Electronic structure probed with positronium: Theoretical viewpoint

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2. Measuring Ps affinity

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  Stay positive.

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- Think like a positron.
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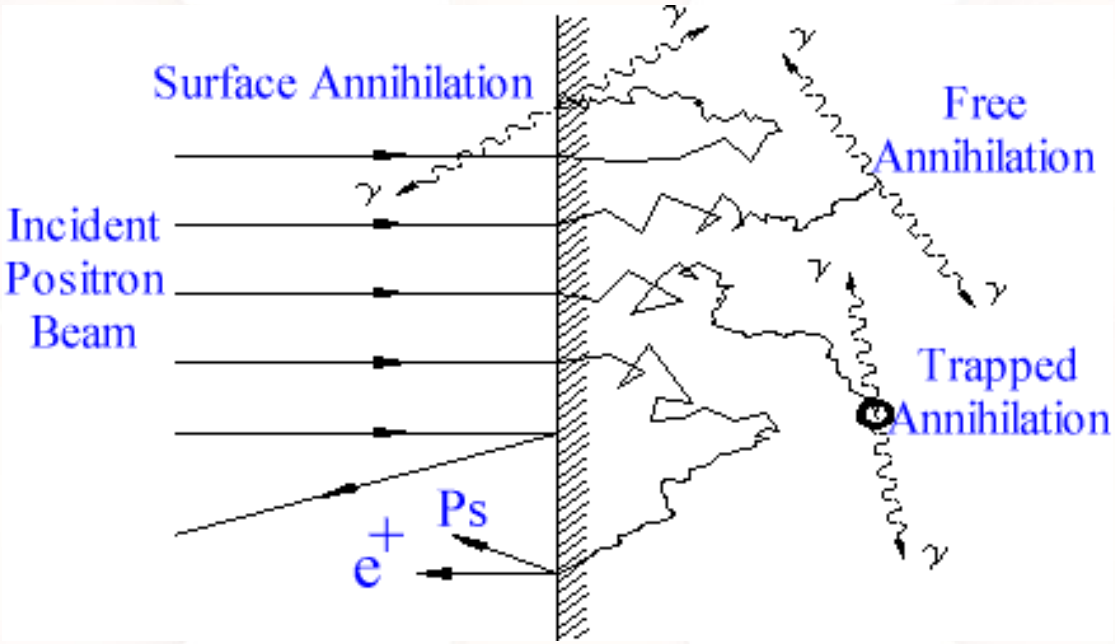
- Positrons may think in high energy way, . . .
  but may also think in low energy way.
- Positrons may get coupled with electrons and form positronium atoms (Ps) which are neutral objects.

Ps formation

- Ps atoms exist in two states:
  - singlet ($S = 0$; para-Ps), lifetime 125 ps,
  - triplet ($S = 1$; ortho-Ps), lifetime 142 ns.
- Many things may happen when a positron enters material via its surface:



- We are not interested in the details of Ps formation in the surface region.

Ps affinity

- The positronium affinity (A_{Ps}) is defined via the electron and positron work functions:

$$\begin{aligned} A_{\mathsf{Ps}} &= \Phi_- + \Phi_+ - E_{\mathsf{Ps}} \\ &= -(\mu_- + \mu_+) - E_{\mathsf{Ps}} \ , \end{aligned}$$

  with E_{Ps} ($\simeq 6.803$ eV) being the Ps binding energy in vacuum.
- Alternatively, A_{Ps} can be expressed via the electron and positron chemical potentials – fundamental material characteristics.
- μ_- and μ_+ can be calculated based on 'some theories'.
- Relations between Φ's and μ's: $\Phi_\pm = \mp\Delta - \mu_\pm$ ($\Delta =$ surface dipole).

- In case we are able to measure A_{Ps} 'at once', we avoid problems when measuring Φ_- and Φ_+ in separate experiments.

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Ps affinity measurement possible ?

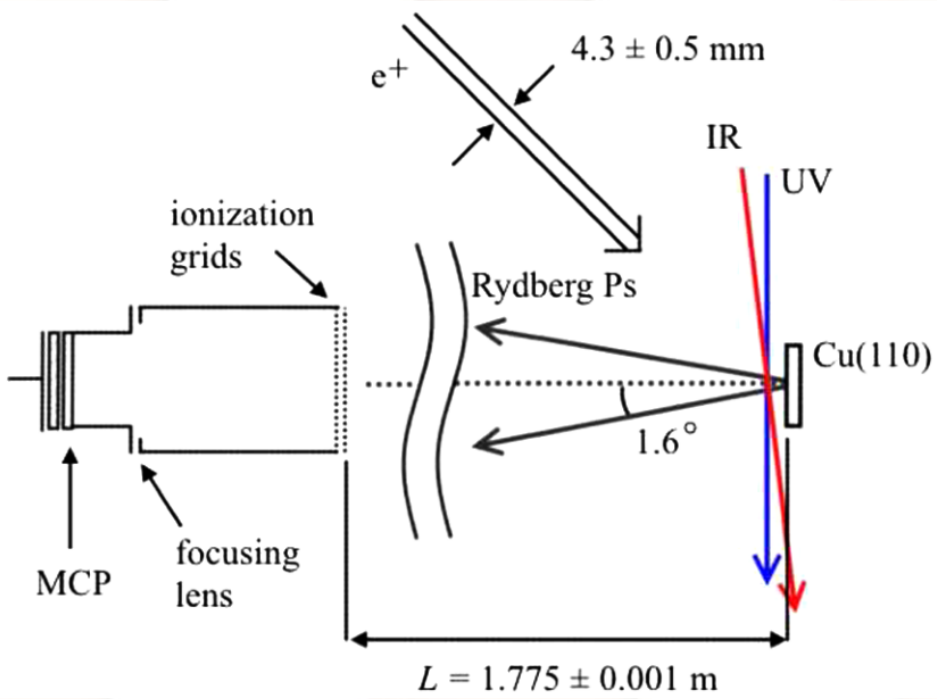
- In a typical positron beam experiment the surface of a material is bombarded with positrons; they thermalize, diffuse and may eventually leave surface as a Ps by capturing an electron.
- The maximum kinetic energy of emitted Ps atoms $E_K = -A_{\mathsf{Ps}}$.
- This means that the necessary condition for Ps to be emitted from a material is that

$$A_{\mathsf{Ps}} < 0 \ .$$

- A_{Ps} is a bulk property and does not depend on the surface at hand (if it is sufficiently clean).
- Since the surface dipoles for electrons and positrons have opposite signs and the same magnitude, it is unimportant that the surface is not perfect because A_{Ps} remains unaffected.

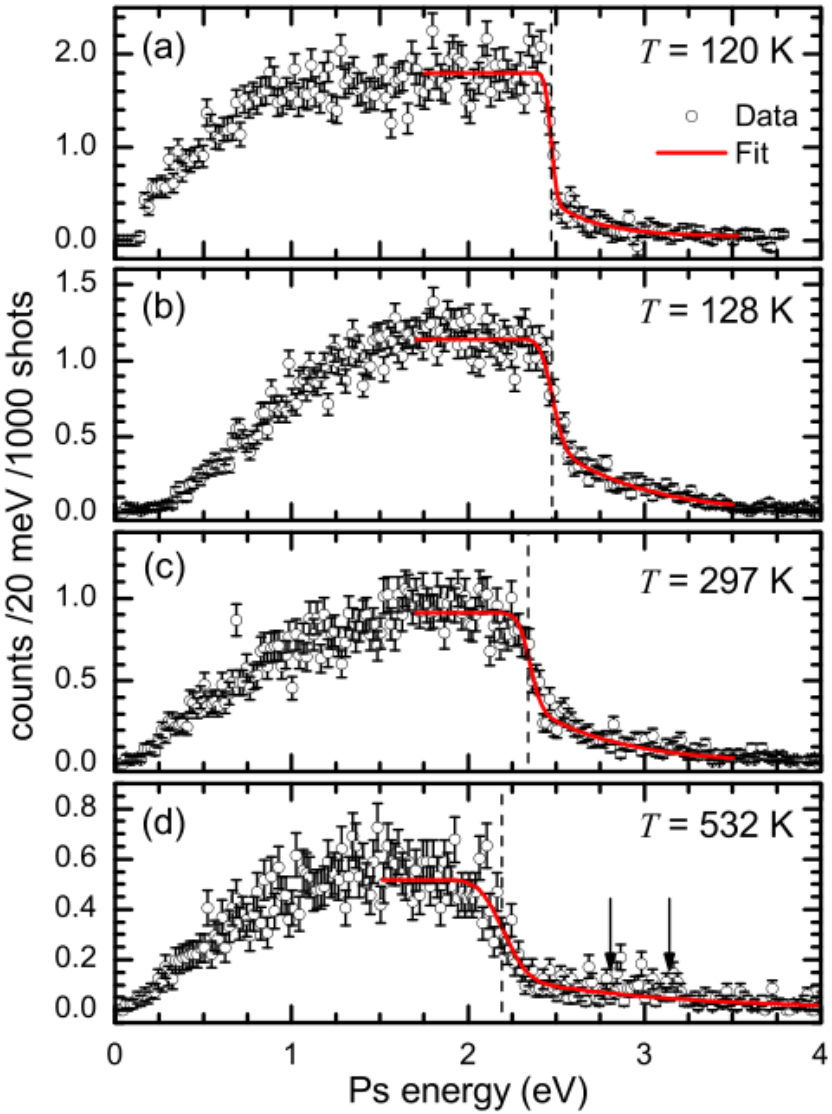
Apparatus at UCR

- The (110) surface of a copper single crystal was studied recently by a positron beam in order to find the Ps affinity.
- The description of the experimental setup at UCR is given in A.C.L. Jones et al., Phys. Rev. Lett. **117**, 216402 (2016).



Experimental spectra

- The spectra of emitted Ps atoms:



- Two implantation energies were tried (3 and 5 keV).
- For the later one a temperature dependence was examined.
- The spectra were fitted with an appropriate dependence in order to find E_K.
- The spectrum at 128 K was analyzed in detail since 'temperature effects' are small.

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Calculations of μ_-

- We employ the standard density functional theory for solids with an appropriate exchange-correlation functional.
- Kohn-Sham equations for electrons:

$$\left[-\frac{1}{2}\Delta_{\boldsymbol{r}} + \phi(\boldsymbol{r}) + V_{xc}[n_-(\boldsymbol{r})]\right]\psi^-_{i\boldsymbol{k}}(\boldsymbol{r}) = \epsilon^-_{i\boldsymbol{k}}\psi^-_{i\boldsymbol{k}}(\boldsymbol{r})$$

  with energy bands $\epsilon^-_{i\boldsymbol{k}}$ and corresponding wave functions $\psi^-_{i\boldsymbol{k}}$. $V_{xc}[n_-(\boldsymbol{r})]$ is the exchange-correlation (many-body) potential.
- The electron density

$$n_-(\boldsymbol{r}) = 2\sum_{\epsilon^-_{i\boldsymbol{k}}<\epsilon_F} |\psi_{i\boldsymbol{k}}(\boldsymbol{r})|^2\,,$$

  where ϵ_F is the Fermi energy.
- Finally, $\mu_- = \epsilon_F$.
- Note: There is also a 'nuclear DFT'.

Calculations of μ_+

- There is a generalization of DFT for electron-positron systems; here we use it in a simplified form.
- Positron Schrödinger equation:

$$\left[-\frac{1}{2}\Delta_{\boldsymbol{r}} - \phi(\boldsymbol{r}) + V_+[n_-(\boldsymbol{r})]\right]\psi^+(\boldsymbol{r}) = \epsilon^+\psi^+(\boldsymbol{r})$$

  with the ground state positron energy ϵ^+ and corresponding wave function ψ^+.
  $V_+[n_+(\boldsymbol{r})]$ is the electron-positron correlation (many-body) potential.
- The electron density

$$n_+(\boldsymbol{r}) = |\psi^+(\boldsymbol{r})|^2 .$$

- Finally, $\mu_+ = \epsilon^+$.

Positron correlation potential

- Recent progress in electron-positron correlation theory by Cambridge, UK group [Drummond et al., PRL **107**, 207402 (2011)] – LDA parametrization of the electron-positron correlation potential (and enhancement factor) based on many-body QMC simulations.
- Our contribution to electron-positron correlation theory [B. Barbiellini and J. Kuriplach, PRL **114**, 147401 (2015)] is used in the following calculations.
- A parameter-free gradient-correction (GGA) was introduced for the positron potential

$$V_+[n_-] = V_+^{\mathrm{LDA}} \exp(-\alpha\epsilon/3) \ ,$$

where ϵ depends on $|\nabla n_-(\boldsymbol{r})|$ and

$$\alpha[n_-] = -\frac{3}{16} \frac{\beta}{V_+^{\mathrm{LDA}}[n_-]} \ .$$

- This V_+ results in a significant improvement of previous empirical GGA schemes.

Theory vs experiment for copper

- A careful analysis of experimental data (128 K) for Cu (110) surface revealed that

$$E_K(128\,\mathrm{K}) = 2.476 \pm 0.010_{stat} \pm 0.013_{syst} \ \text{eV}\,.$$

- As for theory, it can be calculated (using the experimental lattice constant at 128 K) that

$$E_K(128\,\mathrm{K}) = 2.545 \pm 0.010_{num} \pm 0.010_{syst} \ \text{eV}$$

  using the so-called PBEsol XC functional [J.P. Perdew et al., Phys. Rev. Lett. **100**, 136406 (2008)].
- This represents and excellent agreement between theory and experiment (order 10 meV)!!
- Other XC functionals tested gives apparently worse results:
  – LDA: $E_K(128\,\mathrm{K}) = 2.196$ eV
  – GGA PBE: $E_K(128\,\mathrm{K}) = 2.762$ eV.

Meta-GGA calculations for copper

- In order to proceed, we attempted to find out whether some new XC functionals may improve agreement between theory and experiment for copper.
- Here we give first results for the new meta-GGA functional called SCAN [J. Sun, A. Ruzsinszky, J.P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015)].
- SCAN = "strongly constrained and appropriately normed"
- A meta-GGA XC functional depends on the kinetic energy density in addition to the electron density and its gradient.
- First calculations give even better agreement with experiment: difference between theory and experiment is now ~ 0.02 eV.
- In this way are coming to 'chemical precision' of theory/calculations!!
- Measuring A_{Ps} can be used as a sensitive test of XC functionals!

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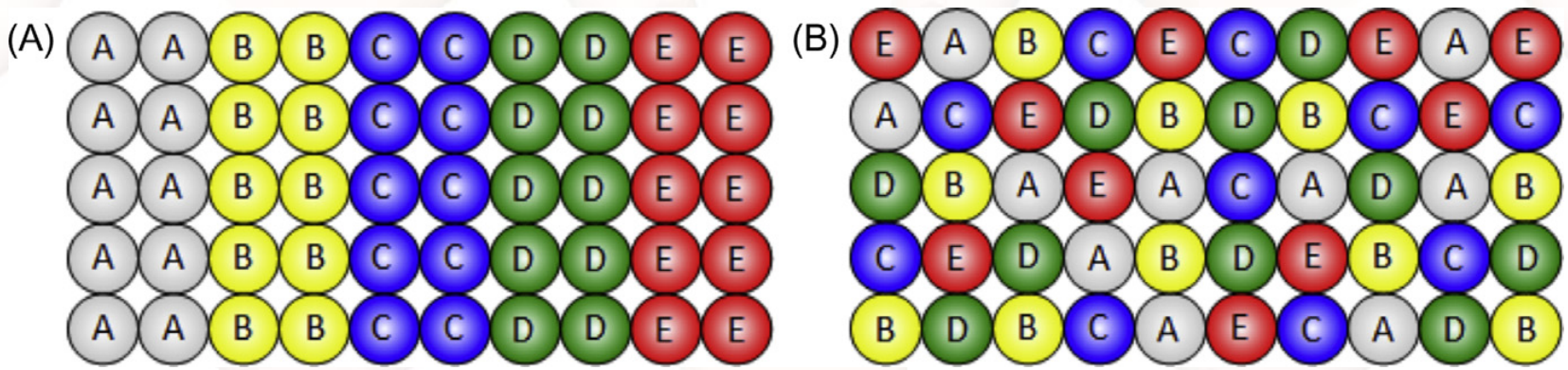
High entropy alloys

- High entropy alloys (HEA) – a new class of materials – exhibit many interesting and unexpected properties which require deeper understanding.

- Apart from defects, bulk electronic structure studies of alloys may also be useful.



High entropy alloys

- The name of HEAs comes from the fact that they exhibit high configurational entropy ($F = U - TS$).
- HEAs consist of several/many metals (at least 4 or 5) in nearly equiatomic concentrations.
- HEAs show very simple crystalline structures (typically fcc or bcc).
- Diffusion in HEAs is supposed to be relatively slow.
- There are large lattice distortions in HEAs.
- Improved mechanical and electrochemical properties are the main point of interest over conventional alloys.

- Information about local order may be obtained via Ps affinity measurements; expected differences in A_{Ps} due to ordering are of order 50 meV for NfNbTaTiZr refractory HEAs.
- The effect of spin-orbit coupling could be important.

Topological materials

- Topological materials are nowadays very popular due to various topological features in their electronic structure.
- We intend to explore some of them and check whether electronic structure is properly predicted using current XC functionals.
- For example, Bi_2Se_3 – a topological insulator – is probably not very prospective because A_{Ps} is likely positive.
- On the other hand, Heusler alloy Co_2MnAl – a half-metal with Weyl points – exhibits a negative $A_{Ps} < -3$ eV.
- Zr_2Te_2P is a candidate for 3D Dirac metal is also going to be examined.
- Na_3Bi is a prospective material for Na-ion battery (anode) material and shows several topological in its electronic structure.

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Conclusions and outlook

- Measuring precisely the Ps affinity provides a unique tool how to find electron chemical potential (supposing that the positron part is determined precisely as well).
- The electron chemical potential is a property that can be derived from the total energy and can be thus calculated using the DFT.
- In this way we can assess (from one point of view) the adequacy of chosen XC functional for a given system.
- The comparison of theory and experiment is becoming exceptionally excellent for copper indicating the quality of new XC functionals.
- More general view is that we can help testing XC functionals by measuring the Ps affinity.
- Interesting materials are being selected for future experiments and studying other features of electronic structure.
- Using spin-polarized beams information about magnetism could be obtained.
- Another direction is to look at electron-positron momentum distribution by using 2D-ACAR measurements.

Thank you!

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