Simulation of properties of positrons trapped at Cu nanoparticles in Fe matrix

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Abstract. Positrons may get trapped in copper nanoparticles embedded in iron, which has been recently well evidenced experimentally. In this contribution we treat this effect theoretically and present an improved approach to simulations of properties of positrons trapped in copper nanoparticles embedded in the iron bcc matrix. The presented approach can be used to determine the size of Cu nanoparticles in model Fe-Cu alloys using coincidence Doppler broadening spectroscopy.

1. Introduction
Cu nanoparticles embedded in the Fe matrix represent an interesting system that can be examined by means of positrons. The reason is that the positron affinity (PA) of Cu is below that of Fe and Cu nanoparticles constitute positron potential wells where positrons can be trapped if nanoparticles are large enough. The experimental evidence of such trapping was reported in [1]. This effect has also practical consequences as the Fe-Cu system serves as a model alloy for reactor pressure vessel steels where Cu-rich precipitates are believed to play the key role in the process of embrittlement (see e.g. [2]).

In principle, nanoparticles could be identified by comparing the measured and calculated positron annihilation response. Recently, an effective computational approach was developed [3; 4], which allows us to calculate characteristics of positrons trapped at Cu nanoparticles as a function of their size. This approach is based on the atomic superposition (ATSUP) method [5; 6] and takes into account the positron affinity difference of the host and particles, which is ordinarily not included in the ATSUP method. In particular, it is possible to determine the positron localization in Cu particles, positron lifetime and binding energy to particles and also high momentum parts of the electron-positron momentum distribution, the last property being a ‘fingerprint’ of positron trapping in Cu nanoparticles. In this contribution the above mentioned approach is further improved by handling properly boundary conditions, which is an important point especially for very small Cu particles. The dependence of the $W$-parameter on the Cu nanoparticle size is presented, which could be used to ‘measure’ the size of Cu nanoparticles in Fe.

2. Computational methods
At the beginning a suitable supercell for calculations has to be selected. The supercell is based on the Fe bcc lattice. Cu particles are introduced into the supercell by replacing appropriate Fe
atoms by Cu. Here we shall study the ‘most compact’ particles only, i.e. those corresponding to the increasing number of nearest neighbor shells of a reference atom in the bcc lattice. Hence, we consider particles having 9, 15, 27, 51, 59, 65, 89, 113 and 137 Cu atoms. It is well known that small Cu particles in the Fe matrix exhibit the bcc structure with the lattice constant very close to that of Fe and Cu particles are coherent with the matrix (see e.g. [2]). Therefore, atomic relaxations around Cu particles are neglected in our approach.

Next, we shall briefly repeat the principle of the computational/simulation method used here according to [4]. The method consists of three steps performed within the framework of the ATSUP technique:

(i) First, the energy \( E_1 \) of positrons in the defect-free matrix material (bcc iron) is determined.

(ii) In the second step, the positron potential in the vicinity of atoms constituting the particle is shifted (by \( \Delta V_2 \)) in order to have the positron energy equal to \( E_1 \). This corresponds to the hypothetical case when the positron affinity difference (\( \Delta A_\pm \)) of the host and particle is zero and the positron is delocalized simultaneously in the host and particle. In this way a reference energy level for the positron potential of atoms constituting the particle is found.

(iii) Finally, the positron potential is further shifted by the energy corresponding to \( \Delta A_\pm \) (i.e. the resulting shift \( \Delta V_3 = \Delta V_2 - \Delta A_\pm \)) and, thereby, the positron potential well with the correct depth is created.

Regarding step (ii) we note that in supercells used for calculations the number of atoms in the particle must be much lower than that of the matrix. In addition, the potential shift \( \Delta V_2 \) for particle atoms is performed at spheres centered at atom nuclei. There is a lower limit for radius \( R \) of such spheres, which corresponds to the situation when the spheres fill up completely the particle volume (i.e. no interstitial space is left among spheres).

In our previous work [4] we have determined the parameters of the model, i.e. \( \Delta A_\pm \) and \( R \) for the Fe-Cu system on the basis of \( \text{ab initio} \) calculations. The resulting values are \( \Delta A_\pm = 0.5 \text{ eV} \) and \( R = 1.6 \text{ Å} \). Readers are referred to [4] for the details of the procedure. We shall use the above parameters in the following.

In order to calculate positron characteristics for regular Cu particles in the Fe matrix in [4], we have employed 2662 atom supercells (i.e. \( 11 \times 11 \times 11 \text{ bcc cells} \) considering periodic boundary conditions (PBCs) for the positron wave function. In the present contribution we check in detail whether such supercell size is sufficient to obtain positron characteristics independent of the supercell size. The reason is that for small Cu particles the corresponding positron potential well is rather shallow and the size of the chosen supercell might not be sufficient.

Such an effect has been reported by Korhonen \textit{et al.} in [7]. The solution is to use a larger supercell or to use PBCs in combination with the so called antiperiodic boundary conditions (ABCs) [7], as explained below, which also saves some computational time. Under PBCs, for a supercell characterized by e.g. \( d_x \) dimension along the \( x \)-axis direction the positron wave function \( \psi \) is not changing its value and sign when considering two positions in space that are shifted just by \( d_x \)

\[
\psi_{\text{PBC}}(x + d_x, y, z) = \psi_{\text{PBC}}(x, y, z) \quad (1)
\]

In the case of ABCs, we however adopt the following rule

\[
\psi_{\text{ABC}}(x + d_x, y, z) = -\psi_{\text{ABC}}(x, y, z) \quad (2)
\]

For small supercells PBCs cause too small positron localization, whereas ABCs result in an overestimate of the positron localization in an open volume defect under study [7]. Then, if an

\[\footnote{For simplicity we consider here a rectangular supercell only.}\]
effective wave function constructed as

$$\psi_{\text{eff}} = \frac{1}{\sqrt{2}} \sqrt{|\psi_{\text{P BC}}|^2 + |\psi_{\text{ABC}}|^2}$$  \hspace{1cm} (3)

is considered, it gives usually apparently more precise positron wave function which matches well – in the close vicinity of the studied defect – the wave function obtained using PBCs for much larger supercell. We shall employ this approach in the present study.

We should yet note that the resulting positron energy corresponding to the wave function $\psi_{\text{eff}}$ is calculated as the arithmetic mean from the values of energies obtained using PBCs and ABCs described above. The high momentum parts of the electron-positron momentum distribution are calculated according to the scheme presented in [8]. The positron density used to calculate the positron lifetime and momentum distribution is taken to be $n_+ = |\psi_{\text{eff}}|^2$. The range of momenta ($p$) used for the calculation of the $W$-parameter is $15 \times 10^{-3} \, \text{m} \cdot \text{e} < |p| < 25 \times 10^{-3} \, \text{m} \cdot \text{e}$. The positron localization in a Cu particle is determined as an integral of $n_+$ over the region where the positron potential is adjusted according to points (ii) and (iii) above. Electron-positron correlations are treated according to a gradient correction scheme developed by Barbiellini et al. [9]. Further computational details are specified in [4]. We further refer to literature [10] concerning the theoretical background of positron calculations.

3. Results and discussions

At the beginning we should state that there is no trapping in Cu particles with 9 atoms. This can be deduced from figure 1 where the dependencies of the positron localization and positron binding energy on the supercell size are plotted. The supercell size is determined by the multiplicative factor that is used to enlarge the (2 atom) bcc unit cell of Fe in the three crystallographic directions. The range of such factors goes from 7 to 25, which corresponds to supercells from 686 to 31250 atoms. Consequently, the supercell size is given in ‘units’ of ‘bcc$^3$’ in the figure. One can clearly see that the positron localization and binding energy approach zero with the increasing supercell size regardless of boundary condition used (‘average’ means the arithmetic mean from PBC and ABC values). This proves that 9 atom Cu particles in iron matrix do not trap positrons. We have discussed this fact already in our work [4], but here an additional proof is given.

![Figure 1](image-url)

**Figure 1.** The dependence of (a) the positron localization and (b) positron binding energy on the supercell size for the 9 atom Cu particle in Fe matrix.

Next, we investigate the 15 atom Cu particle. The results are presented in figure 2 in the way similar to the 9 atom Cu particle. In this case the positron localization and binding energy
converge to some non-zero value with the increasing supercell size. For large supercells the localization is about 38%, whereas the binding energy is still rather small $\sim 0.046$ eV. In figure 2c we also show the positron lifetime which approaches a value being slightly above a calculated Fe bulk value of 113 ps. The just discussed behavior unambiguously show positron trapping at the 15 Cu atom particle in the Fe matrix though the corresponding positron potential well is rather shallow and the positron is not perfectly confined in the particle.

Figure 2. The dependence of (a) the positron localization, (b) positron binding energy and (c) positron lifetime on the supercell size for the 15 atom Cu particle in Fe matrix.

If the differences among examined boundary conditions are checked, it is possible to conclude that for small supercells such differences are rather large and corresponding averaged values still differ non-negligibly from converged ones. In what follows we shall consider that for $11 \times 11 \times 11$ bcc supercell the averaged values for all quantities investigated give already the converged values almost precisely. This further indicates that using the same supercell in our previous work [4] was reasonable except for very small particles (like 15 atom one) where averaged values still deviate apparently from corresponding PBC values.

After studying in detail two particles we now proceed with dependencies for the series of selected particles. Figure 3 shows the dependence of the calculated $W$-parameter on the Cu particle size. One can clearly see that without considering the true positron affinity difference

Figure 3. The dependence of the $W$-parameter on the Cu particle size (diameter) for two computational approaches.
‘no PA’ dependence in the figure) between the particle and matrix the \( W \)-parameter is very close to that for pure Cu even for very small particles, which is connected with the fact that the positron localization for such particles is overestimated. On the other hand, when the positron affinity difference is taken into account (‘with PA’ dependence) in the way described above, the \( W \)-parameter gradually increases, as expected, and becomes closer to the pure Cu value for apparently larger particles compared to the previous case.

This behavior could be, in principle, used to study/determine the (average) Cu particle size in real alloys using coincidence Doppler broadening spectroscopy [11]. The necessary condition would be that saturation trapping occurs in such particles, which does need to be necessarily true in reality. Otherwise the fraction of positrons annihilating at particles would have to be known, which is hard to obtain from experiment. However, simulations of the Cu precipitation process could be of help in this respect [12].

An alternative approach for determining the size of embedded Cu nanoparticles in Fe based on the momentum smearing effect has been proposed at this Workshop [13].

4. Conclusions
Cu nanoparticles embedded in the bcc Fe matrix were studied from the viewpoint of positron annihilation spectroscopy. In particular, we presented a computational/simulation method to determine positron characteristics corresponding to positrons trapped at such nanoparticles. Further work is in progress in order to employ such simulations for estimates of the Cu particle size in real Fe-Cu alloys.

Acknowledgement
We are grateful to M J Puska for his ATSUP code that served as a basis for further developments. This work was supported by the Ministry of Schools, Youths and Sports of the Czech Republic through the research plan MSM 0021620834 and project COST OC 165.

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