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2137-46

Joint ICTP-IAEA Advanced Workshop on Multi-Scale Modelling for Characterization and Basic Understanding of Radiation Damage Mechanisms in Materials

12 - 23 April 2010

Principles of positron annihilation and positron response calculations

J. Kuriplach
Charles University
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Principles of positron annihilation and positron response calculations

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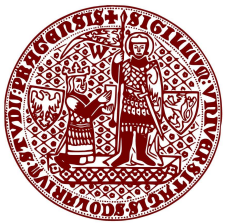
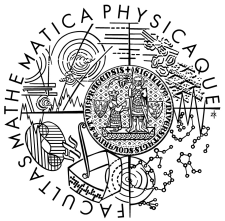
April 20, 2010





Joint ICTP-IAEA Advanced Workshop on Multi-Scale Modelling
for Characterization and Basic Understanding of Radiation Damage Mechanisms in Materials
April 12-23, 2010, ICTP, Trieste, Italy

Lecture outline

Lecture outline

Acknowledgment to people

Charles University in Prague:

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Lecture outline

'Literary description' I

Positron,
elementary antimatter particle having a mass equal to that of an electron and a positive electrical charge equal in magnitude to the charge of the electron. The positron is sometimes called a positive electron or anti-electron. Electron-positron pairs can be formed if gamma rays with energies of more than 1 million electron volts strike particles of matter. The reverse of the pair-production process, called annihilation, occurs when an electron and a positron interact, destroying each other and producing gamma rays.

The existence of the positron was first suggested in 1928 by the British physicist P.A.M. Dirac as a necessary consequence of his quantum-mechanical theory of electron motion. In 1932 the American physicist Carl Anderson confirmed the existence of the positron experimentally.

Annihilation,
in particle physics, the mutual destruction of elementary particles and their antiparticles, with the release of energy in the form of other particles or gamma rays. An example is the annihilation of an electron when it collides with its positively charged antiparticle, a positron.

Basic positron properties and their consequences

- Positron is an antiparticle of an electron:
  mass $= m_e$, rest energy $(m_e c^2) = 511$ keV,
  charge $= +e$, spin $= \frac{1}{2}$.
- Due its positive charge, the positron is repelled from nuclei.
- In materials positrons reside in the interstitial region because they are pushed away from atomic cores.
- Oppositely, electrons are attracted to positrons (and vice versa).
- Under normal experimental conditions, there is at most one positron in a studied sample and electrons pile-up around this positron.
- When a positron and an electron 'meet', they can annihilate producing (most probably) two γ-quanta (with ~ 511 keV energies).
- These γ-quanta carry information about the positron annihilation site (electron density).
- This is the principle how positrons can be used to study materials, including irradiated ones.

Conservation laws for 2γ annihilation: $e^- + e^+ \rightarrow \gamma + \gamma$

- Charge conservation:

$$(-e) + e = 0\,.$$

- Energy conservation:

$$E_- + E_+ = E_{\gamma 1} + E_{\gamma 2}\,.$$

- Momentum conservation:

$$\boldsymbol{p}_- + \boldsymbol{p}_+ = \boldsymbol{p}_{\gamma 1} + \boldsymbol{p}_{\gamma 2}\,.$$

- The energy (momentum) distribution of annihilation γ-quanta reflects the energy (momentum) distribution of e-p pairs.
  The e-p pair distribution can be therefore determined experimentally.
- Angular momentum conservation:

$$(-1)^{L+S} = (-1)^n \quad (n = 2)\,.$$

Positron properties in materials – lifetime

- Positron annihilation (PA) is a statistical process and positron lifetime (τ) is defined as the mean time the positron lives in a material before it annihilates.
- Positrons decay (annihilate) according to the exponential law and the number of positrons (N) at a time t is ($N(t=0)=N_0$)

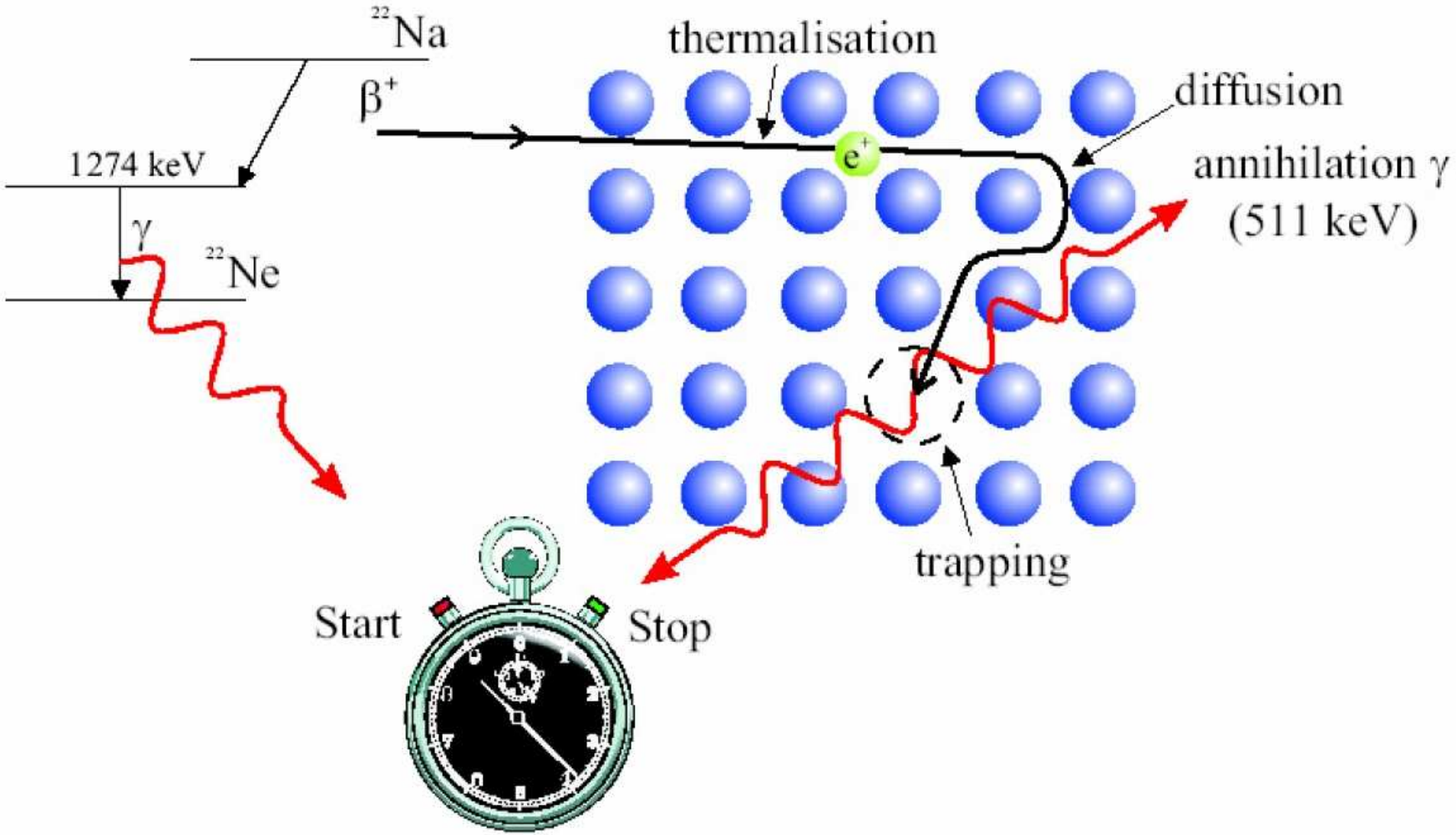
$$N(t) = N_0 \exp(-t/\tau) = N_0 \exp(-\lambda t)\,,$$

  where the decay constant λ ($=1/\tau$) is called annihilation rate.
- PA in many materials is well described by a superposition of several exponential decays, which corresponds to several sites where positrons annihilate.
- The lifetime of positrons in materials ranges from ~ 100 ps to 500 ps.
- Examples of measured lifetimes (in ps) for defect free materials:

Li	290	C($\diamond$)	98	$SiO_2(\alpha)$	~ 270
Al	165	Si	220	ZnO	~ 150
Fe	106	SiC	140	C_{60}	~ 400

Positron properties in materials – lifetime

- How to measure positron lifetime?



Positron properties in materials – lifetime

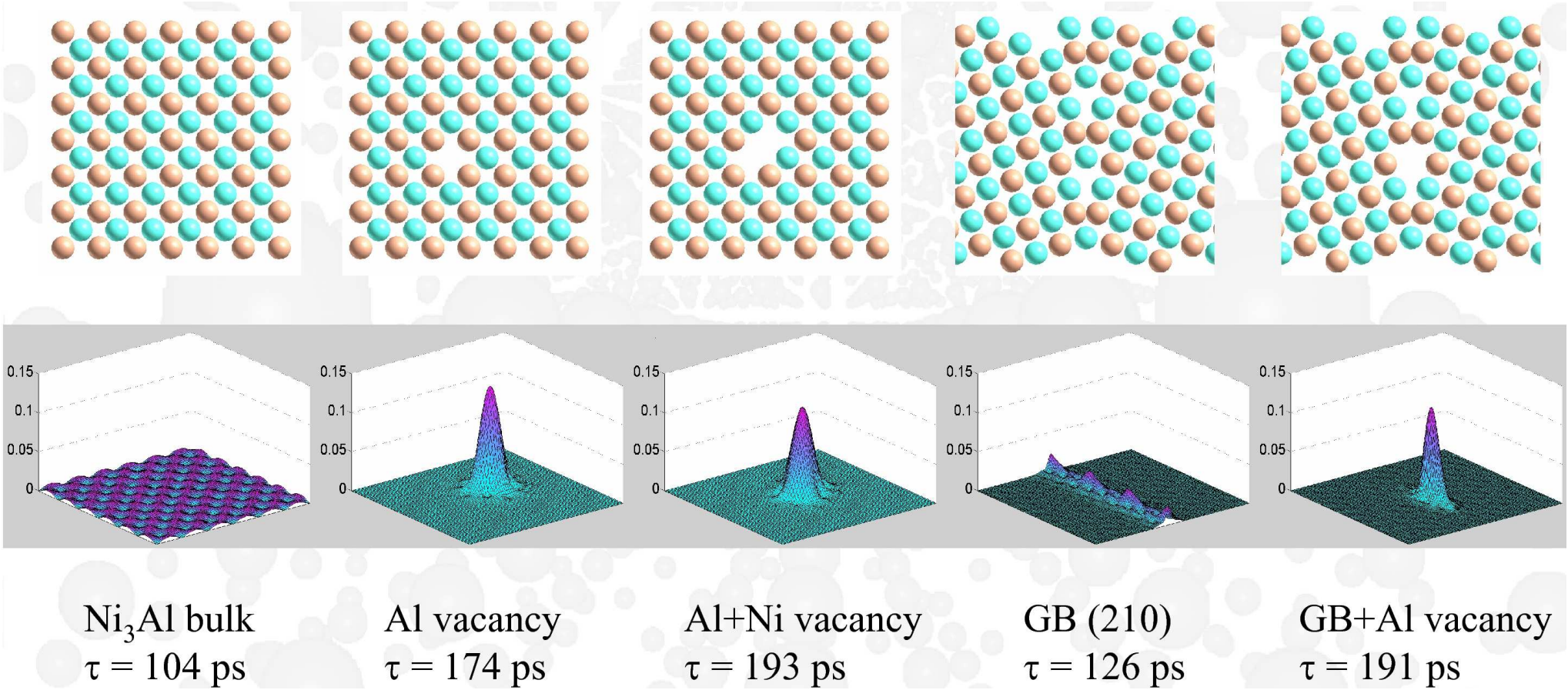
- When an atom is missing (vacancy), positrons 'like' to reside in such places (as repulsion from nuclei is lowered) and may get trapped there.
- This effect constitutes the sensitivity of PA to open volume defects.
- The positron lifetime (annihilation rate) is prolonged (reduced) in open volume defects because of lowering the electron density in open volume defects.
- Examples of bulk and vacancy lifetimes (in ps):

Al	165	V(Al)	240
Cu	115	V(Cu)	180
Fe	106	V(Fe)	175

- **Positron lifetimes are defect specific !!!**

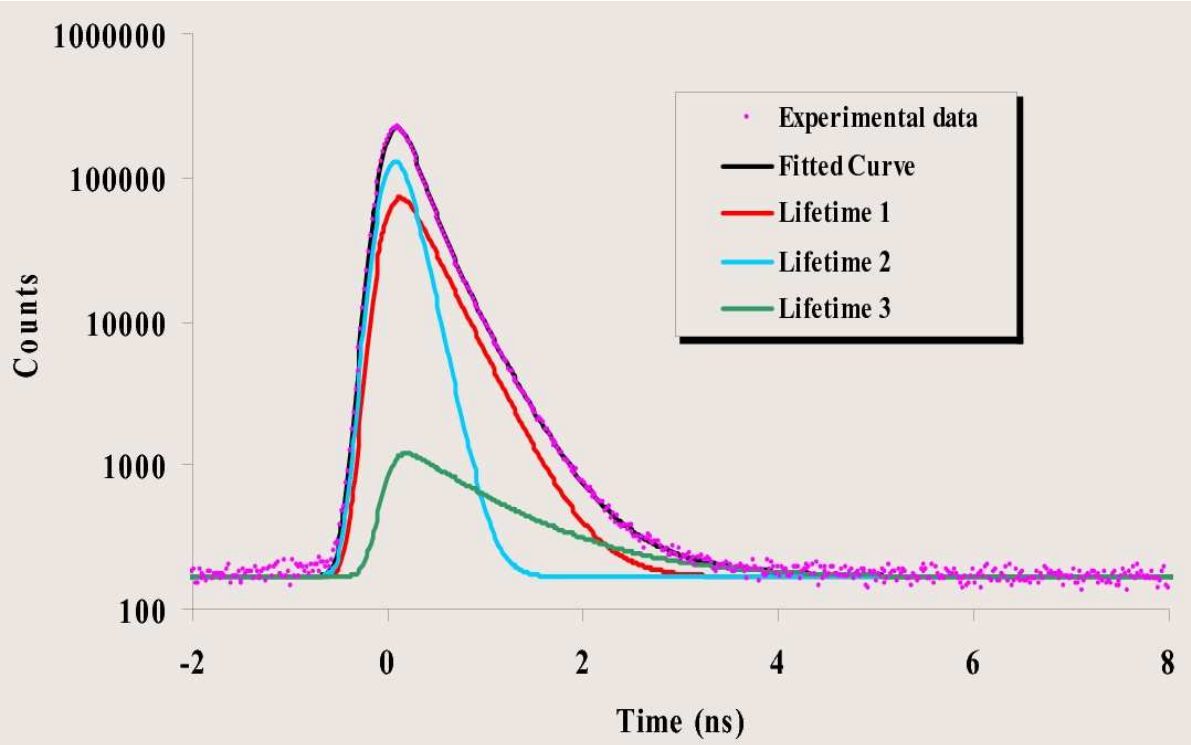
Positron properties in materials – lifetime

- Ni_3Al example:



Positron properties in materials – lifetime

- Measured lifetime spectrum with three lifetime components:



$$f(t) = \sum_{i=1}^{n} N_i e^{-\frac{t}{\tau_i}}$$

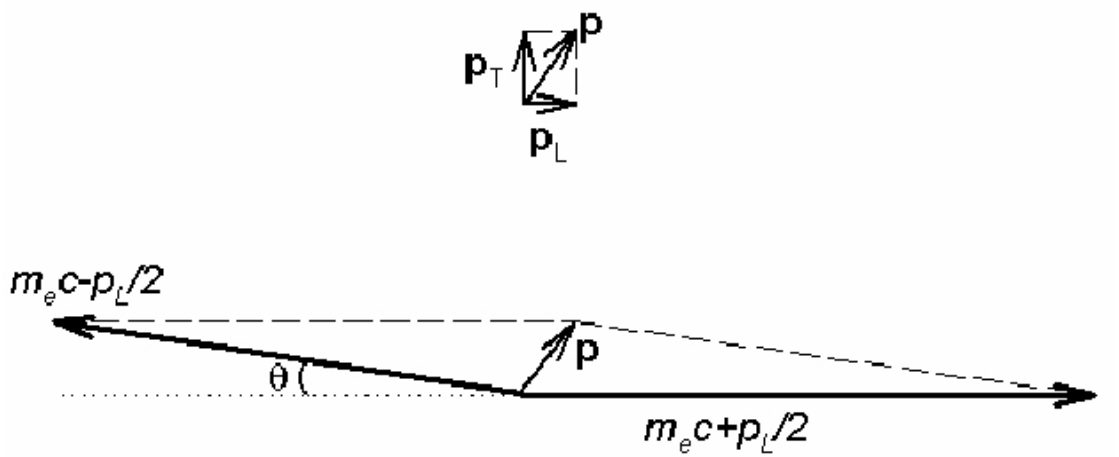
+ convolution with resolution function

Positron properties in materials – momentum distribution

- For 2γ annihilation the relation between the annihilation photon momentum and energy is

$$E_\gamma = |\boldsymbol{p}_\gamma| c \approx m_e c^2 \,.$$

- Doppler shift (Δp_γ) due to non-zero momentum ($\boldsymbol{p}$) of e-p pairs is typically several keV:



$$p_\gamma = m_e c + \Delta p_\gamma$$

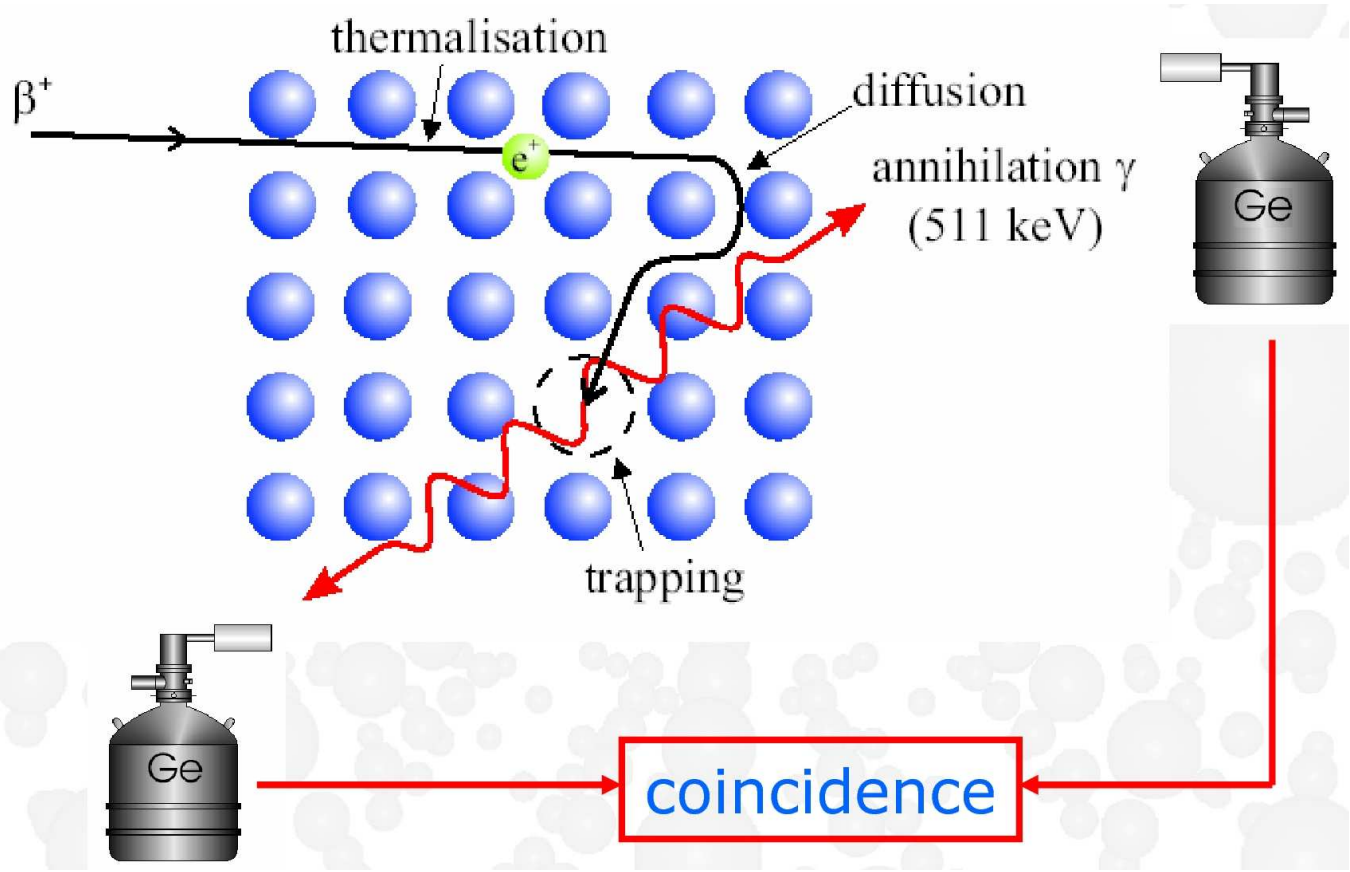
$$\Delta p_\gamma = \pm \frac{1}{2} p_L$$

$$\Theta = \frac{p_T}{m_e c}$$

- When $\Delta E_\gamma = 1$ keV, then $\Delta p_\gamma \doteq 3.92 \times 10^{-3}\ m_e c$.

Positron properties in materials – momentum distribution

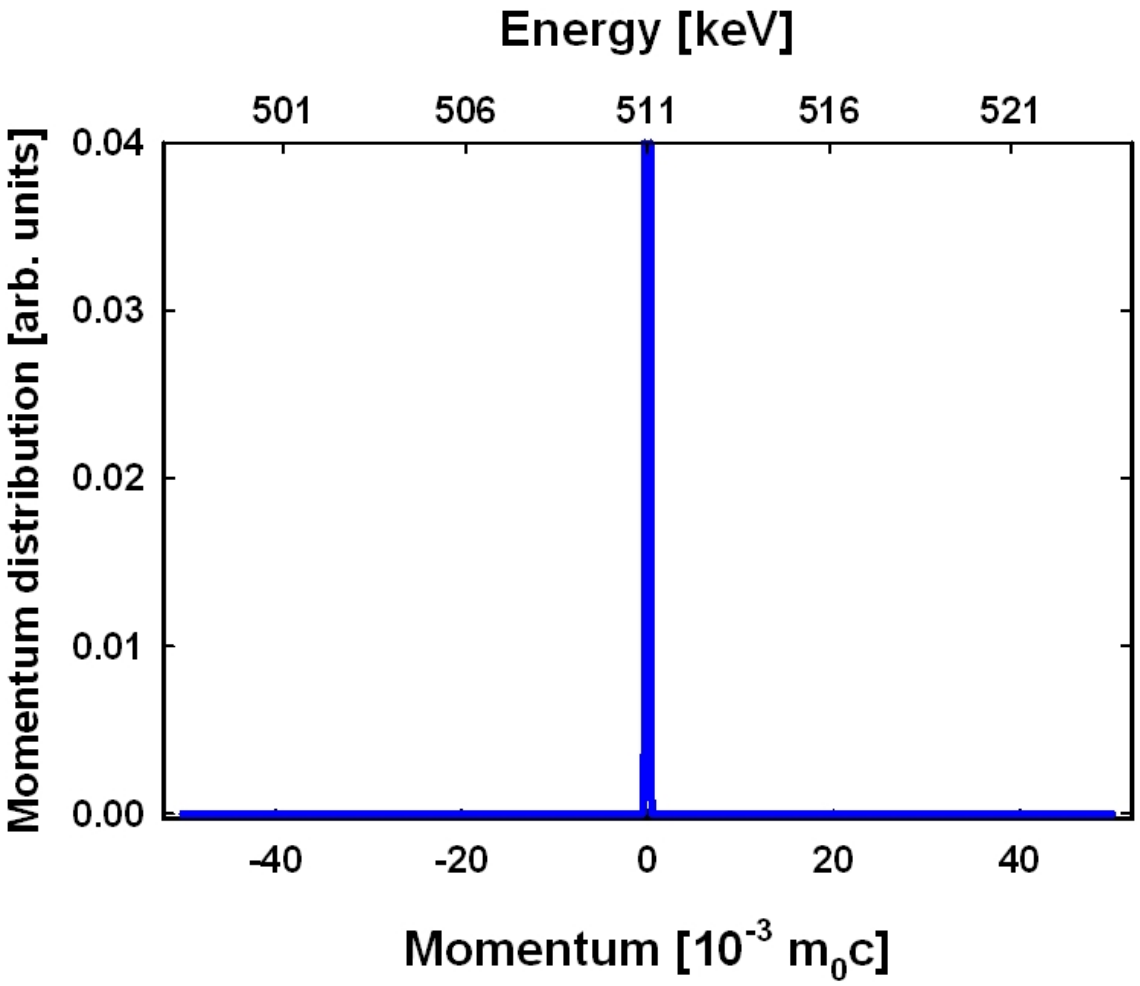
- How to measure momentum distribution of e-p pairs?



- Measuring in coincidence is needed to reduce background and to observe PA with core electrons with higher precision.

Positron properties in materials – momentum distribution

- Definition of line-shape parameters S (shape) and W (wing):



$$S \approx 0.5,\ W \approx 0.1, \qquad \frac{S_{\mathrm{defect}}}{S_{\mathrm{bulk}}} > 1,\ \frac{W_{\mathrm{defect}}}{W_{\mathrm{bulk}}} < 1, \qquad \begin{array}{c} S \rightarrow \text{valence} \\ W \rightarrow \text{core} \end{array}$$

Positron properties in materials – momentum distribution

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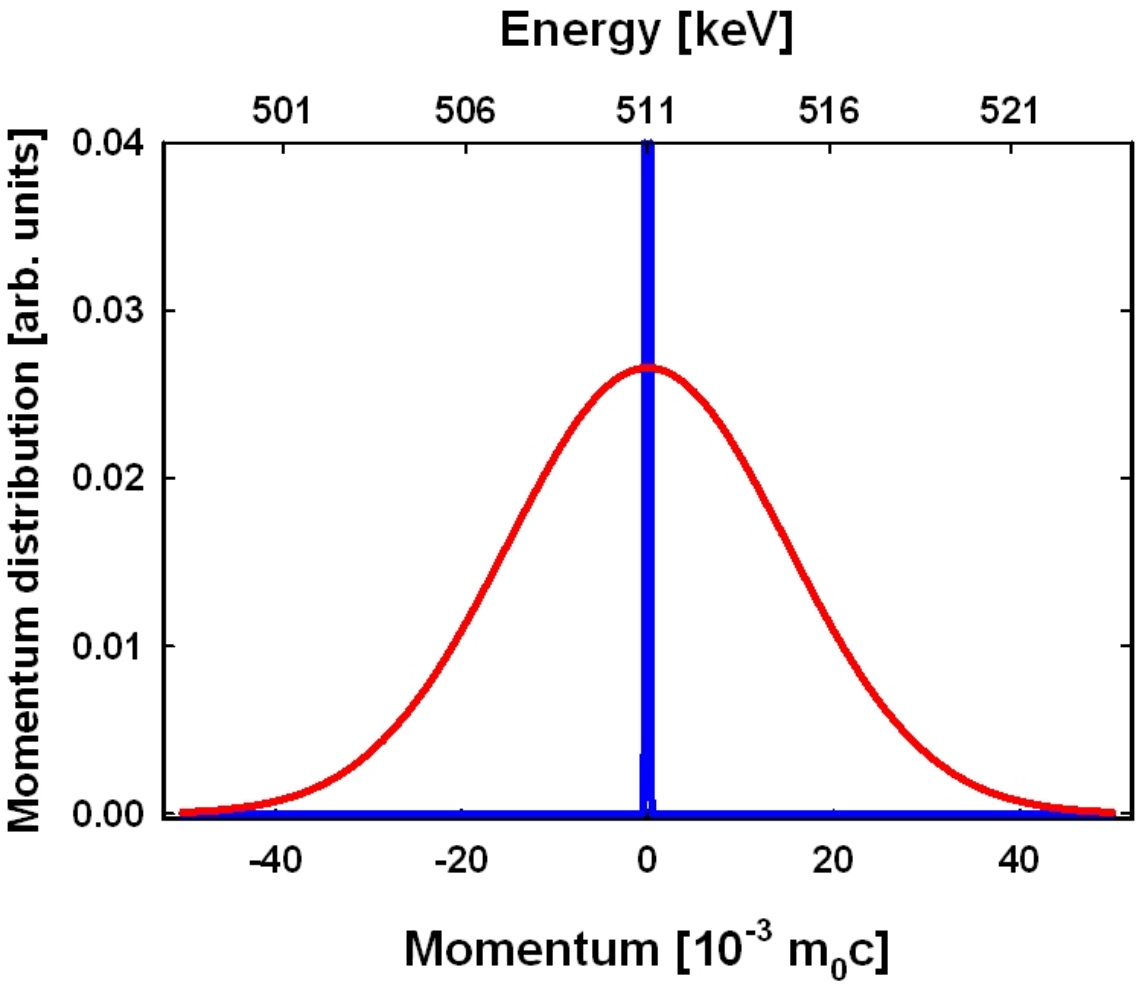

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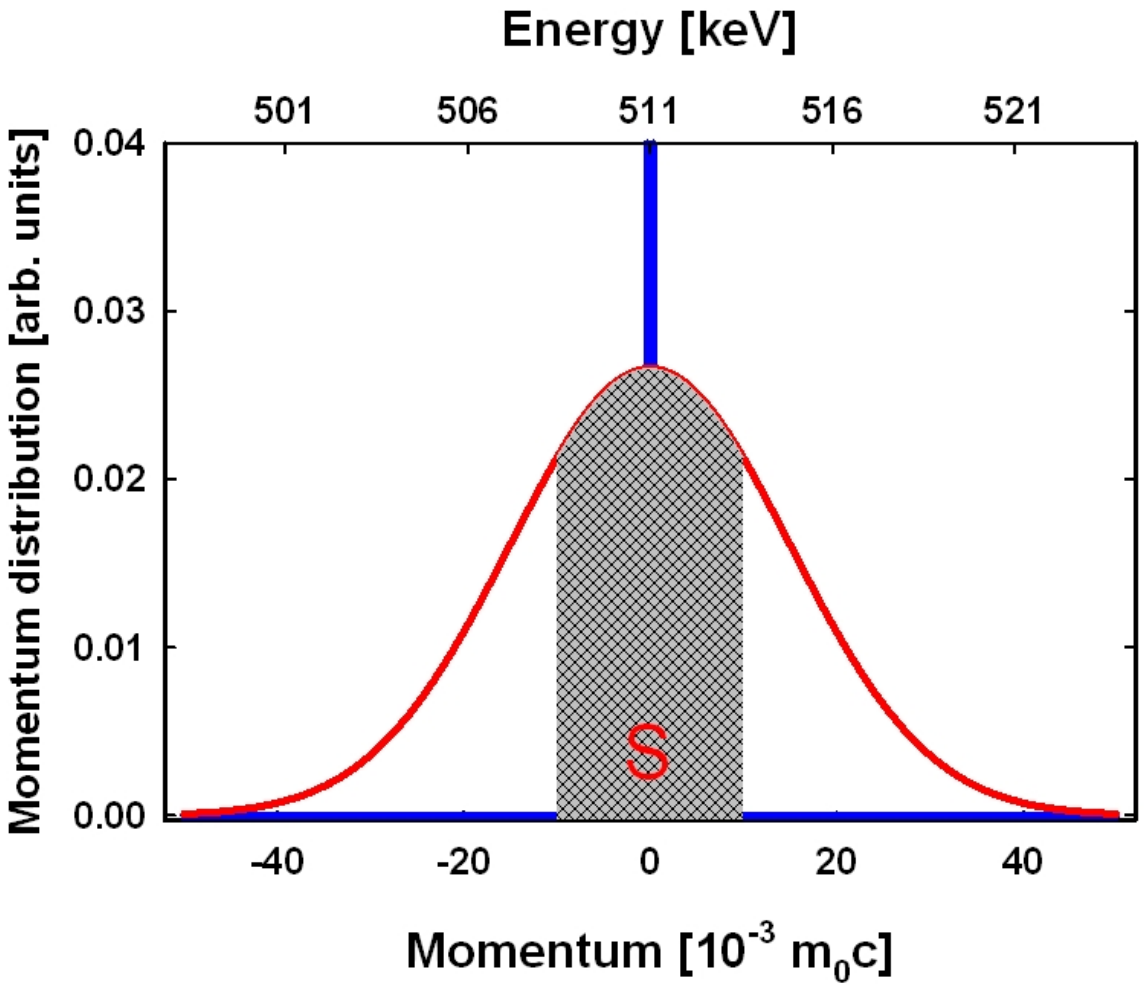

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Positron properties in materials – momentum distribution

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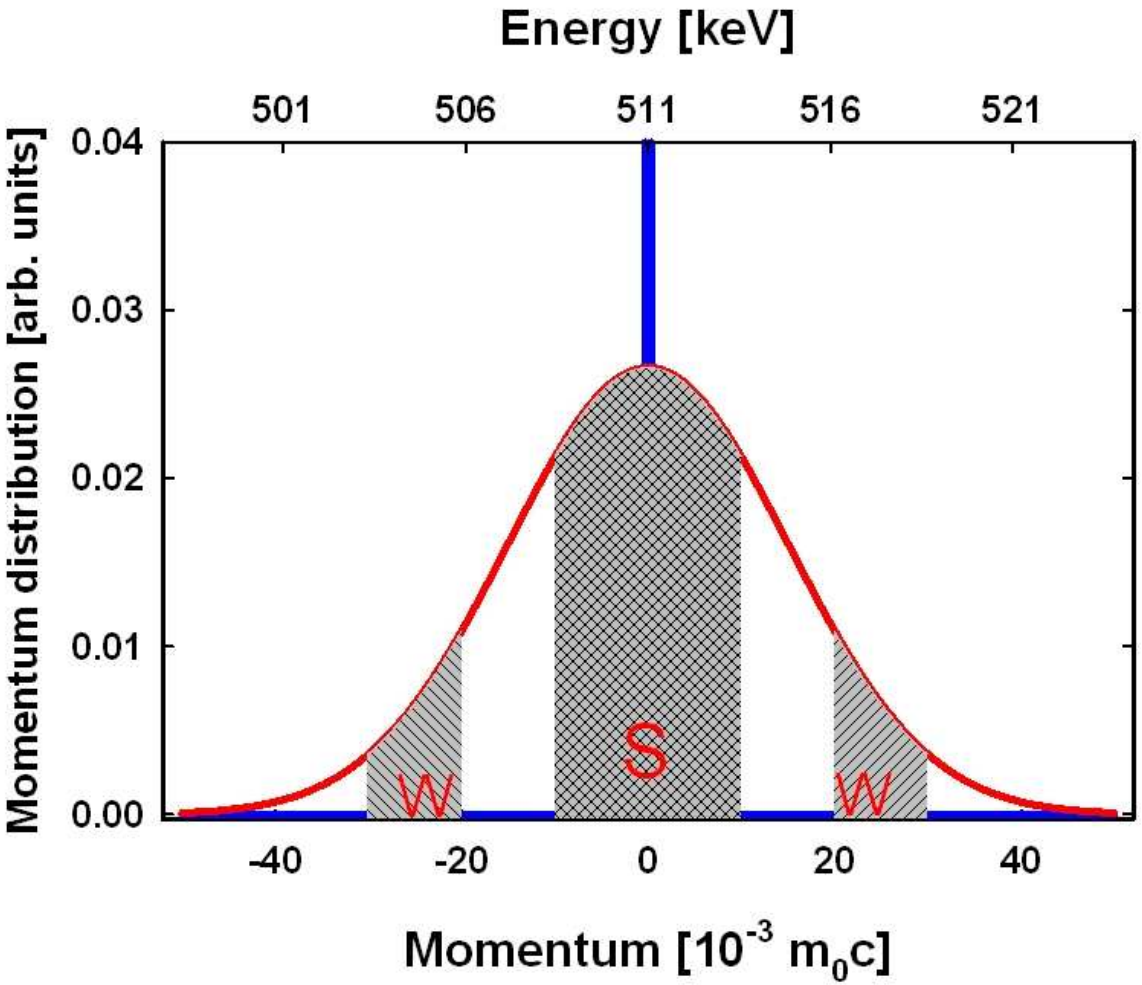

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Positron properties in materials – momentum distribution

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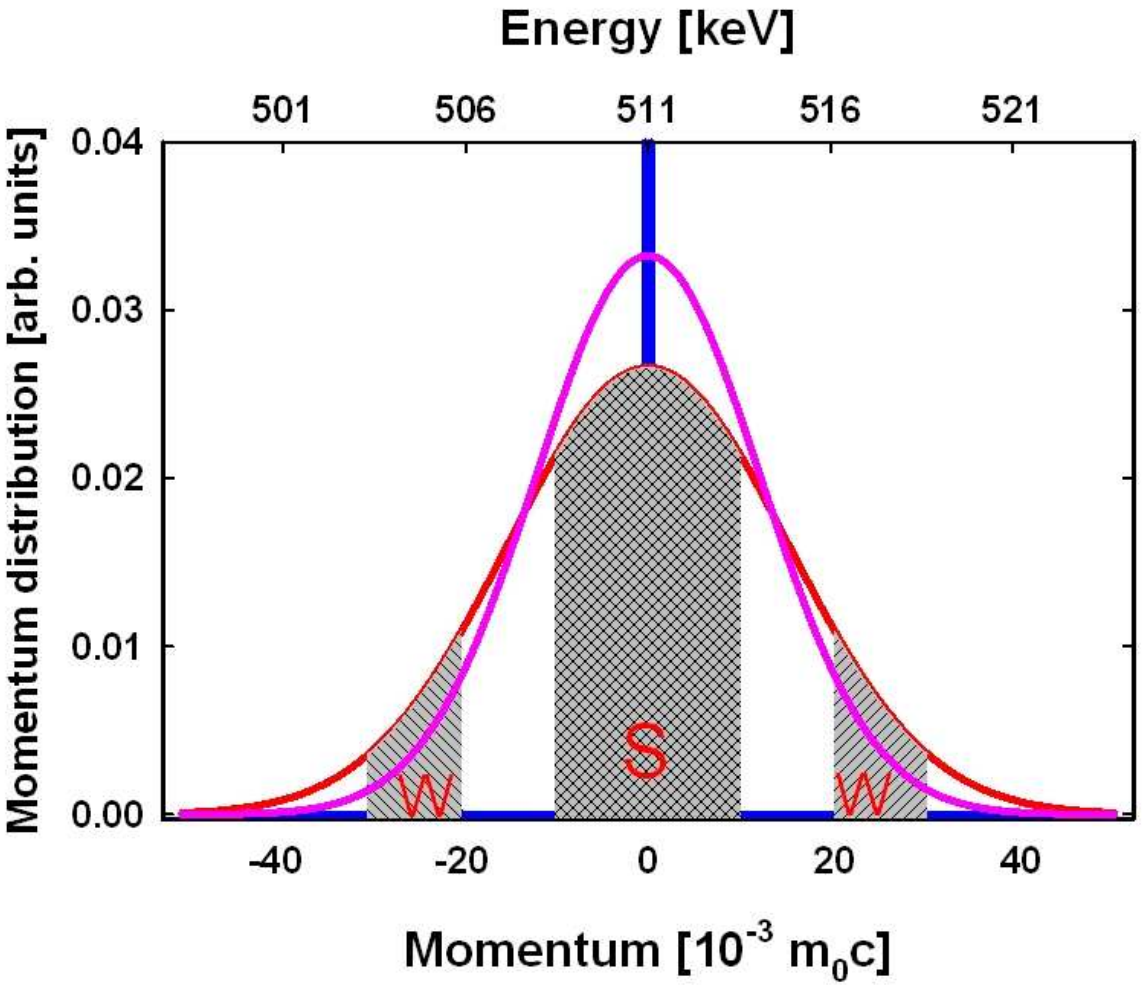
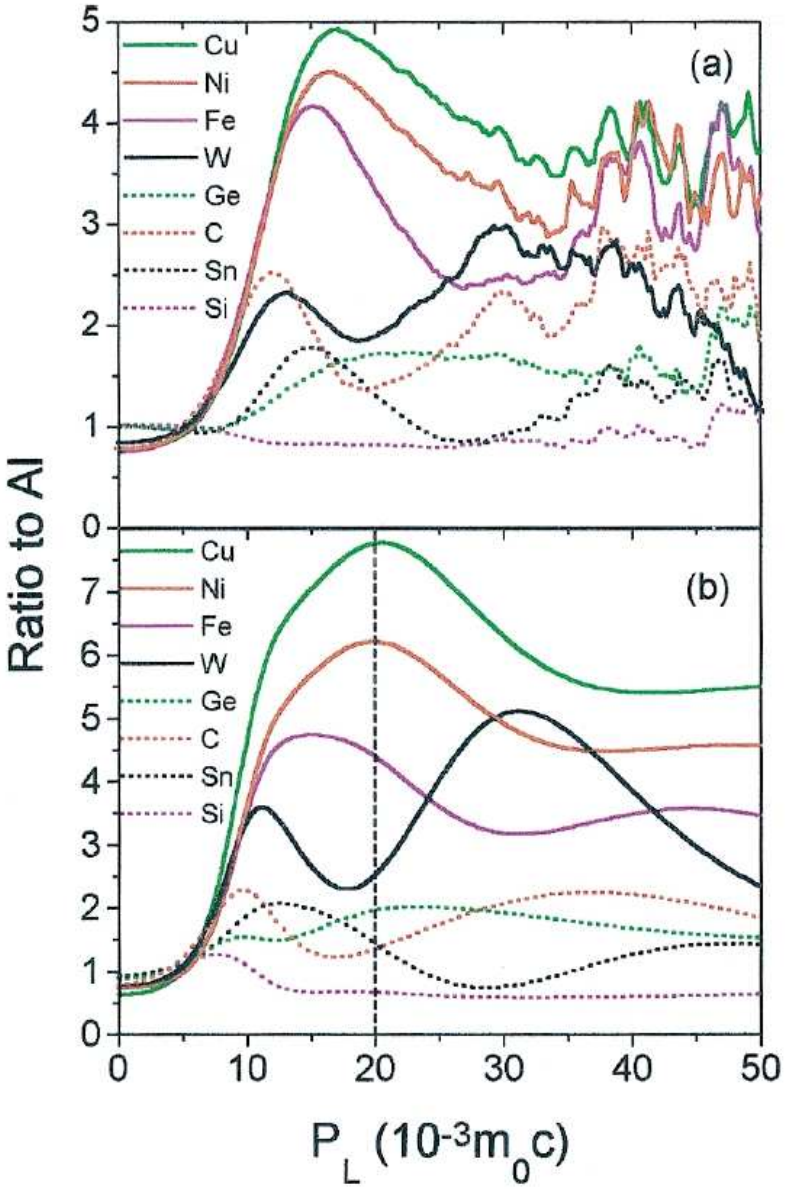


$$S \approx 0.5,\ W \approx 0.1, \qquad \frac{S_{\mathrm{defect}}}{S_{\mathrm{bulk}}} > 1,\ \frac{W_{\mathrm{defect}}}{W_{\mathrm{bulk}}} < 1, \qquad \begin{array}{c} S \to \text{valence} \\ W \to \text{core} \end{array}$$

Positron properties in materials – momentum distribution

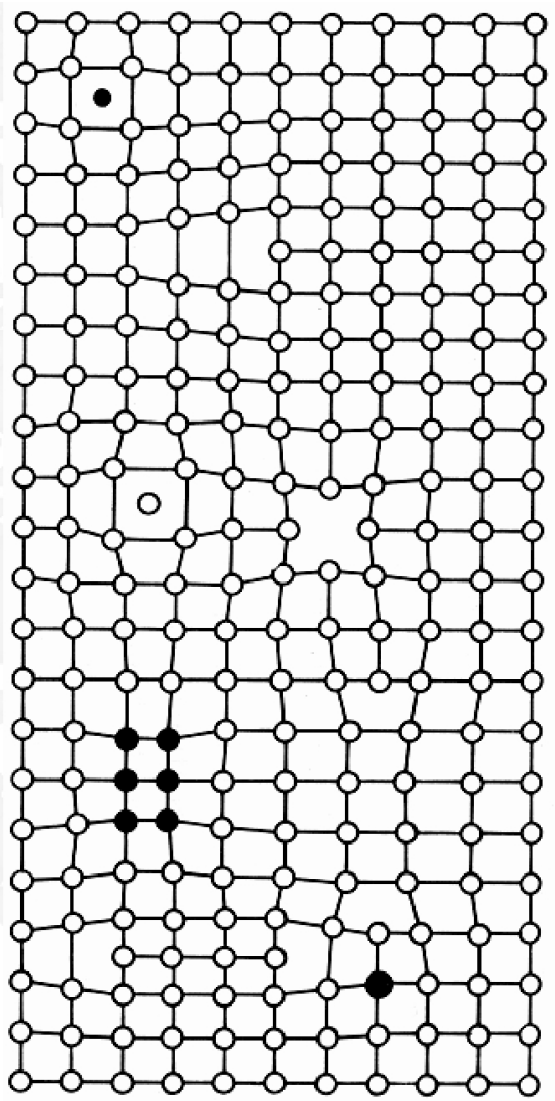
- The W-parameter (high momentum parts of MD) reflects annihilation with core electrons.
- This can be used to study atomic environment of annihilation sites in materials.
- Example: P. Asoka-Kumar et al., Phys. Rev. Lett. **77**, 2097 (1996).



Defects attracting positrons

- Open volume defects:
  - vacancies and their agglomerates (+loops),
  - dislocations (+loops),
  - grain boundaries,
  - stacking faults, etc.
- Some type of precipitates.
- Neutral and negatively charged defects.
- What about irradiation induced defects?

- Positrons insensitive to isolated impurities, interstitials, some precipitates, positively charged defects.



Positronium

- Positronium (Ps) is a bound state of a positron and an electron.
- Ps can, in principle, exist in two states:
  - parapositronium (p-Ps), singlet state ($S = 0$), $\tau = 125$ ps,
  - orthopositronium (o-Ps), triplet state ($S = 1$), $\tau = 147$ ns.
- The binding energy of a Ps (in vacuum) amounts to ~ 6.8 eV $=$ Ry$/2$.
- The numbers of p-Ps's and o-Ps's are in the $1:3$ ratio.
- Ps can be formed in some materials (porous materials mainly).
- Then, the o-Ps lifetime and corresponding intensity allow to estimate the size and concentration of pores (pick-off annihilation).

'Literary description' II

The lifetime of a positron inside a solid is normally less than a fraction of nanosecond. This is a very short time on a human scale, but is long enough to enable the positron to visit an extended region of the material, and to sense the atomic and electronic structure of the environment. Thus we can inject a positron in a sample to draw from it some signal giving us information on the microscopic properties of the material. This idea has been successfully developed in a number of positron-based techniques of physical analysis, with resolution in energy, momentum, or position.

A. Dupasquier and A.P. Mills, Jr.
Positron spectroscopy of solids

Lecture outline

Theoretical background

- Density functional theory ... look at previous lectures.
- From the DFT Kohn-Sham equations can be derived:

$$\left[-\frac{1}{2}\Delta + \frac{\delta E_{xc}[n_-]}{\delta n_-} - \Phi(\boldsymbol{r}) + V_{ext}(\boldsymbol{r})\right]\psi_-(\boldsymbol{r}) = E_-\psi_-(\boldsymbol{r})\,,$$

where

$$\Phi(\boldsymbol{r}) = \int \frac{-n_-(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d^3\boldsymbol{r}' \quad \text{and} \quad n_-(\boldsymbol{r}) = 2\sum_{E_-\leq E_F} |\psi_-(\boldsymbol{r})|^2\,.$$

- How this theory is modified when positrons are included?

Theoretical background

- Two component density functional theory (TCDFT) needs to be used (B. Chakraborty, Phys. Rev. B **24**, 7423 (1981)).
- The basic TCDFT statement is now: the ground-state energy of a system composed of electrons and positrons (and nuclei) is a functional of the electron and positron densities (and nuclear positions).
- From the TCDFT coupled one-particle equations for electrons and positrons can be derived:

$$\left[-\tfrac{1}{2}\Delta + \frac{\delta E_{xc}[n_-]}{\delta n_-} - \Phi(\boldsymbol{r}) + V_{ext}(\boldsymbol{r}) + \frac{\delta E_c^{e-p}[n_-,n_+]}{\delta n_-}\right]\psi_-(\boldsymbol{r}) = E_-\psi_-(\boldsymbol{r})$$

$$\left[-\tfrac{1}{2}\Delta + \frac{\delta E_{xc}[n_+]}{\delta n_+} + \Phi(\boldsymbol{r}) - V_{ext}(\boldsymbol{r}) + \frac{\delta E_c^{e-p}[n_-,n_+]}{\delta n_+}\right]\psi_+(\boldsymbol{r}) = E_+\psi_+(\boldsymbol{r})$$

where

$$\Phi(\boldsymbol{r}) = \int \frac{-n_-(\boldsymbol{r}) + n_+(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d^3\boldsymbol{r}' \quad \text{and} \quad n_+(\boldsymbol{r}) = |\psi_+(\boldsymbol{r})|^2 .$$

because we suppose to have just one positron in the studied system.

Theoretical background

- The TCDFT is quite time and computationally demanding.
- One has to solve a system of coupled equations for electrons and positrons.
- This requires knowledge of the $E_c^{e-p}[n_-, n_+]$ functional (in addition to the E_{xc} one).
- The knowledge of the E_c^{e-p} functional is far from being complete (based on studies electron-positron gas).
- When $n_+ \to 0$, TCDFT can be simplified considerably.
- Then we obtain the so-called 'conventional scheme'.
- In this case, electronic structure (n_-) is not influenced by the presence of positrons and electronic structure can be determined as usual.

Theoretical background

- The positron Schrödinger equation looks as follows:

$$\left[-\frac{1}{2}\Delta + \Phi(\boldsymbol{r}) - V_{ext}(\boldsymbol{r}) + V_{corr}(\boldsymbol{r})\right]\psi_+(\boldsymbol{r}) = E_+\psi_+(\boldsymbol{r})\,,$$

  where Φ depends only on n_-,
  - $V_{corr} = \delta E_c^{e-p}[n_-, n_+]/\delta n_+$ for $n_+ \to 0$ is the so called (electron-)positron correlation potential that depends on the electron density only, and
  - V_{xc} for positrons is effectively cancelled by the positron part of Φ (due to self-interaction).

- Finally, the total positron potential V_+ can be written as

$$V_+(\boldsymbol{r}) = V_{Coul}(\boldsymbol{r}) + V_{corr}(n_-(\boldsymbol{r}))$$

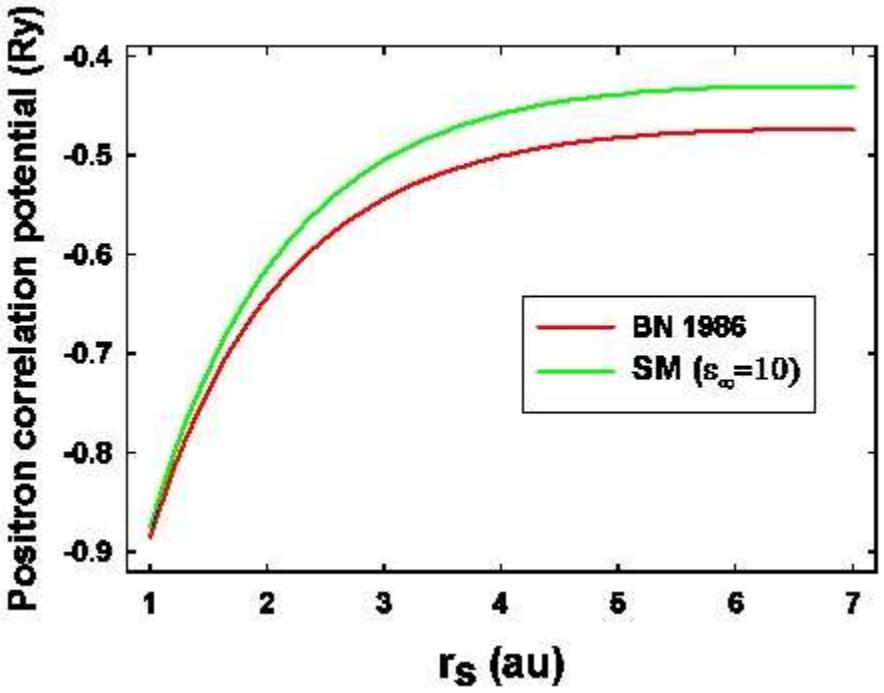
  V_{Coul} being the electron Coulomb potential with opposite sign.

Positron correlation potential

- The most frequently used correlation potential is from Boroński, Nieminen, Phys. Rev. B **34**, 3820 (1986):

$$V_{corr}[\mathrm{Ry}] = -0.6298 - \frac{13.15111}{(r_s + 2.5)^2} + \frac{2.8655}{(r_s + 2.5)}$$

for $0.56 \leq r_s \leq 8.0$ $(4\pi r_s^3/3 = n_-)$ and looks like this



Positron calculation scheme

- The scheme of a typical positron calculation:
  1. The electronic structure of a given system is determined.
  2. The positron potential is obtained using the electron Coulomb potential and density.
  3. The Schrödinger equation for positrons is solved ($\rightarrow \psi_+$, E_+).
  4. Further positron quantities of interest are calculated.

Positron lifetime calculation

- We shall consider that positrons with an intensity of I_+ [m^{-2}s^{-1}] are coming into the sample with volume V [m^3]. The number N of annihilation events per unit time is

$$N = I_+ \sigma n_- V$$

  where σ [m^2] is the cross section for positron annihilation.
- The cross section for 2γ annihilation (QED) is

$$\sigma_{2\gamma} = \frac{\pi r_e^2}{g+1}\left[\frac{g^2+4g+1}{g^2-1}\ln(g+\sqrt{g^2-1}) - \frac{g+3}{\sqrt{g^2-1}}\right]$$

  with the Lorentz factor $g = 1/\sqrt{1-v^2/c^2}$ and classical electron radius $r_e \approx 3\times 10^{-15}$ m.
- If the positron speed is small $(v/c \ll 1)$ then

$$\sigma_{2\gamma} \doteq \pi r_e^2 \frac{c}{v}\,.$$

Positron lifetime calculation

- Using previous formula and $I_+ = n_+ v$ one gets

$$\lambda_{IPM} = 1/\tau_{IPM} = N(n_+ V = 1) = \pi r_e^2 c n_- \,,$$

  i.e. the annihilation rate (in the independent particle model) is proportinal to the electron density.

- However, in reality positrons attract electrons:

$$\lambda = 1/\tau = \pi r_e^2 c n_- \gamma(n_-) \,,$$

  with γ being the so called enhancement factor, assuming also that enhancement depends on n_-.

- For a nonhomogeneous system

$$\lambda = 1/\tau = \pi r_e^2 c \int n_+(\boldsymbol{r}) n_-(\boldsymbol{r}) \gamma(n_-(\boldsymbol{r})) \, d^3\boldsymbol{r}$$

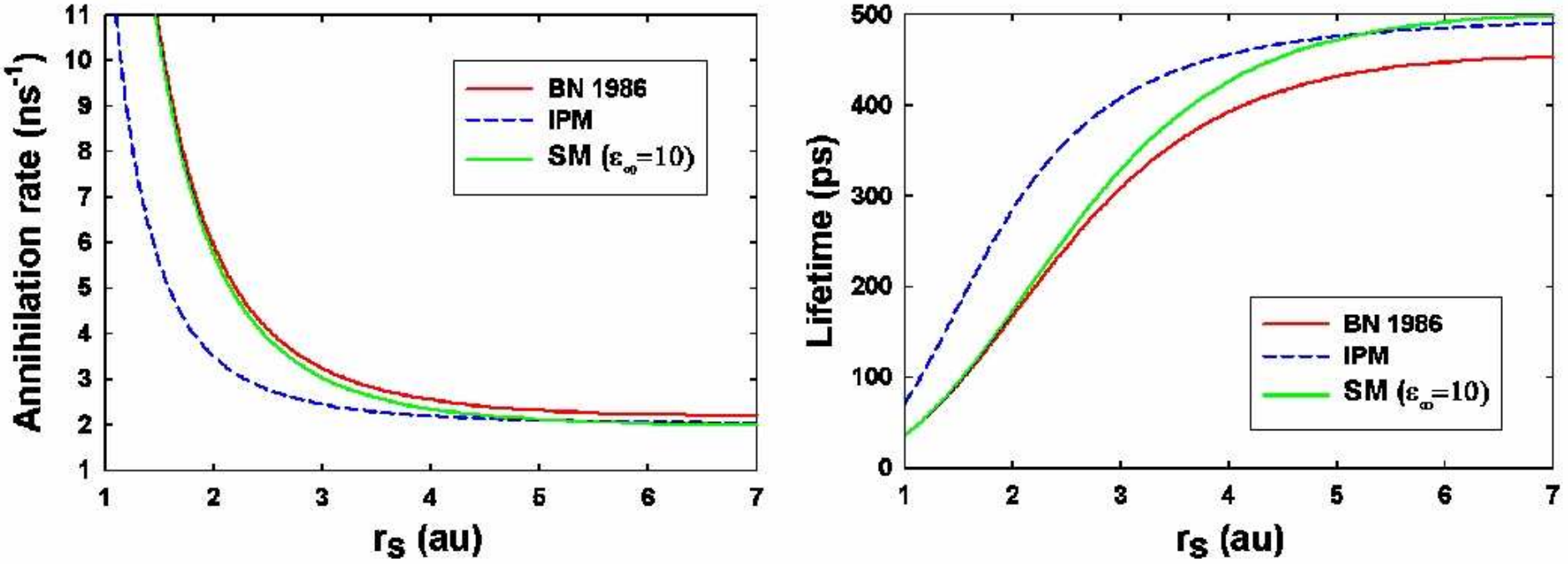
  considering that $\int n_+(\boldsymbol{r}) \, d^3\boldsymbol{r} = 1$.

Positron enhancement factor

- Again very frequently used expression is from Boroński, Nieminen (1986):

$$\lambda = \pi r_e^2 c n_- (1 + 1.23 r_s + 0.8295 r_s^{3/2} - 1.26 r_s^2 + 0.3286 r_s^{5/2} + r_s^3/6)\,.$$

- Dependence of the annihilation rate and lifetime:



- For small densities the annihilation rate (lifetime) approaches 2 ns^{-1} (500 ps) $\doteq \lambda_{p-Ps}/4 + 3\lambda_{o-Ps}/4$.

Momentum distribution calculation

- MD of e-p pairs = MD of annihilation photons is calculated as follows

$$\rho_{2\gamma} = \sum_{E_{-,j} \leq E_F} \gamma_j \left| \int \exp(-i\boldsymbol{p} \cdot \boldsymbol{r}) \psi_{-,j}(\boldsymbol{r}) \psi_{+}(\boldsymbol{r})\, d^3\boldsymbol{r} \right|^2 ,$$

  where $\gamma_j = \frac{\lambda_{ENH}}{\lambda_{IPM}}$ is the state dependent enhancement factor and

$$\lambda_{X,j} = \pi r_e^2 c \int n_+(\boldsymbol{r}) |\psi_{-,j}(\boldsymbol{r})|^2 \gamma_X(n_-(\boldsymbol{r}))\, d^3\boldsymbol{r} \,.$$

- The expression for $\rho_{2\gamma}$ can be simplified when only core electrons are considered. Then, an examination of positron annihilation with core electrons is possible in order to detect atomic environment of annihilation sites.

Positron binding energy to defect

- This is a useful quantity indicating how strong is positron bound to a defect.
- Binding energy is calculated as follows:

$$E_b = E_+(\mathrm{bulk}) - E_+(\mathrm{defect})\,.$$

- When the binding energy is too small, positrons may escape from such a defect (detraping), which depends also on temperature.

Positron affinity

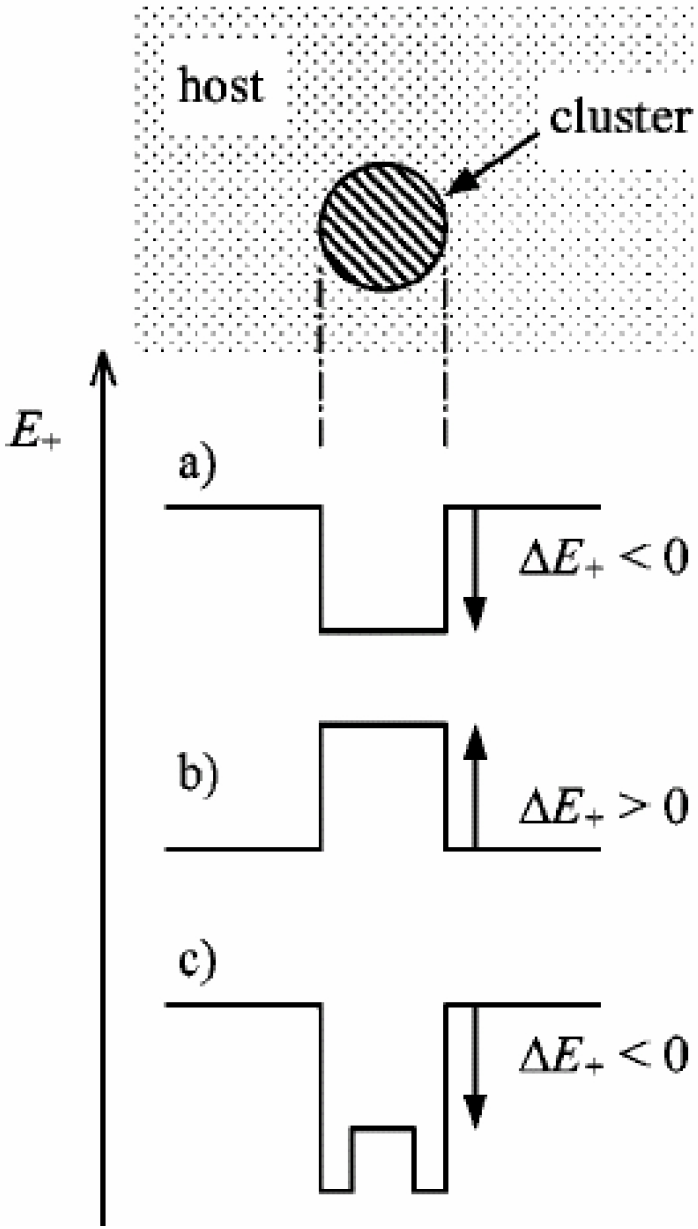
- When we have two materials (phases) in contact, the difference of positron affinities of these materials determines to which material the positron is attracted.
- The positron affinity is defined via electron and positron chemical potentials or work functions:

$$A_+ = \mu_- + \mu_+ = -(\phi_- + \phi_+)\,.$$

- The first expression can be easily calculated because $\mu_- = E_F$ and $\mu_+ = E_+$ considering the same reference level (crystal zero) for electrons and positrons.
- The second expression is more suitaible for measurements.
- The positron affinity of many materials is negative so that positrons may spontaneously escape from such materials (no extra energy is needed).

Positron affinity

- Positron affinity can be interpreted as a generalized positron energy.
- The picture shows ($A_+ \rightarrow E_+$) different cases of positron affinity relations between the host and cluster (precipitate).
- The precipitate can be attractive or repulsive for positrons.



Methods for positron calculations

- Virtually any electronic structure computational method can be adapted for positron calculations (PP (VASP), FLAPW (WIEN)).
- In some cases positron properties can also be obtained with a reasonable precision using a non-selfconsistent electronic structure.
- The so called atomic superposition (ATSUP) method is quite popular for simple and fast positron calculations.
  - It is not a real electronic structure method.
  - The electron density and Coulomb potential are approximated by the superimposed atomic densities and potentials on a regular 3D mesh covering the unit cell.

$$n_-(\boldsymbol{r}) = \sum_{\boldsymbol{R}} n_-^{at}(|\boldsymbol{r} - \boldsymbol{R}|)\,.$$

  - The positron potential is determined using the superimposed atomic Coulomb potential and electron density ($\rightarrow V_{corr}$).

Methods for positron calculations

- - The Schrödinger equation for positrons is solved using the variational principle, i.e. by minimizing the $\langle\psi_+|H_+|\psi_+\rangle$ functional directly on the 3D mesh.
  - A conjugate-gradient method is used for this purpose.
- Comparison of self-consistent methods with ATSUP:

	ATSUP	LMTO		FLAPW	
system	τ (ps)	τ (ps)	A_+ (eV)	τ (ps)	A_+ (eV)
C	94.0	96.7	-2.91	97.0	-2.86
Si	218.4	219.7	-7.14	219.1	-7.08
Fe	101.6	99.6	-3.86	100.9	-4.32
Cu	108.7	104.7	-4.66	106.3	-5.09

Lecture outline

Conclusions

- Positron annihilation is a unique tool to study open volume defects and may detect single vacancies in materials starting from about 1 ppm concentration.
- The size of open volume defects can be determined using positron lifetime.
- The atomic environment of PA annihilation sites can be found using momentum distribution measurements.
- Provided that a precipitate constitute a potential well for positrons, positrons may get trapped in them and can be often detected earlier than with other methods.
- Another advantage is that positrons are 'self-seeking' probes of defects.
- On the other hand, PA is an indirect method and a careful interpretation of experimental data in cooperation with theory is often indispensable.

Conclusions

- PA should be preferably combined with other experimental methods, especially in the case when many types of defects are present in the studied material.
- In irradiated materials, vacancies are primary products of irradiation and are involved in many processes.

- Theoretical methods are available for calculations of various positron characteristics.
- The level of precision of such methods is satisfactory though further improvements are desirable.
- Positron calculations are routinely used to interpret experimental data for basic types of defects.
- For materials with complex defect structure a coupling with structure simulation methods is highly desirable.
- In this case the atomic superposition method is a suitable tool to perform calculations for simulation boxes up to ~ 20000 atoms.

Thank you!