Probing the defects in nano-semiconductors using positrons

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Abstract. Positron annihilation spectroscopy (PAS) is a very useful tool to study the defect properties of nanoscale materials. The ability of thermalized positrons to diffuse over to the surfaces of nanocrystallites prior to annihilation helps to explore the disordered atomic arrangement over there and is very useful in understanding the structure and properties of nanomaterials. As examples, the results of studies on FeS$_2$ nanorods and ZnS nanoparticles are presented. In semiconductor nanoparticles, there are positron trapping sites within the grains also and these are characterised by using appropriate models on the measured positron lifetimes. We have observed vivid changes in the measured positron lifetimes and Doppler broadened gamma ray spectral lineshapes during structural transformations prompted by substitutional effects in Mn$^{2+}$-doped ZnS nanorods. Interestingly, the nanoparticles did not exhibit the transformation, implying the morphologies of the nanosystems playing a decisive role. Quantum confinement effect in CdS nanoparticles was another phenomenon that could be seen through positron annihilation experiments. Coincidence Doppler broadening measurements have been useful to identify the elemental environment around the vacancy clusters that trap positrons. Recent studies on nanocrystalline oxide and sulphide semiconductors are also discussed.

1. Introduction
Positrons are extensively used as probes to explore the defect-related properties and processes in semiconductors. Since a plethora of literature on positron annihilation studies of bulk semiconductors already exists [1], the interpretation of the results of positron annihilation experiments on semiconductor materials composed of nanometer-sized grains is considered simple and straightforward. Still additional complications are bound to arise as the chemical and physical properties of the nanocrystalline semiconductors are generally very different from those of their bulk counterparts. This is not only due to the increased number of atoms on the grain surfaces taking part in the various processes but also due to the changes introduced by increasing concentration of vacancy type defects inside the grains and at their surfaces. In this paper, we review a few such investigations, each highlighting a unique aspect that could be revealed through positron annihilation studies.

2. Experimental details
The samples were synthesized through the normal solvothermal route described in detail earlier [2-9]. Appropriate amounts of the proper reagents were chosen and mixed in the right proportion, followed by rigorous stirring till the final precipitate is formed. It was filtered, washed several times in water or ethanol and then dried in vacuum in an oven at ambient temperature. The products were thereafter
characterized by x-ray diffraction and the crystalline grain sizes were calculated by using the standard Scherrer equation [10]. Crystallites of larger sizes could be produced by heat-treating the synthesized sample at selected temperatures for different intervals of time. The obtained grain dimensions in all the cases were in the nanometer range, spreading over a few to a few tens of nanometers. In some cases, the sizes were also determined from high resolution electron microscopic images (figure 1, for example). The obtained nanostructures were also examined through transmission electron microscopy (TEM) and their morphology varied from simple nanoparticles to bypiramidal shaped nanocones. A few illustrative examples are shown in figures 2(a) - 2(c).

Figure 1. High-resolution electron micrograph of the nanocrystalline (grain size 4.5 nm) cadmium sulphide (CdS) sample.

Figure 2. Transmission electron microscopic (TEM) images of the (a) undoped and (b) 1% Mn²⁺-doped zinc oxide (ZnO) nanocone samples and that of (c) ZnO nanoparticles of diameter 15 nm.

The samples were in powder form and the one for positron annihilation experiments was taken in a glass tube. The £²²Na source of strength about 400 kBq deposited on a thin (~ 4 µm) Ni foil was kept immersed inside the volume of the powdered sample. The sample covered the source from all the sides in sufficient thickness to ensure positron annihilation to occur within it and the glass tube containing the source and the sample was continuously evacuated to remove traces of air and moisture otherwise likely to be trapped in it. This also helped, as demonstrated later elsewhere [8], to prevent quenching of orthopositronium atoms that provide useful information on the intergranular region within the nanomaterials. The positron lifetime data (about 1-1.5 million counts) were collected under the usual experimental settings using a gamma-gamma coincidence setup with a time resolution (full width at half maximum) of 200 ps. For Doppler broadening measurements, a high pure germanium detector with energy resolution 1.14 keV at 511 keV was used. This and another similar detector with identical energy resolution were used on either side of the source-sample assembly for recording the anticollinear annihilation gamma rays to generate the coincidence Doppler broadened spectrum (CDBS) for element-specific identification of the positron trapping sites [11,12].

3. Results and discussion
The positron lifetime data were analyzed using the programs RESOLUTION and POSITRONFIT [13] or, of late, PALSFIT [14]. All the spectra gave satisfactory fit when three exponential components $\tau_1$, $\tau_2$ and $\tau_3$ were resolved with intensities $I_1$, $I_2$ and $I_3$. The lineshape of the Doppler broadened positron
The annihilation gamma ray spectrum was parameterized in terms of $S$ and $W$, respectively representing the area-normalized counts under the segments 0 to 0.6 keV and 1.6 to 4.0 keV on either side of the peak. The CDB spectra were analyzed following the procedure described in the original papers [11,12].

In the following sections, several aspects related to the annihilation of positrons from different sites in nanocrystalline semiconductor materials are discussed. It should be pointed out that the ability of positrons to diffuse through the material after the initial thermalization is the key factor that eventually makes them useful probes to explore the grain surfaces. The average diffusion lengths of thermalized positrons in typical materials range around 10-100 nm [15]. Hence, if the grain sizes are smaller than the thermal diffusion length in the material, large fractions of positrons will diffuse and come out of the grains before annihilation takes place. On the surfaces, positrons get trapped due to the presence of a rich concentration of vacancy type defects, which owe their origin to the highly disordered atomic arrangement. The annihilation characteristics are therefore rich sources of information on the electronic structure and properties of the grain surfaces and interfaces, which are the basic features that distinguish materials of nanocrystalline composition from the coarse-grained bulk material.

![Figure 3.](image1)

**Figure 3.** Peak-normalized positron lifetime spectra of CdS bulk and nanocrystalline (grain size ~ 2 nm) samples.

![Figure 4.](image2)

**Figure 4.** (a) Doppler broadened positron annihilation gamma ray spectra of CdS bulk (closed circles) and nanocrystalline (grain size ~ 2 nm) (open circles) samples. (b) The peak region inside the box in (a) is shown magnified for clarity.

### 3.1. Sensitivity of positron annihilation characteristics to the morphology of nanostructures

In order to demonstrate the sensitivity of positron annihilation to nanocrystalline composition of a given material, the peak-normalized positron lifetime spectra of bulk and nanocrystalline CdS are given in figure 3. The corresponding Doppler broadened gamma ray spectra are presented in figures 4(a) and 4(b). The resolved positron annihilation lifetimes and their intensities (table 1) indicated a conspicuous increase in the value of the defect-specific component $\tau_2$ and the orthopositronium intensity $I_3$ in the nanocrystalline sample. It implies that the positrons entering into the grains successfully diffuse over to the grain surfaces and get trapped into the vacancies or vacancy clusters there. As the grain size decreases, the number of positrons reaching the grain surfaces will increase and the intergranular separation will become large enough to favour enhanced formation of positronium atoms.

| $\tau_1$ (ps) | $I_1$ (%) | $\tau_2$ (ps) | $I_2$ (%) | $\tau_3$ (ps) | $I_3$ (%) | $S$ |
|---------------|-----------|---------------|-----------|---------------|-----------|-----|
| Bulk sample   | 172±4     | 59.3±1.7      | 375±7     | 40.2±1.7      | 1500 (fixed) | 0.5±0.05 | 0.431±0.001 |
| Nanocrystalline sample | 174±4     | 58.9±1.8      | 388±4     | 38.2±1.8      | 1500 (fixed) | 2.9±0.21 | 0.436±0.001 |

Yet another demonstration of the propensity of positrons to open volume regions even in nanocrystalline materials is seen in figure 5 where the positron lifetime spectrum of the sample that
contained a fraction of nanotubes besides nanorods is found less rapidly decaying than that of a sample of nanorods alone [2]. Positron lifetimes can be different in samples of different morphologies of the same nanomaterial and of the same crystalline structure. This is shown schematically in figure 6.

Figure 5. Peak-normalized positron lifetime spectra of two pyrite (FeS₂) nanocrystalline samples, one composed of nanorods and the other a mixture of nanorods and nanotubes.

Figure 6. The mean positron lifetimes in FeS₂ nanocrystalline samples of crystallites with different morphologies.

3.2. Sensitivity of positron annihilation characteristics to nanocrystalline grain size

It is clear from the above discussion that the number of positrons diffusing to the grain surfaces will increase when the grain sizes decrease. The intensity $I₂$ of the lifetime $τ₂$ of trapped positrons will therefore increase. This has been shown in a number of experiments [5, 6, 9]. The magnitude of $τ₂$ may also increase in materials of smaller grain sizes. This is explained as due to the increase in free volume per atom (or, in other words, size of monovacancies) of grains with decrease in sizes [16]. Figure 7 illustrates the $S$ parameter of zinc sulphide (ZnS) nanoparticles continuously increasing with decreasing grain size. A similar behaviour had been observed in metallic nanoparticles also [17]. The nature of variation can sometimes be camouflaged by other accompanying processes such as structural transformation and lattice expansion or contraction at very small sizes of the nanoparticles [16, 18-20].

Figure 7. The $S$ parameter vs grain size of the ZnS nanocrystalline samples: hexagonal (closed circles) and cubic (open circles).

3.3. Sensitivity of positron annihilation characteristics to quantum confinement effects

One of the remarkable features of significant interest in nanoparticles of extremely small sizes is the occurrence of quantum confinement effects. According to the theory put forward by Wood and Ashcroft [21], a nanoparticle consisting of a few tens or hundreds of atoms can behave as a ‘super atom’ with discrete energy bands instead of a continuum and the average one-electron-energy levels split at a normalized Fermi energy ($ε_F$) given by
where $k_B$ is the Boltzmann constant and $T$ the temperature. The number of atoms $N$ in the nanoparticle is calculated assuming the same crystalline structure to hold good as that of the bulk. (The x-ray diffraction patterns have been found to depict still distinguishable peaks although with increased broadening in samples with particle sizes even as small as 2 nm.) In semiconductors, a more decisive parameter is the exciton Bohr diameter that provides a threshold value of the grain size below which the confinement regime becomes relevant. This is of special significance in optical absorption studies where a characteristic blue shift occurs implying a widening of the band gap ($E_g$) expressed as [22]

$$E_{g(nano)} - E_{g(bulk)} = \frac{\hbar^2 \pi^2}{2 \epsilon_0 r^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \frac{1.8e}{4\pi \epsilon_0}$$

where $m_e$ and $m_h$ are the effective masses of the electron and the hole and $m_0$ is the mass of a free electron. $\epsilon_0$ is the permittivity of free space and $\epsilon$ is the relative permittivity of the material. $\hbar$ is Planck’s constant and $e$ is the charge of the electron. The exciton Bohr radius corresponds to the grain radius signaling the onset of quantum confinement effects downward in size, i.e., $r = r_B$ at $E_{g(nano)} = E_{g(bulk)}$. It was thought worth exploring if positron annihilation parameters could exhibit any discontinuities across the said threshold size of the nanocrystalline grains. Positron lifetimes and $S$ parameters were measured in different samples of CdS nanoparticles, each with grains of different sizes confined within a narrow distribution. As shown in figures 8(a) and 8(b), the $S$ parameter and the mean positron lifetime ($\tau_m$) remarkably increased in samples with grains of sizes below the confinement limit ($r_B \sim 3$ nm for CdS). The blue shift observed in the optical absorption spectra confirmed an increase of band gap from 3.7 eV to 4.3 eV in ZnS and from 2.4 eV to 3.1 eV in CdS when the grain sizes were reduced from coarse sizes to about 2.5 nm [3,4]. The widening of the band gap decreases the overlap between the positron wavefunction and that of the high momentum core electrons and consequently the positron lifetimes and $S$ will increase, as shown in the figures.

**Figure 8.** (a) $S$ parameter and (b) the mean positron lifetime versus grain size of CdS nanoparticles.

### 3.4. Positron trapping in crystal vacancies within oxide nanocrystallites

The above discussion are mainly qualitative in nature as they were mainly centered on the perception that the thermalized positrons diffuse from the interior of the nanocrystalline grains to the surfaces and interfaces before their eventual annihilation. This relied on the possibility that no positron trapping sites existed within the grains and the positrons would freely diffuse towards the surfaces. This is true to a great extent in nanoparticles of metals and alloys but not generally in semiconductor nanosystems. The non-stoichiometric defects that are characteristic features especially of oxide and sulphide semiconductors will act as efficient trapping centres for positrons. This is verified through the
application of trapping models, as discussed later. The oxygen and sulfur vacancies, by virtue of their positive charge, repel positrons whereas the cationic vacancies and/or vacancy clusters either neutral or with overall negative charge will trap them. The measured positron lifetimes will be then admixture of those due to annihilation from the crystal vacancies within the grains and in the vacancies on the grain surfaces. The charge specificity of the positrons towards the vacancies is demonstrated in figure 9 that describes the ratio curves generated from the CDB spectra of the corresponding samples and that of annealed Si of purity 99.99%. The curves of CdO, ZnO and NiO depicted a peak at the same electron momentum $p_L = 11.2 \times 10^{-3} m_0 c$, that confirmed positrons encountering the same elemental surroundings in all the samples [5]. In other words, positrons are trapped in the respective cationic vacancies or vacancy clusters formed by the removal of two cations and one oxygen or sulfur ion.

Figure 9. The ratio curves obtained from the coincidence Doppler broadened spectra of a few oxides, indicating that positrons in them encounter identical chemical environments. The corresponding curve for elemental Zn is also shown.

3.5. Positron annihilation characteristics in zinc oxide single crystalline nanobipyramids of base diameters across the thermal diffusion length

In this work, positron annihilation studies were made in ZnO nanocrystals formed with a bipyramidal configuration with the base having a regular hexagonal shape. The measured positron lifetime $\tau_2$ and the $S$ parameter, when plotted against the base diameter of the nanocrystals (figures 10(a) and 10(b)),

Figure 10. (a) Positron lifetime $\tau_2$ and (b) $S$ parameter versus the base diameter of the ZnO nanobipyramids. The insets show the respective variation versus diameters of ZnO nanoparticles.
clearly showed the demarcation of positrons annihilating within and partly on the surfaces of the nanocrystals. The delineation of the lifetimes admixed in a single component was necessitated in the case of nanocrystals with sizes precisely below the thermal diffusion length (~ 52 nm) of positrons in ZnO. Within this limit, the fraction of positrons reaching the crystallite surfaces reduced when their sizes increased, as shown in the insets of the figures. When the sizes of the nanobipyramids are larger than the thermal diffusion length, the positrons are entirely trapped by the crystal vacancies or their clusters within and their lifetimes changed according to the changing sizes of these trapping sites [5].

3.6. Doping effects in zinc sulphide and zinc oxide nanocrystallites

This part discusses about certain interesting aspects came to light when positron annihilation experiments were carried out on samples of nanorods and nanoparticles of ZnS and nanobypiramids of ZnO doped with different concentrations of Mn$^{2+}$ ions. Doping was achieved during the solvothermal synthesis of the samples and the substitution of Zn$^{2+}$ ions by Mn$^{2+}$ ions were verified through energy dispersive analysis of x-rays (EDAX). The exact concentration of Mn$^{2+}$ incorporated in the ZnO lattice could be estimated only in samples of increased doping although the process of intake could be asserted through complementary techniques even in the case of lightly doped samples.

![Figure 11. X-ray diffraction patterns of Mn$^{2+}$-doped (0 at.%, 0.1 at.%, 6 at.% and 20 at.%) ZnS nanorods. Standard patterns of hexagonal and cubic ZnS crystals are also shown.](image)

![Figure 12. (a) $S$ parameter versus concentration of Mn$^{2+}$ ions and (b) $S - W$ plot of ZnS nanorods.](image)

3.6.1. Structural transformation induced in ZnS nanorods due to Mn$^{2+}$-doping. From the x-ray diffraction patterns shown in figure 11, a transformation of the hexagonal wurtzite structure of ZnS nanorods into the cubic zinc blend structure with increased doping by Mn$^{2+}$ ions is evident and the same was investigated through positron annihilation studies as well. The nature of variation of the $S$ parameter with doping and the $S$ vs. $W$ plot are shown in figures 12(a) and 12(b).
These results convincingly proved the ability of positron annihilation techniques to monitor such structural changes occurring in nanomaterials [6,7], notwithstanding the complexities involved in the analysis of the positron lifetime data as discussed later. The said transformation was followed by a substantial increase of the diameters of the nanorods from 12-15 nm to 100-200 nm. This stage was indicated by a reduction of the positron lifetimes $\tau_1$ and $\tau_2$ (figure 13) and is explained as due to the decrease in the number of positrons diffusing and reaching the nanorod surfaces [6].

### 3.6.2. Mn$^{2+}$-doping in zinc sulphide nanoparticles

While the structural transformation discussed above indicated about the strain induced in the zinc sulphide lattice due to substitution of Zn$^{2+}$ by Mn$^{2+}$ of larger ionic radius, successive replacement of Zn$^{2+}$ by Mn$^{2+}$ did not cause such transformation in cubic nanoparticles. On the contrary, positron lifetimes and the $S$ parameter showed changes that differed significantly from those of the nanorod samples (figures 14 and 15). The difference is attributed to the nature of positron trapping defects within the interior of the nanosystems and their evolution during the doping process.

In the previous case of nanorods, the CDB spectra did not show any shift towards the spectrum of elemental Mn (figure 16), which implied that positrons did not reach within the proximity of the doped ions. This suggested that the vacancy-type defects that trapped positrons were zinc monovacancies ($V_{Zn}$) and the Mn$^{2+}$ ions recombined with these vacancies. Positrons were then left with essentially one type of trapping centres, which are the nanorod surfaces. Whereas in the case of Mn$^{2+}$-doped ZnS
nanoparticles, a characteristic shift of the peak of the CDB spectra towards that of Mn is visible (figure 17). The measured positron lifetime \( \tau_2 (= 380 \text{ ps}) \) in the nanoparticles was larger than that (= 329 ps) in nanorods. These observations suggest the presence of vacancy cluster of the type \( V_{Zn-V_{S-V_{Zn}}-V_{Zn}} \) in the undoped nanoparticle sample and the filling of one of the zinc vacancies by the doped Mn\(^{2+} \) ion [8].

![Figure 16. The ratio curves obtained from the CDB spectra of Mn\(^{2+} \)-doped ZnS nanorod samples.](image)

![Figure 17. The ratio curves obtained from the CDB spectra of Mn\(^{2+} \)-doped ZnS nanoparticle samples.](image)

3.6.3. Mn\(^{2+} \)-doping effects in zinc oxide bipyramidal nanocones. In the case of doping the wurtzite zinc oxide crystals with manganese, the introduction of Mn\(^{2+} \) with an ionic radius of 0.8 Å in place of Zn\(^{2+} \) which is 10% smaller than it in size will lead to the invariable impact on its structure. The associated strain in this case is found to manifest as a restricting effect on the size of the nanobypiramids (also called nanocones). For the base diameters of the nanocones decreased when the dopant concentration increased (table 2). This is explained as follows. The increase of dopant concentration increases the strain, which also leads to increase in the internal energy of the crystallite. The easiest approach to minimize the energy is to keep the Mn\(^{2+} \) ions on the surfaces of crystallites as much as possible, and this is possible when the surface to volume ratio is large. The sizes or diameters of the crystallites are therefore decreased. The \( S \) parameter showed a sharp increase (figure 18) and the positron lifetimes too were found sensitive to this anomalous change (figure 19). The characteristic peak of the CDB spectra shifted towards that of elemental Mn, indicating the trapping of positrons in defects decorated by Mn\(^{2+} \) ions (figure 20). As in the case of ZnS, here too a decrease of the positron lifetime in the initial stages of doping proved the conversion of a \( V_{Zn-V_{O-V_{Zn}}-V_{O}} \)-type trivacency to a \( V_{Zn-V_{O-V_{Zn}}-V_{O}} \)-type divacancy by the filling of one of the zinc vacancies by the doped Mn\(^{2+} \) ion. The positron lifetimes thereafter increased by sensing the reduction in base diameters of the nanocones [9] as more and more number of positrons reach out to the nanocone surfaces prior to annihilation.
Figure 18. $S$ parameter versus concentration of Mn$^{2+}$ ions in ZnO nanocones.

Figure 19. Positron lifetimes $\tau_1$ (bottom) and $\tau_2$ (top) versus concentration of Mn$^{2+}$ ions in ZnO nanocones.

Figure 20. The CDB spectra of Mn$^{2+}$-doped ZnO nanocone samples, indicating the shift in the peak of the spectrum of ZnO towards that of Mn on doping.

Table 2. The average diameters of the base of the ZnO nanocones of samples doped with different concentrations of Mn$^{2+}$ ions, as determined from transmission electron microscopic images.

| Concentration of Mn$^{2+}$ ions (at.%) | Bipyramidal base diameter (nm) |
|----------------------------------------|-------------------------------|
| 0                                      | 75                            |
| 0.1                                    | 75                            |
| 0.5                                    | 75                            |
| 1                                      | 55                            |
| 6                                      | 40                            |
| 10                                     | 35                            |
| 15                                     | 25                            |
3.7. The relevance of $\tau_3$ and $I_3$

Normally in bulk semiconductors, the density of electrons is large enough to forbid the formation of positronium atoms. In nanocrystalline materials, however, such a possibility cannot be ruled out as the intercrystalline (or intergranular) region is distinguishable with electron density low enough to favour the formation of positronium by the positrons present there. This feature is found remarkable as the “pick-off” lifetime of the orthopositronium atoms also exhibited systematic variation as functions of the experimental variable chosen as basis for the investigation of the properties of the nanosystem concerned. For example, in the case of the FeS$_2$ nanorod sample discussed in section 3.1., the intensity $I_3$ was 1.2% whereas the same was found as large as 6.0% in the sample that contained nanotubes. A look at the variation of $\tau_3$ and $I_3$ as a function of the grain size in ZnS (both hexagonal and cubic) reveals gradual decrease (figures 21(a) and 21(b)) and is understood in terms of the decreasing number of positrons reaching the intercrystalline region after their initial entry to the grains [3]. When the variation is monitored as a function of the doping concentration, there too a definite trend is visible as, for example, shown in figures 22 for the case of ZnS nanorods. The lifetime $\tau_3$ shows a gradual rise whereas the intensity $I_3$ continuously fall as more and more Mn$^{2+}$ ions are input into the ZnS nanosystems [6-9]. A common reason for the reduction of $I_3$ is the presence of increasing number of Mn$^{2+}$ ions at the intercrystalline region. This is even more evident from the positron lifetime spectra of figure 23, which on analysis showed a drop in $I_3$ from 2.9% to 0.5% on inclusion of 20 at.% Mn$^{2+}$ ions in ZnS nanorods. The behaviour of $\tau_3$ is case-specific and is discussed in the respective contexts [6-9]. Like, for example, the ZnS nanorods reducing the diameters [6] or the ZnO nanobypiramids shrinking the bases [9] during increased doping, the volume of the intercrystalline region increases to result in increased lifetime for the positronium atoms before “pick-off” annihilation takes place.

![Figure 21](image-url) **Figure 21.** The orthopositronium lifetime $\tau_3$ and intensity $I_3$ versus grain size in (a) hexagonal and (b) cubic ZnS nanoparticles.

![Figure 22](image-url) **Figure 22.** The orthopositronium lifetime $\tau_3$ and intensity $I_3$ versus Mn$^{2+}$ concentration in the ZnS nanorods. The data corresponding to the undoped ($x = 0$) sample are shown against 0.01%.
An important question that was recently raised in this particular context is the wisdom in choosing a vacuum surrounding to maintain the source-sample assembly during the experiments. But indirectly this also helped to answer yet another question regarding the location of the positron trapping defects, i.e., inside or outside the nanocrystallites. This is answered using the observations of the following experiment. Positron lifetime and Doppler broadening measurements were performed in one sample of ZnS nanoparticles with grain size about 2 nm in both vacuum and air separately and the peak-normalized positron lifetime spectra are shown in figure 24. The resolved positron lifetimes and their intensities in the two cases are summarized in table 3. Due to the extremely small size of the particles, even a second positronium lifetime ($\tau_2$) as long as 7.29 ns could be obtained with an appreciable intensity of 10.0% besides a lower “pick-off” lifetime component $\tau_3$ of 1.75 ns with 6.6% intensity. On the other hand, when measurements were carried out in air, the longest positronium component completely disappeared and the “pick-off” lifetime $\tau_3$ changed only marginally with intensity 10.7%. The shorter lifetimes $\tau_1$ and $\tau_2$ and their intensities (when normalized to $I_1 + I_2 + I_3 = 100\%$) remained almost unchanged [8]. This shows that a significant fraction of positrons indeed diffused out to the surfaces of nanometer-sized grains and formed positronium in the intergranular region and the positronium lifetime and intensity were quenched by the presence of external gases. Further, the observation that the shorter lifetimes and their intensities were not significantly affected implied effective positron trapping by vacancy clusters within the grains. In other words, it offers proof to the presence of open volume defects inside the nanoparticles. The sharpness of the Doppler broadened lineshape of the spectrum recorded with the source-sample assembly in air is found reduced due to the quenching effect and the $S$ parameter dropped by about 2.2% (i.e., $S_{\text{air}}/S_{\text{vacuum}} = 0.98$).

![Figure 23. Peak-normalized positron lifetime spectra of undoped and 20 at.% Mn$^{2+}$-doped ZnS nanorod samples.](image)

![Figure 24. Peak-normalized positron lifetime spectra of ZnS sample of nanoparticles with average size 2 nm when the measurements were carried out in vacuum and in air.](image)
### Table 3. Positron lifetimes and intensities in the ZnS sample of nanoparticles with average size 2 nm when the measurements were carried out in vacuum and in air.

|        | \( \tau_1 \) (ps) | \( I_1 \) (%) | \( \tau_2 \) (ps) | \( I_2 \) (%) | \( \tau_3 \) (ns) | \( I_3 \) (%) | \( \tau_4 \) (ns) | \( I_4 \) (%) |
|--------|-------------------|--------------|-------------------|--------------|-----------------|--------------|-----------------|--------------|
| In vacuum | 153 ± 2           | 55.1 ± 1.3   | 412 ± 13          | 28.3 ± 1.1   | 1.75 ± 0.10     | 6.6 ± 0.11   | 7.29 ± 0.2     | 10.0 ± 0.3   |
| In air    | 161 ± 2           | 54.4 ± 1.1   | 422 ± 7           | 34.9 ± 1.0   | 1.91 ± 0.10     | 10.7 ± 0.1   | "               | "            |

3.8. The application of trapping models

The issue of the exact number of types of positron trapping sites in nanocrystalline materials is crucial in rightly interpreting the positron lifetimes and intensities. In semiconductor nanosystems, apart from the defects at the surfaces and interfaces, the non-stoichiometric defects within the nanosystems also play an important role and it needs to be specially addressed. In such cases, either of the two lifetimes \( \tau_1 \) and \( \tau_2 \) will include the contributions from the crystal defects within the grains in addition to the defects at the surfaces and interfaces. The most common case is that \( \tau_2 \) is correctly resolved as an independent component representing either one of the two types of defects and \( \tau_1 \) is an admixture of the positron lifetime in the other type of defects besides the bulk and the Bloch state lifetimes. In this case, the validity of this assumption is cross-checked by calculating the value of \( \tau_1 \) using the relation

\[
\tau_1^{cal} = \frac{1 + \frac{\kappa_1}{\lambda_1} \left( 1 + \frac{\kappa_2}{\lambda_p - \lambda_2 + \kappa_1} \right)}{\lambda_p + \kappa_1 + \kappa_2}
\]

(3)

where the annihilation rate \( \lambda = \tau^{-1} \) in the respective cases and the positron trapping rates have the form

\[
\kappa_1 = \frac{\tau_1 (\lambda_p - I_2 \lambda_2) - I_1}{\tau_d - \tau_1}
\]

(4)

and

\[
\kappa_2 = \frac{I_2}{I_1} \left( \lambda_p - \lambda_2 + \kappa_1 \right)
\]

(5)

This model worked in the case of nanoparticles of CdS and ZnS and nanobypiramids of ZnO [3-5]. The same also held good in the cases of Mn\(^{2+}\)-doped ZnO nanocones [9].

Doping of ZnS nanorods and nanoparticles presented a slightly different picture [6,8]. In the former, the normal two-state trapping model gave the best fit to the results, according to the equation

\[
\frac{1}{\tau_1^{cal}} = \frac{1}{\tau_b} + \frac{I_2}{I_1} \left( \frac{1}{\tau_b} - \frac{1}{\tau_2} \right)
\]

(6)

where the second term on the right hand side of the equation gives the rate of trapping of positrons into the defects. This, in corroboration with the observations on the variation of the individual positron lifetimes and their intensities [6,7], gave credence to the view that the Zn\(^{2+}\)-vacancies within the interior of the nanorods are fully occupied by Mn\(^{2+}\) ions. However, identical doping in samples of ZnS
nanoparticles gave results, which were entirely different. The above models failed in this case as $\tau_2$ contained the lifetimes of positrons in both types of defects. The sensitivity of the positron lifetime technique to the individual type of defects is lost in this case and a cumulative trapping rate $\kappa_{12}$ is defined such that the shorter lifetime $\tau_1$ is calculated as

$$\frac{1}{\tau_{1\text{ cal}}} = \frac{1}{\tau_b} + \kappa_{12}$$  \hspace{1cm} (7)

where

$$\kappa_{12} = \frac{1}{\tau_b} \left( \frac{\tau_m - \tau_b}{\tau_2 - \tau_m} \right)$$  \hspace{1cm} (8)

The mean lifetime of positrons $\bar{\tau_m} = (\tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3) / (I_1 + I_2 + I_3)$. An exception to this analysis was encountered in the case of sample doped with the highest concentration (30 at.%) of Mn$^{2+}$ ions in which the formation of Mn-Mn clusters gave rise to one more additional trapping site for positrons and the results were fitted with equations (3), (4) and (5).

The curves illustrating the variation of the trapping rates and thereby the applicability of these models are shown in figures 25(a), 25(b) and 25(c).

**Figure 25(a).** Positron trapping rate $\kappa$ (equation (6)) in the ZnS nanorod samples at different Mn$^{2+}$ doped ion concentration. The data corresponding to the undoped ($x = 0$) sample are shown against 0.01%.

**Figure 25(b).** Positron trapping rate $\kappa_1$ (equation (4); open symbols) and $\kappa_2$ (equation (5); closed symbols) or $\kappa_{12}$ (equation (8); closed symbols) in the ZnS nanoparticle samples at different Mn$^{2+}$ doped ion concentration. The data corresponding to the undoped ($x = 0$) sample are shown against 0.01%.

**Figure 25(c).** Positron trapping rate $\kappa_1$ (equation (4); closed symbols) and $\kappa_2$ (equation (5); open symbols) in the ZnO nanocone samples at different Mn$^{2+}$ doped ion concentration. The data corresponding to the undoped ($x = 0$) sample are shown against 0.01%.
4. Summary and conclusions
The results reported in this paper and the inferences drawn from them prove unambiguously that positron annihilation techniques can be used for the investigation of innumerable features and processes involving semiconducting materials with nanometer dimensions. It is obvious from these studies that positron annihilation offers a wholly non-destructive method for characterizing the vacancy-type defects present both within and outside the nanocrystalline grains. Positron annihilation can complement as a viable spectroscopic tool to support the information available from the other conventional techniques. The success in obtaining distinguishable differences among results of experiments on nanosystems of different morphologies and sizes is a remarkable advantage.

Acknowledgements
The author wishes to thank all the collaborators involved in the experiments discussed in this paper.

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