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Temperature Effect on Positron Annihilation in Condensed Matter*†‡

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An experimental investigation has been made of the temperature effect on the angular distribution of radiation from positron annihilation in matter. The materials chosen were Teflon, fused quartz, naphthalene, and water, for which the most comprehensive studies of the long-lifetime (τ_2) component and its intensity under various conditions have previously been made. The correlation between τ_2 lifetime and intensity and the amount of narrow component in the angular distribution has been studied both in a single phase, and as a function of phase change. Evidence seems conclusive that the so-called temperature effect on angular distributions is in reality a density effect. The underlying cause of the narrow-component enhancement seems in part to be related simply to an increase in positronium production which follows density changes. In quartz, and in water, Teflon, and naphthalene within the present limits of error, the enhancement may be attributed to this cause alone. The narrow component in quartz, Teflon, and naphthalene is found to have a width corresponding to a center-of-mass energy at the time of annihilation of about 10 times the thermal energy for positronium. The water-ice transition shows extremely interesting properties, marked by the appearance of a very narrow and well defined peak in the ice phase. It is suggested this is due to a reduction of the zero-point energy caused by enlargement of cavities in which positronium is trapped. Some anomalies are pointed out in the excisting τ_2 intensity, lifetime, and 3γ annihilation rate as a function of phase change in water.

I. INTRODUCTION[1]

POSITRON annihilation in matter may occur from unbound states through direct annihilation with electrons, or by annihilation from a bound state, the positronium atom. In the latter case, the positronium atom may exist in either the singlet (spin antiparallel) or triplet (spin parallel) states, which gives rise, in free space, to two characteristic mean lives against self-annihilation: 1.25×10^{-10} sec from the singlet state and 1.38×10^{-7} sec from the triplet. These two states will be formed in the ratio $\frac{1}{4}$ to $\frac{3}{4}$. Self-annihilation from the singlet state must occur with emission of 2 quanta, and from the triplet state by emission of 3 quanta.

If positronium is formed in the presence of other matter, the so-called "pickoff" process[2] may occur in which the positron annihilates by 2-quantum emission with an atomic electron of the proper spin orientation. The probability of pickoff depends on the amount of overlap of the positron and external electron wave functions, and therefore should be related to the density of surrounding matter. The lifetime against pickoff will generally be longer than the singlet state self-annihilation time but much less than the triplet self-annihilation time. The effect of the pickoff process is therefore to substantially depopulate the triplet positronium states, giving rise to a "long" lifetime much shorter than that of free-space triplet positronium. Furthermore, the annihilation radiation from the long-lifetime processes will now consist mainly of two quanta rather than three. Such a long-lived two-quantum component in the decay spectrum of positrons annihilating in various insulators, having a lifetime generally a few times 10^{-9} sec, was first discovered by Bell and Graham.[3] Intensity-wise, the τ_2 component was found to comprise about 30% of the area under the lifetime curve and to be the same (with rather wide limits of error) for all materials exhibiting the τ_2 lifetime.

Recent measurements[4] have shown that these data are partially incorrect, however, and that the τ_2 intensity may in fact vary more widely than previously suspected, being ~21% in pure water and as high as 53% in pure fused quartz, and further may depend in part on the presence or absence of impurities.

A temperature dependence in the annihilation processes was also observed by Bell and Graham[3]: a more or less linear dependence of τ_2 lifetime on temperature between $+20°$C and $-196°$C was noted in several substances such as Teflon, although within the (wide) limits of error no change in τ_2 intensity was indicated. Further investigation[5] on Teflon has shown that its τ_2 *vs* T curve levels off between liquid nitrogen and liquid helium temperatures. A similar temperature dependence on the 3γ coincidence rate was observed by Graham and Stewart,[6] and Wagner and Hereford[7] for several substances. Since the 3γ annihilations arise from ^3S positronium which has escaped pickoff, one is merely

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† Part of the data appearing in this article was presented at the Washington Meeting of the American Physical Society, April, 1957. [R. L. de Zafra and W. T. Joyner, Bull. Am. Phys. Soc. Ser. II, 2, 173 (1957).]

‡ Based on part of a dissertation submitted (by R. L. de Z.) to the University of Maryland in partial fulfillment of the requirements for the Doctor of Philosophy degree.

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[1] For a general review of the theory of positron annihilation in matter, see R. A. Ferrell, Revs. Modern Phys. **28**, 305 (1956), and for much pertinent experimental information, the review by S. Berko and F. L. Hereford, Revs. Modern Phys. **28**, 299 (1956). Both articles contain many supplementary references, some given below.

[2] M. Dresden, Phys. Rev. **93**, 1413 (1954) and P. R. Wallace, Phys. Rev. **100**, 738 (1955).

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

[4] R. E. Green and R. E. Bell, Can. J. Phys. **35**, 398 (1957).

[5] Landes, Berko, and Zuchelli, Bull. Am. Phys. Soc. Ser. II, **1**, 68 (1956).

[6] R. L. Graham and A. T. Stewart, Can. J. Phys. **32**, 678 (1954).

[7] R. T. Wagner and F. L. Hereford, Phys. Rev. **99**, 593 (1955).

observing here another manifestation of the temperature dependence of the τ_2 lifetime, however.

In addition to these temperature effects, which apparently are associated with changes in pickoff due to thermal expansion, a temperature effect on the *angular distribution* of annihilation radiation was observed by Stewart.[8] A strong enhancement of the narrow component was found in Teflon at +250°C when compared with the distribution at −196°C. Reason for believing that a relationship exists between the narrow and τ_2 components was furnished by Page *et al.*[9] in their measurements of the angular distribution of crystalline quartz *vs* fused quartz. Crystalline quartz, which shows no τ_2 component,[3] was found to give a very broad angular distribution. Fused quartz, in which the τ_2 component is present, showed a much more peaked distribution.

Although the experimental evidence suggests some identity between the τ_2 lifetime component and the narrow-component radiation, it is clear that pickoff annihilations from the triplet state of positronium, with which the τ_2 component must be associated, should not fall into the narrow component, since they involve relatively high momenta. Magnetic enhancement experiments[10] also bear out the assumption that self-annihilation radiation from ^1S positronium is confined to a rather narrow angular region. It is fairly certain therefore that at least the major portion of the narrow component arises from ^1S self-annihilation, and that the broad component must be attributed to pickoff and direct annihilations.

A possible explanation for the temperature effect on angular distributions was suggested by Ferrell,[11] based on electromagnetic conversion from the $^3S \rightarrow {^1S}$ states. Since that time, the recent remeasurement of τ_2 intensities[4] has removed discrepancies in the data for fused *vs* crystalline quartz which led to the electromagnetic conversion hypothesis. As shown below, it now appears likely that changes in angular distribution brought about by temperature and/or phase changes may be attributed solely to changes in the amount of positronium formed, without the necessity for more complicated mechanisms (although in the case of the water-ice transition, some further assumptions seem necessary and will be taken up in Sec.IV).

In the discussion (Sec. IV) we shall give a simple picture by which variations in the positronium formation mechanism, and thus ultimately in the shape of the angular distribution curve, may be related to density changes in the target material.

II. EXPERIMENTAL

Since nothing was known of the temperature effect on angular distributions except for partial information on Teflon, we have carried out an investigation of the effect in some representative materials for which 3γ rate measurements and/or τ_2 lifetime and intensity information is available for correlation with the angular distribution data. The materials chosen were Teflon, water, ice, and quartz. In addition, a study was made of the effect of crossing the solid-liquid phase change in naphthalene and in water. Previously, the only angular distribution measurements of phase-change effects have been made on fused and crystalline quartz.[9]

A. Apparatus and Techniques

The two-photon angular correlation apparatus was of the usual type (see, for example, reference 9) employing a fixed vertical target and vertical collimating slits, one of which was moved in a fixed series of positions in the horizontal plane by an automatic tracking device. This slit was mounted on a beam pivoted at the target so as always to remain in proper alignment. After each thousand counts, a series of relays were tripped, automatically recording the time elapsed, resetting the scaler, and advancing the slits to the next position. The distance between positions was 0.167 cm. For most of the runs on Teflon, quartz, and ice, a slit width of 0.114 cm was used (0.57 milliradian at the standard distance of 2 meters from the target). For other runs, the slit width was 0.228 cm (1.14 milliradians). Actually, little change was introduced by using the 0.57- rather than 1.14-milliradian slits, due to the basically triangular distribution shape. Ice was a special exception however, as will be discussed below.

No correction for angular resolution has been made on the graphs except for that of Teflon and ice. The effect of the correction is negligible except in regions of high curvature. Since most of the distributions are triangular in shape, the only serious correction occurs at the peak. Even here the change in value at the peak was found to be less than 2% for Teflon, so that it was felt that the labor of making resolution corrections was in general not worthwhile.

No correction has been made for accidental background, since by suitable shielding around the detectors, the ratio of true to accidental counts was kept at about 500/1 using the 1.14-milliradian slits and about 200/1 with the 0.57-milliradian slits. The target face was usually $\frac{1}{2}\times 1$ in. in size, the narrower dimension being along the line of γ-ray observation. Some Compton scattering of the escaping γ radiation will occur, but this is not strongly peaked in the forward direction for 0.5-Mev radiation, and at worst will only produce a nearly uniform background count over a spread of $\sim\frac{1}{2}$ radian. The intrinsic distribution from positron annihilation is on the order of 20 or 30 milliradians. For most of the runs, a source of about 5

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

[9] Page, Heinberg, Wallace, and Trout, Phys. Rev. **98**, 206 (1955).

[10] L. A. Page and M. Heinberg, Phys. Rev. **102**, 1545 (1956) and **107**, 1589 (1957); and S. D. Warshaw, Phys. Rev. **108**, 713 (1957).

[11] Reference 1, pp. 335–336.

millicuries was used, consisting of Na^{22} deposited on the end of a $\frac{1}{4}$-in. diameter stainless steel rod and covered by 1-mil Al foil. For certain runs, a source consisting of Cu^{64} foil was used.

In all cases involving temperature changes, the temperature of the target was measured by a thermocouple imbedded directly in the sample. Temperatures could generally be held steady within 5°C for several hours and all temperatures referred to carry a maximum error of that amount, unless otherwise stated.

For the "peak rate" measurements described below, it was usually necessary to change the target holding arrangement to cover extreme temperature ranges. In this case one or two measurements would be taken at the end of each temperature range with several times the usual statistical accuracy, and the different portions normalized at these points. In addition, over a single temperature range, it was customary to cycle the temperature while taking readings, to minimize any drifts in the counting circuits. (Actually, the circuitry would produce data within the statistical error limits over a period of at least 20 hours, with no visible long term drifts.)

(*i*) *Teflon and Quartz*

For the high-temperature runs on Teflon, the sample was mounted on the end of a copper bar, the other end of which was surrounded by a small electric oven. For the low-temperature Teflon measurements, the sample was mounted in a "spider" placed in front of the source and wedged into a 500-cc beaker which was in turn mounted in a large Dewar and surrounded by dry ice or liquid nitrogen. The beaker was sealed to prevent the accumulation of frost on the sample. Appropriate corrections for attenuation by the nitrogen or dry ice were made when necessary.

With the latter arrangement, it was impossible to use the Na^{22} source, due to space limitations, so a Cu foil measuring about $\frac{1}{2}\times 1\times 0.005$ in. was irradiated and mounted in a lead collimator placed in the beaker. As Cu^{64} has a 12.8-hour half-life, it was necessary to correct for the decay rate whenever a copper source was used.

For the runs made on Teflon under pressure, a sandwich consisting of 3 copper foils 0.0001 in. thick separated by Teflon sheets 0.01 in. thick and backed by heavier sheets of Teflon was irradiated after assembly and loaded into a mechanical press. The foil was kept away from the edges of the sandwich to avoid the possibility of positrons entering and annihilating in the surrounding steel. Pressure was applied by simple tightening of a screw giving a force up to a few thousand pounds. The whole press could be heated by coils running through it, and was cut away to give a maximum thickness of $\frac{1}{8}$ in. of steel at each side along the line of observation of the γ rays. Again any Compton scattering should not materially affect the distribution.

The quartz runs were made in the same manner as those for Teflon except that a Cu^{64} source was used for both the high- and low-temperature runs.

(*ii*) *Naphthalene and Water*

Since the existing apparatus required a vertical target face, and since it was desirable to avoid any change of position in a liquid target face due to evaporation, a small thin-walled vertical reservoir was constructed to hold liquid samples. This consisted of a copper tank with sides 0.01 in. thick which were further tapered towards the front (vertical) face of the tank in order to minimize positron annihilations in the tank walls. The front face, measuring $\frac{1}{2}$ by 1 in., was covered with a nickel foil 0.00004 in. thick. Better than 99% of positrons incident on a foil of this thickness will pass through without annihilation, and the geometry of the tank and source position made it virtually impossible for positrons to reach the tank walls before having annihilated in the material filling the tank. No correction was made to the angular distribution curves for extraneous annihilation, as we feel this should amount to less than 1%. The tank was mounted on the end of a brass rod which could be immersed in a coolant or inserted into a small electric oven to provide temperature changes.

III. RESULTS

A. The Temperature Effect

(*i*) *Teflon*

Figure 1 shows the angular distribution from Teflon at −196°C, +20°C, and +270°C. The three curves have been normalized to equal areas. Stewart's original data[8] indicate a stronger difference between high and low temperatures, but part of this may be due to a change of slit width between his two curves. Later distributions taken by Stewart with constant slit width (private communication) indicate about the same amount of change as shown here. Unless otherwise noted, the error bars on this and all subsequent figures indicate the standard deviation only (based on the square root of the total number of counts). To avoid confusion, in some figures where several curves are shown the number of counts per point is given for each, from which the standard deviation may be derived.

Figure 1(a) is the difference curve obtained from the two temperature extremes. The central area above the dotted line in Fig. 1(a) represents the change in the narrow component, while the total area under the zero line represents the change in the broad component. These two areas must of course agree, since the individual high- and low-temperature angular distribution curves were themselves normalized to equal areas before subtracting.

This type of normalization is the logical one by which to make a comparison between curves, and shows im-

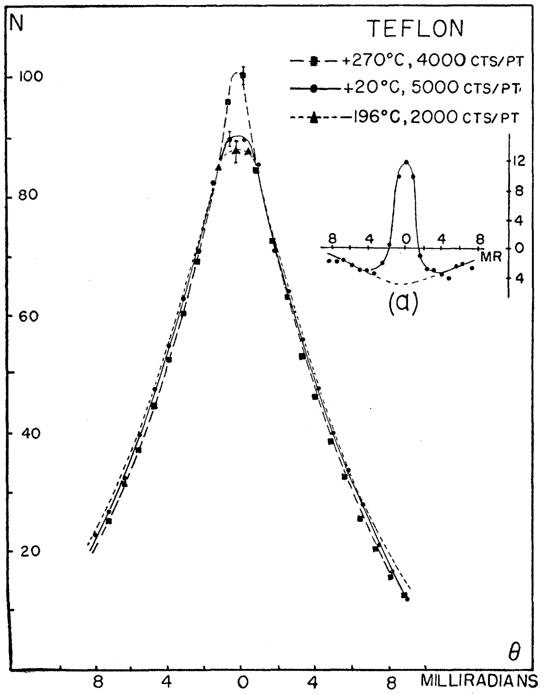

FIG. 1. Angular distribution curves for Teflon as a function of temperature. Slit width = 0.57 milliradian. (a) shows the difference curve obtained from the distributions at −196°C and +270°C. The curves are normalized to equal area.

mediately regions in which relative attenuation and enhancement occur. In Fig. 1, one notes that all three area-normalized curves intersect at a common point on each side of the distribution. This suggests that these points mark the approximate boundaries between distinct narrow and broad components whose *intensities*, rather than distribution shapes, alter to produce the observed changes in angular distribution. This interpretation seems quite reasonable on the basis of different origins for the narrow and broad parts of the distribution as discussed in Sec. I. Thus, for instance, the pickoff mechanism may vary in its efficiency under different density conditions, but the momenta involved would not be expected to change much.

In the following discussions, unless otherwise noted, we shall make the assumption that distinct narrow and broad components exist whose distribution shapes remain relatively constant, and that angular distribution changes are brought about by changes in the relative intensity of these components. It should be noted that if the narrow and/or broad component distribution shapes do change, then one obtains a finite difference-curve area even if no intensity change takes place. Gross changes in shape (e.g., that for ice, see below) are easy to detect and to make allowance for.

Barring changes in shape, the difference curve between two distributions taken under different conditions should give a direct measure of the half-width W_n of the narrow component (from the half-width of the central portion of the difference curve at its half maximum point). Furthermore the ratio of the central difference-curve area [i.e., the part above the dotted line in Fig. 1(a)] to the total distribution area should give the relative fraction of entering positrons involved in producing the observed changes. We shall refer to this difference-curve area ratio as α, and, strictly speaking, mean the experimentally measured quantity, irrespective of whether or not changes in distribution shape may be contributing to its value. There is a certain amount of arbitrariness in the placing of the dotted line across the bottom of the difference curve. We have tried to make it a reasonable approximation to the shape expected for the broad component.

We estimate the central area above the dotted line in Fig. 1(a) to be $(4.7\pm0.8)\%$ of the total angular distribution curve in Fig. 1. (That is, $\alpha=0.047$.) The half-width at half maximum of the portion above the dotted lines gives $W_n=1.3\pm0.2$ milliradians. The error limits in area and half-width take into account possible error in positioning of the dotted line, as well as the purely statistical estimate. From the relation $\theta=P/m_0c$, this value for the half-width indicates a center-of-mass energy at the time of annihilation on the order of

$$E=m_0c^2\theta^2/4=0.21 \text{ ev}.$$

(The 4 appears in the denominator since the positronium mass equals $2m_0$.) Assuming that the narrow component arises only from the self-annihilation of singlet positronium, this would therefore indicate that the positronium energy is about 10 times thermal energy at room temperature at the time of annihilation. More will be said concerning this later.

Figure 2 represents a measure of what we shall call the "peak rate" for Teflon, as a function of temperature. The slits, set at a width of 1.12 milliradians, were placed collinearly with respect to the target, and the counting rate as a function of temperature was recorded for a fixed unit of time.

Three different Teflon samples were used for the data appearing in Fig. 2. Two were obtained from

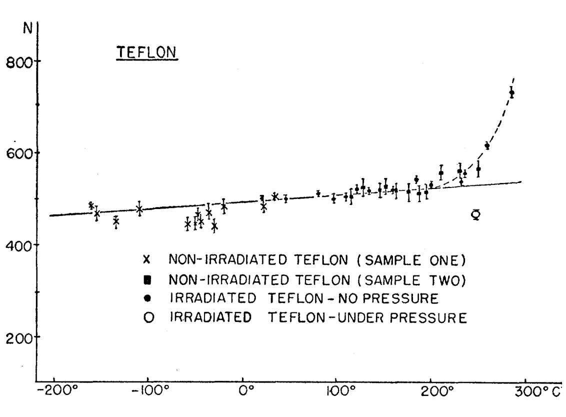

FIG. 2. Peak rate as a function of temperature for Teflon, taken with 1.14-milliradian slit width.

different suppliers and originally used in a preliminary effort to determine whether different samples would show different characteristics. (Slightly different lifetimes have been found in different samples.) Since no substantial difference in behavior of the two samples showed up either in angular distribution or in peak rate, points from both samples are included in Fig. 2. In addition, since it was desired to take a measurement on Teflon under pressure at high temperature, the sandwich described in Sec. II was prepared and irradiated, and data from this also appear in Fig. 2. After irradiation for 24 hours at a neutron flux of $\sim 10^{12}$ cm^{-2}, the Teflon was materially changed in appearance, having turned a light brown and become quite brittle. Nevertheless, its angular distribution curve (Fig. 3) was not particularly changed from that of nonirradiated Teflon, and its peak rate tended to behave just as had that of previous samples. It was reported at the 1957 Washington meeting of the American Physical Society by Lundholm *et al.*[12] (not covered in their abstract) that irradiation of Teflon produces no apparent change in τ_2 lifetime, although a strong drop in τ_2 intensity occurs. It was found that this effect did not appear in Teflon for a total integrated flux ($N \times V \times T$) of less than about 10^{17}, corresponding to a minimum of about 25 hours in the Brookhaven reactor. This is about the maximum length of time that the present sample was irradiated. Since a drop in τ_2 intensity without a change in τ_2 lifetime is indicative of the chemical binding of positrons,[4] one might expect to see a reduction in the narrow component intensity. If anything, the opposite seems to be the case when one compares the high-temperature curve of Fig. 1 with the no-pressure curve of Fig. 3. The data of Lundholm *et al.* were taken at room temperature, however; one really needs to compare distributions and τ_2 intensities at equal temperatures. Further investigation of this would be interesting.

As can be seen in Fig. 2, there is a sharp up-swing in the peak rate above 200° which apparently coincides with the start of a general change in property of the material. At 275° to 300°C, Teflon begins to become translucent and jelly-like with a considerable increase in volume.[13] Heating at or beyond 300°C results in the evolution of poisonous gases, however, and not much work was done at this high temperature.

Immediately after the highest temperature point was taken on the irradiated sample, pressure was applied and a recount taken resulting in a point considerably below the general curve (Fig. 2, at ~250°). An angular distribution was then taken at the same temperature (Fig. 3) which confirmed that the application of pressure will "squeeze out" the narrow component, thus giving a clear indication that the "temperature" effect on angular distribution could in fact be a density effect.

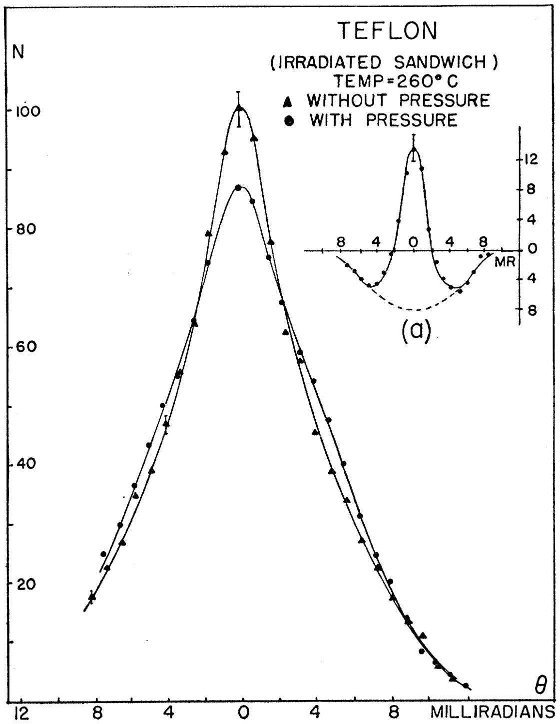

FIG. 3. Angular distribution curves for Teflon at +260°C with and without pressure, normalized to equal area. Slit width = 1.14 milliradians; (a) shows the difference curve.

Figure 3(a) represents the difference curve derived from Fig. 3. The enhancement of the narrow component again falls within roughly the same angular region. The central area above the dotted curve is estimated to be $(8.1\pm0.8)\%$ of the total distribution area, and its half-width at half maximum is 1.5 ± 0.2 milliradians. The higher value for α compared with that found from the temperature difference curves suggests that even less narrow component was present under pressure, despite the elevated temperature, than was present without pressure at liquid nitrogen temperature. (Unfortunately no good estimate of the pressure could be made.) The agreement, within the limits of error, of the half-width values, despite the considerable difference in physical conditions, is interesting and again suggests that we are justified in the assumption that no significant change in the distribution *shapes* has occurred.

(*ii*) *Quartz*

A set of distribution and peak-rate measurements similar to those for Teflon were made on fused quartz (Figs. 4 and 5). Both the angular distribution and peak-rate curves suggest a small change, principally from

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[12] Lundholm, Bjorkland, and Menius, Bull. Am. Phys. Soc. Ser. II, 2, 173 (1957).

[13] It is unfortunate that no τ_2 lifetime measurements on Teflon have been carried out above 200°C. The highest temperature measurements seem to be those of Lundholm *et al.* (reference 12), who stopped at 200°C, somewhat too low to show whether a rapid increase in τ_2 occurs above this temperature, as might be concluded from the peak rate behavior on the basis of a general correlation between the two.

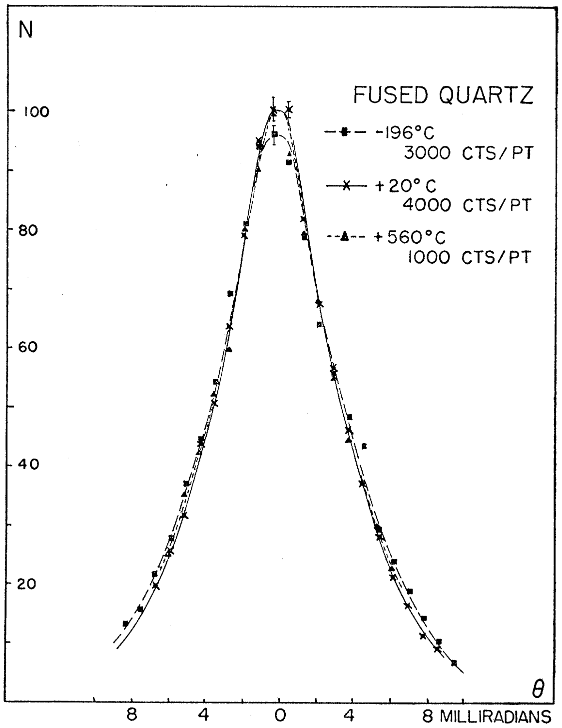

FIG. 4. Angular distribution curves for fused quartz as a function of temperature, normalized to equal area. Slit width =0.57 milliradian.

room temperature to -196°C, although Bell and Graham[3] found no change in τ_2 between these temperatures. Little or no observable change in τ_2 or angular distribution *should* be expected from the density dependence of view, since the coefficient of thermal expansion for quartz is extremely small (1.5×10^{-6} cm^3/degree C). It is possible that the apparent drop-off of the peak curve below room temperature is due partly to faulty normalization at the ends of the ascending and descending temperature runs, in spite of the precautions taken (see Sec. II). We conclude that there may be a temperature effect in quartz (which very exact measurements of τ_2 intensity might reveal), but that its magnitude is at most slight, in keeping with the density-independence hypothesis.

(*iii*) H_2O

Finally, we shall jump ahead for a moment and consider Figs. 6 and 7, showing, respectively, the peak rate measurement as a function of temperature for ice and distilled water, and the density behavior as a function of temperature, neglecting the phase change for the present. H_2O shows interesting variations in density within its two phases and for this reason makes a particularly good test for the density-dependence hypothesis. The curve in Fig. 6 is derived from Fig. 7 on the basis of a density-dependent peak rate, and is seen to be consistent with the experimental points.

B. Effect of Phase Changes

(*i*) *Naphthalene*

To study further the density dependence and the general effect of phase changes on angular distribution, an investigation was made of naphthalene and water across their solid-liquid transitions. It has previously been established by Landes *et al.*[14] that in naphthalene the τ_2 lifetime changes abruptly from 1.2×10^{-9} sec to 2.6×10^{-9} sec as the transition is made from solid to liquid and that furthermore the intensity of the τ_2 component changes from $\sim10\%$ below melting to $\sim30\%$ in the liquid state.

Figure 8 illustrates the peak rate measured for naphthalene, which significantly shows a behavior similar to the τ_2 (intensity *and* lifetime) *vs* T dependence found by Landes *et al.* The melting point of naphthalene is 81°C. The transition temperature is probably sharper than appears in Fig. 8 due to the fact that during heating the temperature around the sides and front of the sample, in contact with the metal tank, would be higher than registered in the center by the thermocouple and vice versa during cooling—thus the thermocouple readings would tend to give an erroneously wide peak-rate transition range.

Figure 9 gives the result of angular correlations taken at 28°C and 86°C. (A partial distribution was also measured at 68°C with less accuracy: it appears to be the same as the distribution at 28°C, as would also be indicated by the peak-rate curve.) The difference curve, Fig. 9(a), indicates an area above the dotted curve of $(9.3\pm1.0)\%$ of the total distribution curve,

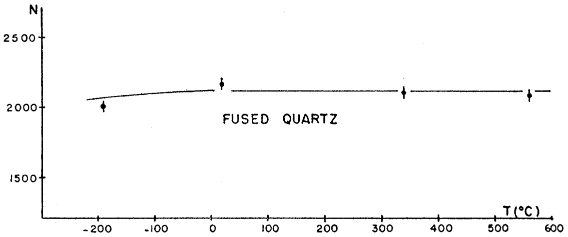

FIG. 5. Peak rate as a function of temperature for fused quartz, taken with 1.14-milliradian slit width.

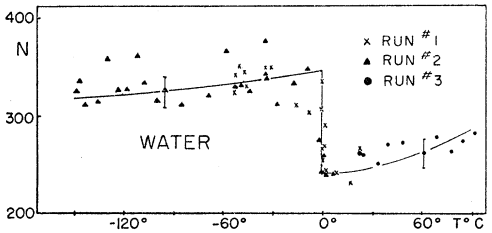

FIG. 6. Peak rate as a function of temperature for water, taken with 1.14-milliradian slit width. The curve is derived from Fig. 7 on the basis of a density-dependent peak rate.

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[14] Landes, Berko, and Zuchelli, Phys. Rev. **103**, 828 (1956).

with a half-width at half maximum of 1.3 ± 0.2 milliradians.

The density of naphthalene changes from 1.14 g/cc in the solid phase to 0.96 g/cc in the liquid phase, or about 16% upon melting, although microscopic density changes can be expected to be even higher. Thus enhancement of the narrow component again follows a decrease in density.

One does not entirely expect that as drastic an effect as a phase change should be comparable in effect with simple density changes in a single phase, but the observations on naphthalene tend to indicate that density changes may be the dominant factor in altering the angular distribution across phase changes. (As we shall see, the total increase in narrow component in liquid naphthalene is ascribable to the increase in positronium production alone, as measured by the τ_2 intensity increase found by Landes *et al.*) With this encouragement we next consider a more critical test of the density-dependence hypothesis.

(*ii*) *Water-Ice*

The results from distilled water are illustrated in Figs. 6 and 10 and show at least two interesting features. First one sees that the "temperature" effect is inverted, although keeping a normal dependence from the *density* standpoint. Thus a general order-disorder dependence, for instance, which has been suggested in the literature, seems to be ruled out. Some further effect seems to be taking place, as evidenced by the now abnormal narrowness of the narrow component. Even though 0.57-milliradian slits were used, the narrowness is so great that most of the observed spread of the experimental points in the central spike is due to the finite resolution of the apparatus, i.e., one is largely measuring the resolution function of the slits. For this reason the correction for angular resolution now becomes important. One may show that the resolution function for 0.57-milliradian slits and a target having the density of ice is very nearly a Gaussian distribution with a half-width of about 0.60 milliradian. The estimated shape of the angular distribution after making the resolution correction is shown by the dotted line in Fig. 10. The narrow component is now found to have a half-width W_n of about 0.35 milliradian, implying an annihilation center-of-mass energy of $E=m_0c^2\theta^2/4=0.015$ ev with a possible error of about a factor of three. This suggests that the narrow spike must arise from completely thermalized positronium (thermal energy$=0.02$ ev). Furthermore, the angular distribution as measured allows an easy separation into narrow and broad components without recourse to comparisons with other curves. When this is done the ratio of narrow-component area to total area (narrow plus broad) is found to be 0.088 ± 0.009. On the other hand, the difference curve between water and ice yields a value of $\alpha=0.077\pm0.01$. Although these values agree within the limits of error, this is accidental and no comparison between them should be made. Strictly speaking, the first quantity is not equivalent to α, and furthermore a large fraction of the value of α here must arise simply from the obvious change in *shape* of the narrow component, aside from any *intensity* changes.

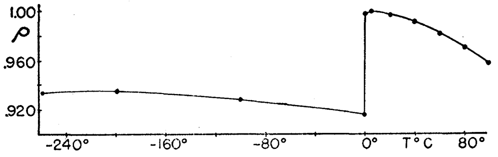

FIG. 7. Density *vs* temperature for water. Derived from data from reference 20 and Dorsey, reference 18.

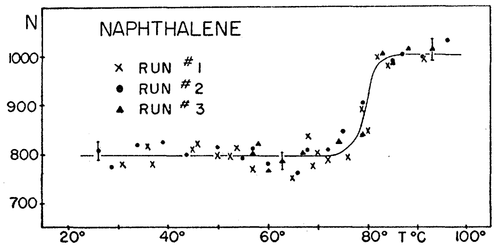

FIG. 8. Peak rate as a function of temperature for naphthalene, taken with 1.14-milliradian slit width. Melting point of naphthalene$=81$°C.

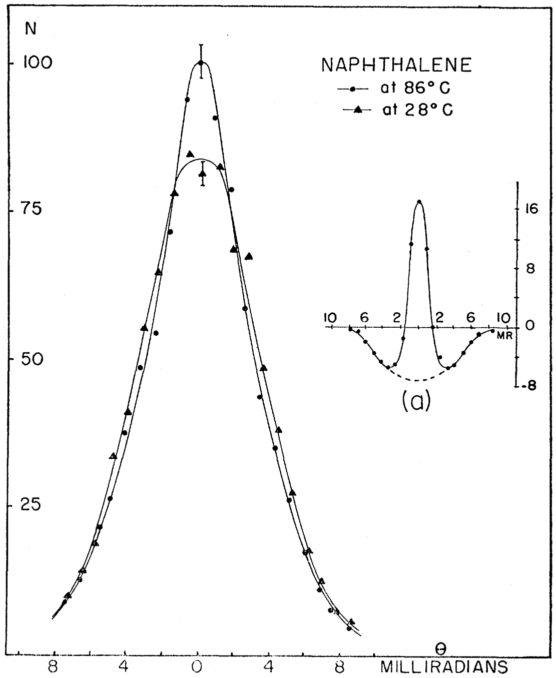

FIG. 9. Angular distribution curves for naphthalene at 28°C and 86°C, normalized to equal areas. Slit width$=1.14$ milliradians. (a) shows the difference curve.

Figure 6, the peak-rate dependence in water, shows $\sim32\%$ increase in the peak rate upon freezing relative to its value for water. In the interest of counting rate,

TABLE I. Data from temperature-induced changes in angular distributions.

Target	α	W_n (milliradians)	E (ev)	$I_2(2)$	$I_2(1)$	$\beta=\alpha-\frac{1}{3}\Delta I_2$
Teflon[a]	0.047 ± 0.008	1.3 ± 0.2	0.21 ± 0.03	?	0.30 ± 0.05[f]	...
Teflon[b]	0.011 ± 0.008	1.1 ± 0.2	0.16 ± 0.07	0.30 ± 0.05[f]	0.30[f](?)	0.011 ± 0.05
Teflon[c]	0.081 ± 0.008	1.5 ± 0.2	0.29 ± 0.04	?	?	...
Quartz	0.178 ± 0.01[e]	1.5 ± 0.2	0.29 ± 0.04	0.53[g]	0[f]	0.001 ± 0.05
Naphthalene	0.093 ± 0.01	1.3 ± 0.2	0.21 ± 0.03	0.29[h]	0.09[h]	0.027 ± 0.04
Water-ice	0.077 ± 0.01	0.35 ± 0.2	0.015 ± 0.3	0.21 ± 0.05[g]	0.21[g](?)	0.077 ± 0.10(?)
	Ratio: $N/(N+B)$	W_n	E (ev)			
Ice[d]	0.008 ± 0.009	0.35 ± 0.2	0.015 ± 0.03	...	...	...

[a] For temperature range −196°C to +270°C.
[b] For temperature range −196°C to +20°C.
[c] At +260°C with and without pressure.
[d] Data measured from single curve. N and B are areas of narrow and broad components. W_n measured after correction for angular resolution.
[e] From data of Page *et al.*, reference 9, after renormalization to equal areas.
[f] From Bell and Graham, reference 3, and T. R. Gerholm, Arkiv Fysik **10**, 523 (1956).
[g] From Green and Bell, reference 4. It is assumed that the intensity (I_2) in ice does not change drastically from that in water.
[h] From Landes, Berko, and Zuchelli, reference 14.

these data were taken with 1.14-milliradian slits: the real change is therefore probably on the order of 3 times this.

It was instructive to extend the peak-rate measurements over a wide temperature range for water, since the density behavior is fairly well known and shows interesting variations. This has already been commented on in Sec. IIIA.

In Table I we present a summary of the experimental measurements of α, the ratio of central difference-curve area to total distribution area; of W_n, the half-width of the narrow component; and of E, the computed value for the corresponding annihilation center energy.

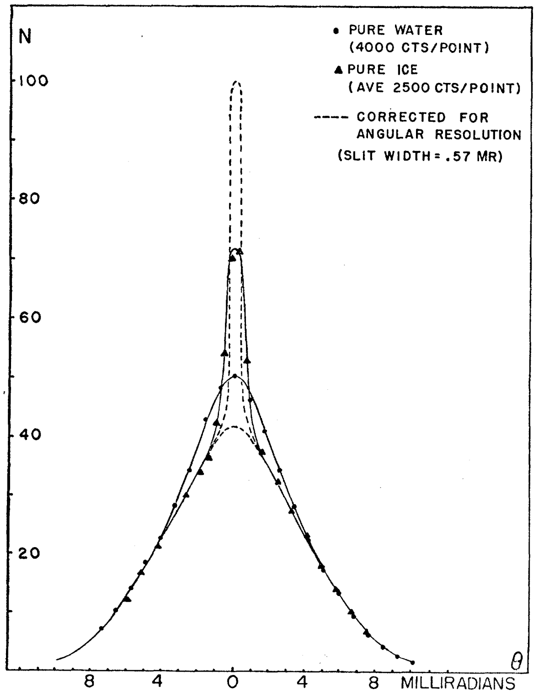

FIG. 10. Angular distribution curves for ice at −40°C and water at 20°C normalized to equal areas. Slit width=0.57 milliradian; (a) shows the difference curve.

In addition, values from various sources are given for $I_2(1)$ and $I_2(2)$, the τ_2 intensities measured for the same physical conditions under which the angular distribution curves were taken. The importance of these values in any discussion of the "temperature" effect will be brought out in the discussion in the next section, as will the significance of the quantity $\beta=\alpha-\Delta I_2/3$, the numerical values of which are tabulated in the last column of Table I.

The value of α for the water-ice transition was derived from the difference curve of Fig. 10. Although the correction for finite slit width was not used, this should not produce an error, since α is an integrated quantity. The value W_n for water-ice is taken directly from the central spike after correction for finite slit width. The error listed for β (naphthalene) is based on an arbitrary assignment of ±0.5 as the error in the τ_2 intensity values measured by Landes *et al.*[14] As mentioned above, much of the value for α (and consequently for β) found from the water-ice comparison curves must arise from the obvious change in the shape of the narrow component, aside from any possible change in τ_2 intensity. In computing β in Table I, it has been assumed that the τ_2 intensity (I_2) does not change drastically from that in water.[3] This may not be correct, but any change should be towards larger I_2 in ice and therefore would reduce β still further towards zero.

IV. DISCUSSION AND INTERPRETATION

It is fairly evident from the experimental results of Sec. III that the "temperature" effect on angular distributions and also the phase-change effects discovered here should be regarded basically as density-dependent phenomena, rather than, say, order-dependent phenomena, as has been suggested by some authors. Accepting this, we must then determine the underlying cause. This appears to be explainable in terms of a density dependence on the amount of positronium formed, and therefore on the number of positrons which may decay by the low-momentum process of self-annihilation from the singlet state of positronium. This may be seen as follows.

We denote the experimentally measured τ_2 intensity by I_2. Then the fraction of entering positrons forming singlet positronium will be $I_2/3$. If I_2 varies from $I_2(1)$ to $I_2(2)$ under different conditions, then the change in the fraction of positrons forming singlet positronium is given by $[I_2(1)-I_2(2)]/3=\Delta I_2/3$. Now let α be the ratio of the difference-curve area to total distribution curve area for angular distributions taken under the same conditions which give $I_2(1)$ and $I_2(2)$. Thus α represents the fraction of the total number of entering positrons being affected. If $\alpha=\Delta I_2/3$, then the change in narrow component is simply that caused by the change in amount of (singlet) positronium present. (We assume as before that the shape of the narrow and broad components is not changing significantly.) On the other hand, if $\alpha\neq\Delta I_2/3$, then the difference $\beta=\alpha-\Delta I_2/3$ would represent that portion of the narrow component not attributable to this cause (i.e., it would represent, for instance, the amount of ${}^1S$ positronium produced by a ${}^3S\leftrightarrow{}^1S$ conversion mechanism). Now from Table I, one sees by the last column that in cases for which complete data exist (quartz and naphthalene), β may easily be taken as zero within the limits of error. In the case of Teflon and water-ice, where sufficiently accurate measurements have not been made on I_2 in one of the temperature or phase extremes, the limits of error, even assuming constant I_2, still allow β to be considered zero. We also note that any objection to our general assumption of the constancy in shape of the narrow and broad components will only reinforce the argument that β may be assigned zero values.

In the case of the water-ice transition, it is highly probable that I_2 is actually not constant across the phase change, in view of the fact that density changes in quartz and naphthalene lead to considerable τ_2 intensity changes. (See also a further discussion of data on the water-ice transition below.) Thus the value of $\beta=0.077$ for water-ice might be considerably reduced. We have assumed I_2 to remain constant in computing β for water in Table I, but suggest a wider limit of error to make up for this. It has already been commented on that in any case the measured value of α, and therefore β, should be reduced on account of the definite change which occurs in the shape of the narrow component here.

Unless considerably more accurate measurements on I_2 and α should show that β may have nonzero values, the necessity is no longer present for introducing a ${}^3S\leftrightarrow{}^1S$ conversion mechanism or other explanation for the narrow-component enhancement brought about through temperature or phase changes. (Until the recent remeasurements of the τ_2 intensity for quartz by Green and Bell,[4] this was not the case.)

In general, the apparent density dependence of the amount of positronium formed may be accounted for by the behavior of the "Ore gap" mechanism.[15] The width of the Ore gap is directly determined by the ionization potential E_i and the lowest excitation potential E_e of the surrounding atoms, along with the positronium binding energy E_p, as shown in Fig. 11. [Here, for the sake of pictorial simplicity, all energies have been plotted as positive. This does not affect any of the arguments since the excitation "potential," etc. may be thought of as the amount of kinetic energy (positive) which must be obtained to excite the atom, etc.] Positronium formation by positrons above the E_e level is unlikely due to the preference for inelastic collisions, and impossible below the bottom of the Ore gap due to lack of sufficient energy for electron capture.

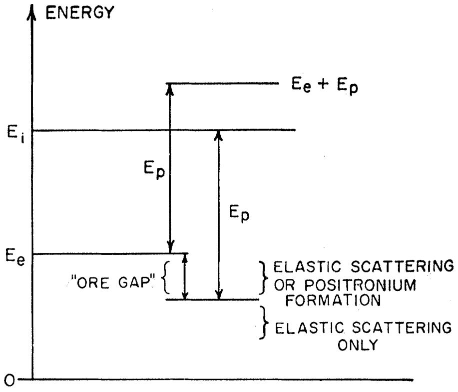

FIG. 11. Energetics of positronium formation. E_i and E_e are the ionization and lowest excitation potentials of the surrounding atoms, and E_p is the positronium binding energy.

If we reasonably assume that positrons will be more or less evenly distributed energy-wise between zero and E_e after undergoing their last possible excitation (inelastic) collision during the slowing down process, then the ratio of the width of the Ore gap to the width from zero to E_e should be fairly indicative of the fraction of entering positrons which will form positronium. As the density increases, the positronium binding energy will decrease due to cramping of the relatively widespread wave function. Thus the width of the Ore gap will decrease with increasing density in a given substance, and the amount of positronium formed will follow suit.

It may be well to point out here some possible narrow-component enhancement mechanisms other than that of increased positronium production, since the present experiments indicate that they probably need *not* be considered as mechanisms seriously influencing the angular distribution of annihilation radiation, except possibly for the last mentioned (iii) below.

(*i*) *The electromagnetic conversion mechanism.*—This was proposed by Ferrell[11] and based on anomalies

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[15] A. Ore, Univ. Bergen Årbok, Naturvitenskap. Rekke No. 9 (1949) and review by M. Deutsch, *Progress in Nuclear Physics* (Butterworths-Springer, London, 1953), Vol. 3, p. 131.

present at the time in data on fused *vs* crystalline quartz. The present results (and the removal of the anomaly by Green and Bell's[4] remeasurements) confirm the rough calculations by Ferrell which indicated that the mechanism would not be important. (These calculations were made under the nonrealistic assumption of a uniform $\mathcal{E}$ field, however, and it was felt at the time that more exact calculations employing a nonconstant field might raise the magnitude of the effect.) Water and ice actually should give an ideal test for the presence of such $^3S \leftrightarrow {}^1S$ conversion, due to the large electric dipole field possessed by the H_2O molecule.[16]

(*ii*) *An actual change in the momentum distribution of the electrons in the material under study.*—This is a possible occurrence across phase changes or as a result of bonds broken by thermal agitation. In the vicinity of defects in insulators one might expect to find less tightly bound electrons. Annihilation with these, either directly or from the ^3S state through pickoff, would reduce somewhat the angular distribution at large angles and enhance it at smaller angles. This could obviously not contribute substantially to enhancement within the true region of the narrow component, but would serve to modify the distribution, and in the process of area normalization lead to a heightening of the central region. (It is important to emphasize that the number of loosely bound electrons need not be large, as positronium in particular would tend to form in defect regions where these electrons would also be found.) This type of effect would lead to nonzero values of β even in the absence of changes in the amount of positronium formed, because of changes in the shape of the broad component.

(*iii*) *A change in the degree of positronium thermalization.*—This could produce an apparent enhancement of the narrow component by decreasing its width and consequently causing an increase in height. This might be brought about in two ways: either by an increase in the efficiency of thermalization or by a change in the ability of positronium to reach thermal energies even in the presence of an efficient thermalizing mechanism. In regard to the first, some calculations by Wallace[2] lend doubt to the idea that positronium is completely thermalized in insulators within its lifetime.[17] Any changes in lattice structure, number of unbound electrons, etc. might then become important in determining the degree of thermalization before annihilation. Wallace does suggest that "ice" should prove one of the most favorable insulators for providing rapid thermalization. This is due to the prevalence of light hydrogen atoms and should not be particularly phase dependent, however.

The second consideration is probably of more importance. Positronium may tend to form and be trapped in defects or holes. Treating the situation at least in crude approximation as similar to that of a particle of mass $M=2m_0$ in a three-dimensional square well, the lowest lying energy level would be given by

$$E=\frac{\pi\hbar^2}{8Mr^2}=\frac{4.6\times10^{-16}}{r^2}\text{ ev cm}^2. \tag{1}$$

Trying the reasonable assumption $r\simeq4$ A, we find that such a trapped positronium atom would be prevented from having an energy <0.29 ev, which is in interesting agreement with the energies indicated in Table I. As thermal or phase-induced local expansions occur, the minimum energy would decrease rapidly due to the r^2 denominator, allowing an apparent enhancement of the narrow component caused in reality by a change in its shape. The validity of the foregoing approach of course depends on the degree to which positronium trapping actually occurs.

Now it is apparent that (*iii*) may lend itself to an explanation of the unusual effect observed in ice (Fig. 10). Here the narrow component corresponds, as shown in Sec. III, to a completely thermalized center of mass at the time of annihilation. It thus appears that in addition to any change in positronium production which may or may not be present, a greater degree of thermalization is also being allowed—apparently due to the greater spacing and lower molecular agitation found in ice as compared with the liquid phase. That this same effect does not seem to occur in other materials may be due to the fact that in other substances *higher* temperatures must be used to obtain lower densities. In particular, the phase-change direction which leads to lower densities in these substances is towards the direction of greater disorganization and molecular agitation; this would keep down the space available to the positronium atoms. Considering naphthalene and quartz in comparison to ice, one finds[18] that the latter has a hexagonal close-packed structure, with $a=4.52$ A and $c=7.32$ A, while naphthalene[19] has a monoclinic C crystal structure with $a=8.24$ A, $b=6.00$ A, $c=8.66$ A, and crystalline quartz[20] a hexagonal structure with $a=5.01$ A, and $c=5.47$ A. Making allowance for the large naphthalene molecule ($C_{12}H_{12}$) and the comparatively large SiO_2 molecule, it is apparent that water in its solid form should have a more open structure, particularly in the c direction. The $\sim5\times5$-A spacing in crystalline quartz is evidently too small to allow

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[16] Recently, R. E. Bell has reported [in an invited talk at the May, 1958 Washington Meeting of the American Physical Society; Bull. Am. Phys. Soc. Ser. II, **3**, 182 (1958)] that τ_2 lifetime quenching data from paramagnetic ions in water cannot be fitted to a theoretical curve which supposes some $^3S \leftrightarrow {}^1S$ conversion to be already present in pure water, thus supporting the conclusions reached here.

[17] Thermalization times in insulators are likely to be rather longer than in metals, since in the latter the high efficiency is due in large part to inelastic collisions with free electrons.

[18] D. M. Dennison, Phys. Rev. **17**, 20 (1921): a review of various and somewhat conflicting structure measurements is given by N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940).

[19] J. M. Robertson, Revs. Modern Phys. **30**, 155 (1958).

[20] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Sec. 2, p. 45.

positronium to exist. Allowing for the finite SiO_2 size, this seems reasonably in agreement with the expectation that the positronium binding energy will become positive when the wave function is too tightly cramped. (In fact it is merely necessary to change the binding energy to the point where the Ore gap no longer exists—see above.)

In conclusion it may be well to point out here some peculiarities in data concerning the water-ice transition. The 3γ annihilation rate is given by

$$R_3 \simeq (\tau_2/\tau_t) I_2 \qquad (2)$$

for the case where τ_2, the lifetime against pickoff, is $\ll \tau_t$, the triplet state lifetime (which is certainly the case for solids and liquids). This 3γ rate has been measured across the water-ice transition by Wagner and Hereford.[21] The data indicate with good accuracy that no sudden change in R_3 occurs at the freezing point. On the other hand, the original intensity data by Bell and Graham[3] indicated that I_2 remained approximately constant in both phases. (This now seems unlikely, however.) If we suppose that accurate measurements will show an increase of I_2 upon freezing—i.e., a "normal" behavior upon decreasing the density, as shown by naphthalene and quartz—then by Eq. (2), τ_2 should decrease in order to preserve the constancy of R_3. In actuality Bell and Graham's original measurements do indicate that τ_2 decreases sharply on the order of 30% upon freezing. But this is quite contrary to the expected behavior of the τ_2 ($\simeq$pickoff) lifetime in the face of decreasing density. On the other hand, if remeasurement should show τ_2 to increase or even stay constant, I_2 would have to behave anomalously. Thus either the R_3 measurements are in error, or an anomaly must unavoidably be present in the τ_2 or I_2 behavior. It is difficult to see what the cause of this might be, but further work on τ_2 intensity and lifetime changes across the phase transition should be quite valuable.

V. SUMMARY

The direct experimental results show the following. In all cases, the enhancement of the narrow component seems to be inversely related to density changes, both across phase transitions and within a single phase, strongly suggesting that the "temperature" effect is really a density effect. The half-widths of the narrow components for Teflon, naphthalene, and quartz all show about the same value, corresponding to an average center-of-mass energy at the time of annihilation of about 10 times the thermal energy for positronium. This is in qualitative agreement with Wallace's estimate[2] that thermalization may not be complete in insulators, although in fact the reason may not be due to an "inefficient" thermalization mechanism, but rather to positronium trapping in defects which results in a comparatively large zero-point energy. It is in any case interesting that these three rather different substances all show very nearly the same narrow-component half-width.

In ice, the narrow component indicates a center-of-mass energy of the same magnitude as the thermal energy. This may be allowed by the rather open nature of the ice lattice, and the fact that the molecules are rather well bound into a lattice structure, leaving a maximum of space available to the positronium atom.

In all cases investigated, the observed enhancement of the narrow component as a function of temperature or phase may be attributed, within the known limits of error, simply to increased formation of positronium brought about by more favorable density conditions, and there is little indication that other mechanisms which might be used to explain a narrow-component enhancement are in fact important.

ACKNOWLEDGMENTS

The authors are particularly grateful to Dr. R. A. Ferrell and Dr. E. A. Stern for many helpful discussions. We wish also to thank E. Hale and W. Isherwood, who at various times took on the lengthy job of translating some of the instrumental data into graphic form.

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[21] R. T. Wagner and F. L. Hereford, Phys. Rev. **99**, 593 (1955), or, for greater clarity in the plotted points, the review article by Berko and Hereford, reference 1, p. 304.