CHAPTER - 1

POSITRON ANNIHILATION STUDY OF DEFECTS IN METALS

This chapter begins with an outline of the basic aspects of the positron annihilation method. Then the physical reasons underlying the application of this method to the study of vacancy type defects, i.e., the trapping of positrons at these defects and the changes in the annihilation characteristics in the trapped state are discussed. The trapping model which forms the basis for the application of the positron annihilation technique to the determination of the vacancy-formation energy in metals is then introduced. Since the main bulk of this thesis is concerned with the study of the annealing behaviour of defects, a general survey of the present understanding of this subject is also presented. The use of positron annihilation technique in the study of the annealing behaviour of defects is then illustrated through a few select examples. This chapter is concluded with a section where the positron annihilation technique is compared with the other experimental methods for the study of vacancy type defects.

There are many review articles that describe the positron annihilation method and its application to the study of defects [1 - 9]. The article by West [1] provides a lucid introduction to this subject.
1.1 The Positron Annihilation Technique

Positrons emitted from a radioactive source like $^{22}\text{Na}$ are injected into the solid where they lose their energy by ionising collisions and phonon-scattering to reach thermal equilibrium in a few picoseconds. The thermalised positrons then annihilate with electrons resulting in the emission of high energy photons which can be detected. According to the laws of quantum electrodynamics, the predominant mode of annihilation of a free positron with an electron is the one which results in the emission of two annihilation photons. These two photons come out with an energy $\sim 0.511 \text{ MeV} (= m_e c^2)$ and in nearly opposite directions. The angular deviation of the two photons from collinearity is related to the electron-positron pair momentum, transverse to the emission direction, according to $\Theta = p_T / m_e c$. The motion of the electron-positron pair also results in the energy of the annihilation photon being Doppler shifted, from the rest mass value of 0.511 MeV, by an amount given by $\Delta E = c p_L / 2$, where $p_L$ is the longitudinal pair momentum i.e., along the direction of the photon emission.

The positron annihilation technique comprises of the measurements of the positron lifetime, the angular correlation and Doppler broadening of the annihilation photons.
This is illustrated schematically in Fig. 1.1. The annihilation rate of a positron in a metal is proportional to the electron density at the site of the positron, and hence a measurement of the lifetime of the positron gives information on the electron density. The angular correlation and Doppler broadening of the annihilation photons is due to the momentum distribution of the electron-positron pair. Because the momentum of a thermalised positron in a solid is nearly zero, these measurements give information on the momentum distribution of electrons in a solid.

The probability of annihilation of a positron with an electron resulting in the emission of two photons is given by

\[
\Gamma (\vec{p}) = \frac{\pi \hbar^2}{8 \pi^3} \int \frac{d\vec{r} \ d\vec{r}'}{\mathbf{r}^2} \exp \left[-i \vec{p} \cdot (\vec{r} - \vec{r}')\right] \times \\
\langle \Phi_0 | \psi_+ (\vec{r}) \psi_+ (\vec{r}') \psi_- (\vec{r}) \psi_- (\vec{r}') | \Phi_e \rangle,
\]

where \(| \Phi_0 \rangle\) is the ground state of the electron system containing the thermalised positron, \(\psi_+\) and \(\psi_-\) are the positron and electron field operators, \(r_0\) is the classical electron radius and \(c\) is the velocity of light [1]. The total annihilation rate, obtained by summing over all the photon momenta, is
Fig. 1.1. Schematic diagram of the positron annihilation technique.
\[ \lambda = \int \gamma(\vec{r}) \, d\vec{r} \]
\[ = \pi \gamma_o^2 \zeta \int d\vec{r} \langle \Phi_0 | \psi^\dagger(\vec{r}) \psi(\vec{r}) \psi^\dagger(\vec{r}) \psi(\vec{r}) | \Phi_0 \rangle \cdot \tag{2} \]

Thus the annihilation rate is given by the expectation value of the electron density at the site of the positron averaged over all the positron positions. The calculation of the annihilation rate of a positron with an electron in a metal is a complicated many-body problem. The electrons tend to pile up around the thermalised positron resulting in a considerable enhancement of the electron density at the site of a positron. The calculation of annihilation rates have been performed within the electron gas approximation and the results are seen to be in good agreement with the experimental values for various metals.

It has been found that though the electron-positron correlation effects are very important in determining the total annihilation rate, the shape of the momentum distribution, \( \gamma(\vec{r}) \), is well described by the independent-particle approximation, where correlations are neglected \[1\]. In this approximation the probability of two photon annihilation is given by
\[ \Gamma_0(p) = \frac{\pi n_0^2}{8 \pi^3} \sum_l \left| \int d\vec{r} \exp(-i \vec{p} \cdot \vec{r}) \Psi_l(\vec{r}) \Psi_+(\vec{r}) \right|^2, \quad (3) \]

where \( \Psi_+ \) is the ground state positron wavefunction and the summation extends over all the occupied electron states \( \Psi_l \). Experimentally it is not practicable to measure the complete 3-dimensional momentum distribution \( \Gamma_0(\vec{p}) \). Instead in the conventional long-slit angular correlation apparatus, only the component of momentum distribution along \( p_z \), a direction that is transverse to the emission direction of the pair of photons is measured. The angular correlation curve is given by

\[ N(p_z) = N(m_0 \cos \theta) = \int \int \Gamma_0(\vec{p}) dp_x dp_y. \quad (4) \]

For a homogeneous electron gas, the angular correlation curve has the shape of an inverted parabola of width proportional to the Fermi momentum. In a real metal the angular correlation curve consists of a parabolic part due to annihilation with the valence electrons and a broad Gaussian part due to annihilation with the core electrons and the high momentum components of valence electrons. From measurements of the angular correlation curves for different orientations of a single crystal, \( \Gamma_0(\vec{p}) \) can be obtained [10]. This contains information on the nature of wavefunctions of electrons and positron (see Eq.(3)) and further from the sharp breaks in \( \Gamma_0(\vec{p}) \) the topology
and the size of the Fermi surface can be inferred [1]. However, in a 'long-slit' angular correlation curve, due to the presence of double integration in Eq.(4), the isotropic high momentum core electron contributions are projected into the low momentum regions, which makes it difficult to observe the anisotropies in the conduction electron momentum distribution and the Fermi surface topology.

Recently, with the advent of 'point-slit' geometry angular correlation machines [11] it has become possible to measure the 2-dimensional angular correlation curve,

\[ N(p_y, p_z) \] given by

\[ N(p_y, p_z) = \int \Gamma_0(\vec{p}) d\vec{p} \quad . \quad (5) \]

Such experiments provide detailed information on the anisotropies in electron momentum distribution and the Fermi surface topology.

In a Doppler broadening experiment, the broadening of the annihilation radiation lineshape, which is due to the component of the electron-positron pair momentum along the direction of emission, is measured using a high resolution germanium detector. The lineshape is given by,

\[ N(\Delta E) = N(c p_x) = \iiint \Gamma_0(\vec{p}) d\vec{p} \quad . \quad (6) \]
It is clear from Eqs. (4) and (6) that in principle the 'long-slit' angular correlation and Doppler broadening experiments provide similar information on the electron momentum densities. However as the momentum resolution of a Doppler broadening experiment is an order of magnitude poorer than that of an angular correlation experiment [12], the former is never used in the study of the electron momentum densities in solids, but the Doppler broadening experiment which has the advantage of being a single detector system with high rates of data accumulation is widely used in defect studies.

1.2 Trapping of Positrons at Defects

In a perfect metal the positron, moving in the Hartree field of the ions and conduction electrons, exists in a well-defined Bloch state. The positron density distribution has nearly a 'Swiss cheese' character with holes around each positive ion due to the strong Coulomb repulsion. The squeezing of the positron to the interstitial regions provides a positive contribution to the ground state energy, as much as 5 eV in some metals. Thus, should additional space be available in the form of a lattice vacancy, dislocation core or void, the positron can relax there with considerable energy advantage.
The trapping of a positron at a vacancy can be understood in terms of a simple physical picture. A vacancy in a metal can be obtained by removing the positron core while allowing the conduction electrons to readjust. In this way a short-ranged negative potential is created which acts as an attractive centre for the diffusing positrons. If the strength of the attractive potential (roughly measured by the product of the depth and range of the potential) is large enough, then a bound state of the positron at a vacancy, is formed i.e., the positron is trapped. It is observed that in most metals, positrons are trapped at vacancies (with a binding energy of the order of 1 eV), the notable exception being the alkali metals where no trapping is observed. This is due to their smaller ion cores, smaller valency \( Z = 1 \), and larger relaxations around a vacancy [2]. In a few cases where the binding is weak, positrons are detrapped from vacancies at high temperatures.

1.2.1 **Positron annihilation characteristics in defects**

A positron trapped at a vacancy sees a smaller electron density and in particular smaller core electron density. This results in the decrease in the annihilation rate (see Eq. (2)) or correspondingly an increase in the lifetime. As an example, the lifetime of positrons trapped at a vacancy in aluminium is 243 psec as against 161 psec in
the perfect metal. For the trapped positron, the fraction of annihilations with the low momentum valence electrons to the annihilations with the high momentum core electrons is also increased. This results in the narrowing of the angular correlation and Doppler broadening curves. In an experiment this narrowing is measured through arbitrarily defined lineshape parameters. In an angular correlation experiment the lineshape is measured through $H$ parameter defined as

$$H = \frac{\int_{-\ell}^{\ell} N(\vec{p}_x) \, d\vec{p}_x}{\int_{-\infty}^{\infty} N(\vec{p}_x) \, d\vec{p}_x}.$$ 

An equivalent parameter in Doppler broadening experiments is called $I$ parameter, defined as the ratio of counts in the central few channels to the total counts in the entire photopeak. In some experiments the ratio of counts in the wing regions to the total counts, called the $W$ parameter, is monitored. (Both $H$ and $I$ parameters increase with the trapping of positrons at defects whereas the $W$ parameter decreases.)

There have been several \textit{ab initio} calculations of annihilation parameters like the lifetime and angular correlation curve for positrons annihilating at defects like vacancies [13–16], dislocations [13, 17] and vacancy clusters [18, 19]. Most of these calculations are based
on the jellium model description of a metal. These have been discussed in detail by Nieminen and Manninen [8]. Calculations in which the presence of the ionic lattice has been explicitly taken into account have been performed by Gupta and Siegel [16]. A brief outline of these calculations is given below.

It is clear from Eqs. (2) and (3) that in order to calculate the lifetime and the angular correlation curve one has to have a knowledge of the electron and positron distribution in the vicinity of the defect. In the jellium model, the presence of a vacancy or a vacancy cluster is simulated by scooping out a spherical hole of radius $a$ in the uniform background of density $n_0$. The resulting charge distribution is given by

$$n_+(r) = n_0 \Theta(r-a),$$

where $\Theta(r-a)$ is a step function: $\Theta(r-a) = 0$ for $r < a$ and $= 1$ for $r > a$. The electrons redistribute due to the perturbation, and the resulting electron density profile and the electrostatic potential are calculated in the Thomas–Fermi statistical approximation [13] or more rigorously using the self-consistent density functional formalism of Kohn and Sham [14, 18, 19]. The positron defect potential is then calculated taking into account (1) the electrostatic potential due to the rearrangement
of electrons around the defect, (2) the decrease in the kinetic energy by an amount equal to the zero point energy of the positron (due to the absence of the ion core) and (3) the positron-electron correlation potential. The positron wavefunction is obtained in this defect potential by solving the Schrödinger equation. The annihilation rate is calculated using the Brandt's local density formula [8] for an inhomogeneous electron gas:

\[ \lambda = \int d \mathbf{r} |\Psi_+ (r)|^2 \lambda_0 \left[ \rho(r) \right] \]  

(7)

where \( \lambda_0 (\rho) = (2 + 134n) \times 10^9 \ \text{sec}^{-1} \) is the annihilation rate in a homogeneous electron gas [20]. In these jellium model calculations, the contribution of the core electrons to the annihilation rate is taken into account by renormalising the valence electron density according to a prescription due to West [21].

The angular correlation curve is calculated either in the independent-particle approximation (Eq. (3)) using the Kohn-Sham wavefunctions [14, 19] or using the mixed density approximation [13]. Most of the ab initio calculations have been performed for aluminium, where there is a good agreement with experiments [8].

The results from such calculations that is of interest to us in this thesis is the variation of
annihilation parameters and in particular the variation of the lifetime as a function of the size of a vacancy cluster [18, 19]. The result taken from the calculations by Haasjarvi et al [18] is shown in Fig.1.2. This illustrates the high sensitivity of the positron lifetime to the size of a vacancy cluster in the range of $1 \sim 5 \, \text{Å}$. This large sensitivity to small clusters is one of the important reasons for the widespread application of the positron annihilation method in the study of the annealing and clustering behaviour of vacancies in metals.

1.3 Determination of the Vacancy-formation Energy

In the previous section, the trapping of positrons at vacancies and the changes in annihilation characteristics in the trapped state were discussed. One of the most fruitful applications of the positron annihilation technique in the defect studies has been the estimation of the vacancy formation energy in metals.

In a metal, the equilibrium concentration of monovacancies at any temperature $T$ is given by

$$C_v = \exp \left( \frac{S_v^f}{R} \right) \exp \left( -\frac{E_v^f}{RT} \right), \quad (8)$$

where $S_v^f$ and $E_v^f$ are the vacancy formation entropy and enthalpy respectively. At low temperatures, when
Fig. 1.2. Variation of positron lifetime in a vacancy cluster as a function of the size of the cluster. These calculations have been carried out in the jellium approximation. From Ref. [18].
the equilibrium concentration of vacancies is small, the positron annihilates from the Bloch state. As the temperature is increased, the concentration of vacancies increases and an increasing fraction of positrons annihilate from the trapped state at vacancies. Ultimately all the positrons annihilate at vacancies. Experimentally this is observed as a sigmoidal variation of the annihilation characteristics (mean lifetime and the lineshape parameters) with temperature.

The results of positron annihilation experiments are analysed in terms of the two state trapping model [22], to estimate the vacancy formation energy. In this model it is assumed that the positron exists in one of the two states, the bulk or Bloch state and the vacancy-trapped state in relative concentrations \( n_b(t) \) and \( n_v(t) \) respectively, with \( n_v(0) = 0 \). The model is described by the set of coupled differential equations,

\[
\frac{d n_b}{dt} = -\lambda_b n_b - \kappa n_b
\]

\[
\frac{d n_v}{dt} = -\lambda_v n_v + \kappa n_b
\]

where \( \lambda_b \) and \( \lambda_v \) are the positron annihilation rates in the bulk and vacancy-trapped state respectively, and \( \kappa \) is the trapping rate from the bulk to the defect-trapped
state. The trapping rate is proportional to the vacancy concentration i.e., \( \kappa = \mu C_v \), where \( \mu \) is the specific trapping rate. The above equations can be solved to yield \( N(t) \), the fraction of positrons in the system at time \( t \):

\[
N(t) = n_b(t) + n_v(t)
\]

\[
= \left( 1 - \frac{\kappa}{\lambda_b + \kappa - \lambda_v} \right) \exp \left[ -\left( \lambda_b + \kappa \right) t \right] + \left( \frac{\kappa}{\lambda_b + \kappa - \lambda_v} \right) \exp \left( -\lambda_v t \right) \tag{10}
\]

The annihilation rate is given by \( -dN(t)/dt \). The annihilation spectrum as measured in a positron lifetime experiment consists of two exponentials with decay constants \( (\lambda_b + \kappa) \) and \( \lambda_v \). The mean lifetime \( \tau \) is given by,

\[
\tau = -\int_0^\infty t \frac{dN(t)}{dt} dt
\]

\[
= \tau_b \left( \frac{1 + \kappa \tau_v}{1 + \kappa \tau_b} \right)
\]

\[
= \tau_b \left( \frac{\lambda_b}{\lambda_b + \kappa} \right) + \tau_v \left( \frac{\kappa}{\lambda_b + \kappa} \right) \tag{11}
\]

where \( \tau_b = \frac{1}{\lambda_b} \) and \( \tau_v = \frac{1}{\lambda_v} \) are the lifetimes in the bulk and vacancy-trapped state respectively.
An expression similar to the above equation can be written for any other annihilation characteristic like the line-shape parameter $I$, since $\left( \frac{\lambda_b}{\lambda_b + \kappa} \right)$ and $\left( \frac{\kappa}{\lambda_b + \kappa} \right)$ are the probabilities for the annihilation in the free and trapped state. Thus,

$$I = I_b \left( \frac{\lambda_b}{\lambda_b + \kappa} \right) + I_v \left( \frac{\kappa}{\lambda_b + \kappa} \right) \quad (12)$$

where $I_b$ and $I_v$ are the lineshape parameters corresponding to annihilation in the bulk and the vacancy-trapped state.

The above equations (11) and (12) can be rewritten to give the trapping rate $\kappa$:

$$\kappa = \mu \gamma_v = \mu \exp \left( \frac{S_v}{kT} \right) \exp \left( -\frac{E_v}{kT} \right)$$

$$= \frac{\lambda_b (\tau - \tau_b)}{(\tau_v - \tau)} = \frac{\lambda_b (I - I_b)}{(I_v - I)} \quad (13)$$

This equation forms the basis for most determinations of $E_v^F$ from positron annihilation experiments. From the measurements of the mean lifetime, $\tau$ or the lineshape parameter, $I$ as a function of temperature, and obtaining the annihilation parameters in the bulk $(\tau_b, I_b)$ and the vacancy-trapped state $(\tau_v, I_v)$ by extrapolations in the low temperature and high temperature regions.
respectively, $\kappa/\Lambda_b$ is evaluated at various temperatures. The slope of the Arrhenius plot of $\ln \left( \kappa/\Lambda_b \right)$ vs $1/T$ gives the vacancy formation energy. The error in the determination of $E_v^F$ due to the uncertain temperature dependence of $\Lambda_b$ and the specific trapping rate, $\mu$, is discussed by Siegel [23].

The application of the positron annihilation technique to the determination of $E_v^F$ is illustrated through the angular correlation studies in copper [24]. The variation in the lineshape parameter with temperature is shown in Fig. 1.3a, and the Arrhenius plot derived from the above measurement is shown in Fig. 1.3b. Such measurements have now been performed in a variety of metals. The most difficult experiments are those in the refractory bcc metals [25].

The two-state trapping model discussed above has been extended to include more than one kind of trap [26]. In particular, such models have been applied to analyse the results from positron annihilation experiments in terms of trapping from mono- and divacancies in equilibrium [27]. The trapping model has also been extended to include the detrapping from shallow traps [26, 28]. This model is discussed in chapter 6.
Fig. 1.3. Estimation of the vacancy formation energy in copper from positron angular correlation measurements [24]. (a) Variation of the normalised peak counts with temperature and (b) Arrhenius plot derived from the above measurements.
1.4 Annealing Behaviour of Defects in Metals

In a metal, defects in excess of the thermodynamic equilibrium concentration can be produced by irradiation with energetic particles, plastic deformation or quenching from elevated temperatures. Irradiation with energetic particles at low temperature produces Frenkel defects, i.e., interstitials and vacancies in equal numbers. Quenching from elevated temperatures results in freezing out of vacancies and the formation of small vacancy clusters. During plastic deformation, apart from vacancies and interstitials, dislocations are also produced in the crystal. When a metal containing this non-equilibrium ensemble of defects is 'annealed', the excess defects disappear by migration to sinks and via vacancy-interstitial recombination. In addition, these defects may also be trapped at impurities or agglomerate to form larger defect clusters before they finally disappear.

The annealing behaviour of defects in metals has been extensively investigated over the last 25 years, mainly through the resistivity measurements. Recently more sophisticated experimental techniques like the diffuse scattering of X-rays, Mossbauer spectroscopy, transmission electron microscopy and positron annihilation technique have been used in order to clarify certain aspects of the
annealing behaviour of defects. As a result of this a fairly good understanding of the annealing behaviour of defects has been achieved. A rich literature and many review articles exist on this subject [29 - 36].

1.4.1 Isochronal annealing stages

In a typical isochronal annealing experiment, the sample is maintained successively at elevated temperatures for a fixed period of time and the changes in the defect concentration is monitored. The isochronal annealing curve for electron irradiated copper is shown in Fig.1.4 [36]. It is observed that the isochronal annealing curve consists of five distinct steps called the annealing stages. The defect reactions occurring in these stages are also shown in the figure.

The stage I consists of five substages, customarily labelled as $I_a$, $I_b$, $I_c$, $I_d$ and $I_e$. In stages $I_a$ to $I_c$ 'close-pair' recombination takes place. These annealing stages are due to the disappearance of those Frenkel pairs in which the interstitial and vacancy are so close that an appreciable interaction exists between them. Stages $I_d$ and $I_e$ are both associated with the free migration of interstitials. Of these, stage $I_d$ corresponds to the correlated recombination, i.e., the interstitial recombines
Fig. 1.4. Isochronal annealing curve in electron-irradiated copper. The various annealing stages and the defect reactions occurring in these stages are indicated. Here $i_i$'s and $v_i$'s refer to the interstitial and vacancy clusters. From Ref. [36].
with its own vacancy of the Frenkel pair, while stage I_c corresponds to the uncorrelated recombination, i.e., the reaction with another vacancy. The defect reactions occurring in these substages have been identified by carrying out annealing experiments on samples containing different initial concentrations of Frenkel pairs. The detailed information on the interstitial structure and migration have come from X-ray diffuse scattering [37] and mechanical relaxation experiments [38]. The freely migrating interstitials can also react amongst themselves to form a di-interstitial or be trapped at impurities, thus surviving at the end of stage I.

In stage II, two processes seem to be important: (1) the growth and rearrangement of interstitial clusters and (2) the detrapping of interstitials from impurities. The experimental techniques that have been most informative about the process occurring in this stage are diffuse X-ray scattering, transmission electron microscopy and Mössbauer spectroscopy. The former two experimental methods have been used to study the clustering of interstitials and the Mössbauer spectroscopy has been used to study the detrapping of interstitials from impurities [39].

Stage III is associated with the migration of vacancies. The freely migrating vacancies annihilate at
interstitial clusters or at an interstitial trapped at an impurity. Some of the vacancies also react amongst themselves to form small vacancy clusters. The experiments that clearly indicate the migration and clustering of vacancies in stage III are the positron annihilation experiments and the diffuse scattering of X-rays. These experiments are discussed in the subsequent sections.

In stage IV the vacancy clusters formed in stage III grow further. This has been seen through the transmission electron microscopy and diffuse X-ray scattering studies. In stage V the interstitial and vacancy clusters anneal out by evaporation of vacancies from the vacancy loops and their subsequent annihilation at interstitial loops. Thus at the end of stage V complete recovery is achieved.

The annealing behaviour of defects has also been explained in terms of an alternative model called the "two-interstitial model" [40]. In this model, stage I is associated with the one-dimensional migration of the crowdion form of interstitial, and stage II is associated with the conversion of the metastable crowdion interstitial to the stable dumbbell interstitial which anneals out in stage III. Stage IV is associated with the migration of vacancies. The two-interstitial model was proposed in order to account for the discrepancy between the
migration energy of the stage III defect and the monovacancy migration energy as obtained from equilibrium measurement, though the relation \( E_v^m = Q^{sp} - E_v^F \), where \( Q^{sp} \) is the activation energy of the self diffusion occurring through the vacancy mechanism and \( E_v^F \) is the vacancy formation energy. The controversy resulting from these two models is not completely resolved but most experiments point to the one interstitial model for defect annealing.

The annealing behaviour of defects so far discussed was for an electron-irradiated fcc metal. In bcc metals the annealing behaviour of defects is more complicated due to the strong influence of impurities [31, 41]. Further the annealing behaviour of defects in cold-worked metals [42] and quenched metals [29, 34] are also different from those of the electron-irradiated metals as the initial defect structures are different. However, annealing studies of defects produced by all the three methods (namely, irradiation, plastic deformation and quenching) are necessary to get a complete understanding of the annealing behaviour of defects.

1.4.2 Isothermal annealing studies

The isochronal annealing studies, that were discussed in the previous section, have helped in identifying the various defect reactions that occur in the different
temperature ranges. In an isothermal annealing study, the annealing behaviour of defects is studied as a function of time at a particular temperature. Such studies provide information on the defect kinetics. The defect kinetics is usually modelled by rate equations similar to those used in chemical kinetics. Such rate equations have been formulated for the various defect reactions like the recombination, migration of defects to sinks, trapping at impurities and clustering of defects [43]. In the following, the annealing kinetics of vacancies in quenched and cold-worked metals will be discussed.

The simplest situation in the annealing of vacancies in quenched metals corresponds to the migration of monovacancies to inexhaustible sinks. The rate equation describing this process is

\[
\frac{dC_{1v}}{dt} = -\alpha D_{1v} C_{1v}, \tag{14}
\]

where \( \alpha \) is a constant depending on the nature and concentration of sinks and \( D_{1v} \) is the monovacancy diffusion constant. In this description of the annealing process, where the vacancy concentration decays exponentially with time, the spatial variation in the concentration of vacancies is disregarded. This is taken into account by modelling the annealing process through the diffusion equation
\[ \frac{\partial C_{1v}}{\partial t} = D_{1v} \nabla^2 C_{1v} \]

with suitable boundary conditions corresponding to various types of sinks. The solution which consists of a sum of decaying exponentials with different time constants, describes properly the initial transients in the decay of the vacancy concentration. The most realistic treatment of the annealing process is one where the discrete atomic jumps are taken into account. This is carried out using the Monte Carlo simulation method. However such studies indicate that the chemical rate theory gives a reasonably good description of the annealing process.

The actual mechanism of annealing of vacancies in quenched metals is more complicated than the above mentioned simple model of migration of monovacancies to sinks \[29,44\]. Some of the complications are: (1) The presence of small amounts of highly mobile divacancies can have a considerable influence on the annealing kinetics, (2) the trapping of vacancies at impurities can also have a significant influence, (3) the vacancies can cluster during their migration and (4) the sink structure can change during the annealing of vacancies at sinks. The rate equations taking into account the clustering of vacancies are described in chapter 3 while those for the annealing of vacancies at variable sink structure are discussed in chapter 5.
The annealing of vacancies to a random array of dislocations, under the influence of their strain fields, is described by the diffusion equation

\[ \frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{j}, \]

with

\[ \mathbf{j} = -D \left[ \nabla C + \frac{C \nabla E}{kT} \right], \quad (15) \]

where \( D \) is the diffusion constant and \( E \) is the elastic interaction energy between a vacancy and a dislocation [45]. The first term represents the flux due to the concentration gradient and the second term the flux due to the drift force \( (-\nabla E) \). It has not been possible to obtain the solution of the above equation for appropriate boundary conditions.

The measured isothermal annealing curves in cold-worked metals have been analysed in terms of the Harper's relation [46]

\[ C(t) = C_0 \exp \left(-Kt^{m_c}\right), \quad (16) \]

which is an approximate solution of Eq. (15) in which the concentration gradient term has been neglected. The value of the exponent \( m = 1/2 \), for an interaction potential varying as \( 1/r^2 \) [45]. It is observed that the experimental
results are in good agreement with Eq. (16) for values of \( m \) between 0.4 and 0.6 \([47]\).

The use of Eq. (16) for analysing the experimental annealing curves has been questioned by Balluffi and Siedman \([45]\). According to these authors, for normal values of the interaction energy, \( E \) it is the gradient term in Eq. (15) that dominates over the drift term and hence Eq. (16), obtained by considering only the drift term, has no physical basis. The annealing behaviour obtained by considering only the concentration gradient follows first-order kinetics. Experimentally this is seldom observed, and departure from first-order kinetics has been attributed to various factors like the presence of an inhomogeneous distribution of dislocations, the change in the dislocation structure during annealing, the change in the efficiency of dislocations as vacancy sinks and the participation of more than one type of vacancy defects in the annealing process.

The isothermal annealing behaviour of cold-worked metals in the stage III region have also been explained in terms of bimolecular defect reaction between the migrating interstitials and immobile vacancies \([48]\).

From the foregoing it is clear that the annealing behaviour of vacancies in quenched and cold-worked metals
is a complicated process rendering it difficult to make a reliable analysis in terms of defects involved and their migration properties.

1.4.3 Analysis of annealing curves

If the defect annealing is governed by a single activated process, the experimentally measured annealing curves can be analysed to estimate the activation energy [43, 49]. If \( p \) is any physical property like the resistivity that is used to monitor the annealing of defects, then for a singly activated process [49],

\[
\frac{dp}{dt} = -K_0 f(p) \exp \left(\frac{-E^m}{RT}\right) \quad (17)
\]

where \( K_0 \) is a constant, \( f(p) \) allows for the interaction between defects and the change in the sink structure, and \( E^m \) is the activation energy for migration. The commonly used methods for obtaining the activation energy are (1) the cross-cut method, (2) the Meechan-Brinkman method and (3) the slope-change method [43, 49]. These are discussed in the following.

Cross-cut method

In this method a series of isothermal annealing curves at \( T_1, T_2 \ldots \) are measured as shown schematically
in Fig.1.5a. A tie line at some constant value of \( p = p_1 \) is
drawn, and the various values of times \( t_1, t_2 \ldots \) at which
the tie line intersects the annealing curves are measured.
The slope of the \( \ln t_i \) vs \( 1/T_i \) plot yields the activation
energy of migration. This can be seen as follows: An
integration of Eq.(17) yields,
\[
\int_{p_0}^{p_1} \frac{d\bar{p}}{f(p)} = -k_b t \exp \left(-\frac{E_M}{kT} \right). \quad \quad (18)
\]
The above equation can be rewritten as
\[
\ln t = -\frac{E_M}{kT} + \ln \left[ -\frac{1}{k_b} \int_{p_0}^{p_1} \frac{d\bar{p}}{f(p)} \right]. \quad (19)
\]

**Meechan-Brinkman method [50]**

In this method the activation energy of migration is
determined by a simultaneous analysis of the isochronal and
isothermal annealing curves, as illustrated in Fig.1.5b. The
isothermal annealing time \( \Delta T_i \) which gives the same
change in \( p \) as the isochronal anneal at a temperature \( T_i \)
is measured. It follows from Eq.(18) that these two
quantities (\( \Delta T_i \) and \( T_i \)) are related according to
\[
\Delta T_i \exp \left(-\frac{E_M}{kT_A}\right) = \Delta t \exp \left(-\frac{E_M}{kT_i}\right), \quad (20)
\]
Fig. 1.5. Schematic of the various experimental methods for the determination of the activation energy: (a) Cross-cut method, (b) Meechan-Brinkman method and (c) Change of slope method.
where $T_A$ is the isothermal annealing temperature and $\Delta t$ is the isochronal annealing time. This equation is used to estimate the activation energy.

**Slope-change method**

Most of the determination of the activation energy from resistivity measurements have been carried out by this method. In this method the annealing temperature is suddenly changed during an isothermal anneal and the ratio of the annealing rates at the two temperatures are determined. These are related to the activation energy through the relation (see Eq.(17))

$$\frac{(d\rho/dt)_T}{(d\rho/dt)_{T_2}} = \exp \left( -E^M \left( \frac{1}{kT_1} - \frac{1}{kT_2} \right) \right) . \quad (2.1)$$

This method is illustrated in Fig.1.5c.

The slope-change method for the determination of the activation energy has the advantage that a single sample is used, whereas in the other two methods at least two samples are required. Thus all the annealing conditions, except the temperature, are kept identical in the slope-change method$. This method however requires that the changes in the defect concentration be monitored quickly
following a change in the annealing temperature and hence cannot be used with positron annihilation measurements.

In this thesis the cross-cut method has been used to estimate the activation energy of migration from the isothermal annealing measurements.

1.4.4 Clustering of defects

It was mentioned in Sec. 1.4.1 that vacancies can cluster during the annealing of quenched, cold-worked or irradiated metals. This clustering can result in the formation of either 2-dimensional vacancy loops or 3-dimensional voids. In contrast, the clustering of interstitials always leads to the formation of 2-dimensional dislocation loops because the large distortions around 3-dimensional clusters make them energetically unfavourable. The clustering of defects is influenced by various parameters like the presence of impurities, gas atoms, stacking-fault energy of the metal, the heat-treatment conditions like the quench temperature, ageing temperature etc. Most of these studies have been made using transmission electron microscopy [51]. The information on the early stages of clustering, that are below the resolution of the transmission electron microscope, have been obtained using the positron annihilation technique and diffuse X-ray scattering experiments. These techniques are compared in Sec. 1.6.
1.5 **Annealing Studies Using Positron Annihilation Technique**

It is clear from the previous section that in order to study the annealing behaviour of defects one requires experimental techniques which provide specific information about the type of defects involved. The resistivity experiments which have been widely used in the annealing studies is non-selective. The measured resistivity has contributions from all the defects present, interstitials, vacancies, defect-impurity complexes, defect clusters, dislocations etc. In comparison, the positron annihilation technique is a selective probe of vacancy-type defects. Furthermore, in a positron annihilation experiment, it is possible to derive certain defect-specific annihilation parameters that can be used to distinguish between various types of defects like monovacancy, dislocation loops and vacancy clusters.

The annihilation rate or the lifetime in a defect is one such parameter that is characteristic of the defect, for example, the lifetime of a positron in a monovacancy in aluminium is $\sim 240$ psec, whereas the lifetime at a vacancy cluster containing ten vacancies is $\sim 400$ psec. The defect-specific parameter, derived from an angular correlation or Doppler broadening lineshape parameter measurements is called the $R$ parameter [52] which is defined as,
\[
R = \left| \frac{I_v - I_v^f}{I_c - I_c^f} \right| = \left| \frac{I_d - I_d^f}{I_c - I_c^f} \right| ,
\]

where \( I_v \) and \( I_c \) are the areas under the peak region and wing regions respectively. The superscripts \( f \) and \( d \) refer to the free annihilation and annihilation from the trapped state at defects. It can be shown that within the framework of the two-state trapping model the \( R \) parameter is independent of the concentration of defects and hence is defect-specific.

It was mentioned earlier in Sec. 1.2.1 that the annihilation characteristics are very sensitive to the size of a vacancy cluster. This, together with the abovementioned features of a positron annihilation experiment, i.e., the selectivity to vacancies and the possibility of evaluating defect-specific parameters, have resulted in wide-spread application of this method to defect annealing studies. In the following a few examples which illustrate the application of the positron annihilation method to annealing studies are discussed. More details can be found in the review article by Gauster [6], where all the experiments have been classified according to the annealing stages. The annealing studies in the cold-worked metals have been discussed by Byrne [53].
The Doppler broadening studies of the annealing behaviour of defects in copper, irradiated with 3 MeV electrons at liquid helium temperature, were carried out by Mantl and Triftshauer [52]. The results taken from their paper are shown in Figs. 1.6 and 1.7. In Fig. 1.6 the parameter $\Delta I_v$, which is the difference between the lineshape parameter $I_v$ and the characteristic parameter $I_v^c$ of the annealed sample, is plotted as a function of the isochronal annealing temperature. The results from the resistivity measurements are also shown in this figure. In stage I, $\Delta I_v$ decreases as the number of vacancies decrease due to recombination with the moving interstitials. The variation in $\Delta I_v$ is nearly parallel to the variation in $\Delta \rho / \Delta \rho_0$. In stage II there is no appreciable change in $\Delta I_v$. In stage III, $\Delta I_v$ increases dramatically, while $\Delta \rho / \Delta \rho_0$ decreases due to further loss of electron scattering centres. The increase in $\Delta I_v$ indicates that the nature of dominant positron traps have changed. This is seen more clearly in the temperature variation of the defect-specific $R$ parameter (see Fig.1.7). The $R$ parameter remains constant during the stages I and II at a value characteristic of vacancies, and increases above stage III to a value different from the characteristic value for vacancies and dislocation loops. The new traps are identified with the small 3-dimensional vacancy clusters, that are formed due to the agglomeration of the migrating
Fig. 1.6. Variation of the Doppler broadening lineshape parameter difference, $\Delta I_v = I_v - I^2_v$, and the resistivity as a function of the isochronal annealing temperature in electron-irradiated copper. Curves 1, 2 and 3 correspond to different initial Frenkel pair concentration. From Ref. [52].
Fig. 1.7. Variation of the defect-specific $R$ parameter as a function of the isochronal annealing temperature in electron-irradiated copper. The values of $R$ parameter for vacancies in thermal equilibrium and dislocation loops are also indicated. From Ref. [52].
vacancies. Further annealing beyond stage III results in a decrease in $\Delta I_v$ due to the disappearance of the vacancy clusters.

The annealing behaviour of defects can be studied in greater detail in a positron lifetime experiment. This is because the lifetime spectra can be analysed into various components to evaluate the annihilation rate in the trapped state and the fraction of the total annihilations in the trapped state. Further, the positron lifetime in the defect-trapped state is a better defined physical quantity than the various momentum distribution parameters in use, and can be theoretically estimated with reasonable certainty. The application of the positron lifetime experiments to annealing studies is illustrated through the experiments of Hautojarvi et al [54] on electron-irradiated iron. Their results are shown in Fig.1.8, where the lifetime in the trapped state, $\tau_2$, and the intensity of this component, $I_2$, which is related to the defect concentration, are plotted as a function of the annealing temperature. In the low-dose sample, between 77 K and 120 K the intensity $I_2$ stays at 100% indicating that all positrons are trapped. The lifetime $\tau_2$ of 170 psec is characteristic of monovacancies in iron. At $\sim$ 140 K the intensity $I_2$ decreases whereas $\tau_2$ remains constant, indicating that vacancy-interstitial recombination has taken place at this temperature. Between
Fig. 1.8. The lifetime $\tau_2$ and intensity $I_2$ of trapped positrons in electron-irradiated $\alpha$-iron as a function of isochronal annealing temperature. The high and low irradiation doses correspond to resistivity increases of 560 n$\\Omega$cm and 220 n$\\Omega$cm respectively. From Ref. [54].
140 K and 205 K $I_2$ and $\tau_2$ remain constant indicating that the monovacancy concentration does not change. At $\sim 220$ K there is a rapid increase in $\tau_2$ and a concomitant decrease in $I_2$ indicating that small vacancy clusters are formed in this temperature region. From the value of lifetime $\tau_2$ which lies in the range of 250 to 300 psec, the vacancy clusters were estimated to contain 2 to 5 vacancies (see Fig. 1.2). In the high-dose sample, no change in $I_2$ is observed at 140 K as the number of vacancies is so large that even after recombination with interstitials, the number of vacancies left in the system is large enough to trap all positrons. This example illustrates the extent of information on the annealing behaviour of defects that can be obtained from a positron lifetime experiment.

Extensive studies on the annealing behaviour of defects in neutron-irradiated [55], electron-irradiated [56] and cold-worked molybdenum [57] have been carried out since the first observation of voids in the neutron-irradiated molybdenum [58]. The variation of lifetime $\tau_2$ with the annealing temperature has been quantitatively analysed [18] to study the growth of vacancy clusters during annealing. This is shown in Fig.1.9. This indicates the potential of the positron annihilation technique for the quantitative study of the vacancy clustering process in metals.
Fig. 1.9. The positron lifetime component, \( \tau_2 \), as a function of isochronal annealing temperature in electron-irradiated molybdenum [56]. The theoretical estimate of the number of vacancies \( N_v \), per microvoid is also shown [18].
1.6 Comparison with Other Techniques

In this section, the positron annihilation technique is compared with other experimental methods that are used for the determination of the vacancy-formation energy and the study of the annealing and clustering behaviour of vacancies in metals.

The use of the positron annihilation technique for the determination of the vacancy-formation energy in metals was discussed in Sec. 1.3. The other method for the determination of the vacancy-formation energy under equilibrium conditions is differential dilatometry [59]. This consists of precise measurements of the length and lattice parameter changes with temperature, which are related to the equilibrium vacancy concentration, \( C_v \) through the relation

\[
C_v = \frac{1}{z} \left( \frac{\Delta L}{L} - \frac{\Delta \alpha}{\alpha} \right)
\]  

(23)

for cubic metals, where \( \Delta L/L \) and \( \Delta \alpha/\alpha \) are the fractional changes in the length and lattice parameter.

With the presently available accuracy for the measurement of these quantities, it is only possible to detect vacancy concentration greater than \( 10^{-4} \). This means that in the temperature range in which the vacancy-formation energy is determined, from the slope of the Arrhenius plot, there
is likely to be a significant contribution from divacancies. This is to be compared with the positron annihilation technique where due to the high sensitivity to vacancies, the variation of the vacancy concentration with temperature is investigated over a range of concentration from $10^{-7}$ to $10^{-4}$ in which the monovacancies predominate. Thus the two techniques can be regarded as complementary to each other with the positron annihilation technique being sensitive to the vacancy concentration in the range of $10^{-7}$ to $10^{-4}$ and the differential dilatometry being sensitive to vacancy concentration beyond $10^{-4}$. By combining the two techniques it is possible to study the temperature variation of the vacancy concentration over a wider range and hence obtain quantitative information about both mono- and divacancies.

In addition to the abovementioned equilibrium methods, the vacancy-formation energy has also been obtained from resistivity measurements on samples quenched from various temperatures [23]. These non-equilibrium measurements however suffer from an inherent disadvantage that the concentration of vacancies quenched in the system is dependent on various parameters like the quench rate, the initial history of the sample etc., which make the vacancy-formation energy obtained from these measurements less reliable as compared to those from equilibrium measurements.
The annealing behaviour of defects in metals have been mainly investigated by resistivity measurements which provides a simple, sensitive and a quick method to monitor the changes in defect concentration during annealing. This method however is non-selective because the measured resistivity has contributions from all types of defects present in the sample. The positron annihilation technique by virtue of its selectivity to vacancies forms a good complement to the resistivity measurements in annealing studies. Furthermore in a positron annihilation experiment, the small vacancy clusters formed during annealing are easily detected and from a measurement of the lifetime in these clusters the average cluster size can be evaluated. The positron annihilation parameters are very sensitive to the size of clusters in the range of 1 - 5 Å. The other experimental method that is used for the study of these small clusters is the diffuse scattering of X-rays. Larger clusters are studied by transmission electron microscopy.

The diffuse scattering of X-rays, which occurs due to the loss of the translational symmetry of a crystal in the presence of defects, is a powerful experimental method for the study of the structure and strength of point defects and their agglomerates [37]. Depending on the scattering vector, different regions of the displacement field of the defect contribute to the diffuse scattering. The
scattering in the region close to the Bragg peak, called Huang scattering, is determined by the long-range displacement field of the defect and has a characteristic $q^{-2}$ dependence ($q$ is the difference between the scattering vector and the reciprocal lattice vector). The Huang scattering is also proportional to the square of the relaxation volume of the defect and hence is more sensitive to interstitial type defects. The changes in the diffuse scattering due to the clustering of defects are: (1) A large increase in the Huang scattering per defect, which is proportional to the size of the defect cluster and (2) a change from $q^{-2}$ to $\sim q^{-4}$ dependence of the scattered intensity. From the measurement of the Huang scattering associated with defect clusters it is possible to evaluate the size of the cluster provided the concentration and relaxation volume are known. Since Huang scattering is predominantly by interstitial type defects it is possible to study the annealing and clustering of vacancies only in the absence of interstitials, like in quenched metals. The results of recent measurements of Ehrhart et al [60] on quenched gold is shown in Fig.1.10. The large increase in the scattered intensity and a change from $q^{-2}$ to $q^{-4}$ dependence reflect the growth of vacancy clusters during the annealing. It has been possible in this experiment to follow the growth of vacancy clusters all the way upto the formation of stacking-fault tetrahedra, which are
Fig. 1.10. (a) Diffuse scattering intensity close to the 422 reflection in quenched gold. (b) Annealing behaviour of Huang scattering intensity $I_H (I_H = I_H(q) \times q^2)$ for the various quenched gold samples:
- Sample 1 ($\Delta \rho_o = 26.2$ n\(\text{m}\text{cm})$: $\triangledown$ Sample 2 ($\Delta \rho_o = 27.0$ n\(\text{m}\text{cm})$
- Sample 3 ($\Delta \rho_o = 27.4$ n\(\text{m}\text{cm})$: ■ Sample 4 ($\Delta \rho_o = 34.2$ n\(\text{m}\text{cm})$
- Sample 5 ($\Delta \rho_o = 34.3$ n\(\text{m}\text{cm})$: and □ Sample 6 ($\Delta \rho_o = 38.0$ n\(\text{m}\text{cm})$.

From Ref. [60].
estimated to contain as much as 500 vacancies. This is to be compared with positron experiments where the lifetime saturates at ~ 50 vacancy cluster (see Fig.1.2). However, Huang scattering experiments suffer from a disadvantage that the clustering of vacancies can be studied only in quenched systems and single crystals are required for these measurements.

The diffuse scattering in the forward direction which is mainly determined by the change in the local atomic density at the defect, is more for vacancies than interstitials. The diffuse scattering in the forward direction has been used to study the clustering of vacancies in electron-irradiated copper [61]. Apart from determining the radius of gyration of vacancy clusters (from the Guinier plots of log (intensity) vs square of the scattering vector), it has also been possible to infer about the geometry of these clusters from the anisotropy of the scattered radiation. The last feature is a distinct advantage over the positron annihilation method where only the average cluster size can be obtained.

The most direct method for observing defect clusters is through transmission electron microscopy [51]. The dislocation loops and the 3-dimensional vacancy clusters locally change the diffraction condition, due to their associated strain fields, and produce diffraction contrast...
images. The lower resolution limit for the visible diffraction contrast images is about 10 Å, which is about 20 point defects in the case of loops and about 50 point defects in the case of 3-dimensional clusters. Thus, the nucleation and the early stages of clustering cannot be observed directly by transmission electron microscopy. However, it has been possible to study the kinetics of nucleation indirectly by observations on fully grown vacancy clusters [62].

To summarise, it is seen that positron annihilation technique is a powerful experimental method for the study of vacancy-type defects. It offers the best method for the determination of the monovacancy formation energy. It also provides useful information about the annealing behaviour of vacancies in metals, and in particular the formation of small vacancy clusters during annealing.

References


D.C. Connors and R.N. West, Phys. Lett. A 30, 24 (1969);


[27] G. Dlubek, O. Brummer and N. Meyendorf, Appl. Phys. 13, 67 (1977)


[41] J. Nihoul, in Ref.[30], p.839

[42] A. Van den Beukel, in Ref.[30], p. 427


[44] K.P. Chik, in Ref.[30], p.183


