Configuration energy analysis of $\beta$-Mg$_2$Al$_3$ cluster structure

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Abstract. Stability of (Mg-Al) clusters in the $\beta$-Mg$_2$Al$_3$ structure has been studied with the use of the effective pair potential of interatomic interactions taken from ab-initio calculations. The total potential energy has been calculated for various possible (Mg-Al) cluster configurations in order to find the optimal ones. The computation has been started from the cluster located at the 8(b) site consisting of 72 partially occupied, overlapping atomic sites, as determined by X-ray studies. The configurations of fully occupied, non-overlapping atomic positions have been selected using the criterion of minimal potential energy. The simulated annealing algorithm has been used for further optimization of the atomic positions in 3D space. The energy optimization leads to the selection of several configurations with the energy close to the minimum. For such structures the configuration entropy has been calculated as a function of the total potential energy. More complex structures, consisting of the optimized clusters and various interface configurations, have been also studied.

1. Introduction
The $\beta$-phase of Mg$_2$Al$_3$ has been originally studied by Samson [1] and more recently in Refs. [2], [3]. The structure is described by the cubic space group Fd-3m (ITA 227) and the final X-ray profile fit is obtained using 23 Wyckoff positions, generating the total of 1832 atomic sites in the unit cell. Part of the sites (840) are considered as fully occupied by Mg or Al atoms with site occupation factor (SOF) equal to one, while the rest are treated as partially occupied (SOF<1). These two subsets of atomic positions exhibit considerable differences in the geometry of local neighborhood. The fully occupied sites obey the mutual distance constraints, i.e. no neighbor is located nearer than the minimum distance evaluated from ionic radii, thus the atoms occupy only non-overlapping positions. The fully occupied fraction forms a set of hexagonal planes [4], perpendicular to [1,1,1] directions, which provide a stable crystalline matrix (fixed framework) for the partially occupied sites.

The partially occupied sites strongly violate the minimum distance rules, since there is an extensive overlapping between neighboring sites, thus they cannot be occupied at the same time (alternative occupation). Fig.1(a) shows the two sets of sites: green (SOF=1) and red/blue (SOF<1). The cross-section on the left shows that the red/blue fraction is located in spherically shaped caverns, centered at the 8(b) positions, and their interconnecting channels. The set of 8(b) positions in the Fd-3m structure forms a diamond-type lattice with sites occupied by the spherical clusters of partially occupied atomic positions and their interconnections (bridges) located along the diamond lattice bonds. The essential part of the partially occupied fraction,
consisting of two spherical clusters and their interconnection is shown in Fig. 1(b). The ionic radii has been reduced to exhibit the details of the structure and the overlapping of atomic positions. A detailed analysis shows that each cluster comprises the central Mg(23) ion (ion numbering after Ref. [1]) at 8(b) position and 72 surrounding sites, which are partially occupied and strongly overlapping. The interface between the clusters, centered around the 16(c) position, consists of twelve well defined pairs of alternatively occupied sites and one double split position (green atoms near the center), giving a total number of 26 positions. The occupation factors listed in Table 2 in Ref. [2] show that the interface part exhibits two alternative forms of the twelve ion configuration (probabilities for each pair sum up to one) and one alternatively occupied Al(21) atom near the 16(c) position.

Figure 1. Model of the structure determined from X-ray diffraction. (a) [110] cross section of the unit cell, (b) Clusters with partially occupied sites. The different types of atoms are distinguished by their size (Al - 20% smaller), the colors denote occupation: green-fully occupied, red-partially occupied by Al, blue-partially occupied by Mg.

The ambiguous nature of the above-mentioned cluster structure can be resolved in two ways. First, it is possible that strongly distorted local clusters emerge with many atoms occupying "interstitial" positions. The second proposition is based on the presence of several forms of well-defined, stable clusters, which occupy at random the spherical caverns in the structure. A strong hint for the second proposition is given by the ordering phase transition to the $\beta'$ phase, with symmetry lowered to the R3m space group. The symmetry analysis shows [5] that the lattice of 8(b) sites splits into two interpenetrating sublattices, occupied by two different types of clusters with possibly different number of ions. Such a suggestion is also expressed by the X-ray study of the $\beta'$ phase [2] and NMR study [3].

The purpose of the present paper is to search for the most stable configurations of Mg-Al clusters, which could be used for a construction of alternative variants of the 8(b) position clusters. The problem of stability of $\beta'$-Mg$_2$Al$_3$ clusters has been studied in [2], by testing the stability of the determined structure and its sensitivity to the Mg/Al substitution. The authors used both the full potential calculations and the effective inter-atomic potential obtained from ab-initio calculations [6]. In the present paper this effective pair potential is used to find the clusters with minimal energy and to construct more complex structures, consisting of both the spherical clusters and the interface parts arranged on the diamond lattice in the Fd-3m structure.
2. Computation Method
The total potential energy has been calculated for various cluster configurations in order to find the optimal ones. In the first stage of calculations, the two types of ions (Mg,Al) are located at atomic sites allowed by the symmetry group determined from the X-ray data, taking into account the minimum distance rules in order to avoid the overlapping. The potential energy of each configuration is computed from following pair interaction formula:

\[ E = \sum_{i=1,\ldots,N}^{j>i} u_{ij}(r_{ij}) \]  

where \( u_{ij} \) is the interaction energy between atoms i and j, taken from authors of Ref. [6]. The corresponding plots of the Al-Al, Mg-Mg, and Mg-Al pair potentials, which can be found in Ref. [2], are essentially different with respect to the minimum distance and potential oscillations with the atomic pair distance. The observed minimum distance values ensure that the energy calculations should be highly consistent with topological analysis based on ionic radii values.

2.1. Divide and conquer scheme for a spherical cluster
The present calculations have been started from the cluster located at the 8(b) site occupied by Mg(23) atom surrounded by 72 partially occupied, overlapping atomic sites. Therefore, in principle \( 2^{72} \) possible configurations should be generated and compared. Such calculations are characterized by a high computational complexity, therefore, we have carried out the search by scanning the configuration subsets with use of the divide and conquer computation scheme, described below. The computational procedure consists of the following steps:

(i) The set of 72 atomic positions is divided into four subsets (four quarters of the sphere), each including 18 atoms. The central Mg atom is added to each quarter, because its interaction with other atoms generate a considerable contribution to the total energy. The program scans all \( 2^{18} \) possible configurations of each quarter.

(ii) For each configuration the energy is calculated from formula (1). If the calculated energy is lower than zero, the configuration is considered as stable and saved, otherwise the configuration is discarded as unstable. If the interatomic separation is smaller then the minimum distance (equal to 0.25092 nm [3]), the energy is taken to be infinite and the configuration is also discarded.

(iii) Each stable configuration of the first spherical quarter is combined together with all stable configurations of the second quarter. This leads to \( n_{q1} \times n_{q2} \) possible configurations, where \( n_{q1} \) and \( n_{q2} \) denote the number of stable configurations of the first and second quarter, respectively. For each combined configuration the total potential energy is calculated and only the configurations with the energy lower than zero are saved.

(iv) The configurations of the entire spherical cluster are created from the combinations of stable configurations of the two half-spheres. The structures with energies less than zero are saved, classified and next sorted to find those with the lowest energies. For the sets of stable structures we have calculated the configuration entropy \( S \) as a function of energy \( E \), according to \( S(E) = \ln g(E) \), where \( g(E) \) is the density of states determined from the histogram of the number of configurations versus energy [7].

2.2. Creation of combined structures
The configurations obtained in Sec. 2.1 have been used to create the more complex structures by constructing the combinations of neighboring clusters and additional interconnecting atoms. First, the configuration of two spherical clusters is created, next the other partially occupied sites are added, which form the interfaces between the previously arranged clusters. Additionally, the
surrounding fully occupied atomic sites are included. This forms an external framework, which additionally stabilizes the entire cluster configuration. All the constructed complex structures are analyzed and the structures with the lowest energy are chosen for further optimization.

2.3. Simulated annealing
The energy optimization performed according to Subsection 2.1 selects the configurations of various classes (atomic compositions) with the energy close to the minimum. In the final stage, the configurations have been additionally optimized by varying the atomic positions in 3D space using the simulated annealing algorithm. Usually the annealing was started at the temperature of 700 K and the temperature was lowered by 1% every 50 steps. In each step, each atom was allowed to move within a 3D box with the box edge initially equal 0.1 nm. The box size was reduced by 0.5% every 150 algorithm steps, if less than 10% of results was accepted.

3. Results
3.1. Spherical clusters surrounding the 8(b) position
The comparison of stable configurations of the spherical cluster shows that it is not possible to create stable clusters consisting of more than 17 atoms (Mg(23) atom plus the surrounding 16 atoms). The limited volume of the spherical cavern, in which the cluster is located, does not allow for the creation of configurations with the number of atoms exceeding 17. This agrees with the estimated mean number of atoms, i.e., 17.32, derived from the X-ray data as a sum of SOF values over all atomic positions in the cluster.

![Figure 2](image)

**Figure 2.** Illustration of three stages of 2xC17+113 cluster construction. (a) Atomic positions as determined from X-ray studies with partial occupation and overlapping (color intensity grows with occupation probability). (b) Atomic cluster configuration as determined by energy selection from fully occupied, non-overlapping positions. (c) Cluster configuration after the random annealing procedure.

The most-stable C17 configuration consisting of 17 atoms and it is formed by the central Mg(23) atom surrounded by 4 Mg(19) atoms and 12 Al(7) atoms. There are six equivalent and symmetry related configurations with the lowest energy and some more configurations attributed to five higher energies levels (within 0.01 eV). The detailed inspection shows that all these configurations are close to the well-known Friauff polyhedron, with Mg(19) atoms shifted from their high-symmetry positions (see Fig.2b). Further adjustment of atomic positions has lead to further energy lowering (see Table 1). The Mg(19) atoms have been slightly shifted to nearby positions, located 0.3067 nm from the central Mg(23), while the Al(7) atoms have been moved to 0.3214 nm from center. The calculated Mg(19) - Mg(23) - Mg(19) angles clearly indicate that
the Mg(19) atoms form a perfect tetrahedron. Together with the Al(7) atoms they form a Friauf polyhedron (see Fig.2b,c). The majority of clusters with energies close to the minimum are those with 16 or 17 atoms. The 16-atom configuration C16 with slightly higher energy comprises the defected C17 polyhedrons with one Al(7) atom missing. Other clusters worth mentioning are the B17 and B16 clusters, that emerge in the structure analysis of the $\beta$-phase [2]. These clusters include a smaller number of Mg(19) atoms that are partially replaced by Al(20) atoms, (B17) or other vertex configurations (B16), with preservation of the triple symmetry axis along [1,1,1] direction.

3.2. Combined structures

The results for the combined clusters are presented in Table 1. The basic clusters are denoted by C17 and C16. The added interface atoms visible in the central part of Fig.2(b) are denoted by I13. As each C17 cluster in the diamond network is connected by four bonds, the other interconnecting atoms have been denoted as SH24. Finally, the framework of fully occupied atomic positions is denoted by FA. It can be seen that for the more complex structures energy per atom goes down since the contribution of the surface energy decreases. The addition of fully occupied positions leads to the further lowering of the energy per atom, what confirms the role of the external framework that stabilizes the entire cluster configuration. The energies of B17 and B16 configurations are initially higher than that of the most stable C17 cluster, which clearly suggests that their important role is reached by the adjustment to the neighboring atoms with SOF=1.

| cluster         | No. of Mg atoms | No. of Al atoms | $E$ [eV] | $E$/atom [eV] | $E$/atom after annealing [eV] |
|-----------------|-----------------|-----------------|---------|--------------|-----------------------------|
| C17             | 5               | 12              | -1.6934 | -0.099612    | -0.146759                  |
| C16             | 5               | 11              | -1.59278 | -0.099549    | -0.146903                  |
| B17             | 2               | 15              | -1.57666 | -0.092745    | -0.115002                  |
| B16             | 4               | 12              | -1.47049 | -0.091906    | -0.138194                  |
| B17 + B16 + I13 | 12              | 34              | -4.80369 | -0.104428    | -0.153859                  |
| C17 + C16 + I13 | 16              | 30              | -5.255129 | -0.114242    | -0.164605                  |
| 2xC17 + I13     | 16              | 31              | -5.39753 | -0.114841    | -0.165422                  |
| 2xC17 + I13 + 2xSH24 + FA | 127 | 92         | -39.73249 | -0.181427    | -0.216556                  |

Table 1. Total potential energy $E$ calculated for the analyzed cluster configurations (cluster labels are explained in text).

Two examples of calculated configuration entropy $S = \ln g(E)$ are displayed in Fig. 3. The right hand side plot refers to all possible configurations of isolated spherical clusters, which contain less than 18 atoms. The left hand side plot includes configurations of the entire 2xC17+I13 complex, which result from the interface variations with the spherical C17 clusters fixed (see Fig.2c). In both the cases, it is visible that the preferred lowest energy configurations are separated by an energy gap from the higher energy configurations, which can be still observed in samples quenched from the temperatures above the $\beta - \beta'$ transition point.
4. Summary
The clusters in the $\beta$-$\text{Mg}_2\text{Al}_3$ structure have been analyzed with use of the effective interatomic potential. The divide and conquer scheme has been used for the selection of low-energy spherical cluster configurations, which were optimized by the simulated annealing algorithm. We have found that the optimal C17 configurations consist of five Mg atoms and twelve accompanying Al atoms, forming a Friauf polyhedron. Alternative 16 and 17 atom configurations with the comparable energy have also been obtained. The results have been used for the creation of complex structures, containing two spherical clusters and the connecting atomic interface. The 2xC17+I13 structure exhibits the symmetry of high temperature $\beta$ phase and contains only a subset of positions found in the X-ray studies. This indicates that the disordered phase includes also some other clusters, which order in the low temperature $\beta'$-phase by preferring the occupation of some Mg(19) sites by Mg and replacing the other by Al ions. Further studies are required for configurations including the entire unit cell with periodic boundary conditions.

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