

# Vacancy clustering in pure metals: some first principle calculations of positron lifetimes and momentum distributions

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**Abstract.** First results of a systematic study on the vacancy clustering process in Al, Cu, Mg and Nb are presented. To this aim first principle calculation of positron lifetimes and positron-electron momentum distributions were performed. We test the reliability of the computational scheme used by comparing some of the calculated results with experimental ones.

## 1. Introduction

Vacancies have a predominant influence on the solid properties because of their important role in the atomic diffusion. When produced in supersaturation, for instance, during quenching, irradiation, or plastic deformation, besides monovacancies, vacancy clusters may be formed. These defects influence structural properties of the solids such as resistance to plastic deformation, solute diffusion, kinetics of thin films growth, etc.

It is well recognized that Positron Annihilation Spectroscopy (PAS) is a powerful tool to study vacancy-like defects. In fact, by measuring positron lifetimes and momentum distributions of the positron annihilation radiation it is possible to obtain information about the open volumes associated with defects and their chemical environment [1]. However, in some cases in which more than monovacancies or divacancies cannot be directly revealed by means of PAS it is necessary to perform *ab-initio* calculations that allow interpreting the experimental results.

In this work, first results of a systematic first principle calculation study on the vacancy clustering process in some pure metals are presented. Specifically, changes in the positron lifetimes and in the CDB positron-electron momentum distributions during vacancy clustering in pure Al, Cu, Mg and Nb were studied. These metals were selected since vacancy-like defects play an important role in: (i) Precipitation processes of Al-based age hardenable alloys; and (ii) Hydrogen sorption kinetic in Nb-doped nanostructured Mg films. These two topics are currently being studied in the Positron Group at IFIMAT (Argentina). In order to check the reliability of the results obtained, when possible some of the calculated results are compared with experimental ones.

## 2. Computational method

### 2.1. Positron calculations

A general introduction to *ab-initio* calculations of positron annihilation characteristics in solids can be found in [2]. In the present work, positron lifetimes and momentum distributions of the annihilating



positron-electron pairs for positrons delocalized in the bulk or trapped in vacancy-like defects were calculated following the procedure developed by Puska and Makonnen based on the VASP code (see [3] and references therein). Positron *ab-initio* calculations have been performed within the frame of the density-functional theory (DFT) [4] which was implemented in the Vienna Ab-initio Simulation Package (VASP) code [5]. The projector augmented wave (PAW) pseudopotential was used to account the electron-ion core interaction, using the local density approximation (LDA) [6] for the exchange-correlation term. In the calculation, the Brillouin-zone of the different structures was sampled using a 6x6x6 Monkhorst-Pack  $k$ -point mesh [7]. For the plane-wave basis set a cut-off of 650 eV was used. The self-consistent calculations were considered to converge when the difference in the total energy of the crystal between consecutive steps did not exceed  $10^{-5}$  eV.

## 2.2. Solid modeling

The periodic structures of the studied elements were simulated using different supercell sizes depending on the element crystal structure. Information corresponding to the crystal structure and lattice parameters used for calculations was taken from experimental data reported in the literature [8]. The unit cell of the crystalline structure has been used as the supercell for bulk calculations. For the calculation in defected materials one or more atoms were removed. In such a case, the supercell should be large enough in order to avoid the defect interaction with its periodic image; therefore, the system describes an isolated vacancy quite well. However, in practice, the size of the supercell cannot be built arbitrarily large. In all cases, we checked whether such supercell size was sufficient to obtain positron characteristics independent of the supercell size. The maximum number of atoms per supercell used to reach convergence was: 256 atoms (64 unit cells) for the fcc crystal structure, 128 atoms (64 unit cells) for the bcc crystal structure and 240 atoms (60 orthorhombic unit cells [9]) for the hcp crystal structure.

In these supercells, when possible, vacancy clusters were created maintaining a spherical or ellipsoidal geometry. Furthermore, for all the studied structures, the volume of the vacancy clusters was estimated. To this aim, an ellipsoid was fitted inside the open volume left by the vacancy cluster.

On the other hand, when generating vacancy clusters the possible relaxation of the crystal lattice was not considered, that is the ions neighboring vacancy agglomerates were not allowed to relax from their ideal position. A more precise calculation of the annihilation parameters could be obtained considering the relaxation of the cluster-neighboring ions and the forces exerted on these ions by the localized positron; however, the study of these effects goes beyond the aim of this work.

## 3. Experimental

Plates of well-annealed high-purity Al, Cu and Mg were used to characterize the bulk state of these elements. Defect signatures were obtained following the procedure described by Somoza *et al.* [10]. The positron lifetime spectrometer was a fast-fast timing coincidence system with a time resolution of 254 ps. A 20  $\mu$ Ci source of  $^{22}\text{NaCl}$  deposited on a thin Kapton foil was sandwiched between two identical specimens. After subtracting the source component, the spectra with about  $10^6$  counts were satisfactorily analyzed using the POSITRONFIT program [11]. The CBD spectra were obtained using two HP-Ge detectors (90% efficiency) with an energy resolution of 1.2 keV at the 511 keV photopeak.

## 4. Result and Discussion

In figure 1, the evolution of the calculated positron lifetime ( $\tau^{\text{calc}}$ ) as a function of the estimated vacancy cluster size for the four studied elements is presented. In this figure, the bottom abscissa indicates the estimated void volume while the top axis indicates the number of vacancies into the cluster. As can be seen in the four panels, all  $\tau^{\text{calc}}$  evolutions show a similar behavior: an initial rapid increase of  $\tau^{\text{calc}}$  for small volumes then reaching asymptotic values for large void volumes. Besides, it can be seen that in all cases, the transition between these two stages occurs for void volumes  $\sim 0.3\text{nm}^3$ . Depending on the crystal structure of the metal, this volume corresponds to different number of vacancies. The  $\tau^{\text{calc}}$  values obtained for perfect lattices and for structures containing monovacancies are in very good agreement with those reported in the literature (see for example [8] and references

therein). Moreover, in the case of Mg the evolution of  $\tau^{\text{calc}}$  is in very good agreement with recently reported results obtained using the non-autoconsistent method [12]. In the same way, the observed increase of  $\tau^{\text{calc}}$  with the growth of the vacancy cluster size for Al shows a good agreement with results reported in [2]. Although the values reported here are systematically lower than those calculated by Puska *et al.*, this difference can be assigned to the method of calculation used in these two works.

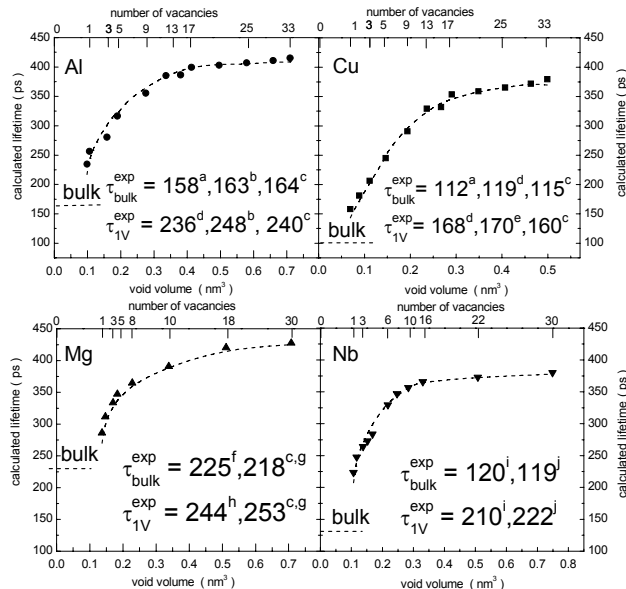


Figure 1: Evolution of the calculated positron lifetimes as a function of the estimated void volume (bottom) and the number of vacancies (top) for the four pure elements studied. Dotted lines are only eye guides.

<sup>a</sup>[13] <sup>b</sup>[14] <sup>c</sup>This work <sup>d</sup>[15]  
<sup>e</sup>[16] <sup>f</sup>[17] <sup>g</sup>[12] <sup>h</sup>[18] <sup>i</sup>[8] <sup>j</sup>[19]

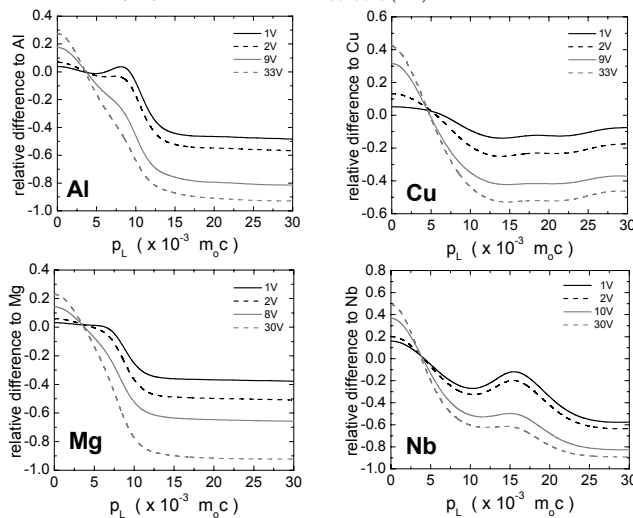


Figure 2: Evolution of the calculated momentum distributions of the annihilating electron-positron pairs in Al, Cu, Mg and Nb containing vacancy-clusters of different sizes. To simulate the experimental CDB spectra, all the calculated curves were convoluted with a Gaussian function ( $FWHM = 1.2 \text{ keV}$ ; that is,  $4.6 \times 10^{-3} m_0 c$ ).

In figure 1, experimental lifetime values measured in pure well-annealed metals and in metals containing monovacancies are also given. As already known, the experimental values for the defect-free bulk and for pure metals containing monovacancies differ with the  $\tau^{\text{calc}}$  in no more than 10%. However, in the case of Mg containing monovacancies this difference increases until about 20%. The same behavior was reported by Folegati *et al.* [18].

In figure 2, the relative (with respect to perfect element) calculated momentum distributions of the annihilating electron-positron pairs in Al, Cu, Mg and Nb containing vacancy clusters of different sizes are shown. To check the goodness of the computational scheme used, when possible it is important to compare these distributions with CDB experimental curves. To this aim, we have compared calculated CDB distributions with the corresponding experimental ones measured in our laboratory. As an example, in figure 3, results of the calculated and experimental relative

ratio curves (with respect to perfect Al) for perfect Cu and Mg are shown. On the other hand, in figure 4 experimental and calculated relative ratio curves for Cu and Mg containing monovacancies were plotted. From figures 3 and 4, it can be concluded that for Cu there is a very good agreement between the experimental and calculated CDB distributions. In the case of Mg this good agreement maintains until about  $10 \times 10^{-3} m_0c$ , the calculated curves qualitatively show the same “structure” as than experimental ones but they are systematically above (or below) the experimental ratio curves. Work in progress will make it possible to go deeper into the analysis and discussion of the results briefly presented in this work.

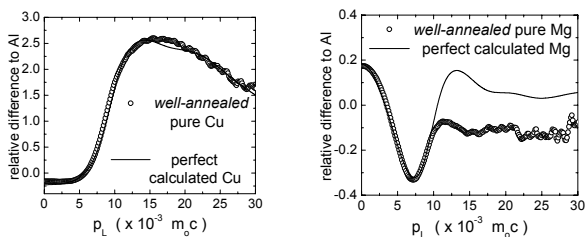


Figure 3: Calculated and experimental Cu/Al relative difference curve (left) and Mg/Al relative difference curve (right).

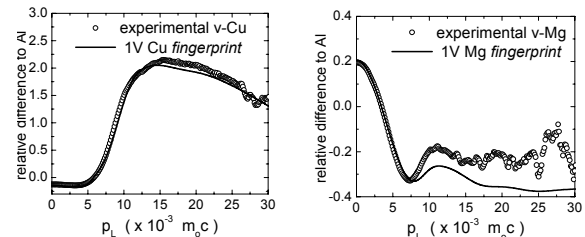


Figure 4: Calculated and experimental CDB curves for Cu monovacancy (left) and Mg monovacancy (right).

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