Ph.D. Thesis

Measurement of Positron Diffusion Constants in Tungsten and Molybdenum by the Observation of Positronium Negative Ions

（ポジトロニウム負イオンの観測によるタンゲステンおよびモリブデン中における陽電子拡散定数の測定）

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Abstract

The positron, the anti-particle of the electron, implanted into metals with the kinetic energy of a few keV loses its energy rapidly and diffuses in metals. Precise studies of positron diffusion in metals have provided information on defects and are important for much research regarding positron science.

The value that characterises the positron diffusion is the diffusion constant, $D_+$. Obtaining $D_+$ requires quantifying the number of positrons which diffuse back to the incident surface via their diffusion motion, $N_S$. Although a few experiments have been attempted to obtain $D_+$, reliability of conventional methods is inadequate due to the difficulty of quantifying $N_S$.

Recently, we developed a new method to accurately quantify $N_S$ by observation of positronium negative ions (Ps$^-$), which consist of one positron and two electrons. The number of emitted Ps$^-$ from the surface is directly proportional to $N_S$ and can be quantified accurately by acceleration with an electric field. This new method enables reliable measurements of positron diffusion in metals.

We applied this new method to measure positron diffusion in polycrystalline tungsten (W) and molybdenum (Mo). This thesis describes the details of the measurement and the results.
Contents

1 Introduction 1

2 Basics 5
   2.1 Positron 5
      2.1.1 Prediction of Existence 5
      2.1.2 Experimental Discovery of the Positron 13
   2.2 Positronium Atoms 15
   2.3 Positronium Negative Ions 16
   2.4 Ps and Ps$^-$ Emission From Metal Surfaces 17
      2.4.1 Positron Work Function 17
      2.4.2 Ps and Ps$^-$ Emission From Metal Surfaces 20
      2.4.3 Ps$^-$ Emission from Alkali-Metal Coated Metal Surfaces 22
   2.5 Fraction Measurements of Ps and Ps$^-$ 25
      2.5.1 Ps Fraction Measurements 25
      2.5.2 Ps$^-$ Fraction Measurements 26

3 Positron Diffusion in Bulk 30
   3.1 Behaviour of Positron in Bulk 30
      3.1.1 Thermalisation 30
      3.1.2 Diffusion 33
   3.2 Conventional Method of Studying Positron Diffusion 36
      3.2.1 Measurement of Line-Shape Parameters 36
      Definition of W-parameter 37
Contents

Definition of S-Parameter .............................................. 38
Measurement of Line-Shape Parameter .............................. 38
3.2.2 Measurement of Reemission Positrons Yield .............. 40
3.2.3 Measurement of Positronium Fraction ....................... 41
3.3 Driving Force of Diffusion ....................................... 43
3.3.1 Generalities ..................................................... 43
  Individual Particles ................................................. 43
  Flux ................................................................. 43
3.3.2 Charged Particle Diffusion in Metals and Semi-Conductors 44
  Electron Diffusion in Metals ...................................... 45
  Electron Diffusion in Semi-Conductors ............................ 45
  Positron Diffusion in Metals ...................................... 46

4 Experiment ............................................................. 47
4.1 Experimental Apparatus .......................................... 47
  4.1.1 Chamber ...................................................... 47
  4.1.2 Slow Positron Source ....................................... 49
    Positron Source .................................................. 49
    Monoenergetic Positron Beam Generation ....................... 50
  4.1.3 Positron Acceleration and Transport ....................... 51
4.2 Sample ............................................................. 54
4.3 Data Acquisition System ........................................... 55
4.4 Production of the UHV Environment .............................. 56
4.5 Experimental Procedures .......................................... 57
  4.5.1 Measurement of Quantity of Incident Positrons .......... 57
  4.5.2 Annealing of the Sample ................................... 59
  4.5.3 Na Deposition ............................................... 60
  4.5.4 Measurement of Ps⁻ Yield .................................. 61
CONTENTS

5 Data Analysis 63
  5.1 Quantity of Incident Positrons ................... 63
  5.2 Yield of Emitted Positronium Negative Ions ........... 64
  5.3 Emission Efficiency of Positronium Negative Ions ........ 68
  5.4 Quantifying $E_0$ .................................. 69

6 Discussion 72
  6.1 Conventional Methods ................................ 72
    6.1.1 Line-Shape Parameter Measurement .................. 72
    W-parameter Observation ................................ 72
    S-parameter Observation ................................ 73
    6.1.2 Measurement of Reemitted Positron Yields .......... 74
    6.1.3 Measurement of Ps atom Yields ..................... 76
  6.2 Advantages of Ps$^{-}$ Observation .................... 77
  6.3 Obtained Values in Our Work ........................... 78
  6.4 Diffusion of Electron and Muons ....................... 79
    6.4.1 Electron Diffusion in Metals ....................... 79
    6.4.2 Muon Diffusion in Metals .......................... 79

7 Acknowledgement 82

A Achievements 88
  A.1 Achievements for ”Development of Methods to Generate Ultra
    Slow Muonium” ........................................ 88
    A.1.1 Oral Sessions ...................................... 88
    A.1.2 Poster Sessions .................................... 89
  A.2 Achievements for ”Measurement of Positron Diffusion in Metals” 90
    A.2.1 Oral Sessions ...................................... 90
    A.2.2 Poster Sessions .................................... 90
    A.2.3 Papers ............................................ 90
  A.3 Awards .............................................. 91
List of Figures

2.1 A positron trajectory observed in a cloud chamber. ........... 14
2.2 Energy spectra of $\gamma$-rays emitted from $o$-Ps $3\gamma$ decay. ........... 16
2.3 Experimental setup for the first observation of Ps$^-$. ........... 17
2.4 Annihilation $\gamma$-ray energy spectra for the first observation of Ps$^-$. 18
2.5 Energy levels of electrons and positrons in metals. ........... 19
2.6 The effect of Cs-coating on the W surfaces. ........... 24
2.7 The annihilation $\gamma$-ray energy spectra for situations representing Ps branching ratio equal to 100\% and 0\%. ........... 26
2.8 Doppler shifted $\gamma$-rays emitted from an accelerated Ps$^-$. ........... 27
2.9 The annihilation $\gamma$-ray spectrum for measurement of accelerated Ps$^-$. ........... 29
3.1 The simultaneous distribution of positron thermalisation process end points. ........... 31
3.2 The simulated and experimentally obtained relations between the mean implantation depth and incident energy. ........... 31
3.3 Simulated and experimentally obtained stopping profiles of implanted positrons into Cu. ........... 32
3.4 Definition of W-parameter. ........... 37
3.5 Definition of S-parameter. ........... 38
3.6 W-parameter plotted against incident positron energy for Cu samples. ........... 39
3.7 Sample chamber for measurement of single-crystal metal surfaces by Wilson and Mills. ...................... 40
3.8 Ps fraction plotted against positron incident energy for Mo(111) sample. ................................ 41
3.9 Energy spectra of reemission positrons for Mo(111) sample. ......................... 42
4.1 Schematic of chamber used in our experiment. ..................... 48
4.2 Schematic diagram of the measurement chamber and the sample holder flange (top-view). ......................... 49
4.3 The capped positron source. ................................ 49
4.4 The surrounds of the positron source capsule. ...................... 50
4.5 Schematic of coils that produce magnetic-field. ................... 51
4.6 The schematic of the $E \times B$ filter’s action. ..................... 52
4.7 The cylindrical electrodes use in the $E \times B$ filter of our apparatus. 53
4.8 Schematic of the accelerate tube. ........................... 54
4.9 Schematic of polycrystalline sample. ............................ 55
4.10 A sample fixed to the centre of a flange. ......................... 55
4.11 The Data Acquisition system of our apparatus. .................. 55
4.12 The schematic of the vacuum system. ............................ 56
4.13 A sample under annealing. .................................... 60
4.14 Schematic of Ps$^-$ emission, acceleration and self-annihilation. 61
5.1 The calculation of number of positrons implanted into the sample. 63
5.2 The $\gamma$-ray energy spectra with the Ps$^-$ emission for the incident positron energies of 1.1 keV, 8.0 keV and 24.0 keV. ............... 66
5.3 Fitting of peak function to the peak due to the Ps$^-$ self-annihilation. 67
5.4 The area ratio $R$ plotted against positron incident energies $E_{e^+}$ (A). ................................. 69
5.5 The area ratio $R$ plotted against positron incident energies $E_{e^+}$ (B). ................................. 70
6.1 Schematic diagram of the apparatus used in the experiment of Wilson and Mills........................................ 75
6.2 Annihilation $\gamma$-ray energy spectra for conditions $f_{Ps} = 0, 1$........................................ 77
6.3 de Broglie wave-length of positive muon and positron........................................ 81
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Properties of $\sigma$-Ps and $\rho$-Ps.</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>List of values of $\phi_{Ps}$ and $\phi_{Ps-}$ for variable metals.</td>
<td>21</td>
</tr>
<tr>
<td>2.3</td>
<td>List of values of $\phi_{Ps}$ and $\phi_{Ps-}$ for alkali metals.</td>
<td>22</td>
</tr>
<tr>
<td>4.1</td>
<td>Parameters of transport coils.</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>List of positron incident energies for measurement with the W(polycrystalline) sample.</td>
<td>58</td>
</tr>
<tr>
<td>4.3</td>
<td>List of positron incident energies for measurement with the Mo(polycrystalline) sample.</td>
<td>58</td>
</tr>
<tr>
<td>5.1</td>
<td>Obtained values of $E_0$ and $n$.</td>
<td>71</td>
</tr>
<tr>
<td>6.1</td>
<td>Obtained values of $E_0$, $n$, diffusion constants, $D_+$ and diffusion length $L_+$.</td>
<td>78</td>
</tr>
<tr>
<td>6.2</td>
<td>Values of $E_0$, $D_+$ reported by previous studies.</td>
<td>78</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

In the present work, we have developed a new method to study positron diffusion in metals. In this method, the dependency of the number of positronium negative ions emitted to a vacuum from the surface of the sample on the positron incident energy is measured. Due to the property of the positronium negative ions, the number can be counted very accurately. Thus, reliable studies of positron diffusion in metals have been enabled.

Positrons implanted into crystals of metals lose their kinetic energies rapidly via the scattering with electrons and phonons. Then, the positrons reach thermal equilibrium with the environment around them and diffuse in the crystals. Due to their positive charge, they feel repulsive forces from the atomic nucleus. Thus, if regions with low positive charge density are in the crystal, positrons are attracted to such regions. A typical example to which positrons are strongly attracted is lattice defects such as vacancies and voids. Positrons trapped by these sites (i.e. their wave functions are localized) annihilate there with electrons. This phenomenon is peculiar to positrons and is not seen with electrons.

Diffusion of positrons in materials is described by the conventional diffusion equation

\[
\frac{\partial}{\partial t} n (x, t) = D_+ \nabla^2 n (x, t) - \lambda_{\text{eff}} n (x, t),
\]
where \( n(x, t) \) is the number density of positron in the position \( x \) at time \( t \), 
\( D_+ \) is the positron diffusion constant and \( \lambda_{\text{eff}} \) is the inverse of the positron effective mean life-time in the bulk of the material \( \tau_{\text{eff}} \) and is written as

\[
\lambda_{\text{eff}} \equiv \frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \kappa C(x).
\]

where \( \tau_b \) is the positron mean life-time in perfect crystal of the material, \( C(x) \) is the concentration of defects and \( \kappa \) is a constant. Thus, the second term on the right side of the diffusion equation corresponds to the property of positrons in materials.

In particular, the measurement of positron diffusion in metal crystals plays a key role in improving the performance of positron moderators. This is because metals (tungsten, copper and so on) are used as positron moderators, which are indispensable for generating monoenergetic positron beams or brightness-enhanced positron beams, which enables research with slow positron beams. Furthermore, the measurement is a key component of researches using positronium (Ps; a bound state consists of a positron and an electron) atoms and positronium negative ions (Ps\(^-\); H\(^-\) like bound state consists of one positron and two electrons). Ps and Ps\(^-\) can be formed from positrons which diffuse back to the incident surface via their diffusion motion after implanted and emitted to a vacuum. Ps and Ps\(^-\) emitted to a vacuum are used for precise studies of quantum electro dynamics (QED), analysis of surfaces and so on. The diffusion of positrons in the bulk influences not only the yields of Ps and Ps\(^-\), but also their kinetic energy distribution. Thus, the information of positron diffusion with high reliability is required.

To study positron diffusion in metals, monoenergetic positrons are implanted into the samples and the ratio \( F_S \) of the number of positrons which diffuse back to the incident surface via their diffusion motion to that of implanted positrons, is used as the function of positron incident energy. In con-
Conventional studies, the major methods listed below were applied to obtain $F_S$.

1. Measurement of line-shape parameters such as W-parameter and S-parameter which reflect the energy distribution of annihilation $\gamma$-rays and is defined from the shape of the distribution,

2. Measurement of number of reemitted positrons emitted from the incident surface, and

3. Measurement of number of Ps atoms emitted from the incident surface.

However, it is difficult to measure $F_S$ accurately and measurements based on these methods are not very reliable.

In the first method, there is uncertainty about the definition of the W-parameter and the S-parameter, especially in the case where the Ps emission occurs. When Ps atoms are emitted, the shape of the annihilation $\gamma$-ray distribution changes. Thus, line shape parameters can not be defined strictly. In the second method, the numbers of annihilation $\gamma$-rays emitted from the sample obtained by comparing the condition in which reemitted positrons are removed and the condition in which these positrons are returned back to the sample. In this method, metal meshes must be placed in front of the sample surface to produce electric fields to realize the two conditions. However, $\gamma$-rays due to the annihilations of positrons which collide with the mesh are the background of the measurement. In the third method, estimation of number of emitted Ps atoms is also problematic. Yields of Ps atoms are measured from the annihilation $\gamma$-ray spectra obtained with the $\gamma$-ray detector. The detector must be calibrated under the assumption that germanium heated to a temperature of 1000 K converts the positrons to Ps atoms and emits them to a vacuum with 100% conversion efficiency. However, no one has verified the appropriateness of this assumption.

We have developed a new method to study positron diffusion in metals. In this method, observation of Ps$^-$ yields is used. The yields are proportional
to the number of positrons that diffuse back to the incident surface. Ps have a negative charge and so we can accelerate Ps easily with an electric field. If we accelerate Ps in the direction of a γ-ray detector, the γ-rays due to the annihilation of accelerated Ps are detected with energy higher than 511 keV (i.e. blue shifted), and we can very clearly separate the signals originating in emitted Ps on the annihilation γ-ray energy spectrum. $F_S$ is obtained accurately and the reliable measurement of positron diffusion in metals becomes available. The only bottle-neck in this method is the lowness of yields of Ps emitted from the surfaces of metal samples. However, this has been removed by alkali metal deposition on to the sample surfaces. This paper describes the details of experiments to measure the positron diffusion in tungsten and molybdenum polycrystalline samples.
Chapter 2

Basics

2.1 Positron

2.1.1 Prediction of Existence

Since the publication of the theory of relativity by A. Einstein, scientists have attempted to seek out physical laws which are invariant (symmetric) for various transformations, for example, coordinate transformation, gauge transformation and non-commutative gauge transformation. In the early stages of these attempts, they tried to construct a theory of relativistic quantum mechanics with the relativistic invariance. Here, the term "relativistic invariance" means that the formations of equations are not changed by the time-space translation and Lorentz transformation.

The Schrödinger equation by which non relativistic quantum mechanics is described is

$$i \frac{\partial}{\partial t} \psi (x) = - \frac{1}{2m} \nabla^2 \psi (x) , \quad (2.1)$$

where $x \equiv t, \mathbf{x}$.

In this chapter, the natural system of units ($\hbar = c = 1$) is employed. The Schrödinger equation is a partial differential equation of one order for time
and of two order for space. The time and space are not treated equally in the equation. To construct the theory of quantum mechanics with relativistic invariance, it is required to find a partial differential equation with the same order for time and space.

A scientist who achieved great success in the study of relativistic quantum mechanics was P. A. M. Dirac [1] [2] [3]. Dirac manipulated the formula

$$E^2 = p^2 + m^2,$$  \hspace{1cm} (2.2)

which is the relationship between the relativistic energy $E$ and momentum vector $p$, to the expression

$$p_\mu p^\mu - m^2 = 0,$$  \hspace{1cm} (2.3)

where the four-vectors of momentum $p^\mu$ is defined as

$$p^\mu \equiv (E, p, p, p) = (E, p_x, p_y, p_z)$$  \hspace{1cm} (2.4)

and $p_\mu$ is defined as

$$p_\mu \equiv \eta_{\mu\nu} p^\nu = (E, -p_x, -p_y, -p_z)$$  \hspace{1cm} (2.5)

$$\eta_{\mu\nu} = \begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. $$  \hspace{1cm} (2.6)

$\eta_{\mu\nu}$ is known as the Lorentz geometric tensor and is invariant. Dirac factorized
Eq. (2.3) and obtained

\[(\gamma^\nu p_\nu + mI_N)(\gamma^\mu p_\mu - mI_N) = 0_N \tag{2.7}\]

$I_N$: A unit matrix of degree $N$

$0_N$: A zero matrix of degree $N$,

where $\gamma^\mu, \gamma^\nu$ are gamma-matrices, defined as matrices which satisfy the anti-commutation relation

\[\{\gamma^\mu, \gamma^\nu\} = 2\eta^{\mu\nu}I_N \tag{2.8}\]

\[\eta^{\mu\nu} = \begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{2.9}\]

From one of the solutions of equation (2.7)

\[\gamma^\mu p_\mu = mI_N, \tag{2.10}\]

via the replacements

\[p^\mu \rightarrow i\partial^\mu \tag{2.11}\]

\[p_\mu \rightarrow \eta_{\mu\nu}(i\partial^\nu) = i\partial_\mu, \tag{2.12}\]

then, the Dirac equation,

\[i\gamma^\mu \partial_\mu \phi (x) = mI_N \phi (x), \tag{2.13}\]

is obtained. $\phi$ is a $N$-component wave function and expressed by $(N, 1)$ matrix.
In Eq. (2.13), $\partial^\mu$ and $\partial_\mu$ are defined with $x^\mu$ and $x_\mu$ as

$$x^\mu \equiv (t, x, y, z)$$  \hspace{1cm} (2.14)

$$x_\mu \equiv \eta_{\mu\nu}x^\nu = (t, -x, -y, -z)$$  \hspace{1cm} (2.15)

$$\partial^\mu \equiv \frac{\partial}{\partial x^\mu} \equiv \left( \frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$  \hspace{1cm} (2.16)

$$\partial_\mu \equiv \frac{\partial}{\partial x_\mu} \equiv \left( \frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right). \hspace{1cm} (2.17)$$

It is evident that the Dirac equation is invariant with respect to the time-space translation. Furthermore, we can verify that the equation is also invariant for the Lorentz transformation via a little long calculation. In the following discussion, the Dirac matrices

$$\gamma_D^0 \equiv \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix}, \gamma_D^j \equiv \begin{pmatrix} 0_2 & \sigma^j \\ -\sigma^j & 0_2 \end{pmatrix}$$  \hspace{1cm} (2.18)

$$\sigma^1 \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma^2 \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma^3 \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$  \hspace{1cm} (2.19)

are employed as the (4, 4) gamma-matrices, although there are an infinite number of gamma-matrices.

According to gauge theory, via the replacements in the Dirac equation Eq. (2.13),

$$\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t} + iqA^0 = \frac{\partial}{\partial t} - ieA^0$$  \hspace{1cm} (2.20)

$$\nabla \rightarrow \nabla - iqA = \nabla + ieA \hspace{1cm} (2.21)$$

$$B = \nabla \times A$$  \hspace{1cm} (2.22)

$$E = -\nabla A^0 - \frac{\partial A}{\partial t},$$  \hspace{1cm} (2.23)
we can obtain the Dirac equation
\[
i \frac{\partial}{\partial t} \phi(x) = \{ \mathbf{\hat{\alpha}} \cdot (-i \nabla + e \mathbf{A}) + m_e \gamma^0 - e A^0 I_4 \} \phi(x),
\] (2.24)

which describes the properties of an electron (mass : \(m_e\), charge : \(-e < 0\)) in the electric and magnetic fields \(E, B\). The operator \(\mathbf{\hat{\alpha}}\) and \(\mathbf{\hat{\alpha}} \cdot (-i \nabla + e \mathbf{A})\) are defined as

\[
\mathbf{\hat{\alpha}} \equiv (\gamma^0 \gamma^1, \gamma^0 \gamma^2, \gamma^0 \gamma^3)
\]
\[
= (\gamma^D_0 \gamma^D_1, \gamma^D_0 \gamma^D_2, \gamma^D_0 \gamma^D_3)
\]
\[
= \left( \begin{array}{ll}
0 & \sigma^1 \\
\sigma^1 & 0
\end{array} \right),
\left( \begin{array}{ll}
0 & \sigma^2 \\
\sigma^2 & 0
\end{array} \right),
\left( \begin{array}{ll}
0 & \sigma^3 \\
\sigma^3 & 0
\end{array} \right)
\]
\[
= (\mathbf{\hat{\alpha}}_1, \mathbf{\hat{\alpha}}_2, \mathbf{\hat{\alpha}}_3)
\] (2.25)
\[
\mathbf{\hat{\alpha}} \cdot (-i \nabla + e \mathbf{A}) \equiv \sum_{j=1}^{3} \hat{\alpha}^j \left( i \partial^j + e A^j \right),
\] (2.26)

respectively.

The equation
\[
E^2 = p^2 + m_e^2
\] (2.27)

has the two independent solutions
\[
E_+ = + \sqrt{p^2 + m_e^2}
\] (2.28)
\[
E_- = - \sqrt{p^2 + m_e^2}.
\] (2.29)

Let \(\phi_{D+}(x), \phi_{D-}(x)\) be the eigen four-component wave functions (expressed by \((4,1)\) matrices) corresponding to the eigen energies of \(E_+, E_-\), respectively, and \(\psi_S(x), \chi_S(x)\) be the eigen two-component wave functions (expressed by
(2, 1) matrices) corresponding to the nonrelativistic (i.e. classical) eigen energy

\[ E_S = \frac{p^2}{2m_e}. \]  

(2.30)

These four wave functions satisfy the energy eigen value equations

\[ \hat{H}\phi_{D+} = +\sqrt{p^2 + m_e^2}\phi_{D+} \]  

(2.31)

\[ \hat{H}\phi_{D-} = -\sqrt{p^2 + m_e^2}\phi_{D-} \]  

(2.32)

\[ \hat{H}\psi_S = \frac{p^2}{2m_e}\psi_S \]  

(2.33)

\[ \hat{H}\chi_S = \frac{p^2}{2m_e}\chi_S \]  

(2.34)

\[ \hat{H} \equiv i\frac{\partial}{\partial t}, \text{ Hamiltonian operator,} \]

and solutions of these equations are

\[ \phi_{D+} \propto \exp \left(-i\sqrt{p^2 + m_e^2}t\right) \]  

(2.35)

\[ \phi_{D-} \propto \exp \left(+i\sqrt{p^2 + m_e^2}t\right) \]  

(2.36)

\[ \begin{pmatrix} \psi_S \\ \chi_S \end{pmatrix} \propto \exp \left(-i\frac{p^2}{2m_e}t\right). \]  

(2.37)

Under the nonrelativistic limitation

\[ \frac{p^2}{m_e^2} \ll 1, \]  

(2.38)

the term \(\sqrt{p^2 + m_e^2}\) is approximated as

\[ \sqrt{p^2 + m_e^2} \simeq m_e + \frac{p^2}{2m_e}. \]  

(2.39)
Thus, the relationships between $\phi_{D+}, \phi_{D-}$ and $\psi_S, \chi_S$ are

\begin{align}
\phi_{D+} &\propto \exp\left(-i (\mp m_e) t\right) \begin{pmatrix}
\psi_S \\
\chi_S 
\end{pmatrix} \tag{2.40} \\
\phi_{D-} &\propto \exp\left(-i (-m_e) t\right) \begin{pmatrix}
\psi_S \\
\chi_S 
\end{pmatrix}. \tag{2.41}
\end{align}

Substituting Eq. (2.40) for Eq. (2.24) and taking the nonrelativistic approximation

\begin{align}
\left| i \frac{\partial \chi_S}{\partial t} \right| &\ll |m_e \chi_S| \tag{2.42} \\
|e A^0 \chi_S| &\ll |m_e \chi_S| \tag{2.43}
\end{align}

into account, we obtain the Pauli equation

\begin{align}
i \frac{\partial}{\partial t} \psi_S (x) &= \left\{ \frac{1}{2m_e} (-i \nabla + e A)^2 I_2 + \frac{e}{2m_e} \hat{\sigma} \cdot \hat{B} - e A^0 I_2 \right\} \psi_S (x) , \tag{2.44}
\end{align}

where the operator $\hat{\sigma}$ and $\hat{\sigma} \cdot \hat{B}$ are defined as

\begin{align}
\hat{\sigma} &\equiv (\sigma^1, \sigma^2, \sigma^3) = \begin{pmatrix}
0 & 1 \\
1 & 0 
\end{pmatrix}, \begin{pmatrix}
0 & -i \\
i & 0 
\end{pmatrix}, \begin{pmatrix}
1 & 0 \\
0 & -1 
\end{pmatrix} = (\hat{\sigma}^1, \hat{\sigma}^2, \hat{\sigma}^3) \\
\hat{\sigma} \cdot \hat{B} &\equiv \sum_{j=1}^{3} \hat{\sigma}^j B^j \tag{2.45}
\end{align}

respectively. The deformation of the Pauli term, $(e/2m_e) \hat{\sigma} \cdot \hat{B}$, in the right hand side of Eq. (2.44) leads to the result,

\begin{align}
\frac{e}{2m_e} \hat{\sigma} \cdot \hat{B} &= 2 \left( \frac{e}{2m_e} \hat{\sigma} \right) \cdot \hat{B} = 2 \frac{e}{2m_e} \hat{S} \cdot \hat{B} = \left. g \frac{e}{2m_e} \hat{S} \cdot \hat{B} \right|_{g=2} \tag{2.47} \\
\hat{S} &\equiv \frac{1}{2} \hat{\sigma} \tag{2.48}
\end{align}
where \( g \) is the Landé’s g-factor. The operator \( \hat{S} \) has the following three properties,

\[
\hat{S}^2 = \hat{S} \tag{2.49}
\]

\[
\left[ \hat{S}^j, \hat{S}^k \right] = \sum_{l=1}^{3} \varepsilon^{jkl} \hat{S}^l \tag{2.50}
\]

\[
\hat{S}^2 = \frac{3}{4} I_4 = \frac{1}{2} \left( 1 + \frac{1}{2} \right) I_4, \tag{2.51}
\]

where \( \varepsilon^{jkl} \) is the Levi-Civita’s totally antisymmetric tensor and defined as

\[
\varepsilon^{jkl} = \begin{cases} 
+1 & \text{when } (j, k, l) \text{ is an even permutation of } (1, 2, 3) \\
-1 & \text{when } (j, k, l) \text{ is an odd permutation of } (1, 2, 3) \\
0 & \text{when } (j, k, l) \text{ is not permutation of } (1, 2, 3).
\end{cases} \tag{2.52}
\]

Hence, we can recognize \( \hat{S} \) as the spin angular momentum operator with the eigen value of \( 1/2 \). It is a great achievement of the Dirac equation that the equation introduces the Pauli term very naturally, although in the province of nonrelativistic quantum mechanics, the term is added to the Schrödinger equation arbitrary. An explanation of the experimental fact that Landé’s g-factor takes a value extremely close to 2 is also achieved by the equation.

The succession of the Dirac equation is not only the illustration of properties of electrons but also the prediction of positron existence. Substituting Eq. (2.41) for Eq. (2.24) and taking nonrelativistic approximations

\[
\left| \frac{i}{\hbar} \frac{\partial \psi_S}{\partial t} \right| \ll |m_e \psi_S| \tag{2.53}
\]

\[
|e A^0 \psi_S| \ll |m_e \psi_S| \tag{2.54}
\]
into account, we obtain

$$i \frac{\partial}{\partial t} \chi_S(x) = \left\{ \frac{1}{2m_e} \left( -i \nabla + eA \right)^2 I_2 - \frac{e}{2m_e} \hat{\sigma} \cdot B - eA^0 I_2 \right\} \chi_S(x) ,$$  

(2.55)

We then take the complex conjugate of Eq. (2.55) and make the operator $-i\hat{\sigma}^2$ act on both sides of the complex conjugated equation from the left. Then, we obtain the equation

$$i \frac{\partial}{\partial t} \left( i\hat{\sigma}^2 \chi_S^*(x) \right) = \left\{ \frac{1}{2m_e} \left( -i \nabla - eA \right)^2 I_2 - \frac{e}{2m_e} \hat{\sigma} \cdot B + eA^0 I_2 \right\} \left( i\hat{\sigma}^2 \chi_S^*(x) \right).$$  

(2.56)

By comparing between Eq. (2.56) and the Pauli equation Eq. (2.44)

$$i \frac{\partial}{\partial t} \psi_S(x) = \left\{ \frac{1}{2m_e} \left( -i \nabla + eA \right)^2 I_2 + \frac{e}{2m_e} \hat{\sigma} \cdot B - eA^0 I_2 \right\} \psi_S(x)$$

which describes an electron (mass : $m_e$, charge : $-e < 0$), Eq. (2.56) is clearly interpreted. The two-component wave function $i\hat{\sigma}^2 \chi_S^*$ corresponds to the particle with the same mass $m_e$ and spin $1/2$ but its charge is $-(-e) > 0$. This particle is called the positron. To explain the meaning or appropriateness of the deformation from $\chi_S$ to $i\hat{\sigma}^2 \chi_S^*$, the quantum field theory is required.

### 2.1.2 Experimental Discovery of the Positron

Positrons were first observed by C. D. Anderson [4] in 1932. Anderson studied cosmic-rays and took many pictures, such as that shown in Fig. 2.1, with the aid of Wilson’s cloud chamber. Some hypotheses about the cause of the track in the picture were developed, such as a hypothesis that the track was caused by a proton or by two electrons. However, these hypotheses were abandoned because of the calculation of the range or lowness of the probabilities. As the result of more precise consideration, the cause of the track was identified as a positron, whose existence had been predicted by Dirac.
Figure 2.1: A positron trajectory observed in a cloud chamber [4]. The positron of kinetic energy 65 MeV entered the lead plate of 6 mm thickness, lost its kinetic energy in the plate and, eventually, penetrated with kinetic energy of 23 MeV.
2.2 Positronium Atoms

The positronium (Ps) atom is a bound state of a positron and an electron. S. Mohorovičić [5] predicted its existence in 1943 and M. Deutsch [6] generated Ps atoms for the first time in 1951 [7]. Ps is a two-particle system which consists of leptons only; thus, it is not affected by the weak and strong interactions, which must be taken into account on the calculations about hadron particle systems. Hence, we can investigate quantum electrodynamics (QED) accurately by the precise observations of its hyper fine structure (HFS) or decay rate.

Ps atoms are classified into two types according to the total spin $S$ of the positron and the electron. Ps atoms with $S = 1$ (i.e. triplet-state; magnetic quantum number $S_z = -1, 0, +1$) are known as ortho-positronium ($o$-Ps). Ps atoms with $S = 0$ (i.e. singlet-state; $S_z = 0$) are known as para-positronium ($p$-Ps).

Emission of photons accompanies the decay of Ps atoms. An odd number and even number of photons are emitted from the annihilation of $o$-Ps and $p$-Ps respectively. The C-parity, which is the eigen value of the charge conjugation operator $\hat{C}$ of a Ps atom before its decay is given as

$$C_{Ps} = (-1)^{l+S}, \quad (2.57)$$

where $l$ is the quantum number of the orbital angular momentum of the Ps atom. The C-parity of $n$ photons $C_{np}$ is given as

$$C_{np} = (-1)^n. \quad (2.58)$$

When a ground state Ps atom (i.e. $l = 0$) decays, an odd number (in most cases 3) of photons are emitted from $o$-Ps ($C_{Ps} = -1^{0+1} = -1$) and an even number (in most cases 2) of photons are emitted from $p$-Ps ($C_{Ps} = -1^{0+0} = 1$).
The C-parity is conserved before and after the decay. The energy of photons emitted from the resting \( o \)-Ps decay is distributed from 0 to 511 keV and from the resting \( p \)-Ps decay is 511 keV. The basic properties of ground state Ps atoms are listed in Tab. 2.1 and an energy spectra of \( \gamma \)-rays from \( o \)-Ps decay are shown in Fig. 2.2.

Table 2.1: Properties of triplet-state positronium (\( o \)-Ps) and singlet-state positronium (\( p \)-Ps).

<table>
<thead>
<tr>
<th>Name</th>
<th>( S )</th>
<th>( S_z )</th>
<th>Mean life-time ( \tau )</th>
<th>Dominate decay mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( o )-Ps</td>
<td>1</td>
<td>(-1, 0, +1)</td>
<td>142 ns</td>
<td>( 3\gamma )</td>
</tr>
<tr>
<td>( p )-Ps</td>
<td>0</td>
<td>0</td>
<td>125 ps</td>
<td>( 2\gamma )</td>
</tr>
</tbody>
</table>

Figure 2.2: The experimental and theoretical energy spectra of the \( \gamma \)-rays emitted from \( o \)-Ps \( 3\gamma \) decay [8]. The data points are the experimental results of Chang et al. The spectra of solid and dashed lines are the predictions based on QED theory of Ore and Powell [9] and Adkins [10] respectively.

2.3 Positronium Negative Ions

The positronium negative ion \( (\text{Ps}^-) \) is a state which consists of one positron and two electrons like the hydrogen negative ion \( (\text{H}^-) \) [11]. In 1946, Wheeler [12]
predicted its existence. The first experimental observation of Ps\(^-\) was performed by Mills [13] in 1981. Figure 2.3 and 2.4 show the experimental setup and obtained annihilation γ-ray energy spectra respectively.

![Experimental setup for the first observation of Ps\(^-\) [13]. Slow positrons were guided by a magnetic field to a carbon film (thickness of 37±17 Å) and emitted Ps\(^-\) were accelerated to the direction of the Ge detector.](image)

Similarly to Ps, Ps\(^-\) are composed of leptons only; thus, they are an ideal platform for testing QED and a number of theoretical studies have been performed. However, a few experiments using Ps\(^-\) have been performed due to its small yield. However, in 2008, this situation dramatically changed. Nagashima et al. [14] found that Ps\(^-\) yields can be enhanced by the deposition of alkali metals to the surfaces of metals from which Ps\(^-\) are emitted.

## 2.4 Ps and Ps\(^-\) Emission From Metal Surfaces

### 2.4.1 Positron Work Function

Figure 2.5 shows the energy levels of positrons and electrons near metal surfaces [15]. The electron work function, \(\phi_-\), is defined as the energy difference
between the state in which an electron has been removed to a distance from the surface of the solid that is large enough that the image force is negligible but small compared to the distance to any other face and the state in which the electron is in the bulk solid. $\phi_-$ can be expressed using the chemical potential of the electron, $\mu_-$, which is defined as the energy of Fermi level with respect to that of crystal zero level, and the effect of the dipole surface layer, $\Delta$, which is caused by the slight tail of the electron wave function from the bulk to vacuum, as follows

$$\phi_- = -\mu_- + \Delta.$$ (2.59)

The energy levels of electrons in the bulk are lower than that of the vacuum; thus, it is impossible that the electrons in metals are emitted spontaneously and the metals lost their electrons of course. The positron work function, $\phi_+$,
is defined using the chemical potential, $\mu_+$, and $\Delta$ as

$$\phi_+ = -\mu_+ - \Delta.$$  \quad (2.60)

Here, we note that $\phi_+$ is defined as the energy level of the bottom of the lowest positron energy band with respect to that of crystal zero level. This is because a thermalised positron settles to the bottom of its allowed band as a delocalised Bloch wave function.

![Electrons and Positrons Diagram](image)

Figure 2.5: Energy levels of electrons and positrons in metals [15].
2.4.2 Ps and Ps$^-$ Emission From Metal Surfaces

Ps atoms can be formed and emitted from surfaces of metal samples bombarded with low-energy positrons [16] [17]. Emission of Ps atoms is energetically allowed if $\phi_{Ps}$, which is the minimum energy required to emit Ps atoms from surfaces to metal, is negative. $\phi_{Ps}$ is given as

$$\phi_{Ps} = \phi_+ + \phi_- - E_{Ps},$$

(2.61)

where $E_{Ps}$ is the Ps binding energy and $E_{Ps} = (1/2) \text{Ry} = 6.8\text{eV}$. $\phi_{Ps}$ is often called the Ps work function, but this naming is not appropriate because Ps atoms can not exist inside metals. In the following discussion, $\phi_{Ps}$ is called Ps affinity. We note that this naming is applicable only for metal surfaces.

The Ps$^-$ affinity, $\phi_{Ps^-}$, is also defined as

$$\phi_{Ps^-} = \phi_+ + 2\phi_- - (E_{Ps} + E_{Ps^-}) ,$$

(2.62)

where $E_{Ps^-}$ is the binding energy of a ground state Ps and an electron. This is the energy difference between the binding energy of Ps$^-$, which is defined as the required energy to break Ps$^-$ up into one positron and two electrons via a quasi-static process, and the binding energy of the ground state Ps atom $6.8\text{eV}$; thus, $E_{Ps^-} \approx 0.33\text{eV}$. Values for $\phi_+, \phi_-$ and $\phi_{Ps}, \phi_{Ps^-}$ calculated using Eqs. (2.61) and (2.62) for the major metals including alkali-metals are listed in Tables 2.2 and 2.3.

As shown in Table 2.2, Ps$^-$ affinities for W(100), W(111) and polycrystalline are negative; hence, the process of Ps$^-$ emission from these surfaces is energetically allowed. In 1983, Wilson and Mills [27] tried to observe the Ps$^-$ emission from a W(111) surface. However they did not succeed the observation and set an upper limit of 0.1% for the Ps$^-$ branching ratio.
Table 2.2: Experimental values of $\phi_+$ and $\phi_-$ and calculated $\phi_{Ps}$ and $\phi_{Ps-}$ for variable metals.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi_+$ (eV)</th>
<th>$\phi_-$ (eV)</th>
<th>$\phi_{Ps}$ (eV)</th>
<th>$\phi_{Ps-}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(100)</td>
<td>-0.16(3) [18]</td>
<td>4.64 [19]</td>
<td>-2.32</td>
<td>1.99</td>
</tr>
<tr>
<td>Al(110)</td>
<td>-0.05(5) [20]</td>
<td>4.06 [19]</td>
<td>-2.79</td>
<td>0.94</td>
</tr>
<tr>
<td>Al(111)</td>
<td>0.065(3)</td>
<td>4.26 [19]</td>
<td>-2.61</td>
<td>1.33</td>
</tr>
<tr>
<td>Ti(polycrystalline)</td>
<td>&gt; 0 [21]</td>
<td>4.33 [19]</td>
<td>&gt; -2.47</td>
<td>&gt; 1.53</td>
</tr>
<tr>
<td>V(polycrystalline)</td>
<td>-0.6(2) [21]</td>
<td>4.3 [19]</td>
<td>-3.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe(polycrystalline)</td>
<td>-1.2(2) [21]</td>
<td>4.50 [22]</td>
<td>-3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe(100)</td>
<td>-1.4(2) [23]</td>
<td>4.67 [19]</td>
<td>-3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe(111)</td>
<td>-1.5(2) [23]</td>
<td>4.81 [19]</td>
<td>-3.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Co(polycrystalline)</td>
<td>0.8 [24]</td>
<td>5.0 [19]</td>
<td>-2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Ni(polycrystalline)</td>
<td>-1.2(2) [21]</td>
<td>5.15(1) [22]</td>
<td>-2.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>-1.0(1), -1.3(1) [21]</td>
<td>5.22 [19]</td>
<td>-2.6, -2.9</td>
<td>2.3, 2.0</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>-1.4(1)</td>
<td>5.04 [19]</td>
<td>-3.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>-0.3(2) [23]</td>
<td>5.10 [19]</td>
<td>-2.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Cu(110)</td>
<td>-0.2(2) [23]</td>
<td>4.48 [19]</td>
<td>-2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>-0.6(2) [23]</td>
<td>4.94 [19]</td>
<td>-2.5</td>
<td>2.2</td>
</tr>
<tr>
<td>Mo(polycrystalline)</td>
<td>-2.2(2) [21]</td>
<td>4.60(15) [22]</td>
<td>-4.4</td>
<td>-0.1</td>
</tr>
<tr>
<td>Mo(110)</td>
<td>-2.1(2) [23]</td>
<td>4.53 [19]</td>
<td>-4.4</td>
<td>-0.2</td>
</tr>
<tr>
<td>Mo(110)</td>
<td>-2.5(2) [23]</td>
<td>4.95 [19]</td>
<td>-4.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Mo(111)</td>
<td>-2.1(2) [23]</td>
<td>4.55 [19]</td>
<td>-4.4</td>
<td>-0.1</td>
</tr>
<tr>
<td>Ag(100)</td>
<td>0.6(2)</td>
<td>4.64 [19]</td>
<td>-1.6</td>
<td>2.8</td>
</tr>
<tr>
<td>Ta(polycrystalline)</td>
<td>-1.2 [18]</td>
<td>4.25 [19]</td>
<td>-3.8</td>
<td>0.2</td>
</tr>
<tr>
<td>W(100)</td>
<td>-3.0(3) [26]</td>
<td>4.63 [19]</td>
<td>-5.2</td>
<td>-0.9</td>
</tr>
<tr>
<td>W(110)</td>
<td>-3.0(2)</td>
<td>5.22 [19]</td>
<td>-4.6</td>
<td>0.3</td>
</tr>
<tr>
<td>W(111)</td>
<td>-2.59 [27]</td>
<td>4.45 [19]</td>
<td>-4.94</td>
<td>-0.82</td>
</tr>
<tr>
<td>Pt(polycrystalline)</td>
<td>-1.8(2) [21]</td>
<td>5.64 [19]</td>
<td>-3.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Au(polycrystalline)</td>
<td>0.90 [28]</td>
<td>5.1 [22]</td>
<td>-0.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Au(111)</td>
<td>&gt; 0</td>
<td>5.31 [19]</td>
<td>&gt; -1.49</td>
<td>&gt; 3.49</td>
</tr>
<tr>
<td>Pb(polycrystalline)</td>
<td>0.90 [28]</td>
<td>4.25 [19]</td>
<td>-1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Pb(100)</td>
<td>2.06 [29]</td>
<td>4.01</td>
<td>-0.73</td>
<td>2.95</td>
</tr>
</tbody>
</table>
Table 2.3: Experimental values of $\phi_+$ and $\phi_-$ and calculated values of $\phi_{Ps}$ and $\phi_{Ps^-}$ for alkali metals.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi_+$ (eV)</th>
<th>$\phi_-$ (eV)</th>
<th>$\phi_{Ps}$ (eV)</th>
<th>$\phi_{Ps^-}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(100)</td>
<td>3.44 [30]</td>
<td>2.93 [30]</td>
<td>-0.43</td>
<td>2.17</td>
</tr>
<tr>
<td>Li(110)</td>
<td>3.51 [30]</td>
<td>2.93 [30]</td>
<td>-0.36</td>
<td>2.24</td>
</tr>
<tr>
<td>Li(111)</td>
<td>3.53 [30]</td>
<td>2.93 [30]</td>
<td>-0.34</td>
<td>2.26</td>
</tr>
<tr>
<td>Na(110)</td>
<td>5.88 [30]</td>
<td>2.70 [30]</td>
<td>1.78</td>
<td>4.15</td>
</tr>
<tr>
<td>Na(111)</td>
<td>5.88 [30]</td>
<td>2.70 [30]</td>
<td>1.78</td>
<td>4.15</td>
</tr>
<tr>
<td>K(100)</td>
<td>4.78 [30]</td>
<td>2.30 [30]</td>
<td>0.28</td>
<td>2.25</td>
</tr>
<tr>
<td>K(110)</td>
<td>4.82 [30]</td>
<td>2.30 [30]</td>
<td>0.32</td>
<td>2.29</td>
</tr>
<tr>
<td>K(111)</td>
<td>4.83 [30]</td>
<td>2.30 [30]</td>
<td>0.33</td>
<td>2.30</td>
</tr>
<tr>
<td>Rb(100)</td>
<td>4.87 [30]</td>
<td>2.26 [30]</td>
<td>0.33</td>
<td>2.26</td>
</tr>
<tr>
<td>Rb(110)</td>
<td>4.82 [30]</td>
<td>2.26 [30]</td>
<td>0.28</td>
<td>2.21</td>
</tr>
<tr>
<td>Rb(111)</td>
<td>4.90 [30]</td>
<td>2.26 [30]</td>
<td>0.36</td>
<td>2.29</td>
</tr>
<tr>
<td>Cs(100)</td>
<td>4.89 [30]</td>
<td>2.14 [30]</td>
<td>0.23</td>
<td>2.04</td>
</tr>
<tr>
<td>Cs(110)</td>
<td>4.94 [30]</td>
<td>2.14 [30]</td>
<td>0.28</td>
<td>2.09</td>
</tr>
<tr>
<td>Cs(111)</td>
<td>4.93 [30]</td>
<td>2.14 [30]</td>
<td>0.27</td>
<td>2.08</td>
</tr>
</tbody>
</table>

2.4.3 Ps$^-$ Emission from Alkali-Metal Coated Metal Surfaces

Whereas a lot of theoretical studies of Ps$^-$ have been vigorously progressed, only a few experimental investigations were performed before 2007. This is because the yield of Ps$^-$ was too few to perform experiments with high statistic precision.

Ps$^-$ affinity for metals, $\phi_{Ps^-}$, can be expressed with $\mu_+$ and $\mu_-$ as

$$\phi_{Ps^-} = \phi_+ + 2\phi_+ - (E_{Ps} + E_{Ps^-})$$
$$= (-\mu_+ - \Delta) + 2(-\mu_- + \Delta) + (E_{Ps} + E_{Ps^-})$$
$$= -\mu_+ - 2\mu_- - (E_{Ps} + E_{Ps^-}) + \Delta.$$  \hspace{1cm} (2.63)
In the deformation above, Eqs. (2.59) and (2.60) are used. Equation (2.63) implies that Ps$^-$ affinity depends on the $\Delta$, which is the effect of the dipole surface layer. Thus, it is expected that reducing $\Delta$ using some method decreases $\phi_{Ps^-}$ and the yield of Ps$^-$ increases.

$\Delta$ is caused by the tail of the electron wave function from the metal surface to the vacuum. Hence, some materials with high polarisability adhering to the metal surfaces diminish $\Delta$. From the expression of the electron work function Eq. (2.59)

$$\phi_- = -\mu_- + \Delta,$$

it is evident that reduction of $\Delta$ leads to a reduction of $\phi_-$. The lowering of the electron work function of metals by depositing an overlayer of alkali metals onto their surfaces has been known and applied to many works, for example, increasing yields of hydrogen negative ions (H$^-$) or secondly electrons from the photocathode of photomultiplier tubes (PMT). Reduction of electron work functions of tungsten by a caesium coating is shown in Fig. 2.6.

In 2008, Nagashima et al. [14] was the first in the world to observe a significant increase in the Ps$^-$ yield from a Cs coated W(100) surface. In this experiment, the target was W(100) foil of 2 $\mu$m thickness, supplied by Aarhus University, and it was supported by a tungsten polycrystalline foil. It was annealed in situ at 1500°C for 30 min by passing electric current through the supporting foil. After cooling to room temperature, Cs was deposited onto the surface of the target using a Cs dispenser purchased from SAES Getters S.p.A.. The conditions of the Cs layers applied were $1.7 \times 10^{14}$ atoms-cm$^{-2}$, $2.2 \times 10^{14}$ atoms-cm$^{-2}$ and $10 \times 10^{14}$ atoms-cm$^{-2}$. Nagashima measured the yields of Ps$^-$ for each condition and the maximum yield was obtained under the condition of Cs layers of $2.2 \times 10^{14}$ atoms-cm$^{-2}$, where the electron work function is the lowest according to Fig. 2.6.

The significant increase in Ps$^-$ yield has enabled various kinds of experi-
Figure 2.6: Experimental values of $\phi_-$ of Cs coated W surfaces [31].
mental research using $\text{Ps}^-$. The photodetachment of $\text{Ps}^-$ is one of these. In 2011, Michishio et al. [32] [33] succeeded in the photodetachment of a $\text{Ps}^-$ by the irradiating laser lights to $\text{Ps}^-$ emitted from the Na coated W(polycrystalline) surface. Development of an energy tunable Ps beam generation based on this research is now progressing.

2.5 Fraction Measurements of Ps and $\text{Ps}^-$

In this section, the methods to detect of Ps and $\text{Ps}^-$ and to quantify their yields are illustrated.

2.5.1 Ps Fraction Measurements

The presence of Ps in the vacuum is identified by the comparison of the obtained $\gamma$-ray energy spectrum and the reference spectrum obtained from the condition in which no Ps atom exits and only $2\gamma$ decays occur. Figure 2.7 shows the annihilation $\gamma$-ray spectra measured by a high energy resolution Ge detector. The spectra in Fig. 2.7 were obtained from an experiment in which slow positrons were implanted into the two different samples. One sample emitted the Ps atoms with 100% of Ps fraction (i.e. $f_{\text{Ps}}$, which is defined as the ratio of quantity of emitted Ps atoms to that of incident positrons, equals 1), and the other did not emit Ps atoms (i.e. $f_{\text{Ps}} = 0$). Due to the continuous energy spectrum for $\alpha$-Ps annihilation $\gamma$-rays from 0 to 511 keV shown in Fig. 2.2, the two spectra shown in Fig. 2.7 are quite different.

In order to quantify the differences in the annihilation $\gamma$-ray spectra, the ratio $R$ is defined as

$$R_{f_{\text{Ps}}} \equiv \frac{T_{f_{\text{Ps}}} - P_{f_{\text{Ps}}}}{P_{f_{\text{Ps}}}},$$

(2.64)

where $T_{f_{\text{Ps}}}$ refers to the integrated counts in the total energy region (for exam-
Figure 2.7: The annihilation $\gamma$-ray energy spectra for situations representing Ps branching ratio equal to 100\% and 0\% [34].

Example, the region of $0-521$ keV and $P_{f_{Ps}}$ is that in the peak region (for example, the region of $501-521$ keV). The Ps fraction $f_{Ps}$ is obtained from the following formula [35] [36]

$$f_{Ps} = \left(1 + \frac{P_1 R_1 - R_{f_{Ps}}}{P_0 R_{f_{Ps}} - R_0}\right)^{-1}$$

(2.65)

where the superscripts 1 and 0 correspond to the cases of $f_{Ps} = 1$ and $f_{Ps} = 0$ respectively.

The annihilation $\gamma$-ray spectrum for the condition $f_{Ps} = 1$ is obtained from the measurement of Ps emission from surface of the Ge target heated to the temperature of 1000 K, under the assumption that the target converts and emits all incident positrons to Ps atoms; however, this assumption has not been verified.

2.5.2 Ps\textsuperscript{−} Fraction Measurements

The quantity of Ps\textsuperscript{−} emitted from the surfaces of metals is also obtained from the annihilation $\gamma$-rays energy spectrum. However, we must note that the energy of a $\gamma$-ray emitted from the self-annihilation of resting Ps\textsuperscript{−} is 511 keV;
hence, it is not possible to distinguish $\gamma$-rays originating in Ps$^-$ from those in single positrons and $p$-Ps atoms. To avoid this problem, the property of Ps$^-$ having a negative charge ($-e < 0$) is used.

![Doppler shifted $\gamma$-rays emitted from an accelerated Ps$^-$](image)

Figure 2.8: Doppler shifted $\gamma$-rays emitted from an accelerated Ps$^-$.  

Figure 2.8 shows the schematic illustration of Ps$^-$ detection. Ps$^-$ formed and emitted to a vacuum from the surfaces of sample metals are accelerated by the electric field between the sample and the acceleration grid, and the accelerated Ps$^-$ decays. Here, let $S$ and $S'$ be the frames of reference fixed to the laboratory and Ps$^-$, respectively, and $+x$ axis direction is defined as the direction of Ps$^-$ acceleration. We focus on the $\gamma$-ray emitted from self-annihilation Ps$^-$ to the direction of angle $\theta$ from the $x$ axis. Let $E$ and $p$ be the Energy and momentum of the $\gamma$-ray observed in $S$, respectively, and let $E'$ and $p'$ be those of same $\gamma$-ray observed in $S'$, respectively. These values are related by the Lorentz transformation given as

$$
\begin{pmatrix}
E'/c \\
p_{x'}
\end{pmatrix} =
\begin{pmatrix}
\gamma & -\beta \gamma \\
-\beta \gamma & \gamma
\end{pmatrix}
\begin{pmatrix}
E/c \\
p_x
\end{pmatrix},
$$

where $\beta$ is the Lorentz factor of Ps$^-$ at the instant of its self-annihilation,
\( \gamma \equiv \frac{1}{\sqrt{1 - \beta^2}} \), and \( \rho'_x \) and \( p_x \) are the \( x \)-components of \( p \) and \( p' \), respectively. From the above, we obtain

\[
E = \frac{m_e c^2}{\gamma (1 - \beta \cos \theta)}.
\] (2.67)

The law of conservation of energy before and after the self-annihilation of \( \text{Ps}^- \) is expressed as

\[
\gamma \cdot 3m_e c^2 = 3m_e c^2 + eW,
\] (2.68)

where \( e \) is the elementary electronic charge and \( W \) is the acceleration voltage which is defined as the absolute value of electronic potential difference between the acceleration grid and the sample. If we define \( \lambda \) as

\[
\lambda \equiv \frac{eW}{3m_e c^2},
\] (2.69)

we obtain

\[
\beta = \sqrt{1 - \frac{1}{\gamma^2}} = \frac{\lambda^2 + 2\lambda}{\lambda + 1}
\] (2.70)

from Eq. (2.68). Therefore the energy of the \( \gamma \)-ray measured by a detector which is fixed to the laboratory is

\[
E = \frac{1}{\lambda + 1 - \sqrt{\lambda^2 + 2\lambda \cos \theta}} m_e c^2.
\] (2.71)

As we can calculate using Eq. (2.71), the energy of \( \gamma \)-ray originating from the self-annihilation of accelerated \( \text{Ps}^- \) is detected as a Doppler shifted value. In particular, if the detector is placed in the region of \(-\pi/2 < \theta < +\pi/2\), the measured energies are higher than 511 keV because the energies of \( \gamma \)-rays are blue shifted. We can distinguish these \( \gamma \)-rays from those originating in single positrons and \( p \)-Ps atoms.
The annihilation $\gamma$-ray spectrum for the measurement of accelerated $\text{Ps}^-$ with 1 kV acceleration voltage is shown in Fig. 2.9. The energy peak of $\gamma$-rays originating in self-annihilation of $\text{Ps}^-$ is clearly separated from the peak at 511 keV. We can quantify the yield of $\text{Ps}^-$ and $\text{Ps}^-$ fraction $f_{\text{Ps}^-}$, which is defined as the ratio quantity of emitted $\text{Ps}^-$ and that of incident positrons, via the integration of the energy peak of $\gamma$-rays from the $\text{Ps}^-$. 

Figure 2.9: The annihilation $\gamma$-ray spectrum for measurement of accelerated $\text{Ps}^-$. The acceleration voltage was 1 kV and $\theta$ was about 30°.
Chapter 3

Positron Diffusion in Bulk

3.1 Behaviour of Positron in Bulk

3.1.1 Thermalisation

Positrons which enter solids with kinetic energy of a few keV lose their energy via the excitation of core electrons [37]. In the case of metals, the excitations of conduction electrons dominate at the lower positron energy range. Through such interactions, the energy of positrons is reduced to a few tens of eV. Slowed down positrons further lose their energy by the electron-hole excitations to the energy of an eV, and then, the scattering of phonons occurs. Eventually, positrons reach thermal equilibrium with solids. This process is called positron thermalisation and the time required for the process is the order of ps, which is much shorter than the typical mean life-time of positrons in solids.

Valkealahti and Nieminen [38] simulated the thermalisation process of positrons and electrons by the Monte Carlo method and obtained the distributions of endpoints of the process. In their simulation, positrons and electrons were implanted into solids of Al, Cu, W and Au with kinetic energy of 1 – 10 keV. A simulated distribution of thermalisation process end points obtained from a condition in which 5 keV positrons are implanted normally into semi-infinite Al is shown in Fig. 3.1. The distribution of depth of positron thermalisation
CHAPTER 3. POSITRON DIFFUSION IN BULK

Figure 3.1: The simulated distribution of positron thermalisation process end points [38]. 5 keV positrons were implanted normally into the semi-infinite Al. The arrow shows the entrance position of the positrons.

Figure 3.2: The simulated and experimentally obtained relations between the mean implantation depth and incident energy of Al [38]. △: results for positrons, ○: results for electrons, ×: mean implantation depth of positron which is experimentally obtained by the beam-foil method [39], +: mean implantation depth of electron which is experimentally obtained by the beam-foil method [40].
end points, $z$, is fitted by the stopping profile proposed by Makhov [41],

$$ P(z) = -\frac{d}{dz} \exp\left(-\left(\frac{z}{z_0}\right)^m\right) = \frac{m z^{m-1}}{z_0^m} \exp\left(-\left(\frac{z}{z_0}\right)^m\right), \quad (3.1) $$

where $m$ is the shape parameter, and $z_0$ is expressed as a function of incident energy, $E_{e^+}$, as

$$ z_0 = \bar{z}(E_{e^+}) \frac{\Gamma((1/m) + 1)}{(1/m) + 1}. \quad (3.2) $$

$ar{z}(E_{e^+})$ is the mean stopping depth and is assumed to be

$$ \bar{z}(E_{e^+}) = AE_{e^+}^{-n}, \quad (3.3) $$

which was originally developed for stopping of electrons. The constant $A$ has been determined empirically to be

$$ A \sim \frac{40 \text{nm-keV}^{-n} \cdot \text{g/cm}^{-3}}{\rho}, \quad (3.4) $$
where $\rho$ is the density of the implantation target material in g·cm$^{-3}$, $\bar{z}$ is in Å, $E_{e+}$ is in keV [39], and the power $n \sim 1.6$ for positrons incident on most materials [42]. Figure 3.2 shows the mean implanting depth as the function of positron and electron incident energy. The stopping profile of 3 keV and 5 keV positrons incident on Cu obtained from simulation and experiment, and the fitted curve of Eq. (3.1) are shown in Fig. 3.3.

### 3.1.2 Diffusion

Thermalised positrons start to diffuse through the lattices in the bulk. The time dependency of positron number density $n(x,t)$ is given by the conventional diffusion equation

$$\frac{\partial}{\partial t} n(x,t) = D_+ \nabla^2 n(x,t) - \nabla \cdot (n(x,t) v_d) - \lambda_{\text{eff}} n(x,t), \quad (3.5)$$

where $x$ is the position in the bulk and $D_+$ is the positron diffusion coefficient. $\lambda_{\text{eff}}$ is the inverse of the effective lifetime of the positron $\tau_{\text{eff}}$ and is expressed using the depth-dependent concentration of defects $C(z)$ and a constant of proportionality $\kappa_t$,

$$\lambda_{\text{eff}} = \frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \kappa_t C(x). \quad (3.6)$$

The second term on the right hand side of Eq. (3.5) corresponds to the advection term of diffusion equations which describe the diffusion in fluids and $v_d$ is the drift velocity of positrons, which depends on the strength of electric fields. The following discussion focuses on positron diffusion in metals; thus, we do not have to consider $v_d$ because an electric field does not exist in metals.

The equation Eq. (3.5) for $v_d = 0$ has been solved and the eigen solution of the equation is expressed as the function of distance from the positron incident...
surface, $z$, as

$$n_K(z,t) = \theta(z) \frac{\sin(Kz) + K\beta \cos(Kx)}{\sqrt{1 + \beta^2 K^2}} \exp(-\delta t) ,$$  \hspace{1cm} (3.7)

where $\beta$ is a coefficient that takes account of internal reflection at the surface and the step function $\theta(z)$ is defined as

$$\theta(z) = \begin{cases} 1 & (z \leq 0) \\ 0 & (z > 0) \end{cases} .$$  \hspace{1cm} (3.8)

The time/space separation constant $\delta$ is related to $K$ in Eq. 3.7 by

$$\delta = D_+ K^2 + \lambda_{\text{eff}} .$$  \hspace{1cm} (3.9)

The wave function of positron $\Psi(z,t)$ is given by the integration of $n_K(z,t)$

$$\Psi(z,t) = \int_0^{+\infty} C_K n_K(z,t) dK ,$$  \hspace{1cm} (3.10)

where $C_k$ is the weight coefficient. If the positron diffusion starts from the initial condition in which all incident positrons exist the positron of depth $z = a$ (i.e. $\Psi(z,0) = \delta(z - a)$), $C_K$ is given as

$$C_K = \frac{2 \sin(Ka) + K\beta \cos(Ka)}{\pi \sqrt{1 + K^2\beta^2}} .$$  \hspace{1cm} (3.11)

The number of positrons which reach the surface via their diffusion motion from the depth $z = a$ is calculated using $D_+$ and $\Psi(z,t)$ as

$$N(a) = \int_0^{+\infty} \left| -D_+ \frac{\partial}{\partial z} \Psi(z,t) \right|_{z=0} \left| \right| dt = \exp \left( \frac{-a}{\sqrt{D_+ \tau_{\text{eff}}}} \right) \frac{1}{1 + \beta/\sqrt{D_+ \tau_{\text{eff}}}} .$$  \hspace{1cm} (3.12)

We express the depth distribution of the point at which the positron ther-
malisation process is complete with the stopping profile $P(z)$. The number of positrons which implant into the metals and diffuse back to the incident surface $N$ is given using $P(z)$ as

$$N = \int_{0}^{+\infty} N(a) P(a) \, da . \quad (3.13)$$

Under the assumption that the shaping parameter $m$ in the Makhov stopping profile Eq. (3.1) equals 1, $N$ is calculated as

$$N = \int_{0}^{+\infty} N(a) P(m; a) \mid_{m=1} \, da$$

$$= \int_{0}^{+\infty} \frac{1}{\bar{z}} \exp \left( -\frac{a}{\bar{z}} \right) \cdot \frac{\exp \left( -\frac{a}{\sqrt{D_{+} \tau_{\text{eff}}}} \right)}{1 + \beta / \sqrt{D_{+} \tau_{\text{eff}}}} \, da , \quad (3.14)$$

and is the Laplace transformation of $N(a)$. Using further assumptions that the positron mean implantation depth $\bar{z}$ is given by Eq. (3.2) and $\beta = 0$, we obtain the ratio $F_{S}$ of the number of positrons that diffuse back to the incident surface to the number of incident positrons, as the function of incident energy $E_{e+}$ as follows:

$$F_{S}(E_{e+}) = \frac{1}{1 + (E_{e+} / E_{0})^{n}} , \quad (3.15)$$

where $E_{0}$ is the incident energy at which 50% of incident positrons return to the incident surface [36] [43]. The values of $D_{+}$, $E_{0}$ and positron diffusion length $L_{+}$ are related by the following equation [34]

$$L_{+} = \sqrt{D_{+} \tau_{\text{eff}}} = A E_{0}^{n} . \quad (3.16)$$
3.2 Conventional Method of Studying Positron Diffusion

Some methods to measure the positron diffusion in metals have been developed. This section illustrates the schematics of three conventional methods. The essence of each method is implanting a monoenergetic positron beam into the sample to obtain $F_S$, which is defined as the ratio of the number of positron that diffuse back to the incident surface to the number of incident positrons, as a function of the positron incident energy $E_{e+}$.

3.2.1 Measurement of Line-Shape Parameters

The energy of $\gamma$-rays emitted from the annihilation of the resting pair of positron and electron is 511 keV. However, the energy of $\gamma$-rays from the annihilation of positrons implanted into materials have a distribution with width because of the Doppler effect with respect to the momentum of positron-electron pairs at the instant of their decay. $\gamma$-rays emitted from the positron-electron pairs which were moving nearer to a $\gamma$-ray detector at the instant of their decay are blue shifted and $\gamma$-rays emitted from the pairs moving away from the detector are red shifted.

Based on these properties, observation of line-shape parameters can measure the distribution of electrons in materials. This method is often used to investigate the vacancy-like defects in crystals. Positrons entered in materials are thermalised and diffuse in the bulk. These diffusing positrons tend to be trapped by defects due to their positive charge. The trapped positrons will annihilate with the valence electrons that has low momentum distribution; thus, the energy width of emitted $\gamma$-ray is smaller. In contrast, in perfect crystals, there is a higher probability that positrons will annihilate with the inner-shell electrons that have large momentum distribution and energy distribution of emitted $\gamma$-rays becomes large.
Energy distribution of annihilation $\gamma$-rays is often quantified by a W-parameter, $W$, and an S-parameter, $S$. W-parameter and S-parameter are defined as follows.

**Definition of W-parameter**

W-parameter, $W$, is defined as the ration of counts in a plain below the 511 keV peak to the total counts in the peak. Figure 3.4 shows an energy spectrum of annihilation $\gamma$-rays.

![Energy spectrum](image)

Figure 3.4: An annihilation $\gamma$-ray energy spectrum. Regions for W-parameter definition are indicated.

$W$ is defined as

$$W \equiv \frac{N_W}{N_T}$$  \hspace{1cm} (3.17)

where $N_W$ and $N_T$ are the summed counts in the regions of W and T in Fig. 3.5, respectively.
Definition of S-Parameter

which is the ratio of counts in a central portion of the 511 keV peak to the total counts in the peak. Figure 3.5 shows an energy spectrum of annihilation γ-rays.

![Energy Spectrum](image)

Figure 3.5: An annihilation γ-ray energy spectrum. Regions for S-parameter definition are indicated.

\[ S \equiv \frac{N_S}{N_T} \]  

(3.18)

where \( N_S \) and \( N_T \) are the summed counts in the regions of S and T in Fig. 3.5, respectively.

Measurement of Line-Shape Parameter

In 1892, Triftshäuser and Kögel [44] studied the defects concentration of a Cu sample irradiated by neutron and He by the observation of line-shape parameter method. They implanted positrons into the sample and measured the W-parameter, \( I_C \) as a function of positron incident energy, \( E_{e^+} \). The range of \( E_{e^+} \) was from 150 eV to 28 keV. They also studied the Cu sample which well
annealed to remove vacancies in the sample. The results obtained are shown in Fig. 3.6.

![Figure 3.6: W-parameter plotted against incident positron energy for Cu samples [44]. The solid line is the fitted curve of Eq. (3.20).](image)

Positrons diffuse back to the incident surface is trapped by their mirror potential (the surface-state), and then, annihilates with the valence electrons. When $E_{e^+}$ is low, most incident positrons diffuse back to the surface; thus, the W-parameter becomes smaller. In contrast, when $E_{e^+}$ is high, most incident positrons annihilate with inner-electron; thus, width of the 511 keV becomes wider and the W-parameter becomes larger.

Triftshäuser fitted the following equation

$$I_C(E_{e^+}) = I_C^\infty - (I_C^\infty - I_C^0) F_S(E_{e^+})$$ (3.19)

$$F_S(E_{e^+}) = \frac{1}{1 + (E_{e^+}/E_0)^n}, \quad n = 1.7$$ (3.20)

to the obtained data, where $I_C^\infty$ and $I_C^0$ are W-parameters of conditions $E_{e^+} \to \infty$ and $E_{e^+} \to 0$, respectively, and $E_0$ is the positron incident energy at which half of incident positrons diffuse back to the incident surface. The value of $E_0$ obtained from the fitting was $E_0 = 7.29 \pm 0.28$ keV.

39
3.2.2 Measurement of Reemission Positrons Yield

In 1983, R. J. Wilson and A. P. Mills, Jr [27] measured the yield of reemitted positron from a W(100) sample bombarded with a monoenergetic positron beam. The schematic of the experimental apparatus used is shown in Fig. 3.7. Magnetically guided positrons were implanted into the sample through three grids placed on the upstream side of the sample. Some of positrons, the thermalised and diffused back positrons, can be emitted as reemitted positrons to the direction of the upstream. NaI scintillation was placed outside the chamber to count the number of $\gamma$-rays emitted from the annihilations of positrons in the bulk. They performed the measurement for the two conditions of 1) reemitted positrons were repelled to the sample and 2) reemitted positrons were transported to the upstream of the chamber by changing the electric potential of the retarding grid. From the comparison of number of $\gamma$-rays for each condition, the yield of reemitted positron was obtained.

In this experiment, they found that increasing positron incident energy $E_{e^-}$ from 1 keV to 3 keV decreased the yield of reemitted positrons. From the

Figure 3.7: Sample chamber for cleaning and characterizing single-crystal metal surfaces of W(110) and Al(100) [27].
assumption that $F_S$ is expressed as the function of $E_{e+}$ as follows,

$$y(E_{e+}) \propto F_S(E_{e+})$$  \hspace{1cm} (3.21)$$

$$F_S(E_{e+}) = \frac{1}{1 + (E_{e+}/E_0)}.$$ \hspace{1cm} (3.22)

They obtained the value $E_0 = 25 \pm 5\text{keV}$.

### 3.2.3 Measurement of Positronium Fraction

In 1987, studies of positron diffusion in molybdenum were performed by the observation of Ps atoms by H. Huomo [45] [46]. The sample studied was Mo(111). They implanted monoenergetic positrons into the sample and measured the Ps fraction as the function of positron incident energy $E_{e+}$.

![Figure 3.8: Ps fraction $f_{Ps}$ plotted against positron incident energy $E_{inc}$ for Mo(111) sample [45].](image)

Figure 3.8 shows the obtained results. They also measured the kinetic
energy distribution of reemitted positrons and the result is shown in Fig. 3.9. The data shown in Fig. 3.9 implies that 5 – 7% of incident positrons are not thermalised completely in the case of \( E_{e^+} = 900\,\text{eV} \). Thus, they analysed the data shown in Fig. 3.8 with changing minimum energy of the analysed energy region, \( E_{\text{min}} \).

![Energy spectra of reemission positrons for Mo(111) sample [45].](image)

Figure 3.9: Energy spectra of reemission positrons for Mo(111) sample [45]. In the case of \( E_{e^+} = 900\,\text{keV} \), a small fraction of positrons are reemitted with the kinetic energy higher than the absolute value of positron work function \( \phi_+ \).

The fitting result with the best agreement to the data was obtained under the conditions \( E_{\text{min}} = 3.5\,\text{keV} \), the shape parameter, \( m \), of Makhov’s stopping profile, Eq. (3.1), equals 2 and the parameter \( n \) in Eq. (3.2) equals 1.55. The optimised value was \( E_0 = 7.5\,\text{keV} \).
3.3 Driving Force of Diffusion

This section describes the driving force of positron diffusion. Two pictures which illustrate motion of individual particles and flux of diffusing material are described first. Then, the driving force of charged particles in metals and semi-conductors are described.

3.3.1 Generalities

Individual Particles

Individual particles in diffusion materials (e. g. ink in water, smoke in atmosphere) perform the Brownian motion (random walk).

Let \( G(x, t) \) be a probability density function which gives the probability that a particle at the positron \( x = 0 \) at time \( t = 0 \) moves to the position \( x + dx \) at time \( t \) as \( G(x, t) \, dx \). Under two assumptions of 1) the motion of the particle does not depend on its history of motion and 2) the diffusion medium is isotropic, \( G \) satisfies the equation

\[
\frac{\partial G}{\partial t} = \frac{s^2}{6\tau} \nabla^2 G, \tag{3.23}
\]

where \( s \) is the norm of \( s \), a position vector of \( x \) viewed from a point of the particle path and \( \tau \) is the time required by its motion of the particle from the initial position \( 0 \) to \( x - s \). Comparing Eq. (3.23) and the Fick’s second low gives a diffusion constant \( D \) as

\[
D = \frac{s^2}{6\tau}. \tag{3.24}
\]

Flux

It is apt to be thought that the flux of diffusion material is cased by the gradient of concentration, \( \nabla n \). However, a gradient of chemical potential plays a key
role to generate the flux actually.

Let us think about vanadium (V) and nickel (Ni) placed separately and heated to the temperature of 500 °C in 1 atm hydrogen gas. Under the condition that solid-soluted hydrogen into V and Ni is in thermal equilibrium with gas-phase hydrogen, concentration of solid-soluted hydrogen in V is about 200 times higher than that in Ni. Then, let the V and Ni be contacted. The diffusion-flux of hydrogen from V to Ni does not occur. Let $\mu_{\text{H}^\text{in}V}$ and $\mu_{\text{H}^\text{in}Ni}$ be chemical potentials of hydrogen solid-soluted in V and Ni, respectively, and $\mu_{\text{H}^\text{in}\text{Gas}}$ be that of gas-phase hydrogen. Due to the thermal equilibrium condition of hydrogen in V, Ni and gas-phase, these three chemical potentials are related as

$$\mu_{\text{H}^\text{in}V} = \mu_{\text{H}^\text{in}\text{Gas}} \quad (3.25)$$
$$\mu_{\text{H}^\text{in}Ni} = \mu_{\text{H}^\text{in}\text{Gas}} \cdot (3.26)$$

Thus, $\mu_{\text{H}^\text{in}V} = \mu_{\text{H}^\text{in}Ni}$ and the hydrogen flux is not caused after V and Ni are contacted. It is to be noted that there are individual hydrogen particles which move from V to Ni or Ni to V.

### 3.3.2 Charged Particle Diffusion in Metals and Semiconductors

The driving forces of charged particle (electron, hole and positron) diffusion in metals and semi-conductors should be discussed in two parts, that of individual particles and that of their flux. The driving force of Brownian motion of individual particles is Coulomb-interaction between these particles and atomic nuclei.

The flux is caused by the gradient of chemical potentials. The chemical potential of charged particles (charge : $e$, electric potential : $\phi$) is expressed
as

\[ \mu_\phi = \mu + q\phi, \quad (3.27) \]

where \( \mu \) is the chemical potential without electric potential. The driving force of the flux of charged particles, \( F_{\text{flux}} \), is calculated as

\[
F_{\text{flux}} = -\nabla \mu_\phi \\
= -\nabla \mu - q\nabla \phi \\
= -\frac{\partial \mu}{\partial n} \nabla n + qE, \quad (3.28)
\]

where \( E = -\nabla \phi \) is an electric field. Equation (3.28) implies that \( F_{\text{flux}} \) can be separated to the driving force of diffusion-flux (the first term) and that of drift-flux (the second term).

**Electron Diffusion in Metals**

There are a vast amount of free electrons in metals. The gradient of electron density, \( \nabla n_{\text{el}} \), is rapidly neutralised. Therefore, the driving force of diffusion-flux is calculated as

\[
-\frac{\partial \mu_{\text{el}}}{\partial n_{\text{el}}} \nabla n_{\text{el}} = -\frac{\partial \mu_{\text{el}}}{\partial n_{\text{el}}} 0 = 0, \quad (3.29)
\]

where \( \mu_{\text{el}} \) is the electron chemical potential. Thus, the diffusion-flux does not occur.

**Electron Diffusion in Semi-Conductors**

In semi-conductors, there are electron diffusion-fluxes. The relationship between electron chemical potential \( \mu_{\text{el}} \) and concentration \( n_{\text{el}} \) is given by

\[
\mu_{\text{el}} = k_B T \ln n_{\text{el}} + \text{Const.}, \quad (3.30)
\]
where $k_B$ is the Boltzmann constant, $T$ is the temperature. The electron diffusion-flux $j_d$ is calculated with mobility, $M$, as

$$j_d = -n_{el} M \nabla \mu_{el}$$

$$= -n_{el} M \frac{\partial \mu_{el}}{\partial n_{el}} \nabla n_{el}$$

$$= -k_B T M \nabla n_{el} . \quad (3.31)$$

From comparing Eq. (3.31) and Fick’s first law, $j_d = -D \nabla n_{el}$, the diffusion constant, $D$, is expressed as the Einstein’s relation,

$$D = k_B T M = \frac{k_B T}{e \nu} , \quad (3.32)$$

where $e$ is the elementally charge, $\nu$ is the electric mobility.

**Positron Diffusion in Metals**

The mean life-time of positrons in metals is on the order of $10^{-10}$ s, and a typical beam-intensity of slow positron beams used in many laboratories is on the order of $10^3 - 10^8 e^+ \cdot s^{-1}$. Therefore, the number of positrons which exist in the metal samples is only one at most.

Positrons in metals perform Brownian motion caused by interactions between positrons and atom nuclei. The driving force of the motion is Coulomb force. On the other hand, due to the slightness of positrons existing in metals simultaneously, there is no positron-flux. Thus, the driving force of the flux can not be discussed.

Some positrons may be trapped by vacancy-type defects in metal crystals, and annihilate there. This phenomenon is peculiar to positrons and is reflected as the annihilation-term in the diffusion equation.
Chapter 4

Experiment

4.1 Experimental Apparatus

We have developed a new method to study positron diffusion in metals by the observation of Ps\(^-\) emission from surfaces of metals [47] [48] and measured the positron diffusion in polycrystalline tungsten (W) and molybdenum (Mo) sample with this method. A slow positron beam apparatus placed at Kagurazaka campus of Tokyo University of Science (TUS) was used in this work. This section illustrates the details of the experimental apparatus and procedures.

4.1.1 Chamber

In our new method to study positron diffusion in metals, we count the number of Ps\(^-\) emitted from the surface of the metal sample. In order to execute our experiment with high statistic precision, alkali-metal must be deposited onto the sample surface to enhance the yield of Ps\(^-\). It is empirically known that a high degree of vacuum is needed in order to maintain the effect of alkali metal deposition. The design of chambers in our apparatus conforms to the ICF standard and is able to produce an Ultra High Vacuum (UHV) environment (typically \(10^{-8} - 10^{-7}\) Pa) inside it.
CHAPTER 4. EXPERIMENT

The chamber consists of three parts

1. Upstream chamber
2. Measurement chamber
3. Sample holder flange

A schematic of the chamber is shown in Fig. 4.1. The upstream chamber contains a positron source, moderator, acceleration grid and $E \times B$ filter (Sec. 4.1.2, 4.1.3). The measurement chamber has ports to attach the Ge detector and alkali-metal sources. The sample holder flange is attached to the down-stream side of the measurement chamber. The flange holds the sample with the molybdenum blocks. These blocks are connected to copper electrodes at the outside of the flange, and we can anneal the sample by the passage of an electric current with the electrodes. A NaI(Tl) scintillation detector is placed behind the flange and a quartz crystal oscillation deposition monitor that monitors the thickness of alkali-metal coating is attached to the flange. A schematic diagram of the measurement chamber and the sample holder flange is shown in Fig. 4.2.
4.1.2 Slow Positron Source

Positron Source

The positron source in our apparatus is radioisotope $^{22}\text{Na}$. $^{22}\text{Na}$ is contained in a capsule as its chloride state (i.e. NaCl) and sealed with a thin titanium film. A photograph of the positron source capsule is shown in Fig. 4.3.
Monoenergetic Positron Beam Generation

The kinetic energy of positrons emitted from $^{22}$Na distributes in the range of $0 - 546\text{ keV}$. In order to generate the monoenergetic positron beam, we have to use the positron moderator to slow down the positrons from $^{22}$Na.

Metals with a negative value of positron work function, $\phi_+$, or solid rare gasses are usually used as the positron moderator. In our apparatus, polycrystalline tungsten is employed as the moderator. $\phi_+$ for polycrystalline tungsten is negative and its absolute value is relatively large (Tab. 2.2), hence, the efficiency of moderation is relatively large.

We use the mesh type moderator (100 mesh/inch, $\phi 10\mu m$) to increase the surface area per unit volume and obtain a high positron moderation efficiency. Commercially available tungsten mesh of diameter $20\mu m$ was electro-polished in NaOH solution. Then, the mesh was annealed at a temperature of 2000K for 45 min to remove the defects in the bulk which behave as positron traps. Seventeen meshes manufactured through the above processes were piled up and placed in front of the $^{22}$Na capsule. The kinetic energy of moderated positrons is about $3\text{ eV}$. The surrounds of the positron source capsule is shown in Fig. 4.4 schematically.

![Diagram of Positron Source and Moderator](image)

Figure 4.4: The surrounds of the positron source capsule.
4.1.3 Positron Acceleration and Transport

There is an acceleration grid at 1 mm downstream of the positron moderator. The electric potential of the positron source and moderator is higher than the accelerator grid. Thus, the kinetic energy of positrons passed through the grid is about 0.1 keV.

These slow positrons are magnetically guided to the downstream of apparatus. The magnetic field is produced by the coils shown in Fig. 4.5. The copper wire of 440 turns is hardened with epoxy resin. Nine coils are equipped to our apparatus and we turn on the electricity as listed up Tab. 4.1. These coils produce a magnetic field of about 100 Gauss on the beam axis. Whereas most positrons emitted from the $^{22}$Na source are slowed down by the positron moderator, a fraction of emitted positrons pass through the moderator mesh and remain motioning with high kinetic energy. In order to eliminate these

Figure 4.5: Schematic of coils that produce magnetic-field. The unit of length in this figure is mm.
fast positrons, our apparatus has the \( E \times B \) filter. As shown in Fig. 4.6, the electric field \( E \) is applied perpendicular to the magnetic field \( B \). In these fields, the trajectory of positrons shifts to the direction which makes a right angle to both \( E \) and \( B \). The value of the shift, \( \Delta y \), in the region where fields \( E, B > 0 \) are applied is given by:

\[
E = \begin{pmatrix} -E \\ 0 \\ 0 \end{pmatrix}, \quad B = \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix}
\]

Table 4.1: Parameters of transport coils.

<table>
<thead>
<tr>
<th>Coil No.</th>
<th>Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
</tr>
<tr>
<td>6</td>
<td>9.5</td>
</tr>
<tr>
<td>7</td>
<td>9.5</td>
</tr>
<tr>
<td>8</td>
<td>9.5</td>
</tr>
<tr>
<td>9</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Figure 4.6: The schematic of the \( E \times B \) filter’s action.
are applied, is given as
\[
\Delta y = \frac{E}{B} \Delta t
\]  
(4.2)

where \( \Delta t \) is the time required to pass through the region where \( E \) exists. Positrons that were not slowed down in the moderator pass through the region with electric field quickly; thus, the shift of their trajectory is too small to pass the aperture placed in the exit of the \( E\times B \) filter. In contrast, positrons with kinetic energy under 0.1 keV required a long time to pass through the \( E\times B \) region; thus, the shift of their trajectory is too large to pass the aperture as well.

We employ cylindrically curved plates as the electrodes to produce an electric field instead of plane ones to avoid the distortion of beam shame due to the potential difference between two electrodes [49]. The positrons passed through the \( E\times B \) filter with kinetic energy 0.1 keV are accelerated by the accelerate tube. A schematic of the accelerate tube is shown in Fig. 4.8. The upstream chamber is electrically isolated from the measurement and sample-preparation chambers by the tube. The electric potential of the upstream

![Cylindrical electrodes](image)

Figure 4.7: The cylindrical electrodes use in the \( E\times B \) filter of our apparatus.
chamber is higher than the downstream chambers and the potential difference is tunable in the range of 0.0 – 29.9 keV. Hence, we can obtain the monoenergetic positron beam of 0.1 – 30.0 keV kinetic energy. Both the measurement and sample-preparation chambers are grounded.

In order to transport positrons to the sample exactly, the trajectory of positrons must be adjusted precisely. We adjust the trajectory with the steering-coils placed close to the downstream of the acceleration tube. Before the experiment, we attach the Micro Channel Plate (MCP) and phosphor screen to downstream of the measurement chamber, and adjust the current of the steering-coils to bring the endpoint of positron beam to the place where the sample will be fixed by the monitoring of the fluorescence on the screen.

### 4.2 Sample

The samples in which positron diffusion was measured in this work were polycrystalline foils of W and Mo. Thickness and purity were 25 μm and 99.95 %, respectively, for both W and Mo samples. The samples were cut out from the sheet of the sample materials. Shapes of the samples were the same for W and Mo. A schematic diagram of the sample shape is shown in Fig. 4.9. A sample cut out was folded down and a deformed one was fixed to centre of the sample holder flange as shown in Fig. 4.10.
4.3 Data Acquisition System

In this work, we count $\gamma$-rays emitted from self-annihilations of $\text{Ps}^-$ and measure their energies to obtain the yield of emitted $\text{Ps}^-$. The data acquisition (DAQ) system of our apparatus is shown in Fig. (4.11). $\gamma$-rays from $\text{Ps}^-$ are detected by the Ge detector in coincidence with the signals from a NaI(Tl) scintillation detector to reduce the background. Electrical signals from the Ge detector are shaped and amplified by two amplifiers and input to a Multi Channel Analyser (MCA). The MCA outputs the digital signals corresponding to the wave height input to it (Analogue to Digital Conversion; ADC).

The signal output from the Ge detector has the time width of about 10 $\mu$s.
In the case that the number of $\gamma$-rays enter the detector per unit time is large, the signals originating in each $\gamma$-ray pile up, and these piled up signals cause background in the high energy region. In order to reduce such background, we use the Pile Up Rejection (PUR) system. This system inputs the veto-signal when the pile up of discrete signal occurs and MCA pauses the ADC sequence.

4.4 Production of the UHV Environment

We can produce an Ultra High Vacuum (UHV) environment in the measurement chamber via proper operation of an oil rotary pump, turbo molecular pumps (TMP) and non-evaporable getter (NEG) pumps. Figure 4.12 shows the schematic of vacuum production systems. One TMP (MITSUBISHI; PT-300) is attached to the upstream chamber and two TMPs (MITSUBISHI; PT-500 and Varian; V-81) are attached to the measurement chamber in series. These TMPs are backed by an oil rotary pump (ALCATEL; M2021SD). Furthermore, two NEG pumps (SAES Getters S.p.A.; CapacitTorr and Vaclab Inc.; MNEG-114) are attached to the chamber.

![Figure 4.12: The schematic of vacuum system.](image)

We pumped the chambers with TMPs and oil rotary pump for a day and
then, baked out the chambers for a few days. The temperature of the baking was about 150°C at the highest point and about 100°C at the lowest point. As the next step, while the temperatures of the chambers were still high, we reactivated the NEG pumps. Eventually, the pressure in the chamber reached to $2.4 \times 10^{-8}$ Pa.

### 4.5 Experimental Procedures

In this section, the procedures of our experiments are described concretely. Schematic processes of the experiment are as follows

1. Measure the number of positrons implanted into sample,
2. Anneal the sample,
3. Deposit Na onto the surface of the sample and
4. Quantify the number of $\text{Ps}^-$ emitted from the surface.

We measured the yields of $\text{Ps}^-$ in the range of positron incident energy, $E_{e^+}$, from 1.1 keV to 30.0 keV. Incident energies for measurements for polycrystalline of W and Mo samples are listed up in Tables 4.2 and 4.3, respectively.

While the experiment was performed, the sample was biased at $-1$ keV with respect to the ground potential to accelerate $\text{Ps}^-$ emitted from the sample surface. Thus, we have to set the kinetic energy of the transported positron to $(E_{e^+} - 1)$ keV to implant positrons with the energy of $E_{e^+}$ keV.

#### 4.5.1 Measurement of Quantity of Incident Positrons

In this work, the positron diffusion coefficient is obtained by the observation of $\text{Ps}^-$ emission efficiency, $f_{\text{Ps}^-}$, as a function of positron incident energy, $E_{e^+}$. 

57
Table 4.2: List of positron incident energies for measurement with the W(polycrystalline) sample.

<table>
<thead>
<tr>
<th>Energy No.</th>
<th>Transport energy (keV)</th>
<th>Incident energy (E_{e^+}) (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>4.0</td>
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<tr>
<td>5</td>
<td>7.0</td>
<td>8.0</td>
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<td>12.0</td>
<td>13.0</td>
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<tr>
<td>7</td>
<td>17.0</td>
<td>18.0</td>
</tr>
<tr>
<td>8</td>
<td>23.0</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Table 4.3: List of positron incident energies for measurement with the Mo(polycrystalline) sample.

<table>
<thead>
<tr>
<th>Energy No.</th>
<th>Transport energy (keV)</th>
<th>Incident energy (E_{e^+}) (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>6.0</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>9.0</td>
<td>10.0</td>
</tr>
<tr>
<td>6</td>
<td>14.0</td>
<td>15.0</td>
</tr>
<tr>
<td>7</td>
<td>19.0</td>
<td>20.0</td>
</tr>
<tr>
<td>8</td>
<td>24.0</td>
<td>25.0</td>
</tr>
<tr>
<td>9</td>
<td>29.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>
Here, $f_{Ps^-}$ is defined as

$$f_{Ps^-} (E_{e^+}) \equiv \frac{N_{Ps^-} (E_{e^+})}{N_{e^+} (E_{e^+})},$$

(4.3)

where $N_{e^+}$ is the number of incident positrons per unit time, and $N_{Ps^-}$ is the number of $Ps^-$ formed and emitted per unit time. It is actually impossible to measure these values. Thus, we measured count rates of $\gamma$-rays originating in annihilation of positrons implanted into the sample $R_{e^+}$ and that of $Ps^-$, $R_{Ps^-}$. $f_{Ps^-}$ is redefined using $R_{e^+}$ and $R_{Ps^-}$ as

$$f_{Ps^-} (E_{e^+}) \equiv a \frac{R_{Ps^-} (E_{e^+})}{R_{e^+} (E_{e^+})},$$

(4.4)

where $a$ is a coefficient proper to the apparatus. The factor of positron and $Ps^-$ transmittance for the $Ps^-$ acceleration grid and position of Ge detector are included in $a$.

As the first procedure of our experiment, we implanted the positrons into the unannealed sample and analysed the annihilation $\gamma$-ray energy distribution. Metals which are not annealed contain the many defects in their bulk. Positrons implanted into such metals are trapped and annihilated to emit 2 $\gamma$-rays. Hence, we can obtain the value of $R_{e^+}$ via the integration of the 511 keV peak in the energy spectrum.

### 4.5.2 Annealing of the Sample

After the measurements of $R_{e^+}$ for each $E_{e^+}$, we annealed the sample in situ to remove defects in the bulk that behave as positron traps. The temperatures and the times for annealing were 1800 K and 30 min for the W(polycrystalline) sample, and were 1500 K, 1800 K and 30 min for each annealing temperature for the Mo(polycrystalline) sample.

We annealed the samples by passage of an electric current. A picture of
sample under annealing is shown in Fig. 4.13. The temperatures of the sample

![Sample under annealing](image)

Figure 4.13: A sample under annealing. The temperature is 1800 K. The silhouette in front of the sample is the $\text{Ps}^-$ acceleration grid. We ensure enough distance between the sample and the grid to avoid deformation of the grid.

were monitored and controlled by the observation of radiation light with an optical pyrometer (KONICA MINOLTA, INC; TR-630).

### 4.5.3 Na Deposition

After cooling down to room temperature Na was deposited onto the surface of the sample in order to increase the $\text{Ps}^-$ yields. The deposition source we used was a Na dispenser purchased from SAES Getter S.p.A. (NA/NF/2.1/17 FT10+10). This dispenser contains $\text{Na}_2\text{CrO}_4$. Pure Na can be emitted to a vacuum by heating the dispenser with an electric current. The thickness of Na deposited on the sample was monitored by the quartz oscillation deposition monitor (INFICON; BK-A0F, 008010G10).

High $\text{Ps}^-$ yields are expected to be obtained when the thickness of Na deposition is 7 atoms-nm$^{-2}$ (2.7 Å) where the electron work function is minimum [31]. However, in this experiment, the thickness of the Na layer was controlled to be 10 atoms-nm$^{-2}$ (4 Å) to stabilise the effect of deposition.
4.5.4 Measurement of Ps\(^-\) Yield

We implanted positron with kinetic energy of \(E_{e^+}\), listed in Tables 4.2 and 4.3 into the annealed and Na deposited W (polycrystalline) and Mo (polycrystalline) samples, respectively, and measured the yields of Ps\(^-\) emitted from the sample for each \(E_{e^+}\). In order to reduce the effect of time dependence of Ps\(^-\) yields due to changes of Na layer states, we changed \(E_{e^+}\) cyclically and observed the Ps\(^-\) emission for each value of \(E_{e^+}\) in a short time interval (300 s for the polycrystalline W sample and 360 s for the polycrystalline Mo sample), and repeated series of the measurements many times to obtain statistically sufficient data.

The schematic of Ps\(^-\) emission, acceleration and self-annihilation is shown in Fig. 4.14. The sample was biased at \(-1.0\) kV with respect to the Ps\(^-\) acceleration grid, which is grounded. Thus, positrons transported to the Ps\(^-\) acceleration grid with kinetic energy \((E_{e^+} - 1)\) keV were implanted into the sample with \(E_{e^+}\) keV. Ps\(^-\) emitted from the sample surface were accelerated by an electric field between the sample and Ps\(^-\) acceleration grid. The energy of \(\gamma\)-rays emitted from the annihilation of accelerated Ps\(^-\) is Doppler shifted for the detector fixed to the laboratory. We placed a Ge detector position

![Figure 4.14: Schematic of Ps\(^-\) emission, acceleration and self-annihilation.](image-url)
where the acceleration $P_s^-$ approaches and detected the blue shifted $\gamma$-rays to measure $P_s^-$ yields.
Chapter 5

Data Analysis

5.1 Quantity of Incident Positrons

As mentioned in Sec. 4.5.1, the number of positrons implanted into the sample for each positron incident energy, $E_{e^+}$, must be obtained in order to calculate Ps$^-$ emission efficiency $f_{Ps^-}(E_{e^+})$. We obtained the number of implanted positrons from the annihilation $\gamma$-ray energy spectra obtained from the measurements in which positrons were implanted into the unannealed sample.

![Integral of spectrum](image1)

Figure 5.1: The calculation of number of positrons implanted into the sample. These graphs were obtained from the measurements in which positrons were implanted into the unannealed sample. The horizontal axis is the half width of the interval of the integration and the vertical axis is the integrated counts. The centre of the interval of the integration corresponds to the energy of 511 keV. The graphs shown on the left and right correspond to the before and after of background-removing, respectively.

Figure 5.1 shows the integration of the annihilation $\gamma$-ray spectra. The
integration of the raw spectrum is shown on the left side of Fig. 5.1. The horizontal axis is the half width of the interval of the integration and its centre corresponds to the energy of 511 keV for each spectra. As we can see from the left side graph of Fig. 5.1, after the half width of the interval of the integration reaches about 100 ch, the integrated counts begins to increase linearly. This implies that the annihilation γ-ray energy spectrum contains a peak its centre is 511 keV and a constant-background. We fitted a linear function to the left side graph of Fig. 5.1 in the region from 300 ch to 500 ch. After removing of the constant-background obtained from the fitting, we got the graph shown on the right side of Fig. 5.1. In this graph, the integration counts converge to a constant value and we recognized the constant value as the area of the 511 keV peak region. The value obtained after the normalization of the 511 keV peak area by the total time of the measurement is the number of detected γ-rays originated in the annihilation of positrons implanted into the sample, $R_{e^+}$. This value is expressed as

$$R_{e^+} = N_{e^+} \frac{\alpha_1}{4\pi} \varepsilon$$

(5.1)

where $N_{e^+}$ is the number of positrons implanted into the sample per unit time, $\alpha_1$ is a solid angle of the Ge detector viewed from the sample and $\varepsilon$ is the detection efficiency of the Ge detector. However, it is not required to know these values concretely as mentioned later.

### 5.2 Yield of Emitted Positronium Negative Ions

The yields of Ps$^-$ emitted from the sample surface are obtained by counting the γ-rays originated in the self-annihilation of Ps$^-$. It is easy to select the γ-rays emitted from the self-annihilation of Ps$^-$, although the Ge detector detects a large number of γ-rays.

As shown in Fig. 4.14, Ps$^-$ emitted from the sample were accelerated
by the electric field between the sample and the Ps\(^-\) acceleration grid. The energy of \(\gamma\) rays emitted from the self-annihilation of Ps\(^-\) and detected by the Ge detector that is fixed to the laboratory is Doppler shifted. The value of the \(\gamma\)-ray energy is given by

\[
E = \frac{1}{\lambda + 1 - \sqrt{\lambda^2 + 2\lambda \cos \theta}}
\]  

(5.2)

\[
\lambda \equiv \frac{eV_{\text{acc}}}{3m_e c^2},
\]  

(5.3)

where \(V_{\text{acc}}\) is the acceleration voltage applied to the sample and \(\theta\) is the angle between the direction of Ps\(^-\) acceleration and the direction of the \(\gamma\)-ray. Figure 5.2 shows the annihilation \(\gamma\)-ray spectra for \(E_{e^+} = 1.1\) keV, 9.0 keV, 21.0 keV and 30.0 keV where the Ps\(^-\) emission occurs. The energy of \(\gamma\)-rays due to the self-annihilation of accelerated Ps\(^-\) is 526 keV and these blue shifted peaks are clearly distinguished from those of at the energy of 511 keV.

The most easiest method to obtain the number of \(\gamma\)-rays due to the self-annihilation of Ps\(^-\) is the summing of the counts of the blue shifted energy peak in Fig. 5.2. However, due to the lowness of counts in the region, it is difficult to accurately estimate the number of \(\gamma\)-rays by the method although the yield of Ps\(^-\) is enhanced by Na deposition. Then, we fitted the function

\[
f(x) = \frac{2\sqrt{2\ln2} S}{\sqrt{2\pi} w} \exp \left( -\frac{4\ln2}{w^2} (x - \mu)^2 \right) + g(x),
\]  

(5.4)

to the energy peak due to Ps\(^-\). The first term of Eq. (5.4) is a Gauß function with mean \(\mu\), full width at half maximum (FWHM) \(w\) and area \(S\). This term corresponds to the resolution-curve of the Ge detector. The second term is a background function and it is known that the formation

\[
g(x) = C_1 + C_2 \tan^{-1} \left( \frac{x - \mu}{w} \right)
\]  

(5.5)

\(C_1, C_2\): Constants.
Figure 5.2: The γ-ray energy spectra with the Ps⁻ emission for the incident positron energies of 1.1 keV, 8.0 keV and 24.0 keV. The Ps⁻ acceleration voltage was $V_{\text{acc}} = 1.0\, \text{kV}$. These spectra have been normalized to the total measurement time. Increase of positron incident energy leads to a decrease of Ps⁻ yields.
expresses the realistic background well. An example of the fitting of Eq. 5.4 to the peak due to the self-annihilation of Ps$^-$ is shown in Fig. 5.3. The value of $S$ obtained by the fitting is $R_{e^+}$ which is defined as the number of detected $\gamma$-rays due to the Ps$^-$ self-annihilation. $R_{Ps^-}$ can be written as

$$R_{Ps^-} = N_{Ps^-} \xi \frac{\alpha_2}{4\pi} \varepsilon,$$

(5.6)

where $N_{Ps^-}$ is the number of emitted Ps$^-$ from the sample per unit time, $\xi$ is the probability that emitted Ps$^-$ reach the Ps$^-$ acceleration grid without annihilating to be accelerated completely, $\alpha_2$ is the solid angle of the Ge detector viewed from the region where the Ps$^-$ self-annihilation occurs and $\varepsilon$ is the detection efficiency of the Ge detector.
5.3 Emission Efficiency of Positronium Negative Ions

Here, we define \( R \) as the ratio \( R_{\text{Ps}^-} \) to \( R_{\text{e}^+} \). \( R \) is expressed as

\[
R = \frac{R_{\text{Ps}^-}}{R_{\text{e}^+}} = \frac{N_{\text{Ps}^-} \xi (\alpha_2/4\pi) \varepsilon}{N_{\text{e}^+} (\alpha_1/4\pi) \varepsilon} = \xi \frac{\alpha_2}{\alpha_1} \frac{N_{\text{Ps}^-}}{N_{\text{e}^+}}. \tag{5.7}
\]

In the deformation of the equation, Eq. (5.1), (5.6) are used. The number of \( \text{Ps}^- \) emitted from the sample surface is proportional to the number of positrons that return to the incident surface after being implanted via their diffusion motion, \( N_S \). \( N_S \) is written with \( F_S \), the fraction of positrons which diffuse back to the incident surface,

\[
N_S = N_{\text{e}^+} F_S. \tag{5.8}
\]

Thus, \( N_{\text{Ps}^-} \) is calculated as

\[
N_{\text{Ps}^-} = r_{\text{Ps}^-} N_S = r_{\text{Ps}^-} N_{\text{e}^+} F_S, \tag{5.9}
\]

where \( r_{\text{Ps}^-} \) is the fraction of the number of emitted \( \text{Ps}^- \) to the number of positrons that diffuse back to the incident surface. Hence, \( R \) is written as

\[
R = \xi \frac{\alpha_2}{\alpha_1} r_{\text{Ps}^-} F_S = R_0 F_S \tag{5.10}
\]

\[
R_0 \equiv \xi \frac{\alpha_2}{\alpha_1} r_{\text{Ps}^-} \text{ = Const.} \tag{5.11}
\]

In general, it is known that \( r_{\text{Ps}^-} \) changes over time; however, the yields of \( \text{Ps}^- \) were monitored and verified to be stable. Thus, in this work, \( \xi (\alpha_2/\alpha_1) r_{\text{Ps}^-} \) is treated as a constant and expresses as the \( R_0 \). The factors of \( \alpha_1, \alpha_2 \) and \( \xi \) are included in \( R_0 \); thus, we do not need to know their concrete values.
5.4 Quantifying $E_0$

Figures 5.4 and 5.5 show the $R$ plotted against the positron incident energies $E_{e+}$ for each sample and annealing temperature. I postulate that the fraction

![Graph showing $R$ plotted against $E_{e+}$ for each sample and annealing temperature.]

Figure 5.4: The area ratio $R$ plotted against positron incident energies $E_{e+}$ (A).

$F_S$, which is defined as the ratio of the number of positrons reaching the incident surface via their diffusion motion to the number of incident positrons, is given by Eq. (3.15) as a function of positron incident energy $E_{e+}$,

$$F_S(E_{e+}) = \frac{1}{1 + (E_{e+}/E_0)^n},$$

where $E_0$ is the positron incident energy at which 50% of incident positrons diffuse back to the incident surface. Under this postulation and Eq. (5.10), $R$ as the function of $E_{e+}$ is written as

$$R(E_{e+}) = \frac{R_0}{1 + (E_{e+}/E_0)^n}. \quad (5.12)$$

The values of $E_0$ and $n$ are obtained by the fitting of Eq. (5.12) to plots in Fig. 5.4 and 5.5. The fitting for the data of Mo(polycrystalline) sample for
Figure 5.5: The area ratio $R$ plotted against positron incident energies $E_{e^+}$ (B).
Table 5.1: Obtained values of $E_0$ and $n$. The parameter $n$ of Mo(polycrystalline) sample is common for each annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_a$ (K)</th>
<th>$E_0$ (keV)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(polycrystalline)</td>
<td>1800</td>
<td>7.4±0.4</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>Mo(polycrystalline)</td>
<td>1500</td>
<td>3.8±0.5</td>
<td>1.7±0.1</td>
</tr>
<tr>
<td>Mo(polycrystalline)</td>
<td>1800</td>
<td>6.0±0.5</td>
<td>1.7±0.1</td>
</tr>
</tbody>
</table>

two different annealing temperatures, $T_a = 1500$ K and 1800 K, was carried out simultaneously under the condition that the parameter $n$ is common for each annealing temperature. Fitted curves are represented in these plots by the red solid curves. Obtained values of $E_0, n$ for each sample and annealing temperature, $T_a$, are listed in Table. 5.1.
Chapter 6

Discussion

It is necessary to obtain the fraction of positrons which diffuse back to the incident surface after their implantation, $F_S$, as a function of positron incident energy $E_{e^+}$ to measure the positron diffusion in metals. This chapter describes the schematics of conventional methods to obtain $F_S(E_{e^+})$ first. Then, the new method we developed is described and shown to be more reliable than those conventional methods.

6.1 Conventional Methods

6.1.1 Line-Shape Parameter Measurement

The energy of one $\gamma$-ray emitted from annihilation of rest positron-electron pairs is 511 keV. However, actual energies of $\gamma$-rays emitted from annihilation of positrons implanted into materials have energy distribution. Thus, distribution reflects the momentum distribution of positron-electron pairs in the instant of their annihilation.

W-parameter Observation

In 1982, W. Triftshäuser and G. Kögel [44] implanted monoenergetic positrons into a Cu sample and measured the W-parameters as a function of $E_{e^+}$. The
fraction $F_S$ is high when $E_{e^+}$ is lower and most positrons diffuse back to the incident surface and annihilate with valence electrons which have relatively low momentum distribution. Therefore, width of the 511 keV becomes wide; thus, the $W$-parameter is larger. In contrast, when $E_{e^+}$ is higher, most implanted positrons annihilate with inner-shell electrons which have high momentum distribution; thus, the $W$-parameter is smaller. Triftshäuser and Kögel postulated that $F_S (E_{e^+})$ is given as

$$F_S (E_{e^+}) = \frac{1}{1 + E_{e^+}/E_0^{1.7}},$$

and the expressed $W$-parameter, $I_C (E_{e^+})$ is

$$I_C (E_{e^+}) = I_C^\infty - (I_C^\infty - I_C^0) F_S (E_{e^+}),$$

where $I_C^\infty$ and $I_C^0$ are the corresponding $W$-parameter values for $E_{e^+} \to +\infty$ and $E_{e^+} \to 0$, respectively.

In the $W$-parameter observation method, a lowness of the energy resolution of the Ge detectors to detect $\gamma$-rays is a problem. Energy resolution of Ge detectors is about 1 keV when the centre energy is 511 keV. $W$-parameter is defined as Eq. (3.17) and the energy width of the region $W$ in Fig. 3.4 is usually set about 2–3 keV. Thus, the energy resolution of the Ge detectors are not enough to $W$-parameter observation. $\gamma$-ray detectors with high energy resolution has not been put to practical use.

**S-parameter Observation**

Positron diffusion in metals is also measured by observation of a $S$-parameter, $S$, as a function of the positron incident energy, $E_{e^+}$. The function, $S (E_{e^+})$, must include effects of positron annihilation in bulk, traps, surface-state and
CHAPTER 6. DISCUSSION

$p$-Ps emitted to a vacuum. $S(E_{e^+})$ is given as

$$S(E_{e^+}) = \frac{S_b (1 - J_S(E_{e^+})) + f_t (S_t - S_b) + J_S(E_{e^+}) (f_{ss}S_{ss} + \alpha f_{Ps}S_{Ps})}{1 - (1 - \alpha) J_S(E_{e^+}) f_{Ps}},$$

(6.3)

where $S_b$, $S_t$, $S_{ss}$ and $S_{Ps}$ are the corresponding S-parameter values for positron annihilations in bulk, traps, surface-state and $p$-Ps atoms, respectively. $f_t$ and $f_{Ps}$ are the fractions of positrons annihilating in traps and as Ps atoms, respectively, and $\alpha$ is a constant. $J_S(E_{e^+})$ is the positron current returning to the incident surface and is given by the Laplace transformation of the positron stopping profile [46].

In the observation of S-parameter, the energy resolution of the Ge detectors is also a problem. S-parameter is defined as Eq. (3.18) and the energy width of the region S in Fig. 3.5 is usually set to about $1 - 3$ keV; thus, the energy resolution of the Ge detectors is insufficient. In addition, Eq. (6.3) does not include the effect of positron reemission. If the effect is included to formula of $S(E_{e^+})$, Eq. (6.3) becomes more complex; thus, it is difficult to carry out exact fitting of obtained data.

6.1.2 Measurement of Reemitted Positron Yields

Some implanted positrons can be emitted as slow positrons. The yield of such positrons, $Y_{e^+}$, is proportional to $F_S$. This property has been used in the experiments to study positron diffusion in metals. In 1983, Wilson and Mills [27] implanted monoenergetic positrons into a W(111) sample and measured $Y_{e^+}$ as a function of $E_{e^+}$. The schematic diagram of their apparatus is shown in Fig. 6.1.

In this experiment, $\gamma$-rays emitted from the sample were counted under the two conditions where reemitted positrons were 1) completely returned back to the sample and 2) removed to the region far from the sample. These two
conditions were realized by the changing of an electric potential of a retarding grid which was placed near the sample. The difference between counts obtained under the two conditions was $Y_{e^+}$. Wilson and Mills postulated that $Y_{e^+}$ is given as

$$Y_{e^+}(E_{e^+}) = \frac{Y_{e^+0}}{1 + E_{e^+}/E_0},$$

(6.4)

where $Y_{e^+0}$ is the yield of reemitted positrons when $E_{e^+} = 0$ keV. They found that increase in $E_{e^+}$ from 1 keV to 3 keV resulted in an approximately 10% decrease in $Y_{e^+}$. The obtained value of $E_0$ from this result was $E_0 = 25\pm5$ keV.

In this method, a retarding grid must be placed near the sample to reflect reemitted positrons to the sample. Some incident positrons, reemitted positrons and Ps atoms are intercepted by the grid and annihilate there. Both the energies of the $\gamma$-rays emitted by the annihilation of the positrons which return back to the sample and those of positrons intercepted by the grid are 511 keV. These $\gamma$-rays with these different origins are not distinguishable in the
energy spectrum. Thus, $\gamma$-rays from the retarding grid resulted in a systematic error of this experiment.

### 6.1.3 Measurement of Ps atom Yields

Ps atoms can be emitted from the samples bombarded with low-energy positrons. The yields of the Ps atoms are also proportional to $F_S$. In 1987, H. Huomo *et al.* [45] measured positron diffusion in Mo(111) sample by the observation of Ps yields as a function of $E_{e^+}$.

The annihilation $\gamma$-ray energy spectra obtained from the conditions $f_{Ps} = 0$ and $f_{Ps} = 1$ are shown in Fig. 6.2. Due to the continuous energy distribution of $\gamma$-rays which originate in $\alpha$-Ps decays, there is significant difference in these spectra in the region of $0 - 511$ keV. Fraction of Ps emission, $f_{Ps}$, is given by following formula

$$f_{Ps} = \left(1 + \frac{P_1}{P_0} - \frac{R_1}{R_0} f_{Ps} R_0 - R_{Ps} f_{Ps} - R_0}ight)^{-1}$$

(6.5)

where $P$ and $T$ are the integrated counts in the peak region (for example, from 501 keV to 521 keV) and the total area (for example, from 0 to 521 keV), respectively. The subscript of $T, P, R$ is correspond to $f_{Ps}$. The calibration parameters $P_1$ and $T_1$, which are $P$ and $T$ obtained under the condition $f_{Ps} = 1$ respectively, are required to calculate $f_{Ps}$. These values are obtained from the observation of Ps emission from the Ge sample that is heated to the temperature of 1000 K, because it is postulated that the 1000 K Ge sample converts all implanted positrons to Ps atoms. However, this postulation has not been verified. Thus, the reliability of positron diffusion measurement in metals by the observation of Ps emission is limited.
6.2 Advantages of Ps$^-$ Observation

We have developed a new method to study positron diffusion in metals by the measurement of Ps$^-$ fraction, $f_{Ps^-}$ as a function of positron incident energy, $E_{e^+}$ [47] [48]. $f_{Ps^-}$ is proportional to $F_S$ and can be measured accurately compared to the line-shape parameter, $Y_{e^+}$ and $f_{Ps}$ mentioned above. Thus, the measurement of positron diffusion in metals with the method is more reliable than in methods.

In the new method, we implant positrons into samples and count the number of Ps$^-$ emitted from the incident surface of the sample. Thus, there is no need to consider effects of positron reemission.

Ps$^-$ can be accelerated by applying an electric field. The energies of $\gamma$-rays emitted from self-annihilation of Ps$^-$ accelerated in the direction of $\gamma$-ray detector are blue shifted and the value of the energy shift can be calculated. The peak of $\gamma$-rays originating in self-annihilation of Ps$^-$ can be distinguished from that of 511 keV in the energy spectra. Thus, numbers of emitted Ps$^-$ can be counted accurately. In addition, $\gamma$-rays of 511 keV energy originating in annihilations of positrons and Ps atoms on the chamber wall or Ps$^-$ acceleration mesh are no longer causes of systematic errors. Furthermore, calibration of
the γ-ray detector, which is indispensable in the measurements of $f_{Ps}$, is not required. Hence, reliable studies of positron diffusion are enabled by this new method.

### 6.3 Obtained Values in Our Work

The values of $E_0$ and $n$ obtained in our work are listed in Table 6.1. The diffusion constants $D_+$ and diffusion length $L_+$ calculated by Eq. (3.16) are also listed. The values of $E_0$ and $D_+$ reported by previous measurements are listed in Table 6.2.

#### Table 6.1: Obtained values of $E_0$, $n$, diffusion constants, $D_+$ and diffusion length $L_+$. The parameter $n$ of Mo(polycrystalline) sample is common for each annealing temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_a$ (K)</th>
<th>$E_0$ (keV)</th>
<th>$n$</th>
<th>$D_+$ (cm$^2$·s$^{-1}$)</th>
<th>$L_+$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(polycrystalline)</td>
<td>1800</td>
<td>7.4±0.4</td>
<td>1.6±0.1</td>
<td>0.22±0.03</td>
<td>52±3</td>
</tr>
<tr>
<td>Mo(polycrystalline)</td>
<td>1500</td>
<td>3.8±0.5</td>
<td>1.7±0.1</td>
<td>0.13±0.09</td>
<td>40±14</td>
</tr>
<tr>
<td>Mo(polycrystalline)</td>
<td>1800</td>
<td>6.0±0.5</td>
<td>1.7±0.1</td>
<td>0.6 ±0.4</td>
<td>87±29</td>
</tr>
</tbody>
</table>

#### Table 6.2: Values of $E_0$, $D_+$ reported by previous studies. The temperature of Mo(111) was 500 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_a$ (K)</th>
<th>$E_0$ (keV)</th>
<th>$D_+$ (cm$^2$·s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(111)</td>
<td>2900</td>
<td>25±5</td>
<td>1.26</td>
<td>[27] [50]</td>
</tr>
<tr>
<td>W(unindicated)</td>
<td>unindicated</td>
<td>&gt; 15</td>
<td>1.4</td>
<td>[51]</td>
</tr>
<tr>
<td>Mo(111)</td>
<td>2300</td>
<td>7.5</td>
<td>1.2±0.1</td>
<td>[45]</td>
</tr>
</tbody>
</table>

The values obtained in our work are smaller than reported previously. A postulation which explains the lowness of these values is the limited annealing temperature $T_a$. The samples used in our work were thin film (25 μm thickness); hence, $T_a$ was limited to 1800 K to avoid deformation of the samples. Due to the lowness of $T_a$, defects in the sample have not been removed completely.
The change of $D_+$ of Mo(polycrystalline) sample supports this postulation. The value of $D_+$ of the sample annealed by the temperature 1800 K is higher than that of the sample annealed by the lower temperature 1500 K.

### 6.4 Diffusion of Electron and Muons

This section describes the difference between the diffusion of positrons and the diffusion of electrons and positive muons.

#### 6.4.1 Electron Diffusion in Metals

The diffusion equation by which simple (that is, not concerning advection, creation and annihilation of diffusion material) diffusion motions is written as

$$ \frac{\partial n}{\partial t} = D \nabla^2 n = D \nabla \cdot (\nabla n), \quad (6.7) $$

where $n = n(x, t)$ is the concentration of diffusing material and $D$ is the diffusion constant. From Eq. (6.7), it is evident that the driving force of diffusion motions is the gradient of the diffusion material concentration. Let us discuss the electron diffusion in metals. In metals, there are a vast amount of free electrons. If there is a slight fluctuation of electron concentration, the free electrons around the fluctuation feel the Coulomb force. These electrons are moved by the force and the fluctuation is uniformed rapidly. There are not electron concentration gradients in metals ($\nabla n = 0$); thus, the electron diffusion does not occur in metals.

#### 6.4.2 Muon Diffusion in Metals

Muons are unstable elementary particle of two charge types ($+e$ for positive muon $\mu^+$ and $-e$ for negative muon $\mu^-$). They have a spin of $1/2$ and their mass is $m_\mu = 105.658 \text{ MeV/c}^2 = (1/9) m_p = 207 m_e$, where $m_p$ is the mass of a
proton. Due to their characteristic mass, positive muon diffusion in metals have intermediate properties between that of H atoms and positrons. Furthermore, information on positive muon diffusion in metals may contribute to the development of methods to generate high intensity ultra slow muon (USM) beams obtained from ultra slow muonium atoms. Several trials to measure the positive muon diffusion in metals have been performed [52] [53].

In 1986, Mills et al. [54] observed muonium atoms (Mu) emission from W foil heated to the temperature of 2800 K and in which positive muons were implanted and stopped. Mu yields $Y_{\mu}$ is given as

$$Y_{\mu} = \rho \sqrt{D_{\mu} \tau_{\mu}^+},$$  \hspace{1cm} (6.8)

where $\rho \text{ cm}^{-1}$ is the stopping density of $\mu^+$ in the W foil, $D_{\mu^+}$ is the $\mu^+$ diffusion constant and $\tau_{\mu^+} = 2.197 \mu s$ is the mean life time of $\mu^+$. The value of $D_{\mu^+}$ obtained by Mills et al. was

$$D_{\mu^+} = 0.002 \text{ cm}^2 \text{ s}^{-1}. $$  \hspace{1cm} (6.9)

There is a large difference between $D_{\mu^+}$ and the positron diffusion constant in a W sample

$$D_+ = 0.22 \pm 0.03 \text{ cm}^2 \text{ s}^{-1},$$  \hspace{1cm} (6.10)

obtained from our work.

The difference between $D_{\mu^+}$ and $D_+$ may be caused by the de Broglie wavelength of the positive muon and positron. Figure 6.3 shows the de Broglie wavelength of positive muon and positron plotted against their temperature. In the case of the positive muon, the de Broglie wave-length is about 5 Å for the room temperature and 2 Å for the temperature of 2300 K, at which Mu emission was observed by Mills et al.. The lattice constant of W is about 3 Å. Thus, positive
muon diffusion can be described in terms of hopping motion. In the case of positron, the de Broglie wave-length is about 300 Å at room temperature and is much larger than the lattice constant of W. If the difference between the diffusion of the positive muon and positron is caused by the difference in their de Broglie wave-length, there may be a relationship between the diffusion constant and the temperature of sample. The de Broglie wave-length of a positive muon of a few K is about 100 Å, which is similar to that of positrons of 300 K temperature. Under the condition of such low temperature, Mu atoms can not be emitted; thus, it is impossible to obtain $D_{\mu^+}$ from the Mu yields. However, the zero field muon spin relaxation method (ZF-μSR) has been established and some experiments to measure the $\mu^+$ diffusion in metal samples have been performed.
Chapter 7

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References


REFERENCES


Appendix A

Achievements

A.1 Achievements for "Development of Methods to Generate Ultra Slow Muonium"

A.1.1 Oral Sessions

1. 鈴木卓越, 神田聰太郎, 南雲一章, 深尾祥紀, 長友傑, 池戸豊, 立花隆行, 中村惇平, 川村成騫, ストラッサー バトラック, 牧村俊助, 藤森憲, 三部勉, 下村浩一郎, 小嶋健児, 鈴木聰, 西山幸生, 齊藤直人, 三個康之, 三宅康博.
東理大学, 東京大学 A, KEK 理研 B, KEK 物構研 C, Open-It D, KEK 計算センター E.
「アルカリ金属を蒸着したタンクステン表面からのミュニウム放出実験 1」.
日本物理学会 2012 年秋季大会. 横浜国立大学. 2012 年 09 月 20 日.

2. 鈴木卓越, 神田聰太郎, 西村昇一郎, 南雲一章, 深尾祥紀, 長友傑, 池戸豊, 上野一樹, 立花隆行, 中村惇平, 川村成騫, ストラッサー バトラック, 牧村俊助, 藤森憲, 三部勉, 下村浩一郎, 小嶋健児, 鈴木聰, 西山幸生, 齊藤直人, 三個康之, 三宅康博.
東理大学, 東京大学 A, KEK 理研 B, KEK 物構研 C, Open-It D, KEK 計算センター E.
「アルカリ金属を蒸着したタンクステン表面からのミュニウム放出実験 2」.
日本物理学会 2013 春季大会. 広島大学. 2013 年 03 月 26 日.

3. 鈴木卓越, 神田聰太郎, 西村昇一郎, 南雲一章, 深尾祥紀, 長友傑, 池戸豊, 上野一樹, 立花隆行, 中村惇平, 川村成騫, ストラッサー バトラック, 牧村俊助, 藤森憲, 三部勉, 下村浩一郎, 小嶋健児, 鈴木聰, 西山幸生, 齊藤直人, 三個康之, 三宅康博.
東理大学, 東京大学 A, KEK 理研 B, KEK 物構研 C, Open-It D, KEK 計算センター E.
APPENDIX A. ACHIEVEMENTS

Department of physics, Tokyo University of Science
"Mu Production from Tungsten and Porous Silicon".
The 8th g-2/EDM collaboration meeting. KEK 東海キャンパス. 2014/07/18

5. 長崎泰之, 鈴木卓爾 (代理発表).
東理大所.
"Muonium emission from surface treated tungsten [2014A0231]".
第 6 回 J-PARC/MUSE 成果報告会. KEK 東海キャンパス.
2015 年 07 月 27 日.

A.1.2 Poster Sessions

Department of physics, Tokyo University of Science,
Institute of Materials Structure Science, KEKA,
Department of physics, The University of TokyoB,
Institute of Particle and Nuclear Studies, KEKC,
Computing Research Center, KEKD.
"Studies of the Effect of Alkali-Metal Coating on Muonium Emission From Tungsten Surfaces".

Department of physics, Tokyo University of Science,
Institute of Materials Structure Science, KEKA,
Department of physics, The University of TokyoB,
Institute of Particle and Nuclear Studies, KEKC,
Computing Research Center, KEKD.
"Observation of Muonium Emission from Alkali-Metal Coated Tungsten Surfaces".
A.2 Achievements for ”Measurement of Positron Diffusion in Metals”

A.2.1 Oral Sessions


A.2.2 Poster Sessions


A.2.3 Papers

Department of physics, Tokyo University of Science. "Development of a method to study positron diffusion in metals by the observation of positronium negative ions". Nuclear Instruments and Methods in Physics Research B 334 (2014) 40-42


A.3 Awards

1. The work indicated as A.1.2-1 was awarded the "Poster Presentation Award".

2. The work indicated as A.2.2-1 was awarded the "The best student presentation award".