

Positron Annihilation Spectroscopy Applied to Materials Science and Engineering

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Keywords: Point defects, Extended defects, Doppler broadening spectroscopy, Positron annihilation lifetime spectroscopy, Structural and engineering materials, Nuclear and irradiated materials, Electronic and photonic materials.

Abstract. The high sensitivity of positrons to directly probe atomic scale defects revealing their structure and characteristics makes it a unique tool in materials science research covering all types of materials from hard to soft matter. This review focuses on applications of positron annihilation spectroscopy (PAS) in hard materials. However, it is not intended as a comprehensive review of the foundations of positron annihilation spectroscopy and description of its techniques. These exist in numerous publications cited in this review. Instead, the aim here is to facilitate employing PAS and interpretation of its measurements by illustrating the advantages, limitations, and challenges and guiding the reader on how to overcome technical problems and how to interpret PAS results in meaningful ways. Applications of PAS in electronic and photonic materials, nuclear and irradiated materials, and engineering materials are discussed. Examples are given to guide the reader on how PAS can be combined with complementary methods to uncover the fundamentals of defect physics and reveal interesting new phenomena in condensed matter.

Introduction

Positron Annihilation Spectroscopy (PAS) is one of the most powerful tools in a wide range of material science research almost covering characterization of all material types from hard to soft matter [1-9]. It is the perfect tool to characterize vacancies in metallic and ionic crystals, voids in porous materials, and free volumes in polymers. After losing its kinetic energy in materials, a positron annihilates with one of the material's electrons emitting 511 keV annihilation radiation; the principles of PAS are based on observing the electron momentum distributions and positron annihilation rates. The first is carried out by measuring the energy and angular distributions of the annihilation photons and the second is done by measuring their emission time relative to the time of positron injection into the medium corresponding to positron lifetime in the medium [10,11]. Measuring the energy and angular distributions of the 511 keV provides information about the electron states and momenta in materials while measuring the lifetime of positron (reciprocal of annihilation rate) provides information about the electron density function at the annihilation site. Because of that, PAS has been extensively used in the past to study electrons states and measure Fermi surfaces in metals and semiconductors [12-17]. However, after the discovery of positron trapping at defects [18], defect spectroscopy has become the predominant application of PAS as positron has unique capability in directly probing atomic scale open volume defects, quantifying them, and further revealing their structure and characteristics [19-21]. These defects play major roles in materials affecting their properties and performance in all applications. In the following I'll briefly discuss the significant role of defects in materials to appreciate how crucial positron spectroscopy of defects is to advance material properties and characteristics in a wide range of fields. A brief survey about defect spectroscopies will be presented and applications of PAS to measure defects in electronic and photonic materials, nuclear and irradiated materials, and engineering materials will be described. Since there are numerous literatures [22-24,1] on principles and description of PAS techniques, this review will mainly focus on the advantages, limitations and challenges of PAS and discuss potential problems that can complicate PAS measurements and analysis. One goal of this review is to

demonstrate how PAS can be strengthened by combining it with other characterization methods such as transmission electron microscopy (TEM) and electrical transport measurements. Examples will be given to show that the impact of PAS can go beyond defect measurements to revealing new phenomena and mechanisms in condensed matter and defect physics.

Defects In Materials-Role and Spectroscopy

Materials contain a variety of point and extended defects. Point defects include vacancy, substitutional, interstitial, Frenkel, and Schottky (Fig. 1). Extended defects include line defects such as edge and screw dislocations, surface defects such as grain and twin boundaries, and volume defects such as voids, cracks, and precipitates. These defects play great roles in materials. Firstly, point defects govern diffusion of atoms affecting the material thermal and transport properties [25,26]. In structural materials, point defects are the building blocks of damage formation. In functional materials, point defects dictate the electrical, optical, and magnetic properties [27-29]. Thus, probing, and characterizing defects is one of the important aspects of material science research. It is vital for the successful development of materials for devices, sensors, and detectors and in understanding damage mechanisms in structural materials to guide the research on improving existing materials or developing new materials suitable for extreme conditions of high mechanical loads, high temperature and pressure, high corrosion rate, high radiation, and high fields.

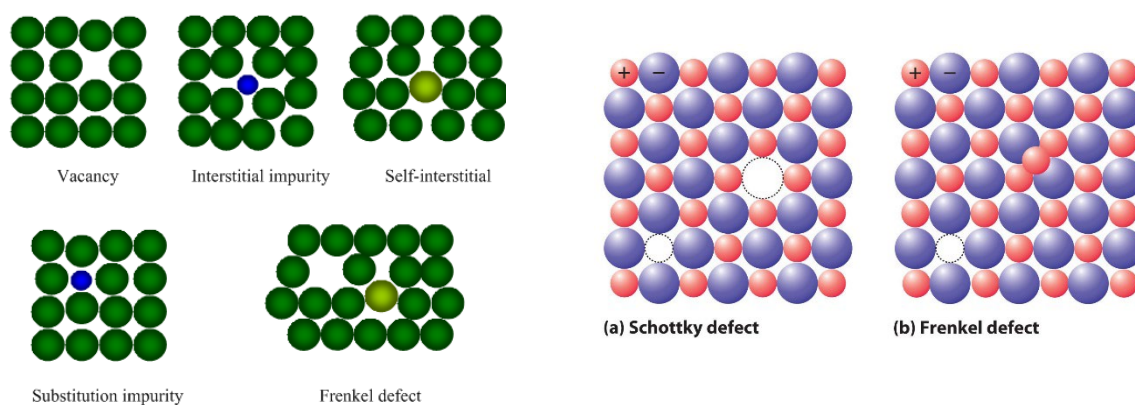


Fig.1. (a): Types of major point defects that may form in any crystal [<https://www.substech.com>] (b): Difference between Frenkel defects and Schottky defects that may form in ionic crystal [<https://chem.libretexts.org>]. Frenkel defects occur when some ions leave their normal position and occupy interstitial sites. Schottky defects occur when the same number of cations and anions are missing from their normal positions forming cation and anion vacancies in equal number.

It is worth to start by a summary of defect spectroscopy methods, however since the list is long, the focus will be on complementary or competitive techniques to PAS. Most defect spectroscopy techniques except for PAS and TEM are indirect, meaning they do not see defects directly, but they measure the change in properties or in the lattice or volume due to the presence of defects. For instance, electrical resistivity [30,31] probes defects through measuring the change in electrical resistivity providing useful information about defect concentrations, their annealing stages and dependence on temperature, but they cannot determine the type of defects or distinguish between them. To probe the presence of defects, measurements must be carried out at low temperature to suppress effect of thermal vibrations on resistivity. The defect concentration in a sample can only be determined by comparing resistivity between the sample and defect free sample. However, electrical resistivity method has been useful in determining the formation enthalpy of vacancies in metals [32]. Optical methods [33-40] that can be used for detection of defects are many, include but not limited to Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), optical absorption spectroscopy, photoluminescence, thermally stimulated luminescence and radiation induced

luminescence. They probe defects through the change in optical properties but are not applicable to all materials such as metals and alloys and often cannot see all defect types present in a sample. Ultrasonic spectroscopies [41,42] measure the effect of defects on the propagation of sound waves; they are not sensitive to small defects or low concentrations. X-ray and neutron scattering techniques [43-46] measure the change in scattering intensities of X-rays and neutrons due to the presence of defects but are highly affected by lattice stresses. Differential dilatometry can probe the presence of defects by measuring the change in volume [47]. Methods that are based on hyperfine interactions that use the electric and magnetic nuclear moments to probe defects include nuclear-magnetic-resonance, electron-paramagnetic-resonance, and perturbed-angular-correlation (PAC) [48-51]. Most of the aforementioned techniques are suited to certain types of measurements or materials but useless to others.

Two methods directly measure defects, TEM, and PAS. TEM directly images defects in materials [52], it can only detect nanometer defect size as conventional high resolution transmission electron microscopy (HRTEM) cannot see single vacancies or small vacancy clusters; it is a perfect tool for nanovoids and can image dislocations and grain boundaries with atomic resolution [53-55]. The associated analytical methods with TEM, such as energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), added great capabilities to TEM [56]. PAS is the other technique that directly probes defects; it has unique capability in seeing atomic scale defects and in measuring low concentration of defects of 10^{-7} [1]. It can measure open volume defects including vacancies, vacancy clusters, and dislocations, complex defects, small voids, and nanoclusters. Standard PAS measurements at room temperature are not applicable for probing interstitials and antistites.

Positron spectroscopy of defects

Two positron spectroscopy methods are commonly used in defect measurements [57], one involves measuring the energy distributions of the 511 keV peak resulting from electron positron annihilation and known as Doppler broadening spectroscopy (DBS). It is based on measuring the Doppler broadening of the 511 keV peak caused by the electron momenta. The other is positron annihilation lifetime spectroscopy (PALS) and based on measuring the lifetime of each positron in the medium from its entrance until death (annihilation). The capability of positron to probe defects is due to positron trapping at defects [58] and the subsequent characteristic changes in DBS and PALS spectra. In brief, positron trapping of defects leads to more annihilation with valence electrons causing less Doppler broadening of the 511 keV peak and longer positron lifetime because of the lower electron density in the vicinity of traps. In DBS the analysis is often reduced to the extraction of two parameters, S and W [1]. S refers to the shape of the 511 keV peak and represents a fraction of positron annihilating with valence electrons. W refers to the wings of the peak and represents a fraction of positrons annihilating with core electrons. Higher defect level leads to more positron trapping at defects and thus higher S parameter and lower W parameter. Accordingly, S parameter has been established as a clear indicator for defect levels in materials. Plotting S versus W is quite useful as it gives insight about changes in defect structures [59]. Simply points lie on the same line in S-W plots represent defects with similar defect structures though their density may be different. Points deviate from the straight line represent defects with different structure. In positron beam experiments, the 511 keV peak is recorded at each positron energy and S and W parameters are extracted and represented as a function of function of positron energy. A S versus positron energy relation gives information about positron diffusion length [60] which can be used to calculate defect density [1]. Further, DBS can give information about the chemistry of defects revealing their chemical environment and identifying the type of impurities by measuring the two emitted 511 keV photons in coincidence [61]. Such measurements reduce the background 4 orders of magnitude revealing positron annihilation with core electrons which are not affected by the crystal field and retain their elemental identity [62]. Since DBS is based on capturing the change in the 511 keV peak shape and measuring its broadening,

it requires measuring the 511 keV photons with very high energy resolution and watch and correct for any drift in the position of the 511 keV peak. Thus, high purity Ge (HPGE) detectors are the appropriate detectors in DBS as they can provide energy resolution close to 1 keV in the vicinity of the 511 keV peak.

PALS measurements provide the most detailed information about defect size and density [63-66]. They can identify the dominant defect groups in a sample revealing their structure, size, and density. Fig. 2 presents different locations where positron annihilates, and the corresponding positron lifetime in Fe. PALS is done by measuring how long each positron lives in the medium before annihilation. By following each positron, a positron lifetime spectrum or positron decay curve is recorded. In defect free material, the spectrum only contains one decay component corresponding to the bulk positron lifetime τ_B in this material. Fortunately τ_B has been calculated for most materials and has been verified by experimental results for many materials. As mentioned above positron trapping at defects lead to longer positron lifetime and additional longer lifetime components. The spectrum is fitted with the sum of exponential decays after convolution with the time-resolution function of the spectrometer and subtracting any background contributions. The extracted lifetime components are related to defect sizes and characteristics, and their intensities can be related to defect concentrations.

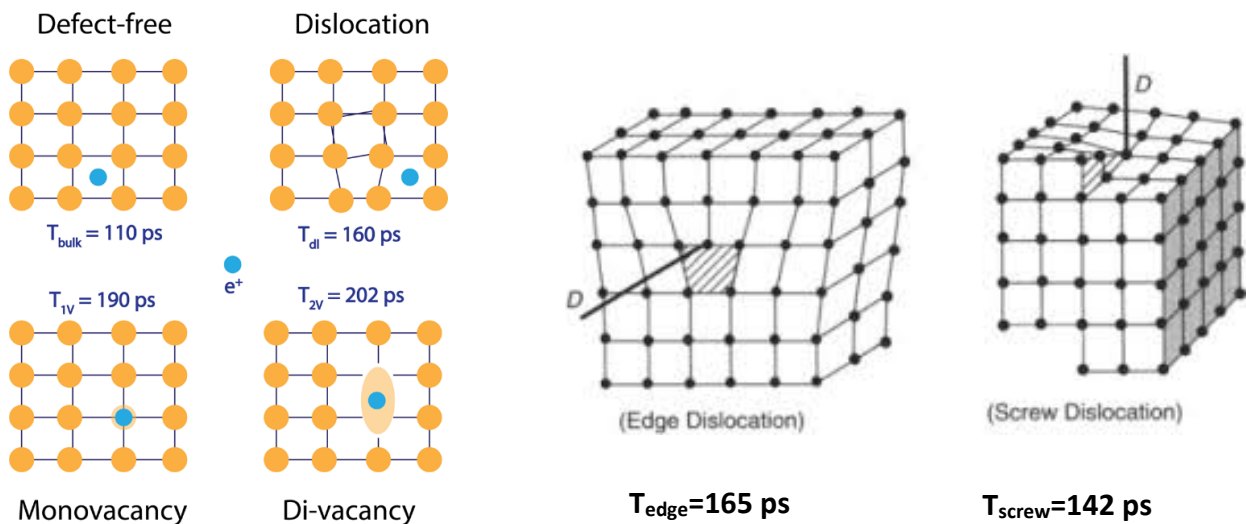


Fig.2. Positron lifetime values in the bulk and in different trapping sites in Fe illustrating the sensitivity of positron lifetime to the structure and type of defects.

Since positron only lives about 100-300 ps in most materials, PALS measurements require very high timing resolution less than 250 ps for metals, semiconductors, and related materials. BaF₂ detectors and plastic scintillators are used for bulk lifetime systems while CeBr₃ scintillator is a better option for positron beam-based PALS because of its high efficiency. Millions of counts are essential to allow a good fit for the spectrum and resolving its lifetime components. However even in case of the inability of resolving individual lifetime components, the average lifetime value extracted from the spectrum can provide insight about the defect size in the samples. It is important to understand that the validity of lifetime measurements is based on assuming one positron in the medium at any instant to prevent overlap of signals from different positrons. This limits the intensity of positron sources that can be used in bulk measurements. In positron beam-based PALS, the positron intensity is low, and only one positron is often present in each pulse; thus, there is no concern on overlapping signals from different positrons.

PAS advantages, limitations, and challenges in material science

The major advantages of PAS are its unique capability in measuring atomic scale defects and its high sensitivity in measuring low concentrations of defects down to 10^{-7} , thanks to its long diffusion length in materials. These two features make PAS an exceptional technique for a wide range of research in materials science. Additionally, it is a nondestructive technique, and the identification of vacancy type defects is straight forward. As mentioned above, positron directly sees open volume defects, not measuring their effect on specific properties such as other methods used for point defects. It has high probability to be trapped in a single vacancy revealing its size and structure; it distinguishes between single vacancy, di-vacancy, and vacancy clusters up to 50 vacancies guided by input from density functional theories (DFT). This makes PAS a powerful tool for damage formation and accumulation studies. Based on DFT results, it can also distinguish between different species of vacancies, for example Ti vacancy vs Sr vacancy and their complexes in SrTiO_3 or Al vacancy versus Y vacancy in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) laser material [67]. This makes PAS an effective tool for electronic and photonic materials. Positron trapping at defects is also sensitive to the charge state of defects rendering it a unique tool in semiconductors. Negative impurities represent shallow traps for positrons, they can be detected only in low temperature PAS measurements. Positron has also a unique capability in characterizing complex defects giving insight about their characteristics and charge states. Dislocations can be detected from PALS measurements as they lead to positron lifetime value higher than bulk lifetime and lower than single vacancy. Finally, many works have shown that positrons are drawn to nanoclusters revealing their structures and chemical identity [68-70], however this is probably dependent on positron affinity for their elements. The analysis of PAS results is straight forward, and defect density and characteristics can be calculated from the measurements by applying positron trapping models as the technique is well supported by theory and results from DFT calculations.

Three methods have been developed to enable PAS measurements in all structures and geometries. PAS can be performed in bulk materials using a standard Na-22 positron source [71] and in thin films, surfaces, and interfaces using slow positron beams and can provide depth resolved defect spectroscopy thanks to the development of variable energy DBS and PALS measurements [72,73]. It can be performed in thick materials up to cm using high energy gamma rays from accelerators - labeled gamma induced positron spectroscopy (GiPS) [73,74]. These various techniques extended PAS applications to a wide range of material science research [75].

The main use of positron spectroscopy of defects in materials science is to detect open volume defects. It is not suitable for probing interstitials or single impurities in materials except negative charge state impurities. As they act as shallow traps for positrons, they can be detected by temperature dependent PAS measurements down to cryogenic regimes, however its applications in this area have been very limited. The biggest limitation in PAS of defects is its poor spatial resolution; it is limited to the positron beam size which is mostly about a few millimeters; this is due to the lack of high intensity positron beams. However, the positron beam at NEPOMUC [76] has been an exception achieving 50 microns resolution. The discussion of spatial resolution for PAS using a Na-22 source is not convenient as it is mainly a probe for bulk samples providing characterization of defects distributed through the entire sample. In depth resolved PAS, the depth resolution is limited by the diffusion length of positrons, which is about 100 nm in most materials, however the presence of high defect levels in materials can reduce its diffusion length to less than 10 nm enabling better depth resolution for defect measurements.

The biggest challenge in PAS is that positrons are scarce. Being antimatter, it is hard to create them and challenging to keep them from annihilation with surrounding electrons. This limits positron beam intensities and thus hinders development of positron microscopy or diffraction applications. In PAS measurements and analysis, certain restrictions must be taken to reduce and eliminate potential errors. For instance, in bulk measurements the positron source must be sandwiched between two identical

samples to prevent 50% contribution from positron annihilation in the surroundings. Thus, PAS cannot be used for investigation of single bulk samples. Additionally in PALS, positron annihilation in the source and cladding materials often contribute $\sim 10\%$ to the measured lifetime spectra and must be accounted for correctly. In DBS, analysis of the 511 keV requires tedious fit for accurate background subtraction because of the asymmetry of the 511 keV peak (Fig.3).

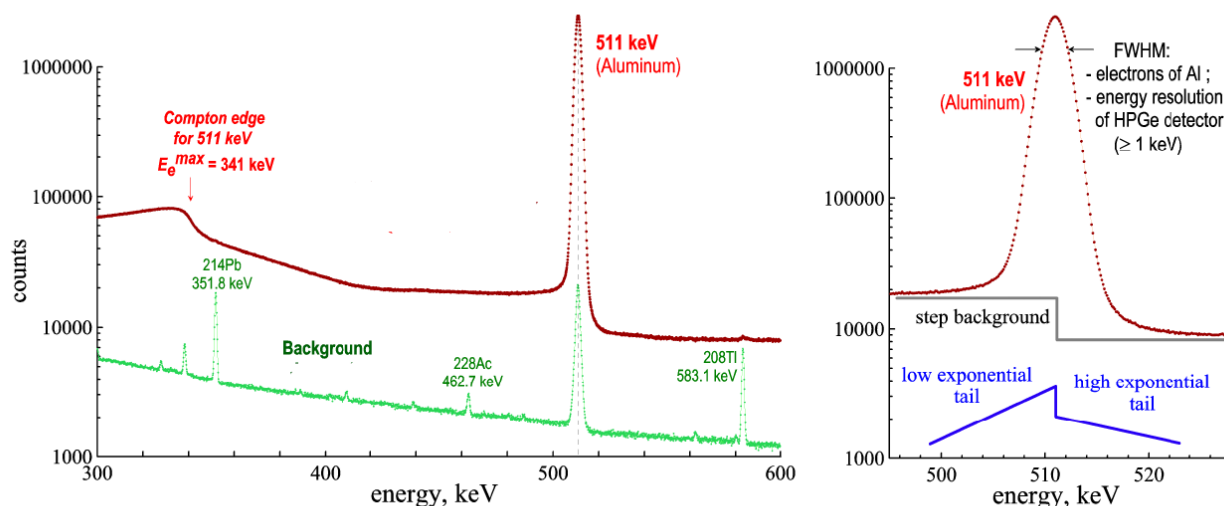


Fig. 3. DB spectrum measured in Al sample showing background contributions and the asymmetry of the 511 keV peak.

Safety precautions must be taken in bulk measurements using unsealed positron sources as they pose potential radioactivity contamination and require one to follow strict radiation safety regulations. Developing intense positron beams is perhaps the greatest challenge preventing PAS from reaching its full capabilities. Saturation of positron trapping occurs in the presence of high defect levels limiting and complicating data analysis. However, many previous studies showed that even in case of saturation of positron trapping at defects, DBS and PALS can still provide useful information about structure and evolution of defects in materials. Despite the aforementioned limitations and challenges, positron has been a very effective tool in material science. In the following I'll give examples of PAS applications and milestones in various material research.

PAS applications in functional materials

The fact that positron trapping at defects depends on the charge state of defects makes PAS a particularly useful tool in semiconductors; it has been very effective to study compensating defects in n-type semiconductors. Almost, PAS has been applied as a research tool in all semiconductors from elemental semiconductors Si, Ge, and their alloy SiGe [77,78] to III-V compound semiconductors including GaAs, GaN, etc [79,80] and oxide semiconductors such as ZnO and Ga₂O₃ [81-84]. It played a major role in understanding their defect physics and identification of compensating defects in them. I refer the reader to a few excellent reviews on defect identification by positron annihilation in semiconductors [2] [85-87].

PAS applications in nuclear and irradiated materials

The first application of positron in defect measurements was to investigate radiation damage induced by neutrons where PAS revealed the fundamentals of defect formation and their recovery in neutron irradiated materials [1]. Since fast neutrons pass through the entire sample thickness, they create

defects in the bulk not confined to specific layers. Thus, neutron irradiated materials are studied using positrons emitted from a Na-22 source. First measurements were carried out in 1972, right after the discovery of positron trapping at defects, and revealed the formation of sub-nanovoids in Mo and Al through PALS and ACAR measurements following neutron irradiation [88,89]. Positron spectroscopy of defects has extended to ion irradiated materials after the development of slow positron and variable energy positron beams, as ion irradiation induced defects are produced within thin layers of micro- or sub-micrometers and cannot be carried out using positrons emitted from the sources with broad energy distributions. Investigation of defects in nuclear and irradiated materials have been well documented in a previous review [1].

PAS applications in engineering materials

PAS offers a nondestructive sensitive tool for stress measurements in engineering materials and for evaluation of damage induced by mechanical loads. Positron is sensitive to dislocations, which are the principal types of defects in plastic deformation. Earlier works [90,91] proved evidence for positron trapping and annihilation at dislocation lines. T. Wider et al. [90] performed in-situ PALS measurements on Cu single crystals during tensile and fatigue tests. They reported threshold shear stress of 10 MPA during tensile test and 8 MPA during test fatigue to be seen by positrons. The 10 MPA corresponds to dislocation density of $3 \times 10^{12} \text{ m}^{-2}$ and mean dislocation spacing of 0.5 μm . Their positron lifetime measurements showed a linear increase in positron lifetime with increasing shear stress above the threshold value and no saturation was observed up to 43.5 MPA. PALS measurements have been also performed on austenitic stainless steel during tensile and fatigue tests and showed the capability of PALS in predicting early failures [91]. In these earlier applications a $^{72}\text{Se}/^{72}\text{As}$ positron source was used to provide higher energy positrons that can be transmitted through relatively thicker depths.

To extend PAS applications to thick engineering materials, accelerator based γ induced positron annihilation spectroscopy (AGPAS) or γ induced positron spectroscopy (GiPs) has been developed [74,92,93] where positrons are created directly inside the sample by pair production, then thermalize, diffuse, and annihilate with the material electrons emitting 511 keV radiation. The technique is based on combining the high penetration of γ -rays with the high sensitivity of positrons enabling defect measurements by PAS in thick materials of several centimeters and providing highly sensitive nondestructive probe for engineering and structural materials [94]. Fig. 4 compares S-parameter versus strain measured by GiPS with stress strain engineering curve of thick steel materials. It is interesting that S parameter- strain curve follows the same behavior of stress-strain curve indicating the sensitivity of positrons to plastic deformation and implying that S parameter can be used as a nondestructive probe for stresses in steel predicting the early stages of material failure. Because of the nondestructive nature of positron probe, this technique has the potential to be developed as a method for quality control of engineering materials. Several methods can be used to generate high energy γ -rays above 1.02 MeV required for PAS and can enable both PALS and DBS [95,96]. The technique has also shown to enable study of transient states in matter using positron annihilation [97].

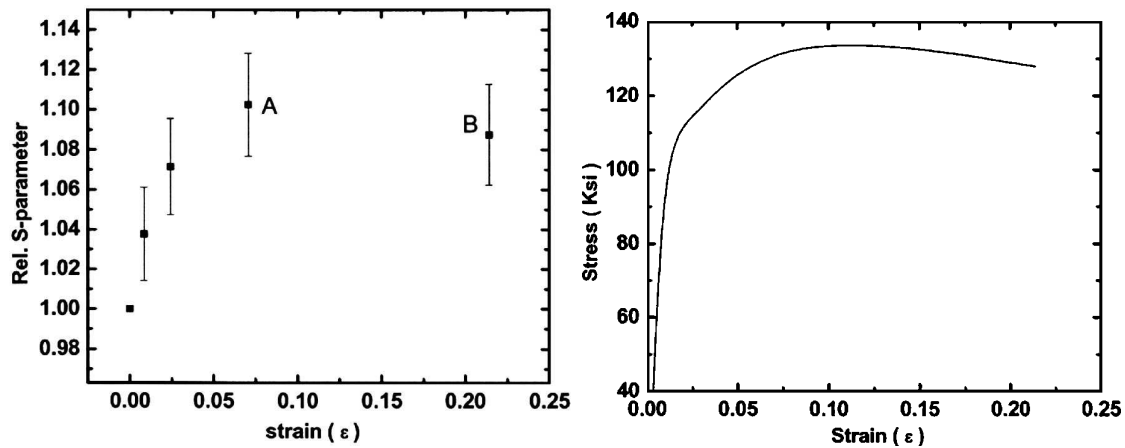


Fig. 4. Comparison of S-parameter vs strain curve with stress strain engineering curve in thick steel material [94] indicating that PAS can be developed as a nondestructive probe for stress measurements predicting the early stages of material failure.

New Physics Revealed by PAS

The high sensitivity of PAS and capability to probe atomic scale defects and measure the change in their structure, size, and characteristics including chemistry and charge state make it a unique tool in materials science revealing new physics in electronic and photonic materials and providing the mechanisms behind interesting phenomena in damage accumulation and recovery. This often requires combining PAS with measuring properties and other characterization techniques. I'll give several examples to illustrate that the impact of PAS can go beyond measuring or characterizing defects in both functional materials and structural/nuclear materials.

In functional materials, PALS measurements revealed an interesting phenomenon of light induced lattice relaxation in SrTiO_3 in the vicinity of vacancies [98,99]. PALS measurements before and after sub-band gap light illumination revealed that light changed the charge state of Ti-O vacancies and induced lattice relaxation and modification in the vacancy size causing large persistent photoconductivity in SrTiO_3 . In undoped a-Si-H, PAS measurements showed that light exposure modified hydrogen trapped in vacancy like defects to be mobile in the Si network [100]. Another example for interesting physics revealed through PAS is the phase transition in fullerene C60 where PALS and DBS showed that the expanding lattice from the C60 molecule undergoes a phase transition, and that three phases coexist over 10 K range [101]. Hydrogen passivation of defects has been detected in many important materials thanks to positron and found to strongly affect their electrical and optical properties [102-105] Figure 6 shows a cartoon illustrating how passivation of Ga vacancies in Ga_2O_3 by 2 H provides shallow acceptors and by 4 H provides shallow donors and DBS measurements revealing the difference between the two complexes [106]

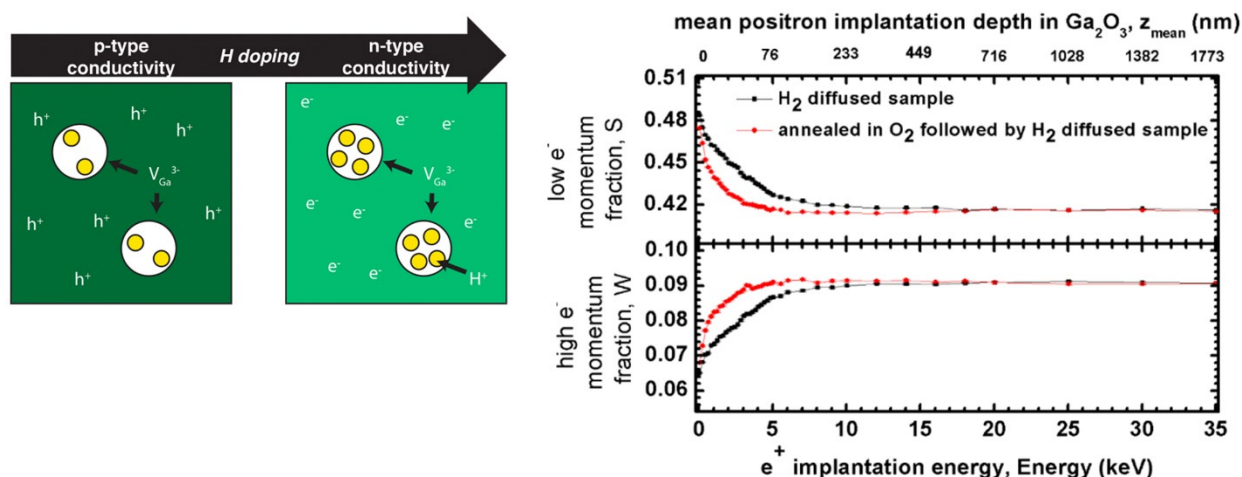


Fig. 5. (a) Schematic showing Ga vacancies passivated by two 2H providing shallow acceptors and Ga vacancies passivated by 4H providing shallow donors in undoped Ga_2O_3 . (b) DBS measurements showing a clear difference between the Ga vacancies with 2H and Ga vacancies with 4H [106]

In irradiated Fe films [107], combining PAS with HRTEM revealed a new unknown mechanism for the interaction of cascade damage with voids in ion-irradiated pure Fe (Fig. 6 a) as combining PAS with HRTEM allows us to measure defect on all length scale from atomic to mesoscale. In Fe/Fe₂O₃ heterostructures, it showed the effect of interface as a sink for radiation induced defects [108]. In FeCr alloys, combining PAS with atom probe tomography (APT) revealed that the high radiation resistance of Fe-Cr is due to the stabilization of individual vacancies and small vacancy clusters next to the Cr atoms (Fig. 6b). The study clearly showed that Cr atoms do not provide a direct sink for interstitials, but they form defect complex with vacancy clusters, which then act as sinks for radiation-induced defects [109]. In concentrated solution alloys, PAS revealed segregation of Ni at the early stages of irradiation [110] and segregation of Cr in deformed alloys [111]. In nickel alloys, impurity-induced vacancy clustering in cold-rolled samples was also revealed by PAS [112]. Such unknown mechanisms and phenomena that can be revealed due to the high sensitivity of positrons to atomic size defects place PAS in an exceptional position to guide the development of novel material systems with high strength and radiation tolerance.

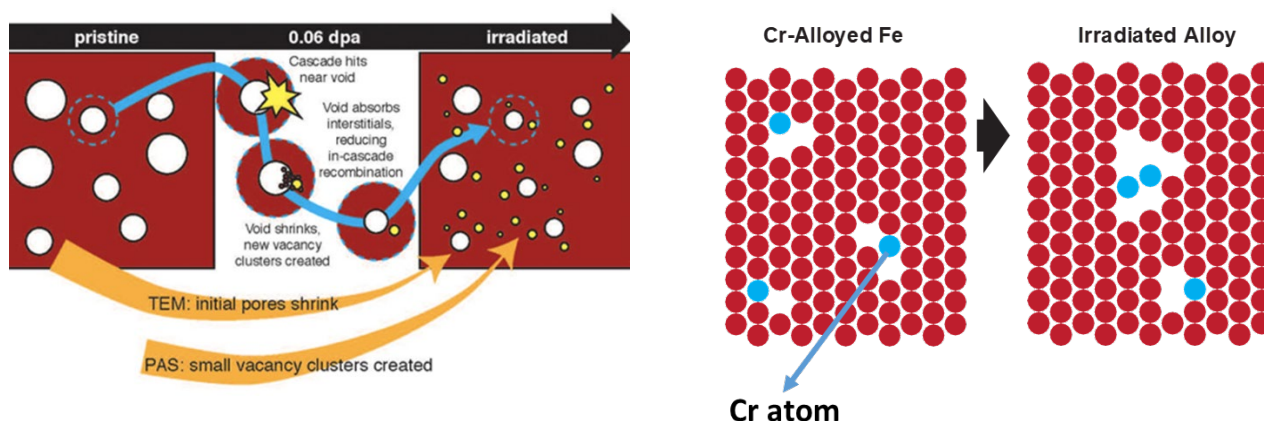


Fig. 6. (a) A cartoon illustrating a mechanism for interactions of radiation induced defects with voids in ion irradiated Fe films revealed by combining PAS and HRTEM. (b) A cartoon shows that the vacancy clusters formed next to Cr atoms in FeCr alloys act as sinks for interstitials and vacancies induced by irradiation and are responsible for the high radiation tolerance of FeCr alloys.

Acknowledgements

The author acknowledges support from: 1- FUTURE (Fundamental Understanding of Transport Under Reactor Extremes), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences 2- TETI (Thermal Energy Transport under Irradiation), an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, 3- the National Science Foundation (NSF) under grant number DMR- 2425965.

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