of the impurity ion is at the normal lattice site for both cases. The theoretical models of Wilson *et al.*[17] and of Quigley and Das[20] are not consistent with these results. Because low-frequency lattice resonant modes are particularly sensitive to the details of the interatomic potential, this disagreement between theory and experiment is not too surprising. No doubt the study of resonant modes will lead to better potential models. The investigation of stress-induced frequency shifts surely will continue to be an important probe of the interatomic potential because the frequency shifts are unusually large: Relative shifts between various polarization components are about 20% for stresses of 5 kg/mm^2. The magnitude of the frequency shifts is understandable in terms of the large energy change associated with a small overlap of ions with filled electron shells.

The major difficulty in interpreting stress shifts quantitatively is still the unknown local elastic constants. For KBr:Li^+, the resonant mode appears to be coupled most strongly to spherically symmetric distortions and progressively less to those of tetragonal and trigonal symmetry. On the other hand, the resonant mode in KI:Ag^+ is most strongly coupled to tetragonal distortions of the surrounding lattice and progressively less to those of spherical and trigonal symmetry. Similar results were obtained for the resonant modes in NaCl:Cu^+. Apparently the appreciable noncentral force components in these latter two cases arise from partially covalent Ag^+ or Cu^+ bonds. Because of this difference in the coupling coefficients between Li^+, on the one hand, and Ag^+ or Cu^+ on the other, the stress coupling coefficients must probe mainly the effective potential of the impurity ion itself in the lattice resonant mode.

ACKNOWLEDGMENTS

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Photoconductivity in Colored Potassium Chloride*

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The photoconductive sensitivity, during the course of bleaching F centers in KCl, was found to vary in much the same way for excitation in the M and N bands as for excitation in the F band, from which it appears that the major effect of bleaching is to decrease the lifetime of photoelectrons. The lifetime of photoelectrons giving rise to the secondary photocurrent was approximately linear with the sensitivity. From the second-order decay of photocurrent, the trapping cross section of α centers at room temperature was found to be about 10^{-13} cm^2. Shallow traps were investigated by means of current glow and isothermal untrapping. Two sets were identified, with depths of about 0.60 and 0.68 eV; the concentration and characteristics vary somewhat between samples.

DURING the bleaching of F centers by means of light which they absorb, in additively colored KCl, some pronounced changes in photoconductive sensitivity have been reported.[1–3] At room temperature, the usual result is a decrease in photoconductive sensitivity which is relatively much greater than is the decrease in F-band height. Markham,[4] and also Hardtke, Scott, and Woodley[2] attributed the reduced sensitivity to the production, during bleaching, of α centers (i.e., negative-ion vacancies) which were assumed to have greater electron-trapping cross section than the traps ultimately filled by the liberated F-center electrons.

Recent work on the photochemical formation of F-center aggregates, and also upon the trapping of electrons by α centers, indicates that the above interpretation is in need of reexamination. It is now clear[5] that the chief products of bleaching at room temperature, the M, R, and N centers, are clusters of two, three, and probably four F centers, respectively; the formation of these products does not result in the production of new α centers. Moreover, during the photochemical process the mobile species appears to be the α center[6] which implies that even those α centers formed may not remain long as isolated traps but rather migrate to join in more complex centers. There is also good

* Supported by the National Science Foundation.
[1] J. J. Oberly, Phys. Rev. 84, 1257 (1951).
[2] F. C. Hardtke, A. B. Scott, and R. E. Woodley, Phys. Rev. 119, 544 (1960).
[3] M. Hirai and A. B. Scott, J. Chem. Phys. 40, 2864 (1964).
[4] J. J. Markham, Phys. Rev. 86, 433 (1952).
[5] See, for example, J. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Co., New York, 1962).
[6] C. Delbecq, Z. Physik 171, 560 (1963).

evidence[7–9] that α centers capture electrons to form excited F centers, so that the trapping cross section of α centers may be smaller, at temperatures where excited F centers readily ionize, than previously supposed.

In addition to the room-temperature result described above, we have also to include in any general theory the effect observed[3] at lower temperatures, where there appears a marked enhancement of sensitivity during the initial period of bleaching, followed by the decrease characteristic of the process at room temperature.

The photoconductive sensitivity may be defined[2] as σ/f, where σ is the conductivity, and f is the number of photons absorbed in unit volume in unit time. Here we express σ in reciprocal time so that σ/f has the dimensions of volume. The sensitivity is given by

$$\frac{\sigma}{f}=\frac{\eta e\mu}{v\sum_i n_i S_i}=\eta e\mu\tau, \tag{1}$$

where η is the quantum efficiency for photo-ionization, and e, μ, and v are, respectively, the charge, mobility, and thermal velocity of an electron.[10] The concentration of a particular kind of electron trap of trapping cross section S_i is n_i, and the summation extends over all kinds of traps in the crystal. The quantity $(v\sum_i n_i S_i)^{-1}$ is the lifetime τ of a photoelectron.

Above -50°C, the photocurrent in colored KCl includes the so-called *secondary* current. The presence of F centers, which themselves trap electrons temporarily near room temperature to form F' centers must be considered in interpreting μ, v, and τ. At sufficiently low light intensity, where the concentration of other traps is independent of the concentration of conduction electrons or F' centers, it may be shown that σ/f is independent of F-center concentration and only the other traps need be included in the summation. The photoelectrons, as they move through the crystal, are temporarily trapped at F centers and returned thermally to the conduction band, perhaps many times, before being finally removed after a time τ by thermally stable traps. It is then convenient to define μ or v as an *effective* mobility or thermal velocity, given by

$$\mu/\mu_c=v/v_c=\tau_c/\tau,$$

where μ_c and v_c are, respectively, the actual mobility and thermal velocity of an electron in the conduction band, and τ_c is the time spent in the conduction band during the entire lifetime τ of the photoelectron. Clearly with this definition, σ/f is the same whether the effective or the actual values are used, since $\mu/v=\mu_c/v_c$; however, it is convenient here to use the effective v, since the entire lifetime τ is readily susceptible to measurement. The effective quantities μ, v, and τ^{-1} are all inversely proportional to the F-center concentration.

There is good evidence[11] that the quantum efficiency for optical ionization of F centers is about unity at -100°C in KCl, at least in unbleached crystals, and it is usually assumed to be unity also at room temperature. The interpretations of the effects of bleaching cited above[2,3] were based on the assumption that η remains constant during bleaching, the effects being due to changes in τ. Others[1,12] have suggested that the effects are due to variation of η, or of both η and τ, during bleaching.

The experiments described here were undertaken (a) to demonstrate whether a variation in τ or η plays the chief role in the effect of bleaching upon the photoconductive sensitivity; (b) to examine in a preliminary way the kinetics of the decay of photocurrent with a view toward examining the role of α centers as traps at room temperature; and (c) to measure the trap-depth or range of depths of the traps reported by Hirai and Scott[3] by means of the "glow current."

EXPERIMENTAL

Photoconductivity, glow-current, and optical-absorption measurements were made in the manner previously described.[3,13] The electrometer output was recorded by means of a Honeywell recorder, Model 153-12YX9, having a time constant of 3 sec. The source of light for bleaching F centers was a tungsten lamp; the light was filtered first through heat-absorbing glass and then through an interference filter supplied by Baird Associates having a transmission peak at 565 mμ with a pass-band half-width of 10 mμ. Light intensity, both for bleaching and photoconductivity, was measured by means of a 12-junction bismuth-silver thermopile supplied and calibrated by Eppley Laboratories, Inc. Following the experiments the thermopile was recalibrated in this laboratory, using an Eppley Laboratory standard lamp; the two calibrations agreed within 2%. The bleaching-light intensity was reduced to desired values by inserting neutral density filters, whose attenuation was known within $\pm 0.5\%$, in the beam. Temperature was measured by means of a copper-constantan thermocouple secured to a copper plate in direct contact with the crystal. During constant-temperature experiments, variations were within ± 1°C of the stated value.

The KCl crystals used were from several sources. Crystals designated A were grown from vacuum-distilled salt supplied by the Anderson Physical Laboratory. Those designated B were grown from Merck

[7] F. Lüty, *Elektronenübergange in Farbzentren, Halbleiterprobleme VI.* (Frederick Vieweg und Sohn, Braunschweig, Germany, 1961.)

[8] H. Fedders, M. Hunger, and F. Lüty, J. Phys. Chem. Solids **22**, 299 (1961).

[9] R. S. Crandall, Phys. Rev. **138**, A1242 (1965).

[10] The sensitivity is often expressed by $\eta\omega_0$, where $\omega_0=\mu\tau$ is the mean electron range in unit electric field.

[11] H. Pick, Ann. Phys. (N. Y.) **31**, 373 (1938).

[12] R. E. Woodley, Ph.D. thesis, Oregon State University, 1965 (unpublished).

[13] M. Hirai and A. B. Scott, J. Chem. Phys. **44**, 1753 (1966).

Reagent KCl which was then further purified by both cation and anion exchange. Both A and B were grown under argon from a melt treated with dry HCl to remove oxygen and hydroxyl ions and displayed no observable absorbance in the range 200–300 mμ. All other crystals were obtained from the Harshaw Chemical Company. The crystals were additively colored, and prior to each experiment each sample was wrapped in aluminum foil, heated 50 sec at 600°C, and quenched between copper blocks precooled in liquid nitrogen. The F-center concentration n_F was found by the use of the Smakula equation in the form

$$n_F = 0.97 \times 10^{16} A_F \text{ cm}^{-3},$$

where A_F is the absorbance per cm at the maximum of the F band at room temperature.

RESULTS AND DISCUSSION

Response to Excitation of Variable Frequency

In order to demonstrate whether a variation in η or τ plays the chief role in the effect of bleaching upon the photoconductive sensitivity, the sensitivity was examined at each of several excitation frequencies as bleaching progressed. Wavelengths of 560, 725, 825, and 1000 mμ, corresponding to the peaks of the F, R_2, M, and N bands, respectively, were used. Figure 1 displays the result. For all four excitation wavelengths, the sensitivity decreased in much the same way. This is not surprising in the case of the curves F and R_2, as it is known[14] that the photoconductivity-response curve for F centers has a long-wavelength tail which extends beyond the position of the R_2 band, so that the decrease in the curve R_2 may arise, to a large degree, from the same source as does the decrease in the curve F. It is also to be noted, however, that the sensitivity for excitation in the M and N bands, where the response for F centers is small,[14] also markedly decreased. Since a variation in τ should have the same effect on sensitivity for all excitation frequencies, it appears likely that the major cause of the decrease is indeed a variation in τ, with, however, some variation (perhaps two- or threefold) in the values of the ratios η_F/η_M and η_F/η_N during the course of bleaching.

If the concentration of traps is large compared to the concentration of photoelectrons, the lifetime of photoelectrons should be independent of their origin, and differences in sensitivity with variation of excitation wavelength should be a direct indication of differences in quantum efficiency. Trap concentrations have previously been estimated[2,3] to be in the range 10^{14}–10^{16} cm^{-3}, while only about 10^{12} photons/cm^3 were used for each photoconductivity measurement. Quantum efficiencies relative to that of the F center (taken as unity), found by comparing the sensitivities in Fig. 1, are given in Table I. Also shown are values estimated by Cole and Friauf[15] on the basis of a similar experiment. The agreement is good except for excitation in the N band, for which we observe a lower quantum efficiency.

TABLE I. Relative quantum efficiencies η for ionization by light of different frequencies.

Band	η, this experiment	η, Cole and Friauf[a]
F	1.0	1.0
R_2	0.6[b]	0.5
M	0.1–0.2[b]	0.15
N	0.1–0.3	0.6

[a] Reference 6.
[b] This is an apparent value only, due to some excitation of F centers in this spectral region.

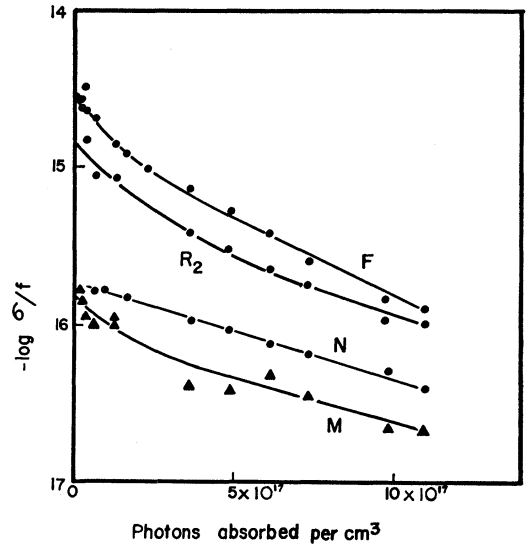

FIG. 1. The photoconductive sensitivity change in additively colored KCl upon F-center bleaching at room temperature. Photoconductivity was excited by four different frequencies (in the F, R_2, N, and M bands) as indicated. Absorbance per cm at the maxima of the F, R_2, and M bands was, respectively, initially: 0.64, 0.00, 0.00; finally: 0.32, 0.07, 0.06. (Base of logarithms is 10.)

First-Order Decay of Photocurrent

A second experiment related the lifetime of the photoelectrons to the sensitivity. If μ and η are constant, by Eq. (1) τ should be linear with σ/f. After the exciting light was shut off, the photocurrents, provided they were less than about 10^{-14} A, so that the concen-

[14] N. Barth, Z. Physik **149**, 370 (1957). [*Note added in proof.* In our experiments, using samples in which the R_2 band was well developed, a peak or shoulder on the curve of photocurrent versus excitation wavelength was generally observed at 725 nm, showing that R_2 centers contribute to the photocurrent. Proper correction for the current due to F centers, which was a large fraction of the total at 725 nm, was difficult to estimate, and the slope of the curve R_2 in Fig. 1 was strongly influenced by variations in the estimated corrections; therefore, we present the uncorrected result.]

[15] G. R. Cole and R. J. Friauf, Phys. Rev. **107**, 387 (1957).

tration of photoelectrons was much less than the concentration of traps, decayed according to a first-order law, viz.,

$$I=I_0\exp(-t/\tau),$$

where I_0 is the current immediately upon shutting off the light at $t=0$ and I is the current at time t.

Samples of crystal A having $n_F\sim10^{16}$ cm^{-3} were subjected to short but intense irradiations with 560-mμ light to produce crystals having a wide range of sensitivities. We assume that μ was not appreciably altered by the short exposures. The time τ was found for each by excitation in the F band at room temperature, and then recording the current after shutting off the light. Since the response time of the recorder was about 3 sec, only lifetimes somewhat longer than 3 sec could be observed. In Fig. 2, the sensitivity is shown as a function of the photocurrent decay time τ, which shows σ/f to vary approximately linearly with τ.

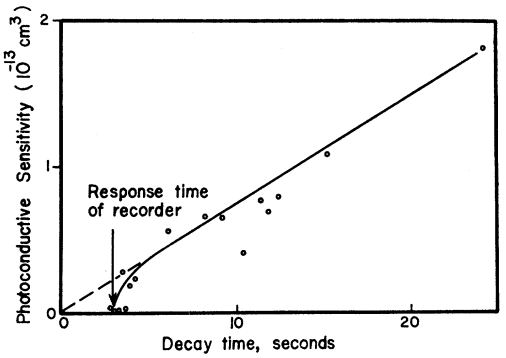

FIG. 2. Relation between photoconductive sensitivity and decay time τ of the photocurrent for small photocurrents, at room temperature.

We conclude from this experiment that variations in sensitivity produced by short exposures arise from changes in τ, not η, for F-band excitation. Considering that τ was of the order of 10 sec, that the lifetime of the F' center at room temperature is reported by Tomura *et al.*[16] to be about 10^{-1} sec, and that the time spent by a photoelectron in the conduction band is negligible compared to these, we see that in this experiment a photoelectron was trapped and released by F centers, on the average, roughly 100 times before combining with a stable trap.

Having the lifetime τ as a function of σ/f, we also find from Eq. (1) that the effective mobility μ is about 10^{-7} cm^2/V sec at $n_F\sim10^{16}$ cm^{-3}.

Second-Order Decay of Photocurrent

At sufficiently high currents, the photocurrent decays, after shutting off the excitation, according to a second-order rate law, that is

$$I^{-1}=I_0^{-1}+k_2t.$$

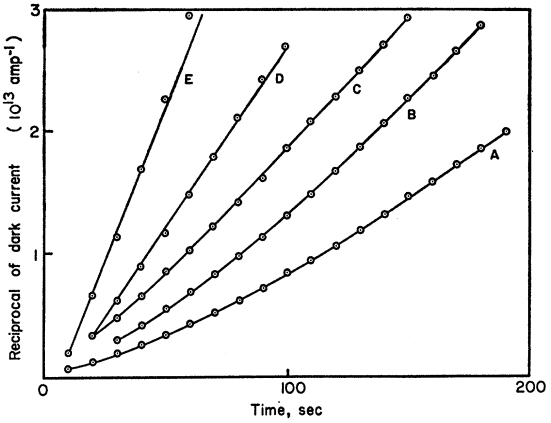

FIG. 3. Second-order decay curves for high photocurrents at room temperature, with degree of bleaching increasing in the order A to E. Absorbance per cm at the maxima of the F, R_2, and M bands was, respectively, A: 0.87, 0.00, 0.00; C: 0.54, 0.02, 0.07; E: 0.45, 0.06, 0.07.

This result is shown in Fig. 3, in which the reciprocal of the current is plotted against time for a Harshaw crystal having $n_F\sim10^{16}$ cm^{-3}, at various stages of bleaching, after excitation with high-intensity light. The slope of the linear portions of the curves is the rate constant k_2. The curvature at $I>2\times10^{-13}$ A in some curves we believe to be due to polarization resulting from the relatively high charges transferred; this effect is most noticeable in curves of low k_2.

The rate of change in the concentration of photoelectrons n (which includes electrons both in the conduction band and those trapped in F centers) after excitation ceases is given by

$$\frac{-dn}{dt}=\frac{n}{\tau}=nv\sum_i n_iS_i. \tag{2}$$

If the excitation is sufficiently intense so that negative-ion vacancies produced by ionization of F centers are the predominant traps, we may approximate the decay rate by

$$\frac{-dn}{dt}=nvn_\alpha S_\alpha, \tag{3}$$

where n_α and S_α represent the concentration and cross section, respectively, of negative-ion vacancies. Then, provided the initial concentration of negative-ion vacancies is negligible compared with that produced by ionization,

$$n=n_\alpha,$$

and the process is second-order. Integration of (2) then leads to

$$n^{-1}=n_0^{-1}+vS_\alpha t=n_0^{-1}+k_2't,$$

[16] M. Tomura, K. Murase, M. Takebayashi, and T. Kitada, J. Phys. Soc. Japan 19, 1991 (1964).

where n_0 is the concentration of photoelectrons immediately following excitation. The constant k_2' is connected to the constant k_2 by

$$k_2'/k_2 = I/n = EAe\mu,$$

where E is the electric field and A is the cross-sectional area of the crystal measured perpendicular to the field. In these experiments E was 430 V/cm and A was 0.30 cm^2. Since μ depends on n_F, it is not strictly constant, but its variation in this situation was neglected.

The initial rate constant k_2 taken from curve A of Fig. 3, is 1.3×10^{11} A^{-1} sec^{-1}, and, taking μ from the first-order result, the corresponding value of k_2' is 2.7×10^{-13} cm^3 sec^{-1}. This is also the product vS_α. We may estimate v from

$$v = v_c\mu/\mu_c.$$

The mobility μ_c in KCl at room temperature was reported by Kalabukov and Sidyakin[17] to be 1.5 cm^2/V sec. Taking v_c to be 10^7 cm/sec, the velocity v is seen to be about 1 cm/sec, so that S_α, according to this analysis, is of the order of 10^{-13} cm^2.

Swank and Brown[18] found the escape frequency of the electron from an excited F center in KCl to be 4×10^{12} sec^{-1}, which leads by the method of detailed balancing to a *capture* cross section for the α center of 3×10^{-14} cm^2 at room temperature, but do not claim better than order-of-magnitude accuracy. A second method for calculating[9] the capture cross section sets it equal to $4\pi e\mu/v\epsilon$, where ϵ is the dielectric constant; this gives the value 6×10^{-14} cm^2.

It must be emphasized, however, that the *trapping* cross section is the capture cross section multiplied by the probability of return to the F-center ground state. This probability can be found for temperatures below 150°K, where return is entirely radiative, from the data of Swank and Brown. Extrapolation to room temperature requires knowledge of the probability of the radiationless transition, which increases rapidly with temperature. Inclusion of this transition in the model of Swank and Brown gives

$$\frac{1}{\eta_T} = 1 + \frac{\tau_0}{\tau_R}\exp\left(\frac{\Delta E_T}{kT}\right) + \frac{\tau_{T,0}}{\tau_0}\exp\left(\frac{\Delta E_T - \Delta E}{kT}\right),$$

where η_T is the probability of radiationless return to the ground state, τ_R is the radiative lifetime, $1/\tau_0$ and ΔE are the escape frequency and activation energy for ionization, and $1/\tau_{T,0}$ and ΔE_T are the frequency factor and activation energy for the radiationless transition. No experimental value of ΔE_T appears to be available. Estimates from configuration coordinate diagrams are not likely to be realistic. If ΔE_T is as small as 0.2 eV, and if $\tau_{T,0}/\tau_0$ is of the order unity, η_T is of the order of 0.1 at room temperature; if ΔE_T is around 0.5 eV, η_T is small compared to the probability of radiative return, which the data of Swank and Brown give as about 10^{-4} at room temperature. Thus, the trapping cross section, calculated from the above capture cross sections, may lie in the range of about 5×10^{-18} to perhaps 5×10^{-15} cm^2.

In previously accounting for the effects of bleaching upon photoconductive sensitivity,[2,3] we have estimated the trapping cross section of the α center to be about 2×10^{-13} cm^2. The second-order photocurrent decay constant leads to a value consistent with this estimate. Clearly, it is difficult to reconcile such a high cross section with the trapping model discussed above.

A second effect upon the magnitude of η_T, described by Lüty,[7] may be of some assistance in this connection. When an excited F center has another F center sufficiently near, the first may return to the ground state by tunneling via the F' state of the second. Thus, η_T increases with F-center concentration, and may also increase during early stages of bleaching if, as Debecq[6] suggests, F centers tend to move together under illumination. If η_T is in fact close to unity and the capture cross section is taken at the upper end of Swank and Brown's stated range of uncertainty, then the trapping cross section may be of the order of 10^{-13} cm^2.

We note from Fig. 3 that, as bleaching progresses, k_2 increases—by about fourfold over the course of the experiment. According to the preceding discussion, k_2 should be a constant, provided that negative-ion vacancies are the only traps which need to be considered, and provided μ is not appreciably altered by the small decrease in F-center concentration. The increase in k_2 with bleaching may be due to a decrease in the mean distance between F centers, according to the argument above. This would imply that bleaching not only reduces the photoelectron lifetime (by increasing the α-center trapping cross section) but also reduces the quantum efficiency for photoelectron production (by increasing the probability of radiationless return to the ground state).

Clearly a more extensive study of the kinetics of photocurrent decay and electron trapping by α centers in the neighborhood of room temperature is to be desired.

Bleaching at −30°C

The enhancement of sensitivity during initial stages of bleaching at −30°C, reported by Hirai and Scott,[3] was attributed to the filling of large-cross-section shallow traps. Their experiments were carried out upon samples from two sources, Harshaw Co. and Tohoku University. However, since the traps may be due to impurities, it seemed worthwhile to extend their measurements to additional samples of differing preparation. Figure 4 shows the variation of σ/f with the total number of photons absorbed in unit volume, at both room temperature and −30°C, for Harshaw crystals

[17] N. P. Kalabukhov and V. G. Sidyakin, Fiz. Tverd. Tela **2**, 2589 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2309 (1960)].

[18] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

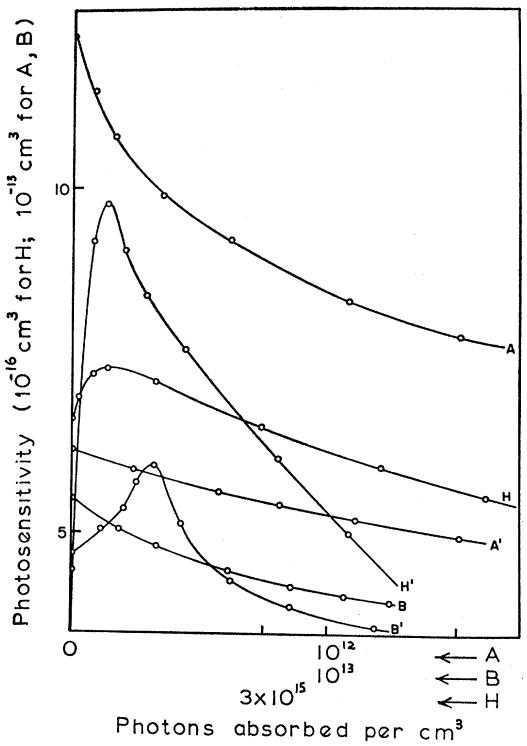

FIG. 4. Effect of bleaching on sensitivity. *A*, *A'*, *B*, *B'*, *H*, *H'*: samples A, B, and Harshaw at room temperature and −30°C, respectively.

and samples A and B. In sample A, no enhancement was observed even at −30°C; the behavior of sample B resembled that of the previous samples, except that the maximum sensitivity was achieved with much less exposure than before; in the Harshaw crystal the enhancement was very marked at −30°C though with the maximum at lower exposure than previously, while at room temperature there was a slight initial enhancement not reported for similar samples by Hirai and Scott. It should be noted that much-lower-intensity bleaching light was used in the present experiments, and the very early rise and fall in sensitivity at room temperature may well have been overlooked in the previous work.

The number of photons absorbed per cm^3 required to attain the maximum sensitivity at −30°C varied greatly even among the several Harshaw samples. It was lowest in samples 1–4, and much the highest in samples 5–7, suggesting that the concentration of the large-cross-section traps is much greater in the last three samples.

The initial sensitivities of crystals A and B were around a thousandfold those of the Harshaw samples at each temperature, implying that electron traps are removed by purification; further, the large-cross-section traps found in Harshaw crystals and crystal B were not detected in the vacuum-distilled material, by bleaching at −30°C.

Glow Current and Trap Depth

To demonstrate the reality of these traps, tentatively referred to as *J* traps, a dark current produced by warming a crystal presumed to contain filled *J* traps was sought.

Colored samples of crystal B and Harshaw crystals 5–7 were bleached at −30°C to the extent necessary to fill the traps *J* (detected as the point of maximum photoconductive sensitivity), immediately cooled to −50°C, and then warmed to room temperature at approximately 4.5 deg/min. The dark current, at a field of about 400 V/cm, as a function of temperature (the so-called *glow current*) is shown for a Harshaw sample in Fig. 5.

The trap depth may be found from the temperature of maximum glow current T_m, using the equation due to Randall and Wilkins and a procedure already described.[13] The trap depth corresponding to the glow current shown in Fig. 5 was 0.563 eV. Trap depths for three additional crystals, and an average value, are given in Table II.

As one test of the Randall-Wilkins model, the sample listed as Harshaw No. 6 was examined using six heating rates between 2.75 and 8.9 deg/min. The peak shifted in the predicted direction with increase in heating rate, from −39 to −26°C, and the trap depth calculated for each heating rate varied less than 1% from the median value.

From the glow curve alone, it is not expected that one could detect the presence of two or more traps having closely spaced depths. A sensitive means of ascertaining whether traps of more than one depth give rise to the glow current is provided by the following experiment: After filling the traps at −30°C, the sample was held at that temperature for varying lengths of time before cooling to −50°C and performing the

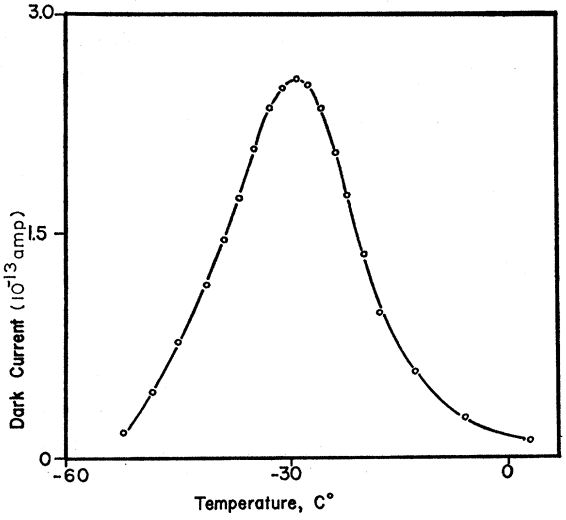

FIG. 5. Glow current from shallow traps in KCl.

TABLE II. Trap depths in KCl.

Sample	From current glow Trap depth, eV	From isothermal untrapping $I_\infty \times 10^{14}$, A	Temp., °C	Lifetime, min	Depth, eV
Harshaw 1	No peak observed		−30	67[a]	0.63[a]
			−20	4.4, 160	0.60, 0.68
			−10	5.0, 180	0.63, 0.71
Harshaw 2	No peak observed		−30	70[a]	0.63[a]
Harshaw 3	No peak observed	6.0	−30	77[a]	0.64[a]
		6.0	−20	9.6, 100	0.61, 0.66
		4.5	−15	5.9, 100	0.62, 0.68
		3.4	−10	3.7, 110	0.62, 0.70
Harshaw 4	No peak observed		−30	85[a]	0.64[a]
Harshaw 5	0.60				
Harshaw 6	0.55		−30	140[a]	0.65[a]
Harshaw 7	0.56		−30	160[a]	0.65[a]
B	0.63		−30	290[a]	0.66[a]
Average	0.59				

[a] Mean value.

glow-current measurement, at a fixed heating rate of 4.5 deg/min. If a range of trap depths is involved, then during the initial holding period shallower traps should become empty and the resulting glow peak will shift to higher temperatures. Figure 6 shows the results of this experiment using a Harshaw sample, which indicates clearly that traps of at least two depths exist. After about 15 min at −30°C, most of the shallower traps were evidently empty, and those remaining gave a current glow peak near 0°C. This value of T_m corresponds to a depth of 0.62 eV.

Those Harshaw samples (1–4) thought to contain a low concentration of J traps all failed to display a detectable glow current, and thus no trap-depth measurement was achieved by this means. The next experiment to be described provided a more sensitive method for crystals of low trap concentration.

Isothermal Untrapping

The rate of emptying of the J traps at each of a series of fixed temperatures was next studied by measuring the time dependence of photoconductive sensitivity after filling the traps by bleaching at −30°C. Crystals were bleached until σ/f reached a maximum; then the bleaching light was turned off, the temperature was adjusted to the desired value, and the photocurrent at fixed excitation intensity was determined at intervals. Figure 7(a) displays the result, for Harshaw sample No. 3, at four temperatures.

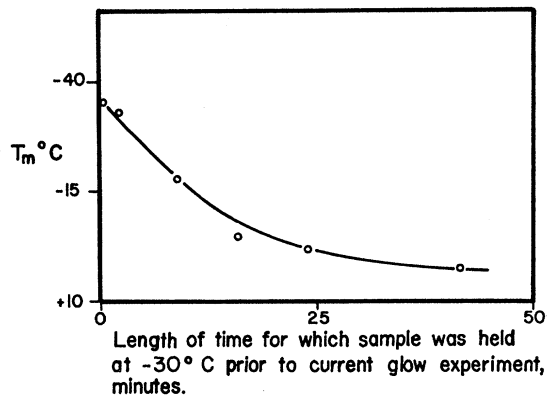

FIG. 6. Shift of glow peak with holding time.

Under the condition that the excitation intensity, applied voltage, and F-center concentration are constant, σ/f is proportional to the photocurrent I in a given sample, and Eq. (1) may be rewritten

$$I^{-1}=c\sum_i n_i S_i,$$

where c is a constant. If we consider the produce nS for all traps other than J traps to remain constant (denoted b) during the above experiment, we may write

$$I^{-1}=c(n_J S_J+b).$$

Since at $t=0$ the J traps are all filled so that $n_J=0$, the initial current is given by

$$I_0^{-1}=cb,$$

while at $t\to\infty$, n_J approaches some fixed value $(n_{J,\infty})$, so that

$$I^{-1}=c(n_{J,\infty}S_J+b).$$

Now, assuming that the filled traps J become empty according to a first-order rate law, we have, for the concentration of empty traps,

$$n_J=n_{J,\infty}[1-\exp(-t/\tau_J)],$$

where τ_J is the lifetime of the filled traps. We can then combine the above relations to obtain

$$\exp(-t/\tau_J)=1-(I^{-1}-I_0^{-1})/(I_\infty^{-1}-I_0^{-1}).$$

Thus a curve of $\log[1-(I^{-1}-I_0^{-1})/(I_\infty^{-1}-I_0^{-1})]$ versus time should be linear, with a slope which yields τ_J.

Such curves derived from the data of Fig. 7(a) are presented in Fig. 7(b). The choice of I_∞ is somewhat arbitrary, as the current limit approached at long times in curves such as those of Fig. 7(a) is not clearly

apparent, but values of I_∞ roughly 0.05×10^{-13} A less than the current at 100 min were taken, as given in Table II for Harshaw sample 3. The curves at the three higher temperatures are distinctly resolvable into two approximately linear portions, indicative of at least two trap depths, as previously indicated by the dependence of glow-current peak on prior holding time. At -30°C, the time of the experiment was insufficient to allow the establishment of a valid slope for the later portion.

The lifetime of the deeper filled traps J is readily obtained from the slope of the later portions of the -10, -15, and -20°C curves of Fig. 7(b), since at large values of the time, the emptying of shallower traps will be essentially complete. The trap depth E and the lifetime τ are related by

$$E=kT\ln(\tau s),$$

where s is a frequency factor characteristic of KCl. Following Dutton and Maurer,[19] s was taken to be 3×10^9 sec^{-1}. The lifetimes and trap depths of the deeper traps found in this way, for Harshaw samples 1 and 3 are given in Table II.

To find the lifetime of the shallower filled traps J, the curve for the later stage was extrapolated to $t=0$. The intercept at $t=0$ equals $\log[1-(I_f^{-1}-I_0^{-1})/(I_\infty^{-1}-I_0^{-1})]$, where I_f is the limit which the current would approach at $t=\infty$ if there were no deeper traps at all. Then a curve of $\log[1-(I^{-1}-I_0^{-1})/(I_f^{-1}-I_0^{-1})]$ was plotted versus time. Such curves were approximately linear. From the slope, τ_J for the shallower traps was found. These lifetimes and trap depths are given also in Table II for two Harshaw samples.

The data obtained at -30°C permitted only a mean lifetime and trap depth to be found, as the slope of the later stage was not established, and extrapolation to find I_f was therefore not possible. The mean values obtained at -30°C, from the initial slope of curves such as those in Fig. 7(b), are given in Table II.

The lifetimes calculated are strongly influenced by the choice of I_∞, so that these are at best rough values. The trap depths, varying with $\ln\tau$, are less sensitive to the choice of I_∞. The trap depth given by the glow experiment, which yielded an average value 0.59 eV, agreed well with the depth of the shallower traps as found by the isothermal untrapping experiment. It is likely that emptying of the shallower traps contributes most noticeably to the glow current.

[19] D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

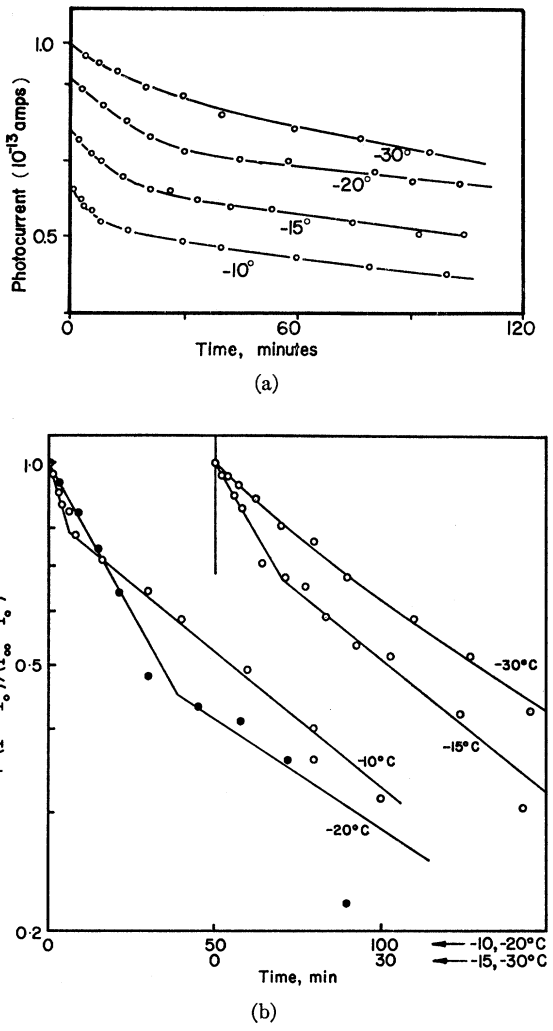

FIG. 7. (a) Effect on photocurrent due to isothermal release of electrons from shallow traps. (b) Variation of $\log[1-(I^{-1}-I_0^{-1})/(I_\infty^{-1}-I_0^{-1})]$ with time.

We conclude that the large-cross-section traps are of at least two types, whose depths lie near either 0.60 or 0.68 eV.

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