Positron Annihilation in Metal Physics

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- History
- Means of Positron Annihilation
- Applications in Metal Physics
Discovery of the Positron

- Positron was predicted in 1928 by Paul A.M. Dirac
- Discovery in 1932 in cloud chamber pictures by C.D. Anderson
- Positronium as bound state of $e^-$ and $e^+$ lightest atom was predicted (1934) and discovered (1951)
- Annihilation in matter was studied beginning in the 40s
- Positrons can be obtained by
  - pair production from gamma radiation ($E_\gamma > 1022$ keV)
  - $\beta^+$ decay from isotopes (mostly $^{22}\text{Na}$)
- First identification of a positron in a cloud chamber
- 5 mm lead plate
- Photo taken by C.D. Anderson
Electron structure of solids can be discovered

- during annihilation: conservation laws must be fulfilled (energy, momentum)
- positron cools down to thermal energies →
- energy of annihilating electron-positron pair = energy of electron
- electron momentum distribution can directly be measured

**The Angular Distribution of Positron Annihilation Radiation**

**Robert Beringer** and C. G. Montgomery

*Sloane Physics Laboratory, Yale University, New Haven, Connecticut*

(Received January 7, 1942)
2D – ACAR (Angular Correlation of Annihilation Radiation)

- now: two-dimensional (position-sensitive) detectors
- measurement of single crystals in different directions:
- reconstruction of Fermi surface possible

\[ N_c(\Theta_x, \Theta_y) = A_c \int_{-\infty}^{\infty} \sigma(\Theta_x m_0 c, \Theta_y m_0 c, p_z) dp_z \]

- sophisticated device available at Univ. Delft
- intense positron source at reactor
- slow (moderated) positrons allow study of near-surface layers
2D-ACAR of Copper

Fermi surface of copper

(Berko, 1979)
Positrons are sensitive for Crystal Lattice Defects

- 1950...1960: in addition to ACAR -> different experimental techniques were developed
- Positron lifetime spectroscopy and Doppler broadening spectroscopy
- end of 60s: lifetime is sensitive to lattice imperfections
  - Brandt et al. (1968): vacancies in ionic crystals
  - Dekhtyar et al. (1969): plastically deformed semiconductors
  - MacKenzie et al. (1967): vacancies in thermal equilibrium in metals
- Positrons are localized (trapped) by open-volume defects

FIG. 1. Positron mean lifetimes in several metals as a function of temperature.
Vacancies in thermal Equilibrium

- Vacancy concentration in thermal equilibrium:
  - in metals $H^F \approx 1...4 \text{ eV} \Rightarrow$ at $T_{m \ [1v]} \approx 10^{-4}...-3 \text{ /atom}$
  - fits well to the sensitivity range of positron annihilation

\[ C_{1v}(T) = \exp\left( \frac{S^F_{1v}}{k} \right) \exp\left( \frac{H^F_{1v}}{kT} \right) \]

**Tungsten**

$H^F = (4.0 \pm 0.3) \text{ eV}$

(Ziegler, 1979)
Determination of Vacancy Formation Enthalphy

THERMAL VACANCIES IN THE NOBLE METALS Cu, Ag, Au, AND IN Pt STUDIED BY POSITRON LIFETIME SPECTROSCOPY

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- Arrhenius-Plot delivers \( H_{1V} \)
- was performed for many alloys
Vacancies and carbon impurities in α-iron: Electron irradiation

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FIG. 1. Positron-lifetime spectra after source-background subtraction in electron-irradiated \(6 \times 10^{18} \text{ e}^-/\text{cm}^2\) high-purity iron at various stages of isochronal annealing. The dramatic occurrence of a long-lifetime component after 230 K annealing is clearly visible.

- positron lifetime is very sensitive for vacancy-type defects
- here: lifetime increases after irradiation
- and further increase after first annealing: vacancy clustering
The positron lifetime spectroscopy

- positron wave-function can be localized in the attractive potential of a defect
- annihilation parameters change in the localized state
- e.g. positron lifetime increases in a vacancy
- lifetime is measured as time difference between appearance of 1.27 (start) and 0.51 MeV (stop) quanta
- defect identification and quantification possible
Positron lifetime spectroscopy

Positron lifetime: time between 1.27 MeV and 0.511 MeV quanta
• much simpler setup
• timing very accurate
• pulse-shape discrimination (suppress “bad pulses”)
• each detector for start & stop (double statistics)
screenshot of two digitized anode pulses

time difference = 2.65471 samples = 663.67 ps
Positron lifetime spectroscopy

- positron lifetime spectra consist of exponential decay components
- positron trapping in open-volume defects leads to long-lived components
- longer lifetime due to lower electron density
- analysis by non-linear fitting: lifetimes $\tau_i$ and intensities $I_i$

Count

\[
N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp \left( -\frac{t}{\tau_i} \right)
\]

\[
\kappa_d = \mu C_d = \frac{I_2}{I_1} \left( \frac{1}{\tau_b} - \frac{1}{\tau_d} \right)
\]

positron lifetime spectrum:

trapping coefficient

trapping rate

defect concentration

As–grown Cz Si

Plastically deformed Si

$\tau_b = 218$ ps (bulk)

$\tau_2 = 320$ ps (divacancies)

$\tau_3 = 520$ ps (vacancy clusters)
Sensitivity limits of PAS for vacancy detection

- **lower sensitivity limit** e.g. for negatively charged divacancies in Si starts at about $10^{15}$ cm$^{-3}$
- **upper limit**: saturated positron trapping
- defect identification still possible
- Then: only lower limit for defect density can be given
Doppler Broadening Spectroscopy

1. Positron lifetime

2. Angular correlation

\[ \Theta_{x,y} = \frac{p_{x,y}}{m_0 c} \]

3. Doppler broadening

0.511 MeV ± \( \Delta E \), \( \Delta E = \frac{p_z c}{2} \)
Measurement of Doppler Broadening

- electron momentum in propagation direction of 511 keV γ-ray leads to Doppler broadening of annihilation line
- can be detected by conventional energy-dispersive Ge detectors and standard electronics
Line Shape Parameters

S parameter:
\[ S = \frac{A_s}{A_0} \]

W parameter:
\[ W = \frac{A_w}{A_0} \]

W parameter mainly determined by annihilations of core electrons (chemical information)
Doppler Coincidence Spectroscopy

- coincident detection of second annihilation $\gamma$ reduces background
- use of a second Ge detector improves energy resolution of system

Martin-Luther-Universität Halle
Doppler Coincidence Spectra

\[ E_1 + E_2 = 2 \, m_0 \, c^2 = 1022 \, \text{keV} \]
Chemical sensitivity due to electrons at high momentum (core electrons)

- a single impurity atom aside a vacancy is detectable
- examples: \( V_{Ga} - Te_{As} \) in GaAs:Te

Martin-Luther-Universität Halle

High Sensitivity of CDBS for thin Layers

\[ I_{\text{ratio}}(E) = (1 - \eta) + \eta \cdot \frac{I_{\text{Sn}}(E)}{I_{\text{Al}}(E)} \]

- Sn layers of different thickness under 200 nm Al
- even very thin layers are visible

C. Hugenschmidt et al. PRB 77 (2008) 092105
Defects in Iron after tensile strength and fatigue treatment

- We performed an extensive study of defects in mechanically damaged iron and steel.
- Positrons are very sensitive: detection of defects already in the Hooks range of the stress-strain experiment.
- Vacancy cluster and dislocations are detectable in both cases.

Somieski et al., J. Physique IV 5, C1/127-134 (1995)
Laterally resolved measurement across Test sample

- Pure Fe sample
- strong damage already for strain < 100% of Hooke’s range -> technically most interesting range
- fraction zone can be predicted from positron measurements

Somieski et al., J. Physique IV 5, C1/127-134 (1995)
Vacancy clusters in semiconductors

- vacancy clusters were observed after neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) → positron lifetime increases distinctly
- example: plastically deformed Ge
  - lifetime: $\tau = 525$ ps
- reason for void formation: jog dragging mechanism
- trapping rate of voids disappears during annealing experiment

Krause-Rehberg et al., 1993
• there are cluster configurations with a large energy gain
• „Magic Numbers“ with 6, 10 und 14 vacancies
• positron lifetime increases distinctly with cluster size
• for $n > 10$ saturation effect, i.e. size cannot be determined

Vacancy clustering during defect annealing

- electron irradiated Fe
- clustering in early stage can be observed
- very sensitive: formation of divacancies and small clusters ($n < 10$)

**FIG. 2.** Positron-lifetime parameters as a function of the isochronal annealing temperature in the low-dose electron-irradiated pure iron.

• plastic deformation in LN2
• only gradual annealing (opposite to electron irradiation)
• two defects:
  - small vacancy clusters \((n < 10)\) - annealing at RT
  - dislocations anneal at 600 K

Precipitation phenomena in Al alloys

- Homogenization at 550°C dissolves Cu in Al
- Quenching to RT: oversaturation of Cu
- Equilibrium cannot be obtained at RT ($\Theta$-Phase: CuAl$_2$)
- Metastable particles are formed: $\Theta''$ (Guinier-Preston-Zones) and $\Theta'$
- Are fully coherent in the beginning
- Have extended strain field
- Obstacles for dislocation motion: hardness increases
- Transition to semi- or incoherent particles: stress field collapses
- Hardness decreases
Positron capture at Precipitates

(a) fully coherent
defect inside
semi-
or incoherent

GPZ in AlZn

(b) Mg-V-Paar in AlZnMg

(c) AlSi
Positron capture in GPZ in Al-Zn (6 at%)

- Quenching of Al-Zn (6at%) from \( \alpha \)-Phase: formation of fully coherent GPZ
- are free of defects (no vacancies, no dislocations)
- 1-dimensional ACAR curves
- Zn-content \( \eta \) of GPZ:
  \[
  N_{\text{AlZn}} = (1 - \eta) N_{\text{Al}} + \eta N_{\text{Zn}}
  \]
- Result: \( \eta = 70\% \)
- formation and dissolution of precipitations can be studied
Age-hardening of Al-Zn(15) at 100°C

- Aging at 100°C: Growth of GPZ
- start to get ellipsoidal
- strong hardness reduction
- positrons detecting dislocation at GPZ
- transition of fully coherent GPZ to semi-coherent $\alpha'_R$-particles
- positron detect directly the first misfit dislocation around the precipitate

R. Krause et al., 1985
Moderation of Positrons

Mean implantation depth of un-moderated positrons from a isotope $^{22}$Na source ($1/e$): Si: 100µm

- broad $\beta^+$ positron emission spectrum
- deep implantation into solids
- not useful for study of defects in thin layers
- for defect depth profiling: moderation necessary
- monoenergetic positrons can be implanted to different depth
Moderation of Positrons

W (110) single crystal foil (negative workfunction)

fraction

annihilation \( \approx 13\% \)

monoenergetic positrons \( \approx 0.05\% \)

fast positrons \( \approx 87\% \)

moderation efficiency: \( \approx 10^{-4} \)

 positron source

fast e+
The Positron Beam System at Halle University

- spot diameter: 5mm
- time per single Doppler measurement: 20 min
- time per depth scan: 8 hours
The positron beam system at Halle University

- beam valve
- differential pumping
- sample chamber
- magnetic beam guidance system
- $^{22}$Na Source
Study of Lubrication Defects

- Study of defects after lubrication treatment
- Steel ball on Cu surface
- Effect of lubricant

Subsurface zones created under lubrication conditions studied by positron annihilation

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Graphs showing positron implantation range (nm) vs. positron energy (keV) for different conditions.
Two intense positron sources available (positrons by pair production)

**NEPOMUC (NEutron induced POsitron Source MUniCh)** at FRM-II
- PLEPS (monoenergetic positron lifetime system)
- PAES (Positron-induced Auger Electron Spectroscopy)
- CDBS (Coincidence Doppler Broadening Spectroscopy)
- SCM (Scanning Positron Microscope)
- user beam line

**EPOS (ELBE Positron Source)** at Research Center Dresden-Rossendorf
- MePS (Mono-energetic Positron Spectroscopy)
- GiPS (Gamma-induced Positron Spectroscopy)
- CoPS (conventional setup using 22Na sources)

at both sites: web-based application system for beam time
Lateral Resolution with Scanning Positron Microscope

- lateral resolution 1...2 \( \mu \text{m} \)
- Positron lifetime spectroscopy
- lateral resolution principally limited by positron diffusion
  \((L_+ \approx 100\text{nm})\)

Munich Positron Scanning Microscope

W. Triftshäuser et al., NIM B 130 (1997) 265
SPM on top of cracked sample

Fatigue-Crack in Al 6013
Trapping at Mg / Si-clusters!

Only dislocations close to crack-tip!

\[ c_{\text{disl}} = 4 \cdot 10^{11} (\tau - 220 \text{ ps})/(240 \text{ ps} - \tau) \text{ cm}^{-2} \]

W. Egger, G. Kögel, P. Sperr, W. Triftshäuser, J. Bär, S. Rödlink, H.-J. Gudladt
EPOS = ELBE Positron Source

- ELBE -> electron LINAC (40 MeV and up to 40 kW) in Research Center Dresden-Rossendorf
- EPOS -> collaboration of Univ. Halle with FZD
- EPOS will be the combination of a positron lifetime spectrometer, Doppler coincidence, and AMOC
- User-dedicated facility
- main features:
  - high-intensity bunched positron beam ($E_+ = 0.5\ldots30$ keV)
  - very good time resolution by using the unique primary time structure of ELBE
  - digital multi-detector array
  - fully remote control via internet by user
Ground plan of the ELBE hall

1: Diagnosestation, IR-Imaging und biologische IR Experimente
2: Femtosekundenlaser, THz-Spektroskopie, IR Pump-Probe Experimente
3: Zeitaufgelöste Halbleiter-Spektroskopie, THz-Spektroskopie
4: FTIR, biologische IR Experimente
5: Nahfeld und Pump-Probe IR Experimente
6: Radiochemie und Summenfrequenz-Erzeugung, photothermische Spektroskopie
Cave 111b

- electron beam line
- electron-positron converter
GiPS: Gamma-induced Positron Spectroscopy

- 3 coincident setups were used: 2 AMOC and 1 CDBS spectrometer
- only coincident detection ensures high spectra quality
The GiPS setup includes 6 Detectors (4 Ge and 2 BaF$_2$)
Example: Water at RT

- Total count rate in spectrum: $12 \times 10^6$

Applications of GiPS since begin of 2009

- neutron irradiated Fe-Cr alloys (highly activated up to 50 MBq $^{60}$Co)
- Reactor pressure vessel steel samples from Greifswald nuclear power station
- Iron samples after mechanical damage (LCMTR-ISCSA-CNRS, Frankreich)
- set of Zircony alloys (Collaboration Mumbai/India)
- porous glass (Chem. Department/Univ. Leipzig)
- biological samples
- liquids
Variety of applications in all fields of materials science:

- defect-depth profiles due to surface modifications (ion implantation; tribology)
- soft matter physics (open volume; interdiffusion; ...)
- porosimetry (e.g. low-k materials - highly porous dielectric layers)
- bulk defects in semiconductors, ceramics and metals
- epitaxial layers (growth defects, misfit defects at interface, ...)
- fast kinetics (e.g. precipitation processes in Al alloys; defect annealing; diffusion; ...)
- radiation resistance (e.g. space materials)
- many more ...

This presentation can be found as pdf-file on our Website:
http://positron.physik.uni-halle.de