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Positron Annihilation in Ca^{2+}-Doped KCl[†]

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A new third positron lifetime (~1.3 nsec) component grows as the square root of the Ca^{2+} concentration. It is attributed to the diffusion of positrons (diffusion constant $D_+(\mathrm{KCl}) \simeq 6\times10^{-3}$ cm^2 sec^{-1}) until annihilation at free-cation vacancies introduced by Ca^{2+} doping.

Recent experimental evidence on metals and insulators has shown that positrons can be trapped in crystal defects to form annihilation or *A* centers where they annihilate with experimentally distinguishable characteristics if they encounter, on the average, electrons of lower density and lower momenta than in the bulk of the crystal.[1] In such cases, positrons offer a method for the study of crystal defects.[2] The present paper contributes further evidence through measurements of the dependence of positron lifetime spectra on the positive-ion-vacancy formation in alkali halide crystals, introduced by Ca^{2+} doping to preserve charge neutrality.

A Na^{22} positron source was sandwiched between a pair of KCl crystals, and the positron lifetime spectrum was measured in a standard fast-slow delayed-coincidence apparatus with an instrument resolution of 360 psec and a decay slope of ~1×10^{-2} psec^{-1}. Five pairs of KCl crystals with various Ca^{2+} concentrations were studied. The method of preparation and assays of other impurities are given by Sibley and Russell.[3] The coincidence spectra were analyzed by a least-squares computer routine, leading to three distinct lifetime components (I_ν, Γ_ν), $\nu = 1, 2, 3$, where I_ν is the component intensity normalized such that $I_1 + I_2 + I_3 = 1$, and Γ_ν the associated decay rate or, equivalently, Γ_ν^{-1} is the lifetime.

The results are summarized in Table I. A significant trend with Ca^{2+} concentration appears in I_3. If one attributes components 2 and 3 to two types of defects at low concentrations, in which positrons are trapped for times that are long compared to Γ_2^{-1} and Γ_3^{-1}, the respective rates κ_2 and κ_3 of positron capture in these defects can be derived from simple rate equations, with the result

$$\kappa_2 = I_2(\Gamma_1 - \Gamma_2), \quad \kappa_3 = I_3(\Gamma_1 - \Gamma_3). \tag{1}$$

Γ_2 and Γ_3 are then the positron annihilation rates characteristic of these *A* centers. The annihilation rate in the crystal bulk γ_c is given by

$$\gamma_c = \Gamma_1 - \kappa_2 - \kappa_3 . \tag{2}$$

These derived quantities are also listed in Table I.

The content of impurities other than Ca^{2+} and the thermal history of the crystals[3] are sufficiently equal that one can attribute $\kappa_2 \sim$ constant to positron traps inherent to the crystals. Only κ_3 varies systematically with the Ca^{2+} concentration. At room temperature, most of the cation vacancies neutralize the divalent impurities by association on adjacent lattice sites. They should be ineffective as positron traps. A small concentration n_v is available as isolated cation vacancies for *A*-center formation. For our crystals one finds[4]

$$n_v \simeq (C/Z_1)^{1/2}\, e^{-E_a/2kT}, \tag{3}$$

where C is the concentration of Ca^{2+} ions, $Z_1 = 12$ (the cation coordination number), E_a the free energy of association between a Ca^{2+} ion and a cation vacancy on nearest lattice sites, and $kT = 2.5\times10^{-2}$ eV at room temperature.

By linear-regression analysis, one finds $\kappa_3 \sim C^{1/2}$ with a correlation coefficient of 0.994 (Fig. 1); the correlation coefficient for $\kappa_3 \sim C$ is only 0.923. The slope in Fig. 1 is $\kappa_3/C^{1/2} = (2.8 \pm 1.0)\times10^{-2}$ [nsec (ppm)$^{1/2}$]$^{-1}$.

The slope can be discussed in terms of two limiting cases of the same physical situation: (i) The positrons interact weakly with the lattice and probe

TABLE I. Characteristics of positron lifetime spectra in KCl:Ca. The data, averaged over several runs, are reproducible to ±5%. Rates are given in (nsec)$^{-1}$. Crystal designations refer to compositions listed in Ref. 3.

Crystal	Ca (ppm)	I_1	Γ_1	I_2	Γ_2	I_3	Γ_3	γ_c	κ_2	κ_3
0302	0	0.50	4.80	0.48	1.88	0.02	0.69	3.32	1.40	0.08
0413 II *b*	0	0.55	5.04	0.43	1.89	0.02	0.51	3.60	1.35	0.09
0613 II	60	0.54	4.73	0.36	1.90	0.09	0.77	3.31	1.02	0.36
0613 III	90	0.46	4.34	0.44	1.84	0.10	0.83	2.90	1.10	0.35
0621 III	400	0.35	4.41	0.46	2.14	0.19	0.86	2.70	1.04	0.67

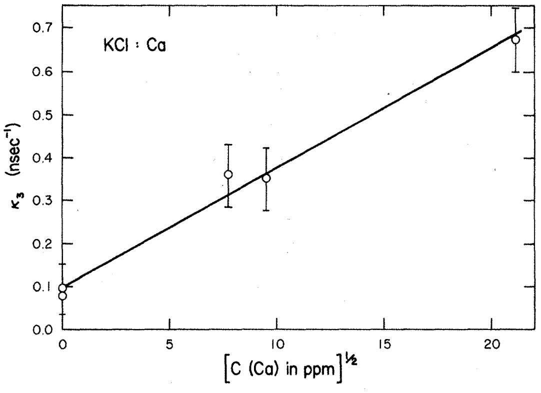

FIG. 1. Positron capture rate κ_3 vs square root of Ca concentration in KCl. The indicated errors are upper bounds.

it as free particles of effective mass m_+^*, velocity v_+, and wavelength $\lambda\!\!\!^- = \hbar/m_+^* v_+ \gg R$; $R \sim (\frac{1}{2}a)$ being the effective vacancy radius comparable to the lattice constant $a(\mathrm{KCl}) = 6.3\,\text{Å}$. Then,

$$\kappa_3 \simeq \rho_{\mathrm{KCl}}\, n_v v_+ \sigma_v\,, \tag{4}$$

where ρ_{KCl} is the reciprocal KCl unit-cell volume and σ_v the positron-capture cross section of the vacancies. Approximately, $\sigma_v = \pi(\lambda\!\!\!^- + R)^2 \xi$; the trapping coefficient ξ depends on the positron wave number inside (K_+) and outside (k_+) the vacancy to lowest order in k_+ as $\xi \simeq 4k_+/K_+$. For $m_+^* \simeq m$, one finds $\sigma_v \simeq 4\times10^{-14}$ cm^2 or $v_+\sigma_v \simeq 5\times10^{-7}$ cm^3 sec^{-1}. (ii) The positrons interact strongly with the anions and diffuse by random walk from site to site until they either annihilate, after a time γ_c^{-1}, in the crystal bulk or are captured by a cation vacancy at the rate

$$\kappa_3 \simeq \rho_{\mathrm{KCl}}\, n_v 4\pi R D_+\,, \tag{5}$$

where D_+ is the positron diffusion coefficient. From the slope in Fig. 1 and Eq. (3), with $E_a \simeq 0.3$ eV,[3] it follows that the values of $v_+\sigma_v$ or $4\pi R D_+$ must be of order $\sim 2.5\times10^{-9}$ cm^3 sec^{-1}. Approximation (i) in KCl seemingly is inconsistent with this result. (However, one should expect it to apply, e.g., in metals.) Therefore, we attribute κ_3 to the diffusion of positrons to Ca^{2+}-induced free-cation vacancies where they annihilate with the lifetime $\Gamma_3^{-1} = 1.3$ nsec. Subject to the large effects of errors in E_a, the diffusion constant for this process is $D_+(\mathrm{KCl}) \simeq 6\times10^{-3}$ cm^2 sec^{-1}.

This number is instructive. Since $D_+ = (a/\sqrt{2}\,)^2 \times (Z_1\tau)^{-1}$, a thermal positron dwells in a unit cell for a time $\tau \sim 3\times10^{-14}$ sec. The positron visits $(\tau\gamma_c)^{-1} \sim 10^4$ unit cells, covers some $a/(\sqrt{2}\,\tau\gamma_c) \sim 5\times10^4\,\text{Å}$ on its random walk, and diffuses over a mean distance $(2D_+\gamma_c^{-1})^{1/2} \sim 2\times10^2\,\text{Å}$ before it annihilates with an electron in the crystal bulk. Still, while in a crystal cell, the positron can form a nearly stable Wheeler compound $\mathrm{Cl}^- e^+$ of binding energy[5] $E = 3.74$ eV in the sense that the dwell time τ is some 10^2 times longer than the eigentime $\hbar/E = 2\times10^{-16}$ sec of the compound.

The question remains as to the nature of the defects appearing as component 2. Apparently here positrons probe traps of concentration $(\kappa_2/\rho_{\mathrm{KCl}} 4\pi R D_+) \sim 30$ ppm which, if voids, must be smaller than the vacancies introduced by Ca^{2+} or otherwise bind positrons less tightly than either an anion (where $\gamma_c^{-1} \simeq 0.3$ nsec) or a cation vacancy (where $\Gamma_3^{-1} \simeq 1.3$ nsec) to cause a $\Gamma_2^{-1} \simeq 0.5$ nsec such that $\gamma_c > \Gamma_2 > \Gamma_3$.

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