POSITRON TRAPPING BY F- AND F'-CENTRES IN KCl

L. Bosi, A. Dupasquier, L. Zappa

JOURNAL DE PHYSIQUE *Colloque* C9, *supplément au n°* 11-12, *Tome* 34, *Novembre-Décembre* 1973, *page* C9-295

POSITRON TRAPPING BY F- AND F′-CENTRES IN KCl

L. BOSI (*), A. DUPASQUIER (*) and L. ZAPPA (**)

Gruppo Nazionale di Struttura della Materia del CNR

Résumé. — On a observé que l'intensité de la composante à longue vie du spectre temporel des positons annihilés dans le KCl additivement coloré décroît par conséquent à la conversion F → F′. L'entité de la réduction montre que les centres F′, ainsi que les centres F, agissent comme pièges pour le positon. Le rapport k'/k des probabilités de capture, pour unité de temps et de concentration, dans les centres F′ et F respectivement, a été estimé à 11,5 ± 5,8.

Abstract. — The intensity of the long-living component in the time spectrum of positrons annihilated in additively coloured KCl was found to decrease when F → F′ conversion occurs. The amount of the reduction gives a strong indication that F′-centres, as well as F-centres, act as positron traps. The ratio between the trapping rates per centre of F′- and F-centres respectively was found to be : $k'/k = 11.5 \pm 5.8$.

1. **Introduction.** — The annihilation of positron in single crystals of additively coloured KCl was first investigated by Herlach and Heinrich [1]. From an analysis of the angular distribution of the annihilation radiation, these authors were led to conclude that an appreciable fraction of positrons is captured by F-centres. Further evidence of the trapping process was obtained by Dupasquier [2], who observed in the time spectrum of positrons annihilated in additively coloured KCl a long-living component (decay rate $\lambda = 0.106 \times 10^{10}\ s^{-1}$), whose intensity increases with F-centre concentration.

Similar observations were made by Mallard and Hsu [3] and by Arefiev and Vorobiev [4] with γ- and electron-irradiated KCl. According to the model proposed in [2] and supported also by the results of the magnetic quenching experiment made by Bisi *et al.* [5], the positron, once captured, forms with the electron of the F-centre a sort of relaxed positronium atom bound to the vacant ion site. The ortho-state of this quasi-positronium gives rise, via 2-γ pick-off annihilation, to the long living component of the lifetime spectrum, while the para-state gives rise to the narrow component of the angular distribution observed by Herlach and Heinrich. So far as F′-centres are concerned, up to the present no experimental information on their interaction with positrons has been available. Yet it can easily be predicted that F′-centres are more effective positron traps than F-centres, being electrically charged. The binding energies of positrons in F′ and in F-centres have been calculated by Berezin [6] : in the first case, the binding energy is twice as large as in the second one. The system formed by the positron with the two electrons of an F′-centre in the lowest energy state is presumed to have a short lifetime, because one of the electrons always has the correct spin direction for fast annihilation in two gamma rays.

The present paper reports the results of an investigation of the effect on the annihilation lifetime spectrum of the reversible F ⇆ F′ conversion in additively coloured KCl at − 100 °C.

The aim was twofold : firstly, to show once more the origin of the long-living component of the spectrum, then to search for evidence of positron capture by F′-centres.

2. **Experimental procedure.** — The measurement of the lifetime spectra was performed in a conventional manner [7] : the prompt time-resolution curve in the conditions of the present experiment has a full width at half maximum of 280 ps ; its logarithmic slope, through at least four decades, corresponds to a half life of 45 ps. Various samples of KCl were used. They were additively coloured following Van Doorn's method [8], cleaved to the desired thickness and quenched, as described in [2], just prior to the measurement. In order to have a (positron source) + (KCl specimen) assembly with an optical absorption in the F-band which would not overpower the sensibility of our spectrophotometer, we used a composite arrangement. The positron source (Na^{22} from a NaCl solution) was deposited on a small polished disc of Brazil quartz. A thin KCl crystal (about 0.5 mm thick) was then placed in direct contact with the source and covered with another quartz disc. As a result, more than 50 % of the positrons were annihilated in the quartz discs, whose thickness was sufficient to stop all the positrons not annihilated in the KCl crystal. As will be explained below, this fact did not disturb our measurement. The source-crystal assembly was now placed in a cryostat with transparent windows and temperature stabilization

(*) Istituto di Fisica del Politecnico, Milano, Italy.
(**) Università degli Studi, Ancona, Italy.

within 2 °C. All preparations were carried out in subdued blue light.

The optical absorption measurements of F-centre concentration were made by means of a Hitachi EPS-3 T spectrophotometer. The F → F′ conversion was maintained at equilibrium conditions by exposing the specimen at − 100 °C to the focused light of a 7158 Philips lamp (150 W) through a combination of optical filters (BG 18 Jenaer Glasswerke Schott & Gen., Mainz + 57 Kodak Wratten). The initial F-centre concentration was restored, when necessary, by irradiation at 88 K with the spectrophotometer light fixed at 600 mμ.

Before starting the experiment, an analysis of the time annihilation spectrum was made ; it revealed the presence of the long-living component with a lifetime of 0.95 ns in strict agreement with the previous results [2]. The experiment consisted in measuring the relative number N of annihilation events occurring between times t_A and t_B ; the instant t_A (= 5.5 ns) was chosen so that the contribution of all shorter components would be negligible, and t_B (= 7.8 ns) so that the contribution of the component under investigation would still be statistically significant. In the above time interval the positrons annihilated in quartz contribute less than 0.25 % to the counting rate. Several counting runs, each of 10 hours, were made alternatively with and without F′-centres, proceeding by the following phases :

i) F → F′ conversion was made as indicated above ; after 20 min the F-centre concentration was measured ;

ii) keeping unaltered both the temperature (− 100 °C) and the F-bleaching light, the time annihilation spectrum was recorded ; the F-centre concentration was then measured for a second time ;

iii) F′ → F conversion was made until the initial F-centre concentration was restored ;

iv) keeping the specimen in darkness at − 100 °C, the time annihilation spectrum was again recorded ; on completion, the F-centre concentration was measured once more.

3. **Experimental results and discussion.** — According to our experimental results, in a positron annihilation spectrum the F → F′ conversion shows itself through an intensity reduction of the long-living component. The lifetime of this component remains, on the contrary, unaltered. The ratio R between the numbers $N(\mathrm{F})$ and $N(\mathrm{F, F'})$ of annihilation events, occurring in the time interval (t_A, t_B), respectively in the absence and in the presence of F′-centres, is therefore equal to the ratio of the intensities of the long-living component in the same conditions. The measured value of this ratio was

$$R = 3.06 \pm 0.33 .$$

Corresponding F-centre concentrations were :

$$n(\mathrm{F}) = 1.8 \times 10^{17}\ \mathrm{cm}^{-3}$$

$$n(\mathrm{F, F'}) = 0.73 \times 10^{17}\ \mathrm{cm}^{-3} .$$

Considered by itself, the above reduction of the F-centre concentration should, according to the results of Dupasquier [2], give rise to an intensity reduction of the long-living component by a factor 2.26. The greater reduction observed here can be explained if the F′-centres act as competitive traps for positrons.

In this case we can write as follows for the intensity I of the long-living component :

$$I = \frac{3}{4} \frac{kn}{a + kn + k'n'} , \tag{1}$$

where kn and $k'n'$ are respectively the capture rates of positrons by F- and F′-centres at concentrations n and n', while a is the rate of all other processes possible for the positron (i. e. annihilation or formation of bound states other than with F- and F′-centres), and the factor $\frac{3}{4}$ takes into account the statistical weight of the ortho-state. To obtain eq. (1) we have assumed that the positrons, once trapped, cannot escape, and that anion vacancies, formed in the same concentration as F-′centres, do not trap positrons.

Substituting in eq. (1)

$$n' = \frac{n(\mathrm{F}) - n(\mathrm{F, F'})}{2} , \tag{2}$$

as imposed by the reaction balance of the F → F′ conversion, and solving for k'/k, the result obtained is

$$\frac{k'}{k} = \frac{2\, n(\mathrm{F, F'})}{\{ n(\mathrm{F}) - n(\mathrm{F, F'}) \}\, I(\mathrm{F})} \cdot \{ R - r \} , \tag{3}$$

where $I(\mathrm{F})$ is the intensity at the concentration $n(\mathrm{F})$ and r represents the value of the intensity ratio to be expected in the absence of positron trapping by F′-centres. Incidentally we note that the above equation implies uniform distributions of F- and F′-centres throughout the crystal. This situation would be obtained if the destruction of F′-centres occurred through the absorption of light quanta and not through thermal instability, because in this case the equilibrium concentrations would not depend on the light intensity. This latter condition was closely approximated in our experiment. In fact, we ascertained that the equilibrium value of the F → F′ conversion does not change significantly when the intensity of the falling light changes by a factor ranging from 1 to 100.

On inserting in eq. (3) $I = 0.095$ and $r = 2.26$, as calculated according to [2], we obtain $k'/k = 11.5 \pm 5.8$, with the error margin allowing for all possible inaccuracies.

The results of the present experiment may be summarized as follows :

i) it is confirmed that the annihilation of positrons trapped in F-centres is responsible for the long-living component observed in additively coloured KCl, since the intensity of this component decreases when bleaching the F-centres, without changing other conditions ;

ii) there are strong indications that positrons are captured by F′-centres with a trapping rate per centre of an order of magnitude larger than that of F-centres.

We may compare the measured value of k'/k with an estimate deduced and explained below.

It can be assumed that the interactions at large distance of a positron with an F-centre and a positron with an F′-centre are similar to those existing between an electron and an F-centre and between an electron and an anionic vacancy (α-centre) respectively. For the positron capture rates per centre in F- and F′-centres we therefore use the expressions given by Pekar [9] for the electron trapping by F- and α-centres. These are :

$$k = 1.1(4\,\pi\mu)\,(KT)^{3/4}\left(\frac{\gamma}{2\,\varepsilon^2\,e^2}\right)^{1/4} \qquad (4)$$

and

$$k' = \frac{4\,\pi\mu e}{\varepsilon}, \qquad (5)$$

where μ is in our case the positron mobility, ε the static dielectric constant, γ the F-centre polarizability, e the electronic charge and K the Boltzmann constant. The ratio k'/k is independent of the positron mobility and is identical to the ratio $k_{\alpha,e}/k_{F,e}$ of the capture rates of an electron by an α- and an F-centre.

Assuming for the ratio $k_{\alpha,e}/k_{F,e}$ at 80 K an average of the values given by various authors [10], [11], [12], i. e.

$$\left(\frac{k_{\alpha,e}}{k_{F,e}}\right)_{80\ K} \simeq 26$$

we have :

$$\left(\frac{k'}{k}\right)_{173\ K} = \left(\frac{k_{\alpha,e}}{k_{F,e}}\right)_{80\ K} \cdot \left(\frac{80}{173}\right)^{3/4} \simeq 15\,.$$

This estimated value is in close agreement with our experimental result

$$\frac{k'}{k} = 11.5 \pm 5.8\,.$$

Finally some indications regarding the value of k' and of the positron mobility μ in KCl may be deduced from our results. During the experiment, we ascertained that the variation of k between + 20 °C and − 100 °C is not greater than 20 %. Ignoring this variation, we assume $k = 0.45 \times 10^{-8}\ cm^3.s^{-1}$, as obtained by Bertolaccini *et al.* [13] from the measurements of [2]. Thus we have

$$k' \simeq 5 \times 10^{-8}\ cm^3.s^{-1}\,.$$

On inserting this value in eq. (5), we have

$$\mu(-\ 100\ °C) \simeq 0.14\ cm^2.s^{-1}.V^{-1}\,.$$

Although only indicative, this datum is relevant since it represents the first experimental information about positron mobility in an ionic crystal.

References

[1] HERLACH, D. and HEINRICH, F., *Phys. Lett.* **31A** (1970) 47.

[2] DUPASQUIER, A., *Lett. Nuovo Cimento* **IV** (1970) 13.

[3] MALLARD, W. C. and HSU, F. H., *Phys. Lett.* **38A** (1972) 164.

[4] AREFIEV, K. P. and VOROBIEV, S. A., *Phys. Lett.* **39A** (1972) 381.

[5] BISI, A., DUPASQUIER, A. and ZAPPA, L., *J. Phys. C* : Solid St. Phys. **4** (1971) L 33.

[6] BEREZIN, A. A., *Phys. Stat. Sol.* (*b*) **50** (1972) 71.

[7] BISI, A., DUPASQUIER, A. and ZAPPA, L., *J. Phys. C* : Solid St. Phys. **6** (1973) 1125.

[8] VAN DOORN, C. Z., *Rev. Sci. Instrum.* **32** (1961) 755.

[9] PEKAR, S. I., *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie Verlag, Berlin) 1954, 154 ff.

[10] COSTIKAS, A. and GROSSWEINER, L. I., *Phys. Rev.* **126** (1962) 1410.

[11] LÜTY, F., *Halbleiterprobleme* **6** (1961) 238.

[12] MARKHAM, J. J., *F-centres in Alkali Halides* (Academic Press) 1966.

[13] BERTOLACCINI, M., BISI, A., GAMBARINI, G. and ZAPPA, L., *J. Phys. C* : Solid St. Phys. **4** (1971) 734