

Nanoclusters in stacking faults in Mg-Y-Zn alloys examined by small-angle X-ray scattering and Extended X-ray Absorption Fine Structure analysis

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Abstract

A coarse-grained picture of segregation layers in MgYZn alloys as a two-dimensional cluster systems bound in stacking faults has been justified by a combined use of Extended

X-ray absorption fine structure (EXAFS), small-angle X-ray scattering, and scanning tunneling microscopy. EXAFS analysis showed an identical relaxed atomic configuration around Y and Zn atoms as a finger print of molecular-like $L1_2$ clusters, characteristic of Long Period Stacking Ordered (LPSO) structures. The fingerprint was confirmed for wide range of compositions of cast ternary alloys containing bulk LPSO structures. The clusters in dilute MgYZn alloys, whose segregation layers were sparsely dispersed in the α -Mg matrix, showed the same fingerprint. The results suggested that the Y-Zn clusters in the segregation layers of Mg-Y-Zn alloys are identical, regardless of the cluster density in the layers or the number of segregation layers.

Keywords

Long period stacking ordered structures; MgYZn alloys ; small-angle X-ray scattering (SAXS) ; extended X-ray absorption fine structure ; two-dimensional cluster system

1. Introduction

The Mg-rich corner of the Mg-Y-Zn alloy system contains long-period stacking ordered (LPSO) structures in the as-cast condition or after long-time annealing. LPSO structures are unique in their phase transformation, because their partial structure, that is, solute clusters consisting of Y and Zn atoms, changes their arrangements and density in the stacking fault planes depending on the composition and thermal history. To understand their nanostructures and formation mechanism, LPSO structures, have been intensively investigated by electron microscopy [1-5], X-ray scattering/diffractions [6-8], first-principles calculations [9-11] and various other approaches [12-14], as a prospective candidate for a strengthening element in light weight structural materials [15]. Well-ordered LPSO phases exhibit stacking structures based on an hcp lattice with periodical stacking faults in close-packed planes, on which $2\sqrt{3} \times 2\sqrt{3}$ superstructure of solute clusters are positioned [3, 4, 9, 16, 17]. Figure 1 shows a schematic of a fully-ordered 18R LPSO structure based on the results of electron microscopy [3-5]. Solute clusters in highly ordered LPSO structures consist of one unit cell of the $L1_2$ cluster, eight Y atoms at the corner sites, six Zn atoms at the face center sites, and an additional interstitial atom at the body-center site, with strongly distorted atomic positions [9-11, 18]; hereafter this will be referred to as the $L1_2$ cluster. The clusters occupy four atomic layers in the body-diagonal direction of the $L1_2$ unit cell. However, experimental studies on the transformation kinetics [6, 7], phase diagram [18] and scanning tunneling microscopy (STM) [13] of Mg-Y-Zn alloys have clarified that the cluster distributions on the stacking faults are often sparser and less ordered. Kurokawa et al. [13] reported direct evidence of such sparse cluster distributions on stacking faults by using scanning tunneling micrographs of cleaved specimens of concentrated samples. Their results led to a coarse-grained cluster

model of segregation layers in the LPSO structure [14], although the structure of poorly ordered clusters has not been comprehensively analyzed yet. To examine the local atomic configurations in such a less ordered structure, the Extended X-ray Absorption Fine structure (EXAFS) is a useful approach. Matsuura et al. [19] reported that the local atomic configuration around Zn in $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy is close to the CsCl type, which does not agree with the later works that used TEM [4,17] or first-principles calculations [9, 10] for fully ordered LPSO alloys. The composition is shown as at %.

Recently, metastable microstructures of Mg with sparsely distributed Y-Zn cluster segregation layers were reported [20]. They were discovered in an attempt to develop dilute MgYZn alloys with the lowest solute composition effective for kink strengthening. An interesting question arises here: whether the nanostructure of such segregation layers are the same for three-dimensional LPSO phases and the sparsely distributed layers in α -Mg grains. To examine the in-plane cluster distance and the periodicity of LPSO structures, small- and wide angle X-ray scattering (SWAXS) measurements were performed. EXAFS measurements were conducted to examine the atomic configurations of the solute clusters. In this study, we analyzed the spatial distribution of clusters using SAXS, and the inner structure of so-called L_{12} cluster identified using EXAFS as a fingerprint of the same structural unit in these alloys.

2. Methods

Cast samples of $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$, $\text{Mg}_{92}\text{Y}_5\text{Zn}_3$, and $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ containing bulk LPSO phases of 14H, 18R or 10H structure in the as-cast state were selected. In-situ SWAXS measurements were performed to examine the evolution of nanostructures, in particular cluster distributions, during the cooling of the alloys from the melt. Plate samples with a

thickness of 0.2 mm were cut from the ingot and heated above the melting temperature before in-situ measurements. Liquid -quenched amorphous $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ ribbons were used to examine transient nanostructures from a supersaturated state to the final LPSO structures. $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ is the typical composition that produces single-phase 18R microstructures after long time annealing. To obtain a dilute composition, $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ rods were prepared by hot pressing the liquid-quenched ribbons at 673 K and subsequently solution treated at 803 K for 173 ks. The microstructures were compared after annealing heat treatments. In-situ measurements and ex-situ heat treatments were performed under vacuum with samples wrapped in graphite sheets.

SWAXS measurements have been performed at BL6A and 10C of Photon Factory, KEK, Tsukuba Japan and BL04B2 and BL40B2 of SPring-8, Hyogo Japan. In-situ measurements were performed during heating process up to the melting point, and then from the melting point down to 623 K to examine the stability and the evolution of the average cluster distribution of the sample. Ex-situ SWAXS measurements were performed for the heat-treatment conditions used for the EXAFS measurements. EXAFS measurements were performed at BL9C and 15A1 of the Photon Factory at the K absorption edges of Zn and Y, using transmission geometry and ionization chambers at room temperature. Absorption data were analyzed using DEMETER software [21]. Atomic positions for the initial values for fitting the EXAFS data were obtained via first-principles calculations, which were also utilized in the estimation of the phase shift using IFFEFIT in DEMETER. Fitting of the EXAFS profiles was made for $30 \text{ nm}^{-1} < k < 120 \text{ nm}^{-1}$, which is reasonable for the energy range of the measurements, and $0.16 \text{ nm} < r < 0.37 \text{ nm}$, corresponding to the nearest neighbor atoms around the Zn atom. From the atomic positions obtained from the first principles calculations, three single scattering paths of Zn-nearest Mg, Zn-Y, and Zn-interstitial Mg were chosen

for the fitting. The atomic positions provided from the first-principles calculations are given as the Supplementary Material.

STM images were obtained for the cleaved sample, which was then transferred for microscopic observation under vacuum [13].

To characterize the atomic configurations of the $L1_2$ clusters and their surroundings, first-principles calculations based on density functional theory were carried out using the Vienna ab initio simulation package (VASP) [22]. The interactions between the electrons and ions were described using the projector-augmented wave method [23, 24]. The exchange-correlation functional was described within the generalized gradient approximation of Perdew and Wang [25]. The valence electron configurations considered in this study were: $3s^2$ for Mg, $4s^2 4p^6 4d^1 5s^2$ for Y, and $3d^{10} 4s^2$ for Zn. We used a 192-atom monoclinic cell of Mg with 18R-type stacking, in which an $L1_2$ -type Y_8Zn_6 cluster was placed in the stacking-fault layers (see Ref. [14] for details). Note that $L1_2$ clusters with and without an interstitial atom of X (X= Mg, Y, or Zn) at the body-center position were examined. The cell parameters and atomic positions were relaxed under zero stress using the Methfessel-Paxton smearing method [26] at a width of 0.2 eV; this was done until the residual forces acting on each atom were less than 3 meV/Å. We adopted a plane-wave energy cutoff of 350 eV and Monkhorst-Pack [27] k -meshes of $6 \times 10 \times 9$, and applied periodic boundary conditions in all directions. The resulting relaxed atomic positions were used as the sources for the EXAFS calculations.

3. Results and discussions

3.1 Cluster distances in MgYZn alloys with LPSO structures

Figure 2 shows the change in the SAXS intensity during cooling the sample from a temperature above the melting point. Therefore, the early stage of the formation

of the LPSO structure begins at higher temperatures with faster diffusion than the previous works, where the as-cast samples were heated from room temperature. Such a gradual change of cluster distance was observed also during heating or isothermal annealing [6, 7, 28-32]. Sharp peaks at $q = 3.4, 4.0$ and 4.8 nm^{-1} correspond to the periodicities of 14H, 18R and 10H respectively, where q is the magnitude of the scattering vector. A broad peak between 5 and 7 nm^{-1} corresponds to the in-plane cluster distance in the segregation layer. The in-situ results showed that the average in-plane distance between the clusters gradually decreased during the measurements, regardless of heating or cooling. This means that the density of the clusters on the segregation layers in the LPSO structures increases continuously during the heat treatments. The reported SAXS results show [6], [29] that as-cast $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ contains both 10H and 18R LPSO structures, and changes to 18R single phase after long time annealing. This transition to longer periodicities with shorter in-plane cluster distances during annealing satisfies the mass balance of the solute clusters.

In Fig.2, the temperature at which the stacking periodicities appear during cooling is in good agreement with that at which the cluster scattering appears for all the sample composition shown here. Therefore, the thermal stability of the periodic segregation layers agrees with that of the in-plane cluster structures examined using SAXS. The average in-plane distance of clusters and the periodicity in the LPSO structures obtained in the present work are summarized in Table I along with the results obtained by previous heating / isothermal studies. The observed longest average cluster distance is larger for the less concentrated alloys. Although the average in-plane cluster distance decreases towards the shortest distance corresponding to the $2\sqrt{3} \times 2\sqrt{3}$ superstructure by annealing, the change is sluggish for dilute alloys. For the direct examination of the cluster

distribution on a segregation/stacking fault layer, Kurokawa et al. [13] measured cleaved MgYZn surfaces using STM, and obtained desired direct images of cluster distribution. Kimizuka et al. [14] proposed a coarse grained picture of two-dimensional cluster distribution. An open question that can be raised here is whether a segregation/stacking fault layer in the LPSO structure can generally be treated as a two dimensional lattice gas system where L_{12} clusters behave as molecular-like units. In-situ synchrotron radiation SAXS measurements are useful for examining the thermal stability of LPSO structures and the manner in which the average intercluster distance changes by annealing, as the average over the macroscopic region. In contrast, STM images provide the direct evidence of sparsely distributed clusters at the segregation layers on cleaved surfaces, though from a limited area and an annealing condition. Therefore, complementary use of the two approaches is advantageous. The SAXS and STM images of the as-cast and annealed ingot samples were compared for as-cast and annealed conditions of the ingot samples to examine the consistency between them. Figure 3 shows the SAXS patterns and STM images of $Mg_{85}Y_9Zn_6$ alloys for the as-cast (a, b) and annealed (d, e) samples. The SAXS patterns show the 6-fold peaks related to two-dimensional arrangements of clusters at the stacking faults. Two sharp rings with weak streaks in the radial direction represent the Bragg peaks attributed to the periodicities of stacking faults in the c-axis direction with segregation in the form of clusters [6]. The SAXS patterns represent the average structure over irradiated volume of approximately $0.3 \times 0.3 \times 0.2 \text{ mm}^3$ in this case. An interesting point is that the SAXS profile of the as-cast sample shows diffuse peaks whose peak position of 5.8 nm^{-1} is smaller than that for $2\sqrt{3} \times 2\sqrt{3}$ superstructure, 6.2 nm^{-1} , by approximately 7 %, still, the former maintains 6-fold symmetry. This suggests that the nearest neighbor cluster position randomly deviates from 6th nearest position to 7th or

9th nearest positions [13], thus keeping average nearest neighbor direction unchanged. This is because they have the crystal orientation of Mg matrix in common, which is the point most contrasting with those in the discussion by Kawasaki and Tanaka on the orientational order in confined colloidal systems [33]. The dark spots in Figs.3 (b) and (e) correspond to the L1₂ clusters [13]. The cluster distribution in Fig. 3(b) is a direct example of a sparser, more poorly ordered cluster arrangement that yields the SAXS pattern in Fig.3 (a). To examine relationship between SAXS patterns and STM images, SAXS patterns were calculated from STM images by,

$$S(\vec{q}) = | \sum_n F(qR) \exp(i\vec{q} \cdot \vec{r}_n) |^2 ,$$

where $\vec{r}_n$ denotes the coordinates of the center of gravity of the n-th cluster and $F(qR)$ is the form factor of the L1₂ clusters. R is the radius of the clusters. Figures 3(c) and (f) show the calculated two-dimensional SAXS profiles. Figures 3 (a) and (c) agree that the peak positions are smaller than that for the $2\sqrt{3} \times 2\sqrt{3}$ superstructure, but still maintain a smooth and diffuse peak with 6-fold symmetry. A quantitative comparison of the peak positions for SAXS and STM requires a large number of STM images to obtain a statistically reasonable average, and will be left for the future work. Still, we may conclude that the SAXS results reflect macroscopically averaged data of sparse cluster distribution on the stacking fault that has been discussed using STM images. After long time annealing, the sample shows $2\sqrt{3} \times 2\sqrt{3}$ superstructure of clusters with some antiphase boundaries in Fig. 3(e). The corresponding SAXS profile of Fig.3 (d) shows sharper 6-fold peaks closer to the $2\sqrt{3} \times 2\sqrt{3}$ positions. The inner sharp rings in the SAXS patterns correspond to the layer periodicity of 10H and 18R for as cast and 18R for annealed sample from the grains with the c axis parallel to the scattering vector.

3.2 Examination of clusters as a unit structure in LPSO structures

To explain the two-dimensional cluster arrangements observed using STM by Kurokawa et al. [13], Kimizuka et al. [14] presented a simulation of cluster distribution based on a coarse-grained model considering effective cluster-cluster interaction energy. They discussed the structure and interactions in comparison with confined colloidal systems [33]. From a CALPHAD viewpoint, Takeuchi et al. proposed a cluster phase diagram also from the experimental cluster configurations obtained from the STM images [34]. These calculations assumed that the so-called L_{12} clusters in the LPSO structures were a constituent subunit of the complex phases, while also behaving as molecules bound to the stacking faults. This idea may be extended to a model in which such clusters are cut from the three-dimensional phase of the LPSO structure, and constitute a metastable two dimensional mesoscopic phase diagram of interacting clusters. In contrast, the Mg-rare earth system is known to form several metastable precipitates called GP zones [35, 36], and tends to segregate rare earth elements at the grain boundary or lattice defects [37]. Therefore, although it is an interesting point and may inspire a novel idea for two-dimensional material self-assembly, we first need to investigate whether the L_{12} cluster, as the unit structure in the two system, is stable and robust enough for a wide range of time, composition, and temperatures. As the most stable atomic configuration of the L_{12} clusters, first-principles calculations [9-11] and HAADF/ABF-STEM [3,4,17,38] results reported a relaxed L_{12} cluster structure with an interstitial atom X at the body-center position of the cluster, Y_8Zn_6-X , for nearly perfectly ordered $2\sqrt{3} \times 2\sqrt{3}$ samples. X is proposed to comprise mostly Mg, and with a smaller probability, Zn [17].

First-principles studies by Saal and Wolverton [9] determined the atomic positions in the cluster which were characterized by a strongly dilated L_{12} cluster, where the atomic distance between the interstitial atom X at the body center position and the Zn

atoms at the face-center position is almost the same as the distance between the face-centered Zn atoms and their nearest neighbor Y atoms at the corner sites as schematically shown in Fig.4. This dilatation resulted in the strong contraction of the distance between the face-center Zn atoms and the nearest Mg atoms just outside the cluster. These atomic positions give $|\chi(r)|$ of the split nearest neighbor, which is characteristic of the relaxed L_{12} clusters in the environmental structure around Zn atoms in the EXAFS analysis, where $\chi(r)$ is the Fourier transform of $k^3\chi(k)$. In contrast, the relaxation does not result in splitting around the Y sites. EXAFS results reflect the signal from the clusters, because the solubility of Zn and Y in the Mg matrix is low. Figure 5 shows the contribution of each scattering path to the Fourier transform of $k^3\chi(k)$ at the Zn K edge calculated by DEMETER using the atomic position obtained from the first-principles results for the fully relaxed state. The atomic positions are unrelaxed (a), (b) or fully relaxed (c),(d), with vacancy (a),(c) or a Mg atom (b),(d) positioned at the interstitial site. The results of the single scattering path for the nearest neighbor sites are shown. For the relaxed structure, the first peaks in Fig. 5(c) and (d) are attributed to the scattering path for Mg atoms just outside the cluster from the Zn atoms, and the second ones are attributed to the path for nearest Y atoms. Due to the outward expansion of Zn sites, the increase in the nearest Zn-Zn distance results in a peak position around 0.4 nm, which was in the region where the single scattering paths for the second nearest neighbor (2NN) and the multiple scattering paths appears. Therefore, Zn-Zn position is not used in the present analysis.

Figure 6 (b) shows $|\chi(r)| = |\text{FT}(k^3\chi(k))|$, obtained as a weighed Fourier transform of the EXAFS function, $\chi(k)$, for the as-cast and annealed $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ samples at the K edge of Zn with k^3 weight and up to $k < 120 \text{ nm}^{-1}$ for transformation. The figure shows that the $|\chi(r)|$ values for the two annealing conditions agree, although the distribution of the

clusters is sparse for the as cast sample. The split nearest neighbor peaks for the two annealed conditions suggest that the atomic arrangements of the $L1_2$ clusters in the LPSO structure are identical for the samples regardless of the average in-plane cluster distance and may be used as a fingerprint for the $L1_2$ cluster. The experimental $\chi(r)$ s were fitted by DEMETER [21], with atomic positions obtained from the first principles calculations as the initial condition. The fitting of $|\chi(r)|$ was performed only for the nearest neighbor region, where the most characteristic pattern of the atomic configuration for the relaxed $L1_2$ cluster appears as shown in Figs.5 and 6(b). As the fitting parameters, atomic distances between the face-center Zn atom and outer Mg atoms, $r_{\text{Zn-Mg}}$, corner Y, $r_{\text{Zn-Y}}$, interstitial Mg, $r_{\text{Zn-inter}}$ are evaluated as independent variables, with the coordination number fixed to the structure model shown in Fig.4, and with a common amplitude variable. The detailed fitting results are presented in the Supplementary Material. Table II compares the nearest-neighbor atomic distances from the Zn atoms for the fully relaxed atomic positions obtained from the first-principles calculations, and those from the fitting parameters for $|\chi(r)|$ of an as-cast $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloy and of the sample after long-time annealing. The distances of $r_{\text{Zn-Mg}}$, $r_{\text{Zn-Y}}$, and $r_{\text{Zn-inter}}$, obtained using first-principles calculations agree with those estimated by fitting the EXAFS results of the $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ samples. In contrast, as shown in Fig.6(c), the $|\chi(r)|$ for the K edge of Y gives single nearest neighbor peak. The fingerprint $|\chi(r)|$ pattern for Zn was also observed for the $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ samples, whose periodicity of stacking faults was strongly disordered. During the formation of the LPSO structures from amorphous ribbons [28, 30], we reported that the formation kinetics of the LPSO structure from such a strongly nonequilibrium condition can be described as a hierarchical phase transformation, consisting of cluster formation and the introduction of stacking faults and spatial arrangements of clusters.

During such a process, randomly nucleated stacking faults result in a random mixture of the stacking sequence of 5(10H) and 6(18R) layers, with the average stacking distances lying in between 5 (4.8 nm^{-1}) and 6 (4.0 nm^{-1}) atomic layers as shown in Fig.7(a) for 583 K. This transient stacking structure appears just above the bifurcation temperature of 550 K and is replaced by the final long-range 18R stacking sequence with rigorously every 6 atomic layers. We may call this stacking state ‘short range stacking order’ (SR-SO) structure instead of LPSO structure [39]. Owing to the sample morphology of the liquid-quenched ribbon, transformations for the EXAFS signal were made with k^3 weight up to $k < 90 \text{ nm}^{-1}$ for the figure. The $|\chi(r)|$ at 583 K in Fig.7(c) agrees with that of the cast $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloys, demonstrating that the atomic structure of the cluster is identical for the two samples. Therefore, the sample with random (short-range) stacking order has the same fingerprint of the L_{12} cluster in common, whereas the $|\chi(r)|$ for the sample annealed at 503 K, where smaller clusters in the supersaturated hcp matrix, does not show a clear splitting of the nearest neighbor peak. From the above results, it is concluded that in $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloys, clusters pinned at stacking faults have a well-defined local structure of the relaxed L_{12} structure with interstitial atoms in common, regardless of whether the clusters are densely or sparsely distributed in the stacking fault plane, even when the stacking sequence is random.

As mentioned in the introduction, considerable attention has been devoted to decrease the amount of solute elements for the kink-strengthened Mg alloys [20]. Figure 8 shows the development of two-dimensional SAXS patterns for $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ alloys (a) immediately after the hot press, (b) after solution treatment and quench, and (c) aging at 623 K for 3.6 ks. Figure 8 (a) shows that thin plate of the LPSO structure formed during hot pressing, with an in-plane cluster peak indicated by a red triangle. Through solution

treatment and quenching, the LPSO structures are dissolved and the sample shows an isotropic scattering intensity profile that monotonically decreases with q . After heat treatment at 623 K, the profiles show a well-defined broad diffraction peak at $q=5.45 \text{ nm}^{-1}$, which corresponds to the in-plane $L1_2$ cluster distance, and dense sharp streaks that extend in the radial direction. The streaks were interpreted as the form factor of very thin segregation layer composed of clusters. Interference peaks may appear in the multilayered segregation layers. However, Fig.8 shows that many streaks appear away from of the origin, and end at a q irrelevant to the 14H or 18R peak position. Considering that the form factor of monolayer segregation on a well-defined crystallographic c-plane gives sharp but weak needle-like scattering, intersection of the form factor with the Ewald sphere lead to a SAXS profile with a segmented streak, which happens to be on the Ewald sphere. Because strengthening has been reported for annealing at 623 K [20], the structure of the cluster was examined using EXAFS. Figure 9 compares $|\chi(r)|$ for the heat-treated $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ alloy with that of the $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloys. The $\chi(r)$ for the dilute alloy shows well -defined split nearest neighbor peaks which agree with those for the $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ samples, confirming well-defined relaxed $L1_2$ clusters identical to those in the well-defined bulk LPSO structures. The present results indicate that sparsely distributed segregation layers in dilute alloy samples, where kink deformation was observed, are composed of cluster layers with well-defined relaxed $L1_2$ clusters identical to those in the perfectly ordered LPSO samples. From the SAXS patterns, the in-plane density of the clusters for the dilute sample was lower than that of the $2\sqrt{3} \times 2\sqrt{3}$ superstructure arrangements.

4. Conclusions

The cluster distribution and structural fingerprint of $L1_2$ clusters in the

segregated layers in MgYZn alloys were examined with the combined use of SAXS and EXAFS for a wide range of compositions, with the help of STM and first-principles calculations. In the segregation layers, the metastable microstructure was characterized by a two-dimensional system of molecular-like L_{12} clusters, regardless of the density of the clusters, periodicity of segregation layers, and number of periods of the layers. The fingerprint of the EXAFS data for the relaxed L_{12} cluster was presented at the K absorption edge of Zn.

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Table I. Segregation / stacking fault layers in MgYZn alloys reported in the preceding and the present works by SAXS.

Composition	Heat treatment	Layer sequence	In-plane q_m (nm ⁻¹)	Reference
9Y-6Zn ingot	673 K~773 K	10H,18R	5.7~6.2	[6,7,31, present]
9Y-6Zn amor.	483 K ~ 673 K	Random, 18R	5.8~6.0	[28,29,30]
5Y-3.5Zn ingot	673 K~773 K	10H,18R,14H	5.2~6.0	[31,present]
2Y-1Zn ingot	673 K~773 K	18R,14H	5.2~6.0	[32,39]
1Y-0.4Zn HP	ss+623K,673 K	single ~ several layers	5.45	[present]

Table II. Atomic distances calculated for fully relaxed state obtained from first principles calculations and the parameters obtained by fitting $\chi(r)$.

	First-principles. /nm	Fit results / nm As-cast	Fit results / nm 673K 2 weeks
r_{Zn-Mg}	0.2801	0.279 $\pm$ 0.0007	0.280 $\pm$ 0.0004
r_{Zn-Y}	0.3019	0.301 $\pm$ 0.0004	0.301 $\pm$ 0.0003
$r_{Zn-interstitial}$	0.3053	0.305 $\pm$ 0.005	0.304 $\pm$ 0.001

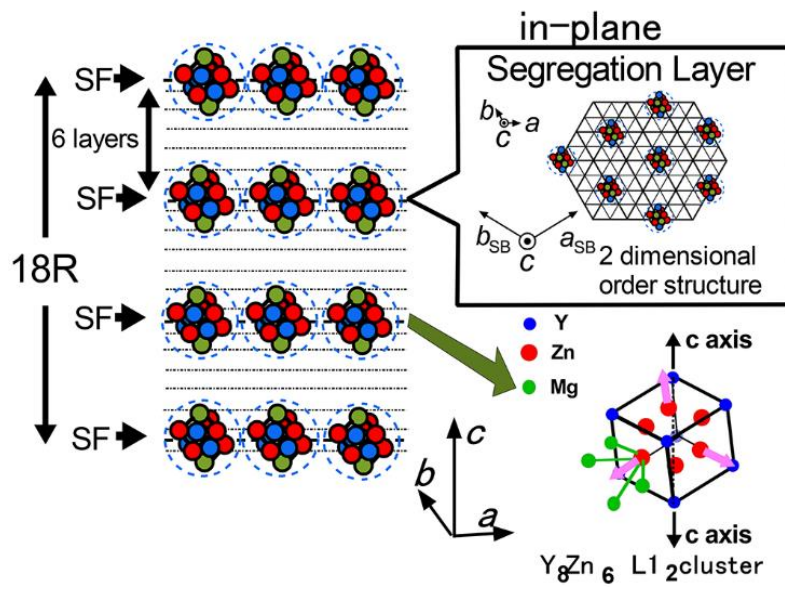


Figure 1. Schematic illustration of 18R long period stacking ordered structure when the structure is perfectly ordered. Modified from the illustration in Fig. 1 of ref.28.

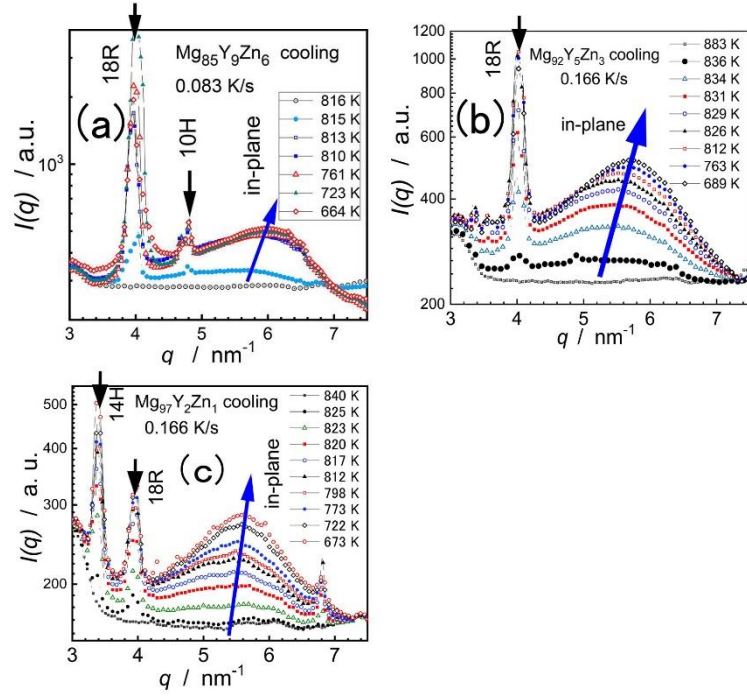


Figure 2. In-situ measurement of SAXS intensity during cooling as-cast MgYZn alloy samples at the cooling rate of 0.083 or 0.166 K/s after melting. The peaks denoted as 18R, 10H and 14H correspond to the segregation periodicities of every 6, 5 and 7 atomic layers in c -direction of the hcp matrix.

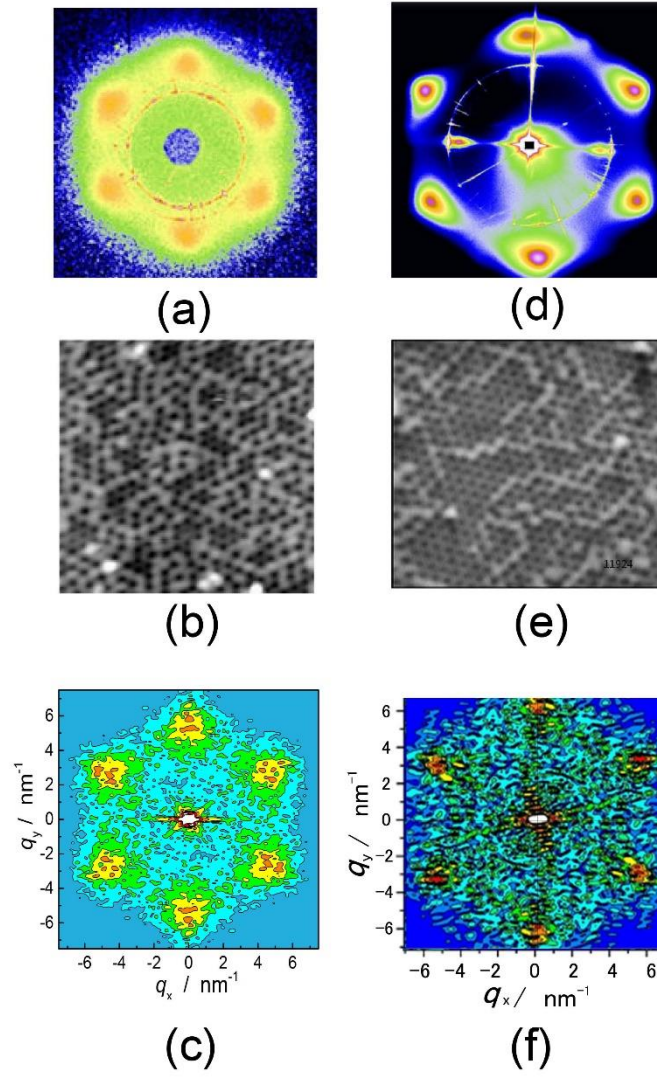


Figure 3. Two-dimensional SAXS and STM patterns obtained for an as-cast ingot (a), (b) and for those after annealing at 673 K for 2 weeks, (d), (e), respectively. STM images show loosely distributed clusters in (b), and fully ordered except domain boundaries for (e). Fourier transformed pictures corresponding to (b) and (e) are shown in (c) and (f). (a) is taken from the same sample as [6].

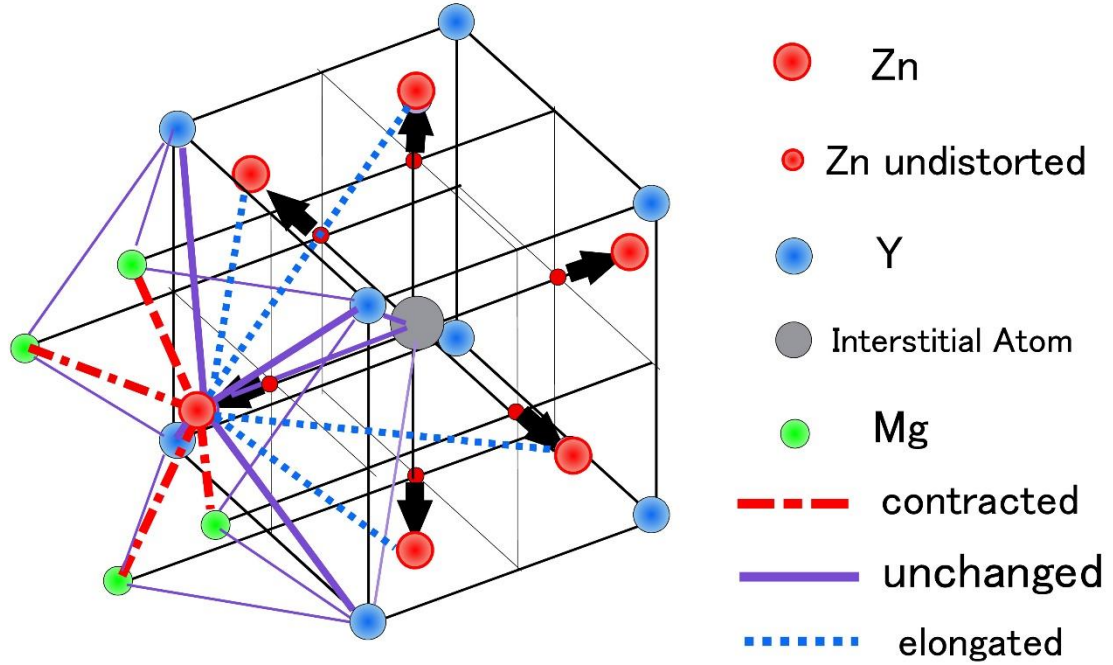


Figure 4. A schematic drawing of the atomic positions of a $L1_2$ cluster and some of its neighboring Mg atoms proposed by STEM analysis of fully ordered LPSO alloys[3,4,17] and first-principles calculations[9,10]. Zn atoms at the face center sites strongly expand outwards, and an interstitial atom is positioned at the body-center site. Distance between the Zn atoms and their neighboring Mg atoms contracts.

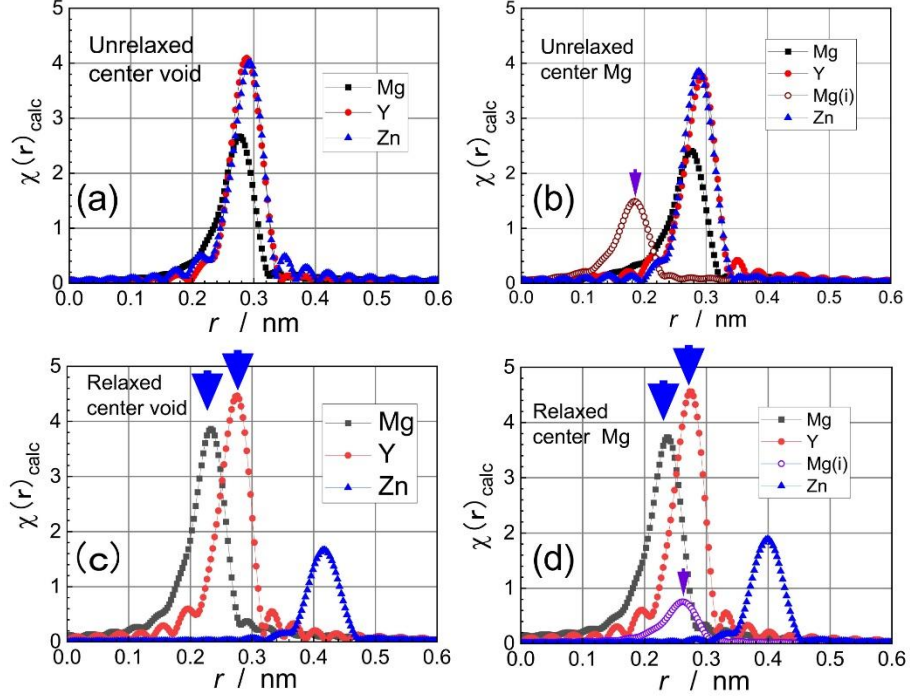


Figure 5. Contribution of the single scattering path processes by the nearest neighbor atoms of Zn to the $|\chi(r)|$ calculated for the unstrained and the fully relaxed cases with Demeter at the K edge of Zn. For the interstitial site, vacancy and Mg are presented, although Mg at the interstitial site in unrelaxed lattice is unrealistic. For the fully relaxed state, split nearest neighbor peaks appear as shown by the arrows. After full relaxation, distance between the nearest neighbor Zn atoms increased to that of the second nearest neighbors due to dilatation. The atomic positions of the relaxed case is the same as the one used for the fitting in Fig.6.

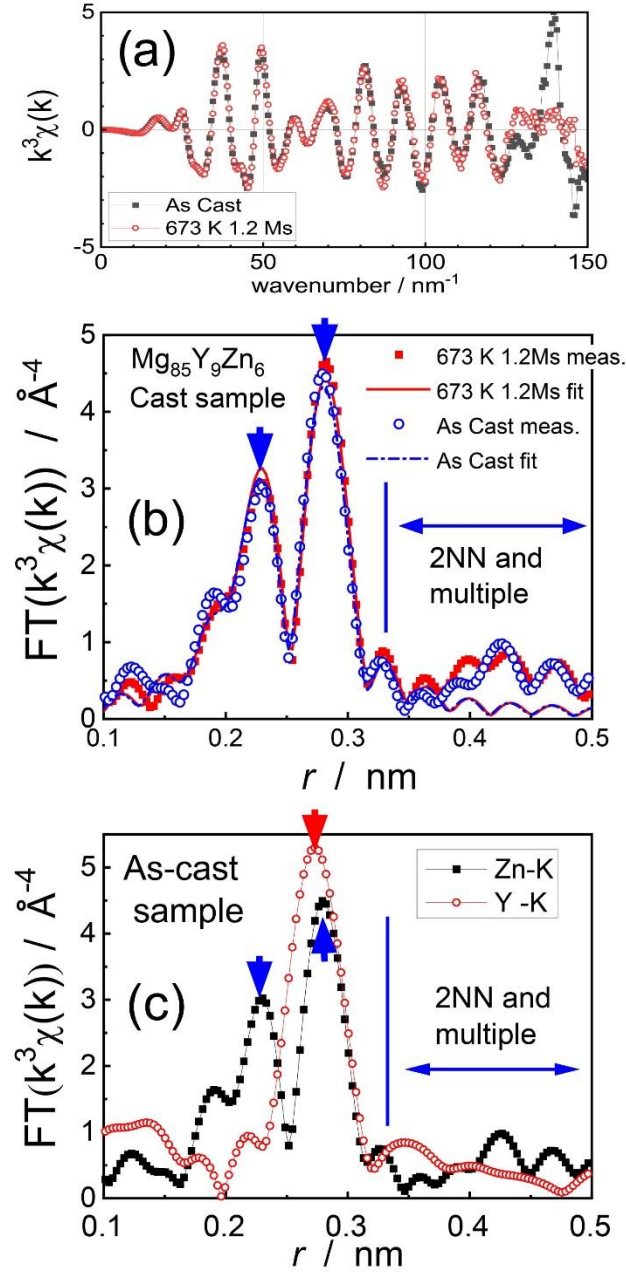


Figure 6. (a) Fourier transform of XAFS oscillation, $k^3 \chi(k)$ obtained from EXAFS measurements for as-cast and well-annealed $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloy samples at Zn K. For the Zn edge (b), fitting results agree with the experimental results. Two peaks shown by the arrows correspond to the nearest neighbor Mg (shorter distance) and the Y (longer distance) of a Zn atom. Local structures around Zn and Y atoms of the as-cast sample are compared in (c). At larger distance, contribution from atoms at second nearest neighbor (2NN) and multiple scattering processes appear.

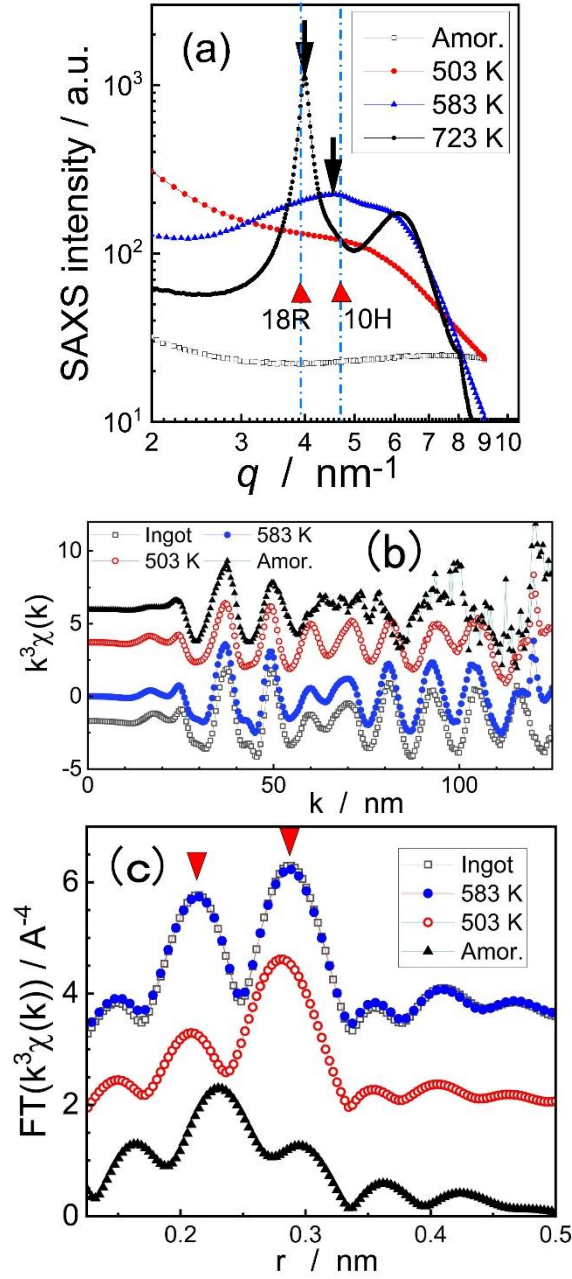


Figure. 7. SAXS profiles and the amplitudes $\chi(r)$ obtained from transmission XAFS at K absorption edge of Zn for $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloy amorphous ribbons after several heat treatments. $\chi(r)$ for 583 K agrees with that for the as-cast ingot sample. Note that the peak position in SAXS profile for stacking periodicity for 583 K lies between 4.0 nm^{-1} and 4.8 nm^{-1} , corresponding to the 18R and the 10H position. It suggests random mixture of 6 and 5 atomic layers. Still the atomic configuration around the Zn atoms agrees with that for as-cast ingot samples. $k < 90 \text{ nm}^{-1}$ was used for all the calculation in Fig.7 (c) due to signal to noise ratio of XAFS data of thin amorphous ribbons.

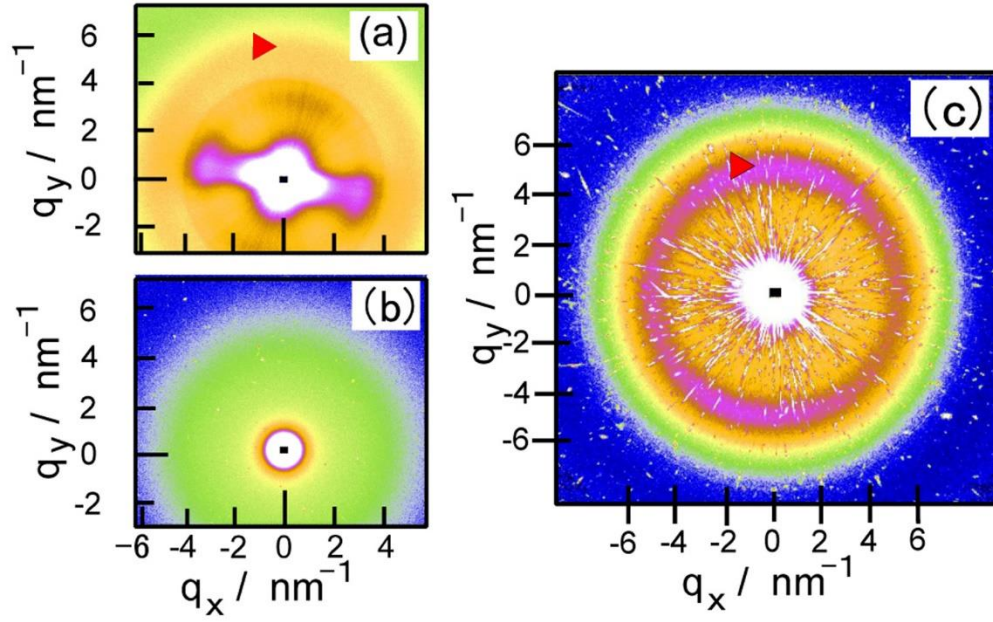


Figure 8. Two-dimensional SAXS patterns of $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ alloy for (a) after hot-pressing at 673 K, (b) solution treated at 803 K, and (c) annealed at 623 K for 3.6 ks. Well-defined diffuse ring corresponding to the in-plane cluster distance was observed at $q=5.45 \text{ nm}^{-1}$ after annealing. Many streaks running in the radial direction were observed instead of Bragg peaks of LPSO structures. The LPSO structure formed by hot pressing dissolved after solution treatments.

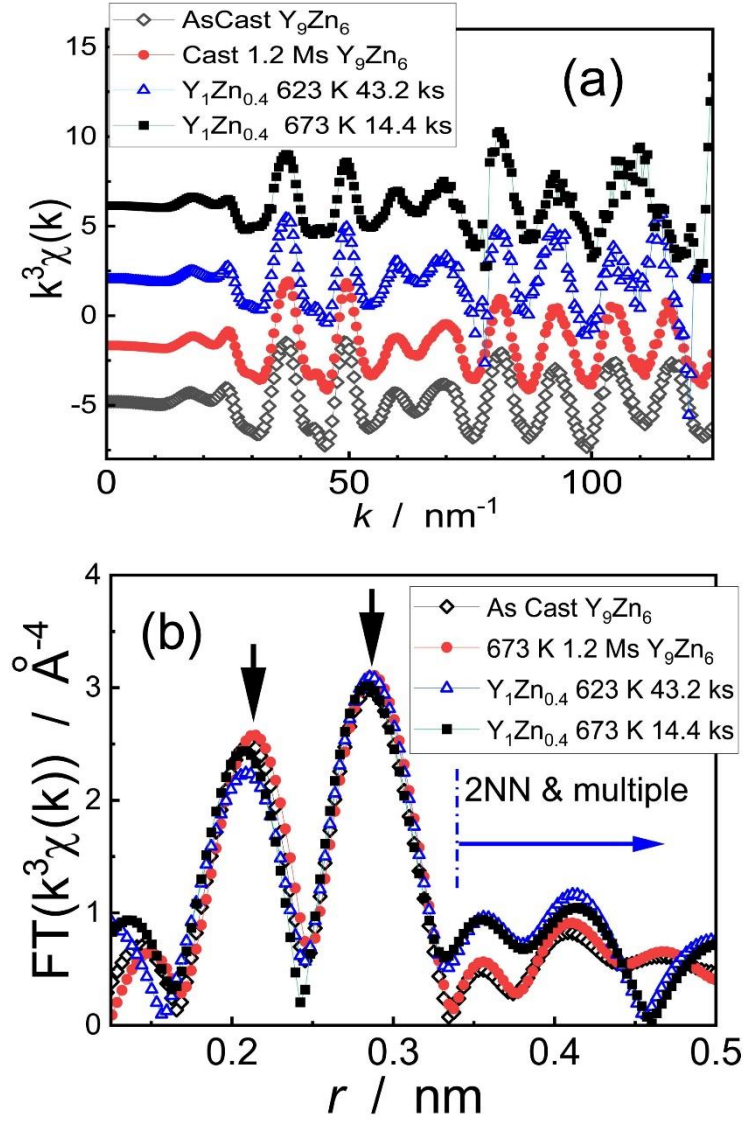


Figure 9. XAFS results at K absorption edge of Zn for $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ alloys after heat treatments. $\text{Mg}_{85}\text{Y}_9\text{Zn}_6$ alloys are also shown for comparison. As shown in Fig.8 (a), quality of XAFS oscillation is poor for $\text{Mg}_{98.6}\text{Y}_1\text{Zn}_{0.4}$ alloys. Still, $\chi(r)$ gives well-defined splitting of the nearest neighbor peak, which has been demonstrated as a finger print of relaxed $\text{L}1_2$ clusters in LPSO structures. At larger distance of $r > 0.3 \text{ nm}$, single scattering processes from the second nearest neighbor atoms and multiple scattering processes appear.