotropy etc.)

1. Introduction

Complex metallic alloys (CMA’s) are intermetallic compounds forming giant elementary cells ($a = 20$–$30$ Å), which usually contain a large number of atoms ($100$–$1000$). Because of very interesting physical properties and potential technological applications they are intensively investigated during the recent years, although some of them have been discovered and partially described some decades ago. Physical properties of these compounds strongly depend on the structure of the unit cell, so it is only natural that the crystal structure and all its structural transformations are being investigated in the first stage. For CMA’s these structures are very complicated, and their investigation is not a simple task. In many CMA compounds the sites with high multiplicity numbers are not fully occupied, and for some of them overlapping atomic positions are found, which are occupied alternatively (split occupation). Fortunately for those parts of the unit cell it is possible to find parameters characterizing these groups of sites in a coarse grained manner, i.e. these sets of atomic positions are collected in separate groups, localized round a small number of special (usually high symmetry) sites. These well-defined groups of sites, with partial occupational disorder in the outer shells, are usually called clusters and may be regarded as structural elements (building blocks), which – similarly to the atoms in regular crystal structures – form higher order lattice structures, leading to the abovementioned large and complex unit cells. A good example of a CMA compound, exhibiting genuinely giant and complex unit cell, is the $\beta$-Mn$_2$Al$_3$ phase, for which the structure investigations [1,2] attribute 1168 occupied
sites to its unit cell. In the present paper it will be used as an example in order to illustrate the application of symmetry analysis method to investigation of complex metallic structures.

The symmetry analysis method based on the theory of group and representations [3] is able to predict all possible channels of structural transformations from a well-known, high symmetry parent crystal structure to structures with reduced symmetry groups, identical with one of subgroups of the initial symmetry group. These symmetry transformations can be described by a small number of parameters, independently specifying the multiplicity and locations of occupied positions as well as other types of physical quantities affected by the crystal transformation. In situations where the microscopic picture is very complicated, as in the CMA compounds, the symmetry analysis method proves to be very helpful.

The symmetry analysis dealing with scalar and vector type functions has been applied to the investigation of the Mg$_2$Al$_3$ transformation from the cubic Fd-3m $\beta$-phase to the rhombohedral R3m $\beta'$-phase [2]. It has been suggested that in the parent $\beta$-phase the Mg and Al atoms occupy 23 different Wyckoff positions, most of them exhibiting multiplicity equal to 96. As some of these positions are partially occupied, the transition to the rhombohedral $\beta'$-phase may follow two alternative routes: the ordering of statistical site occupation factors, distributed over a given orbit of atomic sites, or displacements of atomic positions (the real case may include a combination of these). The first possibility can be described by symmetry analysis of a scalar quantity (changes in the occupation probability), while the other requires a description by polar vector quantities (displacement vectors).

For compounds like CMA's the symmetry analysis offers also a possibility to discuss the structure transformations as a description of symmetry changes (ordering) of tensor quantities, localized on the sets of equivalent positions in the parent high symmetry structure. Such a form of the method has been applied to the discussion of quadrupolar tensor ordering for example in DyB$_2$C$_3$ [4]. As will be shown below in the cubic Mg$_2$Al$_3$ phase there are sets of atomic positions, which form well-defined clusters, and which can be characterized by a second rank tensor – e.g. tensor of inertia, with centers located at the previously mentioned high symmetry Wyckoff positions. These clusters and their respective inertia tensors offer a possibility to describe the transition from Fd-3m to R-3m structure by the symmetry analysis of the cluster ordering and this will be the main subject of the present work.

2. Structural characteristics of $\beta$-Mg$_2$Al$_3$

The renewed interest in the chemical compounds (mostly intermetallics) that are generally labeled as “cluster phases” has been stimulated by their specific structural features, which may lead to low density and some special mechanical properties offering prospects of technological applications. The list of features usually attributed to those cluster phases usually includes [5]:

- the presence of clearly distinguishable nanoscale “building blocks” (clusters), with well-defined local symmetry, sometimes reproducing the crystal structure of other known phases.
- the building blocks are included in the structure, but the interface is not always well-defined (partially occupied sites) and is sometimes used to match-up the incongruences between the local and global symmetry
- the building blocks are sometimes arranged in superstructures of cluster nodes, forming crystal structures with high cell constant values, usually exhibiting high symmetry (cubic or pseudo-cubic) or quasicrystalline arrangements

One of the well-known structures classified as a cluster phase is the $\beta$-Mg$_2$Al$_3$, usually found in the (Mn,Al) alloys with Mg contents lower than the nominal 40:60 ratio (the estimated stability range covers Mg contents between 37.5 and 40%). Its structure has been proposed some decades ago [1] but it is being reexamined in recent years, because there are many questions that has not been properly answered yet, and which can still be of considerable technological importance [2].
2.1. General arrangement of structural elements in $\beta$-Mg$_2$Al$_3$

In the proposed models [1,2] the atomic sites are attributed to 23 non-equivalent Wyckoff positions of the Fd-3m (No.227) space group, that are fully or partially occupied by the Mn or Al atoms. The total number of atomic sites generated from the 23 positions is equal to 1832, but the partial occupation of some of these sites results in the effective number of 1168 atoms located in the unit cell. From the complete list of atomic positions published in Table 1 in [1], that is generally used in the following structure studies, one can find that among the total of 23 positions only 12 are fully occupied by Mg (positions 4,6,15,17,18) or Al atoms (positions 1,2,3,5,16,22). The total number of fully occupied sites is estimated as 840 [2,5]. The structure formed by the fully occupied sites is close to a set of stacked planes, with local hexagonal coordination, which are perpendicular to the [1,1,1] direction of the cubic unit cell. This set of lattice sites is often described more locally as a set of Friauf polyhedra, with some additional polyhedra variants near selected sites [5]. The rest of the atomic positions (992) are only partially occupied and they mainly contribute to the packs of atoms regarded as clusters. Their positions are mainly gathered near five positions in the interior of the unit cell and twelve equivalent positions on the edges of the cube. Some of these edge positions are equivalent, so finally there are eight gathering points of the partially occupied sites per unit cell, which coincide with the locations of 8(b) high-symmetry sites in the crystal.

The structure of $\beta$-Mg$_2$Al$_3$ fully fits the description of a typical cluster phase. Figure 1 shows the proposed cluster allocations in the giant unit cell of $\beta$-Mg$_2$Al$_3$ ($a = 2.82$ nm).

![Figure 1](image)

**Figure 1.** The general view of cluster allocation (a) and the respective [1,1,1] projection (b) of the cluster contribution in the giant unit cell of $\beta$-Mg$_2$Al$_3$.

As can be seen from figure 1 the network of clusters forms a diamond-type lattice, with four nearest neighbors in tetrahedral coordination. Such a lattice has four special directions i.e. [1,1,1], [1,-1,-1], [-1,1,-1] and [-1,-1,1], along which the inter-cluster connections are aligned. The diagonal view shown in figure 1(b) indicates that the structure can be composed of hexagonal prisms (pillars) oriented along [1,1,1] with trigonal prisms as fillers. The neighboring hexagonal prisms are shifted by one third of the crystal period along [1,1,1] direction. The central hexagonal prism is shown in detail in figures 2a and 2b. Starting from the (0,0,0) position and moving along [1,1,1] direction one finds a sequence of high local symmetry positions, namely: two 8(a) sites located symmetrically around 16(c)
position at (0.125,0.125,0.125) and then two 8(b) sites connected through the 16(d) site at (0.625,0.625,0.625) (see figure 2b). The list of atomic positions in the model structure shows that only 8(b) and 16(c) are occupied, while 8(a) and 16(d) are empty. A detailed analysis shows that the 8(a) site lies in the center of a local tetrahedral surroundings formed by fully occupied Al and Mg sites, which do not exhibit close packed configuration features, but which are well stabilized by their surrounding. The 16(c) positions exhibit a local coordination close to hcp, with six neighbors in the \{1,1,1\} plane and two triplets below and above the plane. All the atomic sites near 16(c) are fully occupied. In upper half of the [1,1,1] diagonal, in the close vicinity of the each 16(d) site, there are two Al atoms, separated by a very short distance, which may act as the central core for the surrounding atoms. The atoms located near 16(d) sites are shared with second coordination shell of the well formed cluster of atoms, located at 8(b) sites, forming the interconnecting bridges (see figure 2c and 2d). Therefore the candidates for cluster centers with locally close packed configuration are definitely the sites at 8(b), but to some extent also the 16(d) site surrounding can be treated as a distinct group of partially occupied atomic positions supported by the central core.

![Figure 2](image)

**Figure 2.** The central hexagonal prism of the unit cell (see figure 1b), extracted along [1,1,1] direction, shown in different views (a),(b) in full and after stripping down to the atoms of second (c) and first (d) coordination shells of the 8(b) cluster.

2.2. *High-symmetry 8(b) sites as cluster locations*

The cluster at 8(b) is formed around the Mg(23) atom, located at its centre (see figure 2d). Its first coordination shell consists of 72 atomic sites, attributed to six crystallographic 96(g) positions (12 atomic sites each). Their distances from the centre of the cluster cover the range between 0.282 nm and 0.317 nm, what is consistent with a typical metallic bond length. As can be expected there is no chance for actual placement of 72 atoms in the first coordination shell, with proper distances between them. Especially that some positions definitely overlap and can be only alternatively occupied (split occupation). The total occupation number taken from the experiment [2] summed up over the 6 crystallographic positions is about 1.33, what in fact means that only about 16 atoms (out of 72) are actually present. The set of positions in the first shell can be split into two groups: the four Al positions (7,8,9,10) with total occupation probability summing up to about one, from which only one of every four will be present at a time (12 atoms) and two overlapping Mg19/Al20 positions (in some
structural studies treated as one general metal site) with total occupation summing up to about one third, contributing the total of 4 atoms. The Mg19/Al20 positions are in fact grouped in four separate and closely overlapping sextuplets, so the effective occupation of one atom per each group is quite natural. The second coordination shell (see figure 2c) is located at distances between 0.51 to 0.58 nm from the centre and it also includes six 96(g) positions, from which only one (Mg6) is fully occupied. The rest exhibits only partial occupation, sometimes splitting in pairs with total occupation summing up to one (Mg11/Al12, Mg13/Al14) or half-occupied as Al21. The sites of the second coordination shell are shared with the nearest neighbourhood of the empty 16(d) position, forming a bridge between the neighbouring 8(b) clusters (see figure 2c), aligning with one of the special direction of the cluster networks. Even with partial occupations both coordination shells of 8(b) seem highly symmetrical, with over-all cluster symmetry close to spherical. For the purpose of further analysis the first coordination shell will be called as the A-type cluster.

2.3. Local atomic coordination near the 16(d) sites
The group of atoms located near the 16(d) site on one hand looks like a standalone cluster surrounding the central site and on the other hand play the role of a bridge between the spherical 8(b) clusters. A specific feature of that group is the fact that the central site does not contain any atom, but near that site two split Al21 positions are located, both with occupancy factor close to 0.5. This in fact means that only one Al atom will be present at a time and its actual position will be located near the centre of the cluster. The first coordination shell consisting of Mg13 and Al14 atoms is located at the distances close to 0.25nm. The occupancy factors for the Mg13/Al14 pair sum up to value very close to one. Some structural studies even replace the pair of distinguishable positions with one shared position with occupancy factor equal to one. The arrangements of the atoms in the first coordination shell of 16(d) is far from spherical, definitely exhibiting axial symmetry, with the special symmetry axis aligned with the [1,1,1] or equivalent directions. The central Al atoms together with the surrounding Mg13/Al14 will be further on called B-type cluster.

2.4. Quasi-hexagonal lattice near 16(c) and 8(a) sites
In contrast to the 8(b) clusters the nearest neighbourhoods of the 16(c) sites consist of fully occupied sites, forming a proper close packed configuration, with twelve atoms in the first configuration shell. The configuration closely resembles a hcp arrangement around the central Al22 atom, with six in-plane Al3 neighbours and two Mg4 triplets above and below the plane (the hexagonal plane is perpendicular to the triple [1,1,1] axis - see figure 2a and 2b). The local symmetry at 16(c) is directly related to the presence of the special [1,1,1] axis, but the deviations from the spherical symmetry are very small, as it is usually observed for metallic hcp structures.

At first sight the configuration around 8(a) seems similar to the vicinity of the 16(c) site, however a detailed analysis shows that a different local symmetry is found in the Fd-3m symmetry group. The 8(a) site is not occupied by a single atom, but it is surrounded by a tetrahedron, formed by four Al atoms (the edges formed by Al-Al bonds), with second coordination shell being also a tetrahedron of Mg atoms. Such a local configuration can be by no means treated as a close packed arrangement, therefore it seems that directional features of the Al-Al bonds are responsible for the local energy optimization. However the outraching interatomic bonds seem to fix the group to the quasi-hexagonal matrix formed by the atoms located near the 16(c) sites. A more global analysis actually shows that the quasi-hexagonal network penetrates the whole crystal volume and the only areas that are qualitatively different are the “caverns” in which the spherical 8(b) clusters with the 16(d) connecting cluster are located.

3. Tensor description of clusters as structural elements
A tensors object attributed to the cluster may represent several different physical quantities but the simplest possibility is to consider the tensor of inertia. As its physical nature is very simple it is very
convenient for a demonstration of the cluster symmetry changes during a structural transformation. In the case considered here the tensor of inertia $I$ is calculated from the point mass definition:

$$I_{ij}(\vec{r}_0) = \sum_k m_k \left\{ \delta_{ij} |\vec{r}_k - \vec{r}_0|^2 - (r_{ki} - r_{0i})(r_{kj} - r_{0j}) \right\}$$

(1)

 replacing $m_k$ by the effective atomic masses, attributed to the partially occupied positions ($m_{eff} = m*P$, where $P$ is the respective site occupation factor) in accordance with the symmetry of the atomic orbit. The matrix can be calculated for a selected subset of atoms in the cluster (e.g. individual $n$-th atomic orbit) or summed up over the whole cluster.

3.1. Clusters at 8(b) positions

For the A-type clusters (first coordination shells, located around each 8(b) positions - see figure 2d) in the high-symmetry cubic phase the respective $I$ matrices (the argument $r_n$ runs over all 8(b) sites) take the diagonal form:

$$I_A(r_n) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

$$I_1 = I_2 = I_3 = a$$

$$\vec{n}_1 \perp \vec{n}_2 \perp \vec{n}_3$$

(2)

The $a$ parameter value directly determines the three indistinguishable principal values of the moment of inertia (full degeneration) along three orthogonal, arbitrary principal axes. Such a situation is represented by a spherical form of the inertia ellipsoid, with three indistinguishable, mutually perpendicular principal axes.

3.2. Clusters located at 16(d) positions

The tensors of inertia calculated for the B-type clusters located at the 16(d) sites (the same procedure as for A-type clusters) in the high symmetry cubic phase take the forms shown in table 1.

Table 1. The inertia tensors, their respective eigenvalues and directions of principal axes for various sites of the 16(d) orbit.

| Sites   | Inertia tensor | Eigenvalues        | Principal axes                   |
|---------|----------------|-------------------|----------------------------------|
| 1,5,9,13| $I_B = \begin{pmatrix} b & c & c \\ c & b & c \\ c & c & b \end{pmatrix}$ | $I_1 = b + 2c$ | $\vec{n}_1 = [1,1,1]$ |
|         |                | $I_{2,3} = b - c$ | $\vec{n}_2 \perp \vec{n}_3$    |
| 2,6,10,14| $I_B = \begin{pmatrix} b & -c & -c \\ -c & b & c \\ -c & c & b \end{pmatrix}$ | $I_1 = b + 2c$ | $\vec{n}_1 = [-1,1,1]$ |
|          |                | $I_{2,3} = b - c$ | $\vec{n}_2 \perp \vec{n}_3$    |
As can be seen the 16 sites split into four groups, which are attributed to four direction of the cubic special (symmetry) axis. The allowed directions are the [1,1,1] 3-fold axis and its symmetry equivalent directions i.e. [-1,1,1], [1,-1,1] and [1,1,-1]. For the case of all equal off-diagonal c elements obtained for the 16(d) clusters the single eigenvalue $I_1$ of each tensor takes the highest value, while the other two $I_2$, $I_3$ take lower values. All the inertia ellipsoids have one special principal axis $n_1$, aligned with the 3-fold cubic axis, identical with full rotation symmetry axis of each ellipsoid, while the other two $n_2, n_3$ principal axes are arbitrary, but orthogonal to $n_1$ axis. It means that all ellipsoids are disc-shaped, with the shortest diameter aligned with the corresponding 3-fold symmetry axis.

3.3. Transformation of tensors under symmetry operations

In order to apply the symmetry analysis method one has to know the transformation rules applicable for a given object when the coordinate system is changed or a specific symmetry operation is applied. For a second rank 3x3 tensor the transformation rules can be written in two forms:

$$I'_{ij}(\vec{r}) = \sum_{k,l} d_{ijkl} I_{kl}(\vec{r})$$

(3a)

$$I'_r(\vec{r}) = \sum_s D_{rs} I_s(\vec{r})$$

(3b)

The second version is applicable when the 3x3 matrix is represented by a one dimensional vector of length 9 by a proper re-indexing of components. The elements of the new transformation matrix $D$ can be calculated from the original transformation matrices $d$ [7]. The action of a given space group element $g$ on the tensor of inertia $I$ at a given position $r$ according to the group theory [3] looks as follows:

$$g I(\vec{r}) = \hat{D}(g) I(g^{-1} \vec{r})$$

(4)

The $D(g)$ matrices, executing the tensor transformations under the action of space group symmetry elements, and the resulting tensor components after the transformation can be calculated e.g. by the MODY program [6]. Applying equation (4) and the respective $D(g)$ matrices it can be shown that in the high symmetry cubic structure (Fd-3m) the inertia tensors of A-type clusters localized at 8(b) Wyckoff positions do not change under symmetry operations transforming one 8(b) site into another, equivalent site, thus they take the same diagonal form with equal principal values (see equation 2) for clusters located in all sites within the orbit of 8(b) positions.

On the other hand the application of the $D(g)$ matrices and the equation (4) to the B-type clusters located at the 16(d) in the high-symmetry cubic structure shows that the tensor $I(n)$ located at some 16(d) position number $(n)$, can be obtained by a transformation of the inertia tensor $I(l)$ located at site
(1) using Fd-3m space group elements (see equations 3a,b and 4), as a set of tensors that is invariant under the action of elements of this symmetry space group, for example:

\[
2_x I_{\text{II}}(1) = I_{\text{II}}(2) \quad 2_y I_{\text{II}}(1) = I_{\text{II}}(3) \quad 2_z I_{\text{II}}(1) = I_{\text{II}}(4)
\]

(5)

The obtained results show that in opposition to the A-type clusters, which are characterized by full spherical symmetry, the inertia tensors of 16(d) clusters have a clearly defined principal axis, pointing in different directions at various 16(d) sites, and still they are being equivalent, as the crystal symmetry operations transform the inertia tensors located at different 16(d) sites into each other.

These considerations show that the tensors of inertia can be efficiently used for characterization of clusters localized at some set of Wyckoff positions. Such clusters can be used as a set of structural elements decorating the sites in the elementary cell with a given symmetry space group, thus forming a multi-atom, giant unit cell representing a complicated crystal structure.

4. The symmetry analysis of the Fd-3m => R3m transition in \(\beta\)-Mg\(_2\)Al\(_3\)

The description of tensor objects in the frame of symmetry analysis provides information about the relations between the principal axes of inertia tensor to the crystallographic axes and about the shape of inertia ellipsoids, i.e. about all the properties usually obtained from microscopic data like the positions and masses of individual atoms near a given central site. In the course of a structural phase transition the microscopic variables (the atomic positions and effective masses) may change. Such a change is usually accompanied by a symmetry reduction, i.e. a transition from initial high symmetry space group to the final lower-symmetry group. The symmetry analysis may describe the symmetry reduction process even without knowing the details of the microscopic changes. The symmetry changes observed for the tensor-type objects located in some special sites of the crystal can be described by construction of the respective inertia tensor changes as a linear combination of so called basic vectors of irreducible representations active in a given transition [3,6].

On the other hand one can always calculate the changes of inertia tensor from the microscopic details, i.e. the translations of the atomic positions and the changes in the occupation factors of individual sites. The order-disorder transition which directly affects the occupation factors will change the inertia tensors by modifying the effective masses \(m_{\text{eff}}\) in formula (1). The changes in the occupation probabilities can be alternatively calculated from the symmetry analysis dealing with scalar-type objects like occupation factors.

The aim of the present work is to study the changes of inertia tensors for atomic clusters obtained from both methods, i.e. as the result of microscopic description of cluster deformation, following the ordering of atoms in cubic orbits of partially occupied sites in the Fd-3m => R3m transition, calculated from scalar type symmetry analysis, and the changes of inertia tensor obtained as linear combinations of tensor-type basic vectors of irreducible representation of Fd-3m space group. These calculations show that the description of structural transformations of CMA is possible in the frame of tensor type symmetry analysis even without knowing the microscopic details of the transition.

4.1. Symmetry analysis applied to the occupation probabilities

For testing the equivalence of these two types of descriptions the evolution of two types of clusters has been studied (type A and type B, formed by Mg and Al atoms in the cubic phase, and discussed in the previous section). The A17, A18, A19, A110 and A119 atoms (numbers of atoms and their \((x,y,z)\) parameters are taken after [1]), occupying the 96g Wyckoff positions, form the A-type clusters localized around the 8(b) Wyckoff positions, with the Mg23 atom localized in the center. All the surrounding atoms exhibit partial occupations, which are affected by the symmetry lowering transition. The symmetry analysis applied to the scalar type objects is able to calculate the possible modes of changes for \(\Delta P\) e.g. by using the MODY program. The results of such analysis for the \(\beta \Rightarrow \)}
\[ \beta' \] transition in \( \beta\)-Mg\(_2\)Al\(_3\), obtained for A-type clusters in two neighboring 8(b) sites are given in table 2 below. The results for the remaining six 8(b) nodes can be obtained by the respective centering translations in the FCC lattice.

**Table 2.** Average site occupation factors in the Al\(_7\) sites located around 8(b) positions in the cubic and fully ordered rhombohedral phase

| 8(b) site at (0.5, 0.5, 0.5) | 8(b) site at (0.75, 0.75, 0.75) |
|-----------------------------|---------------------------------|
| **Al\(_7\)** atomic position | **P(cub)** | **\(\Delta P\)** | **P(rho)** | **Al\(_7\)** atomic position | **P(cub)** | **\(\Delta P\)** | **P(rho)** |
| (0.470 0.470 0.600)          | 0.5       | C                 | 1          | (0.780 0.780 0.650) | 0.5       | -C                | 0         |
| (0.470 0.600 0.470)          | 0.5       | C                 | 1          | (0.780 0.650 0.780) | 0.5       | -C                | 0         |
| (0.600 0.470 0.470)          | 0.5       | C                 | 1          | (0.650 0.780 0.780) | 0.5       | -C                | 0         |
| (0.470 0.530 0.400)          | 0.5       | 0                 | 0.5        | (0.780 0.720 0.850) | 0.5       | 0                 | 0.5       |
| (0.470 0.400 0.530)          | 0.5       | 0                 | 0.5        | (0.780 0.850 0.720) | 0.5       | 0                 | 0.5       |
| (0.600 0.530 0.530)          | 0.5       | -C                | 0          | (0.650 0.720 0.720) | 0.5       | C                 | 1         |
| (0.530 0.470 0.400)          | 0.5       | 0                 | 0.5        | (0.720 0.780 0.850) | 0.5       | 0                 | 0.5       |
| (0.530 0.600 0.530)          | 0.5       | -C                | 0          | (0.720 0.650 0.720) | 0.5       | C                 | 1         |
| (0.400 0.470 0.530)          | 0.5       | 0                 | 0.5        | (0.850 0.780 0.720) | 0.5       | 0                 | 0.5       |
| (0.530 0.530 0.600)          | 0.5       | -C                | 0          | (0.720 0.720 0.650) | 0.5       | C                 | 1         |
| (0.530 0.400 0.470)          | 0.5       | 0                 | 0.5        | (0.720 0.850 0.780) | 0.5       | 0                 | 0.5       |
| (0.400 0.530 0.470)          | 0.5       | 0                 | 0.5        | (0.850 0.720 0.780) | 0.5       | 0                 | 0.5       |

The moments of inertia calculated after changes in the site occupation factors (effective masses) are given in Table 3.

**Table 3.** Changes of inertia tensors and the individual I eigenvalues during the Fd-3m => R3m transition.

| Sites | \(I_4\) (cubic) | \(I_8\) (rhom) | \(I_1[1,1,1]\) (rhom) |
|-------|-----------------|-----------------|----------------------|
| 1,3,5,7 | \(\begin{array}{ccc} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{array}\) | \(\begin{array}{ccc} a & d & d \\ d & a & d \\ d & d & a \end{array}\) | \(I_1 = a + 2d\) |
| 2,4,6,8 | \(\begin{array}{ccc} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{array}\) | \(\begin{array}{ccc} a & -d & -d \\ -d & a & -d \\ -d & -d & a \end{array}\) | \(I_1 = a - 2d\) |

The shapes of \(I_8\) (rhom) inertia ellipsoids differ from the spherical form. For the sites 1,3,5,7 the \(I_8\) (rhom)(1) ellipsoid exhibits a disc-like form, while for \(I_8\) (rhom)(2) an egg-like form is observed. In both cases the single principal axis (the full rotation symmetry axis) is directed along [1,1,1]
direction (see table 3), but in the first case the [1,1,1] direction corresponds to the shortest ellipsoid diameter (disc-shaped) while in the second case to the longest (egg-shaped).

Graphical illustration of inertia ellipsoid calculation has been elaborated using the Tensor_Vis program by J.Malinowski [7]. An exemplary visualization, attributed to the 8(b) clusters after the transition, is shown in figure 3.

**Figure 3.** Inertia ellipsoids in the 8(b) sites after the phase transformation: (a) disc-shaped ellipsoid in sites 1,3,5,7 and (b) egg-shaped ellipsoid in sites 2,4,6,8

The moments of inertia calculated for 16(d) clusters after changes in the site occupation factors realized in the $\beta \Rightarrow \beta'$ phase transition take the same form as in the cubic parent structure.

### 4.2. Tensor-type symmetry analysis

The results of the symmetry analysis obtained from the MODY program for tensor-type objects select a three-dimensional $\tau_{10}$ irreducible representation of Fd-3m group as being active in the transition. The respective $k$-vector is obtained as $(0,0,0)$, and the selected set of order parameters is taken as $(c, c, c)$. The output of MODY presenting the tensor-type atomic components of three basic vectors of $\tau_{10}$ irreducible representation is quoted in table 4 below:

**Table 4.** Results from MODY for irreducible representation $\tau_{10}$, dim=3, occurring 1 time.

| Atoms 1,3,5,7 | Matrix elements of basic vectors |
|---------------|----------------------------------|
|               | Ver. 1   | 1       | (0.00, 0.00) | (0.00, 0.00) | (0.00, 0.00) |
|               |          |         | (0.00, 0.00) | (0.00, 0.00) | (0.17, 0.00) |
|               |          |         | (0.00, 0.00) | (0.17, 0.00) | (0.00, 0.00) |
|               | Ver. 1   | 2       | (0.00, 0.00) | (0.00, 0.00) | (0.17, 0.00) |
|               |          |         | (0.00, 0.00) | (0.00, 0.00) | (0.00, 0.00) |
|               |          |         | (0.17, 0.00) | (0.00, 0.00) | (0.00, 0.00) |
The obtained changes of inertia tensors $\Delta I(r)$, calculated as linear combination of tensor-type basic vectors associated with the irreducible representation $\tau_{10}$, active in the transition for the $(c,c,c)$ order parameters are listed in table 5.

**Table 5.** The changes of inertia tensors obtained as linear combination of the basic vectors of the $\tau_{10}$ irreducible representation, active in the $\beta \Rightarrow \beta'$ transition.

| Ver: 1 | 3       |
|--------|---------|
|        | $(0.00, 0.00)$ | $(0.17, 0.00)$ | $(0.00, 0.00)$ |
|        | $(0.17, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |
|        | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |

| Atoms $2,4,6,8$ | Matrix elements of basic vectors |
|-----------------|----------------------------------|
| Ver: 1          | 1                                |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(-0.17, 0.00)$ |
|                 | $(-0.17, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |

| Ver: 1          | 2                                |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(-0.17, 0.00)$ |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |
|                 | $(-0.17, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |

| Ver: 1          | 3                                |
|                 | $(-0.17, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |
|                 | $(0.00, 0.00)$ | $(0.00, 0.00)$ | $(0.00, 0.00)$ |

It can be easily seen, that for $d=d'$ the inertia tensors for A-type clusters in the R3m structure ($I'=I + \Delta I$) calculated from the symmetry analysis stay in full agreement with ones calculated by definition, with proper changes of the effective masses $M_{\text{eff}}$ (see table 3).

The symmetry analysis of the tensor-type objects referring to the B-type clusters, located in the 16(d) positions, does not show the $\tau_{10}$ irreducible representation as the active one. It means that the inertia tensors of clusters localized at 16(d) positions do not change in the order-disorder transition. As can be seen from the discussion of B-type clusters in section 3.2, these clusters already in the cubic, parent structure exhibit deformed (non-spherical) inertia ellipsoids, with the symmetry axis coinciding with the main principal axis $[1,1,1]$, showing a natural preference for transition to rhombohedral symmetry and their symmetry is not affected by the changes of occupation probabilities.

5. Conclusions
The consideration presented in the paper are focused on the problem of symmetry changes for cluster-like objects encountered e.g. in complex metallic alloys. Depending on the nature of the phase transition the symmetry changes may results either from modifications of the site occupation factors or shifts of the atomic positions. For description of the cluster symmetry the simplest tensor class object, namely inertia tensor, has been used. Inertia tensor offers the advantage of two alternative ways of calculating the changes of inertia matrices for a given cluster: directly from a respective formula using...
the positions and effective masses (occupation factors) or a symmetry analysis. The first approach requires the detailed knowledge of the changes in occupation factors and atomic site positions for atoms included in the cluster. The required data can be obtained from the scalar or vector symmetry analysis of the phase transition e.g. by calculation of the ordering mode of site occupation factors within one orbit of symmetry equivalent sites. The calculation has to be done separately for each cluster location. An alternative approach is offered by the tensor-type symmetry analysis. The knowledge of the cluster’s inertia tensor in one site in the high symmetry phase may be used for both calculation of the inertia tensors (their principal axes and moment of inertia eigenvalues) in the other symmetry equivalent cluster locations as well as the changes of inertia tensors of individual clusters resulting from a symmetry reducing phase transition. The second approach does not require the knowledge of detailed atomic data of the cluster, and still the orientation of principal axes relative to the crystal coordinate system and the respective eigenvalues after the transition can be easily calculated. Thus the knowledge of initial and final symmetry groups can be used for construction of a model describing local cluster symmetry changes in each site by specifying the orientation of the local coordinate system and geometrical characteristics (egg-shaped vs. disc-shaped) of the inertia ellipsoid. The considerations presented in this work show that the tensor-type symmetry analysis is able to describe in a very simple way the ordering of clusters (represented by their inertia tensors), accompanying a phase transition even in very complicated, giant-unit-cell structures.

6. References

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