On the early stages of precipitation ~~sequence~~ in dilute Mg–Nd alloys

Anirudh Raju Natarajan^a, Ellen L.S. Solomon^b, Brian Puchala^b, Emmanuelle A. Marquis^{b,*}, Anton Van der Ven^{a,*}

^aMaterials Department, University of California, Santa Barbara

^bDepartment of Materials Science and Engineering, University of Michigan, Ann Arbor

Abstract

We report on a first-principles and experimental study of precipitation in supersaturated solid solutions of Mg-rich Mg–Nd alloys. A cluster expansion Hamiltonian combined with Monte Carlo simulations was used to calculate a metastable HCP temperature-composition phase diagram. Aging studies were performed on dilute Mg–Nd alloys that were then characterized with HAADF-STEM. The early stage decomposition of these alloys is dominated by the thermodynamic stability of different Nd orderings on the HCP crystal structure. The observed progression of Guinier-Preston zones can be rationalized by a successive reduction of the Nd chemical potential. HAADF-STEM studies confirm the appearance of β' -like precipitates, however, the observed Nd ordering does not exclusively consist of zig-zag Nd rows but also contains linear strips of Nd-hexagons at non-periodic intervals. First-principles calculations predict that these orderings are stable compounds that belong to a family of hybrid phases formed by combining the β' ordering with the hexagons of β'' ($D0_{19}$) along the $[010]_{\beta'}$ direction. We label this hierarchy of orderings as β''' . A high degree of degeneracy among the different β''' phases is predicted. This along with a strong composition dependence of the misfit strain is likely responsible for the observed disorder of Nd-hexagon strips. Our experimental and first-principles evidence does not support the formation of Mg_3Nd having $D0_{19}$ ordering. Rather, the features reported as $D0_{19}$ are isolated hexagonal GP rods that show no long-range periodicity. Our study suggests the following precipitation sequence for binary Mg–Nd alloys:

Keywords: magnesium alloys, precipitation, Guinier-Preston, first-principles, statistical mechanics

1. Introduction

Magnesium alloys are promising light-weight substitutes to materials currently used in the automotive and aeronautical industries[1, 2]. The abundance of magnesium in the Earth's crust as well as its low density (relative to steel and aluminum) make it a viable alternative in lowering the weight of structural components[3]. However, poor mechanical properties, corrosion resistance, high temperature strength, formability and creep resistance have limited the commercial use of magnesium alloys.

Improvements to the mechanical properties of pure magnesium can be achieved through alloying and heat treatment, in particular through the process of age-hardening. Mg-RE (rare-earth) alloys are especially attractive due to their high strength at peak aging conditions[2]. As a result, a number of recent studies have investigated the precipitation sequence[4–9] [4–12] and hardening mechanisms[13–21] in magnesium alloys. Nd has proven to be an important alloying element in this respect. The precipita-

tion sequence during aging of Mg–Nd alloys, however, remains controversial, having been the topic of a number of experimental[22–28] and computational[29–33] studies. A recent review reports the following aging sequence[2]:

During typical aging experiments, supersaturated solid solutions (SSSS) containing small amounts of Nd (of the order of 0.5 at. %) are solution treated around 800K and are then aged around 500K. Guinier-Preston zones (GP zones) containing Nd atoms arranged as rods along the HCP c-axis form first in the early stages of precipitation[22, 24]. These rods exhibit local orderings that resemble N's, V's, Λ 's and hexagons when viewed along the $\langle 0001 \rangle$ direction (figs. 1a to 1c). At early times they appear as isolated columns (figs. 1a to 1c) but later self-organize into long chains along the $\langle 10\bar{1}0 \rangle$ direction (figs. 1d and 1e). All orderings proposed in past studies are illustrated as 2-dimensional projections along the $\langle 0001 \rangle$ axis in fig. 1. The red circles in fig. 1 represent columns of Nd atoms along the c-axis of the HCP crystal. Two patterns have been proposed for the chains consisting of V's and Λ 's,

*Corresponding author

Email addresses: emarq@umich.edu (Emmanuelle A. Marquis), avdv@engineering.ucsb.edu (Anton Van der Ven)

with that of Saito (fig. 1e)[22] having shorter distances between the various units than that of Lefebvre (fig. 1d)[24]. The driving forces for the rich array of GP-zone orderings shown in fig. 1 remain a mystery. Throughout this paper, we will refer to the GP zones of Mg-Nd alloys collectively as “GP-rods” and to the linear chains of N’s, V’s, Λ ’s and hexagons as “GP-sheets”. The hexagonal GP-rods[22, 24, 27] are commonly labeled as β'' , corresponding to Mg_3Nd having D0_{19} ordering, as this phase can be viewed as a periodic network of hexagons (fig. 2a) [2]. However, the Nd orderings identified as D0_{19} in past experimental studies never appear as precipitates that are larger than isolated hexagonal units. Here we make a clear distinction between the long-range ordered D0_{19} phase, which we will refer to as β'' , and the isolated hexagons that are seen in the early stages of aging, which we will call hexagonal GP-rods. Such a distinction has also been made in a recent study by Sanaty-Zadeh *et al.*[6] on magnesium alloys containing both neodymium and zinc, where they too report the absence of a long-range ordered D0_{19} precipitate.

(d) VA GP-sheet orderings proposed by Lefebvre *et al.*[24]

(e) VA GP-sheet proposed by Saito *et al.*[22]

Figure 1: Examples of Guinier-Preston orderings in Mg-Nd alloys. The atoms are projected along the $[0001]$ direction of the conventional HCP cell. Only Nd atoms are drawn in red, atoms that are positioned between the grid points are meant to be in the layer above the basal plane.

Upon further aging, a phase having a composition close to Mg_7Nd and an orthorhombic unit cell is observed[22]. This phase, referred to as β' , is an ordering on the HCP crystal (fig. 2b) and forms as plates parallel to the pris-

matic plane. The Nd ordering in stoichiometric β' is shown in fig. 2b and consists of periodically spaced zig-zag rows of Nd (fig. 2c) aligned along the $\langle 010 \rangle_{\beta'}$ direction. Continued aging of the alloy leads to the formation of two other metastable precipitates, β_1 (Mg_3Nd) and β (Mg_{12}Nd)[26, 27]. These have crystal structures that are not HCP based. A microstructure containing both the GP-zones and β' precipitate is thought to yield peak hardness in these alloys[22]. The equilibrium precipitate that is formed at the end of aging also has a crystal structure that is different from HCP and has a composition corresponding to $\text{Mg}_{41}\text{Nd}_5$ [28, 34].

Figure 2: Crystal structures are projected along the $[0001]$ direction of the conventional HCP cell. Only Nd atoms are drawn in red, atoms that are positioned between the grid points are meant to be in the layer above the basal plane.

We report on a combined computational and experimental study of phase stability and precipitation in Mg-rich binary Mg-Nd alloys. We identify the thermodynamic driving forces for the formation of GP-rods and sheets and find that while the experimental GP-orderings are not ground states of the HCP Mg-Nd binary, they are predicted to lower the Nd chemical potential relative to that in a random HCP solid solution. Our first-principles calculations also predict the stability of a family of hybrid orderings that combine features of both β' and β'' , thereby clarifying experimental observations of β' -like orderings containing strips of hexagonal Nd rings. A calculated metastable HCP phase diagram and an analysis of free energies of nucleation predict that the thermodynamic driving force for the formation of Mg_3Nd having D0_{19} ordering is not sufficiently large to expect its formation over other more stable orderings during aging. This is consis-

tent with the absence of precipitates having D0₁₉ ordering exhibiting long-range order. We therefore argue that local orderings identified as D0₁₉ in past studies are more accurately labeled as hexagonal GP-rods.

2. Methodology

2.1. Experimental methodology

A cast Mg-0.40 at.% (2.35 wt.%) Nd alloy was provided by Magnesium Elektron Company, USA. The alloy composition was determined by inductively coupled plasma-mass spectrometry (ICP-MS). Samples were encapsulated in quartz tubes under an argon atmosphere, solution treated at 833K for 24 hours, quenched in water and aged at 523K for 15 minutes and 2 hours. [Aging times were selected from the hardness curve in \[35\].](#) Specimens for transmission electron microscopy were electropolished according to the procedure described by Nie and Muddle[36]. High angle annular dark field (HAADF)- scanning transmission electron microscopy (STEM) images were obtained using a JEOL 2100F microscope operated at 200 kV with a collection angle of 52 mrad and a double-corrected JEOL 3100R05 microscope operated at 300 kV with a collection angle of 74 mrad. All experimental images were adjusted for brightness and contrast with no other manipulations.

2.2. Computational Method

We used first-principles electronic structure methods based on density functional theory (DFT) in combination with statistical mechanics approaches to predict phase stability in the Mg-Nd binary. The rich variety of metastable orderings observed in HCP Mg-Nd binary alloys suggests that configurational degrees of freedom dominate the finite temperature thermodynamic properties of this alloy. A cluster expansion is a useful tool to describe the dependence of the energy of a crystal on configurational degrees of freedom. The state of order among Mg and Nd over the HCP crystal can be tracked by assigning occupation variables, σ_i , to each crystal site i that take a value of 0 if a Mg atom resides at site i and a value of 1 if a Nd atom occupies that site. A particular Mg-Nd arrangement on an N -site crystal is then specified by a vector of occupation variables $\vec{\sigma} = \{\sigma_1, \sigma_2, \dots, \sigma_N\}$. The formation energy of a crystal (relative to some reference state) can be parametrized in terms of polynomials of the occupation variables according to [37, 38]:

$$E_f(\vec{\sigma}) = V_0 + \sum_{\alpha} V_{\alpha} \phi_{\alpha}(\vec{\sigma}) \quad (1)$$

where V_0 and V_{α} are constant expansion coefficients referred to as effective cluster interactions (ECI) and where the cluster basis functions associated with each cluster of sites labeled α are defined as:

$$\phi_{\alpha} = \prod_{i \in \alpha} \sigma_i \quad (2)$$

The first term in eq. (1), V_0 , is equal to the energy of pure Mg for the occupation variables used here. While the cluster expansion extends over all possible clusters of sites α of the crystal, in practice it must be truncated. The ECI of a truncated cluster expansion can be fit to a training set of DFT energies of different Mg-Nd orderings in HCP.

The CASM software package[39–42] was used to construct and parametrize a cluster expansion for the HCP based Mg-Nd binary and to perform Monte Carlo simulations. The total energies of symmetrically unique orderings of Mg and Nd atoms on a HCP structure were calculated with DFT, as implemented in the *Vienna Ab-Initio Simulation Package*[43–47] (VASP). We used the generalized gradient approximation (GGA-PBE)[48, 49] to DFT[50] and projector augmented-wave (PAW) pseudopotentials. An energy cutoff of 450 eV was used for the plane-wave basis. Structures were relaxed with respect to all degrees of freedom. The pseudopotential for magnesium had a $2p^2, 3s^2$ reference valence configuration. A frozen core pseudopotential was used for neodymium where 3 of the 6 valence electrons are placed in the core. This frozen core potential has been shown to capture the thermodynamic and elastic properties of the Mg-Nd alloy[30]. A Γ -centered k -point mesh of $25 \times 25 \times 13$ was chosen for the HCP primitive cell. Meshes were scaled appropriately for larger supercells such that the k -point density remained constant.

A training set of configurations was generated by enumerating all symmetrically distinct Mg-Nd orderings in supercells of the HCP crystal containing up to eight primitive unit cells. We augmented this training set with the energies of dilute perturbations on all the orderings that were found to be ground states in a finite chemical potential range at 0K. For every ground-state configuration we used a 96 atom supercell to systematically enumerate point, pair and triplet anti-site defects of that ordering. We used a genetic algorithm[51] with a cost function given by the leave one out cross-validation score (LOOCV) to pick clusters to be included in a truncated cluster expansion.

The cluster expansion was subjected to semi-grand canonical monte carlo (GCMC) simulations to calculate thermodynamic properties of all the phases that are stable in a finite chemical potential range. Simulations were performed at temperature (T) increments of 20K for a temperature range of $200 \leq T \leq 1000$ and across a range of chemical potentials ($\tilde{\mu} = \mu_{\text{Nd}} - \mu_{\text{Mg}}$) that captured all phase boundaries of interest. For every value of $(T, \tilde{\mu})$, we calculated ensemble averages of thermodynamic quantities over at least 2000 passes. These GCMC calculations were performed on cells consisting of $12 \times 12 \times 12$ and $20 \times 20 \times 12$ unit cells of the primitive cell.

Free energies as a function of Nd composition (x_{Nd}) and temperature, T , were obtained by integrating calculated relationships between chemical potential and concentration and between grand canonical energy and temperature. Phase boundaries of composition versus temper-

ature phase diagrams were then determined by applying the common tangent construction to calculated free energies. To ensure that the free energies were converged with respect to Monte Carlo cell size, we compared the free energies calculated for the β'' phase in the $12 \times 12 \times 12$ cell and in the $20 \times 20 \times 12$ cell. The free energies were found to be within 1meV/atom, indicating that they are sufficiently well converged.

3. Results

3.1. Experimental Results

In the early stages of aging, i.e. 523K for 15 minutes, we find that Nd clusters form as rods along the (0001) direction. Figure 3a shows the formation of GP-sheets consisting of Nd atoms arranged as V, Λ and N units. These units are arranged as long chains with the spacing between Nd columns in adjacent units being close to 0.67 ± 0.02 nm. Figure 3b shows the formation of a single hexagonal GP-rod in a Mg matrix. It is clear from this figure that this hexagonal GP-rod is isolated and is not surrounded by any other patterns. Both these arrangements have also been reported to occur in previous studies [22, 24]. At this stage in the aging heat treatment, there were a number of smaller sized precipitates that consisted of short rows of Nd atoms arranged as hexagons or zig-zags (fig. 4). The individual units of hexagons or zig-zags are separated from each other by a distance similar to that between the zig-zags in β' . We do not observe a regular pattern in the arrangement of the hexagonal and zig-zag rows of Nd atoms.

Figure 3: HAADF-STEM images of a Mg-0.4Nd (at. %) alloy aged for 15 minutes at 523 K with the incident beam parallel to the [0001] zone axis. The figure shows a) VA GP-sheets b) Hexagonal GP-rods

Upon further aging of this alloy, we found that extended precipitates form that are very similar to the previously reported β' phase. However, the precipitates that were observed are found to contain rows of Nd atoms arranged as hexagons (fig. 5), in addition to the zig-zag rows of Nd. Depending on the relative number of hexagonal rings, and zig-zag rows, our micrographs show the formation of β' -like phases with compositions ranging between $x_{\text{Nd}} = 0.125$ and 0.166. Compared to β' ($x_{\text{Nd}} = 0.125$), the precipitates with the higher Nd composition accommodate

the excess as rows of hexagonal Nd-rings. The presence of these hexagonal rows of Nd atoms in the β' precipitate has also been reported in the study by Saito *et al.*[22]. These do not appear to be defects in this precipitate since they are formed as extended chains along the $[100]_{\beta'}$ direction. From the local variations in Nd arrangements, it appears that the expected orthorhombic structure with a Mg_7Nd stoichiometry or a phase composition of 12.5 at. % Nd is not a valid description of these precipitates.

In addition, we also observe the formation of regions in the β' precipitate that seem to have extended hexagonal ordering (indicated with yellow arrows in fig. 5). Due to the complexity of these orderings, interpretation of the STEM images along one orientation can be misleading. To accurately characterize the extended domains of hexagons seen along the [0001] zone axis, imaging of the precipitates was performed along the $[11\bar{2}0]$ zone axis as shown in the inset of fig. 5. In this orientation, hexagonal rings are recognized as 2 [0001] zigzag chains spaced 0.55 ± 0.02 nm apart along a $\langle 10\bar{1}0 \rangle$ direction. While these hexagonal rings extend as columns along the [0001] direction, they do not necessarily extend the entire depth (along [0001]) of the precipitate, as illustrated in fig. 5. Where one hexagonal ring column ends another one begins 0.55 ± 0.02 nm away from the previous column along a $\langle 10\bar{1}0 \rangle$ direction. Viewing this stacking defect along the [0001] zone axis would appear as a wide region consisting of hexagonal rings as in D0_{19} . The frequency of observing this stacking defect and the lack of evidence of D0_{19} ordering when viewed along a $\langle 11\bar{2}0 \rangle$ zone axis confirms that the D0_{19} -like ordering observed along the [0001] zone axis is only an artifact of stacking defects.

Figure 4: HAADF-STEM images of a Mg-0.4Nd (at. %) alloy aged for 15 minutes at 523 K with the incident beam parallel to the [0001] zone axis showing different arrangements of Nd atoms as hexagonal rings and zigzag chains

3.2. 0K Phase Diagram

Phase stability is determined by a global minimum of the free energy. At zero Kelvin, where the entropy is zero, this reduces to minimizing the energy. To assess phase stability in the Mg-Nd binary, we first calculated the formation energies of all the intermetallic compounds reported for this system in the ICSD database[52]. However, since

Figure 5: HAADF-STEM images of a Mg-0.4Nd (at. %) alloy aged for 2 hours at 523 K with the incident beam parallel to the $[0001]$ zone axis showing a β' precipitate with regions of interconnected rows of hexagonal rings (indicated with a yellow arrow). The inset shows the structure of β' along the $[11\bar{2}0]$ zone axes containing stacking defects.

our primary interest is to understand the early stages of precipitation, we also enumerated a large number of symmetrically distinct arrangements of Mg and Nd atoms on the HCP structure. The total energies $E(\vec{\sigma})$ of each configuration $\vec{\sigma}$ were calculated with DFT-PBE allowing all lattice parameters and internal coordinates to relax. Formation energies were calculated relative to pure Mg and Nd, both in the HCP crystal structure, according to:

$$E_f(\vec{\sigma}) = \frac{1}{N}(E(\vec{\sigma}) - N_{\text{Mg}}E_{\text{Mg}}^{\text{HCP}} - N_{\text{Nd}}E_{\text{Nd}}^{\text{HCP}}) \quad (3)$$

where N is the number of atoms in the unit cell of configuration $\vec{\sigma}$, N_{Mg} and N_{Nd} are the number of Mg and Nd atoms and $E_{\text{Mg}}^{\text{HCP}}$ and $E_{\text{Nd}}^{\text{HCP}}$ are the total energies (per atom) of the references in the HCP crystal structure. Analysis of the fully relaxed structures revealed that many of the enumerated configurations in HCP are dynamically unstable and relax to crystal structures that are not HCP. We screened configurations that maintain an HCP crystal structure by inspection of coordination number up to the fourth nearest neighbor shell. After the application of this filter, we were left with 654 structures that had an HCP or near-HCP crystal structure.

Figure 6 shows the formation energies at 0K. The experimental phase diagram indicates the stability of four ordered intermetallic phases: $\text{Mg}_{41}\text{Nd}_5$ (β_e), Mg_3Nd (β_1), Mg_2Nd (C15 Laves phase) and MgNd (B2-CsCl). The Laves phase is observed as a high temperature phase and is not expected to be stable at lower temperatures. The global convex hull shown in fig. 6 is in agreement with these experimental observations[27, 34]. However, since our interest here is in the early stages of precipitation, the relevant convex hull is not the global hull, but rather a metastable convex hull of the orderings that remain in the HCP crystal structure after relaxation.

It is well known that metastable orderings on the crystal structure of the supersaturated solid solution often form first because their nucleation is accompanied by lower interfacial and strain energy penalties. Figure 7 shows the formation energies of the low energy configurations that maintained an HCP parent crystal structure after structure relaxation. The dashed line corresponds to the convex hull. The first phase to appear on the convex hull is the β' ordering (fig. 2b) having a Nd composition of 1/8. The D0_{19} ordering (fig. 2a) at composition 1/4 also appears on the convex hull.

The prediction that β' is on the convex hull of HCP-based orderings is consistent with the experimentally observed precipitates in the initial stages of aging shown in fig. 5. However, close inspection of figs. 4 and 5 indicates that the early HCP-based precipitates are not perfect β' with a Mg_7Nd stoichiometry, but contain excess Nd that are accommodated in linear strips of hexagonal rings that interleave the zig-zag Nd-rows of β' . Furthermore, there is no evidence of a regular distribution of the zig-zag rows and strips of hexagonal rings.

Figure 6: Formation energies of different orderings of Mg and Nd atoms on the HCP crystal structure after structure relaxation with DFT. Formation energies are calculated relative to the energies of Mg and Nd in the HCP crystal structure at 0K. Points colored orange remain HCP after structure relaxation, grey colored points relax into structures that are not HCP. The green points correspond to structures that are on the global convex hull. The red points correspond to configurations on the HCP convex hull

Figure 7: Formation energies of structures that remain HCP after complete structure relaxation in DFT. The structures that are generated by the systematic enumeration of anti-site defect clusters within ordered ground states are colored in brown, purple and green. The hierarchy of structures (β''') generated by combining the β' and the β'' phases are shown in blue. The HCP convex hull (indicated in red) is formed by pure-Mg, β' , $\beta'''_{(0^21)}$, $\beta'''_{(0^31)}$ and β''

While not immediately evident, the β'' ordering (fig. 2a) can be represented as a collection of linear strips of hexagonal Nd orderings as is illustrated in fig. 8c. Viewed in this light, the experimental precipitates of figs. 4 and 5 clearly exhibit features of both β' and β'' . They can be interpreted as a one dimensional ordering of zig-zag Nd rows from β' ~~occasionally~~ occasionally interleaved with a strip of hexagons from β'' . This suggests that a whole family of hybrid orderings can be generated by mixing different fractions of zig-zag rows and hexagonal strips. A "branching" algorithm[53] can be used to systematically enumerate all possible arrangements of zig-zag rows and hexagonal strips. In this algorithm, the first generation of orderings is created by stacking one β' unit and one β'' unit. We will refer to this ordering as $\langle 01 \rangle$, where the 0 refers to β' and 1 refers to β'' . Subsequent generations can then be constructed by taking all the structures in the previous generation and stacking them with either β' or β'' . For example, the second generation consists of $\langle 0^21 \rangle$ and $\langle 01^2 \rangle$. The superscripts refer to the number of times the ordering needs to be repeated. The first three generations of structures that can be constructed with this algorithm are shown in fig. 8. We will refer to this hierarchy of structures as β''' , while referring to a specific ordering in this hierarchy with a subscript (eg. $\beta'''_{(01)}$). This hierarchy of structures includes the parent structures that were used to generate them, i.e. β' (equivalent to $\beta'''_{(0)}$) and β'' (equivalent to $\beta'''_{(1)}$). The precipitates shown in figs. 4 and 5 belong to this hierarchy of orderings, specifically the precipitate shown in fig. 4a corresponds to $\beta'''_{(0^21)}$. The two other experimentally observed precipitates can be generated in the higher generations of the branching algorithm.

The calculated formation energies of β''' orderings are shown in blue in fig. 7. First-principles calculations predict that two β''' orderings ($\beta'''_{(0^21)}$ and $\beta'''_{(0^31)}$) appear on the HCP convex hull. Figure 7 also shows that many other β''' orderings have formation energies residing within 2 meV/atom of the convex hull. This is very close to the numerical accuracy of our DFT calculations and it is therefore not possible to unequivocally identify the true β''' ground states between β' and β'' . The fact that so many β''' orderings are, within the numerical accuracy of the DFT calculations, degenerate with the common tangent between β' and β'' suggests the possibility of a "devils staircase"[53, 54]. This would imply that an infinite, but countable, number of β''' orderings are thermodynamically stable ground states at 0K.

3.3. Transformation Strains

Transformation strains measure the change in lattice vectors of the precipitate relative to that of the matrix. The magnitude of these strains and the resulting strain energy penalty can influence the morphology and stability of coherent precipitates within a matrix. Here we consider the Green-Lagrange strain defined as:

$$\mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) \quad (4)$$

Figure 8: Hierarchy of structures (β''') that can be generated by combining β' and β'' along the $[010]_{\beta'}$ direction. In the schematic crystal structures, the regions that correspond to β' are colored yellow and the regions that correspond to β'' are colored blue. The first three generations that can be constructed using a branching algorithm are shown

$\mathbf{E}$ is a 3×3 matrix that measures the strain of the precipitate phase relative to pure Mg and is invariant to any rigid rotation. $\mathbf{I}$ is the 3×3 identity matrix. The deformation gradient $\mathbf{F}$ is a 3×3 matrix that relates the lattice vectors of a strained unit cell (that of the precipitate phase) to a reference unit cell (that of pure Mg) according to

$$\mathbf{F}\mathbf{P} = \mathbf{S} \quad (5)$$

with

$$\mathbf{P} = \begin{bmatrix} \vec{a} & \vec{b} & \vec{c} \end{bmatrix} \quad (6)$$

where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the lattice vectors (as columns) of the reference unit cell. The matrix $\mathbf{S}$ contains the lattice vectors of the deformed unit cell. Strains reported here are in a cartesian coordinate system with the z -axis parallel to the c -axis and the x axis along the $\vec{a}$ lattice vector of the HCP unit cell. The $\vec{a}$, $\vec{b}$ and $\vec{c}$ axis of the orthorhombic supercell of β' and β''' are oriented along the x , y and z axis of the global coordinate system.

Figure 9 shows the calculated components of the transformation strains for the β' , β''' and β'' phases. Our DFT calculations predict a large misfit along the $\langle 100 \rangle_{\beta'}$ direction (of the order of 10%) for the β' phase. The misfit strains along the $\langle 010 \rangle_{\beta'}$ and $\langle 001 \rangle_{\beta'}$ directions are much smaller (around -1 %). The β'' phase has the same transformation strain (close to 8%) along both the x and y directions due to the symmetry of the Nd ordering. As is clear in fig. 9, the transformation strains of all the β''' phases vary almost linearly as a function of composition between β' and β'' .

The very large misfit strains within the HCP basal plane suggest that the strain energy penalties to form coherent precipitates within the matrix should be very large. This is especially likely for β'' with its large misfit strains in both the x and y direction. Due to the almost linear dependence of the misfit strains as a function of x_{Nd} , there is a small composition interval where β''' phases have a minimal misfit strain both along the z axis (HCP c axis) and the y axis. For example, at a composition of $x_{\text{Nd}} \approx 0.15$, the mismatch along the $\langle 010 \rangle_{\beta'}$ direction between the matrix and the precipitate is close to zero.

The larger misfit strains along the $\vec{a}$ -axis (E_{11}) suggest that precipitates that form as thin plates parallel to the $\{100\}_{\beta'}$ planes would have the least strain energy penalty since they would minimize the interface between the matrix and the precipitate in the $\langle 100 \rangle_{\beta'}$ direction. This is consistent with the thin plate-like precipitate morphologies observed in fig. 4, fig. 5 and previous studies[22].

3.4. Formation of the GP rods

To investigate the driving force for GP-rod and GP-sheet formation, we calculated the 0K formation energies of the various GP orderings observed experimentally in supercells of different sizes. For each pattern, we systematically varied the supercell size thereby probing the extent with which they interact with their periodic images. The overall composition (and densities of these rods) also changes as the size of the supercell is varied. We considered four possible arrangements: (i) Isolated Nd atoms arranged as hexagons, N and V orderings that are periodic along the $[0001]_{\alpha}$ direction (ii) Nd atoms arranged as

Figure 9: Green-Lagrange transformation strains calculated relative to the magnesium crystal for β' , β'' and low energy β''' orderings. The coordinate system used to calculate these transformation strain is shown for the prototype β' phase.

a single zig-zag (fig. 2c), similar to a row of Nd atoms in β' (iii) Nd atoms arranged in a VA pattern with a spacing similar to that specified by Saito *et al.*[22] (fig. 1e) and (iv) Nd atoms arranged in a VA pattern with a spacing similar to that specified by Lefebvre *et al.*[24] (fig. 1d). The formation energies of each pattern is shown in fig. 10. It is clear from this figure that the formation energy of Mg supercells containing GP rods are consistently below the formation energies of supercells with uniformly distributed Nd, showing that there is an energetic preference for Nd clustering. Figure 10 also shows that the formation energies of the GP rods are all above the metastable HCP convex hull. This indicates that the GP-rods are therefore transient patterns that, due to their small size, can form more rapidly than large metastable precipitates such as β' or β''' .

We also calculated the relaxation fields for the isolated GP-rods relative to the ideal HCP crystal (shown in fig. 11). The displacement field of all three GP-rods results in an effective dilation around the cluster as a result of the larger size of Nd atoms. The presence of an isolated “V” rod in a magnesium crystal causes a significant distortion at the edges of the Nd cluster. The introduction of Nd atoms arranged in the shape of a “N” results in a similar response. The hexagonal rods lead to a distortion field that has the expected 6-fold rotational screw axis and is largely dilatational in character. The large dilatational strain fields around the GP rods makes their formation more favorable in regions of tensile stress (as may occur adjacent to a dislocation [55]).

3.5. Cluster Expansion and Finite temperature phase diagram

In the previous sections we described the 0K phase stability of orderings on the HCP parent crystal structure of the Mg-Nd binary. To predict phase stability above 0K, we performed Monte Carlo simulations to an HCP based cluster expansion. The expansion coefficients of the cluster expansion of eq. (1) were fit to a training set of

DFT energies corresponding to 654 HCP Mg-Nd orderings. We selected 25 clusters from a total of 115 clusters using a genetic algorithm. The resulting fit has a root mean square error of 0.007 eV and a LOOCV score of 0.008 eV per HCP primitive unit cell (two atoms). The values of the ECI and some of the clusters that appear in the expansion are shown in figs. 12 and 13.

Our cluster expansion is remarkably accurate in predicting the β' , β'' , and β''' orderings as ground states at 0K. The interaction range of the cluster expansion is large (the largest pair interaction extending $\approx 12\text{\AA}$) compared to typical cluster expansions. It predicts the $\beta'''_{\langle 01 \rangle}$ phase as breaking the convex hull thereby making it stable in a finite chemical potential range. All the other β''' phases are predicted to be degenerate and lie along the convex hull. These configurations have energies that are composition weighted sums of the energies of structures that are stable in a finite chemical potential range. The cluster expansion predicts two sets of degenerate phases, the first set exists between β' and $\beta'''_{\langle 01 \rangle}$, and the second set between $\beta'''_{\langle 01 \rangle}$ and β'' . The degenerate phases are formed by combining the end states according to the branching algorithm of section 3.2 (for example, combining one unit of β' and one $\beta'''_{\langle 01 \rangle}$ gives us $\beta'''_{\langle 021 \rangle}$). Thus an infinite number of degenerate ground states that have a composition corresponding to a rational number can be generated between the end states. An infinite number of ground states is then expected to exist at low temperatures. This is in good agreement with DFT results since formation energies of the β''' phases that were calculated with DFT are within <2 meV of the convex hull (fig. 14). In the real system, it is expected that each of these β''' phases breaks the 0K convex hull. It may be possible to replicate this behavior in our cluster expansion by including longer range interactions, however by including larger clusters in our fit, we would essentially be fitting numerical noise in our DFT data. Thus, we restricted this study to a cluster expansion with the smallest interaction distance that still predicts the lowest order β''' ordering ($\beta'''_{\langle 01 \rangle}$) to be stable in a finite chemical potential window at 0K.

Using the cluster expanded effective Hamiltonian, we calculated free energies by integrating over GCMC data obtained using a $12 \times 12 \times 12$ supercell of the primitive HCP cell. The phase boundaries generated using the common tangent construction are shown in fig. 15. We only considered the free energies of the phases that are stable in a finite chemical potential range at zero kelvin. The cluster expansion only predicts four such phases in the magnesium rich part of the phase diagram: the α -Mg solid solution, β' , β'' and $\beta'''_{\langle 01 \rangle}$. All four phases are found to be stable at finite temperatures. This cluster expansion does not predict any solid state invariant reactions up to the melting temperature of pure Mg. The phase diagram of fig. 15 predicts that any sample with a neodymium composition between 0 and 0.125 is expected to form a two phase mixture of α -Mg and β' .

Figure 10: The formation energies of different GP-rods and GP-sheets that are expected to form in the Mg-Nd alloy calculated with DFT. The dashed line shows the HCP convex hull at 0K.

4. Discussion

The aim of this study has been to resolve the early stage precipitation sequence in Mg-Nd alloys and to determine the thermodynamic driving forces for GP zone and metastable precipitate formation. The later stages of aging in this class of alloys has been discussed in other studies[2, 6, 9–12]. We have shown that the early stages of the aging reaction in Mg-Nd alloys is dictated by the HCP convex hull. Not only are the β' and β'' orderings stable, but there also exists a whole family of thermodynamically stable hybrid orderings that combine features of both phases. We have labelled this family of orderings as β''' . Past experimental studies[22] and HAADF-STEM images collected in this work show ample evidence for β''' formation. Our experimental work shows that a spectrum of β''' precipitates with Nd compositions ranging between $x_{\text{Nd}} = 0.125$ and $x_{\text{Nd}} = 0.166$ are formed, with no evidence for extended β'' . Earlier work[22], however, interpreted the β''' phases as defective β' phases. ~~Our DFT calculations show that they are distinct stable compounds (in HCP), deserving of a separate name. They further~~ We also note that a subset of the β''' orderings at lower Nd compositions contain features reminiscent of antiphase boundaries between different β' translational variants. Antiphase boundaries, however, are generally interpreted as defective structures accompanied by a free energy penalty. Since a large fraction of β''' orderings generated by the branching algorithm have formation energies that lie on the HCP convex hull, these phases should be viewed as distinct phases and not defective orderings of β' containing antiphase boundaries. Our DFT calculations indicate that β''' phases

with a composition close to $x_{\text{Nd}} \approx 0.15$ have a lower transformation strain than β' relative to the Mg matrix, and should therefore require lower strain energy to form compared to β' . We used a cluster expansion combined with grand canonical monte carlo (GCMC) calculations to generate the metastable HCP-based Mg-Nd phase diagram of fig. 15. We also calculated the formation energies of the GP-rods that are observed in the initial stages of aging. The results in fig. 10 clearly indicate an energetic preference to form GP-rods as opposed to a uniform dispersion of Nd in a Mg matrix.

Our first-principles and experimental studies allow us to address several outstanding questions about the metastable HCP Mg-Nd binary. The calculated metastable phase diagram suggests a two-phase coexistence between a Mg-rich solid solution and β' , yet experiments clearly show the formation of a range of β''' phases. Until now it has also not been clear why GP-rods form in this system. Finally, while the experimental work presented in this study clearly shows the formation of Nd units arranged as isolated hexagons, it remains unclear if this is an actual phase that forms during the course of precipitation or if it is a GP zone that is distinct from the β'' phase having long-range D0₁₉ ordering. We address these questions in the following sections.

4.1. Formation of the β''' phase

The experiments in this paper and of previous studies[22] clearly show evidence of β''' formation even after reasonably long aging times. To our knowledge, the presence of a precipitate with only the β' ordering, without the presence

(a) Relaxation field around a "V" GP-rod. The maximum displacement value of an atom is 0.211 Å

(b) Relaxation field around a "N" GP-rod. The maximum displacement value of an atom is 0.242 Å

(c) Relaxation field around a hexagonal GP-rod. The maximum displacement value of an atom is 0.292 Å

Figure 11: Relaxation fields around isolated GP-rods in a $12 \times 12 \times 1$ supercell of the primitive unit cell calculated using DFT. All the displacements have been amplified and are scaled relative to the maximum value of the displacement of an atom after relaxation.

Figure 12: Effective cluster interactions (ECI) for orderings of Mg and Nd atoms on a HCP crystal structure. ECI are grouped based on the number of sites in the corresponding cluster.

(a) Triplet clusters

(b) Quadruplet clusters

Figure 13: The multibody clusters included in the cluster expansion.

Figure 14: Formation energies of the β''' orderings calculated using DFT (blue circles) and the cluster expansion (crosses). All energies are referenced to the formation energies of β' and β''

Figure 15: Temperature-composition phase diagram calculated using the temperature dependent free energies from GCMC simulations. All the colored areas represent single phase regions.

of Nd atoms arranged as hexagons is rarely seen. Nevertheless, based on the phase diagram (fig. 15), only β' is expected to form when quenching into the two-phase field. Figure 15 however corresponds to an incoherent phase diagram and neglects the effect of coherency strain. Inspection of the misfit strains (fig. 9), suggests that β''' structures with a composition close to $x_{\text{Nd}} \approx 0.15$ require transformation strains that are almost the same as that for β' along the $[100]_{\beta'}$ direction but close to 0 along $[010]_{\beta'}$. The lower magnitude of transformation strain along $[010]_{\beta'}$ implies that a smaller strain energy penalty will accompany the formation of the β''' phases around this composition compared to β' . While a rigorous treatment of coherent equilibrium[56, 57] is beyond the scope of this study, the high degree of degeneracy among β' and neighboring β''' phases suggests that coherency strain energy may easily alter the relative stability among these phases, favoring the formation of β''' with the smallest misfit strains instead of β' . The highly anisotropic transformation strains of the β''' precipitates (fig. 9) suggests that plates with wide interfaces along the $[010]_{\beta'}$ and $[001]_{\beta'}$ directions (where the transformation strain is ≈ 0) and a short interface along the $[100]_{\beta'}$ direction (where the misfit is close to 10%) would be energetically preferred. The experimental HAADF-STEM images shown in figs. 4 and 5 confirm that this is indeed the case.

The high degree of degeneracy among the different β''' phases is also likely at the origin of the apparent disorder among zig-zag rows and hexagonal rings observed experimentally. As discussed previously, the numerical errors in our DFT results prevent us from establishing which of the β''' phases are on the convex hull. Furthermore, the very small differences in energies between the various β''' phases are difficult to resolve with a truncated cluster expansion. Our cluster expansion predicts $\beta'''_{(01)}$ to be stable in a finite chemical potential at 0K. All the other β''' phases are degenerate and lie on the convex hull (without breaking the hull) at 0K.

We explored the effect of these zero kelvin degeneracies at finite temperature by calculating the free energy of $\beta'''_{(021)}$, which at 0 Kelvin is degenerate with respect to a two phase mixture of β' and $\beta'''_{(01)}$. The calculated free energy for this phase was based on GCMC results collected in a $20 \times 20 \times 12$ supercell of the primitive HCP simulation cell. The free energies of $\beta'''_{(021)}$, β' and $\beta'''_{(01)}$ are compared at 800K in fig. 16. The free energy of $\beta'''_{(021)}$ is less than an meV above the common tangent. This difference is within the limit of the accuracy enforced in our GCMC simulations. In view of these very small energy differences, the metastable phase diagram between $x_{\text{Nd}} = 0.125$ and 0.25 cannot be resolved. The high degree of degeneracy of the free energies of the β''' phases and their sensitivity to coherency strain energy motivates the phase diagram shown in fig. 17 where we have shaded the region in which any of the degenerate β''' phases can form. The shaded region in the phase diagram signifies the existence of an infinite, but

countable, number of β''' phases, each having a different ratio of zig-zag and hexagonal strips.

Figure 16: Calculated free energies for α -Mg, β' , $\beta'''_{\langle 021 \rangle}$, $\beta'''_{\langle 01 \rangle}$, $\beta'''_{\langle 012 \rangle}$ and β'' at 800K. Common tangents are shown as dashed lines. The energies are referenced to the 0K energies of pure-Mg(HCP) and Mg_3Nd having β'' ordering.

Figure 17: Metastable phase diagram for the Mg-Nd alloy showing a region between $x_{\text{Nd}} = 0.125$ to $x_{\text{Nd}} = 0.25$ where an infinite, but countable, number of β''' phases are expected to exist. This region is hatched to schematically indicate that the exact nature of the phase transitions and transition temperatures in this region remains unclear.

4.2. Formation of the GP rods

The Guinier-Preston zones in Mg-Nd alloys consist of highly ordered clusters of Nd atoms arranged as rods along the c -axis of the HCP crystal and patterned similar to N,V and hexagons in the basal plane (fig. 1). Figure 10 shows that the formation energies of the GP rods do not lie on the HCP convex hull. It is however clear from this figure that the energies of the clustered patterns are lower than that of a random dispersion in a Mg matrix.

To quantify the driving forces for Nd clustering, we consider the change in the Nd chemical potential upon formation of GP rods and sheets. To this end, it is convenient to envision two types of Mg solid solutions. One consists of Nd uniformly distributed over the substitutional sites of HCP Mg. At dilute concentrations, interactions between Nd can be neglected. The free energy of this solid solution can then be approximated with an ideal solution model according to

$$\Delta\bar{G}^{SS} = k_B T (x_{\text{Mg}} \ln x_{\text{Mg}} + x_{\text{Nd}} \ln x_{\text{Nd}}) + E_{\text{Nd}}^{\text{point}} x_{\text{Nd}} \quad (7)$$

where $\Delta\bar{G}^{SS}$ is the free energy of the solid solution per atom, k_B is Boltzmann's constant, T is the temperature, x_i is the mole fraction of component i , and $E_{\text{Nd}}^{\text{point}}$ is the energy change associated with replacing a Mg atom in a pure magnesium HCP crystal with a Nd atom (using pure Mg and pure Nd, both in the HCP crystal structure, as reference states).

Another type of solid solution could consist of pure Mg with a random distribution of GP rods. The GP rods are too small to be considered as distinct precipitates. Rather, they can be viewed as similar to large molecules dissolved in a solvent. Experimental evidence suggests that the GP rods and sheets in Mg-Nd alloys are very long along the c -axis[22]. Hence each GP-rod or sheet ties up a large number of Nd atoms. While the free energy for this solution should account for the configurational entropy associated with all possible ways of distributing GP rods and sheets, this entropic contribution will be substantially smaller than that of a random solid solution having the same number of Nd atoms. We can therefore neglect the configurational entropy arising from all the different ways of arranging the GP-rods and approximate the free energy of this solution, $\Delta\bar{G}^\gamma$, using 0K formation energies. Based on our DFT supercell calculations (fig. 10) at dilute Nd concentrations, the rods are non-interacting and their energy can be approximated as having a linear composition dependence:

$$\Delta\bar{G}^\gamma \approx E_{\text{Nd}}^\gamma x_{\text{Nd}} \quad (8)$$

E_{Nd}^γ is a constant that can be fit to DFT calculated formation energies of each GP-rod in supercells of different sizes.

The free energies (eqs. (7) and (8)) can be used to estimate the chemical potential of Nd in either of the hypothetical solid solutions according to

$$\mu_{\text{Nd}}^\phi = \Delta\bar{G}^\phi + (1 - x_{\text{Nd}}) \frac{\partial \Delta\bar{G}^\phi}{\partial x_{\text{Nd}}} \quad (9)$$

where $\Delta\bar{G}^\phi$ is the free energy of phase ϕ . Graphically this corresponds to the intercept of the tangent to $\Delta\bar{G}^\phi$ with the free energy axis at $x_{\text{Nd}} = 1$. Nd will tend to cluster into GP rods if it can lower its chemical potential relative to that of a non-interacting solid solution.

The chemical potentials of Nd in a non-interacting random solid solution and in a solution containing different

Figure 18: The chemical potentials of Nd in solutions containing different GP-rod and GP-sheet patterns. The chemical potential of Nd in the non-interacting random solid solution is evaluated for a composition of $x_{Nd} = 0.005$ and a temperature of 520K. The largest driving force exists for the formation of the VA GP-rods with a spacing as suggested by Lefebvre *et al.*[24]. The isolated clusters of Nd atoms arranged as N,V or hexagons have the smallest driving force.

nano rods are shown in fig. 18. It is clear from this figure that isolated units of N,V or hexagons have the smallest driving force to form. Nevertheless, the combination of a finite driving force as well as the requirement of a small number of Nd atoms to assemble N,V or hexagonal rods is likely the reason that they are observed as the first patterns during the decomposition of the SSSS.

Longer aging times allows for more Nd diffusion, leading to the formation of the larger GP-sheets, which are accompanied by the largest drop in chemical potential. Since all the GP-sheets that have been explored in fig. 18 would require similar amounts of diffusion, we do not expect that the GP sheets with the spacing as suggested by Saito *et al.*[22] or the zig-zag ordering investigated by Issa *et al.*[31] will form. Only the GP-rods with the larger spacing between V's and Λ 's (as suggested by Lefebvre *et al.*[24]) are expected as these are accompanied by the largest drop in Nd chemical potential. The measured spacings between Nd atoms in adjacent V, Λ units for these GP-rods, calculated with DFT, is $6.9\text{\AA}$, in excellent agreement with the experimental value of $6.7 \pm 0.2\text{\AA}$. We note that if entropic contributions arising from the different ways of arranging GP-rods were taken into account, the chemical potential drop upon forming GP-rods and sheets will only become larger than that shown in fig. 18.

In addition to the thermodynamic driving force to form these patterns, the strain fields around the isolated GP-rods (fig. 11) could interact favorably with extended defects such as dislocations in the material. Many GP rods and sheets are likely attracted to stress fields that are tensile in nature as their energy would be lowered further.

4.3. Is β'' formed during the aging sequence?

Past studies have discussed the formation of β'' (having $D0_{19}$ ordering) as part of the precipitation sequence of dilute Mg-Nd alloys [2, 22, 24, 27, 30, 31], sometimes even attributing the peak strength in this alloy to the formation of this phase. Our metastable HCP-based phase diagram, however, indicates that aging these alloys should only lead to the precipitation of β' , or as described above to a β''' phase if coherency strains are able to alter relative stabilities. In fact, the nano sized precipitates that form in the early stages of aging (fig. 4) are closer in appearance to the β''' phases at a composition of $x_{Nd} = 0.166$ than they are to that of β'' .

The Nd orderings identified as β'' in past studies are usually no larger than isolated Nd hexagons and do not exhibit the long-range order expected of a $D0_{19}$ precipitate. One possibility is that these local orderings are β'' nuclei and form due to a significantly larger driving force to nucleate β'' compared to that of either β' or β''' . Figure 19a schematically illustrates a graphical representation of the nucleation driving force to form a β phase in a supersaturated solid solution α . Figure 19b shows calculated nucleation driving forces for β' , β''' and β'' for a supersaturated α -Mg alloying with $x_{Nd} = 0.5\%$. The free energies

(a) Schematic drawing showing the nucleation driving force to form a β precipitate from a supersaturated solid solution of the α phase.

(b) The nucleation driving force for the formation of β' , β''' and β'' from a dilute Mg-Nd solid solution calculated using the free energies obtained with GCMC. The nucleation driving forces are calculated at 520K and 620K.

Figure 19

of the degenerate β''' were approximated by linearly interpolating between the the free energies of the β' , $\beta'''_{(01)}$ and β'' .

As is clear in fig. 19b, the nucleation driving force to form the β'' phase is not especially large to favor its formation over that of β' or any of the β''' orderings. In fact at higher temperatures, it is less than that of β' . As shown in fig. 9, the misfit strain to form coherent β'' in pure Mg is very large in all three directions. Hence we expect that the coherency strain energy penalty of coherent β'' precipitates should be larger than that of β' or that of β''' having compositions close to β' . The lack of an overwhelming nucleation driving force coupled with the large strain energy accompanying the coherent formation of β'' suggests that the observed Nd hexagon rods are not incipient β'' precipitates. Instead, we argue that they are more accurately labeled as hexagonal GP-rods, which as shown in the previous section are transient orderings that lower the Nd chemical potential relative to a disordered solid solution. Given the large strain energy penalty to form β'' , and the lack of experimental evidence for a long-range ordered β'' precipitate, it is appropriate to remove the $D0_{19}$ phase from the Mg-Nd precipitation sequence and replace it with GP-rods. As aging continues, the hexagonal GP-rods will either dissolve, liberating Nd to form larger GP-sheets, or serve as nucleation sites for β''' formation as suggested in fig. 4. In the figure, the hexagonal, V and N GP-rods are arranged such that locally, a β''' ordering is formed.

5. Conclusion

We have performed a combined experimental and first-principles study to elucidate the precipitation sequence in magnesium neodymium alloys. We have established that while the GP rods and sheets observed during early aging are not ground state orderings on the HCP crystal structure, their formation from a random solid solution is accompanied by a reduction of the Nd chemical potential. HAADF-STEM imaging has shown that the early precipitates are not perfectly ordered β' , but instead consist of Nd zig-zag rows interleaved by strips of Nd hexagons. The presence of Nd hexagons results in a range of precipitate compositions between $x_{Nd}=0.125$ and 0.166. First-principles DFT calculations predict that the observed Nd orderings correspond to stable compounds that belong to a family of hybrid orderings consisting of different fractions of β' and β'' ($D0_{19}$). These hybrid orderings, which we have labeled β''' , are highly degenerate with each other and with β' . Their misfit strains relative to the HCP Mg matrix are sensitive to composition, suggesting that coherency strain may play an important role in selecting a particular β''' ordering. The precipitates observed in this study and previous studies[22, 24], are consistent with these orderings and range in composition from $x_{Nd} = 0.125$ (β') to $x_{Nd} \approx 0.166$. While Nd has a tendency to form hexagonal clusters, no experimental evidence was found to support the formation of long-range ordered β'' precipitates having $D0_{19}$ ordering. A cluster expansion Hamiltonian was combined with Monte Carlo simulations to calculate a metastable HCP temperature-composition phase diagram. Neither the metastable phase diagram nor calculated nucleation driving forces support the formation of β'' precipitates having $D0_{19}$ ordering in dilute Mg-Nd alloys. We therefore argue that the hexagonal arrangements of Nd atoms observed during the early stages of aging should not be identified as $D0_{19}$, which has long-range order, but rather as hexagonal GP-rods.

Our study motivates the following precipitation sequence for dilute binary Mg-Nd alloys:

where β''' includes the β' phase and ranges in composition from $x_{Nd} = 0.125$ to $x_{Nd} \approx 0.166$

6. Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award #DE-SC0008637 as part of the Center for PRedictive Integrated Structural Materials Science (PRISMS Center) at University of Michigan. Resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User

Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 are gratefully acknowledged. All plots were made using the `matplotlib` library[58].

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