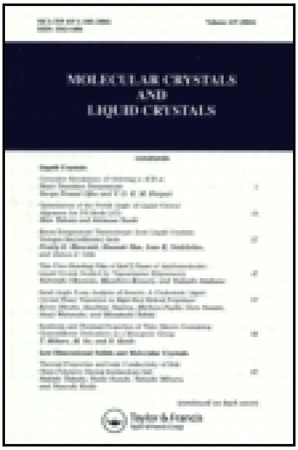

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# Vacancy Formation Energies in Plastic Crystals Using Positron Annihilation Techniques

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# VACANCY FORMATION ENERGIES IN PLASTIC CRYSTALS USING POSITRON ANNIHILATION TECHNIQUES

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Abstract  Ortho-positronium annihilation has been used to assess vacancy formation energies and vacancy concentrations in several plastic crystalline solids. In general, the ortho-positronium lifetimes showed a gradual increase with temperature at low temperatures consistent with normal lattice expansion, coupled with sudden larger increases at the brittle-plastic phase transformation. In most solids, at about $0.7T_m$, a larger sigmoid increase occurred indicative of the trapping of ortho-positronium in thermally generated defects in the lattice. The lifetimes in the defect state are consistent with the conclusion that the defects are of a size equivalent to vacant lattice sites. On this basis and using the defect trapping model devised for metals, activation energies for vacancy formation were evaluated for adamantane, bicyclooctane, succinonitrile and dl-camphene.

The data are consistent with a vacancy concentration of $10^{-7}$ to $10^{-3}$ vacancy fraction over the range $0.7T_m$-$T_m$ (melting temperature)

## INTRODUCTION

In the development of the understanding of the defect properties of molecular solids it has been demonstrated that the dominant point defect is a molecular vacancy. This conclusion has been reached following detailed examinations of the pressure, temperature and isotope-mass dependence of self-diffusion[1]. Supportive, but less definite evidence has been adduced from the limited number of studies of differential expansivity and excess specific heat[1]. Self-diffusion reflects the combination of both the formation and migration properties of the defect in the solid. Unfortunately, the two contributions cannot be separated for molecular solids. The latter techniques reflect the formation properties of the defects but they are of limited accuracy. There is a need for more detailed and accurate information on the separate formation and migration parameters of vacancy defects in molecular solids.

In the study of the properties of point defects in metals a novel technique which has recently evolved is the examination of positron annihilation[2]. A positron injected into the metal undergoes annihilation with an electron of the material with the emission of two $\gamma$-quanta of energies 0.51MeV mutually at $\sim$180° to each other. In samples containing vacancies or vacancy clusters the positrons may become trapped at these electron deficient regions thus increasing the lifetime of the positron with respect to its bulk lattice value. The sensitivity of the positrons to such defects has allowed the determination of vacancy formation and migration energies.

In many molecular solids, prior to annihilation, a fraction of the injected positrons form a positron-electron bound state, positronium (Ps). This species can exist in two forms; either as the shortlived p-Ps (spins antiparallel) which decays with a lifetime of 0.125ns, or the long-lived o-Ps (spins parallel). In free space this latter species decays with a lifetime of 140ns. In condensed matter annihilation may also proceed by the overlap of the positron of o-Ps with an electron of the medium of opposite spin. This so-called pick-off annihilation process often dominates and reduces the lifetime of o-Ps to the order of a few nanoseconds. The observed decay rate is sensitive to small changes in the electron and therefore molecular density of its environment. This feature of the annihilation of positrons in molecular materials could provide a satisfactory probe of defect and structural properties. Before this study, the method had been used successfully for the examination of the defect properties of ice[3] and the detection of phase transformations in organic crystals.

The principal aim of the present study was to make, for the first time, a detailed assessment of the applicability of the positron annihilation technique to the determination of vacancy concentrations and vacancy formation energies in those molecular solids known as plastic crystals[1]

## EXPERIMENTAL

### MATERIALS

The 'plastic crystals' examined covered the full range of these materials as defined by entropy of fusion (0.7R-2.5R). As we have speculated elsewhere[1], this increase in entropy of fusion parallels a decrease in macroscopic plasticity and hence variation in defect nature.

The compounds were: cyclohexane (F); pivalic acid (F); succinonitrile (B); camphene (B); norbornylene (H); bicyclooctane (F); hexamethylethane (B) and adamantane (F). (F, B, C and H denote the structure of the upper temperature (plastic) phase - FCC, BCC, simple cubic or HCP). All solids were purified to better than 100ppm total impurity content (usually <1ppm). Within this range no influence of impurity content on positronium lifetimes was found. Impurities did influence phase transformation behaviour however. A detailed examination of this influence has been made for dl-camphene and cyclohexane[4].

Single and polycrystalline samples yielded similar lifetime data. This was confirmed for specific samples by cycling, initially single crystal samples, through the brittle/plastic phase transformation. Fracture to form a polycrystalline mass inevitably occurs during this procedure. Annealing effects were noted in the transition region in some cases. Outside this region single crystal and fractured samples showed equivalent behaviour.

## MEASUREMENTS AND DATA ANALYSIS

Measurements were made using the positron lifetime technique[2]. A positron source ($\sim 20\mu Ci\,^{22}NaCl$) encapsulated between thin Kapton or nickel foils was sandwiched between 2 discs of the material to be studied, 1cm diameter x 0.5cm thick. The source-sample sandwich was mounted in a thermostatically controlled chamber or cryostat.

A fast-fast coincidence lifetime spectrometer with a time resolution of FWHM = 0.4ns was used for the measurements. Lifetime spectra were accumulated over a 15-20 hour period to give $\sim 4 \times 10^6$ counts in a spectrum. Measurements were made during several successive increasing and decreasing temperature scans.

Data were analysed using the computer programme POSITRONFIT[5]. The spectrum could be resolved in an unconstrained analysis, into three or four lifetime components depending on the precision of the data. Specific details are given in the separate publications refering to each material. For most solids the lifetimes obtained were consistent with those expected for the following annihilation processes. (The numbers as subscripts define parameters noted subsequently).

1. p-Ps $\tau_1$ = 0.125ns
2. free positron $\tau_2$ = 0.3 - 0.4ns
3. o-Ps pick off (bulk) $\tau_3$ = 1 - 1.8ns
4. o-Ps pick off (defect) $\tau_4$ = 1 - 3ns

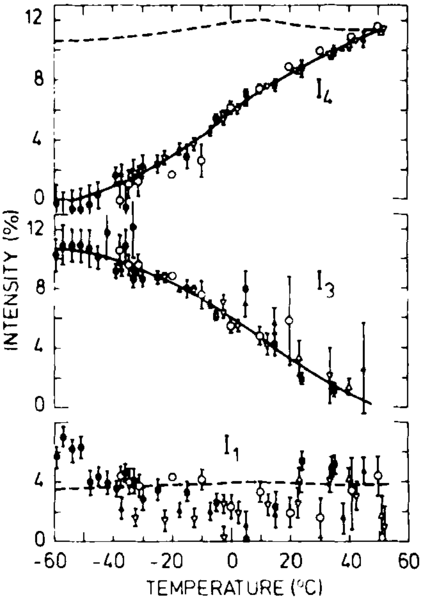


FIGURE 1. The relative intensities of ortho-($I_3$,$I_4$) and para-($I_1$) positronium decay processes in succinonitrile. The upper dotted curve is $I_3$+$I_4$ i.e. total ortho-positronium yield. The lower dotted curve shows the agreement of $\frac{1}{3}(I_3+I_4)$ with the $I_1$ data.

Hexamethylethane and norbornylene also gave evidence of an additional lifetime which we were unable to define and which interfered to some extent with the analysis.

Lifetimes consistent with processes 3 and 4 dominated at high temperatures. This, plus the expected relationship between the intensities of the positronium processes[2]

$$I_1 = {}^1/_3(I_3 + I_4)$$

which was observed in all cases (e.g. Figure 1) within reasonable experimental error, coupled with angular correlation measurements in some cases, gave the final confirmation that we were observing a positronium formation in the solids.

## RESULTS

Most materials yielded the characteristic variation of o-Ps lifetime with increasing temperature, viz a linear increase at lower temperatures with sudden changes in the vicinity of phase transformations, giving way to a sigmoid increase at temperatures approaching the melting temperature ($\sim 0.7T_m$), e.g. Figure 2. The first two increases can be associated with normal lattice expansion. The last is associable with the activated formation of trapping centres (vacancies?) in the crystal lattices.

The apparent exceptions to this pattern of behaviour were cyclohexane[7] and pivalic acid[8]. In cyclohexane[7], following the expected increase in lifetime at the phase transformation, a non-linear (but not sigmoid) increase occurred; the increase continuing to melting. The overall change in lifetime was small however and the true shape could have been masked by experimental inaccuracies. With pivalic acid, the sigmoid increase does probably occur but interference from the phase transformation ($0.9T_m$) and the increase in lifetime associated with this, complicates the situation.

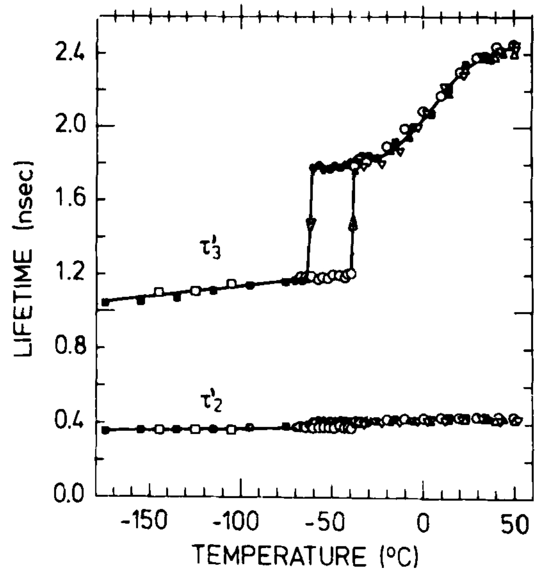


FIGURE 2. The variation of ortho-positronium lifetime $\tau_3$ and the lifetime of positrons not forming positronium $\tau_2$ with temperature for succinonitrile.

These experimental problems precluded an assessment of vacancy parameters in these two cases. This observed sigmoid behaviour in the remaining solids is so similar to that noted for positron annihilation in metals at high temperatures that it would seem only reasonable to accept that a parallel process is occurring for the positronium in molecular crystals viz. trapping and annihilation from a defect state. This would also parallel the findings for ice[3]. We believe this defect to be a lattice vacancy. As we note above, this is the most likely defect to form in a molecular crystal. Additionally, the lifetime for o-Ps pick off annihilation from the defect state is consistent with this interpretation. Briefly, the reasoning is as follows. The lifetime of positronium in the trapped state would be expected to increase with an increase in defect volume (decrease in electron density at the defect).

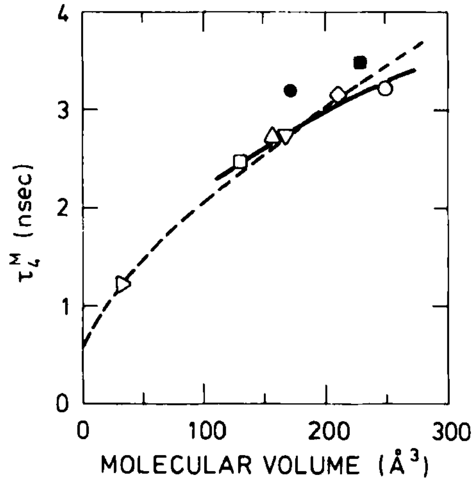


FIGURE 3. The correlation between the longest lifetime at - or extrapolated to - the melting point, $\tau_4^M$, and molecular volume, $\Omega$. The open symbols are associated with the lifetime of ortho-Ps trapped in a vacancy of volume $\Omega$. The closed symbols represent materials where also trapping into divacancies apparently takes place. The full curve is drawn through the open symbols (apart from the point for ice) to guide the eye. The dashed curve is the result of a simple model calculation. The symbols are for the following materials: ▷ ice; □ succinonitrile; Δ norbornylene; ∇ cyclohexane; ◇ adamantane; O dl-camphene; ■ hexamethylethane; ● pivalic acid.

This arises because the overlap between the positronium and surrounding molecular electrons will decrease. Thus the pick-off annihilation rate falls. The trend found experimentally is shown in Figure 3. Here we speculate that the defect volume can be approximated to the molar volume, an equivalence confirmed by studies of the pressure dependence of self-diffusion[1]. The variation can be explained qualitatively on the basis of a simple vacancy model[8] based on a spherical potential (dotted line in Figure 3).

All experimental points fall satisfactorily close to the predicted variation with the exception of $\tau_4$ for pivalic acid and hexamethylethane. In both cases we have strong evidence from both isotope-mass effect experiments and the influence of pressure on self-diffusion to indicate that these lattices contain a significant proportion of divacancies in equilibrium. Thus the defect volume will be, on average, higher than the molar volume. The defect volume for these materials predicted from the curve (Figure 3) is satisfactorily in agreement with the possible vacancy/divacancy concentration obtained from the other studies.

On this basis we have assumed that the responsible defect is a vacancy and proceeded to assess the temperature dependence of the concentrations of these defects on the basis of the simple trapping model[2] usually applied to the trapping of positrons in metals.

Except for norbornylene and hexamethylethane which, as indicated above, have additional lifetime components which interfere with the accurate definition of $\tau_3$ and $\tau_4$ and cyclohexane which shows no sigmoid change, the data for the remaining materials fit well with this model (e.g. Figure 4). Values of ln $\chi$, the trapping rate, a factor proportional to the defect concentration, were plotted against reciprocal temperature in an attempt to evaluate the activation energy

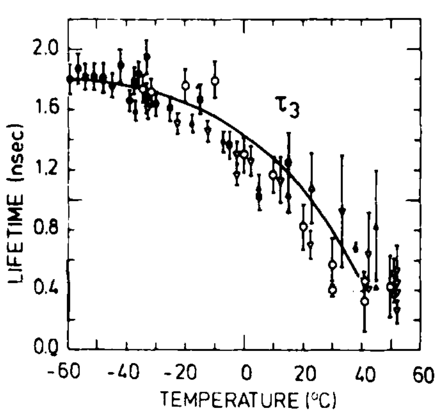
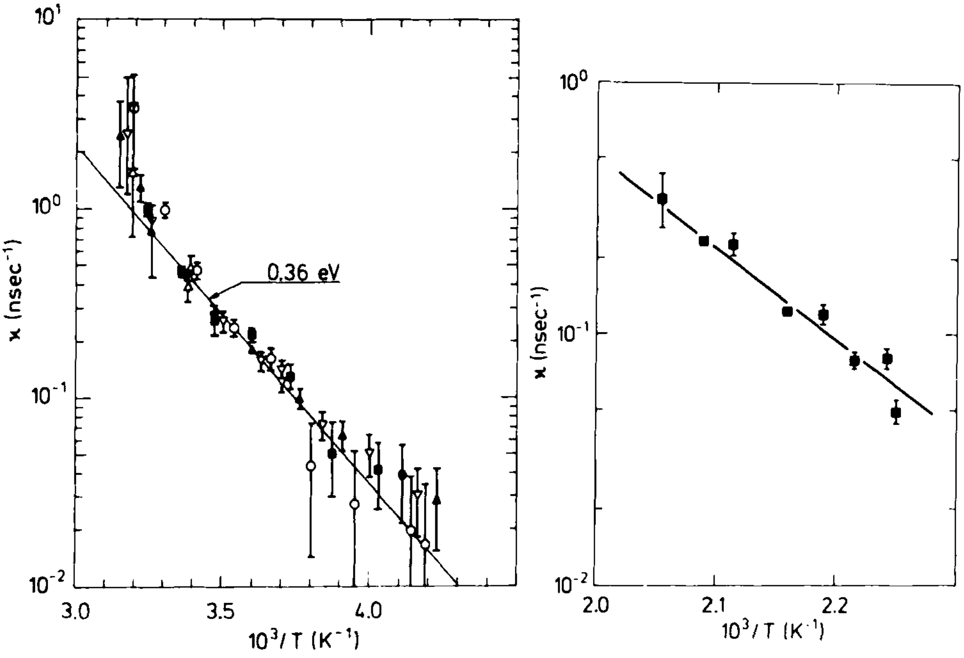


FIGURE 4. Variation of $\tau_3$ for succinonitrile with temperature. The full line through $\tau_3$ represents values calculated for the trapping model and defines the applicability of this model to this system.

for vacancy formation (Ev) (e.g. Figure 5).

For adamantane[9] (Figure 5b), the log $\chi$, $1/T$ plot was linear and yielded $E_v = 70 \pm 8$ kJ $mol^{-1}$ in good agreement with other theoretical and experimental predictions[1]. This agreement, for our most crystalline substance is excellent confirmation of the basis of our experiments.

The plots for the remaining materials for which an analysis can be done show a systematic curvature (e.g. Figure 5a) but can be fitted to a straight line over a reasonable temperature range, within experimental error. The resulting activation energies are noted in Table 1 where they are compared with the activation energy for self-diffusion ($E_d$), which we have argued is $2E_v$[1] and the lattice energy, $L_s$, the likely energy of vacancy formation[1].



(a) (b)

FIGURE 5. The trapping rate $\chi$ for ortho-positronium as a function of reciprocal temperature for a) Succinonitrile b) Adamantane

TABLE 1 Vacancy formation energies in plastic crystals

| | $E_v$ | $E_d$ | $L_s$ | $S_f/R$ |
|---|---|---|---|---|
| | | kJ mol$^{-1}$ | | |
| Adamantane[9] | 70 | 139 | 66 | 2.5 |
| Bicyclooctane | 53 | - | 51 | 2.3 |
| Succinonitrile[10] | 35 | 70 | 70 | 1.5 |
| Camphene[11] | 32 | 96 | 52 | 1.2 |

Agreement with the above predictions is best for the solids of high entropy of fusion, $S_f$ and worst at the opposite extreme. This may well reflect the true situation and indicate that our previous speculations on the magnitude of $E_V$ in these solids are in error. We note however that it is for the more plastic materials that the discrepancy arises and the very plastic materials which defy analysis. Cyclohexane, for example, can be defined as being 10 times more plastic than adamantane[1]. We see two possibilities which could account for this, both of which could provide an additional contribution to the annihilation of o-Ps and which would have to be taken into account in order to extract the thermal vacancy contribution prior to the evaluation of $E_V$.

Firstly, there may be an effect of dislocations. These have been noted to influence the positron annihilation process in deformed metals[2]. On handling, passage through the phase transformation or thermal cycling,considerable numbers of dislocations could form in the softer materials. These would not necessarily anneal out. These and their associated vacancy clouds could give a background contribution to the o-Ps annihilation in the plastic phase. The apparent lack of sigmoid variation in $\tau_4$ for cyclohexane could arise from this contribution. It could also influence the shape of the variation in succinonitrile and camphene.

Alternatively, it is possible that o-Ps could become self-trapped in the solid. This is a well-defined process in liquids. The repulsive forces of Ps effectively blow a hole in its environment in which it can sit with an increase in lifetime. It is tempting to consider that such a process could occur in the softer crystals. This could again interfere in a similar manner to that indicated for the dislocations.

Further work is in progress to assess the possible interference from these sources.

In addition to the information quoted above we also note that some idea of the vacancy concentration $C_V$ can be derived from our experiments. For metals, the inception of the sigmoid increase in lifetime occurs at $C_V = 10^{-7}$. In all the present materials the inception occurs at $0.7T_m$ (the melting temperature). Thus, accepting a direct parallel and our calculated $E_V$ we speculate that $C_V$ for the plastic crystals lies in the range $10^{-7}$-$10^{-3}$ vacancy fraction over the temperature range $0.7T_m$-$T_m$ (melting temperature).

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