Positron Annihilation in Alkali Halides*

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The time annihilation spectrum of positrons in most alkali halides is measured. Positrons appear to decay through at least two different processes which lead to a complex time annihilation spectrum. The first component is conceivably due to positrons which annihilate when free; the second, which occurs with an intensity I_2 between 25 and 85%, is characterized by a mean life τ_2 whose amount ranges between 4×10^{-10} and 8×10^{-10} sec. From the whole set of the collected data, empirical regularities can be extracted; the annihilation rate λ_2 appears simply correlated with the molecular density n within each halides series, according to the relation: $\lambda_2 = \lambda_0 + \alpha n$. λ_0 decreases, passing from fluorides to bromides, and α turns out to be simply proportional to the square of the radius of negative ion. The τ_2 component is sensitive to the application of a static magnetic field; the magnetic quenching, however, is appreciably lower than what would be expected if one attributes this component to the decay of a free positronium atom.

I. INTRODUCTION

POSITRON annihilation studies so far have been carried out on several materials; the series of alkali halides, however, have been neglected as far as concerns lifetime measurements, despite the simple structure of these crystals and the intrinsic interest connected with the possibility of capture of the positron by the negative ion. Bell and Graham,[1] in their pioneer work on positron lifetime in different substances, found in NaCl a qualitatively similar result to those in metals. No other measurements have since been reported; the only notice is quoted by Wallace,[2] according to which positrons live in a fluoride longer than in an iodide. The energetics of positronium formation in ionic crystals was discussed by Ferrel,[3] who showed that the formation of a positronium atom is energetically not permitted; essentially this is simply due to the fact that there is no room in the crystals for a positronium atom. Ferrel also discussed the possibility that the positron might be captured by the negative ion and was led to the conclusion that a bound positron should have a lifetime roughly varying with the cube of the ionic radius. The existence of a bound system consisting of a neutral chlorine atom, an electron, and a positron was first suggested by Wheeler[4]; an accurate mathematical treatment was given by Simons.[5] Ferrel has given an analysis of the angular distribution of annihilation quanta, based on his model of a bound positron; his arguments have been discussed by Lang and de Benedetti.[6] At present, several results are available on the angular distribution of photons from electron-positron annihilation from alkali halides. In particular, Stewart and Pope[7] were led to the conclusion that if the positron is

to be represented by a single-particle wave function, it must not be considered as localized on any negative ion. In any case it seems that nobody has considered the possibility that positrons in ionic crystals can be annihilated through different processes occurring with nearly equal probability.

It is our intention to report in this paper the results of an extensive investigation on positron lifetimes in alkali halides. In fact, a previous measurement[8] has clearly shown the need to get a large empirical background in order to throw more light on the ultimate fate of positrons in ionic crystals.

II. EXPERIMENTAL METHOD

The experimental setup used in this work has been described in a preceding paper[9] and employs a nanosecond Vernier time-delay analyzer. We shall not describe its features here but wish only to mention the improvement made to the nanosecond analyzer, consisting of a time range expansion so that delays up to 4×10^{-8} sec are now measurable.

The positron emitter used was Na^{22}; one drop of high specific activity solution of $Na^{22}Cl$ was dried on an aluminum foil (0.18 mg/cm^2 thick) sandwiched between the specimens under investigation; their thickness was sufficient to stop all positrons. The specimens were multicrystalline analytical reagent-grade chemicals; in two cases (NaCl, KCl) single crystals were used too. The whole process was carried out in a glove dry box and the sandwich source-specimen was enclosed in a Lucite, hermetically sealed container. All the containers were equivalent to one another.

The technique and the experimental method used in this work for the measurement of magnetic quenching of τ_2 component in KCl was previously described in a paper which reported the results of magnetic quenching experiments on positronium in plastic materials.[10]

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[1] R. E. Bell and R. L. Graham, Phys. Rev. 90, 644 (1953).
[2] P. R. Wallace, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1.
[3] R. A. Ferrel, Rev. Mod. Phys. 28, 308 (1956).
[4] J. A. Wheeler, Ann. N. Y. Acad. Sci. 48, 219 (1946).
[5] L. Simons, Phys. Rev. 90, 165 (1953).
[6] G. Lang and S. de Benedetti, Phys. Rev. 108, 914 (1957).
[7] A. T. Stewart and N. K. Pope, Phys. Rev. 120, 2033 (1960). This article gives references to earlier works.

[8] A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. 131, 1023 (1963).
[9] A. Bisi, A. Fasana, E. Gatti, and L. Zappa, Nuovo Cimento 22, 266 (1961).
[10] A. Bisi, A. Fiorentini, E. Gatti, and L. Zappa, Phys. Rev. 128, 2195 (1962).

III. RESULTS

A. Annihilation Rates

The inspection of the time spectrum of positrons annihilating in alkali halides shows that the decay is complex. An example is reported in Fig. 1, where at least two components are clearly distinguishable: The first, τ_1 (as a matter of fact it cannot be shown to be single), is the one distorted by the resolution of the apparatus, the second, τ_2, is the main object of our work. Both in cases where the complexity of the spectrum is easily seen, and in those where it is less easily seen, the analysis of the spectral shape, made with the aid of the first three moments, has shown unambiguously the composite nature of the decay. The
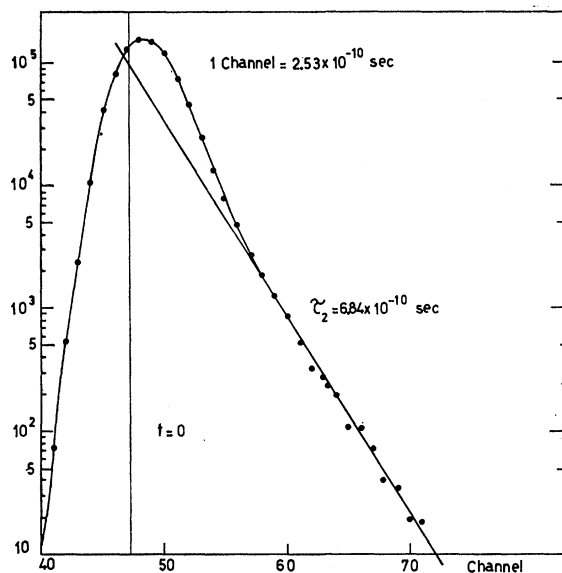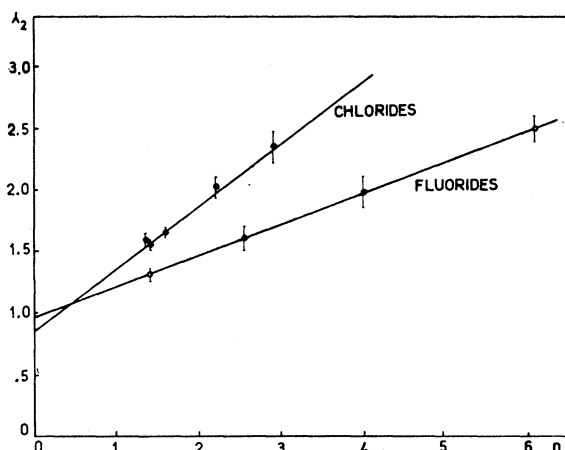

FIG. 1. Time spectrum of positrons annihilating in CsBr.

FIG. 2. Annihilation rate λ_2 (units: 10^9 sec^{-1}) of long-lived positrons in alkali chlorides and fluorides as a function of molecular density n (units: 10^{22} cm^{-3}).

method of the moments, however, was not used to deduce the lifetime of the component and its intensity. Lifetimes were obtained by reading them directly from the logarithmic slopes of the recorded curves; intensities too were obtained from the graphs. In some cases the decaying part of the curve is not fitted with a single exponential owing to the presence of a rather flat tail. If one draws a reasonable straight line through the points of the tail, a τ_3 component is obtained whose intensity does not attain 1%. No comments can be made at present on this tail; the fact that it has not been observed in all specimens indicated that it was not instrumental. Perhaps a third process of annihilation could show itself with a very weak probability.

Table I collects the results (we wish to emphasize that the results with multicrystalline specimens and single crystals were identical) and shows the following
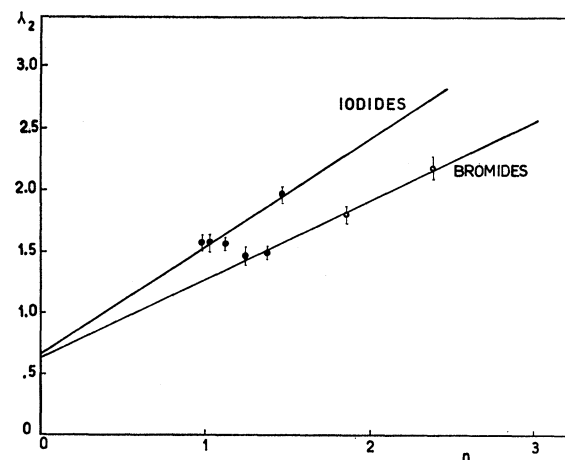
TABLE I. Long lifetimes of positrons in alkali halides; n indicates the molecular density, τ_2, I_2, τ_3, and I_3 indicate mean lives and intensities of the long-lived components.

Halide	$n \times 10^{-22}$	$\tau_2 \times 10^{10}$ sec	I_2 (%)	$\tau_3 \times 10^9$ sec	I_3 (%)
LiF	6.04	4.02±0.20	70±15	2.7	0.8
NaF	4.00	5.05±0.35	49±5	2.5	1.4
KF	2.57	6.20±0.40	33±7	2.7	0.4
CsF	1.42	7.60±0.21	46±5	···	···
LiCl	2.94	4.25±0.25	30±10	···	···
NaCl	2.23	4.96±0.24	52±15	2.0	0.9
KCl	1.60	6.07±0.12	50±15	···	···
RbCl	1.37	6.27±0.19	31±10	···	···
CsCl	1.42	6.39±0.18	25±4	···	···
LiBr	2.40	4.58±0.20	85±10	3.6	1.0
NaBr	1.87	5.56±0.20	34±7	3.6	0.9
KBr	1.39	6.73±0.22	37±7	···	···
CsBr	1.26	6.84±0.33	31±4	···	···
NaI	1.48	5.11±0.18	61±9	3.3	1.2
KI	1.13	6.40±0.21	43±7	···	···
RbI	1.00	6.36±0.18	56±15	3.9	0.2
CsI	1.05	6.36±0.29	25±4	3.9	0.8

FIG. 3. Annihilation rate λ_2 (units: 10^9 sec^{-1}) of long-lived positrons in alkali iodides and bromides as a function of molecular density n (units: 10^{22} cm^{-3}).
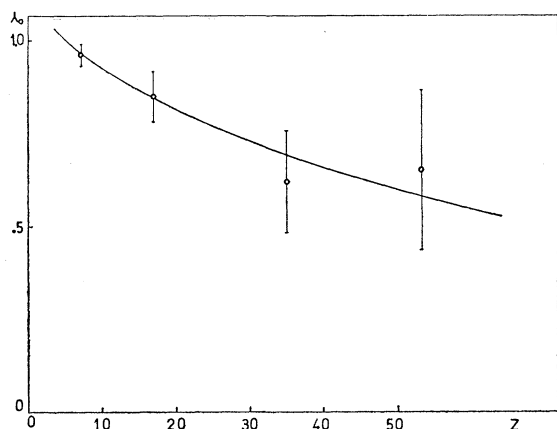
FIG. 4. Extrapolated value λ_0 (units: 10^9 sec^{-1}) of annihilation rate to zero molecular density as a function of the atomic number of the negative ion.

empirical regularity: Within each series of alkali halides, the lifetime decreases with increasing molecular density. A graph (Figs. 2 and 3) where the annihilation rates λ_2 are plotted against molecular densities n clearly shows that the points fit a straight line for each series. It follows that we can write the following equation:

$$\lambda_2 = \lambda_0 + \alpha n \qquad (1)$$

and deduce from the graph λ_0 and α for each series. We found that λ_0 decreases and α increases when passing from fluorides to iodides. In order to express this relationship, we tentatively chose the simplest quantities that characterize the negative ion, i.e., atomic number Z and ionic radius r. The best fits are obtained between λ_0 and Z and between α and r. Figures 4 and 5 illustrate these relationships, the second of which is simply expressed by the equation

$$\alpha = K r^2,$$

where $K = 1.90 \times 10^2$ cm sec^{-1}.

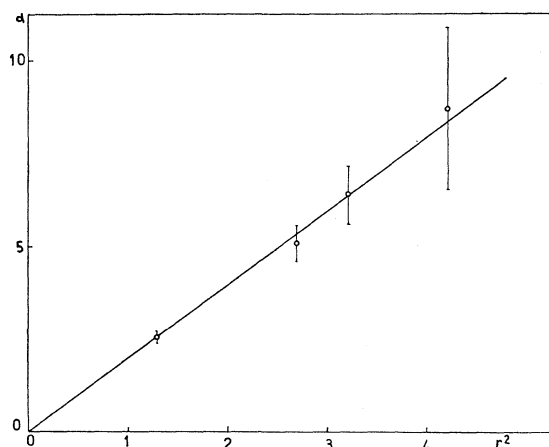FIG. 5. α as a function of the square of the negative ion radius r [see Eq. (1)]. Units: α in 10^2 cm^3 sec^{-1}, r in 10^{-8} cm.

As far as regards the intensity I_2 of the τ_2 component, the size of the experimental errors do not permit us to establish the existence of empirical regularities. Perhaps there is a tendency for smaller positive ions to show a greater intensity.

B. Magnetic Quenching

The influence of a magnetic field on the hyperfine structure of a free positronium atom is well known[11]: It consists of a mixing of the magnetic substates with $m = 0$ and hence of a quenching of the orthostates. As far as concerns magnetic quenching of positronium in solids, a recent investigation[10] has shown that in Teflon and Lucite the measured quenching and the predicted one are identical within experimental errors. It means that at least in these polymeric materials, the positronium
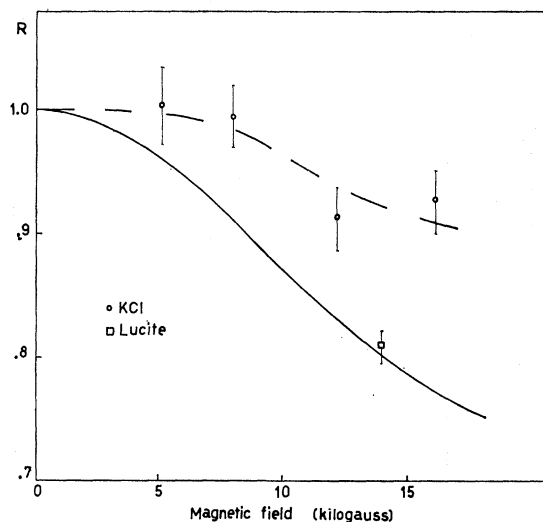

FIG. 6. Relative intensity of the τ_2 component in KCl with and without magnetic field. The full line gives the quenching for a free positronium atom.

atom behaves as though it were free or, more exactly, the solid does not perturb the hyperfine splitting. We have made a magnetic quenching experiment on the τ_2 component and have chosen for that purpose the single-crystal KCl as a specimen, because in this case the weak τ_3 component is absent. Clearly our aim was to establish whether the τ_2 component arises from the decay of a system having the same features as the orthopositronium in polymeric materials. We shall not deal here with the detailed theory of the experiment as it has been already described in the quoted paper.[10]

The measurements consisted of several recording runs of time spectra taken alternatively with and without field. From the spectra we have evaluated the ratio R of the numbers of those events which have survived a prefixed time $t_1 = 3.30 \times 10^{-9}$ sec, with and without

[11] O. Halpern, Phys. Rev. 94, 904 (1954).

field. The results are reported in Fig. 6 where the full line gives the quenching R which one would expect if the τ_2 component arose from orthopositronium decay. As may be seen, all the experimental points lie much above the calculated curve; to check that this fact does not originate from the experimental setup, we have repeated the experiment, all conditions remaining unchanged, with positrons in Lucite. In this case the results quite agree with the expectations; the corresponding experimental point is also reported in the same graph.

Clearly, the assumption that in alkali halides a bound system can be formed with the same properties as the free positronium is seriously contradicted by this experiment.

IV. DISCUSSION

We wish now to give a tentative sketch of the ultimate fate of positrons in alkali halides.

It is reasonable to assume that a fraction of positrons, when slowed down, annihilates freely as in metals, with a lifetime of about 2×10^{-10} sec; these positrons certainly contribute to the τ_1 component. Moreover, we are forced to assume that the remainder of the positrons, a fraction as large as 50%, annihilate through a different process where the negative ion plays a prevailing role.

This picture is supported by the fact that the measured annihilation rates λ_2 display a regular behavior within each alkali series. The relation between λ_2 and the molecular density n is certainly empirical in nature and this fact must be kept in mind in discussing Eq. (1), where the annihilation rate is expressed as a sum of two terms. In effect, if Eq. (1) is no more than an interpolative formula which accounts quite well for the experimental results, there is no place for further comments on it. On the contrary, if we attribute to it a precise physical significance, we must conclude that the positrons responsible for the τ_2 component annihilate through two competitive processes. The first is described by a partial rate which is independent of the molecular density and the second by a partial rate simply proportional to n. A simple assumption comes forth spontaneously from these considerations, i.e., that of a positron

bound into a system with one or more electrons; in this case the positron can annihilate with one of its own electrons (annihilation rate λ_0) and with an electron of surrounding atoms (annihilation rate proportional to n).

The assumption of a bound system is sustained by the complexity of the annihilation time spectrum and moreover by the results of the magnetic quenching experiment. It is, in fact, implausible that a quenching can exist for free positrons; for instance, we have ascertained that a magnetic field has no influence at all on positrons annihilating in metals. On the other hand, the amount of the observed quenching prevents us from identifying the bound system with a positronium atom, as already emphasized in the preceding section. This does not exclude the possibility that the positron can be bound primarily to one electron. Here we are using the word "positronium" in its original significance, i.e., a positron-electron bound system in free space described by the well-known wave functions.[12]

An attractive assumption is that in alkali halides, Wheeler[4] compounds are formed similar to those studied by Simons,[5] i.e. $(\mathrm{Cl}\ e^-)e^+$ or $(\mathrm{Cl})(e^-e^+)$. In contrast with the suggestion contained in our previous paper,[8] however, the present results seem to favor the formation of systems of the type $(\mathrm{Cl})(e^-e^+)$—a complex where the two particles in parenthesis are more closely bound to one another than the third. In fact, the other possible systems, of the type $(\mathrm{Cl}\ e^-)e^+$, where the negative ion had zero-orbital and spin-angular moment, could not account for the existence of a magnetic quenching. Otherwise, the good agreement between the measured λ_0 value for chlorides and the annihilation rate predicted by Simons for this last system on the assumption that the probability of antiparallel spin is 1:4 could favor at first sight, $(\mathrm{Cl}\ e^-)e^+$. The high intensity of the τ_2 component, however, and the absence in the time spectra of another component with comparable intensity and longer lifetime, furnish a further argument which suggests taking into greater consideration a system like $\mathrm{Cl}(e^-e^+)$ than $(\mathrm{Cl}\ e^-)e^+$.

[12] H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin 1957), Vol. XXXV, p. 88.