Atomic structure of pre-Guinier-Preston and Guinier-Preston-Bagaryatsky zones in Al-alloys

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Abstract. We present results on the structure of nano-sized particles (Guinier-Preston (GP) and Guinier-Preston-Bagaryatsky (GPB) zones) in Aluminum alloys. Precipitates of alloying elements like Cu, Mg, or Si hinder the motion of dislocations and, thus, are responsible for the strength of AlCuMg- and AlMgSi-alloys - used e.g. as AA2024 (old aircrafts) and AA6013 for the fuselage of the new Airbus A380, respectively. We will discuss the role of quenched-in vacancies for diffusive motion at room temperature (RT) enabling the growth of the precipitates. Using positron annihilation spectroscopy (PAS) – both lifetime and Doppler broadening – gives information on the local atomic environment in the vicinity of vacancies. On the other hand X-ray absorption fine structure (XAFS) spectroscopy is capable of characterizing the local atomic environment around selected elements (Cu, Mg). We will interpret the measured data by comparing them to numerical calculations of PAS and XAFS spectra. However, reliable numerical calculations of spectroscopic quantities are only possible provided that relaxed atomic positions are used as an input. We calculate those employing the ab-initio code SIESTA. Thus, considering decomposition of Al-alloys, we obtain extremely valuable information on the earliest stages, forming immediately after solution heat treatment and quenching, i.e. during the first few minutes of storage at RT.

1. Introduction

The hardening process in Al-alloys was discovered about 100 years ago by Alfred Wilm [1] in 1906. Wilm tried to harden different Al-alloys like steel: performing a solution heat treatment followed by quenching in water at room temperature (RT). But while steel is hardened immediately by this process it did not work for the Al-alloys Wilm was investigating. One day he had done the quenching process he left the samples for hardness testing in laboratory over a weekend. When he returned after a couple of days and did the hardness testing, the strength of the samples had increased significantly. This way Wilm found the AlCuMg alloy, which is still used in a similar composition as AA2024 for the fuselage of airplanes [2].

However, Wilm could not explain why some samples showed a higher strength than others. It took another 30 years until Guinier and Preston discovered by the new method of X-ray diffraction, independently from each other, that in pure AlCu alloys Cu precipitates as monoatomic platelets on the (100)-directions in fcc Al – named nowadays Guinier-Preston (GP) zones [3, 4]. However, the Cu platelets became visible in the X-ray spectra first after some hours

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of room temperature storage following the solution heat treatment and quenching. Once the metastable phases (precipitates) have reached a certain size of some nanometers they can be imaged nowadays – at least for atoms with a significantly larger atomic charge $Z$ than Al – by high resolution transmission electron microscopy (HRTEM) \[5\]. However, it is still extremely difficult to get atomic resolution pictures or selected area diffraction patterns of the earliest stages, where precipitates are smaller than 1 nm, and especially for alloying elements like Mg or Si neighboring Al in the periodic table.

Even after 100 years of technical application of these materials, it is still unclear when during the first minutes following the quenching process the first few-atom agglomerates grow to small sub-nanometer sized clusters of solute atoms, how their atomic structure looks like, and what the exact role of quenched-in vacancies is. Even though the first clusters formed consist of just a few atoms, they have a significant influence on the final strength of some aluminium-alloys. Hence, AlCuMg and AlMgSi alloys are still subject of numerous investigations (for a review see e.g. \[6\]).

We know that the precipitation process starts immediately after the heat treatment and quenching forming a supersaturated solution (SSS) of the alloying elements. The formation of the agglomerates is believed to happen by diffusion via quenched-in vacancies. This is supported by the observation that once very heavy elements like lead (Pb) are added to the alloy, the precipitation process is delayed, since these large atoms capture vacancies.

Since positron annihilation spectroscopy (PAS) is a unique tool to detect vacancies and vacancy-like defects in metals, aluminum alloy were systematically investigated – first by Dlubek an co-worker at the end of the 1970s \[7\] (for recent reviews see \[8, 9\]).

However, it was discovered recently that one has to freeze the decomposition process immediately after quenching to prevent the sample from changing during the course of taking one single spectrum within positron annihilation lifetime spectroscopy (PALS) or measuring the momentum distribution with Doppler broadening of the annihilation radiation (DBAR) \[10\].

Even if freezing the stage of early decomposition is possible, the problem remains to identify the atomic surrounding of vacancies and solute atoms to characterize the kind of cluster they have been forming. We have to note here that the relative concentration of quenched-in vacancies and solute atoms is about 1/1000. Hence, we need an additional method characterizing early precipitates of few atoms without a vacancy attached, and thus, possible not able to trap positrons. Recently, the method of X-ray absorption fine structure (XAFS) spectroscopy has been re-invented after more than 25 years for the characterization of the surrounding of selected elements in Al-alloys \[11, 12\].

In this paper we will show how the experimental methods PAS and XAFS can be combined with numerical simulations of obtain a characterization of early decomposition stages in Al-alloys.

### 2. Review of existing methods

While the measurement of pure well annealed metals has been proposed as a way obtaining a fingerprint in the momentum distribution measured by positron annihilation \[13\], we are convinced that these attempts did show the correct route but turned out to be insufficient.

To our mind the main problem is that in well annealed metals the positrons ‘see’ a totally different electronic density and momentum distribution as if the positron is localized in a vacancy or a vacancy-like defect, e.g. a vacancy solute-atom pair or precipitates containing structural vacancies. However, taking this route only a rough qualitative analysis is possible. We can detect certainly the influence of several alloying element in e.g. the momentum distribution of a AlMgSiCu alloy, as displayed in figure 1 involving a single Ge-detector with the setup and data analysis as described in \[14, 15\]. One can clearly see the influence of Cu-additions in AA6013. However, any qualitative analysis is impossible, i.e. identifying which solute atom is attached to
Figure 1. Pure elements – well-annealed samples as ratio to Al bulk (right) and AlMgSi(Cu)-alloys at the so called T6-state of maximum hardness (left side). The temperature treatment for T6-state is 180$^\circ$C for 4h after solution heat treatment and quenching. In comparison to the pure elements (right) we can see clearly the influence of Cu-additions in the alloy AA6013 – the only one containing copper. Please, note the different scale for copper (right).

the vacancies where the positron is localized, what would the atomic structure of precipitates be.

It has been tried to overcome this problem by using samples of the alloying elements (Cu, Mg, Si) where the positron is localized in vacancy defects, in order to mimic the density and momentum of electrons around vacancy-solute atom pairs in aluminum alloys. However, the reference samples should be prepared in such a way that they show single component spectra. Otherwise it will be very hard to extract exactly the correct momentum distribution for the vacancy defects - even if a parallel measurements of the momentum distribution and the positron lifetime are performed.

However, the main problem remains the sample preparation. We have to ensure that only one type of defect – namely the mono-vacancy – will be created, and additionally, at a concentration leading to complete positron trapping. To the authors knowledge there are only three methods of sample preparation existing to achieve this goal: in-situ measurements at high temperature of thermally generated vacancies (see for a review [16, 17]), low temperature electron irradiation (see e.g. [18]), and quenching from a temperature just below the melting point.

For the first case the main experimental challenge is due to the problem of sealing the positron source and mounting the detectors close enough to the sample – especially for positron lifetime measurements. However, PALS measurements have been done – to the authors knowledge – only for noble metals like Cu, Ag, Au, while for e.g. refractory metals like W, Mo or Ta only measurements of the momentum distribution exist [19].

For the other two case the main experimental problem is that in most metals, e.g. the noble series (Cu, Ag, Au) but also in Al, Fe, Ni, Zn, Mg and for many others, vacancies are highly mobile at room temperature. Exceptions are found for refractory metals with a high melting point (W, Mo, Ta) but also for Pt. This means a low-temperature electron or proton irradiation experiment is necessary, where the samples have to be kept cold and transferred to the PAS measurement without warming them up. However, in rare cases even the liquid nitrogen temperature of 77 K would be insufficient for preventing vacancies to become mobile.
Quenching experiment exhibit the additional difficulty that a certain amount of vacancies is lost during the quench or may agglomerate to form vacancy clusters.

On the other hand, for In or Ga their melting point is so low that even at room temperature a measurable amount of thermal vacancies exists. Hence, for determining the positron annihilation properties for the bulk of these materials one would have to cool the samples.

However, even if it is possible to prepare all reference samples in an accurate way and perform all the measurements at a sufficient accuracy, the main problem cannot be circumvented by experiments alone. The electron density (measured by PALS) and the electron momentum density (measured by DBAR) cannot be exactly interpolated from e.g. mono-vacancies in pure copper (12 nearest neighbors) to a vacancy solute atom pair like Cu in Al. This is due to the fact that certain relaxations of atoms around a vacancy occur, which can only be estimate accurately by ab-initio calculations [20, 21]. Additionally, the electron density, and thus also the electron momentum density, changes by an energetically favorable redistribution of charge in the solid.

Nevertheless, those experiments, as described above, are indispensable for testing the calculation schemes involved in producing spectra to compare to experiment. Even nowadays the calculation schemes suffer from many approximations resulting in deficiencies describing the properties of solids exactly.

3. Experimentals

Two high purity Al alloy has been investigated: one containing 1.7at% of Cu (named AlCu in the following) and one with 1.87at% of Cu and additionally 1.78at% Mg (named AlCuMg in the following). The latter has a similar composition as AA2024. The alloys were solution heat treated at 560°C for 30 minutes and then rapidly quenched into water at room temperature. For the PAS measurement the samples was taken out of the water, mounted to a holder, and immediately cooled to −40°C. The time delay until the samples reached a temperature of 0°C was less than 2 minutes. The samples for XAFS measurement were taken out of the water and immediately cooled in liquid nitrogen. They were kept at temperatures below −70°C throughout transportation to BESSY and mounting to a cryostat for the synchrotron measurements (for details see [10, 12]). All XAFS measurements were taken at the 7T-MPW-mags synchrotron beamline at BESSY in Berlin. The XAFS spectra were recorded at the Cu K-edge in fluorescence mode. For the energy range from 8900 to 9400 eV each one of the 1000 points per spectrum contains about 10⁵ counts.

During all measurements the samples were kept at −40°C during the measurements to assure that all decomposition kinetics was frozen [22]. In order to simulate natural aging, the samples were then exposed to room temperature (RT) for increasing time intervals and cooled again to −40°C for the measurement as shown in figure 2.

![Figure 2](image_url)

**Figure 2.** Measurement sequence: after solution heat treatment (1) the samples were quenched into water at RT. Measurements (3) were taken while the samples were cooled to −40°C. In between different measurements the sample were exposed successively to increasing time intervals at room temperature (natural aging).
The positron lifetime spectra were taken with a conventional fast-fast coincidence setup employing BaF$_2$ detectors with a FWHM time resolution of about 230 ps. Collecting about 17 million counts per spectrum guaranteed a reliable data analysis. Each sample was arranged in sandwich geometry embedding a $^{22}$Na Al-foil source (30 $\mu$Ci) between two identical alloy disks. The Doppler Broadening of the annihilation radiation (DBAR) has been measured at a temperature of $-40^\circ$C with a $^{68}$Ge source employing a single pure Ge-detector as described in [14, 15].

4. Numerical methods

4.1. SIESTA method

For the calculation of the total energies and the structural relaxations we used the ab-initio code SIESTA [23]. This code implements the density functional theory (DFT) in the local density approximation (LDA). The Brillouin-zone is sampled by a Monkhorst-Pack (MP) mesh. In contrast to other established ab-initio DFT-methods, instead of a plane wave basis, a local Gaussian basis set is employed within the split-valence method [24].

For our calculations we used a DZP basis set for the atomic valence orbitals of Al and Cu. The corresponding pseudo potentials were generated using the Troullier-Martins flavor without any core-corrections (for details see [25]).

Usually, testing the employed pseudo potentials involves Al in Al bulk crystals and Cu in Cu bulk crystals. However, we also tested the generated pseudo-potentials for the Al-Cu interactions by calculating the coherent and semi-coherent precipitation phases $\Theta$ and $\Theta'$ (see details in [25]). Additionally, we calculated vacancy formation energies for mono-vacancies in bulk Al and bulk Cu (108 atom supercells), leading to values close to experimental data or other ab-initio calculations (see [25] for details and references).

As atomic structure of the equilibrium S-phase we assumed an orthorhombic crystal structure (symmetry group Cmcm) with lattice parameters $a = 400$ pm, $b = 923$ pm, and $c = 714$ pm for Al$_2$CuMg [6].

4.2. Positron lifetime and momentum distribution calculations

We utilize here structures of Cu-platelets relaxed with the first-principles method SIESTA (see section 4.1). Then theoretical calculations of positron annihilation parameters are performed employing free atomic wave functions using the method introduced in refs. [26, 27] in the improved version of [28]. The momentum distribution is obtained by summing up the contributions from each core electron state weighted with its partial annihilation rate. The partial annihilation rate is calculated within the generalized gradient approximation (GGA) of electron-positron correlation [29]. The calculation of positron lifetimes is performed using the local-density approximation (LDA) scheme employing Boronski-Nieminen enhancement [30].

The supercells for positron calculations were created by embedding the SIESTA-relaxed atoms (3 unit cell containing 108 atoms) in larger cells extended with bulk lattice atoms to ensure the localization of the positron wave function. Thus, one avoids interactions of the simulated positron with its periodic replica. The localization of the positron inside the calculation cell is ensured by cutting the supercell with relaxed atoms at a plane with the greatest possible distance to the defect and inserting a number of ideal unit cells. A sufficient size of the supercell has been found by increasing the size until the positron lifetime did not longer change by a significant value – here chosen with 0.2 ps. A similar scheme has been used to find the right number of real space grid points for the calculation. For the mini-Guinier-Preston zones (GPZ) $5 \times 5 \times 5$ unit cells with 500 atoms have been employed (16 real space grid points per unit cell) (for more detail see [25]).
4.3. XAFS-calculations with FEFF-8.2
By employing the FEFF-8.2 code [31] we obtained the simulated XAFS-spectra presented here. The full multiple scattering calculation involved a cluster of at least 87 atoms, corresponding in fcc-Al to about six shells of atoms around the scattering center. A Debye-Waller factor \( T = 233 \text{K} \) has been employed to take into account the atomic vibrations due to the finite sample temperature (the typical measurement temperature to freeze in the decomposition [12]). A discussion of typical deviations between measured and calculated XAFS-spectra has been presented in [32].

5. Results
The relaxations around an isolated Cu atom in the Al matrix shows up as a decrease in the distances of nearest neighbor atoms from 286.34 pm to 280.5 pm, which is 2.0% less than the ideal bond length in fcc Al [25]. This result is in good agreement with other ab-initio calculations [33] and XAFS experiments for dilute AlCu-alloys giving 280 pm [34].

5.1. Pre-Guinier-Preston zones in AlCu
It is well established experimentally that Cu precipitates in Al as mono-atomic platelets on the (100)-planes in fcc Al (see e.g. the textbook by Haasen [35]). Hence, we consider different structures of small Cu-disks up to 5 Cu atoms arranged as closest neighbors on one face of an fcc cube (see Figure 3). However, it has been shown recently that 3D-clusters are less stable than 2D-platelets of Cu [21].

After the first stage of decomposition when the first atom pairs have formed, the precipitates have to grow under Cu-poor conditions – compared to the stoichiometry of the the stable Al\(_2\)Cu-phase \( \Theta \). Hence, we calculated some structures of Cu-disks containing vacancies. Additionally, it is experimentally well established that one detects in as-quenched pure AlCu- AlCuMg-alloys positron lifetimes which should be related to an open volume of about one mono-vacancy in Al. Hence, it may be that at least a fraction of GP zones contains structural vacancies as shown in figure 4.

For mini-GPZ with or without vacancies we estimated the positron binding energy \( E_b \) to the precipitates as the difference of the total energy of the positron in Al-bulk. As we can see from figure 3 it is increasing for the GPZ without structural vacancies with the size of the precipitate reaching some 100 meV for infinitely extended GPZ. If vacancies are involved, the binding energy is decreasing with the number of Cu-atoms in the GPZ (figure 4). This may be related to the enhanced relaxation of Al-atoms towards the Cu disk with increasing number of Cu atom.

A more detailed view on the relaxation features is given in the following figures (Figure 5 and 6). Generally, we find relaxations of Cu atoms away from each other within the (100) habit plane and strong relaxation of Al-atoms above and below the habit-plane towards the Cu-platelet. For a more detailed discussion see [25].

When one Al-atom is embedded in 4 Cu atoms on a (001)-plane in Al we did not observe any pronounced relaxation. This is in contrast to the other cases where Cu atoms are on NN positions. However, this structure is more than 0.5 eV less favorable in energy than 4 Cu atoms in closest positions on an (001)-plane in Al as in figure 6 [25].

Concerning the comparison to experimental methods we find that the positron wave function is generally localized around Cu atoms for ideal, i.e. not vacancy containing, precipitates (see Figure 3). The relaxation features creating more open space in between the Cu atoms enhance this effect (see Figure 3 - right). However, the positron lifetime is only slightly changed in the range from 165 to 168 ps. Thus, ideal or relaxed GPZ without structural vacancies cannot explain the experimental findings of 220 ps after quenching and storage at room temperature [36].
Precipitates containing vacancies lead to calculated positron lifetimes of about 220 ps – in agreement with the experimental data (see Figure 4). When comparing the two configurations of four Cu, one with a vacancy inside and besides the Cu-atoms, one can see that the location of the vacancy besides (220...230 ps) is more compatible with experiment than inside the disk (205 ps). Indeed the former structure is also more stable [33].

Figure 7 shows a XAFS spectrum in terms of the fine-structure function $\mu(E)$ which is defined in the usual way after subtraction of a smooth background function.

Concerning XAFS measurements and calculations we can see from figure 7 that there is a good correspondence between measured and calculated XAFS spectra for a pure AlCu sample where the applied heat treatment ensured the formation of the equilibrium $\Theta$-phase ($Al_2Cu$). Other phases like the metastable $\Theta'$ or $\Theta''$ did not fit. For the atomic structure of the $\Theta$ or $\Theta'$ phase we refer to [35] or [25].

Measurements of as-quenched samples of the pure AlCu alloy showed that even during the quenching process Cu-pairs and possibly also triples must have formed, which becomes evident simply by statistical considerations. Figure 8 shows a superposition of XAFS spectra for isolated Cu atoms and for a pre-GPZ displayed in figure 5.

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**Figure 3.** Early stages of GP-zones without vacancies in the (001)-plane of the Al-lattice: shown are atomic positions, positron densities, lifetimes, and binding energy $E_b$ of the positron as well as Doppler spectra for the atomic configurations (from top to bottom). The momentum distribution is obviously changed by substitutional Cu-atoms – especially when the size is above three Cu-atoms, while the positron lifetime is largely unaffected. It stays very similar to that in Al-bulk.

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This usually means a coincidence in the positions and height the maxima and minima of the XAFS spectra.
Figure 4. Early stages of GP-zones with one vacancy in the (001)-plane of the Al-lattice: Atomic positions, positron densities, lifetimes, and binding energy $E_b$ of the positron as well as Doppler spectra of the displayed atomic configurations (from top to bottom). As expected the momentum distribution is changing from the left to the right towards more Cu-rich environment. The positron lifetime, on the other hand, is only affected significantly, if the vacancy is either inside the or outside the Cu-disk. Here the binding energy is decreasing with the number of Cu atoms.

Figure 5. Mini-GPZ consisting of 5 Cu atoms (red): atomic structure as calculated with SIESTA. The strong relaxation of Al-planes (grey) above and below the Cu-platelet towards it results in some Al-Cu bond length shortened to less than 270 pm.
Figure 6. Mini-GPZ consisting of 4 Cu atoms (red) and a vacancy (open circle): atomic structure as calculated with SIESTA. The strong relaxation of Al-planes (gray) above and below the Cu-platelet towards it is not changed much by the presence of the vacancy.

Figure 7. XAFS spectrum from the Al 1.7at.% Cu alloy heat treated for 1 hour at 350°C (green dots) in comparison to FEFF-8.2 calculations of the Θ-phase (straight line).

5.2. Pre-Guinier-Preston-Bagaryatsky zones in AlCuMg - PAS
Guinier-Preston-Bagaryatsky (GPB) zones are named after Yu. A. Bagaryatsky who investigated AlCuMg alloys by X-ray diffraction both after natural aging [37] and artificial aging [38]. Bagaryatsky proposed a certain structure for the arrangement of Cu and Mg atoms in small nanometer-sized cluster, which has been later questioned by many authors according to their own X-ray diffraction results.

In a recent paper it has been shown by both XAFS and PAS that the atomic configuration in the technical AlCuMg alloy AA2024 showed after 10 – 80 hours aging at room temperature that the atomic environment seen by positrons must be very similar to a vacancy on the copper sublattice of the equilibrium S-phase (Al2CuMg) [39]. But the equilibrium S-phase is formed first after heat treating the AlCuMg alloys for some hours at temperature above 200°C, so it had not yet formed in our samples. However, it has been shown by Nagai et al that the momentum distribution 1 hour after quenching is very similar to that when the S-phase must have been formed according to their temperature treatment [40].

Now, very recently it could be shown that changes during the first minutes after quenching are detectable by PAS [10]. The samples measured by PALS and DBAR in this work were prepared according to the procedure described in section 3. For all papers published previously
Figure 8. XAFS spectrum from the pure Al 1.7at.% Cu alloy in the as-quenched state (blue dots) in comparison to FEFF-8.2 calculations (straight lines) of an isolated Cu atom and a pre-GPZ as displayed in figure 5 (middle Cu taken as scattering center). The straight red line is a superposition of the spectra for the single Cu atoms and the pre-GPZ (50% each).

Figure 9. AlCuMg alloy: Mean positron lifetime during RT storage. Only the as-quenched state did not show a single-component lifetime spectrum and, i.e., complete trapping.

Figure 9 shows the changes during the first minutes of aging at room temperature. The lifetime spectrum is composed of two components – the longer one close to the known value for vacancies in Al: about 240 ps. After one minute of room temperature storage we detect a jump in the average lifetime from 188 to more than 220 ps, which can hardly be explained by the creation of defects. Rather the trapping potential may change as described below.

6 220 ps is typical for vacancy solute atom pairs or structural vacancies inside precipitates (see figure 4).
Decomposing the spectrum according to a simple two-component trapping model, where the trapping fraction amounts to 0.30, and a trapping coefficient of \(10^{14}\, s^{-1}\) [44], we obtain a quenched-in concentration of mono-vacancies in the order of \(2 \times 10^{-5}\) per atom. This is a reasonable fraction of the original concentration of thermal vacancies at the temperature for the solution heat treatment. As similar value has been found for AlMgSi alloys [10].

Figure 10. Before complete trapping is observed, the positrons are trapped by vacancy-solute complexes (left). After decomposition started structural vacancies inside agglomerate (right side) may be a better candidate. Gray circles: Al atoms; yellow circles: solute atoms.

However, it is difficult to identify the atomic structure of the defects detected by PALS alone. We can just assume that the signal must arise from vacancy-solute-atom pairs since isolated vacancies become mobile in pure Al at about 220 K. In principal, there are several possibilities to interpret the observed incomplete trapping of positrons during the first minutes of RT aging: The positrons could be scattered by the solute atoms [45], meaning that the diffusion length is effectively reduced so that not all positrons can reach a vacancy-solute pair during their lifetime.

During the ongoing decomposition the solute atoms aggregate. Thus, the number of scattering centers would decrease, the positrons could diffuse farther and the fraction of trapped positrons would increase, leading to the complete trapping observed (figure 10 – left).

Another possibility would be that at the beginning of RT aging the trapping is transition limited [45]. The agglomeration of solute atoms around the vacancies would then change the attractive potential sensed by the positron, leading to an increasing trapping probability (right side of figure 10). A decision may be possible according to DBAR measurements.

In figure 11 we present measurements of the same AlCuMg sample material by DBAR, as described in section 3 employing the tool of high-momentum analysis (HMA) [14, 15]. In comparison to numerical calculations we can reveal a possible atomic structure of the defects responsible for positron trapping.

We tried many different planar configurations of Cu or Mg atoms attached to the vacancy. However, none of these simple vacancy-solute atom pairs – even with two Cu or Mg atoms attached on both sides of the vacancy – would fit the experimental data; neither did any considered structure model for the metastable S’-phase do the job.

Thus, we propose here – inspired by the old work of Bagaryatsky [37, 38] – the first attempt of a 3-dimensional structural model for the initial stage of decomposition, i.e. an atomistic model of possible Cu-Mg-clusters formed, which may be the pre-cursor of the growing GPB-zones (see figure 12). However, up to now we could only employ ideal coordinates from the fcc Al lattice, while there is work in progress determining relaxed positions by ab-initio calculation.

Considering that the bump in the displayed momentum distribution between 7 and \(10 \times 10^{-3}\, m_0c\) is an artifact of the employed calculation scheme, this model could be a first building block of the long sought atomistic structure of Guinier-Preston-Bagaryatsky zones. We will propose a probable structure in a forthcoming paper, once we find support by experimental work.

5.3. Pre-Guinier-Preston-Bagaryatsky zones in AlCuMg - XAFS
XAFS measurement were analyzed in terms of the fine-structure function \(\chi(k)\) which is defined in the usual way as the difference between the measured absorption coefficient and a smooth
Figure 11. AlCuMg alloy (symbols) in comparison to calculations of the momentum distribution (straight line) involving a small cluster of 1 Cu and 4 Mg atoms around a vacancy as shown in figure 12.

Figure 12. Atomistic model of a small cluster of 1 Cu (red) and 4 Mg atoms (green) around a vacancy (open circle) employing unrelaxed coordinates in fcc Al (Al atoms in gray). For this structure the DBAR calculation in figure 11 has been performed.

background function representing the absorption of an isolated atoms divided by the jump of the absorption coefficient at the threshold energy of the Cu K-edge energy. The applied method of data analysis is described in details elsewhere [46]. Furthermore the Fourier transform of the fine-structure function yields a pseudo radial distribution function (PRDF) of the next neighbors of the absorbing atoms.

Figure 13. X-ray absorption fine-structure (XAFS) data after processing: For the ternary AlCuMg three different stages of decomposition are shown. During the first eight hours of room temperature storage the XAFS spectra change drastically (see figure 14). Relaxation processes around Cu-atoms are revealed by the pseudo radial distribution function (figure 14). They start after eight minutes of RT storage.
Figure 13 shows the spectra for three different stages of decomposition of an AlCuMg sample: the as-quenched state, after 8 hours room temperature aging, and Cu embedded in S-phase precipitates (sample treatment: 1 hour at 350°C).

Note that the as-quenched state differs significantly from the other two. Zero-crossing points are shifted towards higher wavevectors and the amplitudes change as well. These systematic changes are also reflected in the Fourier transform (see figure 14). The sample exhibits an increasing relaxation of the first shell of NN atoms towards the absorbing Cu atom with increasing storage time. This can be seen from a shift of the center of the first peak of the respective PRDF towards smaller distances. After eight minutes of RT storage the onset of the relaxation process is detectable for the AlCuMg alloy continuing during the following hours of RT storage.

This is in good agreement with PAS measurements described in section 5.2 showing changes of the atomic surrounding of vacancies during the first few minutes. Additionally, results of Starink et al point to the same feature, who detected Cu-rich cluster in an AlCuMg alloy after 15 minutes of RT storage by atom probe investigations [47].

Finally, we present a comparison of the sample (1 hour 350°C) resembling the stable S-phase with FEFF-calculations.

Figure 15 shows the XAFS spectrum for the S-phase state as in figure 13 without the division of the jump of the absorption coefficient at the threshold energy of the Cu K-edge energy for better showing the features at the absorption edge. We can see a good agreement with the FEFF-calculation for the S-phase confirming the reliability of the calculations. Unfortunately, since so far no atomistic model for pre-GPG zones is existing, we cannot present any calculations here.

6. Summary

For aluminum alloys containing Cu and Mg we could demonstrate the sensitivity of both XAFS and PAS to the very early stages of decomposition – just a few minutes after quenching.

Besides possibly atom probe methods XAFS is one of the few tools which can give reasonable information about the first stages during the ongoing decomposition process. In conjunction with numerical simulation methods even the atomic structure of few atom clusters can be revealed.

PAS on the other hand is unique in showing the atomic surrounding of quenched-in vacancies and their fate during the ongoing decomposition process. However, as soon as PAS detects complete trapping information on the density of defects is lost. Nevertheless, their atomic structure may be revealed by combining positron lifetime spectroscopy (PALS) with Doppler broadening of the annihilation radiation (DBAR) in comparison to numerical simulation tools.
PAS measurements of samples immediately cooled after quenching showed that the distribution of solute atoms is altering significantly during the first few minutes after quenching.

This is confirmed by XAFS showing in the case of the AlCuMg alloy that the first relaxation process involving the Cu atoms occurs just after a few minutes of RT storage following the quenching. Interpreting this as the formation of the first agglomerates is supported by recent atom probe investigations [47].

We may have found the first building block of the mysterious Guinier-Preston-Bagaryatsky zone – named pre-Guinier-Preston-Bagaryatsky zone – which has been constructed as a 3-dimensional arrangement of Cu and Mg atoms according to the guidelines suggested by Bagaryatsky more than 50 year ago. We hope that our structural model the GPB zones (to be presented elsewhere) will find support by further measurement.

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Figure 15. XAFS spectrum from the AlCuMg alloy heat treated for 1 hour at 350°C – S-phase state (red dots) – in comparison to FEFF-8.2 calculations of the S-phase (straight line).
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