Theoretical calculation of positron affinities of solute clusters in aluminum alloys

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Abstract. We have performed theoretical calculations of positron states for solute clusters in aluminum alloys to estimate the positron affinity of solute clusters. Positron states of solute clusters in aluminum alloys were calculated under the electronic structures obtained by first-principles molecular orbital calculations using Al158 -X13 clusters. We defined the positron affinity of the solute clusters by the difference in the lowest potential sensed by positrons between the solute clusters and Al bulk. With increasing atomic number of 3d metals, the annihilation fraction of the solute clusters rapidly increases at Mn and shows a maximum at Ni. A similar trend is observed for 4d metals. The localization of positron at the solute clusters mainly arises from charge transfer from Al matrix to solute clusters. The positron affinity defined in this work well represents the localization of positron at the solute clusters in aluminum alloys.

1. Introduction
It is well known that positron annihilation spectroscopy is a very sensitive tool for vacancy-type defects in solids. However, if solute atoms have a stronger affinity to positrons than the matrix atoms, the positron wave-functions are localized at the solute clusters. Nagai et al. have investigated ultrafine Cu precipitates in a very dilute Fe-Cu alloy using coincidence Doppler broadening (CDB) method and have found that the wave functions of all positrons are entirely confined within the nanosize Cu precipitates [1]. They also reported that positrons are trapped at solute clusters in Al-Zn and Al-Ag alloys [2]. On the other hand, Puska et al. reported calculated positron affinities of elemental metals [3]. Although the positron affinities of elemental metals were calculated using their own structures, the calculated positron affinities agree well with the experimental results reported by Nagai et al.: the solute atoms have a stronger positron affinity than the matrix atoms in Fe-Cu, Al-Zn and Al-Ag alloys. Bharathi et al. have calculated positron annihilation characteristics of Zn clusters in Al matrix [4]. It was found that positrons form a bound state for Zn clusters and the positron lifetime decreases with increasing Zn cluster size, which agrees with the positron affinities calculated by Puska et al. However, it is not clear that the positron affinities of elemental metals are applicable to any alloys. In the present work, we have calculated positron states of solute clusters in aluminum alloys to estimate positron affinities of solute clusters.
2. Computational method

In order to obtain the electron density and potential for calculations of positron wave-functions, the discrete-variational (DV) Xα cluster method using a program code SCAT [5, 6] was employed. We used the model clusters composed of 171 atoms as an aluminum matrix. The orbital populations were calculated based on the Mulliken population analysis [7].

The three dimensional potential $V_s(r)$ sensed by the positron is constructed as a sum of the electron static potential $V_e(r)$ due to the nuclei and the electrons, and a correlation potential $V_{corr}(n(r))$ describing the electron-positron correlation:

$$V_s(r) = V_e(r) + V_{corr}(n_-(r)),$$

where $n_-(r)$ is the electron density. For the density dependence of $V_{corr}(n(r))$, we used the interpolation formula of Boroński and Nieminen [8]. The Schrödinger equation for the positron was solved by the finite-difference method [9]. The positron lifetime $\tau$ is calculated as the reciprocal value of the positron annihilation rate $\lambda$ by

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

where $r_0$ is the classical electron radius, $c$ is the speed of the light, $n_+(r)$ is the positron density and $\gamma(r)$ is the enhancement factor describing the short-range pileup of the electron at the positron. For the enhancement factor, we used the interpolation formula [8]. Annihilation fractions of solute clusters were obtained using the Mulliken population analysis.

3. Results and discussion

3.1. Difference in positron lifetimes between solute clusters and solid solutions in Al-Zn alloys

To confirm the localization of positrons at solute clusters, positron lifetimes of Zn clusters were compared to those of solid solution models in which Al and Zn atoms are randomly distributed. The arrangement of Zn atoms was determined so that the pair-correlation functions were close to those in perfect random alloys up to the fifth neighbor shell [10]. Figure 1 shows calculated positron lifetimes of Zn clusters and solid solutions in the Al-Zn alloys as a function of the number of Zn atoms in $\text{Al}_{171-x}\text{Zn}_x$. Structural relaxations were not considered in either the Zn clusters or solid solution models.

![Figure 1. Positron lifetimes of Zn clusters and solid solutions in Al-Zn alloys](image-url)
The positron lifetimes of the Zn clusters are shorter than those of solid solution models. This result indicates that positrons are localized at the Zn clusters, which results in the shorter positron lifetimes of the Zn clusters. Even in the smallest Zn cluster, Zn13, there is a significant difference between the Zn cluster and solid solution. Therefore, the solute clusters composed of 13 atoms were employed for positron state calculations in the present work.

3.2. Annihilation fractions of clusters composed of 13 solute atoms in Al alloys

The annihilation fraction of solute clusters directly indicates the degree of localization of positrons at solute clusters. Figure 2 shows calculated annihilation fractions of solute atom 13 clusters in the Al alloys. With increasing atomic number of 3d metals, the annihilation fraction of the solute clusters rapidly increases at Mn and shows a maximum at Ni. A similar trend is observed for 4d metals. Figure 3 shows positron densities around the Ca13, Fe13 and Ni13 clusters. In the case of the Ca13 cluster, the annihilation fraction is 1.6 % and the positron density at the Ca13 cluster is close to zero. With increasing annihilation fraction from the Ca13 to Ni13 clusters, the positron density at the solute clusters becomes larger, which clearly indicates that the localization of positrons at the solute clusters increases with increasing annihilation fraction of the solute clusters.

Figure 2. Annihilation fractions of the solute clusters in Al alloys as a function of the atomic number of the solute atoms.

Figure 3. Positron densities around (a) the Ca13, (b) Fe13 and (c) Ni13 clusters. Annihilation fractions of the solute clusters are written on the top of each panel.
3.3. Potentials sensed by positrons and positron affinities

Although the annihilation fraction of the solute clusters directly indicates the degree of localization of positrons at the solute clusters, it does not have a physical meaning and strongly depends on the concentration or size of the solute clusters. Therefore, the annihilation fraction is not suitable for a parameter to estimate the positron affinities of the solute clusters.

The important factor to determine the distribution of positrons is the potentials sensed by positrons defined by equation (1). The potentials sensed by positrons for various sizes of the Zn and Ag clusters are shown in Figure 4. The lowest potentials sensed by positrons are not sensitive to the size of solute clusters. Thus, in the present work, we define the positron affinity of the solute clusters by the difference in the potentials sensed by positrons between the solute cluster and Al bulk as shown in Figure 5.

**Figure 4.** Potentials sensed by positrons around the solute clusters in (a) Al-Zn and (b) Al-Ag alloys.

**Figure 5.** Definition of the positron affinity of the solute cluster.
3.4. Relationship between positron affinities and annihilation fractions

The positron affinities and annihilation fractions of the solute clusters are shown in Figure 6. In order to fit the scale to the annihilation fractions, the positron affinities are plotted from positive to negative values. The positron affinities show a similar trend to the annihilation fractions. Especially, the change in annihilation fractions in the 3d metals is well reproduced by the positron affinities. However, there is a significant difference on the left side of the 4d metals. For example, although the Mo cluster has almost the same positron affinity as the Co cluster, the annihilation fraction of the Mo cluster indicates that positrons are not localized at the Mo cluster. There is another difference in the magnitude between the positron affinities and annihilation fractions. The positron affinities of the 4d metals are larger than those of the 3d metals. However, the annihilation fractions are similar to each other. These discrepancies mainly arise from the difference in width of the potentials in the solute clusters.

Figure 7 shows the potentials sensed by positrons around the interstitial regions in the Co and Mo clusters and Al bulk. In the Co and Mo clusters, the depths of the potentials are almost the same values. However, the width of the potential in the Mo cluster is smaller than that of the Co cluster and Al bulk. As a result, the positrons are not localized at the Mo cluster. The difference in width of the potentials arises from the screening of the ion cores by d-electrons. The screening of the ion cores by 4d-electrons in the Mo clusters is weaker than that by 3d-electrons in the Co clusters. The depth and width of the potentials sensed by positrons in the 3d and 4d metal clusters are shown in Figure 8. The depth of the potential of the 4d metals is always larger than that of the 3d metals. On the other hand, the width of the potential of the 4d metals is always smaller than that of the 3d metals. Thus, the 3d and 4d metals show similar trends for the annihilation fractions despite the difference in the positron affinities. In order to improve accuracy of the positron affinities, not only the difference in depth of the potentials but also the difference in width of the potentials should be considered. We will try to define the positron affinity in which the width and depth of the potentials are taken into account in a future study.

![Figure 6](image_url)

**Figure 6.** Correlation between positron affinities and annihilation fractions of solute clusters in Al alloys.
3.5. Difference in positron affinities between elemental metals and solute clusters in Al alloys

Figure 9 shows the positron affinities defined in the present work and those for elemental metals reported by Puska [3]. The positron affinities of elemental metals are shifted to set the value of Al to zero. The overall trend is quite different because the positron affinities for elemental metals are calculated for their own structures. A common feature is a decreasing trend in the middle of the 3d and 4d metals. The decreasing trend mainly arises from the increase in the screening of ion cores by d-electrons. The positron affinities for elemental metals show an increasing trend in the left side of the 3d and 4d metals. This trend is mainly due to the decrease in the atomic radius. The positron affinities for elemental metals have been used for estimation of positron affinities of solute clusters in Fe-Cu, [1] Al-Zn and Al-Ag [2]. In these alloys, the atomic radius of the solute atoms is comparable to that of the matrix atoms. Therefore, the positron affinities for elemental metals are applicable to the solute clusters in these alloys.

In order to clarify the origin of the positron affinities of the solute clusters, the positron affinities are compared to the charge transfers from Al bulk to the solute clusters in Figure 10. The change in the charge transfer is almost the same as that in the positron affinities. In the present work, the positron affinities are defined by the difference in the potentials sensed by positrons between the solute clusters and Al matrix. Thus, the difference in the potentials sensed by positrons mainly arises from the charge transfers from Al bulk to the solute clusters.
4. Conclusions
Positron affinities of solute clusters in aluminum have been calculated for Al-X\(_{13}\) clusters using first-principles molecular orbital calculations. Positron affinities defined by the difference in the potentials sensed by positrons well represent the localization of positrons at the solute clusters. Compared to the positron affinities of elemental metals, the overall trend in those of the solute clusters is quite different because the positron affinities for elemental metals are calculated for their own structures. A common feature is a decreasing trend in the middle of the 3d and 4d metals, which arises from the increase in the screening of ion cores by d-electrons. The difference in the potentials sensed by positrons is mainly due to the charge transfer from Al bulk to the solute clusters. The change in width of the potentials needs to be considered to improve accuracy of the positron affinities.

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References
[1] Nagai Y, Hasegawa M, Tang Z, Hempel A, Yubuta K, Shimamura T, Kawazoe Y, Kawai A and Kano F 2000 Phys. Rev. B 61 6574
[2] Nagai Y, Tang Z, Ohkubo H, Takadate K and Hasegawa M 2003 Rad. Phys. Chem. 68 381
[3] Puska M J, Lanki P and Nieminen R M 1989 J. Phys.: Condens. Matter 1 6081
[4] Bharathi A and Chakraborty B 1988 J. Phys. F: Met. Phys. 18 363
[5] Adachi H, Tsukada M and Satoko C 1978 J. Phys. Soc. Jpn. 45 875
[6] Ellis D E and Painter G S 1970 Phys. Rev. B 2 2887
[7] Mulliken R S 1955 J. Chem. Phys. 23 1833
[8] Borowski E, Nieminen R M 1986 Phys. Rev. B 34 3820
[9] Puska M J, Nieminen R M 1983 J. Phys. F 13 333
[10] Mäder K A, Zunger A 1995 Phys. Rev. B 51 10462