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Defect structure studies using positron annihilation spectroscopy

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Abstract. The positron annihilation method is a new addition to the range of sensitive complementary nuclear techniques available for materials' research. The preferential sensitivity of positrons towards micro-defect domains which are not assessable by other techniques makes it an attractive tool for many materials science problems. The present paper is intended as a brief introduction on the principle of measurements and its potential is exemplified with the help of results on some metallic and ceramic systems.

Keywords. Defect structure studies; positron annihilation spectroscopy; sensitive complementary nuclear techniques.

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1. Introduction

The existence of the positron, the antiparticle of the electron was predicted by Dirac (1930) and experimentally verified by Anderson (1932). An electron-positron pair is unstable and the annihilation photons constitute the signal through which the information on the behaviour of positrons in condensed matter; including their interaction with imperfections, is obtained.

Positron annihilation spectroscopy has many advantages in the study of condensed matter. It is a non-destructive method. It is now well established as a technique for the study and characterisation of defect microstructures (Doyama and Hasiguti 1973; Seeger 1976; Byrne 1980; Wiffen and Spitznagel 1982).

The physical basis of positron interaction in condensed matter is well described by various authors (West 1973; Hautojarvi 1979; Brandt and Dupasquier 1983). A brief account of the positron annihilation mechanism and the principle of measurement techniques is presented here along with some applications in metals and ceramics.

2. Positron dynamics in solids

Positrons are usually obtained from radio-nuclide sources such as ^{22}Na, ^{64}Cu, etc. which emit positrons with sufficient energy to penetrate most materials to a few hundred microns. On implantation, positrons get thermalised rapidly ($\approx$ 1 psec) by a succession of ionization and phonon scattering events. The thermalisation times are usually much shorter as compared to the mean lifetime of positrons in solids (Kubica and Stewart 1975).

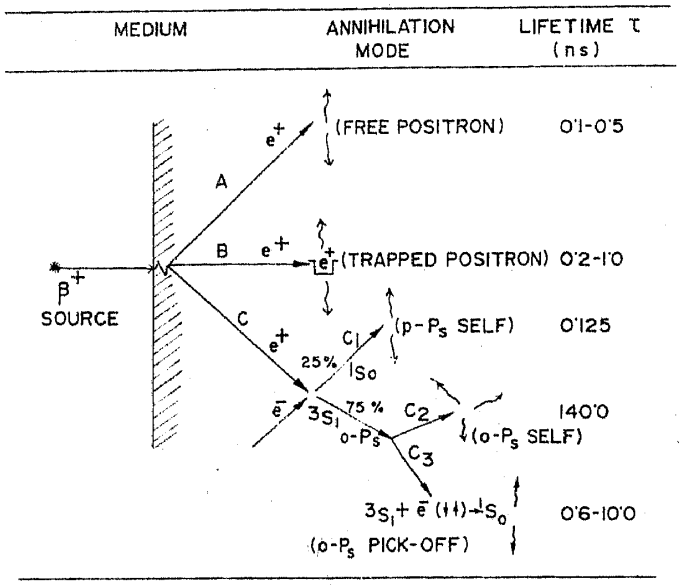

Figure 1. Positron annihilation modes in solids: (A) free annihilation, (B) trapping at point defects and (C) positronium formation and subsequent decay by (C_1) para, (C_2) ortho and (C_3) pick-off annihilation processes.

The injected positrons are distributed in the medium in various possible states. Figure 1 summarises schematically the experimentally observable alternative annihilation modes. Path A represents the annihilation of positrons with free electrons into two γ-rays of 511 keV each, in approximately 0·1 to 0·5 nsec depending upon the density of the free electrons in the solid. Positron wave functions can be localized at point defects (path B). Since the electron density at these sites is lower than in the perfect crystal, the mean lifetime of the trapped positrons becomes longer (0·2–1·0 nsec) than that of the free positrons. These two annihilation modes are typical for metals.

In insulators, positrons can capture an electron (path C) to form positronium, Ps, the hydrogenic two body $e^+ - e^-$ system (BE = 6·8 eV).

In a diamagnetic medium, the positronium distribution is initially in the singlet (p–Ps) and triplet (o–Ps) states in the ratio of 1 : 3. The intrinsic lifetime of p–Ps is 0·125 nsec, about the same as the free positron lifetime in dense metals, whereas for o–Ps it is 140 nsec. However, o–Ps in solids decays mainly by a competing mechanism called the 'pick-off' process, where the positron in the o–Ps suffers a 2γ annihilation in collision with a valence electron having opposite spin (path C_2). Therefore, the o–Ps lifetime is shortened to a few nano seconds (0·6 to 10·0 nsec), which is again a function of the electron density in the medium.

Both the positron and the positronium have a strong tendency to get localised in the regions of low electron density. This localization is reflected in the subsequent annihilation radiation and thus provides the basis for using positrons as a probe for the study of defects in solids.

3. Principle of PAS measurements

Positron, either free or bound, interacts with more than one electron in different energy states in a many particle system. Basically two kinds of information are obtained: (1) that

related to the electron density and (2) that of the distribution of electrons in momentum space. Thus, three different types of measurements can be performed: (i) positron lifetime or more specifically, the positron decay spectrum; (ii) angular correlation of the direction of the photon emitted during 2γ-annihilation; (iii) doppler broadening of 511 keV annihilation radiation.

The time delay between the injection of positrons (marked by the 1·28 MeV nuclear γ-ray using a ^{22}Na source) and the detection of 511 keV annihilation photon in the solid, measured over a large number ($\approx 10^5$) of individual events constitutes the lifetime spectrum (Smedskjaer and Fluss 1983). From such time distributions, one can deduce the decay rate of positrons from experimentally distinguishable states in the material. For ionic solids, like alkali halides and metal oxides, generally two or three lifetime components are obtained. The fastest component τ_1 is assigned to free and p–Ps decay, while the longer ones τ_2 and τ_3, to the pick-off annihilation of o–Ps in the crystalline and disordered regions respectively (Bertolaccini *et al* 1971; Brandt and Paulin 1968).

If the centre of gravity of the annihilating electron-positron pair is at rest, two γ-rays must be emitted with exactly equal energy (511 keV) and in opposite directions. However, because of the non-zero momentum of the pair, the photons deviate from collinearity, *ie*; the two γ-rays are emitted in directions $\pi \pm \theta$ radians. In addition, the energy of the annihilating photon undergoes a Doppler shift $(511 \pm \Delta E)$ keV. Since the momentum of the thermalised positron is very small relative to that of the electron, the distribution of θ in angular correlation and ΔE in the Doppler broadening experiments therefore represent essentially those of the crystal electrons, both core and valence. The higher momentum core electrons contribute proportionally more to the largest values of θ and ΔE. Therefore, the γ–γ angular correlation curves and Doppler broadened spectra are both more sharply peaked for solids containing defects and trap positrons, since there are fewer core electrons at the defect site (Doyama 1979).

For quantitative analysis of defects in solids, parameters deduced from PAS measurements are employed with the help of trapping models (Brandt 1967; Bergersen & Stott 1969).

4. PAS study of vacancy concentrations in metals

PAS has a distinct advantage in the study of vacancy concentration in metals, because it is possible to carry out these studies under thermal equilibrium conditions and at very low vacancy concentration ($\approx 10^{-6}$) where only monovacancies dominate the whole equilibrium ensemble.

The common observation in metals is that the positron annihilation parameter shows a typical S-shaped curve: a thermal expansion effect at low temperatures which gets superimposed with a vacancy trapping effect at higher temperatures and a saturation near the melting point, where it is assumed that all the positrons get annihilated from the trapping sites (MacKenzie *et al* 1967; McKee *et al* 1972; Triftshauser 1975; Seegers *et al* 1978). Figure 2 shows the typical lineshape parameter dependence for Cu as a function of temperature (Fluss *et al* 1980). For evaluating E_v, the formation energy of a vacancy, the experimentally measurable quantities F_b and F_v which represent the specific values of positron annihilation parameter, F (*eg* lifetime,

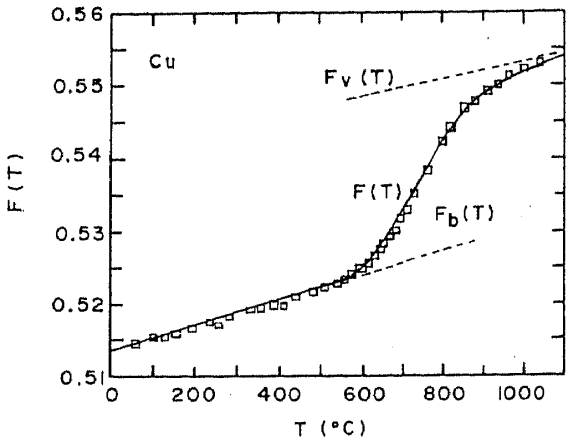

Figure 2. The experimental (□) Doppler-broadening lineshape parameter $F(T)$ as a function of temperature T, and the monovacancy two-state trapping model fit to the data (solid curve). After Fluss *et al* 1980.

ratio of the peak height to the area of angular correlation curve, line-shape parameter etc.), in the free and trapped states respectively, are used in an Arrhenius relationship.

$$\ln\left[\frac{F-F_b}{F_v-F}\right] = -\frac{E_v}{kT} + \ln(A\tau_b) \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, A is a constant and τ_b is the lifetime for the perfect lattice. The values of E_v determined from PAS technique are found to be in good agreement with those obtained from other experiments (Siegel 1978; Doyama 1979; West 1979).

5. Radiation damage studies

Study of radiation damage is important from the point of view of understanding the behaviour of point defects in solids. The sensitivity of the positron annihilation spectroscopy technique to vacancies and their aggregates has made it particularly useful in elucidating the recovery processes in metals and alloys after neutron and electron irradiation (Mogensen *et al* 1972; Cotterill *et al* 1972). From the PAS data, it is possible to identify the migrating entity and determine the average dimensions of vacancy clusters or microvoids, which are below the limit of conventional electron microscopy (Seeger 1973; Petersen *et al* 1975; Mantl and Triftshauser 1975).

Irradiation at low temperatures predominantly results in the production of single vacancies and interstitials. The defect recovery in copper crystals (Mantl and Triftshauser 1975) irradiated by 3 MeV electrons at 10 K, was followed by residual resistivity and Doppler broadening parameters expressed in terms of I_v (corresponding to valence electrons) and I_c (corresponding to core electrons) (figure 3). The initial drop in resistivity indicates that the number of trapping sites for positrons is reduced. Thus, the increase in I_v and the corresponding decrease in I_c can be interpreted as due to the aggregation of vacancies into small three-dimensional clusters, which eventually collapse into vacancy loops, often observed in electron microscopy studies. These results thus support the vacancy model of stage III for migration of point defects

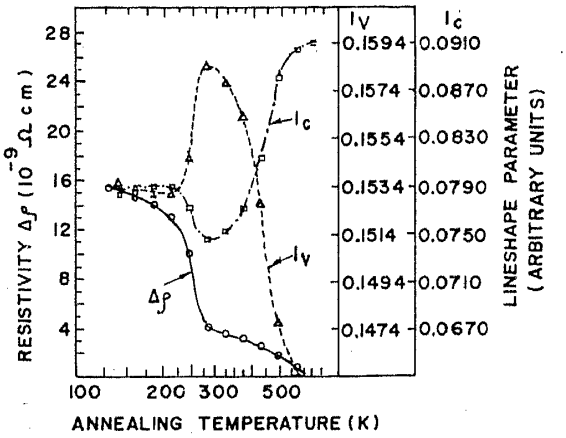

Figure 3. Dependence of the lineshape parameters I_v and I_c, and the electrical resistivity for electron irradiated copper, as a function of the annealing temperature. (After Mantl and Triftshauser 1975).

(Schilling and Sonnenberg 1973). This was further verified in the case of copper from measurement of positron lifetimes (Hinode *et al* 1978).

6. Defects in non-metals

In non-metals, the positron annihilation modes are quite complex—usually characterised by two or more decay components—and the reason for this has still not been established. However, positron annihilation behaviour in molecular solids like polymers, ionic solids like alkali halides, oxides and the silicate glasses is explained, partly because of the observations made with other conventional techniques (Walker 1979; Dupasquier 1979). As positron trapping by defects is the basic phenomenon, the established analytical methods are equally effective in analysing the PAS results.

The formation of a Ps-like bound state is no longer speculative and several confirmatory experiments, involving measurements under different atmospheres (Steldt and Varlashkin 1972), three-to-two photon relative yield measurements (Sen and Patro 1969), magnetic quenching experiments (Yam *et al* 1978; Judd *et al* 1979) etc., have helped to reveal the annihilation mechanism. Figure 4 shows the γ-γ angular correlation results on pure and doped polycrystalline samples of ThO_2. An increase in the peak counting rate in the presence of transition metal impurities represents the enhancement in the 2γ annihilation events compared to that in pure ThO_2. This is attributed to the increase in the pick-off quenching rate of *o*–Ps in the presence of these ions.

7. Positron annihilation in fine powders

Positronium formation in metal oxide powders was first reported for Al_2O_3, MgO, CaO and ZnO (Kusmiss and Stewart 1967). The angular correlation curves showed a low intensity narrow component attributed to the annihilation of *p*–Ps, formed on or near the surface of the finely divided powder particles. Earlier observations of long time components ($\tau_3 \simeq 3{\cdot}5$ ns, $I_3 \simeq 6\%$) observed for alkaline-earth oxides (Bussolati and Zappa 1964) and the additional intermediate component ($\tau_2 \simeq 0{\cdot}5$ ns, $I_2 \simeq 12\%$)

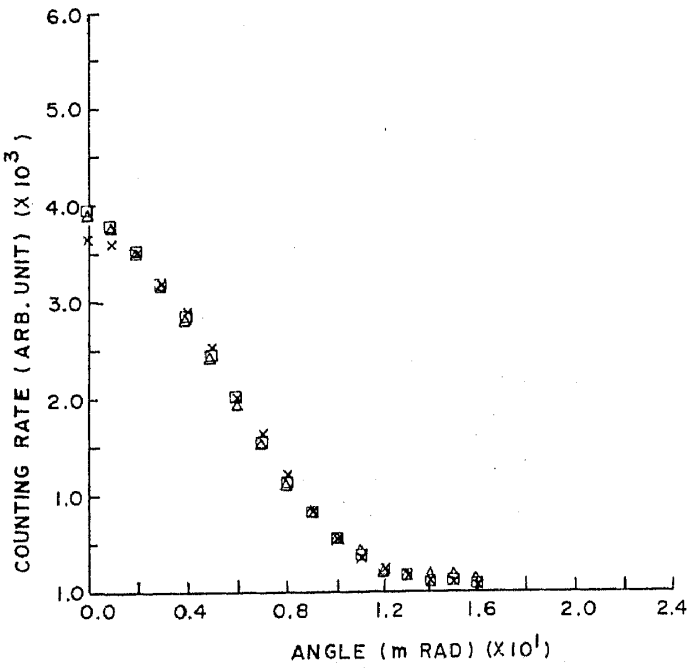

Figure 4. Angular distribution of annihilation photons in ThO_2: pure (X) and doped with TiO_2 (Δ) and Fe_2O_3 (□).

obtained in several oxides and fluorides (Paulin and Ambrosino 1967) also gave a clear evidence for the decay of a Ps-like bound state in the medium.

The most remarkable feature observed is that the annihilation characteristics are strongly dependent on the particle size of the powders. For ZrO_2 powders (Mitsuhashi *et al* 1972), it was found that the positron life time is insensitive to its allotropic modification but is dependent only on the particle size. Life time components τ_1 and τ_2 were found to increase as the particle size becomes small.

Brandt and Paulin (1968) demonstrated a strong dependence of life time spectra on particle size of MgO, Al_2O_3 and SiO_2. The systematic narrowing of the angular correlation curve (Steldt and Varlashkin 1972) and the increase in the pick-off life time component τ_2, (Baranowski *et al* 1977) with decreasing particle size of MgO powders are also consistent with the results of previous authors. The decrease in mean life time with improvement in crystalline perfection is a general phenomenon observed in metal powders (Noguchi and Miyata 1979), graphite (Iwata *et al* 1981), diamond (Mokrushin and Breusov 1980), etc.

Figure 5 shows the life-time results on microcrystalline ThO_2 powders (Upadhyaya *et al* 1982a). A linear plot correlating τ_1 and τ_2 with crystallite size deduced from X-ray line broadening, established that the finer particles correspond to a higher defect density. The annihilation probability for both free (τ_1) and *o*–Ps pick-off (τ_2) processes is reduced in the pseudo-amorphous powders due to lower than average electron density. With increasing crystalline perfection, the free volume at the trapping site decreases which enhances the overlap of the positron wave function with that of the valence electrons in the medium. Deviation in the value of the positron parameter from that of the single crystal state is thus a quantitative measure of the degree of disorder in the powdered state. This leads to the suggestion that a reexamination of the intrinsic

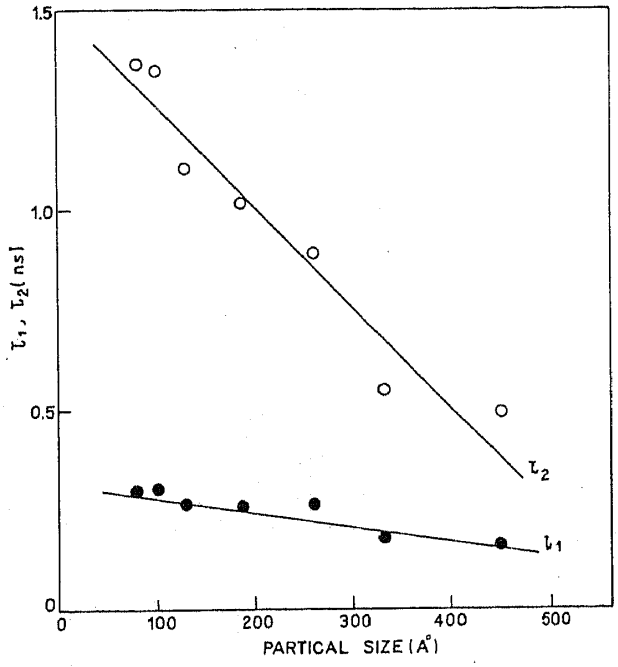

Figure 5. Positron lifetime components τ_1 and τ_2 versus primary particle size (measured by X-ray diffraction line broadening method) correlation for finely divided thoria powders.

values of positron life times reported so far by employing powder samples may be needed.

Another important aspect of positron dynamics in fine powders is concerning their diffusion mechanism—both from the point of view of moderation as well as trapping (Barko *et al* 1979; Brandt 1974). The injected positrons after thermalization and Ps formation scan the powder grains isotropically. The rate of trapping at defects and the escape rate at the surface are proportional to the diffusion constant of the migrating species. Assuming the Ps to be formed with equal probability inside a small insulating solid of spherical shape, the escape rate can be derived. The relative intensity of the life time component assigned to the surface, when expressed as a function of particle size enables one to calculate the Ps diffusion constant (D_+). For oxides, it was found to be of the order of 10^{-5} cm^2 sec^{-1} (Brandt and Paulin 1968; Upadhyaya *et al* 1982b), which is about three orders of magnitude smaller than for metals (Paulin *et al* 1974; Matsuoka *et al* 1980; Noguchi and Miyata 1979).

Positron diffusion constant in powders can also be measured using the following expression (Brandt 1974)

$$Y = (D_+ \tau_b)^{1/2} Sd \tag{2}$$

where Y is a comprehensive life time parameter, τ_b the intrinsic value of life time in the solid and the quantity Sd, which is the product of the specific surface area of the powder and the theoretical density, is equivalent to the inverse of the mean particle diameter.

The values of the escape probability I_S and Y for thoria powders are plotted in figure 6 (Upadhyaya *et al* 1982c). It shows an increase in the intensity of the surface life time component with increasing surface area. The slope of the Y *vs* Sd graph yields the Ps diffusion constant in thoria as 80×10^{-5} cm^2 sec^{-1}, equivalent to a Ps diffusion length of about 60 Å.

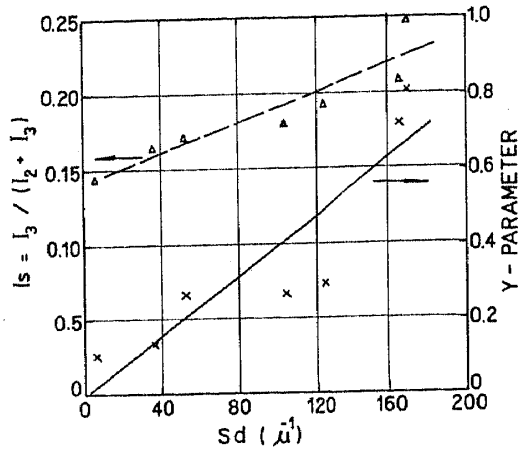

Figure 6. *Sd* product *vs* (i) escape probability (*Is*) of *o*–Ps to the powder particle surfaces and (ii) and *Y*-parameter dependence for thoria powders.

Summary

Positron annihilation spectroscopy has made a significant impact in our understanding of the defect structure in solids. The favourable combination of properties possessed by positrons makes them specially valuable as probes of microscopic and atomic scale imperfections. It has been found to be a sensitive tool for the study of electron structure in metals and also has a great potential in the study of point defects—especially lattice vacancies. This selective nature of the interaction has helped in explaining various metallurgical phenomena. The defect recovery processes associated with the irradiation damage and various thermomechanical treatments in metals and alloys have been investigated to great advantage.

PAS has successfully utilized oxide powder systems, primarily as a suitable medium to test and rationalize experimentally the predictions of quantum electrodynamics about the positronium formation and its decay reactions. In this process, it has contributed to our understanding of defect structure in ceramics, in much the same way as it has in metals. Results cited here elucidate the role of material fineness on Ps-dynamics, *ie*, the diffusion constant, pick-off annihilation rate, etc., employing a medium which has been well characterized by a variety of conventional techniques.

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