layer potential on the low-potential side becomes gentle with an increase in $R$, i.e., with an increase in the Debye length of the trapped ions.

In summary, the dynamics of a bounded beam-plasma system is understood systematically. An electron-beam injection into a plasma induces the Buneman instability and the subsequent nonoscillatory Pierce instability. The sudden potential drop due to the latter instability evolves to result in the laminar double layer, because it is accompanied by collisionless ion trapping.


[1]O. Buneman, Phys. Rev. 115, 503 (1959).

[2]T. D. Mantei and D. Gresillon, Phys. Rev. Lett. 40, 1383 (1978).

[3]J. S. DeGroot *et al.*, Phys. Rev. Lett. 38, 1283 (1977).

[4]K. Saeki *et al.*, in *Proceedings of the Thirteenth International Conference on Physics of Ionized Gases, Berlin, September 1977* (Physical Society of the German Democratic Republic, Leipzig, 1977), p. 783.

[5]S. M. Hamberger and J. Jancarik, Phys. Rev. Lett. 25, 999 (1970).

[6]M. V. Nezlin *et al.*, Zh. Eksp. Teor. Fiz. 55, 397 (1968) [Sov. Phys. JETP, 28, 208 (1969)].

[7]J. R. Pierce, J. Appl. Phys. 15, 721 (1944).

[8]P. Coakley *et al.*, Phys. Rev. Lett. 40, 230 (1978).

[9]B. H. Quon and A. Y. Wong, Phys. Rev. Lett. 37, 1393 (1976).

[10]A. B. Mikhailovskii, Zh. Tekh. Fiz. 35, 1945 (1965) [Sov. Phys. Tech. Phys. 10, 1498 (1966)].

[11]J. P. Blewett and E. J. Jones, Phys. Rev. 50, 464 (1936).

[12]N. Sato *et al.*, Appl. Phys. Lett. 24, 300 (1974).

[13]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1960), p. 104.

[14]I. B. Bernstein, J. M. Green, and M. D. Kruskal, Phys. Rev. 108, 546 (1957).


# Positron Annihilation Study of Defects in Succinonitrile


M. Eldrup and N. J. Pedersen
*Chemistry Department, Risö National Laboratory, DK-4000 Roskilde, Denmark*

and

J. N. Sherwood
*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G11XL, United Kingdom*


(Received 23 July 1979)


Positron lifetime and angular correlation measurements have been made on the plastic crystal succinonitrile. They confirm the phase transition at $234 \pm 1$ K. In the plastic phase the average orthopositronium lifetime increases with temperature and saturates at the highest temperatures. This is interpreted as orthopositronium trapping in thermally created defects, probably vacancies. A defect formation energy of $0.36 \pm 0.1$ eV is deduced. This is lower than predicted values of the vacancy formation energy.


Much use has been made of the positron annihilation technique (PAT) for the examination of point defects, in particular in metals,[1] but also in ionic solids[1] and ice.[2] Although the technique has been applied to a number of organic molecular crystals[3,4] it has only recently been attempted to obtain intrinsic defect properties from the results.[5] In many molecular crystals a fraction of the injected positrons will form positronium (Ps). It is possible that this species may become localized in regions of lower than average electron density. Thus Ps may act as a probe for vacancies and vacancy clusters in these solids as do positrons in metals. If so, this would open the way for detailed studies of the formation and migration energies of such defects to supplement the rather sparse existing information[6] and to aid in the elucidation of self-diffusion mechanisms.[6] In this Letter we report on positron lifetime and angular correlation measurements in the *plastic crystal*[7] succinonitrile, $CNCH_2CH_2CN$ (SN). This material has a low-temperature brittle monoclinic phase (II) which at[8] 233 K transforms into the plastic body-centered-cubic phase[6] (I) with a simultaneous decrease in density. A close similarity is found between the temperature dependence of ortho-Ps lifetimes in the high-temperature plastic phase of this material and that for positrons which are being trapped in thermally created vacancies in metals.

For the lifetime measurements, high-purity (< 1-ppm total impurity) melt grown SN monocrystals were mounted on each side of a 20-$\mu$Ci $^{22}$NaCl source encapsulated in Kapton foil (1 mg cm$^{-2}$). The time resolution of the two lifetime spectrometers used was 0.35–0.4 ns full width at half maximum (FWHM). Angular correlation measurements were made with a conventional long-slit spectrometer[1] with 1-mrad slits and an external 15-mCi $^{22}$Na source. In both systems the sample was mounted in a liquid-nitrogen cryostat ($T$ control ± 0.5 K).

The lifetime spectra were analyzed using the computer program POSITRONFIT.[9] Unconstrained analyses indicated the presence of a short-lived component (lifetimes, 0.05–0.2 ns with large uncertainties) which probably arises from para-Ps.

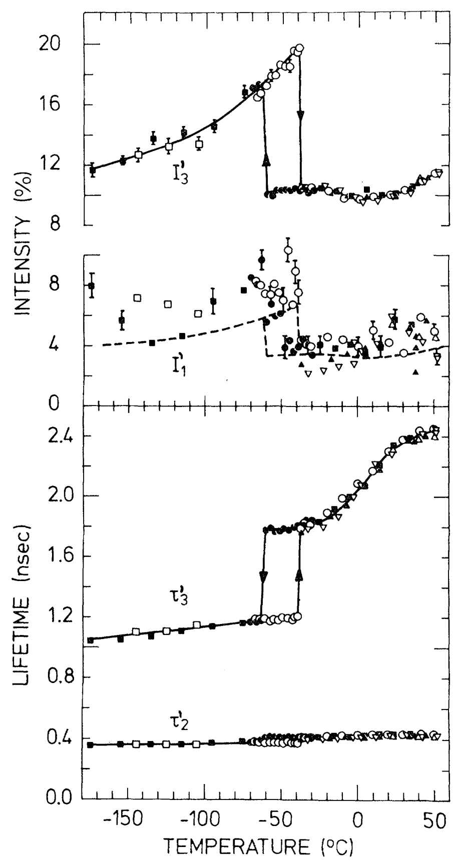


FIG. 1. Lifetimes and relative intensities derived from a three-term analysis with $\tau_1'$ fixed at 0.12 nsec. The filled symbols are for decreasing temperature and the open ones for increasing temperature. Triangles and the other symbols are from two different spectrometers. The sequence of measurements was filled circle, open circle, filled square, open square, open triangle, filled triangle, and open inverted triangle. The dashed curve for $I_1'$ is $\frac{1}{3}$ of the full curve for $I_3'$. The typical error bars shown are statistical estimates.

Hence, an analysis for three lifetime components was made, the shortest lifetime $\tau_1'$ being fixed at 0.12 ns, the intrinsic para-Ps lifetime. The results are shown in Fig. 1. We associate the $\tau_3'$, $I_3'$ component with ortho-Ps and the $\tau_2'$, $I_2'$ component with positrons not forming Ps.

The phase transformation is clearly defined at 234 ± 1 K (Ref. 8, 233 K) with some hysteresis. Despite a large scatter in $I_1'$, the values for phase II are higher than those for phase I. Allowing for errors in assessing such low-intensity components, $I_1' = \frac{1}{3} I_3'$ which supports the assignment of $\tau_3'$ and $I_3'$ to ortho-Ps.

The angular correlation curves seem to contain no or only very-low-intensity narrow components. They are essentially Gaussians (~9.2 mrad FWHM), at low temperatures slightly flattened and at high temperatures slightly peaked. They give no clear indication of the phase transformation. Since the lifetime data give evidence that Ps is formed in both phases in SN, the lack of narrow components characteristic of delocalized[2] para-Ps suggests that Ps annihilates from a localized state at all temperatures.

In the present context, the most interesting feature of Fig. 1 is the sigmoid change of $\tau_3'$ with temperature. This is very similar to the variation of positron lifetimes observed for metals.[1] By analogy, we propose that the variation results from the trapping of ortho-Ps in thermally activated defects which provide more empty space for Ps than it experiences in the bulk and therefore give rise to a longer ortho-Ps lifetime (i.e., the saturation value $\tau_3' = 2.45$ ns).

From the simplest version of the defect-trapping model as usually applied to metals,[1] we have, for ortho-Ps,

$$I_4 = I_{\text{o-Ps}} \kappa / (\lambda_b - \lambda_t + \kappa), \tag{1}$$

$$\tau_3 = (\lambda_b + \kappa)^{-1}, \quad \tau_4 = \lambda_t^{-1}, \tag{2}$$

where $I_{\text{o-Ps}}$ is the ortho-Ps yield, $I_4$ is the measured intensity of the trapped component, and $\lambda_b$ and $\lambda_t$ and the annihilation rates in the untrapped and trapped state, respectively. $\kappa$ is the trapping rate and $\tau_3$ is the lifetime in the untrapped state.

To test the applicability of the model, the lifetime spectra from phase I were analyzed for four lifetime components, keeping $\tau_4 = 2.45$ ns and $\tau_1 = 0.12$ ns. The results are shown in Fig. 2. The sum, $I_3 + I_4$ ($I_{\text{o-Ps}}$) shown by the upper dashed curve is essentially constant (11.3 ± 0.7)%. With the data from Fig. 2 for $I_4$ and $I_3 + I_4$ (dashed curve), $\kappa$ and $\tau_3$ were calculated from Eqs. (1)

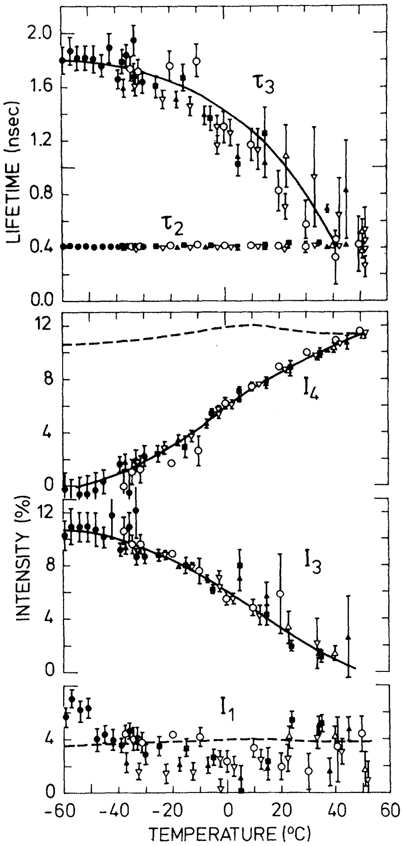


FIG. 2. Lifetimes and relative intensities derived from a four-term analysis with $\tau_1 = 0.12$ nsec and $\tau_4 = 2.45$ nsec. The full curves for $I_3$ and $I_4$ are drawn to visually best fit the points. The sum of these two curves is the upper dashed curve. The full curve for $\tau_3$ is calculated from the trapping model. The dashed $I_1$ curve for is 1/3 of the $(I_3 + I_4)$ curve.

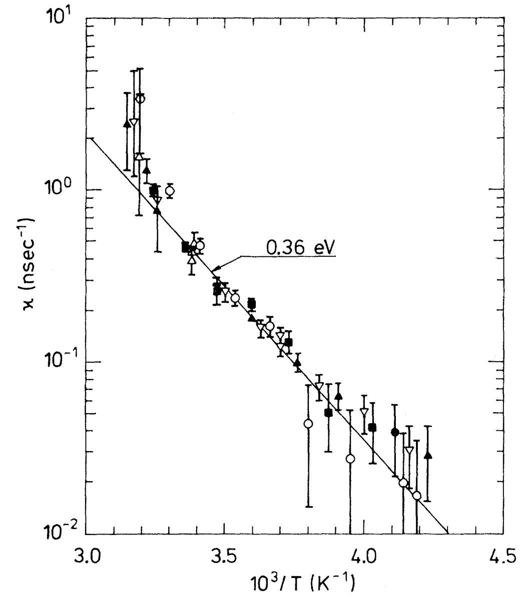


FIG. 3. The trapping rate, $\kappa$, for ortho-Ps, as deduced from the trapping model, Eq. (1), against the inverse absolute temperature.

and (2) ($\lambda_b^{-1} = 1.80$ ns, $\lambda_t^{-1} = 2.45$ ns). Using the smoothed curve for $I_4$ we obtain the full curve drawn for $\tau_3$ in Fig. 2. It agrees well with the experimental points. Thus, the trapping model can consistently describe the ortho-Ps data.

The trapping rates, $\kappa$, calculated from the experimental $I_4$ values, are plotted in Fig. 3 against the inverse temperature. The slope of the best straight line is equivalent to an activation energy of 0.36 eV.

The most likely candidate for the defect which gives rise to the trapping is the lattice vacancy. Expansivity data indicate vacancy concentrations $\sim 10^{-3}$ at the melting point in Sn.[6] Also, a lifetime of 2.45 ns is approximately that which would be expected for ortho-Ps in an unrelaxed SN vacancy of volume $\Omega = 131$ Å$^3$ [cf. saturation lifetime in *dl*-camphene = 3.2 nsec ($\Omega = 251$ Å$^3$), ortho-Ps lifetime in an ice vacancy[2] = 1.2 ns ($\Omega = 33$ Å$^3$)].

The dislocation density is expected to depend strongly on the prehistory of the sample (e.g., whether it has been taken through the phase transition or not). Therefore, trapping in dislocations cannot explain the observed reproducible temperature dependent ortho-Ps trapping.

If we assume—as it is usually done[1]—that the trapping rate, $\kappa$, is proportional to the vacancy concentration, $C_v$, and allow for uncertainties a arising from, e.g., possible effects of divacancies and temperature-dependent bulk and vacancy ortho-Ps lifetimes we obtain a vacancy formation energy $E_v^f = 0.36 \pm 0.1$ eV.

Estimates of $E_v^f$ for molecular solids yield values in the range $E_v^f \sim 0.5L_s - 1L_s$, where $L_s$ is the lattice energy of the solid. Thus for SN, $E_v^f \sim 0.36-0.73$ eV. Values at the upper end of this range are believed to be more dependable[6] and are consistent with the results of recent self-diffusion studies[10] which yield activation energies for self-diffusion $E_d = E_v^f + E_v^m \sim 1.10-1.46$ eV, where $m$ refers to migration. Accepting this last comment on dependability, there are some obvious discrepancies. Maybe the reason for this shall be found in the relationship between $\kappa$ and $C_v$. The fact that the data are consistent with the trapping model suggests that there is a transition of Ps from one state (a localized "bulk" state) to another state (the vacancy state) at a rate which is roughly time independent. This trapping rate may depend on temperature and vacancy concentration. For trapping of positrons (which are delocalized) into metal vacancies (which have a rather low concentration) it is generally believed[1] that $\kappa = \mu C_v$, where the specific trapping rate $\mu$ does not depend on temperature and $C_v$. This may not be true for trapping of localized Ps into vacancies of higher concentration in molecular crystals. If the propagation of Ps to the vacancies is a thermally activated diffusionlike motion one would expect $\mu$ to depend on temperature. If, on the other hand, some Ps get trapped by a tunneling mechanism, one would expect $\mu$ to depend on $C_v$, i.e., $\kappa$ and $C_v$ would not be proportional. Thus, although lattice vacancies may be the fundamental cause of the increase in $\tau_3'$, more knowledge is required of both the mechanism of the trapping process and, consequently, the nature of the localized bulk state of Ps.

Various possibilities for this localized state seem to exist, at least in the plastic phase. Maybe even the "best" crystals available today contain imperfections or impurities which will act as shallow traps for Ps. Especially the influence of dislocations may be important. These form and multiply with great ease in plastic crystals.[6] One might also speculate that Ps could become self-trapped in these crystals. In the plastic phase SN exists as a dynamic equilibrium of three conformers (two gauche 82%, one trans 18%). Changes between these forms (activation energy[11] 0.1 eV) could create regions in which Ps could become localized. Maybe Ps could stabilize such an open region.

Work is proceeding on other plastic crystals. Preliminary results for camphene and adamantane also show changes in the ortho-Ps lifetime which can be associated with trapping in vacancies and are consistent with a trapping-model description.

The analogies between results on defects in plastic crystals and in metals should make the plastic-crystal studies interesting also to workers in the field of metal defects.

We wish to thank O. E. Mogensen for many discussions, S. J. Lund for his support, and A. Bønke Nielsen for her technical sssistance. The financial support of the Science Research Council and North Atlantic Treaty Organization are most gratefully acknowledged.

[1] *Positrons in Solids*, edited by P. Hautojärvi (Springer, Berlin, 1979).

[2] O. E. Mogensen and M. Eldrup, J. Glaciol. 21, 85 (1978); M. Eldrup, O. E. Mogensen, and J. Bilgram, J. Glaciol. 21, 101 (1978).

[3] R. M. Singru, K. B. Lal, and S. J. Tao, At. Data Nucl. Data Tables 17, 271 (1976).

[4] W. Brandt and J. Wilkenfeld, Phys. Rev. B 12, (1975), and references therein.

[5] T. Goworek and C. Rybka, Phys. Status Solidi (b) 83, K91 (1977).

[6] *The Plastically Crystalline State*, edited by J. N. Sherwood (Wiley, London, 1979).

[7] J. G. Aston, in *Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. Labes, and A. Weissberger (Interscience, New York, 1963), Chap. 9.

[8] C. A. Wulff and E. F. Westrum, Jr., J. Phys. Chem. 67, 2376 (1963).

[9] P. Kirkegaard and M. Eldrup, Comput. Phys. Commun. 7, 401 (1974).

[10] J. Bruce, D. Lightbody, and J. N. Sherwood, unpublished work.

[11] P. P. Ho and R. R. Alfano, Phys. Rev. A 17, 1161 (1978).