Positron annihilation in alkali-halide crystals with defects

A. A. Vorob'ev, K. P. Aref'ev, and S. A. Vorob'ev

Nuclear Physics, Electronics, and Atomation Research Institute at the Tomsk Polytechnic Institute
(Submitted October 29, 1974)
Zh. Eksp. Teor. Fiz. **68**, 1486–1490 (April 1975)

Positron annihilation is investigated in electron-bombarded alkali-halide single crystals KCl (42%)–KBr (58%), KCl, KBr, and NaCl containing cation vacancies. The main annihilation characteristics (angular distribution of annihilation radiation, 3γ-annihilation probabilities, time distribution of positron annihilation) are found to vary with the crystal defect content. The experimental data obtained can be satisfactorily explained by the model of a "positron-exciton" complex near the cation vacancy.

PACS numbers: 78.70.B

INTRODUCTION

Much factual material has been accumulated by now, offering evidence that the characteristics of positron annihilation in alkali-halide crystals are sensitive to structural defects of the crystals.[1-3] The simplest case for the interpretation of the experimental data is annihilation of positrons in a sample in which mainly one selected type of defect is induced, say F centers.[1-4]

A more complicated case is the annihilation of positrons in radiation-colored alkali-halide crystals,[2,5] where a complex of defects is induced (electron and hole color centers, complexes of cation-anion vacancies, etc.).[6] Comparison of the angular distributions of the annihilation radiation in radiation-colored and additively-colored KCl single crystals[5] has demonstrated the effectiveness of the capture of positrons by V_2 hole color centers, which include cation vacancies, as established in [7]. Effective capture of positrons by cation-anion vacancy complexes and by the complex comprising a Ca^{++} impurity and a cation vacancy is demonstrated in [8,9]

However, the physical nature of the positron states coupled with defects containing cation vacancies is not clear.[5,10]

In this paper we present the results of the measurement of the principal annihilation characteristics (angular distribution of the annihilation radiation, probability of 3γ annihilation, and temporal distribution of positron annihilation) in defect-containing alkali-halide crystals containing cation vacancies (the solid solution KCl(42%)-KBr(58%), or KCl, KBr, and NaCl single crystals, exposed to an electron beam). These comprehensive measurements yield more complete information on the positron states connected with defects that contain cation vacancies.

EXPERIMENTAL PROCEDURE AND RESULTS

The angular distribution of the annihilation radiation was measured with a parallel-slit-geometry setup[11] with a geometric resolution $\Delta\theta \approx 0.8$ mrad. To measure the probability of the 3γ annihilation we used a Ge(Li) detector of 25 cm^3 volume, with a resolution 6 keV. The temporal distribution of the positron annihilation was measured with a setup having a resolution 0.54 nsec.

The KCl, KBr, and NaCl were bombarded with 2-MeV electrons in an ESG-2.5 MeV electrostatic generator at a current ~0.5 $\mu A/cm^2$ for 4 and 20 minutes. The concentration of the induced color centers was determined by measuring the optical-absorption spectra.

The table lists the following measured characteristics of positron annihilation in real and defective alkali-halide single crystals: the intensity I_N of the narrow component in the correlation annihilation-radiation curves, the intensity $P_{3\gamma}$ of the 3γ annihilation, the components (τ_1, τ_2, τ_3) of the positron lifetime in samples with defects and their intensities $I_{1,2,3}$, and the F-center concentration. The data indicate that the annihilation characteristics in samples with defects are different than in real crystals. The same results, namely the appearance of a narrow component in the correlation curves of the annihilation radiation, the increase of the probability of the 3γ annihilation, and the changes of τ_2 and τ_3, all obviously provide evidence that the positrons are captured by cation-anion vacancy complexes, as is the case in the solid solution KCl(42%)-KBr(58%), and by V_2 centers, as is the case in electron-bombarded KCl, KBr, and NaCl. A comparison of the dependences of the intensities of the narrow component in the correlation curves of the annihilation radiation I_N and the third long-lived component of the positron lifetime I_3 on the concentration of the F centers in the electron-bombardment KCl crystals (see the table) with the analogous dependences for additively-colored KCl[12,13] offers evidence that the positrons are more effectively captured by the V_2 centers. On the other hand, the increase of the probability of the 3γ annihilation in defective samples in comparison with real crystals (table) indicates that the positron state that takes place upon capture of positrons by cation-anion vacancy complexes of V_2 centers is similar to the positronium state, but its characteristics differ significantly from the characteristics of free positronium and depend on the type of the crystal and on the type of the defect in which the cation vacancy enters. This evidenced by

Characteristics* of positron annihilation in real and defect-containing alkali-halide single crystals.

Substance	I_N, %	$P_{3\gamma}$, %	τ_1, 10^{-10} sec	τ_2, 10^{-10} sec	τ_3, 10^{-9} sec	I_1, %	I_2, %	I_3, %	^nF, 10^{17} cm^{-3}
1	2	3	4	5	6	7	8	9	10
KCl	0,0	0.42	2.0	5.26	1.2	48	50±5	2.0	—
KBr	0,0	0.43	3.3	7.40	--	76	24±5	--	—
NaCl	0,0	0.44	2.0	5.54	--	71	29±4	--	—
KCl(42%)—KBr(58%)	3.0±0.5	0.81	2.5	7.20	--	79	21±5	--	—
KCl [4 min] **	4.8±1.5	0.42	2.0	5.25	1.14	43	51±5	6.2	0.7±0.15
KCl [20 min]	8.4±1.5	0.94	2.0	5.20	1.16	43	47±5	10.4	2.6±0.25
KBr [4 min]	4.0±1.5	0.43	3.3	7.75	--	82	18±4	--	0.6±0.1
KBr [20 min]	8.0±1.5	0.52	3.3	7.57	--	77	23±4	--	2.0±0.2
NaCl [4 min]	6.8±1.5	0.44	2.0	4.95	--	78	22±4	--	2.0±0.2
NaCl [20 min]	16.3±2.0	0.91	2.0	7.15	--	74	26±4	--	6.6±0.5

*The errors of all the quantities in columns 3–7 and 9 are the same and their respective values are: ±0.04, ±0.16, ±0.20, ±0.20, ±5, and ±0.8 for $P_{3\gamma}$, τ_1, τ_2, τ_3, I_1, and I_3, respectively.

**The quantities in the square brackets are the bombardment times.

the satisfaction of the equality[14]

$$P_{3\gamma}=\frac{1}{372}I_1+\frac{\tau_2}{\tau_t^0}I_2+\frac{\tau_3}{\tau_t^0}I_3. \quad (1)$$

Here $\tau_t^0 = 1.4 \times 10^{-7}$ sec is the lifetime of the free orthopositronium.

DISCUSSION OF RESULTS

Let us analyze the results on the basis of the model described in the earlier papers.[15,10] The proposed model presupposes formation of a system (e^+-exciton) near the cation vacancy, a fact that can be regarded as a "positronium" state in which the positron is attracted by the vacancy and the electron by the hole. Let us estimate the energy condition for the formation of such a "positron-exciton" complex near a cation vacancy. It takes the form

$$E^+=U_{exc}-E, \quad (2)$$

where E^+ is the kinetic energy of the positron localized on the vacancy E_{exc} is the exciton-production energy (~6 eV[16]), and E is the binding energy of the positron-exciton complex in the crystal and is equal to $E_0 + \Delta E$, where E_0 is the binding energy of the free positron-exciton complex, and ΔE is the energy of the affinity of this complex to the crystal.

On the other hand, the condition of dynamic stability is

$$E^+-U_{exc}<(-E_0^+), \quad (3)$$

where $(-E_0^+)$ is the energy of the ground state of the positron in the crystal and E_0^+ is the affinity of the positron to the crystal. Combining (2) and (3), we obtain the conditions for the formation of a positron-exciton complex near a cation vacancy

$$U_{exc}-E<E^+<U_{exc}-E_0^+. \quad (4)$$

The quantity $\Delta = -E_0^+ + E$ is to a certain degree a measure of the probability of production of a positron-exciton complex near a cation vacancy in a crystal. It follows from the inequality (4) that the condition for the production of such a complex is

$$E>E_0^+. \quad (5)$$

Let us check on the satisfaction of the inequality (5). To this end we estimate E_0 approximately as the binding energy of a free positronium ion $e^-e^+e^-$ relative to decay into positronium and a free electron,[17] whence $E_0 \approx 0.326$ eV. The affinity energy of the positron-exciton complex near the cation vacancy to the crystal we express in the form

$$\Delta E=E_c^+-E_M^++E_{exc}^--E_M^-. \quad (6)$$

Here E_c^+ is the energy of the positron affinity to the cation vacancy, which can be estimated as equal to the binding energy of an electron in an F center (~2 eV[18]); E_M^+ and E_M^- are the Madelung corrections to the energy of the exciton ground state coupled with the cation vacancy and of the excited electron. In first-order approximation we have

$$E_M^+\approx 25/2a \text{ [eV]}, \quad E_M^-\approx 25/a \text{ [eV]},$$

where a is the distance between ions in Angstrom units; E_{exc}^- is the energy of the affinity of the excited electron to the anion (~1 eV[18]). The affinity of the positron to the crystal will be estimated at $E_0^+ \approx 0$, since it is shown in [19] that positron in alkali-halide crystals are quasifree, and this also is confirmed by the experimental value of the effective mass of the positron ($m_+^* \approx M_0$).[10]

Thus, the quantity Δ is essentially positive. We can therefore conclude that the formation of a positron-exciton complex near a cation vacancy is energywise allowed and, as follows from the inequality (4), the energy E^+ of a positron moving around a cation vacancy ($\gtrsim 1$ eV) is sufficient for the formation of this complex. In our case we have a positron-exciton complex near a cation vacancy, which cannot move over the crystal.

Let us consider the main properties of this positron-exciton complex near a cation vacancy, as applied to the results obtained by us (see the table) and the results obtained for positron capture by cation vacancies in KCl + Ca.[9]

1) The overlap of the wave functions of the excited electron and of the positron in the positron-exciton complex near a cation vacancy will be smaller than in positronium, i.e., $|\Psi(0)|^2/|\Psi_{Ps}(0)|^2 = \alpha < 1$. For this complex we can assume in rough approximation the value of the mass of the free electron as the effective mass of four particles (cation vacancy, positron, electron, hole), and the dielectric constant can be set at $\epsilon = 1$. We can then tentatively compare the result with the overlap of the wave functions of the electrons and positrons in the positronium ion $e^-e^+e^-$, which is close to the density of positronium.[20] We thus find that in the positron-exciton complex near the cation vacancy we have $\alpha \approx 0.5$. This fact explains the anomalously strong magnetic quenching of the intensity I_3 of the third long-lived component of the positron in KCl + Ca, which was observed in [9], in comparison with the quenching of free positronium.

2) The rates of annihilation of a positron with an excited electron of an anion, λ_s^A and λ_t^A (the singlet and triplet states, respectively), decrease in comparison with positronium, since they are proportional to $|\Psi(0)|^2$. In this case, however, λ_s^A and λ_t^A are bounded by the exciton lifetime ($\tau_0 = 1/\lambda_0$). The rate of annihilation of a positron from the triplet state of a positron-exciton complex near the cation vacancy will be determined mainly by the pick-off annihilation process. Thus, it is obvious that $\lambda_t = 1/\tau_3$, i.e., even in real alkali-halide crystals there is a fraction of positrons captured by cation vacancies and forming a positron-exciton complex near a cation vacancy. The changes of τ_2 and I_2 in KCl(42%)-KBr(58%), KBr, and NaCl crystals with defects (see the table) indicate that the component τ_3 is close to τ_2, and as a result the mean value of these temporal components is observed. As to the rate of annihilation of a positron from a singlet state of this complex in a crystal, a rate determined by the annihilation of the positron with the excited electrons, it will be smaller than that of free positronium, and can therefore be close to the rate of annihilation of free thermalized positrons, i.e., what is obviously observed in experiment is the average annihilation rate ($\lambda_S = 1/\tau_1$) due to both processes. The annihilation of positrons from a singlet state of this complex will lead to the appearance of a narrow component in the correlation curves of the annihilation radiation, and this indeed took place in the experiment (see the table), inasmuch as the energy of the excited electron is much lower than that of the valence electrons with which

the positrons from the triplet states of this complex are annihilated.

3) The probability of 3γ annihilation from the triplet state of the positron-exciton complex takes the form

$$P_{3\gamma}=I_t\lambda_0/\lambda_t=I_3\lambda_0/\lambda_t. \quad (7)$$

If we take as a rough approximation the lifetime of the free exciton in alkali-halide crystals (10^{-8} sec[16]) to be equal to the lifetime of the exciton bound with the positron near the cation vacancy ($\tau_0 = 1/\lambda_0$), then it follows from (7) that the yield of the 3γ annihilation in crystals with defects is increased, as is indeed observed by us in experiment (table).

4) Since the binding energy of the positron with the excited electron in the positron-exciton complex near the cation vacancy is small (0.3 eV), it follows that this formation is unstable, as is evidenced by the fact that the equation $I_N = I_3/3$ is not satisfied in KCl crystals with defects (see the table), but is satisfied for positronium.[14]

Thus, the model of a "positron-exciton" complex near a cation vacancy results in satisfactory agreement with the experimental results obtained in the present work and with those described in the literature for alkali-halide crystals containing cation vacancies in the defects. This obviously proves that the positron-exciton complex is actually produced near a defect containing a cation vacancy, and that positrons are effectively captured in alkali-halide crystals by defects containing cation vacancies.

[1]D. Herlach and F. Heinrich, Phys. Lett. **31A**, 47 (1970).
[2]K. P. Arefiev and S. A. Vorobiev, Phys. Lett. **39A**, 381 (1972).
[3]W. Brandt and H. F. Waung, Phys. Rev. B. **3**, 3432 (1971).
[4]E. P. Prokop'ev, Fiz. Tverd. Tela **14**, 2924 (1972) [Sov. Phys.-Solid State **14**, 2520 (1973)].
[5]A. A. Vorobiev, K. P. Arefiev, and S. A. Vorobiev, Appl Phys. **3**, 241 (1974).
[6]Van Buren, Defects in Crystals (Russ. transl.), IIL, 1962.
[7]V. F. Pichugin, Dissertation TPI, Tomsk (1973).
[8]A. A. Vorobiev, K. P. Arefiev, and S. A. Vorobiev, Phys. Stat. Sol. (b), **53**, K 133, (1972).
[9]W. Brandt, A. Dupasquier, and G. Dürr, Phys. Rev. B. **6**, 3156 (1972).
[10]A. A. Vorobiev, Yu. M. Annenkov, K. P. Arefiev, and S. A. Vorobiev, Phys. Stat. Sol. (b), **57**, K27 (1973).
[11]K. P. Aref'ev, S. A. Vorob'ev, and Yu. A. Timoshnikov, Fiz. Tverd. Tela **13**, 922 (1971) [Sov. Phys.-Solid State **13**, 770 (1971)].
[12]D. Herlach and F. Heinrich, Helv. Phys. Acta **45**, 10 (1972).
[13]A. Dupasquier, Lett. Nuovo Cim. **4**, 13 (1970).
[14]V. I. Gol'danskiĭ, Fizicheskaya khimiya pozitrona i pozitroniya (Physical Chemistry of the Positron and of Positronium), Nauka (1968).
[15]A. A. Vorob'ev, K. P. Aref'ev, and S. A. Vorob'ev, Tezisy dokladov XI Evropeĭskogo Kongressa po molekulyarnoĭ spektroskopii (Abstracts, 11th Europ. Congress on Molecular Spectroscopy), Tallin, 1973, No. 64.
[16]A. A. Vorob'ev, Ionnye i élektronnye svoĭstva shchelochnogaloidnykh kristallov (Ionic and Electronic Properties of Alkali-Halide Crystals), TGU, Tomsk, 1968.
[17]W. Kolos, C. C. J. Rootham, and R. A. Sack, Rev. Mod. Phys. **32**, 178 (1960).
[18]A. A. Vorob'ev, Tsentry okraski v shchelochnogaloidnykh kristallakh (Color Centers in Alkali-Halide Crystals), TGU, Tomsk, 1968.
[19]P. Hautojärvi and R. Nieminen, Phys. Stat. Sol. (b), **56**, 421 (1973).
[20]G. Ferrante, Phys. Rev. **170**, 76 (1968).

Translated by J. G. Adashko
161