PHYSICAL REVIEW B VOLUME 27, NUMBER 4 15 FEBRUARY 1983

Interactions between self- and solute trapping of photocarriers in Pd-doped AgCl

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(Received 7 October 1982)

EPR studies on ultraviolet-irradiated crystals of AgCl:Pd have confirmed earlier results on AgCl:Cu for the existence of an energy barrier in the self-trapping of the photohole. The height of this barrier is near 1.8 meV. Migration of the self-trapped hole was found to be athermal for temperatures below 30 K; above 35 K the self-trapped hole hops, with a diffusivity given by $D = 7\times10^{-7}\exp(-61\text{ meV}/kT)$ cm^2/sec. This suggests that the value of the electron transfer integral is about 1% of the energy of the phonons involved, that the bandwidth for the self-trapped hole is of the order of 2 meV, and that the binding energy of the hole is approximately 0.1 eV. The dependence on temperature of the efficiency of photoproduction of various trapped-carrier palladium centers was determined, and was correlated with the migration of the self-trapped hole. The presence of a small amount of Fe^{2+} "tracer" served to indicate those decay processes that were due to thermal release of trapped holes.

I. INTRODUCTION

The properties and interactions of both ionic and electronic point defects are, in many ways, perhaps better understood for silver chloride and silver bromide than for any other ionic materials. In part, this is due to the very high mobility of the interstitial component of the intrinsic cation Frenkel defect; it has thus been possible to characterize in detail the properties of the lattice defects, even to the extent of determination of the temperature dependence of the formation enthalpies (see, for example, Friauf[1] and Jacobs *et al.*[2]). Further, because of the indirectness of the electron energy gap, large photocarrier lifetimes can be achieved so that semiconductor-type experiments, as well as optical studies of electronic defects, thereby become feasible (the photocarrier-phonon interaction in the silver halides has recently been reviewed by Kanzaki[3]). It is therefore not surprising that the dynamics of the trapping of photocarriers in the silver halides should be of interest, not only because of its relevance to the effects of solute ions in the photographic process, but also for its own sake.

This paper is concerned with the properties of self-trapped holes in silver chloride, and with the interactions of these with photocarriers trapped at divalent palladium ions, with or without a nearby charge-compensating cation vacancy. Several types of carrier trapping are found in silver chloride. First, even in the absence of impurity ions, the hole becomes self-trapped below liquid-nitrogen temperature. The resulting localized state, first reported by Höhne and Stasiw,[4] is centered on a cation site, forming Ag^{2+}; relaxation of the neighboring chlorides produces a center tetragonally distorted along the [100] axis. A second type of trapping is the hydrogenlike binding of a carrier in the Coulombic field of a defect with a net charge (e.g., a divalent ion). Because of the large dielectric coefficient and relatively small effective masses in AgCl, this Coulombic binding is very weak, only a few hundredths of an electron volt, as shown by Brandt and Brown.[5] As a result, such centers are stable only near absolute zero, and will be of no further interest here. A third process involves the incorporation of the carrier into an inner shell, the *d* or *f* shell of a transition ion, resulting in trap depths of the order of several tenths of an electron volt. Since such solutes exist in AgCl typically as substitutional divalent ions, charge compensated by a cation vacancy (Ag^{+}_{vac}), the location of the vacancy can play a major role in determining the stability of the trapped carrier. Thus, in the AgCl:Pd^{2+} system of interest in the present work, Eachus and Graves[6] have shown that the isolated Pd^{2+} ion is a deeper trap for photoelectrons than is the electrically neutral next-nearest-neighbor complex $Pd^{2+}(Ag^{+}_{\mathrm{vac}})$. Moreover, this neutral complex can also act as a hole trap, whereas, as expected, the positively charged free palladium ion cannot. Additionally, the behavior of Fe^{2+}, which is also present in our crystal, is particularly interesting: It does not capture electrons, but can acquire a hole, upon which the resulting ferric ion moves into an interstitial position and becomes stabilized by either four nearest-neighbor cation vacancies[7] or only three, if the temperature is too low for immediate formation of the more stable configuration.[8] These two centers will be referred to as $\mathrm{Fe}^{3+}_{\mathrm{cubic}}$ and $\mathrm{Fe}^{3+}_{\mathrm{trig}}$, respectively.

In the case of the self-trapping of the hole in silver chloride, earlier results from this laboratory[9] have demonstrated that this involves an activation energy, as had been proposed theoretically by Sumi and Toyozawa[10] and by Mott and Stoneham.[11] In our previous experiment, the specimen was doped both with Cu^{2+}, which served as a source of holes upon illumination with 435-nm blue light, and Cu^{+} which acted as a hole trap to compete with the self-trapping process. It was shown that the self-trapping process is indeed thermally activated, with an energy barrier of 1.7 meV. The purpose of the work described in the present report was to extend these earlier experiments in several ways. First, in these new studies both photoholes and electrons are produced with the use of band-gap excitation. Second, the crystal was doped with Pd^{2+} instead of copper; palladium represents a useful dopant for this type of experiment because, as shown by Eachus and Graves[6] and by Zhitnikov *et al.*,[12] one thereby introduces traps for both electrons and holes (in our experiment, we need an electron trap to prevent recombination with the holes). Third, in the present experiment, results are also obtained on the kinetics of the migration of the self-trapped hole. In addition, a detailed investigation of the effects of irradiation temperature on the types of centers produced will be shown to correlate well with the migration dynamics of both holes and cation vacancies, thus corroborating and extending somewhat Eachus and Graves's study of competitive trapping. Finally, the presence of several parts per million (ppm) of Fe^{2+} in our crystal will be seen to provide a useful indicator of which type of carrier is freed when an increase in temperature results in the recombination of trapped electrons and holes.

The Pd^{2+} ion has a $4d^8$ electronic configuration, so that paramagnetic centers are produced upon capture of either an electron or a hole. Although one of its isotopes has a nuclear spin of $\frac{5}{2}$ ($^{105}\mathrm{Pd}$, 22% natural abundance), neither the electron-paramagnetic-resonance (EPR) spectra reported by Eachus and Graves nor those obtained in the present work show any hyperfine splitting due to interaction with this nuclear moment. All three irradiation-produced paramagnetic species, Pd^{+}, $\mathrm{Pd}^{+}(\mathrm{Ag}^{+}_{\mathrm{vac}})$, and $\mathrm{Pd}^{3+}(\mathrm{Ag}^{+}_{\mathrm{vac}})$, were earlier shown each to have a [100] axis—the first because of a Jahn-Teller relaxation[6,13] and the other two because the cation vacancy is at a next-nearest-neighbor site. The resulting EPR spectra were satisfactorily interpreted by Eachus and Graves in terms of the superhyperfine interactions with the four nearest chloride ions (with nuclear spin $I=\frac{3}{2}$) in the plane perpendicular to the distortion axis, ignoring the fact that one-fourth of the Cl^{-} ions have a nuclear magnetic moment different from that of the dominant $^{35}\mathrm{Cl}$. This gives rise to the following spin Hamiltonian:

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)+\sum_{i=1}^{4}[A'_{\parallel}S_z I_z+A'_{\perp}(S_y I_y+S_x I_x)].$$

$A'_{\parallel}$ and $A'_{\perp}$ are the components of the superhyperfine-interaction tensor, and the z axis coincides with the [100] axis of elongation. The spectra obtained in the present work are consistent with the configurations attributed to the various EPR centers by Eachus and Graves, and we have adopted their assignments.

II. EXPERIMENTAL

The AgCl crystals used in this work were produced by Mr. C. B. Childs of the University of North Carolina from high-purity deoxygenated material doped with PdCl_2. They were grown from the melt at 1.0 mm/h with the use of the Bridgman method, under an atmosphere of 80 mm of fractionally distilled chlorine and 680 mm of ultra-high-purity nitrogen. Subsequent spectroscopic analysis of the samples used here showed a Pd^{2+} concentration of 40 ppm, and also the presence of 2.6 ppm of iron, which in the crystal presumably existed as substitutional Fe^{2+}. The crystals were oriented by means of Laue back-reflection methods. They were then gently cut with a fine-toothed jeweler's saw in the shape of a parallelepiped, with the major axis along [110], polished on successively finer papers, and then etched to remove the remaining surface damage. All handling of the specimens, including procedures during EPR runs, was carried out under yellow safelights.

Paramagnetic centers were produced by high-intensity irradiation of the crystals while in the cavity of a Bruker ER200 EPR spectrometer with the use of a narrow band centered on 375 nm. This wavelength is short enough to excite electrons across the band gap at low temperatures. The irradiation and measurement temperatures could be varied by means of an Oxford Instruments continuous-helium-flow refrigerator. After each irradiation, the EPR spectra, at 9.439 GHz, were usually taken at 14.5 K, although some studies of the thermal decay of centers were made at the decay temperature without periodically cooling down to 14.5 K.

III. RESULTS AND DISCUSSION

A. Self-trapped hole

If $\mathrm{AgCl{:}Pd}^{2+}$ is irradiated with band-gap light at a temperature well below 60 K, three strong EPR

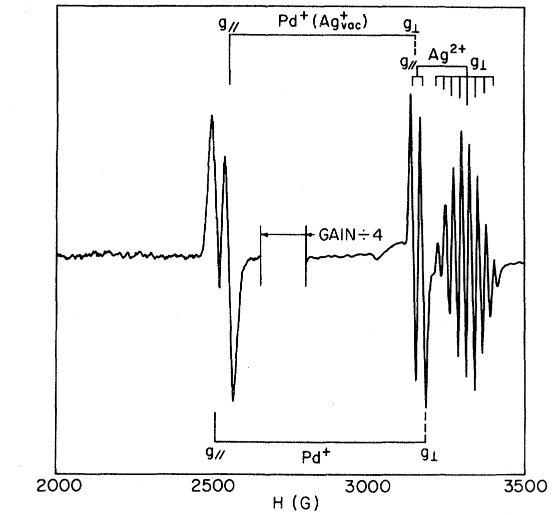

FIG. 1. EPR spectrum, measured at 14.5 K, after irradiation at 14.5 K with 375-nm light for 20 min.

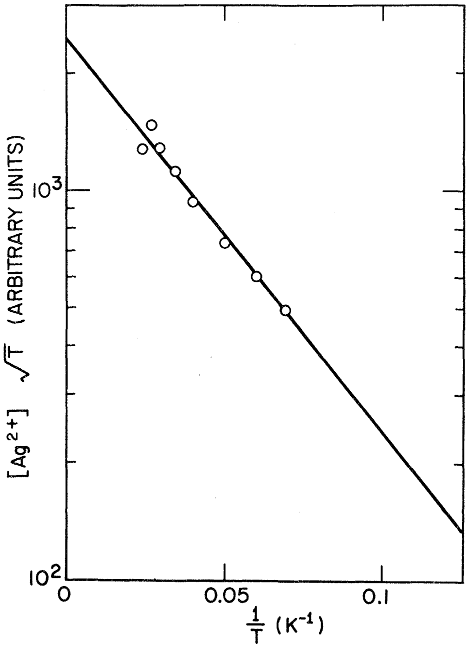

FIG. 2. Arrhenius plot of the temperature dependence of the number of irradiation-produced self-trapped holes.

spectra are produced, as shown in Fig. 1. The holes become self-trapped, and recombination is inhibited by the trapping of electrons at Pd^{2+} and Pd^{2+} (Ag^{+}_{vac}). The assignments indicated on Fig. 1 for the two palladium centers are those deduced by Eachus and Graves.[6] The values of spin-Hamiltonian parameters derived for these centers from our results are given in Table I.

An experiment was performed to corroborate, with this different system, the earlier measurement[9] on AgCl:Cu of the activation barrier involved in the transition of the hole from the free state to the localized self-trapped state. The crystal was exposed to a series of identical 5-min irradiations at temperatures in the range 14.5—37 K. The lower limit of this range is imposed by the tunneling process that appears near 10 K, while the upper limit is determined by the onset of thermally activated hopping of the self-trapped hole, which renders their spectrum unstable as they decay out. After each exposure, the resulting EPR spectrum was measured at 14.5 K, and the crystal was then annealed at 50 K to restore it to its original state. As was argued in our previous paper, one expects that the number of self-trapped holes produced by each 5-min exposure will increase with increasing temperature of irradiation as $T^{-1/2}\exp(-E/kT)$, where E is the energy barrier opposing the transition to the self-trapped, localized state. The data obtained here are shown in Fig. 2, and they are clearly consistent with this expectation. The activation energy derived from Fig. 2 is 2.0±0.3 meV, which may be compared with the 1.7±0.1 meV obtained earlier with copper-doped AgCl. The present determination is less precise because of complications due to the overlapping of EPR lines of the many types of centers that are present. The two sets of data, however, are consistent, thus corroborating the model proposed.

TABLE I. Spin-Hamiltonian parameters of photoproduced centers in AgCl:Pd, Fe. (The values of A and A' are all in units of 10^{-4} cm^{-1}.)

Center	g_{11}	$g_{\perp}$	A_{11} (hyperfine	$A_{\perp}$ interactions)	A'_{11} (Cl super-hyperfine	$A'_{\perp}$ interactions)
Ag^{2+}	2.141±0.001	2.041±0.001	24.7±1	31.3±1		
Pd^{+}	2.665±0.001	2.139±0.001			7.4±1	7±1
$Pd^{+}(Ag^{+}_{vac})$	2.643±0.001	2.141±0.001			6.6±1	
$Pd^{3+}(Ag^{+}_{vac})$	2.020±0.001	2.017±0.001			33.6±1	6±1

The kinetics of the decay of the self-trapped hole signal was studied by following the decrease, with increasing time of aging, of the intensity of a particular EPR line, while holding the crystal at some fixed temperature in the range 14—50 K. In each case, the concentration of self-trapped holes was found to decrease by a first-order exponential decay, as would be expected if the number of final hole traps greatly exceeds the number of holes. Also, the total EPR spectrum of the crystal was monitored during a thermal bleaching at 40 K, and it was found that, as the Ag^{2+} centers disappear, not only do the concentrations of trapped-electron centers [Pd^+ and $Pd^+(Ag^+_{vac})$] concomitantly decrease, but also that those of two other hole centers, $Pd^{3+}(Ag^+_{vac})$ and Fe^{3+}_{trig}, increase. This appearance of new trapped-hole centers explains why the decay of the self-trapped hole is of first order, rather than the second-order kinetics that would result from recombination of equal numbers of holes and electrons. Furthermore, this demonstrates that the decay of the self-trapped hole is by means of its own migration, rather than as a result of the thermal release of trapped electrons, as Eachus and Graves had originally suggested.

The temperature dependence of this migration of the self-trapped hole is shown in Fig. 3, in the form of an Arrhenius plot of the time constant for the first-order decay of the corresponding EPR signal. There are two sharply delineated regimes: For temperatures greater than 35 K the data fit a simple thermal-activation relation, $\tau=\tau_0 \exp(H/kT)$, while for temperatures below 30 K, the migration rate of the self-trapped hole is almost independent of temperature and actually increases slightly as the temperature is lowered.

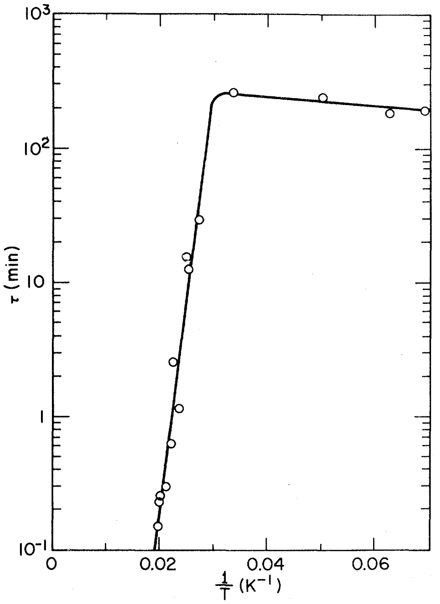

FIG. 3. Temperature dependence of the time constant for the exponential thermal decay of the concentration of self-trapped holes.

In the high-temperature "classical" region the data of Fig. 3 yield $\tau_0 = 8.5\times10^{-6}$ sec and $H = 61\pm3$ meV. This activation energy almost surely describes the hopping process, a phonon-assisted tunneling, rather than the depth of the self-trap, since the activation energy for hopping is expected to be considerably less than the trap depth.[14–16] To proceed further, we must ask whether, for the range of temperature above 35 K, those phonons involved in the hopping are essentially classically excited; this sets in at approximately one-third of the corresponding characteristic temperature θ. Since the self-trapped hole is localized within a single unit cell of the crystal, the pertinent phonons are primarily those of short wavelength on or near to the Brillouin-zone surface. If these are mainly the acoustical phonons, then their energies range from about 4 to about 13 meV,[17] and $\theta/3$ would run from 16 to 52 K. Thus, for many of these, the classical region of Fig. 3 is above $\theta/3$. In such a "high-temperature" regime, to a rough approximation the activation energy for hopping is expected to be about one-half of the binding energy of the self-trapped hole.[14,16,18] We may thus conclude that in AgCl the binding energy of the self-trapped hole is approximately twice 61 meV, or about 0.1 eV.

We can deduce further information about the hopping process from the magnitude of the preexponential factor τ_0. For random migration to a random distribution of fixed sinks, the relaxation time τ is given by $\tau=1/(4\pi rND)$; here r is the capture radius, which must be close to 1.5×10^{-8} cm for non-Coulombic traps, N is the density of traps, which must be somewhat less than our dopant concentration of about $10^{18}/cm^3$, and D is the diffusion coefficient of the hole, which will have the form $D_0 \exp(-H/kT)$. Inserting the experimental value of τ_0 (the exponential factors containing H cancel), we find that $D_0 \approx 7\times10^{-7}$ cm^2/sec. But D_0 is also equal to $(\frac{1}{6})\lambda^2 z \nu P$, where λ is the unit jump distance (about 3×10^{-8} cm), z is the number of equivalent jump directions possible from a given site (12 for the fcc lattice of AgCl, ν is a characteristic atomic vibration frequency (about 3×10^{12}/sec), and P is a factor that represents the probability that a hole will successfully make the jump when the necessary thermal energy is provided to the ions. The factor P consists of the product of two factors which are each less than unity: (a) the probability that the highly localized polaron can make the jump during the short time that the ions about an adjacent site are suitably relaxed,[14,15] and (b) the probability that the presence of the necessary thermal energy H actually does produce a set of ion relaxations that results in an energetically suitable site in the adjacent unit cell. From the value of 7×10^{-7} cm^2/sec for D_0, one obtains for P the value 10^{-4}. The fact that this is considerably less than unity is consistent with the idea that the wave function of the self-trapped hole in AgCl is highly localized within one unit cell, so that the electron transfer integral is small compared to the phonon energy.

For example, let us take the energy of the pertinent phonons to be about 6-meV, and suppose that we ignore the ion-configuration factor, item (b) above. Then, in the approximation of Eq. (64) of Emin's 1975 paper,[14] but including a factor of 12 for the number of crystallographically equivalent hopping directions, one estimates the electron transfer integral to have a value of about 1% of the 6-meV acoustical phonon. This, however, is perhaps an underestimate, since the ion-configuration factor may be substantially less than unity, and our result for the electron transfer integral will go inversely as the square root of that factor. In any event, with a coordination number of 12, one obtains from this value of the transfer integral a bandwidth for the self-trapped hole of the order of 2 meV.

Turning now to the low-temperature decay, apparent in Fig. 3 for temperatures below about 30 K, the almost completely athermal nature of this process is indicative of propagation within this very narrow small-polaron band of states. An earlier suggestion[19] that this phenomenon might be obscured in real crystals by the strain effects of background defects is perhaps not applicable here because well-annealed AgCl crystals can often have very low dislocation densities. Also of interest is the quite sharp transition seen in Fig. 3 around 30–35 K, much more abrupt than deduced from calculations based on model systems.[18]

The slight temperature dependence that is found for this process indicates that the mobility of the small polaron decreases with increasing temperature. This is presumably the result of the superposition of several weak effects: the effects of temperature on the width of the small-polaron band[14] and on the scattering of polarons by phonons and by defects, both charged and uncharged.

B. Photoproduced palladium centers

In order to study the temperature dependence of the relative efficiencies of photocarrier trapping at the various types of impurity-ion centers, the crystal was exposed to a sequence of 20-min ultraviolet irradiations, each at a successively higher temperature, from 10 to 225 K. The complete EPR spectrum was recorded at 14.5 K after each exposure. No thermal annealing at a high temperature was provided between one uv exposure and the next; this was dictated by the desire to preclude the premature accumulation of the $\mathrm{Fe}^{3+}_{\mathrm{cubic}}$ center. We thus assume that upon prolonged exposure to ionizing radiation at the next higher irradiation temperature, the centers originally present at the lower temperature come to the new steady-state distribution characteristic of this higher temperature. In contrast with the study of the self-trapping of the hole (described in Sec. III A), the irradiation periods here were long enough to approach saturation of the concentrations of paramagnetic centers. Also, for irradiation temperatures above about 40 K, there was considerable decay of the self-trapped hole during the irradiation so that the EPR spectrum measured after quenching to 14.5 K really is a reflection of a dynamic steady-

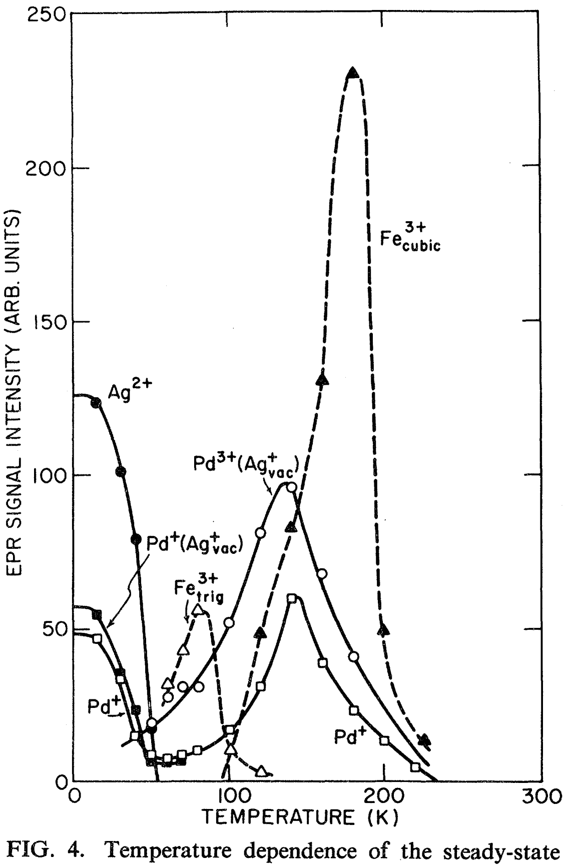

FIG. 4. Temperature dependence of the steady-state concentrations of centers produced by prolonged ultraviolet irradiation. The constant of proportionality between EPR intensity and defect concentration varies from one center to another. Thus, the very intense Fe^{3+} signals do not imply large concentrations, as compared to the palladium centers.

state set up in the irradiation field.

The results of this experiment are shown in Fig. 4. The EPR intensities plotted in this figure are those for characteristic lines taken with the magnetic field parallel to a [100] axis of the crystal. The assignments of the centers are those deduced earlier by Eachus and Graves, and are completely consistent with the present results. The spin-Hamiltonian parameters derived from the fitting of our results are listed in Table I.

For irradiation temperatures below about 30 K, the photoelectrons are trapped at both Pd^{2+} and $Pd^{2+}(Ag^{+}_{vac})$ centers, while those holes which survive recombination become self-trapped. Since the self-trapped hole is not very mobile at these temperatures, further recombination is inhibited. Similar to previous results of Eachus and Graves,[6] we find no substantial trapping of the hole by $Pd^{2+}(Ag^{+}_{vac})$ at low temperatures. This is strange, since at higher temperatures uv irradiation produces considerable amounts of $Pd^{3+}(Ag^{+}_{vac})$. It is therefore not unlikely that, as in the case of the self-trapping process, an activation energy barrier must be surmounted in order for a hole to become trapped at the neutral $Pd^{2+}(Ag^{+}_{vac})$ center; such a barrier would exist if considerable ion relaxation were necessary to provide a bound state for the hole.

For irradiation temperatures higher than 30 K, the hopping mobility of the self-trapped hole becomes increasingly significant, so that during the irradiation fewer trapped photocarrier centers survive until the cool down to 14.5 K. Thus, Fig. 3 shows that the concentrations of all three paramagnetic centers fall synchronously as the irradiation temperature is increased from 30 to 60 K, at which point only very small amounts of centers of any type are formed. At still higher temperatures of irradiation, however, large numbers of centers are once again produced. The self-trapped hole is now too mobile to be retained, and three new trapped-hole centers appear: $Pd^{3+}(Ag^{+}_{vac})$, Fe^{3+}_{trig}, and at still higher temperatures, Fe^{3+}_{cubic}. The $Pd^{3+}(Ag^{+}_{vac})$ has been shown earlier by Eachus and Graves to have a [100] axis, and therefore to be a next-nearest-neighbor complex. Its EPR spectrum, here measured at 14.5 K, is shown in Fig. 5.

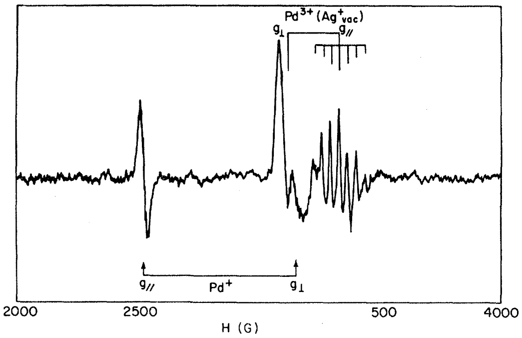

FIG. 5. EPR spectrum of the complementary electron and hole palladium centers produced by uv irradiation at approximately 100 K. The spectrum was measured at 14.5 K. The vacancy in the $Pd^{3+}(Ag^{+}_{vac})$ complex occupies a next-nearest-neighbor site.

The rising efficiency of these hole-trapping centers at temperatures above 60 K precludes complete recombination, so that large concentrations of electron centers also appear once again, but this time only as Pd^{+} (the palladium-vacancy complex is now seen only as a hole trap). When the temperature of irradiation, however, begins to approach 200 K, the concentrations of all trapped-carrier defects decrease toward zero. Clearly, this is the result of recombination following the thermal release of one of the two types of carrier, either holes from the $Pd^{3+}(Ag^{+}_{vac})$ or electrons from the Pd^{+} centers. Now, in Eachus and Graves's crystals, which also contained a small amount of copper (a very stable trap for holes), the Pd^{+} center was observed at temperatures as high as 250 K. Hence, our decrease in efficiency for production of palladium centers, as the irradiation temperature increases above 140 K, must be due to the instability of $Pd^{3+}(Ag^{+}_{vac})$ against loss of the hole. In fact, we were never able to see the broad line at 225 K which Eachus and Graves assigned to Pd^{+}, although we monitored the EPR spectrum both at 225 K and at 14.5 K, after irradiation at 225 K. It thus seems likely that their crystals contained compensating hole traps more stable than in our specimen, and copper is a likely choice.

There are two curious features of Fig. 4: (a) the dip, near 60 K, in production efficiency versus temperature, and (b) the temperature dependences of the concentrations of the two ferric centers. The first of these, the dip, is much more pronounced here than in the results of Eachus and Graves, perhaps because of the difference between the hole-trapping properties of Cu^{+} and Fe^{2+}. This anomaly at 60 K can be understood in terms of the necessity to form stable hole centers if recombination is to be prevented. At low temperatures, this is accomplished by the self-trapping process, and at high temperatures (e.g., in the range from about 100 to 150 K) by the formation of $Pd^{3+}(Ag^{+}_{vac})$. At intermediate temperatures, however, neither of these two mechanisms is operative: The temperature is too high to prevent migration of self-trapped holes, but too low to promote substantial formation of immobile $Pd^{3+}(Ag^{+}_{vac})$, presumably because of an activation energy barrier. That the resulting recombination is determined by the migration of holes, rather than by thermally released electrons, is demonstrated by the rise in concentration of Fe^{3+}_{trig} as the number of self-trapped holes decreases.

The other strange aspect of Fig. 4, the temperature ranges of the appearances of the two different iron centers, can be interpreted in terms of the dynamics of the cation vacancies which are needed to form these centers. This is discussed in more detail elsewhere.[20]

A brief exploration of the isothermal decay at the irradiation temperature was carried out for the several palladium centers. By monitoring the entire EPR spectrum, rather than just following the time dependence of a particular line or lines, one could observe the rise of new centers as old ones disappeared. For aging temperatures higher than 70 K, the EPR spectra were periodically taken at 14.5 K, whereupon the specimen temperature was again returned to its original value.

For temperatures of irradiation and aging in the range 30—50 K, even though the self-trapped holes disappear by a simple first-order process, the electron centers, Pd^+ and $Pd^+(Ag^+_{vac})$, decay by a more complex route, involving at least two processes. The time constants for both of these processes are considerably greater than that for the decay of the self-trapped hole. The EPR spectra show that, during this aging, two new hole centers appear, $Pd^{3+}(Ag^+_{vac})$ and Fe^{3+}_{trig}. Thus the loss of self-trapped holes is not simply by means of recombination with trapped electrons; instead, some holes are transferred to other centers, where they are stored for longer times.

For temperatures above 70 K, the paramagnetic centers consist mainly of the complementary pair, Pd^+ and $Pd^{3+}(Ag^+_{vac})$. In the dark, there is very little decay until the temperature exceeds about 170 K, above which one sees both centers disappearing together by means of what appears to be a superposition of two first-order processes. During the first of these processes the concentration of the Fe^{3+}_{cubic} "tracer" grows to saturation, demonstrating that the decay proceeds through migration of holes thermally freed from the $Pd^{3+}(Ag^+_{vac})$, and not by electrons from the Pd^+. Eachus and Graves also performed decay experiments on $Pd^{3+}(Ag^+_{vac})$ and found a single first-order process. Since their aging temperatures were some 50 K above the range of our experiments, it is perhaps not surprising that they did not observe the faster of the two processes. It is not clear, however, why one should find first-order, rather than second-order, kinetics. Perhaps this indicates the importance of other traps for the carriers.

ACKNOWLEDGMENTS

We wish to thank Mr. C. B. Childs for the preparation of the palladium-doped silver chloride single crystal. We are grateful to Professor J. P. Hernandez for a number of insightful discussions. This research was supported by the National Science Foundation, Grants Nos. DMR-78-09198 and DMR-81-21418.

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