Positron Annihilation Centers in NaCl[†]

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The intensity of the long-lived component in the positron lifetime spectrum of NaCl is found to be correlated with the x-ray-induced growth and thermal annealing of the *V*-region color centers. If this lifetime component is attributed to positrons annihilating on defects, called annihilation or *A* centers, the data indicate that *V*-center formation reduces *A*-center formation. The results suggest that positron-annihilation measurements can serve as an important complement to color-center measurements in the study of defects in ionic crystals.

Certain characteristics in the lifetime spectra of positrons annihilating with electrons in solids can be correlated well, but not unequivocally, with defect concentrations.[1] Qualitative evidence was presented earlier that the longer lived of the two positron-lifetime components observed in NaCl can be modified reversibly by changing the color-center concentration through ionizing radiation.[2] More recent studies on crystals with color centers, introduced irreversibly by excess alkali concentrations, appear to be in accord with this observation.[3-5]

This Letter reports systematic measurements that link positron-lifetime spectra to color-center concentrations in NaCl crystals subjected to a sequence consisting of (1) x-ray–induced coloring, (2) white-light bleaching, and (3) thermal annealing. The data exhibit a strong correlation between the long-lived positron-lifetime component and the concentration of "*V*-region" color centers. The results suggest that positron-annihilation measurements can become an important new technique for the study of defects and color centers in solids.

The long-lived component in the positron-lifetime spectra of alkali-halide crystals has been attributed to positrons trapped over periods $>10^{-9}$ sec by crystal defects, forming annihilation or *A* centers.[1] *A* centers can be resolved experimentally as distinct components of lifetime spectra if the annihilation rate for positrons trapped in *A* centers is appreciably longer than the annihilation rate in the bulk of the crystal. The conceptually simplest *A* center is a positron trapped in a positive-ion vacancy. The simplest *F* center consists of an electron trapped in a negative-ion vacancy. In this sense the positron *A* center forms, albeit only for the short time until the positron annihilates with an electron ($\sim 10^{-9}$ sec), the antimorph of the electron *F* center.

The kinetics of *A*-center formation can be characterized by four processes: (1) A positron thermalized in the bulk of the crystal annihilates at the rate γ_c. (2) In competition with (1), the positron can be trapped by a defect at the rate κ to form an *A* center. (3) A positron in an *A* center annihilates at the rate γ_a. (4) In competition with (3), the positron can escape from the *A* center into the bulk of the crystal at the rate λ. The parameters γ_c, γ_a, and λ are characteristics of the crystal and its defects. The trapping rate κ is related to the defect concentration available for *A*-center formation, n_d, by $\kappa = \nu\rho_c n_d$ where, at least in first approximation, the product of the volume capture rate ν and the reciprocal unit-cell volume ρ_c can also be treated as a time-independent characteristic of the crystal.

The solution of the coupled differential equations describing processes (1) to (4) yields the probability $p(t)$ that the positron entering the crystal at the time $t=0$ has not annihilated with an electron at the time t:

$$p(t)=\frac{\gamma_c-\Gamma_2}{\Gamma_1-\Gamma_2}\exp(-\Gamma_1 t)+\frac{\Gamma_1-\gamma_c}{\Gamma_1-\Gamma_2}\exp(-\Gamma_2 t), \quad (1)$$

where the rates Γ_1 and Γ_2 are given by

$$\Gamma_{1,2}=\tfrac{1}{2}\{\gamma_c+\gamma_a+\kappa+\lambda \pm[((\gamma_c+\kappa)-(\gamma_a+\lambda))^2+4\kappa\lambda]^{1/2}\}. \quad (2)$$

The subscript 1 refers to the plus sign, and 2 to the minus sign.

In the following, the observed intensity of the long-lived component, I_2, is identified with the term $(\Gamma_1-\gamma_c)/(\Gamma_1-\Gamma_2)$. Since I_2 is in fact distinguishable experimentally, it follows that $\lambda \ll \gamma_a$, or

$$\Gamma_1=\gamma_c+\kappa;\quad \Gamma_2=\gamma_a. \tag{3}$$

The concentration n_d of defects available for the formation of A centers characterized by γ_a can be deduced from measured quantities through the capture rate[1]

$$\kappa=\nu\rho_c n_d=(\Gamma_1-\Gamma_2)I_2=(\gamma_c-\gamma_a)I_2/(1-I_2). \tag{4}$$

The measurements are guided by the following concepts. F centers and V centers are formed by ionizing radiation. The processes leading to radiation-induced F-center formation in alkali halides are not completely understood.[6,7] F centers are thought to be formed by electron capture in association with one or more defect reactions, such as the breakup of defect clusters or the separation of defects from dislocations. Capture of electrons by isolated anion vacancies is the simplest and possibly an idealized form of F-center formation. Similarly, the nature of many of the types of centers contributing to the broad V-region absorption is not understood, although there is wide acceptance of the idea that most of the V-region centers are formed by hole caputre.[7] The conceptually easiest idea is the formation of the idealized, but not experimentally established, prototype of a V center: a hole captured by an isolated positive ion-vacancy. These uncertainties as regards color-center formation notwithstanding, it is clear that the role of any defect that can function as a positron A center would be modified if it were converted into a color center by electron or hole capture. Specifically, if the defects involved in positron annihilations are progenitors of either the F or any of the V centers, the conversion of such defects into color centers should be detectable as a change in the long-lived component of the lifetime spectrum. For example, the trapping of a hole on any hole-center precursor could render it inoperable as an annihilation center. I_2 should then decrease with increasing optical density in the spectral range of the V bands, i.e., with increased V-center concentration n_V, while $\Gamma_2=\gamma_a$ remains unchanged. The quantity

$$\Delta_2\equiv[I_2/(1-I_2)]_1-[I_2/(1-I_2)]_0 \tag{5}$$

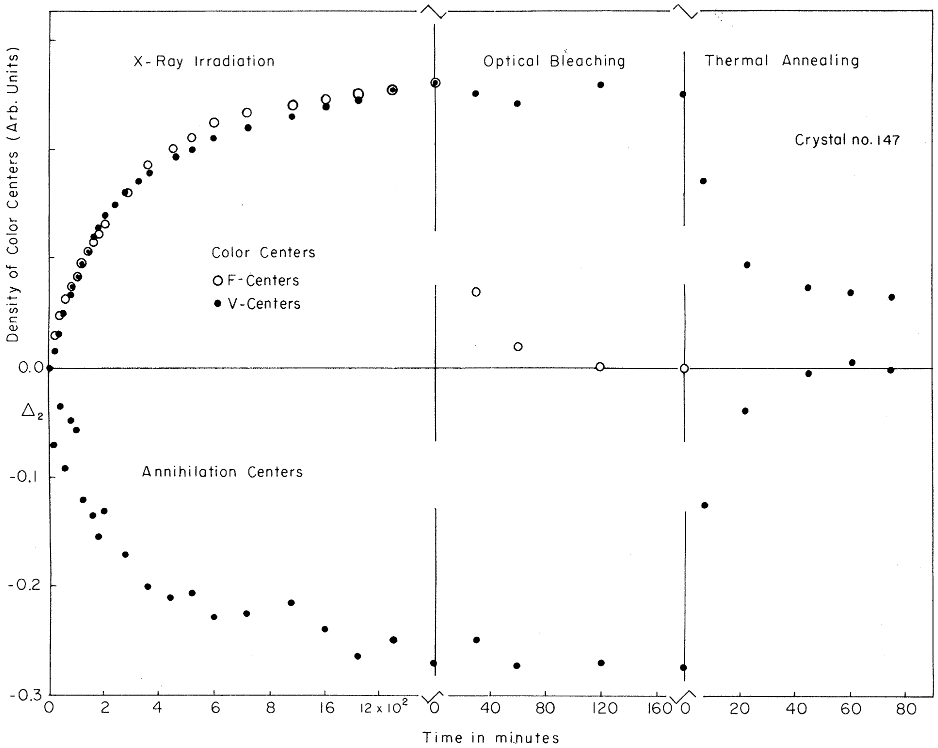

FIG. 1. Growth and annealing curves for the F- and V-center concentrations in NaCl and the change of I_2 as expressed by Δ_2 [Eq. (5)]. The relative uncertainty of the points is comparable to their scatter about a smooth dependence on duration of treatment; the data are reproducible to ±5%.

should depend on n_V as

$$-\Delta_2=[\nu\rho_c/(\gamma_c-\gamma_a)]n_V. \qquad (6)$$

The subscripts 0 and 1 refer to the data as measured on the untreated and treated crystals, respectively.

Pairs of NaCl single crystals of dimension $1\times1\times0.2$ cm^3 were cleaved from a Harshaw boule. The optical-absorption and positron-annihilation spectra were recorded at room temperature after treatment for given time intervals in three phases: (1) room-temperature (RT) x-ray irradiation at ~1.5×10^2 R/min with a W cathode at 50 kV; (2) RT optical bleaching in white light from a fluorescent lamp; (3) annealing at 480°C.

The concentrations of the F centers and the centers in the V region, n_F and n_V in arbitrary units, are assumed to be proportional to the optical absorption in these regions. The F-center absorption was determined from the height of the F band at 465 nm and the V-region absorption from the total "area" under the absorption curve in the region between 190 and 360 nm. The positron-lifetime spectra were measured in a standard manner by a fast-slow delay coincidence apparatus with a Na^{22} positron source sandwiched between the crystal pair. The prompt spectrum had a half-width of 360 psec and a decay slope of ~1.1×10^{-2} psec^{-1}. The positron-lifetime spectrum was computer analyzed, after unfolding of the prompt spectrum, in terms of two principal lifetime components (I_1, Γ_1) and (I_2, Γ_2). A weak (<2%), slowly decaying component remained unchanged during the experiments and was subtracted out with the random-coincidence background. By averaging over the measurements on the four crystal pairs investigated we find that $\gamma_c=3.43\pm0.08$ nsec^{-1} and $\gamma_a=2.22\pm0.08$ nsec^{-1}, independent of the experimental conditions in the three phases of the experimental cycle. The initial values of $I_2=1-I_1$ in our thin samples are 0.50 ± 0.05. We found that $I_2\sim0.3$ in thick crystals, presumably because the cleaving introduces a larger defect concentration in thin crystals than in thick crystals over the range of positron penetration.

Figure 1 shows the results for one crystal pair. The scales in the upper part are adjusted so that the optical densities are equal in magnitude to $-\Delta_2$ [Eq. (5)] at the maximum x-ray–exposure time in phase (1). Through Δ_2 the decrease of the intensity of the long-lived component I_2 is apparently correlated equally well with n_F and n_V. However, white-light bleaching in phase (2) reveals a specific correlation between the V-region absorption and I_2: n_F vanishes, while n_V and Δ_2 remain unchanged.[8] Annealing at 480°C in phase (3) removes most of the V-region coloring and restores Δ_2 to its initial value. That is, annealing reduces the otpical absorption in the V region and increases the long-lived component in the positron-lifetime spectrum. The same behavior is found in the four crystal pairs so investigated. Figure 2 summarizes the results. Within the experimental scatter, it confirms the linear relation between Δ_2 and n_V anticipated by Eq. (6).

One can estimate an effective defect concentration available for A-center formation by setting $\kappa_0=4\pi RD_+\rho_c n_d$, where $R\sim3$ Å is the capture radius of the defect and $D_+\simeq6\times10^{-3}$ cm^2/sec is the positron diffusion constant in alkali chloride, as extracted from positron-lifetime data of Ca^{2+}-doped KCl crystals.[9] From the measured trapping rate $\kappa_0=1.2\pm0.1$ nsec^{-1} one obtains $n_d\simeq20$

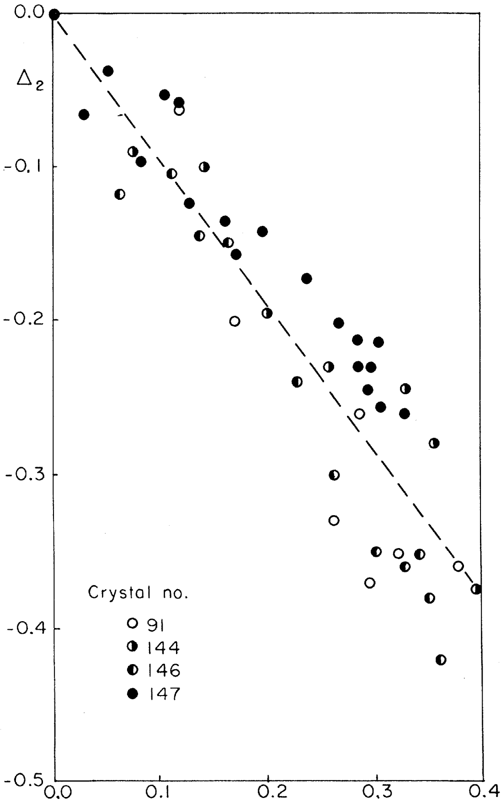

FIG. 2. The measured decrease in the long-lived component I_2 of the positron-lifetime spectrum as expressed by Δ_2 [Eq. (5)] versus the V-center concentration as measured by optical absorption for four NaCl crystal pairs. The uncertainty in the points is comparable to their scatter about the dashed line.

ppm. This value is larger than one would expect if only isolated positive-ion vacancies were to contribute; based on thermodynamic considerations[10] for our levels of crystal purity, they should be present only in concentrations ~1 ppm. The proportionality factor between Δ_2 and n_V in Eq. (6) as estimated from positron data becomes $4\pi R D_+ \rho_c/(\gamma_c - \gamma_a) \simeq 5\times 10^{-2}$ ppm^{-1}; the V-center concentration scale of the abscissa in Fig. 2 is then given in units of ~20 ppm.

In conclusion, the long-lived component of the positron-lifetime spectrum in NaCl crystals can be attributed to the trapping of positrons on potential V-region color centers. The principal evidence for this is the experimentally demonstrated fact that the quantity κ, which is a measure of the concentration of defects available for A-center formation, decreases as the V-region absorption increases; annealing of the samples restores both the optical absorption and κ to their original values. This is consistent with the premise that most of the V centers stable at room temperature are defects with trapped holes, and that hole trapping renders defects inoperable as sites for positron annihilation with distinctly resolvable rates.

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Excitons in Indirect Electroabsorption*

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Exciton effects have been included in a calculation of the indirect differential electroabsorption coefficient at the fundamental optical absorption edge of Ge. The theory is in very good agreement with experiment; this is the first successful attempt to obtain a quantitative fit to electroabsorption data. The theoretical fit yields a value of 0.6701 eV for the indirect band gap of Ge at 296°K.

In recent years modulation spectroscopy has become a powerful experimental tool for investigating the optical properties of solids.[1,2] In spite of tremendous experimental advances, theories[3] of modulation spectra have been limited to the one-electron approximation, with the result that quantitative agreement between experiment and theory has yet to be obtained. The development of theoretical techniques[4] for evaluating the optical absorption by Wannier excitons in a uniform electric field makes it possible to go beyond the one-electron approximation and to calculate $\Delta\alpha(\omega, F)$, the electric-field-induced change in the optical absorption. In this Letter we report the results of the first calculations to include electron-hole correlations in the evaluation of the differential absorption coefficient at the indirect edge of Ge.

The indirect transitions in Ge and in Si represent an ideal test for a theory of electroabsorption because (a) the zero-field Elliott theory[5] is known to agree well with experiment,[6] (b) energy conservation forbids many of the broadening processes which complicate the spectra at higher optical thresholds, and (c) the energy-band structures are well known.[7] Therefore, we have calculated the indirect phonon-assisted electroabsorption for these materials and have compared