

Positron Annihilation in Copper, Silver, Gold and Thallium Halides.

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Summary. — A complex decay was found for positrons annihilating in Cu, Ag, Au and Tl chlorides, bromides and iodides. The time spectra are characterized by two components, with lifetimes about $2 \cdot 10^{-10}$ s and $4 \cdot 10^{-10}$ s. Their relative intensities, when summed, become nearly equal to 100% of the total number of counts, thus proving that none of these components can arise from the formation and decay of a positronium atom in ortho- and para-states.

1. — Introduction.

Much experimental work has been recently done on the annihilation of positrons in alkali halides. Measurements have been performed on angular correlation ^(1,2), time annihilation spectra ^(3,4), and three quantum yield by means of a triple coincidence method ⁽⁵⁾.

The time spectra analysis showed that competitive processes must contribute, with comparable probability, to the annihilation in alkali halides. In fact the time spectra can be resolved into two components; the mean life of the short-lived component is $\tau_1 \simeq 2 \cdot 10^{-10}$ s, while that of the long-lived one lies in the range from 4 to $7 \cdot 10^{-10}$ s.

⁽¹⁾ A. T. STEWART and M. K. POPE: *Phys. Rev.*, **120**, 2033 (1960).

⁽²⁾ A. T. STEWART and R. MARCH: *Phys. Rev.*, **122**, 75 (1961).

⁽³⁾ A. BISI, A. FIORENTINI and L. ZAPPA: *Phys. Rev.*, **131**, 1023 (1963).

⁽⁴⁾ A. BISI, A. FIORENTINI and L. ZAPPA: *Phys. Rev.*, **134**, A 328 (1964).

⁽⁵⁾ A. BISI, C. BUSSOLATI, S. COVA and L. ZAPPA: *Phys. Rev.*, **141**, 348 (1966).

This result and those arising from experiments on magnetic quenching and three quantum decay were interpreted assuming that a bound system, different from the free positronium atom, can be formed and survive.

Theoretical considerations now available can be summarized as follows. NEAMTAN and VERRAL⁽⁶⁾ showed that in a LiH crystal, an electron can be captured by a positron forming a distorted positronium atom: these authors suggested that a similar event may occur also in alkali halides. Bound states of a positron with a negative ion, or a polaron state were proposed and investigated by GOL'DANSKII *et al.*^(7,8). More recently BRANDT proposed a model in which a positron becomes bound to a cation vacance⁽⁹⁾.

In spite of all these experimental and theoretical works, the behaviour of positrons in ionic crystals before annihilation is still scarcely understood.

In this paper we report the results of time spectra analysis of positrons annihilating in heavy metals (Cu, Ag, Au and Tl) monohalides. These compounds are similar to alkali halides, but their chemical bond is not so highly ionic. The aim of our search was to ascertain whether the time spectrum has a complex structure and whether this structure displays a behaviour which can be connected with the ionic character of the chemical bond. We wish to point out that the chemical behaviour of the four quoted metals is very similar; their monohalides are moderately ionic, the covalent character increasing when the difference in electronegativity between halogen and metal decreases.

2. - Experimental procedure.

We used ²²Na as a positron emitter; a high-specific-activity droplet of ²²NaCl solution was dried on a thin silver or deltamax foil (1.5 mg/cm²) and then covered with an identical foil. Silver or deltamax were chosen because they resist reasonably well to the chemical corrosion caused by the investigated substances. The source was then sandwiched between the specimens under investigation. The specimens were multicrystalline analytical reagent grade chemicals (supplied by the BDH Laboratory Chemicals Division, Poole, England); their thickness was sufficient to stop all positrons. Particular care was taken to avoid photolytic darkening of photosensitive compounds, and to prevent their oxidation or hydration. The manipulation of powders has been carried out in darkness, and, when necessary, in a glove dry box, in which

(6) S. M. NEAMTAN and R. I. VERRAL: *Phys. Rev.*, **134**, A 1254 (1964).

(7) V. I. GOL'DANSKII, G. DAREWYCH and E. P. PROCOP'EV: *Žurn. Ėksp. Teor. Fiz.*, **47**, 659 (1964) (English transl.: *Sov. Phys. JETP*, **20**, 440 (1965)).

(8) V. GOL'DANSKII and E. P. PROCOP'EV: *Fiz. Tverd. Tela*, **6**, 3301 (1964) (English transl.: *Sov. Phys. Solid State*, **6**, 2641 (1965)).

(9) W. BRANDT: *Proc. of the Wayne Conference on Positron Annihilation* (Detroit, 1965).

a high-purity argon flow was maintained. The sandwich source-specimen was then hermetically sealed in a black lucite container. Notwithstanding these precautions the strong reactivity of the gold halides caused the alteration of AuBr and AuCl samples, so that we limited ourselves to the investigation of AuI.

The time spectra were obtained measuring the delays between the prompt 1.28 MeV γ -rays accompanying the β^+ decay of ^{22}Na and one of the annihilation quanta. The γ -rays were detected by Naton 136 plastic scintillators ($1\frac{1}{2}$ in. diam \times 1 in. thick) coupled with XP 1021 photomultipliers: the delays between the suitably shaped photomultiplier pulses were measured and classified by a time to pulse height converter coupled to a 512-channel pulse-height analyser. Energy selection and pulse pile-up rejection circuits were provided in both channels.

The over-all resolution curve of the apparatus, measured by a ^{60}Co source, was fitted by a Gaussian curve with FWHM $3.5 \cdot 10^{-10}$ s.

To analyse complex spectra we employed a maximum-likelihood method, in which allowance was made for finite time resolution, background and finite width of pulse height analyser channels.

The same method was recently adopted by BERTOLACCINI *et al.*; further details are given in their paper ⁽¹⁰⁾.

3. - Results and discussion.

All the examined halides display time spectra having a complex structure, which can be resolved into three components.

As usual, we classify these components according to their mean lives τ ; the first component is characterized by a mean life τ_1 of about $2 \cdot 10^{-10}$ s; the second by a mean life τ_2 of about $4 \cdot 10^{-10}$ s and the third by a mean life τ_3 ranging from 16 to $32 \cdot 10^{-10}$ s.

Mean lives and relative intensities I_1, I_2, I_3 of the three components are reported in Table I. We have quoted errors greater than the standard errors on the mean of several measurements; in fact, systematic errors could prevail in some of our measurements. They arise mainly from the accuracy achievable in calibrating the time-delay scale and from the approximations made in analysing the spectra.

The intensity I_3 is very low, of the order of 1% or less, so that in many cases it is hardly distinguishable from the background. We are not able to make any comments on this component whose origin could be attributed to impurities contained in the specimen under investigation. We wish to recall that a very faint component has been found also in some alkali halides ⁽⁴⁾.

⁽¹⁰⁾ M. BERTOLACCINI, A. BISI and L. ZAPPA: *Nuovo Cimento*, **46 B**, 237 (1966).

TABLE I. — *Lifetimes of positrons in Cu, Ag, Au and Tl halides. τ_1 , τ_2 , τ_3 indicate the mean lives; I_1 , I_2 , I_3 indicate the relative intensities.*

Halide	$\tau_1 \cdot 10^{10}$ s	I_1 (%)	$\tau_2 \cdot 10^{10}$ s	I_2 (%)	$\tau_3 \cdot 10^{10}$ s	I_3 (%)
CuCl	1.81 ± 0.09	40 ± 3.0	3.33 ± 0.15	57 ± 2.5	24.2 ± 1.5	0.3 ± 0.1
AgCl	1.81 ± 0.09	53 ± 6.5	3.86 ± 0.15	46 ± 2.0	18.0 ± 1.7	1.3 ± 0.1
TlCl	1.97 ± 0.10	64 ± 6.5	3.67 ± 0.15	38 ± 3.5	22.8 ± 2.6	0.3 ± 0.1
CuBr	1.73 ± 0.09	30 ± 5.0	3.81 ± 0.15	62 ± 3.5	18.9 ± 2.5	0.7 ± 0.2
AgBr	1.82 ± 0.09	34 ± 6.0	3.47 ± 0.15	60 ± 4.0	18.9 ± 3.0	1.5 ± 0.4
TlBr	2.21 ± 0.11	51 ± 5.0	3.65 ± 0.15	43 ± 4.0	32.0 ± 5.0	0.2 ± 0.1
CuI	1.83 ± 0.09	30 ± 3.0	3.79 ± 0.15	68 ± 3.5	20.8 ± 4.0	0.5 ± 0.1
AgI	1.66 ± 0.08	32 ± 6.0	3.70 ± 0.15	71 ± 2.0	32.9 ± 4.0	0.5 ± 0.1
AuI	2.19 ± 0.25	27 ± 6.0	3.86 ± 0.20	76 ± 5.0	22.5 ± 1.0	1.0 ± 0.2
TlI	2.25 ± 0.10	41 ± 5.0	3.76 ± 0.15	50 ± 3.5	23.6 ± 4.5	0.2 ± 0.1

A typical time spectrum, from which the long-lived tail has been subtracted, is shown in Fig. 1. As can be easily seen, the spectrum can be resolved in two components of comparable intensity; their values, when summed, attain, within the experimental errors, 100% of the total number of counts. Therefore, it

appears that only two competitive processes are responsible for the fate of the positron.

From the data reported in Table I, it is apparent that the lifetime τ_2 is practically the same for all halides, within the limits of experimental errors, while the shorter lifetime τ_1 displays slight variations from one substance to another. An attempt to correlate τ_1 with the simplest properties of the halides shows that this lifetime slightly decreases with increasing molecular density. This is seen in Fig. 2, where the decay rate λ_1 together with the decay rate λ_2 , is plotted as a function of the molecular density n .

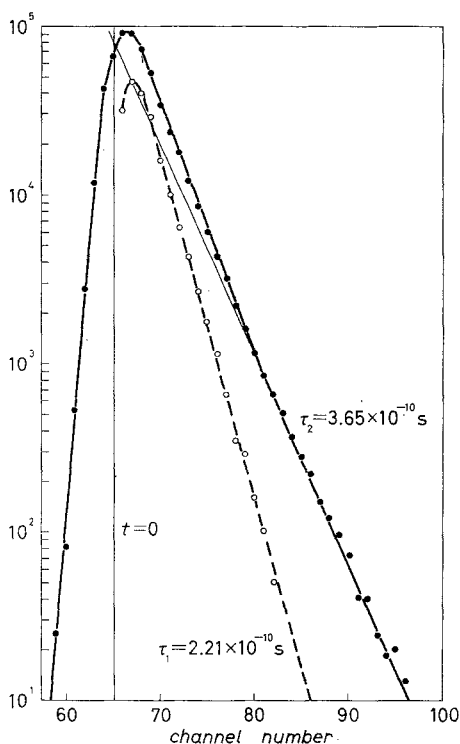


Fig. 1. — Time spectrum of positrons annihilating in TlBr (the weak long-lived tail was subtracted). 1 channel = $1.056 \cdot 10^{-10}$ s.

However it must be kept in mind that the accuracy of the τ_1 measurements is poor, owing to the fact that the shape of the spectrum is appreciably influenced by the finite instrumental resolution in the region where this component predominates.

A sharper correlation can be observed between the intensities I_1 and I_2 and the electronegativity of the halogen. Using Pauling's values for electronegativities, we obtain for each cation the graphs shown in Fig. 3.

A more comprehensive picture can be obtained by correlating I_2

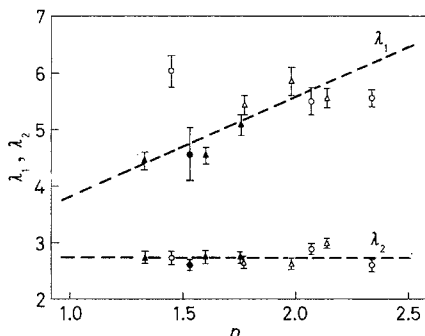


Fig. 2. - Decay rates $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$ (units: 10^9 s^{-1}) plotted against molecular density (units: 10^{22} cm^{-3}): Δ copper halides; \circ silver halides; \bullet gold halides; \blacktriangle thallium halides.

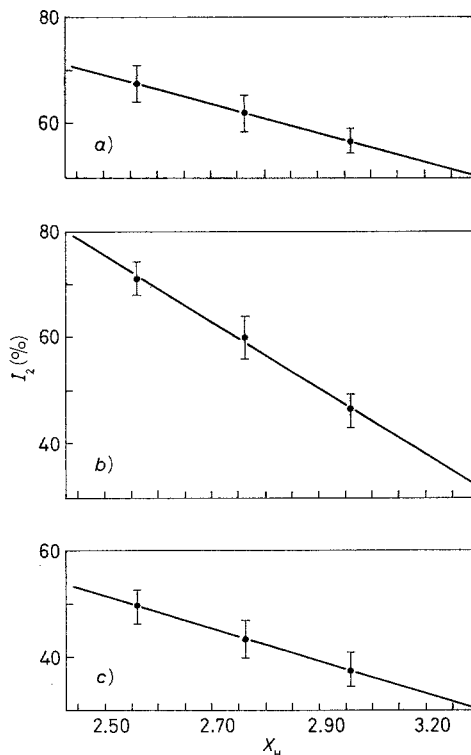


Fig. 3. - Intensity of the second component I_2 in Cu, Ag, and Tl halides, as a function of Pauling's electronegativity of the halogen: a) copper halides; b) silver halides; c) thallium halides.

with the fraction of ionic character ϵ of the compound. The result is shown in Fig. 4. The ϵ values were calculated according the following equation:

$$\epsilon = 0.16 (x_{\text{H}} - x_{\text{M}}) + 0.035 (x_{\text{H}} - x_{\text{M}})^2$$

given by HANNAY *et al.* ⁽¹¹⁾, where

x_{H} is the electronegativity of the halogen,

x_{M} is the electronegativity of the metal.

⁽¹¹⁾ N. B. HANNAY and C. P. SMYTH: *Journ. Amer. Chem. Soc.*, **68**, 171 (1946).

We used the x values given by SANDERSON⁽¹²⁾, calculated from the stability ratios. All the points pertaining to Cu, Ag and Au halides can be fitted by a straight line, while the I_2 values of Tl halides give points (not shown in the Figure)

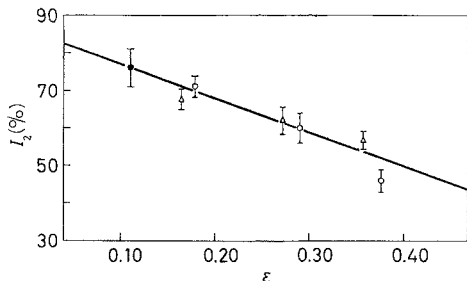


Fig. 4. — Intensity of the second component I_2 in Cu, Ag and Au halides as a function of the ionic character ε : Δ copper halides; \circ silver halides; \bullet gold halides.

which fall well under the straight line. This is not surprising because the electronic structure of the outer shell of the thallium positive ion is different from that of copper, silver and gold ions: Cu^+ , Ag^+ and Au^+ have eighteen electrons, Tl^+ has two more electrons (a chemically inert s -electron pair).

On the ground of the above results, we wish to discuss briefly the process which could be responsible for positron annihilation in our compounds.

Any interpretation has to take into account that the sum of the intensities of the two components gives 100%. This fact rules out the conventional interpretation of positron annihilation in nonmetallic materials, *i.e.* that positronium formation in ortho- and para-states and its decay act as the only competitive process to the free positron annihilation. It is the first time that positrons were observed to behave in such a way, so that we are forced to make a working hypothesis. We attribute the τ_1 component to the annihilation of positrons when free and the τ_2 component to the formation and decay of a positron bound system quite different from the free positronium atom. The following two arguments agree with our model: *a*) the mean life τ_1 appears to decrease with increasing molecular density of the medium; *b*) the I_2 intensity decreases with increasing electronegativity of the halogen; this can be accounted for as follows. A strong difference in electronegativity between constituents of a diatomic crystal indicates that the anion has a compact structure; in this case, it is likely that the positron interacts with it as a whole. If the electron attraction exerted by the cation increases, the stiffness of the spherical structure of the anion is perturbed. An incoming positron has therefore a greater probability to encounter electrons far from the ion center and to capture them, forming a bound system, more or less distorted by the nearest ion. If such a system is responsible for the longer-lived component τ_2 , then the sense of the intensity variation agrees with the observed one.

(12) T. A. SANDERSON: *Chemical Periodicity* (New York, 1960), p. 34.

RIASSUNTO

L'annichilazione di positroni in cloruri, bromuri e ioduri di Cu, Ag, Au, e Tl risulta complessa. Gli spettri temporali sono caratterizzati da due componenti con vite medie da circa $2 \cdot 10^{-10}$ s a $4 \cdot 10^{-10}$ s. La somma delle intensità relative di queste due componenti costituisce il 100% del numero totale dei conteggi: ciò prova che nessuna di esse può essere originata dalla formazione e successivo decadimento di un atomo di positonio negli stati orto e para.

Аннигиляция позитронов в галоидах меди, серебра, золота и таллия.

Резюме (*). — Был обнаружен сложный распад при аннигиляции позитронов в хлоридах, бромиды, йодидах Cu, Ag, Au и Tl. Временные спектры характеризуются двумя компонентами, с временами жизни около $2 \cdot 10^{-10}$ сек и $4 \cdot 10^{-10}$ сек. Их относительные интенсивности, после сложения, дают результат, приблизительно равный 100% от общего числа измерений, следовательно, это доказывает, что эти компоненты не могут возникнуть от образования и распада позитрония в орто- и парасостояниях.

(*) *Переведено редакцией.*