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Positron Lifetime Spectra in Molecular Substances*

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Earlier quantum-mechanical model calculations show, and experiments have confirmed, that at low and intermediate temperatures the long lifetime of orthopositronium atoms (*o*-Ps) against electron pickoff in a molecular lattice rises with the free volume, because the overlap between the positron component of the *o*-Ps wave function and the wave function of the lattice electrons responsible for pickoff decreases with increasing lattice spacing. An extension of this model to higher temperatures, where the influence of lattice vibrations becomes important, predicts a shortening of the pickoff lifetime relative to its value in a cold lattice of the same free volume. In fact, under favorable conditions, on heating, the rise with free volume can be overshadowed by the decline due to thermal density fluctuations such that a maximum in the pickoff lifetime develops at a characteristic inversion temperature. In search for such maxima, lifetime spectra of positrons annihilating in three organic insulators (polyethylene, polytetrafluoroethylene, glycerol) were measured with high resolution over wide temperature ranges, and decomposed into three components. On analysis, the data reveal that the relative intensities of the components with the longest and shortest lifetimes, in their dependence on temperature and pressure, vary as the free volume. At elevated temperatures the longest lifetime in polytetrafluoroethylene exhibits a maximum which is interpreted to be a manifestation of the thermal motion of the lattice molecules.

INTRODUCTION

THE study of positron annihilations in molecular substances has taken a new turn with the decomposition of the decay spectra into three components.[1,2] Contrary to what had been anticipated, the component with the shortest resolved lifetime comprises more than one-half of all annihilations in the substances investigated so far and, as the temperature is increased, the long-lifetime component grows in intensity at the expense of the shortest-lifetime component.

Positrons when slowed down in a substance may form positronium (Ps) over a range of kinetic energies of order $\frac{1}{2}$ Ry, the Ore gap. The annihilation spectrum reflects the various modes open to the positrons for annihilation with the electrons in the substance.[3] A fraction of the positrons drops through the Ore gap and annihilates as "free" positrons with electrons of the lattice. All other positrons form either para-Ps (antiparallel spins) or ortho-Ps (parallel spins), in diamagnetic substances presumably in the ratio 1 to 3. Positrons bound in *p*-Ps annihilate with the electrons to which they are bound into 2γ quanta, in 0.125 nsec. Positrons bound in *o*-Ps annihilate predominantly via para decay with electrons of the lattice, i.e., by electron pickoff, since the self-annihilation rate into 3γ quanta is some hundred times slower than the pickoff rate. From these considerations a fairly straightforward picture emerges of the structure of the lifetime spectrum of positrons annhilating in substances where Ps can be formed. It has a long-lifetime component attributed to the pickoff annihilation of positrons bound in *o*-Ps, with lifetimes typically ranging from 2 to 4 nsec, and fractional intensities of 10 to 30% of all annihilations. This long-lifetime (τ_2) component was discovered by Bell and Graham[4] and has since been the subject of many investigations. All other annihilations appeared unresolved as the short-lifetime (τ_1) component. However, it is clear that the *p*-Ps pendant of the *o*-Ps component must be part of it, comprising ~3–10% of all annihilations with lifetimes ~0.125 nsec. The remaining annihilations, 60–80%, could then be expected to derive from annihilations of free positrons with lattice electrons having an intermediate lifetime of ~0.5 nsec.

The analysis of our annihilation spectra in molecular substances such as polyethylene or polytetrafluoroethylene (Teflon) does not support this simple picture. In Sec. 2 we report the underlying experimental data. Sections 3 and 4 present our preliminary interpretation for discussion and further confirmation.

This investigation started as a search for a maximum in the lifetime of the pickoff component as a function of temperature. Such maxima were predicted to occur[5] whenever the effect of the thermal motion of the lattice molecules, which shortens the lifetime, outweighs the accompanying increase in free volume, which lengthens the lifetime.[6] The data reported in Sec. 2 exhibit such a maximum. The interpretation is given in Sec. 4.

1. EXPERIMENTAL

The measurements of positron lifetime spectra were performed in a standard manner. Na^{22}-enriched NaCl was placed between two slabs of the material under investigation either directly, or incapsulated in 0.23-mil

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* Work supported by the U. S. Atomic Energy Commission.

[1] I. Spirn, W. Brandt, G. Present, and A. Schwarzschild, Bull. Am. Phys. Soc. **9**, 394 (1964).

[2] A. W. Sunjar, Bull. Am. Phys. Soc. **9**, 394 (1964).

[3] For recent reviews and extensive references, see P. R. Wallace, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1; M. Deutsch and S. Berko, in *Beta and Gamma Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1965), p. 1583 ff.

[4] R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).

[5] W. Brandt, NYU Report, 1963 (unpublished).

[6] W. Brandt, S. Berko, and W. W. Walker, Phys. Rev. **120**, 1289 (1960), henceforth referred to as I.

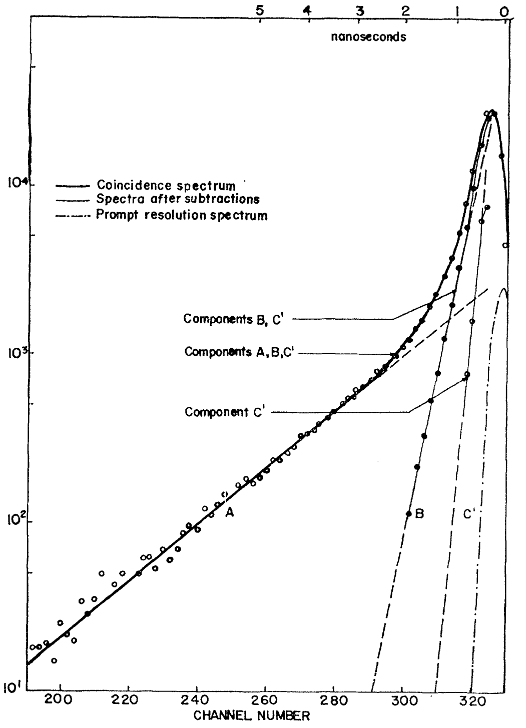

FIG. 1. Typical delayed-coincidence spectrum of positrons annihilating in polyethylene at room temperature. The three components can be identified by the straight lines. In this experiment the width at half-maximum of the prompt resolution curve was set to be 0.42 nsec.

aluminum foil. This assembly was packed into a thermally controlled aluminum sample cell. The temperature was regulated by two cartridge heaters inserted in the aluminum block and by cooling coils attached to the outer surface of the cell. Asbestos insulated the cell from the environment. The temperature could be kept constant to ±0.5°C at any value between -185 and $+350$°C.

The time delay between the 1.28-MeV γ quantum emitted less than 10^{-2} nsec after a positron is ejected from a Na^{22} nucleus, and the 0.5-MeV annihilation quanta is measured by the coincidence apparatus described elsewhere.[7] The optimum resolving time of the apparatus, as gauged by the full width at half-maximum of the prompt spectrum from a Co^{60} source, was 0.21 nsec. In the experiments described below the windows were set to register the upper 60% of the Na^{22} Compton electron spectrum, giving a resolving time of 0.42 nsec.

The first material investigated was commercial-grade polyethylene $(-CH_2-CH_2-)_n$. Disks were cut from sheets and thermally cycled in the sample cell. At our rate of heating and cooling, typically 1°/min, we did not observe thermal hysteresis in the annihilation spectra. At temperatures over 200°C, discoloration of the samples set in, and no data taken above such temperatures were retained. In different samples only such temperature data were retained where after heating or cooling the annihilation spectra were reproducibly the same at the reference room temperature. We did not find any discernable differences between the lifetime spectra of positrons annihilating in two types of polyethylene (Alathon 14 and Alathon 34) with comparable densities (0.92–0.93 g/cm^3 at room temperature).[8] Samples of polytetrafluorethylene (Teflon TFE fluorocarbon polymer),[8] $(-CF_2-CF_2-)_n$, in disk form were packed into the sample chamber and thermally cycled in the same manner as the polyethylene samples. No effort was made to re-establish the 18–20°C transition.[9] Finally, glycerol 99% c.p. was distilled into a glass sample holder with a centrally affixed Na^{22} source and then sealed. This avoided difficulties associated with the hydroscopic properties of glycerol, delayed chemical decomposition at elevated temperatures, and kept the oxygen content small and constant.

A typical annihilation spectrum with a total of 10^6 counts is shown in Fig. 1. Except in a few favorable cases, graphical decomposition of such spectra is difficult to perform reliably and reproducibly. Therefore we employed the computational method developed by Cummings.[10] In brief, it fits a series of exponentials to the data points by successive iterations until a suitable convergence criterion is satisfied. The calculations were performed on the IBM 7094 computer of the New York University Computing Center. The results of the analysis are given in terms of the lifetimes of the components, and their relative intensities. In our analysis, we searched for the minimum number of components required to obtain the optimum fit to the experimental curves. Most of the spectra required the decomposition

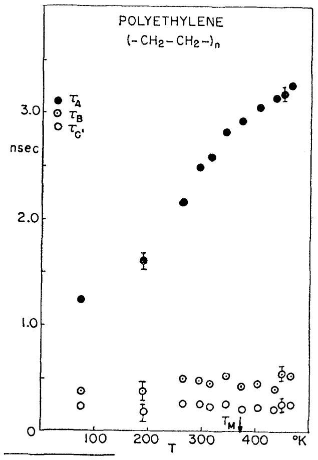

FIG. 2. The mean lifetimes of the three components resolved in the annihilation spectrum of positrons in polyethylene as a function of temperature. T_M refers to the approximate melting point.

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[7] G. Present, A. Schwarzschild, I. Spirn, and N. Wotherspoon, Nucl. Instr. Methods **31**, 71 (1964).

[8] We are grateful to E. I. du Pont de Nemours and Company, Inc., for providing us with the material.

[9] G. Fabri, E. Germagnoli, and G. Radone, Phys. Rev. **130**, 204 (1963).

[10] J. B. Cummings, Brookhaven National Laboratory Report No. 6470, 1962 (unpublished). For details of our analysis and evaluation of errors, see I. Spirn (unpublished).

into at least three components. This does not preclude the possibility that the shortest lifetime component so resolved is not a composite of several unresolved modes of decay. In fact in the discussion of the data, we shall always assume that it contains the *p*-Ps pendant of the *o*-Ps pickoff component in accordance with spin statistics. But if we analyze the spectra by insisting on, say, four components, one of which having the *p*-Ps lifetime 0.125 nsec, the program gives as good a fit to the data as the analysis into only three components. It is difficult then in a clear-cut manner to assign errors to the lifetimes and intensities so determined because they derive in part from external experimental sources, in part from a certain lattitude of the program in the assignment of the parameters characterizing each component. For example, the latter occasionally introduces spurious but small (compared to the effects under investigation) correlations between the parameters of different components. The errors stated in the following are conservative estimates of these compounded uncertainties in the sense that they generally exceed the scatter of the experimental points about the smooth curves representing the changes of these parameters with experimental conditions.

2. RESULTS

Figure 2 shows mean lifetimes of the three resolved components *A*, *B*, and *C′* in polyethylene, and their temperature dependence. Each point represents the mean of many measurements. The error flags give representative uncertainties of the points throughout the temperature range investigated. The two shorter lifetimes $\tau_B \simeq 0.50$ nsec and $\tau_{C'} \simeq 0.25$ nsec are independent of the temperature. The lifetimes τ_A increase sharply with temperature. They agree with the measurements of Kohonen,[11] except that the decomposition of the spectra into three components yields slightly larger τ_A values than obtained if only two components are resolved. Figure 3 depicts the corresponding intensities i_A, i_B, and $i_{C'}$ of the three components. At low temperatures, the intensities stay essentially constant. At temperatures above 200°K, $i_{C'}$ begins to drop, from its high initial value of ~0.6, to ~0.3 at the highest temperatures investigated. Concurrently i_A starting from ~0.1 grows to become larger than $i_{C'}$ at high temperatures. The component i_B remains constant within experimental error over the entire temperature range.

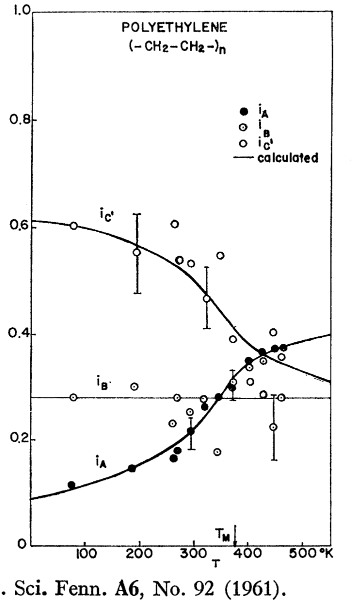

FIG. 3. The relative intensities of the three components resolved in the annihilation spectrum of positrons in polyethylene as a function of temperature. The calculated curves are discussed in Sec. 4.

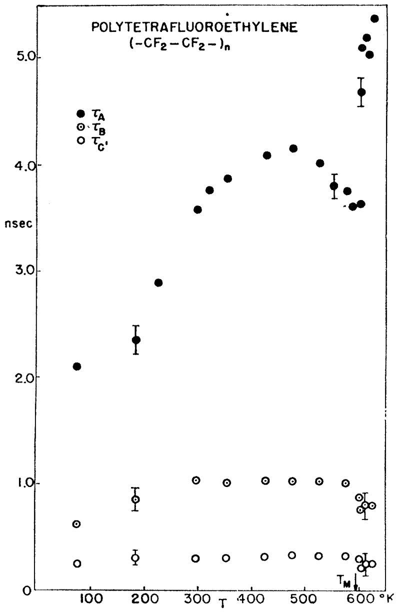

FIG. 4. The mean lifetime of the three components resolved in the annihilation spectrum of positrons in polytetrafluoroethylene (Teflon) as a function of temperature.

Figure 4 summarizes the corresponding lifetimes in Teflon up to temperatures where thermal degradation sets in. At the low temperatures they agree with earlier measurements.[6] At intermediate temperatures, a distinct maximum develops beyond which τ_A declines until melting. As did Fabri *et al.*,[9] we see a sudden reversible increase of τ_A within a few degrees of the melting point. The intermediate τ_B appears to increase slightly in coming from low temperatures and to drop somewhat near the melting point. Similar trends appear in the temperature dependence of $\tau_{C'}$. Figure 5 shows the intensities, which exhibit a temperature dependence similar to that in polyethylene, although the changes occur at higher temperatures and over a smaller temperature range. Moreover, i_B appears to rise slightly at the higher temperatures.

We extended earlier measurements on glycerol[6] in the amorphous phase to higher temperatures, as shown in Fig. 6. From 77 to 425°K the two short lifetimes are constant with values $\tau_B = 0.48 \pm 0.10$ nsec and $\tau_{C'} = 0.25 \pm 0.06$ nsec. We confirmed the rise of τ_A up to temperatures near the crystalline melting point 290°K, but

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[11] T. Kohonen, Ann. Acad. Sci. Fenn. A6, No. 92 (1961).

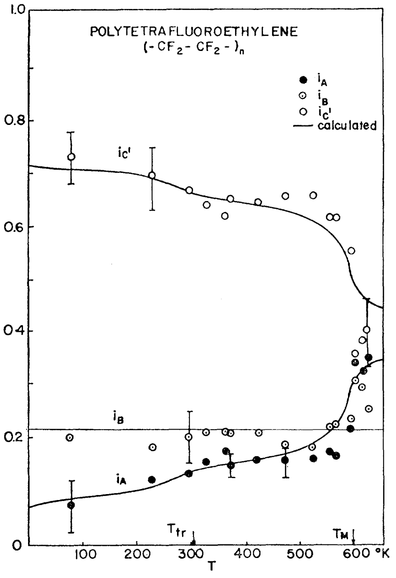

FIG. 5. The relative intensities of the three components resolved in the annihilation spectrum of positrons in polytetrafluoroethylene (Teflon) as a function of temperature. T_{tr} refers to the onset of the crystalline transition. The calculated curves are discussed in Sec. 4.

observe a sharp change to a weak temperature dependence at higher temperatures. The slight discrepancy between the τ_A and the earlier data indicates the effect of the present decomposition into three components. The two sets of data coalesce as τ_A becomes large compared to τ_B and $\tau_{C'}$. The intensities are given in Fig. 7, with trends similar to those observed in Figs. 3 and 5.

3. INTENSITIES

The relative magnitudes of the intensities and their dependence on temperature, shown in Figs. 3, 5, and 7, reveal new details about the processes underlying the positron annihilation spectra in molecular substances. Because of the relative magnitude of the energies relevant for the Ore gap, $\sim\frac{1}{2}$ Ry, as compared to thermal energies, and because of the small effects of the confinement in a lattice on the stability of positronium atoms,[12] one is led to discard changes in the positronium formation cross sections as the primary reason for the large variations of i_A and $i_{C'}$ with temperature. The near constancy of i_B bears this out, if one attributes this component to the annihilation of positrons which have not formed Ps. The lifetime of these "free" positrons τ_B is inversely proportional to the overlap of the positron-electron wave functions and therefore is determined primarily by the affinity between e^+ and the atoms of the lattice. It should be comparable in magnitude, as it is, to the spin averaged Ps lifetime, $\sim$0.5 nsec, and fairly insensitive to changes in the lattice structure. Normalizing the experimentally resolved components,

$$i_A+i_B+i_{C'}=1\,, \tag{1}$$

we attribute the fraction $i_A+i_{C'}=1-i_B\simeq$const to the annihilation of Ps atoms.

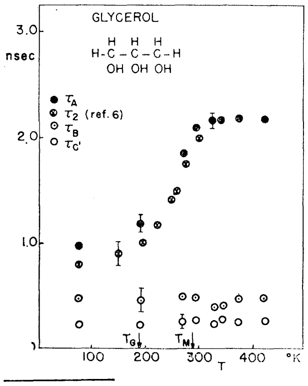

FIG. 6. The mean lifetime of the three components resolved in the annihilation spectrum of positrons in amorphous glycerol as a function of temperature. T_G refers to the glass transition temperature, T_M to the crystalline melting point. The comparison with previous data (I) illustrates the shifts of the τ_A relative to the τ_2 resulting from a two-component decomposition.

We again identify i_A with the pickoff annihilations of o-Ps atoms in the free volume of the lattice, as amplified further in Sec. 4. But since $i_{C'}>(i_A/3)$, the component $i_{C'}$ must be the sum of several unresolved components. One of them comes from annihilations of positrons bound in o-Ps, because we find experimentally in diamagnetic substances that i_A increases with increasing temperature at the expense of $i_{C'}$. Therefore we anticipate that if differentiated by origin, $i_{C'}$ comprises at least three components.

$$i_{C'}=i_{C1}+i_{C3}+i_D\,, \tag{2}$$

where i_{C3} refers to o-Ps atoms in some state with a pickoff rate higher than that in i_A; i_{C1} and i_D are the corresponding intensities for p-Ps. Because of spin statistics the fraction

$$i_A+i_{C3}=\tfrac{3}{4}(i_A+i_{C'}) \tag{3}$$

derives from o-Ps annihilations, and

$$i_{C1}+i_D=\tfrac{1}{4}(i_A+i_{C'}) \tag{4}$$

from p-Ps annihilations.

The experiments show that an equilibrium exists between i_A and i_{C3} (and presumably between i_D and i_{C1}), which can be shifted by heating. We introduce the probability P_{cr} that Ps atoms once formed with relative yield η will find themselves in domains of the substance with free volume larger than some critical value v_{cr}. Here they annihilate as component A (or D). They annihilate as component $C3$ (or $C1$) in the dense domains of the substance with a probability $(1-P_{\mathrm{cr}})$. Let the coincidence experiment be triggered at the time $t=t_0$, and the Ps atoms be formed at $t=t_1$. The time dependence of the Ps population in the two components becomes

$$\begin{aligned} n_A(t)+n_{C3}(t)=i_A\exp[-(t-t_0)/\tau_A]\\ +i_{C3}\exp[-(t-t_0)/\tau_C]\,, \end{aligned} \tag{5}$$

where we have identified the measured i_A, i_{C3} with

$$\begin{aligned} i_A&=\eta_{o\text{-Ps}}P_{\mathrm{cr}}\exp[-(t_0-t_1)/\tau_A]\,,\\ i_{C3}&=\eta_{o\text{-Ps}}(1-P_{\mathrm{cr}})\exp[-(t_0-t_1)/\tau_C]\,. \end{aligned} \tag{6}$$

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[12] See Ref. 6, Appendix.

One estimates the time $|t_0-t_1|$ to be so short that $|t_0-t_1|/\tau_A \lesssim |t_0-t_1|/\tau_C \ll 1$, and therefore $\eta_{o\mathrm{Ps}}=i_A+i_{C3}$ within experimental error. Although we expect the same equations to hold for i_D and i_{C1}, only their sum is of interest for the relation between the experimentally resolved components, and therefore

$$\begin{aligned} i_A &= (i_A+i_{C'})\tfrac{3}{4}P_{\mathrm{cr}}\,, \\ i_{C'} &= (i_A+i_{C'})[1-\tfrac{3}{4}P_{\mathrm{cr}}]. \end{aligned} \tag{7}$$

The space between the molecules, in units of the excluded volume occupied by the molecules, i.e., the reduced free volume, is larger than some v_{cr}^* with the probability

$$P_{\mathrm{cr}}=\exp(-v_{\mathrm{cr}}^*/v_f^*)\,, \tag{8}$$

where v_f^* is the reduced average free volume per molecule. Using the respective density-temperature curves,[13] we plot Eq. (7), with Eq. (8), in Figs. 3, 5, and 7, having chosen v_{cr}^* to be 0.3, 1.0, and 0.4, respectively. If compared in terms of the changes in reduced free volume, the isothermal decrease of i_A with pressure as measured by Stump and his co-workers[14] agrees with our temperature data. In light of the studies of Turnbull and Cohen[15] on the significance of Eq. (8) and of its relevance to the present problem,[16] we conclude that density fluctuations in the substance are the determining factor for the observed interrelation between i_A and $i_{C'}$.

One might ask to what extent this scheme can account for the narrow component in the 2γ angular-correlation data, which appears to be primarily density-dependent and should be attributed to the self-annihilation of p-Ps atoms.[17,18] The fraction of all annihilations attributable to this process is equal to $[i_D+i_C\tau_C/(\tau_C+\tau_D)]$. By the measurements presented here this quantity in polyethylene is 0.16 at room temperature and increases between −196 and +200°C by 0.03±0.01. In Teflon, it is 0.17 at room temperature and increases between −196 and +270°C by 0.04±0.01. The latter value is to be compared with the quantity $\alpha=0.047\pm0.008$ obtained from angular-correlation measurements on Teflon by De Zafra and Joyner.[18]

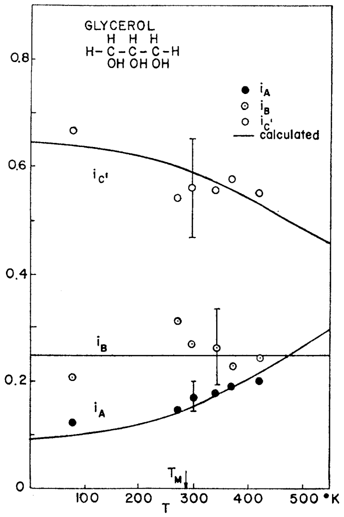

FIG. 7. The relative intensities of the three components resolved in the annihilation spectrum of positrons in amorphous glycerol as a function of temperature. The calculated curves are discussed in Sec. 4.

4. LIFETIMES

In the previous paper I[6] it was shown that at low and intermediate temperatures the lifetime τ_A of o-Ps for electron pickoff from the lattice increases on heating because of the accompanying change in free volume. The overlap between the positron component of the o-Ps wave function and the wave function of the lattice electrons responsible for pickoff decreases with increasing lattice spacing, and hence τ_A increases. This effect is confirmed by experiment.

At higher temperatures we expect the influence of lattice vibrations and of density fluctuations generally to become important. Thermal fluctuations cause a smearing of the electron-density distribution in the lattice, effectively raising the electron density in the free volume. This shortens τ_A relative to its value in a cold lattice of the same free volume. Indeed, under favorable conditions the increase on heating of τ_A with the free volume can be outweighed by the decrease

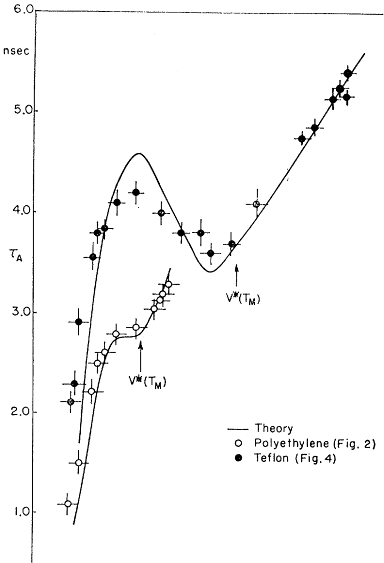

FIG. 8. Comparison of the calculated lifetimes τ_p with τ_A.

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[13] E. Hunter and W. G. Oakes, Trans. Faraday Soc. **41**, 49 (1945) (polyethylene); F. A. Quinn, D. E. Roberts, and R. M. Work, J. Appl. Phys. **22**, 1085 (1951) (polytetrafluoroethylene); A. K. Schulz, J. Chem. Phys. **51**, 530 (1954) (glycerol).

[14] R. Stump, Bull. Am. Phys. Soc. **2**, 173 (1957); R. K. Wilson, P. O. Johnson, and R. Stump, Phys. Rev. **129**, 2091 (1963).

[15] D. Turnbull and M. H. Cohen, J. Chem. Phys. **31**, 1164 (1959); **34**, 120 (1961).

[16] W. Brandt, *Proceedings of the Positron Annihilation Conference, Detroit, 1965*, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, to be published).

[17] A. T. Stewart, Phys. Rev. **99**, 594 (1955).

[18] R. L. de Zafra and W. T. Joyner, Phys. Rev. **112**, 19 (1958).

caused by the thermal motion in such a manner that a maximum develops.

The present investigation was undertaken for the purpose of finding such maxima in the temperature dependence of τ_A. It is clear from Fig. 8 that polyethylene just fails to develop a discernable maximum before melting. Teflon with its high melting point has a maximum outside experimental errors. In all three substances investigated, a different regime prevails above the crystalline melting point.

For a more quantitative discussion of the lifetime curves it is instructive to extend the model developed in I to include thermal effects. The spin-averaged pickoff annihilation rate Γ_p is given by

$$\Gamma_p=\pi r_e^2 c\int \rho_{\mathrm{Ps}+}(\mathbf{x})\rho_L(\mathbf{x})d^3x\,, \tag{9}$$

where r_e is the classical electron radius, c is the velocity of light, $\rho_{\mathrm{Ps}+}(\mathbf{x})$ is the density of a positron bound in a Ps atom, and $\rho_L(\mathbf{x})$ is the density of the electrons bound to the atoms in the lattice L. At finite temperatures, the lattice atoms oscillate about their equilibrium positions with a temperature-dependent mean-square amplitude $\langle u^2\rangle$, i.e., $\rho_L(\mathbf{x})$ is to be identified with the thermal average of the electron density ρ_{0L}, while in the harmonic approximation $\rho_{\mathrm{Ps}+}(\mathbf{x})$ remains unchanged. In each lattice cell, of volume v_1, the average electron density becomes

$$\rho_\mu(\mathbf{x})=(2\pi\langle u^2\rangle)^{-\mu/2}\int \rho_0(\mathbf{x}-\mathbf{u})\exp(-\tfrac{1}{2}u^2/\langle u^2\rangle)d^\mu u\,, \tag{10}$$

where $\mu=1$, 2, 3 refers to the conditions of planar, cylindrical, and spherical cell symmetries, respectively. Following I, we insert in to Eq. (10) the hard-core density ρ_0 of a molecule of radius r_0 and volume v_0, and integrate. We expand in terms of $(r-r_0)/r_0$ and insert into Eq. (9). On integrating term by term we obtain

$$\Gamma_p=\Gamma_{1p}+\mu\pi r_e^2 c v_0\rho_0\sum_{m=1}^{\infty}\frac{(1;2;m)}{(2m)!}\, r^{2m-1}\rho_{\mathrm{Ps}+}^{(2m-1)}(r_0)\left(\frac{\langle u^2\rangle}{r_0^2}\right)^m\,, \tag{11}$$

using the abbreviation $\rho^{(n)}(r_0)=(d^n\rho(r)/dr^n)_{r=r_0}$. The first term is the same as Eq. (14) of I,

$$\Gamma_{1p}=\Gamma_{0p}/[1+F(S,v^*)]\,, \tag{12}$$

where

$$\Gamma_{0p}=\pi r_e^2 c\rho_0 \tag{13}$$

is a constant, and

$$[1+F(S,v^*)]^{-1}=\int_{v0}\rho_{\mathrm{Ps}+}(\mathbf{x})d^3x \tag{14}$$

depends only on the dimensionless parameter

$$S=(4m/\hbar^2)U_0r_0^2$$

and on the reduced volume $v^*=v_1/v_0$. U_0 is the hard-core cell potential. We introduce

$$\xi_0^2(S,v^*)=S-(4m/\hbar^2)r_0^2E(S,v^*)\,, \tag{15}$$

where $E(S,v^*)$ is the energy of the Ps atom in the lattice. It is a property of our hard-core cell model that

$$\rho_{\mathrm{Ps}+}^{(2n-1)}(r_0)=(2\xi_0/r_0)^{2n-2}\rho_{\mathrm{Ps}+}'(r_0)\,. \tag{16}$$

Inserting Eq. (16) into Eq. (11) yields

$$\Gamma_p=\Gamma_{0p}\frac{1+G(S,v^*)\{\exp[2\xi_0^2(S,v^*)\langle u^2\rangle/r_0^2]-1\}}{1+F(S,v^*)}\,, \tag{17}$$

where

$$G(S,v^*)=\mu v_0 r_0\rho_{\mathrm{Ps}+}'(r_0)/4\xi_0^2\int_{v0}\rho_{\mathrm{Ps}+}(\mathbf{x})d^3x\,. \tag{18}$$

Although we have made extensive calculations of $G(S,v^*)$, for the present purpose the interpolation formula

$$G(S,v^*)\simeq\tfrac{1}{2}[1-\tfrac{1}{2}\tanh(\mu-1)/\xi_0(S,v^*)] \tag{19}$$

suffices, since it is exact in the limits $\xi_0\to 0$ and $\xi_0\to\infty$, and has a maximum error of some 10% only when $\xi_0/(\mu-1)\simeq 1$, for $\mu=2$, 3. With the functions $\xi_0^2(S,v^*)$ and $F(S,v^*)$ as given in I we can compare $\tau_p=\Gamma_p^{-1}$, Eq. (17), with τ_A provided we specify the dependence of $\langle u^2\rangle$ on temperature.

In keeping with the spirit of the model developed here, it is sufficient for estimating $\langle u^2\rangle$ to make use of the Lindemann melting criterion as derived by Pines.[19] We write

$$\langle u^2\rangle/r_0^2=v^{*(2/\mu)}\gamma_M T/T_M\,,\quad \Theta_{\mathrm{D}}<T\leq T_M\,, \tag{20}$$

where γ_M is the critical value of $\langle u^2\rangle/r_1^2$ for which melting occurs and Θ_{D} is the Debye temperature. Consequently in the melt,

$$\langle u^2\rangle/r_0^2=v^{*(2/\mu)}\gamma_M\,,\quad T>T_M\,. \tag{21}$$

At very low temperatures $\langle u^2\rangle$ becomes constant, and Γ_p depends only on v^*.

Figure 8 compares the pickoff lifetime $\tau_p=\Gamma_p^{-1}$ as calculated from Eq. (17) with the experimental τ_A of polyethylene and Teflon. Similar results are obtained for glycerol. We have chosen $\mu=2$, $\tau_{0p}=\tau_C$, and $S=25$. The numerical values of γ_M which give the best fit to the data of Teflon and polyethylene are close to those typical of alkali metals ($\frac{1}{16}$) and noble metals ($\frac{1}{12}$), respectively.

On balance, then, the picture underlying Eq. (17) accounts for the essential features of the long-lifetime measurements. The initial sharp rise is fairly insensitive to the temperature; it derives from the drop in the overlap integral as the Ps atoms begin to recede from the lattice molecules into the developing free volume. As the free volume grows further the concurrent thermal

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[19] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 34 ff.

broadening of the electron-density distribution affects the small residual overlap so strongly that a maximum can appear before melting sets a limit on the thermal amplitudes. From then on the electron density in the free volume declines and the lifetime rises.

It remains to discuss briefly τ_B and $\tau_{C'}$. In Sec. 3 we were led to identify the component B with the annihilation of positrons which did not form Ps, because of the magnitude of τ_B and the small variations of τ_B and i_B with temperature. Even the slight trends with temperature discernable in Figs. 2 and 4, if significant, would be consistent with this interpretation for reasons similar to those advanced for the changes in τ_A, if consideration is given to the differences in the affinities between a molecule and a positron on one hand and a positronium atom on the other. The small values of $\tau_{C'}$ are comparable to the lifetime of Ps^- and reflect the high pickoff rates in the ordered domains of the lattice[6]; indeed the values of τ_A as plotted in Fig. 8 extrapolate [redacted] to just such short lifetimes as $v^*(T) = 1+v_f^*(T)$ approaches the tight-packing (t.p.) value $1+v_{\mathrm{t.p.}}^*$. [redacted]

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Molecular Distribution and Elasticity in Crystals

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The well-known fluctuation-compressibility theorem for fluids is generalized to crystalline solids. It is pointed out that in anisotropic media, fluctuating local strains induce long-range pair correlations. The resulting anomalous contributions to the theorem's pair-correlation-function integral are related to certain components of an elastic tensor for the crystal. Detailed knowledge of particle-singlet and pair equilibrium distributions alone thus provides constraints on, but does not wholly determine, the solid's elastic constants.

I. INTRODUCTION

ONE of the central results in the statistical-mechanical theory of classical fluids is the density-fluctuation theorem[1] relating the isothermal compressibility κ to an integral of the difference between the pair distribution function, $\rho^{(2)}(r_{12})$, and the product of singlet distribution functions, $\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)=\rho^2$:

$$\begin{gathered}\rho^2 kT\kappa=\rho+\int d\mathbf{r}_{12}[\rho^{(2)}(r_{12})-\rho^2],\\ \kappa=(1/\rho)(\partial\rho/\partial p)_T,\quad \rho=N/V.\end{gathered}\tag{1}$$

The local density-fluctuation integrand refers to an infinite isotropic and homogeneous system, which normally ensures integrability. One of the persistent interests in relation (1) concerns critical phenomena; for the liquid-vapor transition the anomalous behavior of κ at the corresponding critical point is thus related to a long-range nonintegrable tail of the integrand, and hence to critical opalescence.[2]

The isothermal compressibility κ measures the elastic response of a fluid to an isotropic stress. Indeed, this quantity is essentially the single elastic constant that fluids possess. It is the aim of this article to examine the modification of Eq. (1) required by crystalline substances where there may be up to 18 independent elastic constants.

An interesting and evidently characteristic feature of solids that emerges from the analysis below is that the density fluctuation integrand corresponding to $\rho^{(2)}(r_{12})-\rho^2$ possesses long-range character, decaying to zero as the inverse distance cubed. This behavior (unlike the exponentially damped behavior expected for fluids under normal circumstances) has nothing to do with critical phenomena, but arises from local stress fluctuations. The long-range crystalline-phase "tail" requires careful handling, and indeed holds the key to proper modification of Eq. (1) in the presence of direction-dependent elastic properties.

II. DEDUCTION

DeGennes[3] has remarked that Eq. (1) represents for fluids the long-wavelength limit of a more general

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[1] L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) **17**, 793 (1914); J. Yvon, *Fluctuations en Densité*, Actualités Scientifique et Industrielles, No. 542 (Hermann et Cie., Paris, 1937).

[2] M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

[3] P. G. deGennes, Nuovo Cimento **9**, Suppl. 1, 240 (1958).