Materials Science Forum Vols. 445-446 (2004) pp. 132-134
online at http://www.scientific.net

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Theoretical study of positron annihilation in nanoclusters in Al-Cu system

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Keywords: Positron annihilation in nanoclusters, positron affinity, atomic superposition method, Al-Cu alloys, Guinier-Preston zones

Abstract. Positron annihilation at Cu-rich nanoclusters in the Al-Cu system is studied theoretically. For this purpose we employ the atomic superposition method and shift the positron potential at the nanocluster's place by a certain amount related to the positron affinity difference of the Al host and the nanocluster. In general, this approach appears to be very efficient for calculations of properties of positrons annihilating in embedded nanoclusters.

1 Introduction

Nanoclusters embedded in a host can be conveniently studied using positron annihilation (PA) techniques [1]. A necessary prerequisite is that positrons may get trapped in such nanoclusters. PA characteristics then reflect nanoclusters' atomic and electronic structure. So far the theoretical approach employed to examine PA in embedded clusters was based on the notion of the positron affinity (A_+). To be more specific, if ΔA_+ is the difference of positron affinities of the host and (coherent) cluster, then $\Delta A_+ > 0$ ($\Delta A_+ < 0$) means that the cluster represents a potential well (barrier) for positrons [2]. ΔA_+ can be calculated using ab initio electronic structure methods considering crystal structures of the host and cluster. However, direct computational studies of PA in embedded nanoclusters would represent a difficult task because of large supercells involved, and ab initio based studies are, thereby, restricted to very small clusters. The Al-Cu system is a well known age-hardening system and is also very important for practical applications. Here we calculate the positron lifetime and positron binding energy for several types of Cu clusters embedded in the Al matrix using an approach described below.

2 Computational method

In this contribution we take advantage of the simplicity of the affinity approach and combine it with the so-called atomic superposition technique [3] (ATSUP) that is very efficient for positron calculations, but it neglects electron charge transfer effects (see [3] for further details). The ATSUP method was already used in the past for studying positron trapping at small Zn clusters embedded in the Al matrix [4]. However, the effects due to the Fermi level alignment of the host and cluster (there is a charge transfer at the host-cluster interface) were not taken into account. We attempt to simulate an influence of such effects on PA properties using a three-step procedure: (i) The energy (E_1) of delocalized positrons in the host (without any cluster) is determined. (ii) The positron potential in the vicinity of cluster's atoms is shifted in order to get the positron energy equal to E_1. In this way a reference level for the cluster's positron potential is found. Simply, if there is no positron affinity difference, the positron levels of the host and the cluster should be the same. (iii) The additional positron potential shift – that is equal to the positron affinity difference of the host and the cluster – is applied.

The purpose of these three steps is to create a potential well that has the correct depth, i.e. the difference of positron levels of the host and the cluster approaches the ΔA_+ value for large clusters, as required by the positron affinity concept applied to the interface of two materials.

As for numerical implementation, the shift of the potential is performed at 3D mesh points inside spheres centered at nuclei of atoms for which the shift should be applied. All spheres

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Table 1: Calculated positron lifetimes (τ) and binding energies (E_b) for small Cu clusters and vacancy related defects in Al. Bulk lifetimes for Al and Cu are also given.

system	τ [ps]	E_b [eV]
bulk Al	168	–
1 Cu	166	0.10
2 Cu	164	0.17
3 Cu	161	0.23
4 Cu	157	0.30
bulk Cu	152	–
V	244	2.13
V-Cu	242	2.39

Table 2: Calculated positron properties for models of GP1 (rows 2-7) and GP2 (eighth row) zones in Al. Values for bulk Cu are also specified (last row). Results for vacancies are in last two columns.

system	τ [ps]	E_b [eV]	τ [ps]	E_b [eV]
5 Cu	159	0.21	238	2.44
9 Cu	157	0.29	234	2.26
13 Cu	156	0.32	233	2.19
21 Cu	156	0.33	232	2.03
25 Cu	156	0.33	232	2.00
29 Cu	156	0.34	232	1.98
77 Cu	152	0.27	218	1.63
bulk Cu	152	–	198	0.47

have the same radius (R) and its value will be discussed below. The shift requested in item (ii) above is found 'manually' by trying several its values and running the code for them. The forms [5] of the positron correlation potential and enhancement factor were used in all calculations.

3 Results and discussion

For testing purposes we first examine small Cu clusters having from 1 to 4 atoms. Clusters are simply created by replacing Al atoms in the perfect Al fcc lattice by Cu ones (lattice relaxations were neglected). The most compact cluster configurations were selected. 108 atom supercells are used in calculations. The positron affinity difference of Al and Cu was determined using A_+ values taken from [2] and is equal to 0.40 eV. In order to find an appropriate value of the parameter R (see above), for 2 and 4 atom clusters we performed a set of calculations with different R's and compared resulting positron wave functions with those obtained using first principles pseudopotential (PP) calculations [6] carried out with the same supercells. This 'matching procedure' results in $R \simeq 4$ Å (this is about the same as the lattice constant of fcc Al). In turn, ATSUP calculations with this value satisfactorily reproduce PP based positron wave functions for 1 and 3 atom clusters. One impurity atom can hardly be considered as a different phase that can be characterized by the positron affinity. Nevertheless, the current approach seems to describe reasonably well this case.

Results of positron calculations for small Cu clusters are collected in Table 1. Bulk positron lifetimes for Al and Cu are specified as well. The lifetime for Cu was calculated for the hypothetic Cu lattice with the lattice constant of Al (because of neglected relaxations for Cu clusters). The lifetime for clusters should approach this value when the size of clusters increases. Here we have too small clusters to see the saturation behavior, but we observe the correct trend. This also applies to positron binding energies which gradually increase with the cluster size and should approach $\Delta A_+ = 0.4$ eV for large clusters. The calculated vacancy lifetime (see Table 1) agrees well with that given in the literature [3]. The Cu-vacancy pair also gives a similar value. Both values could be slightly modified by lattice relaxations. Regardless of such relaxations, the calculated values indicate that a lifetime of ~ 205 ps – often found in quenched Al-Cu alloys [7] – does not correspond to the single vacancy or Cu-vacancy pair, but to some more complicated defect (see also below).

We now apply our computational method to Guinier-Preston (GP) zones in the Al-Cu system [8, 9]. In these calculations we use the same parameters as above (i.e. $R = 4$ Å, $\Delta A_+ = 0.4$ eV) and a 2400 atom supercell created by extending the fcc cell of Al by $10 \times 10 \times 6$ times along three cubic crystallographic directions (see Fig. 1). As for GP1 zones, we select the $\{001\}$ plane in the middle of the cell and replace gradually Al atoms by Cu ones considering nearest neighbor shells of the atom in the center of the plane. In this way we obtain GP1 models containing 5, 9, 13, 21, 25 and 29 Cu atoms (Fig. 1). The results of positron calculations are given in Table 2 together with those for the cases when the central Cu atom is removed in order to model a vacancy. Again, lattice relaxations were not considered. We may see that the lifetime (binding energy) of positrons trapped in GP1 zones decreases (increases) with the increasing number of Cu atoms. The lifetime is approaching 156 ps, which is a little bit more than the Cu bulk lifetime specified in the last row. This is due to the annihilation of positrons with electrons of Al atoms present in planes adjacent to the Cu one. A similar explanation applies to the binding energy. In Fig. 1 the positron density is plotted in a plane going through a GP1 zone (29 Cu atom model). One may clearly see positron localization in this GP zone. Regarding GP1 zones with vacancies, positron lifetimes as well as binding energies are substantially larger compared to the previous cases due to positron trapping at the vacancy. Nevertheless, these lifetimes are rather close to that of the single vacancy in Al (see Table 1). This is again due to the presence of Al atoms in the neighborhood of the vacancy.

As for GP2 zones, we examined just one model case based on [9] where GP2 zones are found to be three Cu {001} adjacent planes surrounded by two Al planes slightly enriched by Cu. If we neglect a small Cu content in the latter planes, we can model GP2 zones just by three adjacent Cu planes. Here we consider the configuration created from the GP1 zone model with 29 Cu atoms by adding 24 Cu atoms into each of two adjacent {001} planes. The calculated lifetime (see Table 2) coincides with that for the bulk Cu because positrons mainly annihilate with electrons of Cu atoms. Similarly, the vacancy lifetime (218 ps) is apparently smaller than those found for GP1 zones, but it is still larger than that for the Cu vacancy (198 ps) given also in the table. On this basis we may speculate that a lifetime of about 205 ps mentioned above corresponds to positron annihilation in a vacancy surrounded mainly with Cu atoms.

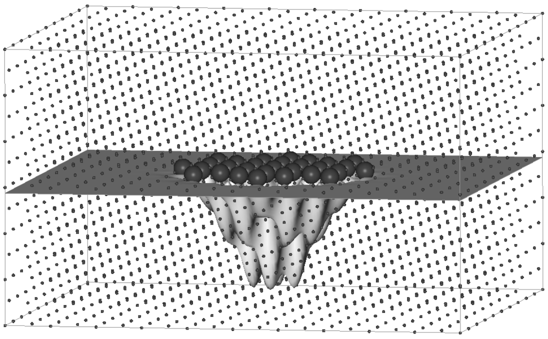

Fig. 1. A model atomic configuration of the GP1 zone in the Al-Cu system. Small points (larger spheres) represent Al (Cu) atoms. The positron density in a plane going through the center of the GP1 zone is also plotted.

In conclusion, the above described computational approach appears to be very useful when studying the complex defect structure in the Al-Cu system. It is highly desirable to perform such calculations for realistic atomic configurations, and ab initio based structure relaxations for simple defect structures are already in progress. It would also be very helpful to perform positron calculations for complex defect structures and the procedure employed in [10] for the Al-Zn system could be perhaps used (cf. also [11]). The approach used in this contribution can also be applied to other systems containing nanoclusters, like Fe-Cu [1], in order to predict their PA characteristics.

Acknowledgements

We thank M.J. Puska for providing us with his ATSUP code which served as a basis for developments. This research was supported by the Ministry of Education of the Czech Republic (project OC 523.70 within the framework of the COST Action 523 – “Nanostructured materials”).

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