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# SLOW POSITRON SURFACE STUDIES

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## Abstract

Positron-electron annihilation in condensed matter provides a way to investigate the electronic structure, the annihilation characteristics depending on the electronic structure of the environment sampled by positrons. The relatively recent production of intense low energy positron beams has made the study of surfaces with positrons possible. The near surface region can be studied by implantation of slow monoenergetic positrons via positron electron annihilation and, in addition, via positron diffusion length measurements. This is a powerful method to study vacancy type defects in the near surface region because positively charged positrons are normally very efficiently trapped by vacancy defects. The experiments reviewed in this tutorial paper show that, by using slow positron beams, one can study (i) vacancy profile defects in the near surface region, vacancy defects at interfaces, (ii) electron momentum density, electron density of states and magnetism at surface, and (iii) surface structure.

Key words: Positron annihilation, Slow positrons, Positronium, Surface, Vacancy defects, Work function, Metals.

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## Introduction

The last decade has seen much exciting progress in the area of slow positron beams and, more recently, in their applications to the studies of surfaces. The first experiment designed to study positron annihilation at solid surfaces was reported in 1974 (Canter et al. 1974). Progress in the understanding of the positron surface interaction was linked to the production of intense slow positron beams under ultrahigh vacuum conditions ($10^{-9}$-$10^{-10}$ Torr). The first experiment of this type (Mills 1978) was rapidly followed by others which began clarifying the various processes of positron surface interaction (Mills et al. 1978, Lynn 1979, Mills 1979a). Some of these processes can be used as tools to analyse the surface. This is a new area of research, and the few experiments already completed with slow positrons have raised some interesting possibilities.Let us simply mention:

- implantation of slow positrons in the near surface region ($<<10^4$ A ) provides a unique method to study vacancy type defects in the near surface region (for a review see Mills 1983, Lynn 1983).

- positron annihilation at surfaces can be used to study the momentum densities of surface electrons (Howell et al. 1985, Lynn et al. 1985) and to investigate surface magnetism (Gidley et al. 1982).

- low energy positron diffraction (LEPD) and reemitted positron energy loss spectroscopy (REPELS) allow investigations of surface structure in a way comparable to low energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS) (Canter and Lynn 1984).

This paper explains and illustrates some of these various applications. It is organized in the following way. The first section gives the necessary background for understanding positron annihilation studies in materials. The second section presents technical aspects of slow positron beam production. The third section describes some of the processes of positron

surface interaction used to study surface or near surface region. The fourth section gives examples of vacancy defects studies in the near surface region. The fifth section reviews experiments that investigate surface structure.

## Positron annihilation in condensed matter

In this section, we recall how information on the electron density and the electron momentum density in materials can be drawn from positron-electron annihilation.

### Background

The existence of positrons was predicted by Dirac (1930) in his relativistic theory of electrons and discovered by Anderson (1932). Positrons are the antiparticles of electrons. This means that they have the same mass, the same spin but an opposite charge and that a positron-electron pair may annihilate into gamma-rays or may be produced by gamma-rays. In matter, positron-electron annihilation limits the positron existence. The positron lifetime, defined as the average time of the positron existence in materials, depends on the electronic density and ranges typically from $10^{-10}$ to $10^{-8}$ s. The annihilation gamma-rays carry away the momentum of the annihilating pair. Their energy and angular distribution is related to the momentum distribution of the annihilating pairs.

The annihilation process is studied from the number of emitted photons, two or three, from their energy and angular distribution or from the positron lifetime spectrum (see, for example, Hautojarvi 1979). In materials, positrons can annihilate from various states. The local electronic environment sampled by the positrons depends on these various states.

Positrons can be used as a bulk probe or as a surface probe according to the type of sources which are used. In bulk studies, the conventional positron sources are $\beta^+$ radioactive isotopes of long half lives (table 1). The source ($10^4$ to $10^6$ $e^+/s$) are placed near the studied samples or in contact with them. The $\beta^+$ decay positrons are emitted with a continuous energy spectrum and their energy (E<1 MeV) is sufficiently high for deep implantation (10 to a few 100 μm) in the sample. Surface studies require low energy positrons which are produced by moderating $\beta^+$ decay positrons in a target called a moderator. After production, the slow positrons are collected into a beam focused on the sample. Bulk studies are often referred to as standard positron studies because they began to develop as early as 1950. By comparison, the development of the technique to produce slow positrons took a long time. Slow positron beams sufficiently intense ($10^5$ $e^+/s$) to study solid surfaces were obtained only in 1974 (Canter et al. 1974).

An interesting property of positrons, due to their positive charge, is their ability to be trapped by vacancy type defects in matter. Positrons are a very useful probe of vacancies and of small vacancy clusters of n vacancies (n = 1, 2 ....30). Positron studies of defects are mainly developed in metallic compounds where they provide unique and useful information on vacancy clustering and vacancy-impurity interaction. In semi-conductors, where positron annihilation begins to be applied to defect studies, several interesting results have already been obtained. The positron behaviour in insulators is more complex than in metals and positron annihilation studies of defects are less advanced.

Positron annihilation in condensed matter is a huge field of investigation and numerous reviews have been published : see, for example, Wallace 1960, Goldanski 1968, West 1973, Seeger 1973, Brandt 1974, Hautojarvi 1979, Berko 1980, Siegel 1980, Byrne 1980, Stewart and Roellig 1967, Hasiguti and Fujiwara 1979, Doyama 1980, Coleman et al. 1982, Brandt and Dupasquier 1983, Jain et al. 1985.

### Annihilation from different states

After penetration in a solid, $\beta^+$ decay or slow positrons reach thermal energy in a very short time (a few $10^{-12}$ s) compared to their lifetime (Lee Whiting 1955 and , more recently, Brandt and Arista 1979, 1982, Brandt and Dupasquier 1983, Valkealathi and Nieminen 1983, 1984). Positrons are therefore thermalized when they annihilate. Electron-positron ($e^+$-$e^-$) pairs can annihilate from either unbound or bound states. A bound $e^+$-$e^-$ pair forms an atom called positronium. Hereafter, positron annihilation refers to the annihilation of unbound $e^+$-$e^-$ pairs and Ps annihilation to that of bound pairs. Ps annihilation occurs in non metallic materials. It is normally observed in insulators and at solid surfaces and was first discovered by Deutsch (1951). The mechanisms of positronium formation are still discussed (Mogensen 1979).

Table 1. $\beta$+ radioactive isotopes.

| Source | E endpoint (MeV) | Production | Half-lives | Fraction $\beta^+$ (%) |
|---|---|---|---|---|
| $^{22}Na$ | 0.54 | $^{24}Mg(d,\alpha)$ | 2.6 y | 90 |
| $^{58}Co$ | 0.47 | $^{58}Ni(n,p)$ | 71 d | 15 |
| $^{64}Cu$ | 0.65 | $^{63}Cu(n)$ | 12.8 h | 19 |
| $^{68}Ge$ | 1.88 | $^{66}Zn(\alpha,2n)$ | 275 d | 86 |

Positrons have annihilation characteristics distinct from positronium atoms. Unbound $e^+$-$e^-$ pairs, which are for 1/4 in para-spin state (S=0) and for 3/4 in ortho-spin state (S=1), annihilate into two Γ-rays because the 2Γ-annihilation cross-section (Ore and Powell 1949) is by more than two orders of magnitude larger than the 3Γannihilation cross section (Dirac 1930). Ps atoms self-annihilate from either para or ortho-states because in Ps the energy levels are doublets formed by a singlet para-state (S=0, p-Ps) and a triplet ortho-state (S=1, o-Ps). According to the selection rules, the p-Ps annihilate into two Γ-rays and the o-Ps state into three Γ-rays. In addition, the momentum and electron densities sampled by positrons in unbound pairs (Ferrell 1956, Chang Lee 1958, Taa Pra Sad 1973, Berko 1983) are different from those encountered in Ps pairs (Taa Pra Sad 1973, Dupasquier 1979, 1983).

Positively charged positrons are strongly repelled by positive ions in materials and they can be trapped in vacancy type defects which are regions where the ion density is lower than average. The annihilation characteristics of localized positrons are quite different from those of delocalized positrons in the perfect lattice and depend on the type of defects. "Vacancy defect spectroscopy " with positrons is based on this phenomenon.For instance, positron lifetimes in metals are typically about $10^{-10}$ s in bulk, $2 \times 10^{-10}$ s in vacancies, $5 \times 10^{-10}$ s in cavities. The increase of the lifetime reflects the lower electronic densities sampled by positrons localized in vacancy defects.

Positrons reveal the presence of vacancy type defects when the defect concentration is sufficient. For example, positrons detect vacancies in metals for concentrations above $5\times10^{-7}$/at ( Mackenzie et al. 1967) and cavities of diameters d≈40-50 A for concentrations above $10^{-8}$/at (Cotterill et al. 1972). The positron trapping in defects is characterized by a trapping rate proportional to the defect concentration: $k=\mu c$. The trapping rate per defect, $\mu$, depends on the type of defect and is often called specific trapping or capture rate.

## Annihilation parameters

Two kinds of annihilation parameters may be determined for the different positron states : (i)the positron lifetime (i.e.the inverse of the annihilation rate) and (ii) the distribution of the momenta of the electron-positron pairs.

Positron lifetime. The lifetime spectrum of positrons, n(t), is by definition the probability that, after penetration in a material at t=0, the positron has not yet annihilated with an electron at the time t. The lifetime spectrum corresponds to a single exponential decay component when positrons annihilate from one single state. When positrons can occupy several states, n(t) is generally a sum of exponential decay components:

$n(t) = \Sigma_i I_i \exp[-t\lambda_i]$ with $\Sigma_i I_i = 1$.

$\lambda_i$ characterizes the disappearance rate in the state i and $I_i$ the corresponding intensity. The average positron lifetime $\tau$ is given by the sum $\Sigma_i I_i \lambda^{-1}{}_i$. Annihilation from unbound pairs gives rise to lifetimes in the range $(0.1\text{-}0.5)\times10^{-9}$ s. Ps self annihilation gives rise to two lifetimes corresponding to p-Ps annihilation and to o-Ps annihilation. For the ground state in vacuum, the lifetimes are respectively of $0.125\times10^{-9}$ s for the p-Ps and of $140\times10^{-9}$ s for the o-Ps. In matter, the positron of the Ps atom can annihilate with an electron of the medium. This process, called electron pick-off, reduces considerably the o-Ps lifetime from $140\times10^{-9}$ s to $(1 \text{ to } 4)\times10^{-9}$ s.

From positron lifetime measurements, it is usually possible to determine the various positron annihilation states and so to investigate the concentration and the structure of vacancy defects.

Energy and momentum of positron-electron pairs. At the time of annihilation, the emitted photons carry away the total energy and momentum of the electron-positron pair. The photon energy spectrum for o-Ps annihilation is quite different from that measured for p-Ps or positron annihilation. In o-Ps annihilation, the three photons have a continuous energy distribution from 0 to $\approx mc^2$ ($mc^2$=511 keV, electron mass energy). In p-Ps or positron annihilation, the two photons are emitted in nearly opposite directions with the respective energy $mc^2+\delta E$ and $mc^2-\delta E$ and a simple relation exists between the energy of the photons and the momentum of the pair. The energy broadening $\delta E$ and the deviation $\delta\theta$ from the colinearity are proportional to a component of the pair momentum:

$$\delta E = cp_{//}/2 \qquad \text{tg}(\delta\theta) = p_\perp/mc \approx \delta\theta \qquad (1)$$

$p_{//}$ is the momentum component along the emission direction of the Γ-rays . $p_\perp$ is the momentum component perpendicular to the emission direction of the Γ-rays.

The momenta in the p-Ps ground state are very small. Therefore, the annihilation of delocalized thermalized p-Ps in a medium is characterized at low temperature by a very sharp peak centered at zero momentum value.

For positron annihilation, the delocalized positrons mainly encounter conduction or external core electrons of kinetic energy $E_-$<100 eV. One calculates, for example, with $E_+$ = 1/40 eV and $E_-$=100 eV, a total momentum $p=20\times10^{-3}$ mc which leads to $\delta E \lesssim 5$ keV and $\delta\theta \lesssim 20\times10^{-3}$. The momentum distribution of the electron-positron pairs mainly reflects the momentum distribution of electrons because the thermalized positrons have a narrow Maxwellian momentum distribution. From energy and angular correlation measurements, it is therefore possible to determine the momentum distribution of electrons which annihilate with positrons. In metallic compounds, Fermi surfaces can be studied from annihilation of delocalized positrons. They are investigated by angular correlation measurements which provide better momentum resolution than energy measurements.

When several annihilation states are in competition, the momentum distribution is an

average of the momentum distribution in the different states. It is usually difficult to resolve the various componenets. Consequently, in vacancy defect studies, energy and angular correlation measurements are therefore less powerful ways for identifying unknown defects than positron lifetime measurements.

Experimental techniques

As seen above, one can perform three kinds of experiments to study positron annihilation : 1) positron lifetime measurements; 2) measurements of the energy of the $\Gamma$-annihilation radiations ; 3) measurements of the angular correlation of two $\Gamma$-annihilation radiations . The techniques used in these three types of experiments are shortly described below. For more details, the reader is referred to the references given above.

Positron lifetime. In positron lifetime measurements, one measures the number of annihilations which occur at time t after the positron penetration in the material. Positron lifetime measurements require a signal which marks the entrance time of the positron in the target and a signal which marks its annihilation time.

In standard bulk studies, a $^{22}Na$ radioactive source is sandwiched between two similar specimens in close contact with them. The entrance of the positron in the specimens is marked by the 1.28 MeV $\Gamma$-ray emitted with the positron . The time t between the detection of the 1.28 MeV $\Gamma$-ray in a scintillator and the detection of the subsequent 0.511 MeV annihilation $\Gamma$-ray in a second similar scintillator is measured by using a conventional time-to-amplitude converter and a mutichannel analyser.

In surface studies, where the target is far away from the positron source, one uses the detection of secondary electrons ejected by the incident positron hitting the surface. These secondary electrons are detected in a channel electron multiplier which delivers the start signal for the time-to-amplitude converter (Gidley et al. 1982, Lynn et al. 1984). Such spectrometers have broader resolution function than the spectrometers using the 1.28 MeV $\Gamma$ - rays as the start signal.

The lifetime spectra are analysed by fitting the data to a sum of exponential components convoluted with the resolution function of the spectrometer. In bulk studies, the different exponential components can be resolved with a high accuracy, which provides a powerful method to identify vacancy defects. This is not the case in surface studies where some of the decay components must be constrained (Lynn et al. 1984). The construction of positron lifetime spectrometers using pulsed and bunched slow positron beams ( pulse width around $10^{-10}$ s) is in progress (Mills 1980a, Schodlbauer 1985). Such spectrometers will give more accurate lifetime measurements in surface studies.

When Ps annihilation competes with positron annihilation, different methods are used for extracting the Ps fraction from the lifetime measurements (Dupasquier 1983). Sometimes the detection of $3\Gamma$-annihilation, which provides a unique signature of Ps annihilation (see above), is preferred to evidence Ps annihilation. The $3\Gamma$-rays are generally detected in coincidence in three energy sensitive detectors at 120° from one another ($E_\Gamma \approx 341$ keV since $p_{Ps} \approx 0$).

Energy measurements. One counts the number of $\Gamma$-rays emitted with a given energy E. Energy measurements are generally performed using Ge(Li) or intrinsic high purity Ge detectors with energy resolution around 1 keV. NaI(Tl) scintillators with higher efficiency but lower energy resolution (40 keV at 511 keV) are also used.

The entire energy spectrum is recorded for the study of the 3 $\Gamma$-annihilation. The energy profile has the typical shape seen in figure 1 with a marked peak around 511 keV. Generally, only a fraction of electron-positron pairs annihilate from positronium state. One has therefore to extract the fraction of positronium annihilation contributing to the energy spectrum.

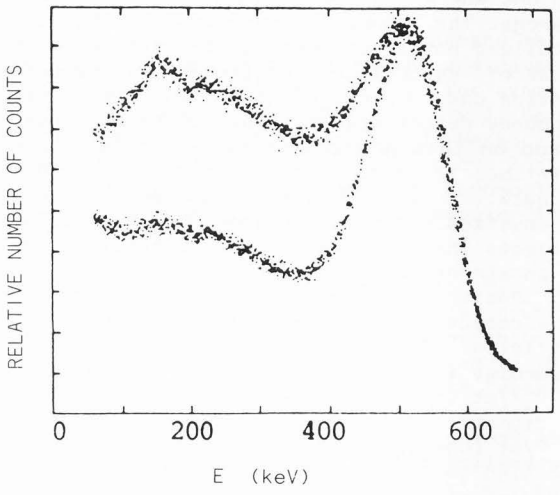



Figure 1 Energy spectrum of annihilation radiations in presence of x% (upper curve) and 0% (lower curve) of o-Ps. The peak region corresponds to the range 485 to 530 keV. After Lynn (1983).

The determination of the Ps annihilation fraction is based on the change of the probability of annihilation events in the 511 keV peak between 100 % of Ps annihilation and 0 % of Ps annihilation (figure 1). This method is usually used to determine the fraction of Ps annihilation in surface studies. A detailed and critical analysis of this method has been recently given by Schultz et al. (1984).

Only the Doppler broadening of the 511 keV $\Gamma$-rays, i.e. the energy profile in the peak region (figure 1), is measured for positron or p -Ps annihilation studies using a high resolution Ge detector.

Angular correlation of 2 $\Gamma$-annihilation radiation. In $2\Gamma$-ACAR experiments, the two $\Gamma$-rays emitted in nearly opposite directions are

detected in coincidence in a pair of similar counters. The number of coincidences is recorded as a function of the angles between the two directions of the $\Gamma$-rays. According to the type of counters, one obtains a counting rate proportional either to a one dimensional (1D - ACAR) projection or to a two -dimensional (2D-ACAR) projection of the electron momentum distribution.

In 1D-ACAR, the $\Gamma$-rays detectors are usually NaI (Tl) scintillators behind lead slits which define the resolution width of the apparatus. In 2D-ACAR detector, systems sensitive to the impact position of the $\Gamma$-ray are used : multidetectors of 64 NaI (Tl) scintillators (Berko et al. 1977, Berko 1980),multiwire proportional chamber (Manuel 1983), Anger camera (West 1980). The momentum resolution obtained in angular measurements , about $\delta p \approx 0.4\ 10^{-3}$ u.a.m., is one order of magnitude higher than in energy measurements.

In metals, Fermi surfaces can be reconstructed from 2D-ACAR profiles measured in single crystals with different orientations. The 2D-ACAR technique is unique to study Fermi surfaces in alloys (Berko 1983). The 2D-electron positron momentum distributions have been recently measured at metallic surfaces using Anger cameras (Lynn et al. 1985, Howell et al. 1984, 1985).

Summary

In this section, we have introduced some basic aspects of positron annihilation and described the standard measurements perfomed to study positron annihilation in materials. Positron lifetime measurements give information on the electron density in materials. Energy or angular correlation measurements yield information on the momentum density of electrons which annihilate with positrons.

Annihilation characteristics depend on the positron state in materials. Positrons are trapped by vacancy defects in localized states. This provides a way for investigating vacancy type defects via positron annihilation.

Positrons are widely used in condensed matter for measuring Fermi surfaces and for investigating vacancy type defects on an atomic scale. In solutions, chemical reactions between ions and positrons, or Ps atoms, are studied.

We will see in the following sections how information on the positron diffusion length can be obtained from the implantation of slow positrons in a solid. We will also see how the measurement of the flux of positrons diffusing to a surface can be used for investigating vacancy type defects in the near surface regions ($<<10^4$A ).

## Slow positron beam production

In a slow positron apparatus, the low energy (0-3 eV) positrons, after production, are accelerated to various energies (0-100 keV) and collected into a beam before striking a target. For surface studies, these operations are performed under ultra-high vacuum ($10^{-9}$-$10^{-10}$ torr). Since the first experiment using a slow positron beam under ultra-high vacuum, several other beams of this type have been constructed (see, for example, Lynn and Lutz 1980, Rosenberg et al. 1980, Trifsthauser and Kogel 1982, Howell et al. 1982, Vehanen et al. 1985). A slow positron apparatus can be divided into three parts (figure 2a): 1). a source chamber where the low energy positrons are produced, 2). a transport line in which the slow positrons are accelerated and guided by electrostatic or magnetic systems, and 3). a target chamber where the experiments are performed. These three parts are shortly described hereafter.

Source chamber

In the source chamber, fast positrons, obtained either from a $\beta^+$ radioactive source ($E<1$ MeV) or from $e^+$-$e^-$ pair produced from Bremsstrahlung, are converted into low energy positrons through a solid moderator. In the existing systems various $\beta^+$ radioactive sources are used : $^{11}C$, $^{58}Co$, $^{22}Na$, $^{64}Cu$, $^{68}Ge$, with activities of several tens mCi. For pair-production positrons, the source chamber is associated with a high energy electron accelerator providing 100-200 MeV electrons. Electrons are stopped in a thick ($\approx$1cm) target, positioned close to the moderator, and generate Bremsstrahlung from which $e^+$-$e^-$ pairs ($E\approx 10$ MeV) are produced (Howell et al. 1982, 1983, Begeman et al. 1982, Graff et al. 1984).

Materials for which positrons have a negative affinity can be used as moderators. After penetrating into the moderator the fast positrons slow down and thermalize. A fraction of the positrons stopped near a surface can diffuse to this surface before annihilation and escape from the target at nearly thermal energies. The efficiency of the moderation, $\varepsilon$, is defined as the ratio of the number of reemitted slow positrons per unit time to the number of positrons emitted from the source. $\varepsilon$ is expected to be of the order of the ratio of the diffusion positron length $l_+$ ($l_+\approx 0.1$ µm) to the mean implantation depth $z^*$ ($z^*\approx 0.1$ to 100 µm).

A detailed review of the development of moderators can be found in Mills 1983. First attempts for producing slow positrons by moderation were reported as early as 1950, but until 1972 the efficiency of the moderation was too low for application of positron beams to surface studies. Canter et al. (1972) reported an efficiency around $3\times10^{-5}$ with a moderator consisting in MgO-coated gold foils arranged in a Venetian blind geometry. The low energy positron beam obtained with this moderator was sufficiently intense to study the interaction of slow positrons with solid surfaces (Canter et al. 1974). Investigations of the positron reemission process from a solid surface struck by slow positrons in ultra-high vacuum enabled one to guide the choice of materials to be used as moderator (Canter and Mills 1982, Mills 1983, Lynn 1983, Vehanen et al, 1983). Metallic ultra-pure single crystals are at the present time

considered as excellent moderators providing efficiencies around $10^{-3}$ (table 2). We will see below that the reemitted slow positron yield depends critically on the bulk and surface properties of the moderator.

The slow positrons can be emitted from the moderator either through the entrance surface of the incident fast positrons, or, through the opposite surface. In the case of reemission through the entrance surface, the stopped positrons diffuse in the direction opposite to their initial penetration direction and the emission is often referred to as "back reemission". Most of the existing beams use the "back reemission geometry". The advantage of this geometry is to reduce the fraction of non thermalized reemitted positrons to the small fraction of backscattered incident positrons. "Forward emission" is considered to build very intense ($> 10^{64}$ $e^+$/s) beams. The high brightness of such beams is achieved by successive stages of moderation, acceleration and focusing (Mills 1980b, Canter and Mills 1982, Mills and Wilson1982, Lynn and Wachs 1982, Mills 1983, Lynn and Frieze 1983, Frieze et al. 1985a).

In spite of the loss of intensity, the positron beam brightness increases after a moderation process due to the important reduction of the beam energy and, for some moderators, of the beam angular divergence. The emission cone around the normal of the surface and the energy distribution of positrons depend on the nature of the moderator. For example, for a single Cu (111) crystal with partial sulfur overlayers, one has $\delta\theta \leq 15°$, $\delta E \leq 0.25$ eV (Mills 1979a, 1979b, 1980c). In many cases, the slow positrons are reemitted in a narrow cone (a few 10°) around the normal to the surface with narrow energy (FWHM $\leq$ 0.1 eV) distribution (Fischer 1984). As regards the applications of the beams, such properties of the moderator, in addition with the efficiency coefficient, can be interesting to consider when choosing a moderator.

An interesting property of the moderation process is that the reemitted slow positrons can be partially polarized when the initial fast positrons are polarized. It is the case for decay positrons and their polarization can be partially preserved during the interaction with the target (Zitzewitz et al. 1979). It is possible to obtain slow positron beams with polarization up to 0.5 (Van House et al. 1984, Van House and Zitzewitz 1984). Such beams are interesting for surface magnetism investigation.

Transport line and target chamber

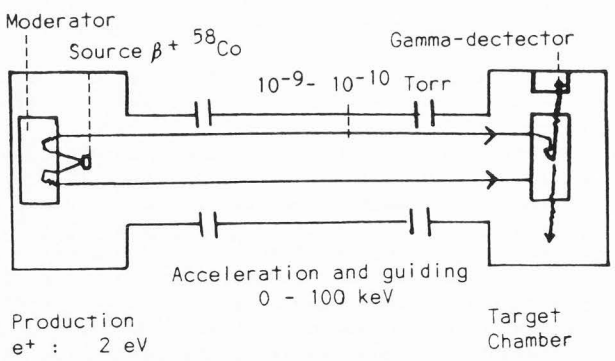
The transport system and the equipment of the target chamber depend on the experiments to be performed with the beam. Electrostatic focusing gives better angular resolution and so is appropriate for angle resolved studies, but it is less simple to construct and operate than magnetic focusing.

Different methods are used to shield the target from the positron source. Technical information can be found in the references given above and in Canter and Mills 1982.

In addition to the devices required for a given experiment, the target chamber is generally equipped with an ion gun for surface cleaning and with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) for surface characterization.

## Positron-surface-interaction

Various interaction processes are possible when slow positrons strike a solid surface. For details, the reader is referred to the recent theoretical articles of Feder 1980, Jona et al 1980, Oliva 1980, Nieminen and Oliva 1980, Pendry 1980, Read and Lowy 1981, Read 1983, Nieminen 1983, 1984, Canter and Lynn 1984, Platzman and Tzoar 1987, and to the reviews by Lynn 1983, Mills 1983. Some of these processes can be used as surface analysis tool. In this section, we



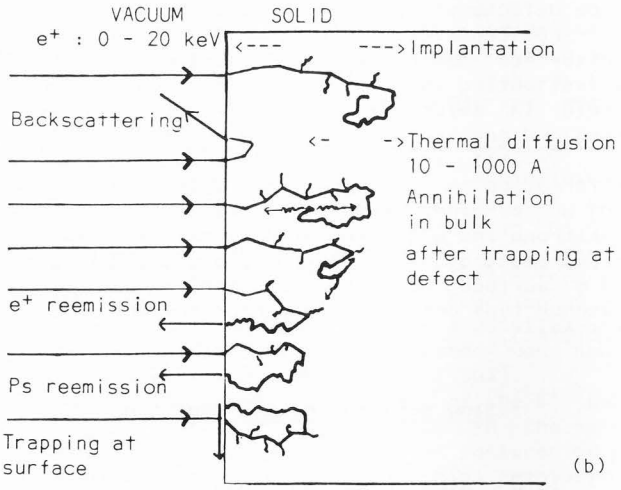




Figure 2 Scheme of a slow positron apparatus (a) and of positron surface processes (b).

give the principles of measurement related to these processes.

When positrons hit a target, a small fraction reflects elastically or inelastically while most of them penetrate into the crystal. The diffraction pattern of elastically backscattered positrons was first observed at single crystal surfaces by Rosenberg et al. (1980). The low energy positron diffraction (LEPD) can be used in analogy to electrons to study surface structure. Within the target, positrons slow down through inelastic collisions with electrons and finally thermalize and begin to diffuse. In the course of their diffusion, positrons can encounter different fates (figure 2b):

- annihilation inside the target either in a bulk delocalized state or in a localized state after capture in a vacancy type defect
- return to the entrance surface, where, according to the material, they can be (i) reemitted into vacuum either as positron or as Ps atom after pick-up of an electron; (ii) trapped in the induced "image" potential well just outside the surface; (iii) reflected within the target.

Surface and near surface regions ($<<10^{-6}$ m) can be investigated by measuring, as a function of the positron incident energy E, one of the annihilation parameters (see above), the slow positron yield $Y_{e+}$ or the positronium yield $Y_{Ps}$. $Y_{e+}$ (and respectively $Y_{Ps}$) is defined as the fraction of incident positrons which are reemitted as slow positrons (resp. Ps atoms). The quantities, $Y_{e+}$, $Y_{Ps}$, are proportional to the probability F(E) that positrons diffuse back to the entrance surface and consequently yield information on the positron diffusion in the near surface region via F(E) :

$$Y_i = Y^o_i \times F(E) \qquad i = (e^+, Ps) \qquad (2)$$

A similar relation holds for the fraction of positrons captured in the surface state $Y_{ss}$. $Y^o_{Ps}$, $Y^o_{e+}$ and $Y^o_{ss}$ are the probabilities that a positron at the surface undergoes one of the processes of interaction and are sometimes referred to as branching ratios. The branching ratios are the low energy limit, E--->0, of the yields Y and can be determined by extrapolating the experimental data at very low incident energy (E << 30 eV).

The calculation of the probability F(E) is at the basis of the interpretation of experiments where $Y_{Ps}$ (or $Y_{e+}$) are measured. We give below a short description of the theoretical frame work of this calculation.

Slow positron emission

Positron reemission is the process underlying the production of slow positrons. Slow positrons are spontaneously ejected from materials for which the positron work function $\Phi_+$ is negative (Hodges and Stott 1973a, Nieminen and Hodges 1976). $|\Phi_+|$ is the energy necessary to extract a positron from the bulk far outside into the vacuum. The expression of the positron work function $\Phi_+$ is analogous to that of the electron work function $\Phi_-$ .

$$\Phi_+ = -D - \mu_+ \qquad \Phi_- = D - \mu_- \qquad (3)$$

$\mu_-$ is the electron chemical potential
$\mu_+$ is the positron chemical potential
D is the electrostatic surface dipole.

The positron work function is experimentally determined from the measurements of the energy distribution of the emitted slow positrons (Mills et al. 1978). The positrons emerge from the surface with a maximum energy equal to $|\Phi_+|$. If the positrons undergo no inelastic process while escaping through the target surface, their energy distribution results from the Maxwellian distribution of their thermal energy within the target. Consequently, the positrons have an energy distribution with a narrow spread of ≈3/2 kT and are emitted in a narrow cone (a few 10°) around the normal to the surface (Nieminen and Oliva 1980). This is the case for the majority of slow positrons reemitted from Cu, Al (Murray and Mills 1980a) and from W, Ni (Fischer 1984). However, the distribution of the energy component perpendicular to the surface also presents in some cases a low energy tail (W,Ni,Cr) which results from inelastic interactions between the escaping positrons and the surface (Wilson, 1982 1983, Wilson and Mills 1983a, 1983b, Fischer et al. 1983). Fischer et al. 1983 demonstrated that the analysis of the energy loss in the reemitted positron spectrum can yield information on surface structure in a parallel way to electron energy loss spectroscopy.

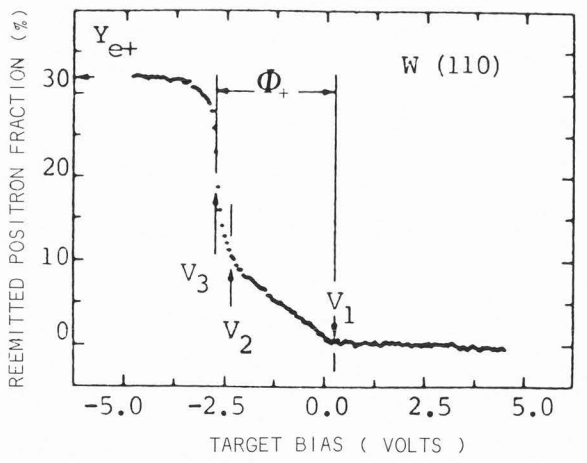



Figure 3 Integral energy distribution of reemitted positron fraction for a W(110) surface struck by 2 keV positrons. The positron fraction is measured versus the target voltage $V_T$ with respect to the retarding grid. The positron yield at 2 keV is the maximum reemitted fraction obtained here at $V_T \leq V_3$. The positron work function is defined as the energy difference $-|e(V_3-V_1)|$. The reemitted fraction between $V_2$ and $V_1$ results from positrons undergoing inelastic processes during their reemission from the surface. After Schultz et al. (1983).

To measure the reemitted positron energy and the positron yield $Y_{e^+}$, the positrons emerge towards a retarding grid located in front of the target which is biased at various voltages $V_T$ with respect to the grid. The number of annihilations in the target is counted with a gamma energy sensitive detector as a function of the target bias. When the target is more positive than the grid, the reemitted positrons escape from the target and the counting rate $n(V_T)$ is low. When the target is biased negatively, the reemitted positrons with an energy lower than $|eV_T|$ are retarded and return to the target. The counting rate increases when $V_T$ becomes more negative and reaches a maximum for $|eV_T| \geq |\Phi_+|$ (figure 3). In figure 3, the positron work function $\Phi_+$ is determined as $|e(V_3-V_1)|$. $V_3$ is the voltage at the maximum of the differential curve $n(V_T)$ and $V_1$ is the voltage just sufficient to obtain the minimal value of $n(V_T)$. The slow positron yield $Y_{e^+}$ is the ratio of the difference between the maximum counting rate ($V_T \leq V_3$) and the minimum counting rate ($V_T \geq V_1$) to the maximum counting rate.

As seen in table 2, the experimental determination of the positron work function (Mills 1978, 1979c, 1980, 1983 and for review Mills 1983, Mills et al. 1978, Murray and Mills 1980c, Lynn and Lutz 1980, Lynn et al. 1981, Wilson and Mills 1983a, 1983b, Schultz et al. 1983) are generally in good agreement with the calculated values (Hodges and Stott 1973a, Nieminen and Hodges 1976, Nieminen and Oliva 1980, Flechter et al. 1983). Negative positron work functions were determined for several metals : Al, Co, Cu Ni, Pt, Ta and W. The slow positron branching ratios, $Y^o_{e^+}$, are about 30 %.

In analogy to the electron work function, the positron work function can be used to study changes in the surface structure which affects the surface dipole D (Murray et al. 1980, Schultz et al. 1983).

Positronium emission

It was known from studies on positron annihilation in bulk that positronium was emitted from oxide powders (Paulin and Ambrosino 1968). Studies of positron annihilation at surfaces were however necessary to understand the role of the surface in this process.

Canter et al. (1974) were the first to report that positronium was abundantly formed when slow positrons interacted with various solid surfaces (metals, oxides, insulators). The positronium formation process was clarified from experiments on clean metal crystals (Mills 1978, Lynn 1979) in ultra-high vacuum ($10^{-9}$-$10^{-10}$ torr). A high fraction of positronium annihilation is observed for very slow positrons (0-2 keV) hitting clean metallic surfaces. As positronium annihilation is not observed in metallic bulk (Hautojarvi 1979), this demonstrates that Ps is formed at surfaces in metals. Ps annihilation is still detected for positrons implanted deeper in the materials at ranges comparable to the length diffusion of positrons ($z^* \approx 1_+ \approx 0.1 \mu m$). This shows that the positrons which have diffused back to the surface are involved in the Ps emission process. Spontaneous positronium emission is possible from most metals because the Ps work function $\Phi_{Ps}$ (Nieminen and Oliva 1980) is generally negative (table 2) :

$$\Phi_{Ps} = \Phi_+ + \Phi_- - E_B \qquad (4)$$

where $E_B$ is the binding energy in the ground state : $E_B = -1/2$ Ryd $= -6.8$ eV. The Ps branching ratio $Y^o_{Ps}$ is temperature dependent (Canter et al. 1974, Mills 1978 ) and follows an Arrhenius type profile with activation energies around 0.1-1 eV (Lynn 1979, Mills 1979b, Lynn and Welch 1980). This phenomenon (figure 4) is attributed to thermal desorption of $P_s$ atoms . The Ps atoms originate from the association of positrons trapped in the surface state with electrons near the Fermi surface (Lynn 1979, Mills 1979b, Chu et al, 1981). The existence of two mechanisms for positronium formation is consistent with positronium velocity measurements performed for a Cu (111) surface (Mills and Pfeiffer 1979). At room temperature, Ps atoms are ejected with energy $E \approx 3$ eV. At higher temperature, the fraction of Ps ejected

Table 2. Theoretical and positron work functions $\Phi_{+,th}$, $\Phi_{+,exp}$, theoretical electron work function $\Phi_{-,th}$, positron branching ratio $Y^o_{e^+}$ and activation energy $E_a$ in different metals. After Mills (1983) and Vehanen et al. (1983).

| | $\Phi_{+,th}$ | $\Phi_{+,exp}$ | $\Phi_{-,th}$ | $\Phi_{Ps}$ | $Y^o_{e^+}$ | $E_a$ |
|---|---|---|---|---|---|---|
| Al(100) | $-0.5_a$ | $-0.19(2)_b$ | $4.41(3)_i$ | -2.58(3) | 0.21 | $0.49_j$ |
| Al(110) | $-0.3_a$ | $-0.05(5)_c$ | $4.28(3)_i$ | -2.57(6) | 0.09 | $0.40_c$ |
| Al(111) | $+0.1_a$ | $-0.04(1)_d$ | $4.24(3)_i$ | -2.60(3) | 0.14 | $0.41_j$ |
| W(110) | | $-2.96 \pm 0.2_e$ | $5.25 \pm 0.2_i$ | -4.25 | | |
| W(111) | $-2.1_f$ | $-2.59(1)_g$ | $4.47(2)_j$ | -4.92 | | |
| Cr(100) | $-2.2_f$ | $-1.76(10)_k$ | $4.46(6)_h$ | -4.10 | | |

a Nieminen and Oliva 1980
b Murray and Mills 1980b
c Mills 1983
d Vehanen et al. 1983
e Schultz et al. 1983
f Nieminen and Hodges 1976
g Wilson and Mills 1983
h Grepstadt et al. 1976
i Strayer et al. 1973
j Lynn 1980

increases and a new velocity component appears corresponding to E≈0.14 eV at 790° C.
Pick off annihilation for o-Ps is not possible probably because of the high ejection Ps velocities: the time spent in the near surface where pick-off would be possible is too short.

The positronium yield $Y_{Ps}$ is easy to measure (see below) and is often chosen as the measured parameter for surface studies.

Surface state

Positron annihilation in a surface state was theoretically proposed by Hodges and Stott (1973b) to explain the long experimental lifetimes due to cavities in neutron irradiated molybdenum (Cotterill et al. 1972). The image force gives rise to a potential well just outside the surface, sufficiently deep to trap positrons (Hodges and Stott 1973b). The positron binding energy in the surface state, $E_{ss}$, can be experimentally determined from the Ps thermal desorption process (Lynn 1979, Mills 1979b, Murray and Mills 1980a, Lynn and Welch 1980, Rosenberg et al. 1980). The activation energy $E_a$ of this process is related to $E_{ss}$ and is given by (Mills 1979b, Lynn 1979) :

$$E_a = E_{ss} + \Phi_- - E_B \qquad (5)$$

The experimental values of $E_{ss}$ deduced from $E_a$ and $\Phi_-$ measurements, $E_{ss}\gtrsim 3$ eV, can be compared to calculations (Nieminen and Hodges 1978, Barberan and Echenique 1979). In Al (Lynn 1979, Mills 1979b) they are in good agreement with the theoretical predictions for different crystallographic surface orientations (Nieminen and Puska 1983). Nieminen and Puska (1984) have also investigated the positron localization in vacancies on Al surfaces and found that the trapping is very weak.

A positron lifetime of 580±10 ps was recently measured for the surface state at a Al(110) surface at 300 K (Lynn et al. 1984). This experimental value is in qualitative agreement with theoretical predictions : 630 ps (Nieminen and Puska 1984) and 540 ps (Nieminen and Hodges 1978). Modifications of the surface structure could be investigated by such measurements. However, such possibilities have not yet been exploited, partly due to the difficulties arising from the resolution function of the lifetime spectrometers (see above).

Back diffusion to the surface

The probability F(E) that the positrons while diffusing return to the surface is related to their initial incident energy E, which governs their implantation profile in the target, p(z,E). The more energetic they are, the higher is the chance of their being deeply implanted and the smaller the probability that a fraction of positrons diffuse back to the surface.

After penetration in a solid with an initial energy (E≤1 MeV) the life history of positrons divides into two periods. During the first one, $t\leq 2\times10^{-12}$s, positrons lose their energy through ionization and electronic excitation and reach energies around a few eV's. During the second period, positrons approach thermal energies via phonon scattering. Their motion can be described by a one dimensional diffusion equation (Brandt 1974, Lynn 1980, Mills and Murray 1980, Nieminen and Oliva 1980, Frieze et al. 1985b). One can consider that the initial density distribution n (z, t=0) is given by the stopping profile p(z,E) (for a discussion of this point see Mills and Wilson 1982).

$$D_+ \frac{\partial^2}{\partial z^2} n_E(z,t) = \frac{\partial}{\partial t} n_E(z,t) + \lambda\, n_E(z,t) \qquad (6)$$

$$n_E(z,0) = p(z,E) \quad ; \quad \int_0^\infty dz\, p(z,E) = 1.$$

$D_+$ is the positron diffusion constant; $\lambda$ is a bulk removal rate, $\lambda=\lambda_b+k$, due to annihilation at rate $\lambda_b$, and possibly to positron capture in vacancy defects at the rate $k=\mu c$; k is constant when the defect concentration is homogeneous. k becomes dependent on z in non-homogeneous materials: for instance, after ion irradiation, a defect profile c(z) exists in the near surface region and as the nature and the density of defects change along z, one writes $k = \mu(z)c(z)$.

At the entrance surface, the positrons can disappear from the bulk at a total rate $\nu$. The total depletion rate at the surface is the sum of the rates of the processes which remove positrons from the metal, : $\nu_{e^+}$ for positron emission, $\nu_{Ps}$ for Ps emission and $\nu_{ss}$ for capture in the surface state. The diffusion flux balances the depletion rate at the surface (z = 0), which implies the boundary condition :

$$\left|J(0,t)\right| = \nu n_E(0,t) \qquad \text{or}$$

$$-D_+ \frac{\partial}{\partial t} n_E(0,t) = \nu n_E(0,t) \qquad (7)$$

The total loss probability of positrons at the surface is

$$Y(E) = \nu F(E) = \nu \int_0^\infty dt\, n_E(0,t) \qquad (8)$$

From the solution n(z,t) of the diffusion equation, one obtains the following expression for F(E) :

$$F(E) = (\nu+(D_+\lambda)^{1/2})^{-1} \int_0^\infty dz\, p(z,E)\, f(z) \qquad (9)$$

with $f(z) = \exp[-z/(D_+\lambda^{-1})^{1/2}]$

F(E) is proportional to a Laplace transform of the stopping profile, where the Laplace variable is the inverse of the positron diffusion length, $l_+=(D_+\lambda^{-1})^{1/2}$, ($\lambda$ constant). The probabilities $Y_i$ corresponding to the various processes are given by :

$$Y_i = Y_i^o\, F(E) \quad \text{with } i: e^+, \text{ Ps, or ss} \qquad (10)$$

The expressions (10) and (9) show that, for a given stopping profile in the target, the quantities $Y_i$ depend on the positron diffusion coefficient in the bulk $D_+$, on the defect structure in the near surface region via $\lambda$, and

on the surface structure via $Y^o$. A large diffusion coefficient and the absence of vacancy type defects favour the positron diffusion back to the surface. In the experiments where the escape rate at surface is diffusion limited, i.e $\nu >> (D_+\lambda)^{1/2}$ , the yields become :

$$Y_i = Y_i^o \int_0^\infty dz\ p(z,E)\ f(z) \qquad (11)$$

If the dependence of the stopping profile p(z,E) on the positron incident energy is known, one can extract the positron diffusion length $l_+$ in the bulk from the variations of the yields $Y_i$,(i=$e^+$, Ps), versus the positron incident energy E. This method was used to investigate diffusion coefficient in well annealed metals (Mills 1978, Lynn and Welch 1980, Lynn 1980, Mills and Wilson 1982 and see reviews by Mills 1983, Lynn 1983), in semi-conductors (Mills 1978, Jorch et al. 1981, Jorch 1982, Nielsen et al. 1984) and applied to the determination of the vacancy formation enthalpy via the temperature dependence of the positron diffusion length (Lynn and Welch 1980, Lynn and Lutz 1980).

For the analysis of the experimental data (mainly $Y_{Ps}$), an exponential stopping profile is usually assumed (Mills 1978, Mills and Murray 1980,Lynn and Welch 1980,Schultz and Lynn 1982):

$$p(z,E) = z^{*-1} \exp[-(z/z^*)] \qquad (12)$$

The mean implantation depth $z^*$ is related to the incident positron energy via a power law in analogy to the electrons (Lynn 1980): $z^*=AE^n$ The constants A and n are characteristic of each material (Mills and Wilson 1982, Valkealathi and Nieminen 1983) and usually of the order: $n\approx1.5$ and $A\approx4.10^{-6}$ $g.cm^{-2}.keV^{-n}$. For example, Mills and Wilson (1982) reported in Al n=1.6(-0.8, +0.15), $A=3.36\times10^{-6}$ $g.cm^{-2}.keV^{-n}$ and in Cu n= 1.43 (-0.11,+0.07),$A=4.40\times10^{-6}$ $g.cm^{-2}.keV^{-n}$ for the quantity $z^*\exp(-1/2)$. Writing the diffusion length $l_+$ as $l_+=AE^n_o$, one obtains for $Y_i$:

$$Y_i = Y_i^o\ [\ 1+ (E/E_o)^{\ n}]^{-1} \qquad (13)$$

The experimental curves $Y_{Ps}$ or $Y_{e+}$ versus the positron incident energy are fitted by expression (13) with n, $E_o$ and possibly $Y^o_i$ as adjustable parameters. As previously mentioned, instead of being an adjustable parameter, $Y^o_i$ can be estimated as the limit of the data at very low incident energy.

The analysis with an exponential profile was successfully applied to several experiments where the data were obtained for positron maximum energy below 6 keV. Recently, at higher energies, ($E \lesssim 100$ keV), the exponential approximation to the stopping profile failed (Nielsen et al. 1984). A better representation of the implantation profile consistent with recent Monte Carlo calculations of the stopping profile (Valkealathi and Nieminen 1983, 1984) is given by

$$p(z) = m\ z^{m-1}\ z^{*-m} \exp[-(z/z^*)^m] \qquad (14)$$
$$m \approx 1.9$$

Nielsen et al. (1984) found in the case of silicon that the positron diffusion coefficient varies by about 17 % owing to the choice of the stopping profile.

In the experiments designed to explore defect profiles near the surface (Trifsthauser and Kogel 1982, Kogel and Trifsthauser 1983, Vehanen et al. 1985), $\lambda$ depends on z in the equation (9). An accurate knowledge of the stopping profile is required to extract the defect profile from the data. Vehanen et al. (1985) proposed to investigate depth profiles via the quantity K(E) :

$$K(E) = \frac{[Y_{Ps}(E)/Y_{Ps}(0)]_b - [Y_{Ps}(E)/Y_{Ps}(0)]_d}{[Y_{Ps}(E)/Y_{Ps}(0)]_b} \qquad (15)$$

which is less sensitive to the shape of the stopping profile than $Y_{Ps}$ (E). The subscripts b and d refer to the quantities measured in the well annealed specimen (b) and in the damaged specimen (d). K(E) is the relative fraction of positrons which become trapped during the diffusive motion back to the entrance surface. The diffusion equation is resolved numerically for various depth profiles c(z) and the results are fitted to the quantity K(E).

Summary

In summary, we comment on the figure 4 which illustrates the energy and temperature dependence of the positronium yield , $Y_{Ps}(E,T)$ First, one notes in this figure that, at any temperature, $Y_{Ps}$ decreases when the incident energy of positrons increases. This is due to the smaller part of positrons which diffuse back to the entrance surface when E increases. $Y_{Ps}$ is mainly dependent on surface process at low energy (28 eV), while at higher energy, it results from the combination of diffusion and surface processes. So, the temperature dependence is different at low and high energy. At low energy (28 MeV), the increase of $Y_{Ps}$ with increasing temperature is explained by the surface process of Ps thermal desorption. At higher energy, the bulk influences the temperature dependence of $Y_{Ps}$. The influence of the bulk is particularly strong at high temperature, ($T > 600$ K), because of the thermally generated vacancies. Positrons get trapped in the vacancies, which prevents them from returning back to the surface : $Y_{Ps}$ decreases strongly at high temperature. At lower temperature, ($T \lesssim 600$ K), the fraction of positrons which are retained in the vacancies is too small to mask the increase of the branching ratio $Y^o_{Ps}$ : $Y_{Ps}$ varies as $Y^o_{Ps}$. The competition of the two processes results in a maximum in the curves. This maximum decreases when E increases since the positrons are stopped more deeply inside the target.

## Defect studies in the near surface region

We present here examples of defect studies performed with slow positron beams.

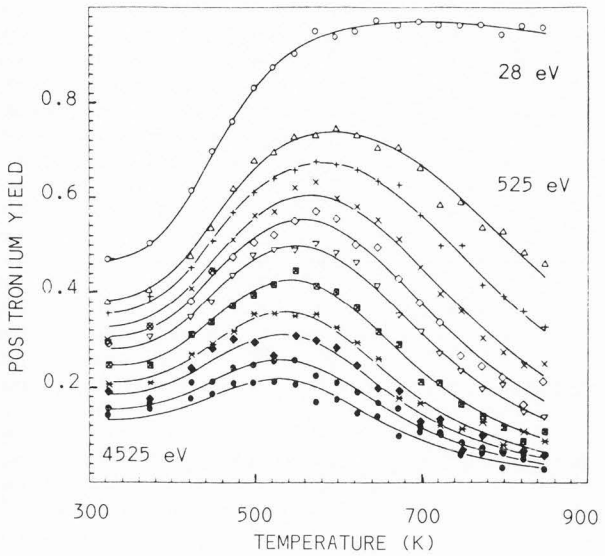



Figure 4 Positronium yield in Al(110) versus sample temperature at various incident energies. After Lynn(1983).

Vacancy defects in metals

Thermal vacancies. We give an example of the determination of the vacancy formation enthalpy in Al, based on the measurements of the positron diffusion length versus temperature (Lynn and Welch 1980, Lynn and Lutz 1980, Lynn 1983). The quantity measured is the positronium yield. The parameter $E_o$ related to the positron diffusion length by power law, $l_+=AE_o^n$, is extracted from the curves $Y_{Ps}$ (E) according to equation (13). Figure 5 shows its temperature dependence . The decrease of $E_o$ when the temperature increases means that the positron diffusion length decreases. This is due to the positron trapping in the thermally generated vacancies. The curve $E_o$ (T) is fitted by the expression :

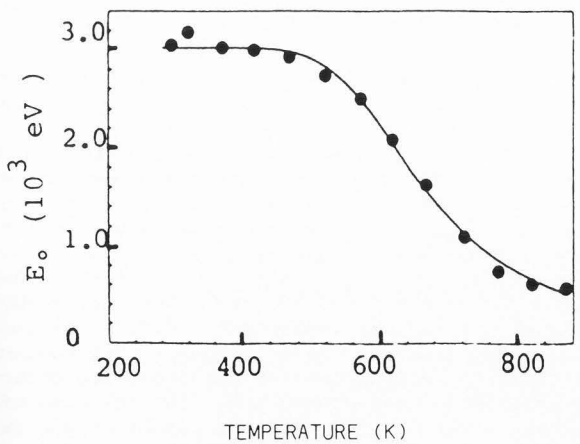



Figure 5 Parameter $E_o$ in Al(110) versus sample temperature. The positron diffusion length l+ is related to $E_o$ by $l+ = A\ E_o^n$. After Lynn 1983.

$$E_o=A^{-1/n}\ (D_+\lambda_b^{-1})^{1/2n}\ (1+\lambda_b^{-1}\ \mu\ c_{IV}(T))^{-1/2n}$$

$$n\neq 0,\ c_{IV}(T) = \exp(S^F_{IV}/k)\exp-(H^F_{IV}/kT) \qquad (16)$$

$\mu$ is the specific trapping rate per vacancy; $S^F_{IV}$ and $H^F_{IV}$ are the vacancy formation entropy and the vacancy formation enthalpy. The fitting parameters are $\lambda_b^{-1}\ \mu\ \exp(S^F_{IV}/k)$ and $H^F_{IV}$. The quantity $A^{-1/n}\ (D_+\lambda_b^{-1})^{1/2n}$ is extracted from the $Y_{Ps}(E)$ data recorded at room temperature : $E_o$ (300 K) = $A^{-1/n}\ (D_+\lambda_b^{-1})^{1/2n}$ = 2.45 keV. The best fit is obtained for $\lambda_b^{-1}\ \mu\ \exp(S^F_{IV}/k)$ = 1.25 $10^6$ and $H^F_{IV}$=0.62 eV. The value 0.62 eV is consistent with previous determinations, 0.62 to 0.66 eV, obtained from measurements of bulk positron annihilation parameters.

Vacancy defect profiles. In aluminium, Vehanen et al. (1985), studied defect profiles resulting from (0.2-3.6 keV) $Ar^+$ sputtering of Al(110) surface by measuring the positronium fraction versus the incident positron energy (0 to 20 keV, $\delta E \leq 0.1$ keV). The decrease of the Ps yield after sputtering (figure 6) reveals the presence of vacancy defects. In figure 6 the sputtering with 3 keV $Ar^+$ at incident angle 75° produces the highest positron trapping. The trapped fraction of back-diffused positrons, K (E) (see above) is calculated from the $Y_{Ps}$ (E) data and fitted for different defect profiles. It is found that defect profiles have a typical width of 15 A followed by an exponential tail extending to 50.... 100 A . The point defect concentration near the surface saturates to values at about 0.5-5 % depending on the sputtering conditions. The defect production rate is found sensitive to the temperature. It increases when temperatures are above the vacancy migration temperature.

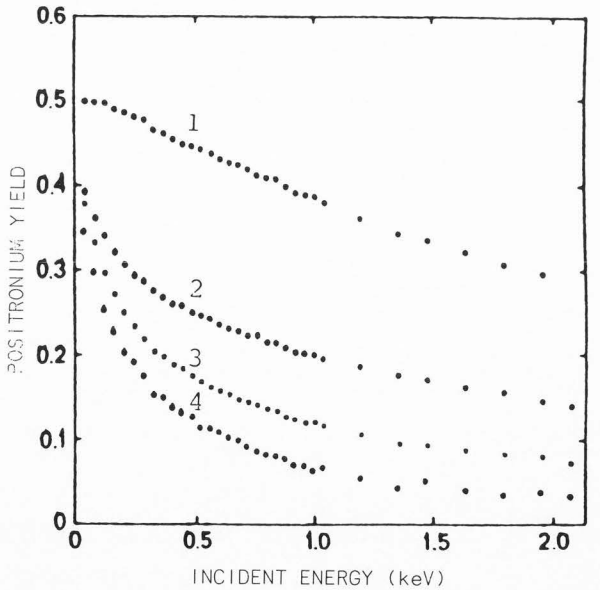



Figure 6 Positronium yield in Al(100) crystal versus positron incident energies before (1) and after Ar+ sputtering at various incident energies and angles: 400 eV 30° (2), 800 eV 60° (3), 3 keV 75° (4). After Vehanen et al.(1985).

Trifsthauser and Kogel (1982) studied the effect of He irradiation in nickel by Doppler broadening measurements.

Vacancy defects at metallic interfaces. Schultz et al. (1983) investigated the deposition process of evaporated copper on a clean W(110) single crystal by measuring the positron work function $\Phi_+$ and the slow positron yield $Y_{e+}$. They characterized also the surface structure at various stages of the process by LEED and AES measurements. Their work is the first and still unique application of slow positron beams to the study of metallic interfaces.

Figures 7.a to 7.c show the evolution of $\Phi_+$ and $Y_{e+}$ for various states of the Cu/W(110) system. Figure 7.a corresponds to the annealed W(110) single crystal, from which about 33% of positrons are reemitted. Approximately 70 % of these reemitted positrons have the energy $|\Phi_+|$=2.94±0.2 eV. After the deposition of a 1.5 Cu monolayer fraction -determined from AES measurement- the steep part of the curve is smooth (figure 7.b). The energy distribution of the reemitted positrons spreads and only 30 % of them are reemitted with an energy equal to $|\Phi_+|$. $|\Phi_+|$ is lowered to 2.61±0.2 eV and the positron yield $Y_{e+}$ decreases markedly to 12 %. After the deposition of a few monolayers, LEED measurements indicate the formation of a Cu(111) surface. The reemitted positron energy distribution (figure 7.c) is analogous to that observed from a clean Cu(111) single crystal. $\Phi_+$ is higher than for the W(110) surface, $\Phi_+$=-0.64±0.2 eV and 90 % of the reemitted positrons have the maximum energy $|\Phi_+|$. However, the positron yield of 10%, is lower than in pure Cu, by more than a factor of two. It recovers the value of 28 % characteristic of a clean Cu(111) single crystal after annealing at 1225 K.

The authors ascribed the decrease in $Y_{e+}$ (figure 7.a to 7.c) to positron trapping due to open volume defects associated to the Cu/W (110) interface. The main argument leading to associate the defects to the interface is that these defects disappear at temperatures much higher than the characteristic temperature - around 600 K-at which vacancy defects in copper are dissolved. After comparison of their results with previous LEED and thermal desorption studies, the authors proposed that incomplete coverage of the first monolayer is at the origin of defects.

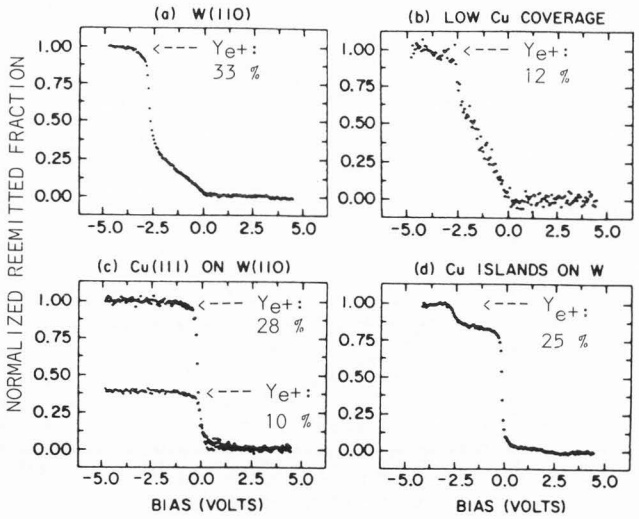



Figure 7 Integral energy distribution of reemitted positrons at various formation stages of the system Cu/W(100). After Schultz et al. (1983).

Figure 7.d was obtained after heat treatments causing incomplete desorption of the copper overlayers. The two steps in figure 7.d correspond to positron work functions of the same order than for Cu(111) and for W(110) surfaces. According to the authors, the appearance of these two steps indicate the existence of three dimensional copper islands remaining on the W(110) surface. The fraction of remaining copper is estimated from the curve to be around 80% in good agreement with the AES determination of 78 %.

Amorphous metals/alloys. In the amorphous metals/alloys ($F_{40}Ni_{40}P_{14}B_6$, $Fe_{82}B_{12}Si_6$, $Cu_{30}Zn_{70}$, $Cu_{50}Zn_{50}$, $Gd_{67}Co_{33}$) the presence of intrinsic vacancy type defects was monitored by measurements of the positron diffusion length (Vehanen et al. 1984). The positron diffusion length is extracted from the Ps fraction versus the incident energy. In the initial state, the diffusion length $l_+ \approx 10$ A is very short compared to typical diffusion length in well annealed metals, ≈1000 A . The authors ascribed this short diffusion length to positron trapping into open volume defects. The evolution of the positron trapping with the temperature suggests the existence of several types of open-volume defects. In addition, the authors found that the concentration of defects (or their specific trapping rate) is lower in metal-metalloid glasses than in metal-metal glasses. They attributed this difference to the presence of boron atoms, which, in metal-metalloid, can fill the open-volume defects.

Vacancy defects in non metals

Amorphous oxide layers. Lynn and Lutz (1980) studied the Ps fraction variation induced by the growth of an oxide layer on Al(111) surface after oxygen exposure $3\times10^{-4}$-1 torr.$s^{-1}$. They noted the formation of amorphous thick oxide overlayers 5-10 A and followed the recrystallisation of this oxide layer after heating above 700 K (Lynn 1980).

Crystalline and amorphous ice. As positrons, positronium can be used to study vacancy defects in insulators. Eldrup et al. (1983,1984) studied the fraction of positronium emitted from crystalline or amorphous ice after $Ne^+$ sputtering and annealing. In the case of ice, the thermalized positrons cannot escape as positron ($\Phi_+ > 0$) nor positronium because the minimum energy required to ionize an electron is higher than the Ps binding energy. Therefore, the emitted positronium arises from the fraction of positronium which is formed in the bulk and diffuses back to the surface. The authors fitted

to the data $Y_{Ps}(E)$ an expression similar to equation (11) but where the positron diffusion coefficient is replaced by the Ps diffusion coefficient and where an additional term takes into account the probability of the Ps formation in the bulk. By this method, they obtained the first direct measurement of the positronium diffusion coefficient in ice. The authors attributed the strong decrease of the positronium yield $Y_{Ps}$ after $Ne^+$ irradiation (figure 8) to inhibition of Ps formation in the presence of defects. Progressive recovery of $Y_{Ps}$ occurs after annealings.

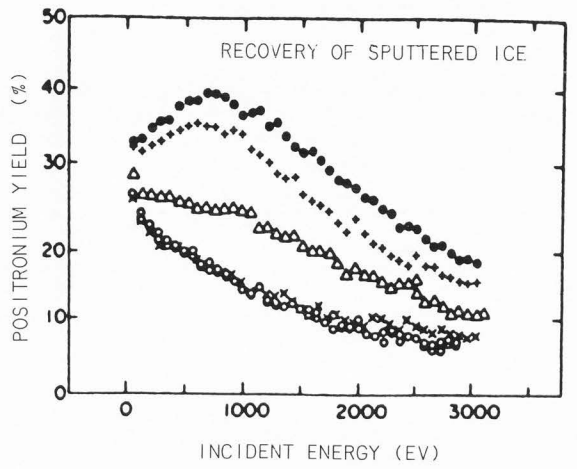



Figure 8 Positronium yield versus incident positron energy in crystalline ice after Ne+ sputterring and subsequent annealings: as sputtered o, annealed in the range 50-117 K x, 118-137 K △, 137-145 K +, 145-149 K ●. After Eldrup et al. (1983, 1984).

## Surface structure investigation

In this section, we report some experiments in which properties of the surface have been investigated.

### Surface magnetism

Gidley et al. (1982) demonstrated that in Ni surface magnetism can be investigated by using a polarized beam of low energy positrons. A clean (110) single crystal is magnetically saturated parallel or antiparallel to the direction [111] and struck with polarized slow positrons (0.3-1.5 keV, $Pe_+$=0.5±0.03). The fraction of positronium formed depends on the respective polarization of positrons and electrons. At room temperature $P_{e-}$ was found to be 2.5±0.3 % and decreased to near zero after adsorption of an oxygen monolayer. $P_{e-}$ disappears for temperatures above the Ni Curie temperature. The critical exponent of the surface layer magnetization obtained by fitting a power law to the curve $P_e(T)$ is 0.7±0.1, in good agreement with the predicted values.

### Electron density of states at the surface

Mills et al.(1983) showed that it is possible to investigate the electron density of states at the surface by measuring the Ps velocity spectrum. The theoretical basis of this experiment is developed by Platzman and Tzoar (1987).

### Electron-positron momentum densities at surfaces

Howell et al. (1984, 1985) and Berko et al. (1985) reported the first 2D-angular correlation measurements of the positron - electron pairs annihilating respectively at the (121) surface of a single copper crystal and at the (100) surface of an Al single crystal. The coincidence counting rate is low in these experiments which require intensities of the slow positron beam higher than in usual applications (> $10^7$ $e^+/s$). Figure 9 shows the positron-electron momentum distribution obtained for copper at 740 eV and 18 keV. It clearly demonstrates that the momentum density of the annihilated electrons is much narrower at the surface (704 eV) than in the bulk (18 keV). At the surface, the momentum density is resolved into a positronium momentum distribution and a positron-electron momentum distribution arising from positrons trapped in the surface state.

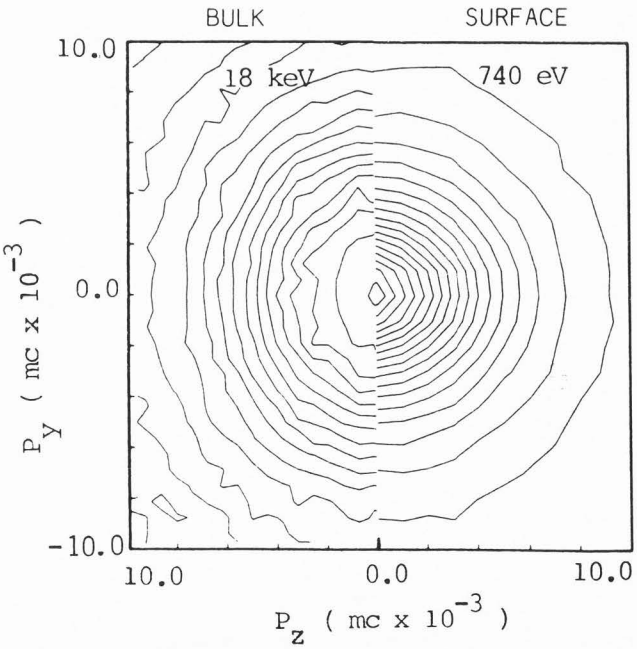



Figure 9 Momentum distribution of electrons annihilating with positrons at surface (704eV) and in the bulk (18keV) in a single crystal of copper. After Howell et al. (1984).

### Low energy positron diffraction (LEPD) and reemitted positron energy loss spectroscopy (REPELS)

The elastic and inelastic processes that positrons encounter at a surface can be used to investigate the surface atomic structure. The

reader can find a comparison of these processes with the analogous electron processes in Canter and Lynn 1984.

LEPD. Rosenberg et al. (1980) were the first to observe LEPD with low energy (20-400 eV) positrons from a Cu(111) solid surface. Mills and Platzman (1980) reported first order Bragg-reflection from Al(111) and Cu(111) surfaces observed for ≈10 eV positrons. Weiss et al. (1983) measured LEPD from Cu(100) surface with an angular resolution much higher than previously (Rosenberg et al. 1980) and compared LEED and LEPD profiles obtained in similar conditions (figure 10) from a Cu(111) surface at equal angle of incidence. The relative strengths of the elastic scattering of positrons and electrons depend on the target atom and the incident energy (Feder 1980). Recently, Frieze et al. (1985a) using a slow positron (2 -500 eV) beam of high brightness (D=1 mm, θ=1° at 100 eV instead of D≈5 mm and θ≈5° in previous studies) obtained the first multispot LEPD pattern from a W(100) crystal and compared it with a multispot LEED pattern recorded under similar conditions.

The comparison between the experimental data and the calculated LEPD intensity profiles (Weiss et al. 1983) leads to the conclusion that the elastic mean free path is shorter for positrons than for electrons at low energies. This comparison confirms also that the models of the LEED process can be used for LEPD after changing the sign of the Coulomb potential and suppressing the exchange potential (Jona et al. 1980).

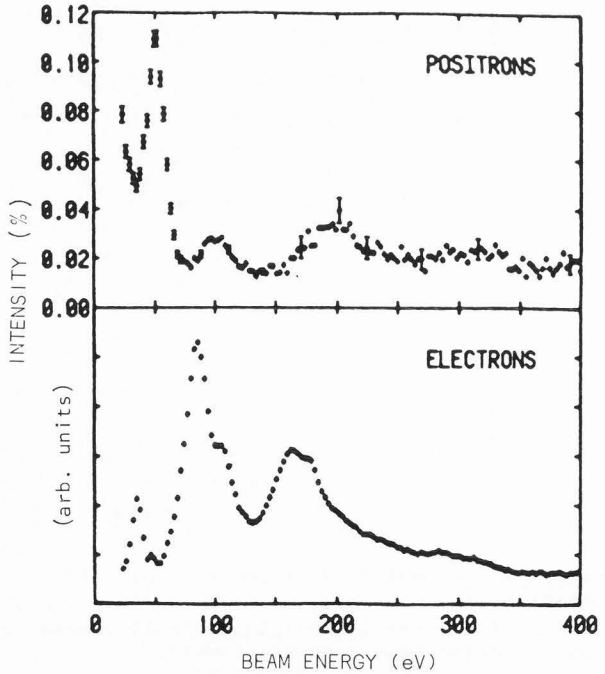



Figure 10 LEPD and LEED intensity profiles from a Cu (110) surface at equal angle of incidence and scattering (30° from the normal) versus the beam energy. After Weiss et al.(1983), Canter and Lynn (1984).

The calculations of LEPD intensity are simplified by the lack of exchange term, the reduction of the correlation term between the positron and the core electron, and the reduction of the elastic mean free path. This can be considered as an advantage of LEPD technique over LEED (Canter and Lynn 1984).

REPELS. Fischer et al. (1983) observed the vibrational excitations of carbon monoxide on Ni (100) from energy loss spectrum of reemitted positrons. The energy loss peaks at (57 and 248) $\times 10^{-3}$ eV (energy resolution 7 %) are in agreement with previous results obtained by electron energy loss spectroscopy.

## Conclusion

Variable energy slow positron beams offer various new possibilities for studying the near surface region and surface structure for both basic and applied research.

They provide a powerful and unique way of investigating vacancy type defects in the near surface region. The potential of such investigations is shown by the experiments described in this tutorial paper. Vacancy defects can be studied in absorbed overlayers, at metal-metal, metal-semiconductor and metal-insulator interfaces.

Slow positron beams can be used to study electron densities of states, electron momentum densities and magnetism at the surface.

They provide methods -alternative to those using electron beams- for surface structure analysis: low energy positron diffraction, reemitted positron energy loss spectroscopy, positron work function measurements. Positron and electron response can be studied under similar conditions. Comparison of their respective responses yields a better understanding of surface properties. Further increases in beam brightness are to be expected. Positron microscopy may be possible but would require high intensity beams of diameter less than 30 μm and divergence less than 1°.

Understanding the interaction of positrons with surfaces is in itself a highly interesting problem of solid state physics. Theories describing the microscopic mechanism of the positron-surface interaction are still lacking.

This paper has concentrated on the applications of slow positron beams to solid surface studies. Our final remark is to note that the study of the structure of the positronium and negative Ps ion in atomic physics is based on the use of slow positron beams (for a review, see Mills 1981, 1983).

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## Discussion with Reviewers

P. Hautojarvi: How many positrons can you have at the same time in a sample?

Author: The positron lifetime and the positron diffusion length are so short that, with the low intensity of positron sources used in standard experiments , one can consider that there is only one positron at only one time.

P. Hautojarvi: What kind of information is it possible to get on the structure of defects by slow positron beams?

Author: With the present quality of the beams, the defect profile of a vacancy type defect distribution can be determined in the near surface region. However, information on the size and the configuration of the vacancy defects is not yet available from lifetime measurements using beams. The lifetime spectrometers using beams are in progress and this information can be expected in the near future.