Simple model of Mg$_2$Al$_3$: β and β’ phases

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Abstract: Two crystalline phases: β and β’ of the Mg$_2$Al$_3$ alloy are compared. There are three types of structural domains, whose structures are based on sets of hexagonal layers. The main chain contains 11 layers. It does not undergo any transformation during a phase transition from the β’-phase to the β-phase. Conversely, during this process, shorter chains vanish and transform into clusters, whose atomic positions are occupied partially. Any two adjoining domains merge in a coherent way. It does not apply to the third domain. At its border structural defects appear. They are the seeds of clusters emerging in the β-phase.

1. Introduction

The Samson structure, β-Mg$_2$Al$_3$, is one of the most complex intermetallic structures (Samson, 1965, Feuerbacher et al., 2007). Its cubic elementary cell (Fd-3m, no. 227 space group) contains 1168 atoms which are distributed over 1832 atomic positions. About 75% of atoms (879 to be exact) form the firm framework of the structure - 528 of them are Al and 351 are Mg. By “the framework” or “skeleton atoms” we understand a set of Samson’s positions which are occupied by atoms with the probability of 100%. The remaining 289 (25%) atoms partially occupy 953 positions with the average occupation probability of 30%. They form clusters arranged in an elementary cell in a tetrahedral lattice. Their structure has been described in detail in (Feuerbacher et al., 2007) and the following references and in (Sikora et al., 2008). The lattice constant of the Samson structure is gigantic: $a_c=2.8242(1)$ nm. When cooled down, at the temperature of 214°C (with the cooling rate of 5°C/min), the structure undergoes a phase transformation to the rhombohedral β’-Mg$_2$Al$_3$ (space group R3m, no. 160, which is a subgroup of the Fd-3m group - index 4) with $a_r=1.9968(1)$ nm, $c_r=4.89114(8)$ nm. It should be pointed out that the constant $c_r$ of the rhombohedral structure is practically equal to the length of the main diagonal of the cubic structure $a_c \sqrt{3} = 4.89166$ nm $\approx c_r$. Additionally, the ratio $a_c / a_r = \sqrt{2}$, which means that the frame of the unit cell is the same for both: cubic and rhombohedral structure.

Stacking of hexagonal layers in the structure of β-Mg$_2$Al$_3$ has been published recently (Wolny et al., 2008). In that paper we pinpointed the fact that there were three structural domains distributed along the main diagonal ([111] direction) of a cubic unit cell. The relative positions of the centers of these domains were shifted by 1/3 of the diagonal length. All length values were given in relation to the $z$ axis unit of the hexagonal reference frame, which is equal to the length of the main cubic diagonal - for the β cubic phase, or its equivalent, lattice constant $c$ - for the β’ rhombohedral phase. It was proved, that the core of a domain consists of eleven parallel and evenly distant hexagonal planes occupied by skeleton atoms. 75% of the β phase atoms and 100% of the β’ phase atoms are the skeleton ones. All skeleton atoms form a set of 22 parallel and evenly distant hexagonal layers. The set is clearly illustrated by the figures introduced in the further part of the paper.
For the purposes of the structural analysis presented in this paper we use atomic positions obtained from the gigantic elementary cell (Samson, 1965, Feuerbacher et al., 2007). These positions are widely accepted by different teams of crystallographers. Consequently, we adopted this model for our study of the structure, aiming at discovering some simple rules that would allow us to reconstruct such complex structures.

2. Hexagonal layers

Figures 1 a&b show the positions of all Al and Mg skeleton atoms of inner part of domain-I for $\beta$-Mg$_2$Al$_3$ projected onto the base layer. With great accuracy only the hexagonal sites marked by A, B and C are occupied by Al atoms (figure 1a). The Mg atoms behave similarly (figure 1b).

![Figure 1. The skeleton Al (a) and Mg (b) atoms projected onto the plane (111) for the cubic structure of $\beta$-Mg$_2$Al$_3$. All the atoms fit to the nodes of hexagonal network.](image)

Figures 2a&b outline an exact sequence of layers. The whole structure is divided into three domains. In figures 2a&b, only domain I is presented in details, because its structure is identical to the structure of domains II and III. These domains are represented here only by a set of lines: thick ones (Al atoms) and thin ones (Mg atoms).

Their relative shift along the z-axis is equal to 1/3. The whole set consists of 22 parallel and equally distant layers. Some of them are occupied by the skeleton atoms. The rest is filled by atoms forming clusters – the structures whose atomic positions are occupied with the probability less than one. The distance between two layers equals 1/22 \(\approx 0.0788\). The figures show only the skeleton atoms, which lie inside domains (\(r \leq 0.22\)): Al atoms – thick lines and open circles; Mg atoms – thin lines and full circles.

In case of the $\beta$-Mg$_2$Al$_3$ phase (figure 2a) the Al atoms are arranged into 11 layers forming the main chain. Only these layers are occupied by the skeleton atoms. The Mg atoms which are associated with the Al layers form atomic complexes denoted with $\alpha$, $\beta$ and $\gamma$ symbols. The $\alpha$ complex consists of three hexagonal layers containing some A-type knots, which are occupied in a sequence: Mg/Al/Mg (see also figure 3a). Within the middle layer, among Al atoms, there are gaps occupied by Mg atoms. The outer Mg layers are shifted by around 0.06 with respect to the Al layers, because the atomic radius of Mg atoms is nearly 12% larger than the Al one. Consequently, Al gaps are too small for Mg atoms. There is not enough space for them within a common hexagonal layer. Mg atoms are situated either above or below a hexagonal Al layer. The $\beta$ and $\gamma$ complexes closely resemble the $\alpha$ complex, however in their case, these are positions B (\(\beta\)) or C (\(\gamma\)) that are taken. It is also worth emphasizing that for each complex (\(\alpha\), \(\beta\) and \(\gamma\)) the ratio Mg/Al is equal to 2/3, which is in accordance with the chemical compositions of the alloy Mg$_2$Al$_3$. 

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Figure 2. The sequence of 22 hexagonal layers and their arrangement within particular domains: I, II and III. Thick lines indicate Al layers, thin ones – Mg layers. All three domains are identical. They are shifted by 1/3 along the z axis with respect to each other. The structure of the inner area ($r \leq 0.22$) of the first domain is outlined in details in the figure. Open circles are associated with Al atoms and full circles with Mg atoms. In case of the $\beta$-phase (a) the skeleton atoms form 11 layers of the main chain. In case of the $\beta'$-phase (b), in addition to the main sequence, there are also shorter ones: layers 13'–15' and 17'–18'.

Among the $\alpha$, $\beta$ and $\gamma$ complexes, there are hexagonal layers of type A, B or C partially filled by Al atoms, which are interspersed with a gap. The resulting sequence of 11 layers of the main chain is as follows: $1\alpha2B3\gamma4A5\beta6A7\gamma8A9\beta10C11\alpha$. The middle part of this chain consists of a regular sequence: $3\gamma4A5\beta6A7\gamma8A9\beta$ within which Al atoms occupy A positions whereas Mg atoms are put in B or C positions in alternate layers. The periodic set of 11 hexagonal layers can also be described by Friauf polihedra, as it is shown in figure 3c. This is an energetically stable sequence. However, it is not consistent with the chemical composition of the alloy. If it filled the whole space, the ratio Mg/Al would achieve the value 1/2 and the Mg atoms would be in deficiency. The chemical balance is restored by Mg atoms scattered within outer parts of the structural domains. It should be emphasized that the factual chemical composition of the studied sample was not fully stoichiometric – it was equal to Mg$_{38.5}$Al$_{61.5}$ (Feuerbacher et al., 2007).

Half of the domain is occupied by two clusters containing most of the atoms with SOF<1. As it is shown in figure 3b, a Mg atom occupies the centers of hexagonal rings of Al atoms. The size of Mg atom is bigger than the size of Al atom making the lattice constant for the hexagonal lattice greater than for the hexagonal lattices of skeleton layers.

Figure 3. Local arrangement of atoms for a periodic set of 11 hexagonal layers (a) and for aperiodic clusters (b) for $\beta$-Mg$_2$Al$_3$. Decoration of periodic set of hexagonal layers by Friauf polihedra (c). Light balls – Al atoms, dark ones – Mg atoms.
The structure gets heavily defected above room temperature. The defects destroy the initial periodic sequence of layers. At higher temperatures Al atoms can easily swap positions between A and B (layer 2) or C (layer 10). It does not involve a considerable amount of energy. For a perfect set of close-packing of spheres such energy would be equal to zero. Therefore, Al swaps can easily occur at temperatures which are only slightly higher than room temperature. This kind of structural defect terminates the main chain of hexagonal layers and consequently layers 2B and 10C are the second to last layers in this chain.

The set of layers of the rhombohedral phase $\beta'$-Mg$_2$Al$_3$ is outlined in figure 2b. As in previous figures, only the inner atoms ($r \leq 0.22$) are highlighted there. Similarly to the cubic phase, this structure also has 11 hexagonal layers arranged in a sequence of the main chain. Additionally, the structure contains some shorter chains (three-layer long $13'-14'-15'$ and two-layer long $17'-18'$). They are not observed in the high temperature phase ($\beta$). These short chains occupy positions situated between 22 layers of the main chain, which are described above. The transition between positions of the main chain’s layers to the positions of the short chains’ layers is realized by successive Al-Mg swaps in consecutive layers.

All the atoms that belong to the 11 layer-long main chain occupy A, B or C hexagonal positions (figure 2). Only layer 17 is occupied by those Al atoms that can be found in ~C positions. These positions do not belong to the set of hexagonal structure’s knots. Nonetheless, they are quite close to them. A similar atomic arrangement can be observed in the case of layer ~20’ (figure 2b) where Al atoms occupy positions ~B.

The single domains of two phases: $\beta$ and $\beta'$ of Mg$_2$Al$_3$ are compared in figure 4. The transformation from the high temperature phase ($\beta$) to the low temperature phase ($\beta'$) results in reducing the symmetry of a single domain. A symmetrical domain becomes asymmetric and the clusters break apart into short chains of hexagonal layers of different sizes. Depending on the size of the chain, the observed process undergoes at different temperatures. Instead of classical phase transition one observes a diffuse-controlled transformation, which also depends on the annealing time of the sample.

![Figure 4](image.png)

*Figure 4. Comparison of single domains of $\beta$ and $\beta'$ phases in Mg$_2$Al$_3$. A set of 22 layers and two aperiodic clusters are marked in the figure.*

### 3. Relative shift of the domains

The structure of Mg$_2$Al$_3$ consists of three domains shifted with respect to each other along the $z$ axis by 1/3. Within the base plane these domains form a hexagonal set. It is shown in figure 5, where one
can find the projected atomic positions of all domains forming layers 9B. As a reference frame for each domain a hexagonal lattice type A (thin lines) is marked in the figure.

Figure 5. Layers 9B of neighboring domains are drawn within a common plane. The centers of the domains form a superstructure marked with thick lines. The base hexagonal lattice is marked with thin lines. The superstructure is 22/3 ≈ 7.3 times larger than the base hexagonal lattice.

An average lattice constant $a_0$ can be established by adjusting the hexagonal lattice to the atoms’ coordinates. Having done that for 11 consecutive layers of the main chain, the value of this constant can be estimated as $a_0 \approx 0.1368$. This value is identical to the lattice length $a$ of close-packed spheres arranged along $c_h$ into 22 hexagonal layers.

Equal distances between atoms, regardless of their lying strictly within hexagonal layers or outside them, are proved by an assumption proposed also by Steurer (2007), which states that atoms are stacked into almost a close-packed structure. The value of nearest neighbors distance obtained for Al atoms projected into hexagonal plane is equal to 0.273 nm (i.e. equal to $a_0$) which is very close to the nearest neighbors distance observed for the FCC aluminum structure (0.286 nm). A slightly lower value of that quantity measured for Mg$_2$Al$_3$ (of about 4%) can be explained by low roughness of the basic plane.

The behavior similar to the Samson structure has already been observed in some other complex phases, e.g.: Cu$_4$Cd$_3$ (Anderson, 1980) or NaCd$_3$ (Yang, Anderson & Stenberg, 1987), where the regions corresponding to the hexagonal domains consisted of fragments of the Laves phase structures. The Laves structures are frequently described in terms of the stacking of hexagonal layers.

It also seems that the skeleton atoms, which are forming hexagonal layers, play an important role for other Laves phases. For example, there should be a certain simple explanation of the commensurate modulated vectors for Mg$_2$Al$_3$ and Mg$_{17}$Al$_{12}$ described by Donnadieu et al. (2002).

4. Conclusions
Mg$_2$Al$_3$ structure consists of three types of hexagonal rod-like domains. The core of each domain contains the main chain of 11 evenly distant hexagonal layers occupied by skeleton Al atoms arranged into a sequence: 1α2B3γ4A5β6A7γ8A9β10C11α. The building element of the structure consists of hexagonal chains of aluminum atoms completed with dimmers of magnesium atoms, as it was shown in the figure 3. The connection between such complexes is realized by hexagonal Al layers, for which every second atomic position is empty. An arrangement of such building blocks can be also described by Friauf polihedra, which are very common for the Laves phase structures. The resulting structure of 11 layers is rather stable and does not change during the transition from the low temperature phase ($\beta'$) to the higher temperature one ($\beta$). The most important problem is, however, the chemical composition of the core of the eleven layers. The corresponding value of the chemical composition is MgAl$_3$ rather than Mg$_2$Al$_3$ and the magnesium atoms are in deficiency. The Mg atoms are mostly located in the outer part of the domains.

The most common defect, which ends the well ordered sequence of hexagonal layers in a single domain, is associated with the process of atomic swap – an exchange of positions between an Al atom...
and a Mg one. This atomic disorder makes one chain of hexagonal layers end and another chain begin. Due to the Al-Mg swap, the shorter few-layer-long chains are formed. These short chains of layers are shifted with respect to the main chain and they occupy intermediate positions for β’-phase. At high temperature such short chains become unstable and transform into clusters, whose crystal positions are only fractionally occupied (β-phase).

A refinement process conducted upon all the layers of the main chain allowed us to ascertain the average value of the lattice constant for the hexagonal lattice equal to \(a_0 = 0.1368\), when measured in relative units or 0.2732 nm. Assuming that \(a_0\) is also the diameter of an Al atom of a close-packed structure, we obtain the distance between hexagonal layers equal to 0.2223 nm. Such value fits perfectly to the distance between 22 layers along the \(z\) direction (i.e. \(c/22 = 0.2223\) nm). This means that size of the unit cells of both rhombohedral (β’) and cubic (β) phases is fully determined by the close packing of Al skeleton atoms.

The three rod-like domains have identical structures. They are shifted along the \(z\) axis by 1/3 of the period. In case of symmetrical domains (β-phase) their sequence is: I, II and III, which leads to the FCC unit cell. In case of asymmetrical domains (β’-phase), even if the domains are in the same sequence as for cubic structure, the symmetry of the unit cell is reduced to rhombohedral.

In the base plane there is a hexagonal superstructure which periodicity is 22/3≈7.3 times bigger than the hexagonal lattice constant for Al atoms in a single domain. Such superstructure of domains together with the symmetry of individual domains are responsible for cubic or rhombohedral symmetry of an average unit cell.

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References
[1] Anderson S 1980 An alternative description of the structure of Cu₄Cd₃ Acta Crystallographica B36 2513-2516
[2] Donnadieu P et al 2002 Commensurately modulated states in the Mg-Al system Philosophical Magazine A82 297-316
[3] Feuerbacher M et al 2007 The Samson phase, β-Mg₂Al₃, revisited Z. Kristallogr. 222 259-288
[4] Samson S 1965 The crystal structure of the phase β-Mg₂Al₃ Acta Crystallographica 19 401–413
[5] Sikora W et al 2008 Symmetry analysis in the investigation of clusters in complex metallic alloys Journal of Physics: Conference Series 104 012-023
[6] Steurer W 2007 A lecture on CMA-NoE Annual Meeting Santorini Greece
[7] Wolny J et al 2008 Stacking of hexagonal layers in the structure of β-Mg₂Al₃ Philosophical Magazine Letters 88 501-507
[8] Wolny J et al 2001 Phason and phonon contribution to diffraction pattern of \(\sqrt{3}×\sqrt{3}\)-type hexagonal layers Philosophical Magazine A81 301-310
[9] Yang Q-B et al 1987 An alternative description of the structure of NaCd₂ Acta Crystallographica B43 14-16