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Positron Annihilation in Ca^{2+}-Doped KCl–Temperature and Magnetic Field Effects[*]

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The temperature dependence of the positron lifetime spectra shows, contrary to expectations based on earlier work, that all positive-ion vacancies introduced by Ca^{2+} doping can act as traps for positrons in which they annihilate with a distinct long lifetime. Magnetic quenching of the long-lifetime component indicates that in this state the positron wave function overlaps with a partially spin-polarized wave function of crystal electrons.

A previous paper[1] reported lifetime spectra of positrons annihilating in Ca^{2+}-doped single crystals of KCl. A new third long-lived component, of mean lifetime ~ 1 nsec, appears with an intensity that grows with the molar Ca^{2+} concentration C. This finding was confirmed recently by Hsu *et al.*[2] The spectra were analyzed to extract the rate κ_3 for positron capture in defects that are available at concentration $n_d(C)$ such that

$$\kappa_3(C)=\chi\rho_{\mathrm{KCl}}\,n_d(C)\ , \qquad (1)$$

where χ denotes the volume rate related to the positron propagation rate in the crystal and ρ_{KCl} is the reciprocal KCl unit-cell volume.

For definiteness, one adopts the following model for Ca^{2+}-doped KCl crystals.[3] Ca^{2+} ions replace K^+ ions substitutionally in the KCl lattice. To preserve charge neutrality a positive-ion vacancy is formed for each implanted Ca^{2+} ion. Most vacancies are associated with a Ca^{2+} ion on nearest positive-ion sites. At finite temperatures T, a fraction of the vacancies are free; i.e., they are removed from Ca^{2+} sites by more than one nearest-neighbor distance. If positrons can be trapped by all Ca^{2+}-induced vacancies, then $n_d = C$. If, however, they can be trapped only in free vacancies, the mass-action law predicts that at thermal equilibrium

$$n_d \simeq (C/Z_1)^{1/2}\, e^{-E_a/2kT}\ , \qquad (2)$$

where $Z_1 = 12$ is the cation coordination number and $E_a(\mathrm{KCl}) \simeq 0.3$ eV is the free energy of association between a vacancy and a Ca^{2+} ion.

Reference 1 presented data measured at room temperature T_R, which showed a C dependence of κ_3 closer to $\kappa_3 \propto C^{1/2}$ than to $\kappa_3 \propto C$, and thus supported the idea that positrons annihilating with the long lifetime are trapped preferentially in free vacancies. If this is so, Eq. (2) predicts a strong increase with temperature of n_d and hence, through κ_3 [Eq. (1)], a strong temperature dependence of the positron lifetime spectra with the possibility of an independent determination of E_a.

We measured lifetime spectra in the range from $T_R = 290$ °K to $T = 980$ °K for two crystal pairs of the same origin as those studied in Ref. 1. One set was doped with $C = 150$ ppm of Ca, the other with $C = 400$ ppm. A sandwich of two single crystals with an interjacent ^{22}Na activity deposited on a 1-mg/cm^2 mica foil was held in a quartz cell by gently packed dry KCl powder, sealed under vacuum, and placed in a furnace with automatic temperature control. The thermally insulated assembly was placed between the two scintillator-photomultiplier γ-ray detectors of a standard fast-slow coincidence apparatus, with a 350-psec prompt resolution and a decay slope of 10^{-2} psec^{-1}. The spectra were resolved into three distinct components by the same least-squares computer routine as employed in Ref. 1.

As Fig. 1 shows, the results are not consistent with a κ_3 that depends on the temperature through n_d as given by Eq. (2). Only a weak temperature dependence appears which is barely above the experimental uncertainties in κ_3. If one were to attribute this trend only to changes in n_d (keeping χ constant), it would mean that $E_a = 0.03$ eV at most, in contradiction to theoretical and other experi-

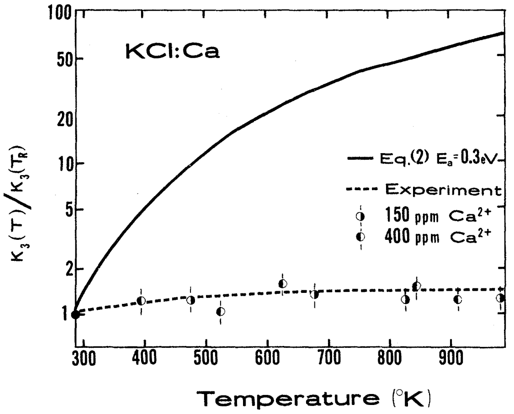

FIG. 1. Positron capture rate at temperature T relative to that at room temperature T_R, $\kappa_3(T)/\kappa_3(T_R)$. The solid curve is the T dependence expected from Eq. (2) with $E_a=0.3$ eV. The experimental points linked by the dashed curve were measured for KCl crystals doped with Ca^{2+} concentrations of 150 and 400 ppm.

mental evidence which supports values of $E_a = 0.3$ eV or greater.[3,4]

In the course of this study we determined with higher accuracy than in Ref. 1 the κ_3 values of all crystal pairs at T_R and, in particular, that of the 400-ppm crystal pair because it probes the C dependence of κ_3 most critically. We find, on better statistics, the value κ_3(400 ppm)$= 1.2 \pm 0.1$ nsec^{-1} which is significantly higher than the value 0.7 nsec^{-1} reported in Ref. 1. The other κ_3 values remained essentially unchanged. As can be seen in Fig. 2, the present set of κ_3 values supports a linear dependence $\kappa_3 \propto C$. This, then, is consistent with a temperature-insensitive n_d because it implies that all positive-ion vacancies introduced by Ca doping are available as potential positron traps, irrespective of their position in the lattice relative to the Ca^{2+} sites. We calculate that the binding of a positron in an associated vacancy is not significantly reduced by the proximity of the Ca^{2+} ion. This result can be viewed as a consequence of the fact that the effective dipole moment of an associated Ca^{2+}-vacancy pair in the lattice is some 15 times larger than the minimum dipole moment (equal to 0.639 a.u.)[5,6] required for the binding of an electronic particle to a dipole. The volume rate $\chi = 2\times 10^{-10}$ $\text{cm}^3\,\text{sec}^{-1}$ corresponding to the straight line in Fig. 2, if analyzed along the lines suggested in Ref. 1, leads to a diffusion coefficient $D_+ \simeq 5 \times 10^{-4}$ $\text{cm}^2\,\text{sec}^{-1}$, and to a dwell time for the positron in the unit KCl cell of 3.5×10^{-13} sec. This reinforces one of the main conclusions reached in Ref. 1, namely, that the positron moves through the crystal by tunneling from unit cell to unit cell with dwell times that are some 10^2–10^3 times larger than the eigentime of the Wheeler compound PsCl.

To further elucidate the properties of the positron-annihilating centers formed by positron trapping in Ca^{2+}-induced defects, we measured the magnetic field dependence of the lifetime spectrum. The experiments were performed with an apparatus of a broadened time resolution (~700 psec) imposed by the light pipes necessary for the removal of the photomultipliers from the magnetic field.

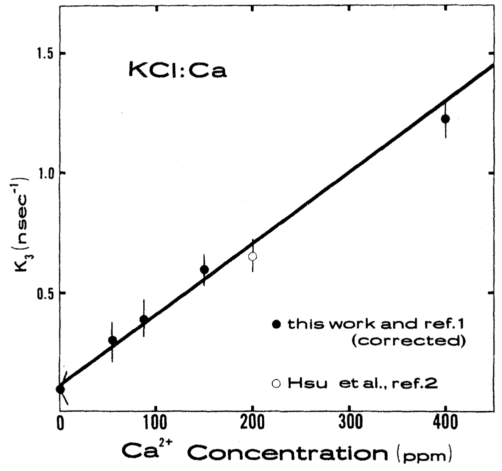

FIG. 2. Capture rate κ_3 of positrons in KCl at T_R, as a function of the Ca^{2+} concentration C. The straight line corresponds, by Eq. (1), to $n_d = C$ and a volume rate $\chi = 2\times 10^{-10}$ cm^3/sec.

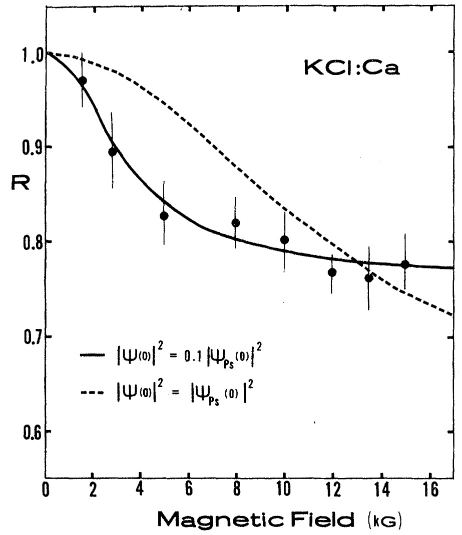

FIG. 3. Magnetic quenching of the long-lived component in KCl doped with 400-ppm Ca^{2+}. Curves are calculated according Ref. 7. Dashed curve: positronium *in vacuo*. Solid curve through experimental points: $|\psi(0)|^2 = 0.10\,|\psi_{Ps}(0)|^2$.

The long-lived component was nevertheless clearly resolved from the shorter ones. For a discussion of the magnetic field effect on the positron lifetime spectra, we resort to the procedure employed previously in magnetic-quenching experiments.[7] One calculates the ratio R of the number of annihilations with field on and field off in a given interval of delayed-coincidence times chosen such that in this range the contribution of the short-lived components can be neglected.

The points in Fig. 3 show the results for the $C = 400$ ppm crystal pair. The intensity of the long-lived component so probed is clearly reduced by the static magnetic field. This suggests that the wave function of positrons trapped in Ca^{2+}-induced defects overlaps with an unpaired-spin component in the wave function of the crystal electrons near the trap.

The extent of the positron and unpaired-electron overlap can be deduced from the magnetic-quenching data as follows. A theoretical value of R can be calculated, according Ref. 7, with the overlap, expressed by the unpaired-electron density at the positron, $|\psi(0)|^2$, as the only adjustable parameter. With a least-squares-fitting procedure to our data one finds $|\psi(0)|^2 = (0.10 \pm 0.01)|\psi_{\mathrm{Ps}}(0)|^2$, where $|\psi_{\mathrm{Ps}}(0)|^2$ is the overlap in the ground state of positronium *in vacuo*. The resulting R is drawn in Fig. 3 (solid line). The quenching ratio R for positronium *in vacuo* is shown for comparison (dashed line).

The overlap with an unpaired electron is much more pronounced when positrons annihilate at the F centers in additively colored KCl crystals. Although the long lifetimes are nearly the same, one finds here a distinctly different quenching curve corresponding to $|\psi(0)|^2 = (0.29 \pm 0.04)|\psi_{\mathrm{Ps}}(0)|^2$.[8] The significance of these differences as regards the electronic structure of the positron annihilation centers is under study.[9] It is apparent that magnetic quenching offers an effective method for differentiating in solids between long-lived positron states of different origins but of otherwise very similar annihilation characteristics.

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Electric Field Effects in Optical and First-Derivative Modulation Spectroscopy

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The large selection of electroreflectance data available in the literature enables surface field effects on optical and first-derivative modulation spectra to be estimated for most materials. A method for doing this is presented.

Since the first experimental investigations of the electroreflectance effect, it has been recognized that surface electric fields in a semiconductor or insulator could influence the values of optical "constants," determined either directly by means of normal- or non-normal-incidence techniques or indirectly by means of first-derivative techniques.[1] Yet in most such experimental measure-