

# Theoretical Calculation of Positron Trapping by Embedded Nanoclusters

Wenfeng Pan, Bin Zhao, Renqi Zhang, Ning Qi, Bo Wang, and Zhiquan Chen\*

Hubei Nuclear Solid Physics Key Laboratory, Department of Physics, Wuhan University, Wuhan 430072, P. R. China

E-mail: [chenzq@whu.edu.cn](mailto:chenzq@whu.edu.cn)

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The trapping and annihilation characteristics of positrons in nanosized solute atom clusters (Mg, Ag, Au) embedded in Al crystals were studied by theoretical calculations based on the atomic superposition model (ATSUP). The results confirm the effective confinement of the positron wavefunction inside clusters with a diameter less than 1 nm, which contain only a few atoms. With increasing nanocluster size, the trapping of positrons is gradually enhanced leading to an increased positron annihilation lifetime. Our results suggest that positron lifetime spectroscopy should be a sensitive probe for Ag, Au and Mg nanoclusters in Al matrix.

## 1. Introduction

Nanosized clusters of solute atoms formed in the aging process of alloys play an important role in the hardening of alloys [1]. However, during the early stage of the aging process the size of the cluster is too small to be detected by conventional probes such as transmission electron microscopy. It was recently demonstrated that nanoclusters embedded in alloys can be effectively detected by positron annihilation techniques when the positron affinity of the nanocluster is lower than that of the matrix [2]. Several experimental and theoretical works have been reported on the study of nanoclusters in Al-Cu and Al-Zn alloys by positron annihilation techniques. It was found that positrons are confined in Cu, Zn nanoclusters which have a lower positron affinity than Al atoms [3, 4]. There have been relatively few theoretical calculations of nanoclusters in Al-Ag, Al-Mg and Al-Au alloys compared to experimental studies. In our work, we have used the atomic superposition model (ATSUP) to calculate the positron density distribution and annihilation lifetime in Al-Mg, Al-Ag and Al-Au alloys. Confinement of the positron wavefunction in the nanoclusters was observed, and the positron lifetime changes with increasing cluster size, suggesting enhanced trapping of positrons.

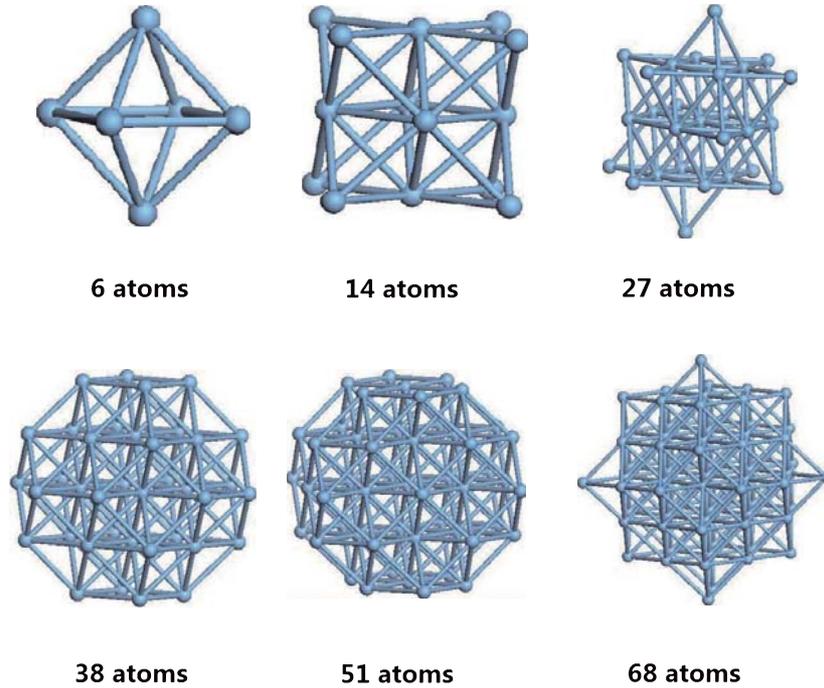
## 2. Computational methods and models

The positron annihilation lifetime calculation is performed using the atomic superposition (ATSUP) method. The crystalline charge density  $n_-(r)$  and Coulomb potential  $V_c(r)$  is constructed by superimposing individual atomic charge densities and potentials:

$$n_-(r) = \sum_i n_{at-}(|r - R_i|), \quad V_c(r) = \sum_i V_{at}(|r - R_i|), \quad (1)$$

where  $n_{at-}$  and  $V_{at}$  are the free-atom electron density and atomic Coulomb potential, respectively, and the  $R_i$  runs over the occupied atomic sites. The three dimensional potential  $V_+(r)$  is written as a sum of the Coulomb potential  $V_c(r)$ , and the positron-electron correlation energy  $V_{corr}(n_-(r))$ :

$$V_+(r) = V_c(r) + V_{corr}(n_-(r)), \quad (2)$$



**Fig. 1** Constructions of nanoclusters with different numbers of atoms embedded in an Al matrix.

where  $n_-(r)$  is the electron density. The positron-electron correlation energy  $V_{\text{corr}}(n_-(r))$  is obtained using the Boroński-Nieminen parametrization [5]. The positron annihilation lifetime is then the reciprocal value of the annihilation rate  $\lambda$ :

$$\lambda = \pi r_0^2 c \int n_+(r) n_-(r) \gamma(r) dr, \quad (3)$$

where  $r_0$  is the classical electron radius,  $c$  is the speed of light,  $n_+(r)$  and  $n_-(r)$  are the positron and electron density, and  $\gamma(r)$  is the so-called the enhancement factor which is determined by the local density approximation [6].

The positron annihilation characteristics were computed in a 256 atom supercell created by extending the Al FCC cell by  $4 \times 4 \times 4$  times along the three cubic crystallographic directions. The nanoclusters were simply created by replacing Al atoms in the perfect Al FCC lattice considering nearest neighbor shells of the atom in the center of the plane to be the most compact atomic configurations (Fig. 1). No lattice relaxations were considered in the calculation.

### 3. Results and discussion

#### 3.1 The positron annihilation characteristics in Al-Mg alloys

To simulate embedded Mg clusters in an Al matrix, we constructed clusters containing 6, 14, 27, 38, 51 and 68 Mg atoms in the 256 atom supercell by replacing Al atoms with Mg. It was reported that Mg nanoclusters embedded in an Al matrix are fully coherent with the Al matrix [7], so Mg nanoclusters embedded in Al adopt the FCC phase despite its bulk phase being HCP and the positron annihilation lifetimes of Mg are calculated using the lattice constant and space group of Al for Mg clusters. Results of positron annihilation lifetime for Mg clusters are shown in Fig. 2. The positron annihilation lifetime increases gradually with increasing Mg cluster size. For 68-atom Mg clusters, the positron annihilation lifetime is 183.6 ps, which is much lower than the lifetime in pure Mg with

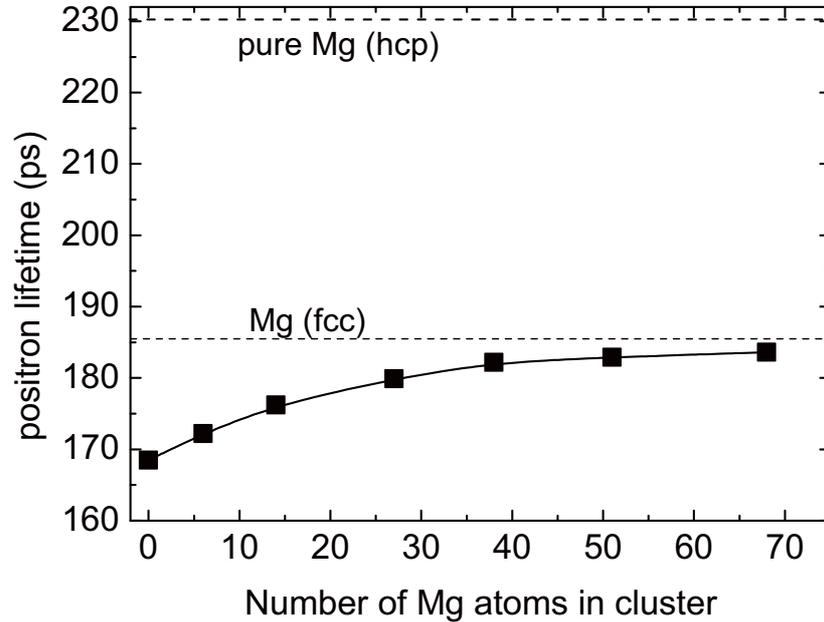


Fig. 2 Positron annihilation lifetime of Al with different sizes of Mg clusters.

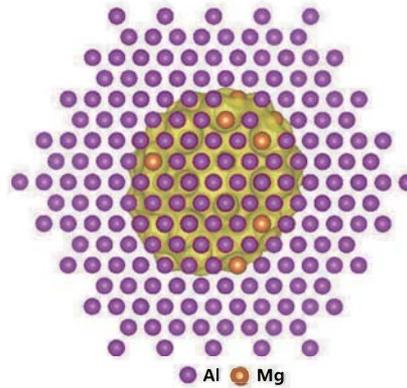


Fig. 3 Positron density distribution in a 68-atom Mg cluster embedded in an Al matrix.

a hexagonal close-packed structure (230.6 ps) but is very close to the lifetime in pure Mg (185.1 ps) calculated using the lattice constant and space group of Al. Similar results have been also reported for Zn nanoclusters in an Al-Zn alloy [4]. A simple theoretical model predicted that the minimum radius of clusters that will effectively trap positrons can be estimated by the following relationship [8]:

$$r [\text{nm}] = \frac{0.31}{\sqrt{\Delta A_+ [\text{eV}]}} \quad (4)$$

where  $\Delta A_+$  is the difference in positron affinity between the cluster and matrix. The difference of positron affinity between Al and Mg is 1.77 eV (see Table I), so the predicted minimum diameter of a Mg cluster that can trap positron is 0.46 nm from Eq. (4). For 27-atom Mg clusters, the diameter is larger than 0.46 nm, so the positron will be effectively trapped. The positron lifetime of 27-atom Mg clusters (see Fig. 2) is also close to the pure FCC Mg. Figure 3 shows the positron density distribution

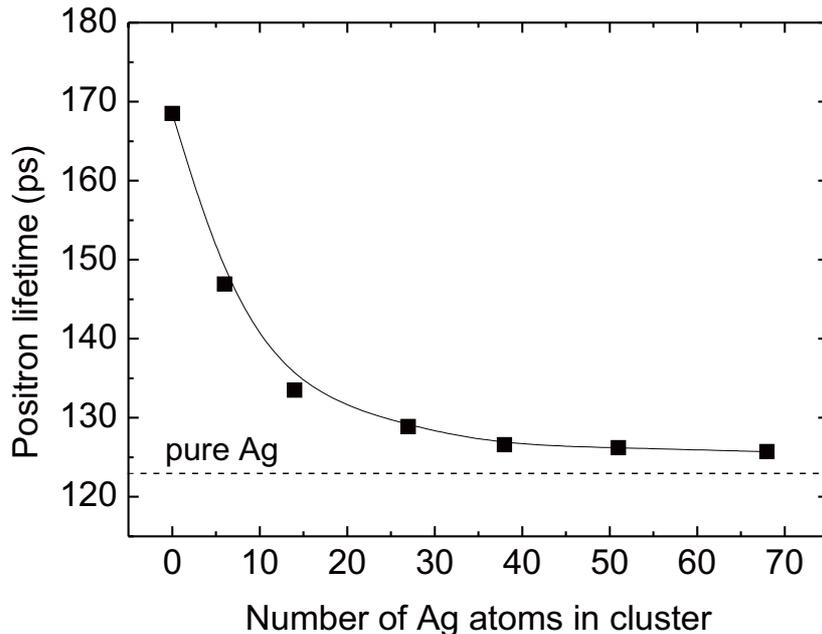
in a 68-atom Mg clusters. The yellow colored region represents the positron wavefunction. Almost all positrons are confined inside the Mg cluster mainly due to the lower positron affinity towards Mg ( $-6.18$  eV) compared to Al ( $-4.41$  eV) as listed in Table I.

### 3.2 The positron annihilation characteristics in Al-Ag alloys

In the Al-Ag system, we constructed Ag nanoclusters with the same sizes as Mg nanoclusters outlined in the previous section in the Al matrix. These clusters are fully coherent with the surrounding Al matrix as confirmed by three-dimensional atomic imaging [11]. The corresponding calculated positron annihilation lifetimes for the constructed system are shown in Fig. 4. The calculated positron lifetime of pure Al is  $168.5$  ps, while it is  $123.8$  ps for pure Ag. It can be clearly seen that with the increasing sizes of Ag clusters, the positron annihilation lifetime decreases gradually. For 68-atom Ag clusters, the positron lifetime reaches  $125.7$  ps. This is much shorter than that of pure Al but is nearly the same as that of pure Ag. This indicates that positrons are nearly fully confined in the 68-atom clusters. Even for Ag clusters with only 38 atoms, the positron lifetime is already very close to that of pure Ag. It indicates clearly positron localization at 38-atom Ag clusters because the diameter these clusters is about  $0.8$  nm, which is larger than the minimum diameter of Ag clusters ( $0.64$  nm) obtained from

**Table I** Some relevant parameters of Al, Mg, Ag and Au:  $a$  is the lattice constant and  $A_+$  is the positron affinity [9, 10],  $\Delta A_+$  is the relative positron affinity defined as  $\Delta A_+ = A_+(\text{cluster atoms}) - A_+(\text{Al})$ . Negative value of  $\Delta A_+$  means that the clusters represent a potential well for positrons.

Element	Space group	$a$ [nm]	$A_+$ [eV]	$\Delta A_+$ [eV]
Al	FM3-M	0.405	$-4.41$	0
Ag	FM3-M	0.409	$-5.36$	$-0.95$
Mg	P63-MMC	0.321	$-6.18$	$-1.77$

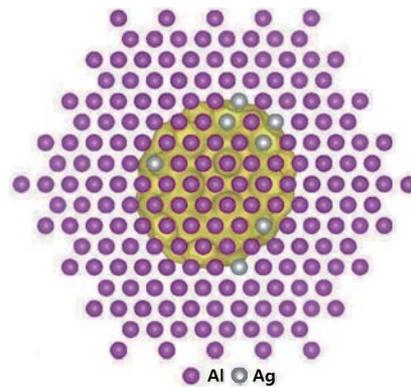


**Fig. 4** Positron annihilation lifetime of Al with different sizes of Ag clusters.

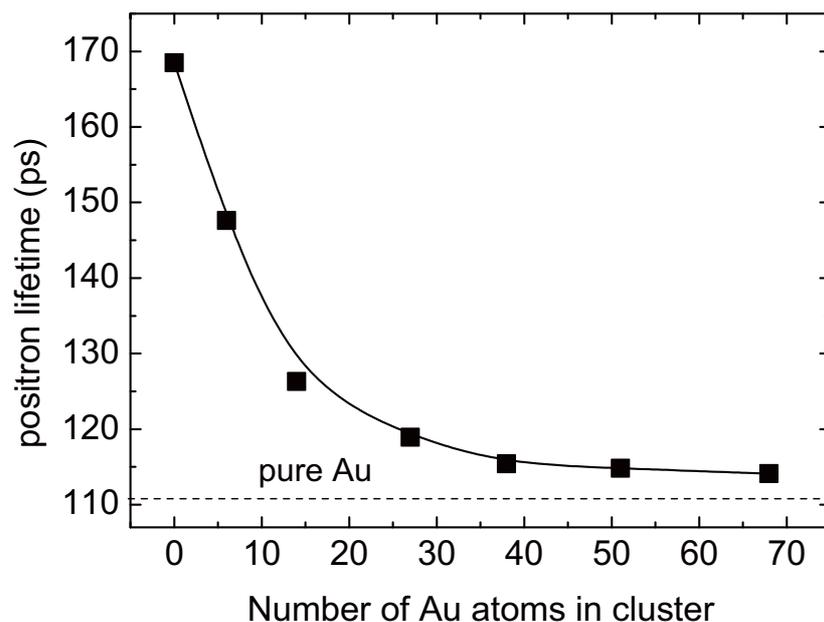
Eq. (4). Figure 5 shows the positron wavefunction distribution in 68-atom Ag clusters embedded in an Al matrix. It can be clearly seen that the positron wavefunction is almost fully localized inside the 68-atom clusters. The outmost Ag atoms of the cluster appear outside of the region of positron wavefunction. This explains why the positron annihilation lifetime in these 68-atom clusters approaches that of pure Ag.

### 3.3 The positron annihilation characteristics in Al-Au alloys

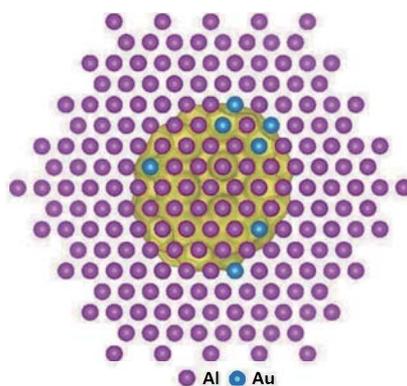
In the Al-Au system, the positron annihilation lifetime (see Fig. 6) decreases as a function of cluster size from 168.5 ps in the pure Al matrix to 114.8 ps in the Al matrix containing a cluster with 68 Au atoms. This is similar to the change of positron lifetime in Al-Ag alloys. Since the positron lifetime of a 68-atom Au cluster is very close to that of pure Au (111.0 ps), positrons are well-localized in the Au clusters. The positron density of this system (Fig. 7) also confirms confinement of



**Fig. 5** Positron density distribution in a 68-atom Ag cluster embedded in an Al matrix.



**Fig. 6** Positron annihilation lifetime of Al with different sizes of Au clusters.



**Fig. 7** Positron density distribution in a 68-atom Au cluster embedded in an Al matrix.

positrons inside the Au cluster. The diameter of 68-atom Au clusters is less than 1 nm, which means that positron can be a sensitive probe for Au clusters with size below 1 nm. This has been verified by experimental results [9]. The estimated minimum diameter for Au clusters to confine positrons effectively is 0.48 nm calculated by Eq. (4). Thus, the positron lifetime of 27-atom Au clusters with a diameter of about 0.60 nm is close to that of pure Au.

#### 4. Conclusion

Theoretical studies of positron localization and annihilation were performed for aluminum alloys with different embedded nanoclusters (Mg, Ag and Au). The positron wavefunction distribution indicates effective confinement of positrons in these clusters. With increasing cluster size, the trapping of positrons is gradually enhanced. When the cluster size approaches around 1 nm, positrons show almost full localization inside the clusters, and the positron lifetime is close to that of the pure solute (Mg, Ag and Au). Our results indicate that the trapping of positron in nanoclusters can be predicted by theoretical studies, which can provide important guidance to analyze the process of precipitation in alloys by positron annihilation spectroscopy.

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