Positron Annihilation in Solid and Molten Alkali Chlorides

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The time annihilation spectra of positrons were measured in solid and liquid NaCl, KCl, and CsCl at
temperatures between 295 and 1223°K. An abrupt change of the spectral shapes is observed at melting.
It was possible to show that the so-called A-center model, which is based on the assumption that the positron
can be captured by a lattice defect, can account for this effect. In the framework of the A-center model, an
effective electron number has been calculated which increases when passing from LiCl to CsCl.

I. INTRODUCTION

THE formation of positron bound states in alkali
halides was discovered some years ago by Bisi,
Fiorentini, and Zappa[1,2] by means of the lifetime
technique. The time annihilation spectra were recently
reexamined with an improved timing apparatus by
Bussolati, Dupasquier, and Zappa,[3] who obtained more
accurate lifetime and intensity values for the various
spectral components (this work will be referred to as I
in the following).

As far as regards the nature of the bound states,
Ferrell[4] has shown that Positronium formation is
energetically unfavored and the results of angular
correlation[5] and three-quantum decay yield measure-
ments[6] confirm that Positronium is not formed in
alkali halides. Gol'danskii and Prokop'ev[7-9] have
proposed three different bound-state models: (1) the
system e^+-anion, (2) self-trapping of the positron in a
polaronic bound state, and (3) positron capture by a
lattice defect (annihilation center or A-center model).
Brandt[10] has studied the vacancy A-center model, i.e.,
the bound system e^+-cation vacancy; this model seems
to be supported by quite recent measurements in NaCl
after plastic compression and after x-ray irradiation.[11]

In the present paper, we report the results of an
experimental investigation in which the annihilation
characteristics have been studied in some alkali
chlorides (NaCl, KCl, and CsCl) by means of the life-
time technique, observing temperature and phase-
transition effects. The obtained results are discussed
with reference to the A-center model.

II. EXPERIMENTAL PROCEDURE

The positron emitter (about 50 μCi of Na^{22} from a
carrier-free NaCl solution) was dispersed in the salt
under investigation. The salt specimens were multi-
crystalline analytical reagent-grade powders. Each
specimen was introduced in a quartz vial, dehydrated
in vacuum for 36 h at about 100°C below the melting
point, hermetically sealed, and then left to cool down
to room temperature. The quartz vial was 20 mm in
i.d.$\times$30 mm high; a conservative estimate of the
positron escape probability ensures that the fraction of
annihilations in the quartz walls is less than 2%. In the
reduction of the experimental data, the effect of this
fraction has been neglected.

The measurements were performed at various tem-
peratures, starting from room temperature, rising
stepwise up to the melting point and beyond it, and
then going slowly back to room temperature. The
heating was obtained by means of a small resistence
furnace (outer diameter 50 mm) inserted between the
scintillation counters. The temperature of the furnace
was automatically controlled within $\pm$10°C. Water
cooling of the scintillators and of the photomultipliers
was provided.

The time-measuring setup has been previously
described.[12] The over-all resolution curve, measured
with a Co^{60} γ-ray source, has sides simulating a simple
exponential decay through at least four decades. The
full width at half-maximum (FWHM) is 3.0×10^{-10} sec
and the logarithmic slope of the sides corresponds to a
half-life of 5×10^{-11} sec.

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TABLE I. Mean lives and intensities of positrons in alkali chlorides at various temperatures.

Salt	T (°K)	Phase	τ_1 (10^{-10} sec)	τ_2 (10^{-10} sec)	τ_3 (10^{-10} sec)	I_1 (%)	I_2 (%)	I_3 (%)
NaCl	295	fcc	3.20±0.22	6.70±0.27	···	79±8	17.1±1.5	···
	423	fcc	3.15±0.22	6.50±0.26	···	68±7	25.0±1.5	···
	523	fcc	3.25±0.23	6.72±0.27	···	80±8	22.9±1.5	···
	723	fcc	3.50±0.24	6.75±0.27	···	78±8	20.3±1.5	···
	973	fcc	3.63±0.25	6.64±0.27	···	77±8	17.7±1.5	···
	1123	liquid	···	4.90±0.19	···	···	100 ±5	···
	1123	liquid	···	4.80±0.19	···	···	104 ±5	···
KCl	295	fcc	2.89±0.20	6.68±0.27	···	62±6	41.2±3.0	···
	673	fcc	3.48±0.24	7.92±0.32	···	65±6	37.9±3.0	···
	1083	liquid	3.07±0.21	9.09±0.36	···	49±5	53.9±3.5	···
CsCl	295	sc	1.64±0.16	4.44±0.18	12.3±0.50	29±4	62 ±4	10.1±0.5
	573	sc	1.70±0.16	4.71±0.20	13.4±0.55	21±3	75 ±5	10.3±0.5
	778	fcc	2.12±0.16	5.60±0.22	13.5±0.55	22±3	57 ±4	19.4±1.0
	873	fcc	2.18±0.16	5.10±0.20	13.9±0.55	20±3	60 ±4	24.7±1.2
	973	liquid	···	3.70±0.25	12.1±0.50	···	68 ±7	37.0±1.8
	1073	liquid	···	3.35±0.23	10.1±0.40	···	61 ±6	44.2±2.2
	1153	liquid	···	3.34±0.23	7.5±0.30	···	56 ±6	46.5±2.3

The analysis of the spectral shapes was performed by fitting a sum of exponential functions with a least-squares method; a 7040 IBM computer was used. The first approximation values were obtained by a maximum-likelihood method, described in a previous paper.[13]

III. RESULTS

All the results of our measurements are collected in Table I. The quoted errors are conservative estimates, greater than the statistical scatter of the obtained results, in order to take into account some possible systematic errors that could arise from the time calibration of the time-amplitude converter, from the data analysis procedure, and from the annihilations in the walls of the quartz container.

The spectral components pertaining to the solid phase are numbered in order of increasing lifetimes as in paper I. For the sake of simplicity, the same indexes are also used for the liquid phase, although a sharp discontinuity occurs at the melting point and it is questionable to ascribe to the same origin components pertaining to different phases. The chosen numeration rests on the A-center model we discuss in Sec. IV.

The long-lived tail in the spectra of NaCl and KCl, quoted in paper I, has been found to disappear after a prolonged high-temperature dehydration. In consequence of this result, we can confirm the spurious origin of the tail and attribute it to moisture collected on the surface or even inside the grains.

The investigated salts display a somewhat different behavior and the main peculiarities observed may be summarized as follows:

(a) NaCl: Two components are resolved at all temperatures below the melting point. The shortest

[13] M. Bertolaccini, A. Bisi, and L. Zappa, Nuovo Cimento **46**, 237 (1966).

lifetime displays a slight increase with increasing temperature, while no temperature effect is observed in the second lifetime. The relative intensities do not follow a monotonic trend. After melting, the time spectrum becomes simple: An unique exponential decay is observed, with a mean life intermediate between those in the solid and an intensity equal to 100% within the achievable accuracy. It is to be noted that, after cooling, all the annihilation characteristics are restored to their initial values; this reversibility also holds in the case of the other salts. Two typical spectra are shown in Figs. 1(a) and 1(b); in Fig. 2, the measured mean lives are reported as functions of the temperature.

(b) KCl: Measurements were performed at three different temperatures. The spectra are resolved into two components in both cases of the solid and the liquid salt. The mean life τ_1 in the liquid is shorter than the mean life τ_1 in the solid at $T=673$°K.

(c) CsCl: This salt undergoes a solid-state phase transition from the simple-cubic (sc) to the face-centered-cubic (fcc) structure at $T=742$°K. The spectra pertaining to both phases can be analyzed into three components. An abrupt increase of τ_2 is observed at the phase transition, whereas τ_3 remains nearly unaffected. After melting, only two components can be distinguished, with relative intensities summing up to 100%. The shortest mean life is intermediate between the first two mean lives in the solid. The longer living component has a mean life that approaches the mean life of the third component in the solid near the melting point and then decreases markedly with increasing temperature. In Fig. 3, we report the mean lives in CsCl as functions of the temperature.
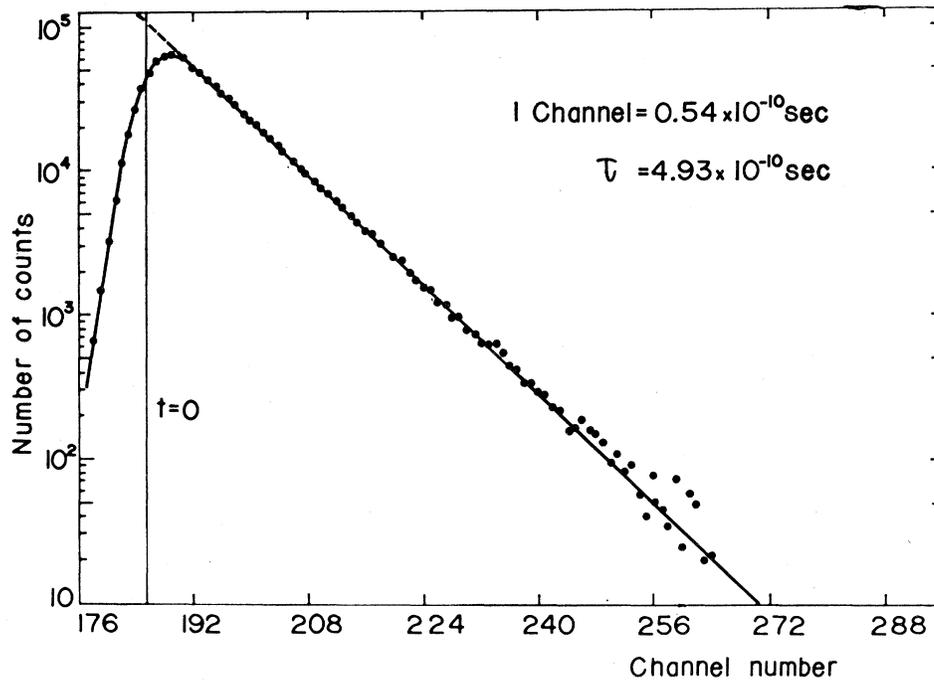
IV. DISCUSSION

The results exposed in Sec. III show that the number of components decreases at melting from two to one in
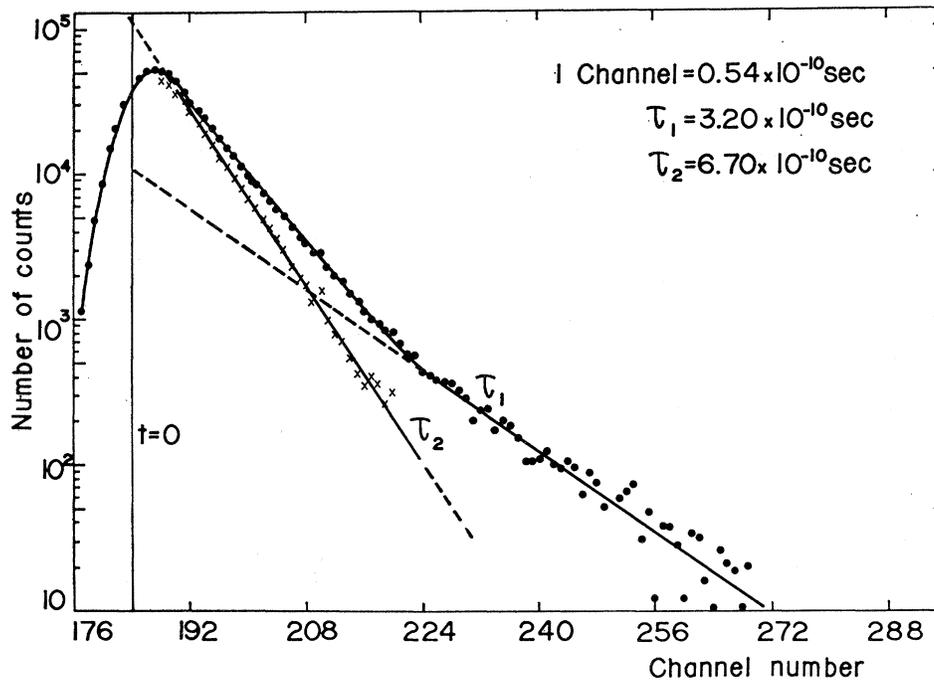
FIG. 1. (a) Time spectrum of positrons annihilating in solid NaCl at 295°K.
(b) Time spectrum of positrons annihilating in liquid NaCl at 1123°K.

the case of NaCl and from three to two in the case of CsCl.

It is difficult to understand this behavior on the basis of a model attributing the various spectral components to positrons bound in different energy levels of the system $Cl^- e^+$. Should this system be formed in the solid phase, it would be stable in the liquid phase, too. It could not be dissociated by thermal collisions because

of its high binding energy: 3.74 eV for the fundamental state (in vacuum), after Simons's calculations,[14] and no less than 2.39 eV for the first excited state (inside a halide crystal), after the estimate given in Paper I.

On the contrary, an explanation can be given if it is assumed that a trapping process by lattice defects (*A* centers) is effective. It is to be noted that the vanishing of one spectral component after melting is not to be attributed to the absence of *A* centers in the liquid, but can be justified by an enormous increase of the trapping and escape probabilities. This will be clear from the following discussion.

We assume that, at the time *t* after the injection in the material and after instantaneous thermalization, the fraction $n_1(t)$ of positrons is free and the fraction $n_2(t)$ is trapped in *A* centers. Following Brandt's[10] suggestion, the *A* centers involved could be positive ion vacancies. The n_1 positrons may annihilate when free or be captured by *A* centers; conversely, the fraction n_2 may annihilate when bound in the trapping center or escape from it. If a third component is also present in the time spectrum, it could be caused by the existence of a second type of *A* centers; for instance, chemical impurities or chlorine molecular complexes (Cl_2, Cl_2^-) resulting from a stoichiometric unbalance.

We indicate by $n_3(t)$ the positron fraction trapped at the time *t* by *A* centers of the second type. We assume that the annihilation rates, the capture rates in the
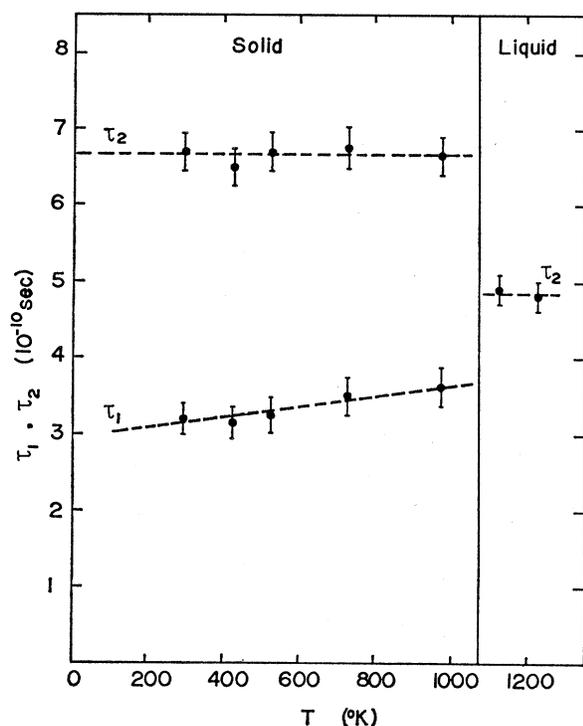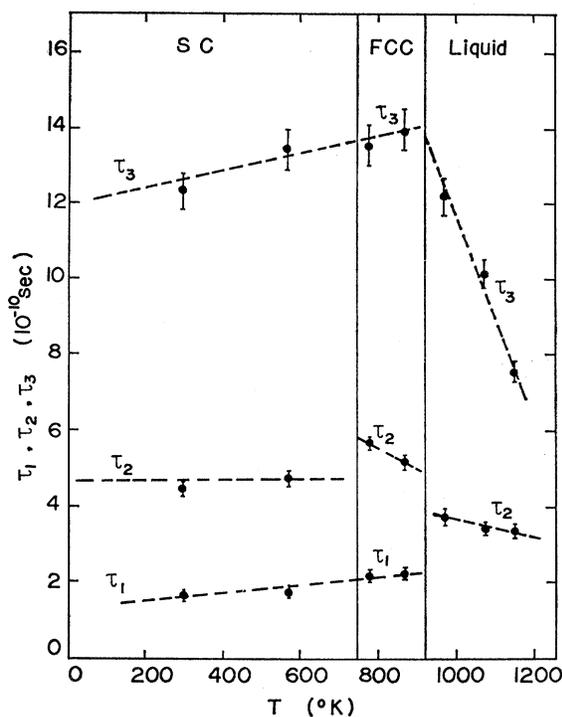

FIG. 3. Mean lives in solid and liquid CsCl.

first- and second-type *A* centers, and the escape rates are constant in time; the possibility of a direct transition $n_2 \rightarrow n_1$ is neglected. With these hypotheses, the population balance between the possible states is described by a simple system of differential equations, from which the following observable annihilation rates $\Gamma_i = \tau_i^{-1}$ are obtained:

In the two-components case,

$$\Gamma_1 = \tfrac{1}{2}(\gamma_1 + \gamma_2 + \kappa + \lambda + \{[(\gamma_1 + \kappa) - (\gamma_2 + \lambda)]^2 + 4\kappa\lambda\}^{1/2}),$$
$$(1a)$$
$$\Gamma_2 = \tfrac{1}{2}(\gamma_1 + \gamma_2 + \kappa + \lambda - \{[(\gamma_1 + \kappa) - (\gamma_2 + \lambda)]^2 + 4\kappa\lambda\}^{1/2}).$$

In the three-components case,

$$\Gamma_1 = -p_1,$$
$$\Gamma_2 = -p_2, \qquad (1b)$$
$$\Gamma_3 = -p_3,$$

where p_1, p_2, p_3 are the roots of the equation

$$\mathrm{Det} \begin{bmatrix} p+\gamma_1+\kappa+\kappa' & -\lambda_1 & -\lambda_2 \\ -\kappa_1 & p+\gamma_2+\lambda & 0 \\ -\kappa_2 & 0 & p+\gamma_3+\lambda' \end{bmatrix} = 0. \quad (2)$$

The symbols used in Eqs. (1a), (1b), and (2) have the following meaning:

γ_1: annihilation rate for untrapped positrons;

γ_2, γ_3: annihilation rates for trapped positrons;

κ, κ': capture rates for first- and second-type *A* centers;

FIG. 2. Mean lives in solid and liquid NaCl.

[14] L. Simons, Phys. Rev. **90**, 165 (1953).

λ, λ': escape rates from first- and second-type centers. If we assume that the number of positrons captured by A centers, during slowing down, is negligible, so that $n_1(0)=1$, $n_2(0)=0$, and $n_3(0)=0$, the lifetime spectrum $s(t)$ becomes, in the two-components case,

$$s(t)=I_1\Gamma_1 e^{-\Gamma_1 t}+I_2\Gamma_2 e^{-\Gamma_2 t}, \qquad (3')$$

where the intensities I_1, I_2 are given by

$$I_1=(\gamma_1-\Gamma_2)/(\Gamma_1-\Gamma_2),$$
$$I_2=(\Gamma_1-\gamma_1)/(\Gamma_1-\Gamma_2); \qquad (4')$$

and in the three-components case,

$$s(t)=I_1\Gamma_1 e^{-\Gamma_1 t}+I_2\Gamma_2 e^{-\Gamma_2 t}+I_3\Gamma_3 e^{-\Gamma_3 t}, \qquad (3'')$$

where the intensities I_1, I_2, I_3 are given by

$$I_1=\frac{\gamma_1[\Gamma_1-(\gamma_2+\gamma_3+\lambda+\lambda')]+\Gamma_2\Gamma_3-\gamma_2\kappa-\gamma_3\kappa'}{(\Gamma_1-\Gamma_2)(\Gamma_1-\Gamma_3)},$$

$$I_2=\frac{\gamma_1[\Gamma_2-(\gamma_2+\gamma_3+\lambda+\lambda')]+\Gamma_3\Gamma_1-\gamma_2\kappa-\gamma_3\kappa'}{(\Gamma_1-\Gamma_2)(\Gamma_3-\Gamma_2)}, \qquad (4'')$$

$$I_3=\frac{\gamma_1[\Gamma_3-(\gamma_2+\gamma_3+\lambda+\lambda')]+\Gamma_1\Gamma_2-\gamma_2\kappa-\gamma_3\kappa'}{(\Gamma_2-\Gamma_3)(\Gamma_1-\Gamma_3)}.$$

It is easy to see from Eqs. (1a) and (4') that, if we take the limit for $\kappa\to\infty$ and $\gamma\to\infty$, we have $\Gamma_1\to\infty$ and $I_1\to 0$. The annihilation rate Γ_2 becomes

$$\Gamma_2=f\gamma_1+(1-f)\gamma_2, \qquad (5)$$
where
$$f=\lambda/(\kappa+\lambda). \qquad (6)$$

An analogous result can be obtained in the three-components case. For $\kappa\to\infty$ and $\lambda\to\infty$, we have $\Gamma_1\to\infty$ and $I_1\to 0$; the annihilation rates of the residual components can be obtained from Eq. (1a) after replacing γ_1 with $\bar{\gamma}=f\gamma_1+(1-f)\gamma_2$, κ with $\bar{\kappa}=f\kappa'$, λ with λ', and γ_2 with γ_3. The above results are independent of any assumption on initial values for n_1, n_2, and n_3.

The asimptotic case $\kappa\to\infty$ and $\lambda\to\infty$ describes adequately the actual situation in a liquid halide. In fact, it is easy to see that λ and κ after melting become much greater than the characteristic annihilation rates γ_i. An approximate evaluation of κ is given by

$$\kappa=\pi r_A^2 v_{th}\rho_A, \qquad (7)$$

where r_A is the effective capture radius of the first-type A center, ρ_A is the number of A centers per unit volume, and v_{th} is the thermal velocity of the positron. It is well known that the fundamental properties of liquid alkali halides are satisfactorily accounted for by the "hole model."[15-17] In this model, the structure of the liquid

is described as a nearly regular assembly of ions, among which a number of holes (i.e., vacancies, in the usual solid-state physics language) is mixed at random. The total volume of the holes is approximately equal to the volume change at melting. From the known value of the fractional change in volume $\Delta V/V\simeq 0.2$, we get $\rho_A\simeq 2\times 10^{21}$ cm^{-3}, about a factor of 10^3 higher than the defects concentration in thermal equilibrium before melting. The capture radius r_A can be roughly estimated as being equal to the cation radius, i.e., $1\div 2$ Å. Inserting the above values in formula (7), and setting $v_{th}(10^3 °K)\simeq 2\times 10^7$ cm sec^{-1}, we obtain

$$\kappa=1\div 4\times 10^{12} \text{ sec}^{-1}.$$

A lower limit for λ is represented by the rate of vacancy disappearance, as a consequence of the ions transfer from lattice sites into vacancies. Thus,

$$\lambda\geq\nu e^{-E/KT}, \qquad (8)$$

where $\nu(10^{13}$ sec$^{-1})$ is the frequency of thermal vibrations and E is the activation energy for the transfer process. E is roughly given[18] by

$$E=\tfrac{1}{5}H/N_A, \qquad (9)$$

where N_A is Avogadro's number and H is the activation heat of viscous flow (about 10 kcal mole^{-1}). At $T=1000°K$, the exponential factor is about $\tfrac{1}{3}$, so that we have $\lambda\geq 3\times 10^{12}$ sec^{-1}. The annihilation rates γ are of the same order of magnitude as the measured rates Γ, i.e., less than 10^{10} sec^{-1}. A factor of 10^2 or more is then to be expected between the capture and escape rates and the annihilation rates in ionic liquids. Thus, as we have already anticipated, the A-center model can account for the behavior observed in NaCl and CsCl. However, in KCl, the number of components does not change after melting; this fact seems to be at variance with the theory, although the observed decrease of τ_1 is in predicted sense. At present, we have no arguments to explain this disagreement.

Some interesting informations on the positron behavior in solid alkali halides can be extracted from the experimental data in the framework of the A-center model. The characteristic annihilation rate for untrapped positrons can be calculated using Eqs. (4') or (4''), provided the assumption made on initial conditions is correct. We have, for the two-components case,

$$\gamma_1=\Gamma_1-I_2(\Gamma_2-\Gamma_1), \qquad (10a)$$

and for the three-components case,

$$\gamma_1=\Gamma_1-I_2(\Gamma_2-\Gamma_1)-I_3(\Gamma_3-\Gamma_1). \qquad (10b)$$

The other parameters can not be calculated without additional assumptions, the number of the unknowns being greater than the number of available independent

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[16] W. Altar, J. Chem. Phys. **5**, 577 (1937).
[17] R. Fürth, Proc. Cambridge Phil. Soc. **37**, 252 (1941).

[18] S. Glasstone, K. J. Saidler, and H. Eyring, in *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941), p. 489.

TABLE II. Annihilation rates for free positrons deduced from measured mean lives and intensities in the framework of the A-center model.

Salt	T (°K)	$(\rho/M)\times10^2$ (mole cm^{-3})[a]	γ_1 (10^9 sec^{-1})	Paper
LiCl	295	4.88	3.29±0.12	Paper I
NaCl	295	3.70	2.71±0.11	Paper I
	295	3.70	2.84±0.19	Present paper
	423	3.67	2.76±0.17	Present paper
	523	3.59	2.71±0.17	Present paper
	723	3.49	2.58±0.15	Present paper
	973	3.37	2.52±0.16	Present paper
KCl	295	2.66	2.79±0.11	Paper I
	295	2.66	2.65±0.15	Present paper
	673	2.59	2.26±0.13	Present paper
RbCl	295	2.31	3.06±0.13	Paper I
CsCl	295	2.37	3.25±0.14	Paper I
	295	2.37	3.18±0.24	Present paper
	573	2.27	2.52±0.21	Present paper
	778	1.87	2.27±0.15	Present paper
	873	1.84	2.05±0.14	Present paper

[a] The density values are taken from Ref. 19.

equations. A simple approach has been attempted by Brandt,[10] who postulated that the escape probability from A centers may be neglected in ionic crystals. With this assumption, the following equations hold:

$$\kappa = I_2(\Gamma_2 - \Gamma_1), \tag{11}$$

$$\kappa' = I_3(\Gamma_3 - \Gamma_1). \tag{12}$$

However, the product $I_2(\Gamma_2 - \Gamma_1)$, calculated from our experimental results, does not increase monotonically with temperature, as would be expected, because κ is proportional to the concentration of vacancies. We remember that in our experiments no thermal hysteresis was observed; therefore, the equilibrium conditions were presumably reached. We think that more sophisticate assumptions are necessary for a full comprehension of the argument.

[19] *Molten Salts Handbook*, edited by G. J. Jantz (Academic Press Inc., New York, 1967).

TABLE III. Effective number of electrons per ion couple.

Salt	ξ
LiCl	15.0±0.5
NaCl	16.6±0.6
KCl	21.6±2.0
RbCl	29.4±1.2
CsCl	27.5±2.0

According to Eqs. (10a) and (10b), we have calculated the γ_1 values from the experimental results of this paper and Paper I. These values are collected in Table II, where the molar density ρ/M is also reported. A correlation between γ_1 and molar density must be expected if the untrapped positrons can move freely from an ion to another. In this case, according to Dirac's[20] theory of annihilation, γ_1 should be given by the equation

$$\gamma_1 = \pi r_0^2 c \xi N_A \rho/M, \tag{13}$$

where r_0 is the classic electron radius, c is the light velocity, N_A is Avogadro's number, and ξ is the effective electron number per couple of ions of opposite sign. By inserting the γ_1 values of Table II in Eq. (13), we may obtain the effective electron number ξ that results in being nearly constant for each salt, but increases when passing from LiCl to CsCl. The mean values of ξ for various chlorides are collected in Table III. The increase in ξ could indicate that the positron wave function is more concentrated on the negative ions the greater the dimensions of the positive ions surrounding them. Unfortunately, an adequate theory of the positron states in a perfect ionic crystal is still lacking and the above conjecture can not be confirmed.

ACKNOWLEDGMENT

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