exhibit dispersion, i.e., a variation of the phase velocity with wavelength. This behavior is very similar to that found with bulk vibrational modes. We have also found for the monatomic cubic lattice considered here that a critical wavenumber generally exists in the Rayleigh wave region. For wavenumbers greater than the critical wavenumber the atomic displacements exhibit a phase reversal between successive layers parallel to the surface.

A sufficient number of interactions has been chosen in our model to permit the fitting of an arbitrary set of elastic constants. Since the interactions are assumed to be short-range, however, one must hold certain reservations concerning the validity of the quantitative results for ionic crystals such as NaCl or KCl where long-range Coulomb forces are important.

Work is currently underway on the generalization of the lattice theory to face- and body-centered cubic lattices as well as to diatomic cubic lattices and the diamond and zinc-blende lattices. It is hoped that a unified treatment can be obtained of both Rayleigh-type waves and the optical surface waves.

ACKNOWLEDGMENT

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Decrease of *F*-Center Photoconductivity Upon Bleaching*

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A quantitative study of the rapid decrease in photoconductivity accompanying the relatively less rapid bleaching of *F* centers in additively colored KCl is reported. The experimental observations agree, except during very early stages of bleaching, with an equation for the variation of sensitivity with total light absorbed derived upon the assumption that negative-ion vacancies are created and traps of smaller cross section are filled during bleaching. Except during early stages, where several kinds of traps may be present in low concentration, only one kind of trap other than the negative-ion vacancy need be considered.

The effects of added divalent ions, both positive and negative, upon photoconductivity are reported.

INTRODUCTION

When *F* centers in an additively colored alkali halide crystal are destroyed by irradiation with light which they absorb, the photoconductivity of the crystal is reduced relatively much more than is the optical absorption.[1,2] In one experiment previously reported,[2] for example, the photoconductivity was reduced by about 80% during bleaching, while the number of *F* centers, as given by the absorbance, was decreased by only 10%. The decrease in photoconductivity produced by bleaching is hereafter referred to as *fatigue*.

The sensitivity of a photoconductor depends both upon the ratio of conduction electrons produced to quanta absorbed (that is, upon the quantum efficiency, η) and upon the average lifetime of a conduction electron, τ. Oberly ascribed the fatigue to a decrease of η with bleaching, and proposed that two types of *F* centers may exist: a soft center which is photoconducting and readily bleached by light ($\eta=1$), and a hard center which is not photoconducting ($\eta=0$), nor capable of being bleached, but continues to absorb light. Accordingly, the photoconductivity would undergo a sharper decrease during bleaching than the optical density and approach a zero value as the "soft" centers are destroyed. Markham[3] attributed the diminishing photoconductivity to a decreasing τ instead of η, and suggested that the decreased electron lifetime was caused by an increase in negative-ion vacancy concentration as *F* centers were decomposed.

This report describes experiments carried out to provide quantitative information regarding the fatigue of photoconductivity during bleaching. The data were consistent with equations for the variation in sensitivity with light absorbed, developed upon the assumption that as bleaching proceeds traps of small cross section, initially present in the crystal, are filled and negative-ion vacancies of large cross section are created. There appears to be no necessity to assume the existence of two types of *F* centers.

EXPERIMENTAL

(a) Sample Preparation

All measurements were conducted at room temperature in the *F* band of single crystals of KCl. The

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[1] J. J. Oberly, Phys. Rev. 84, 1257 (1951).

[2] G. W. Neilson and A. B. Scott, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 297.

[3] J. J. Markham, Phys. Rev. 86, 433 (1952).

majority were performed on crystals obtained from the Harshaw Chemical Company. Spectrographic analysis of the purity of similarly prepared KCl samples from the same company can be found elsewhere.[4] A few additional measurements were conducted on single crystals grown from doubly-recrystallized reagent grade KCl. In two instances the melt was charged with divalent ions—0.05 mole % $SrCl_2$ and 0.13 mole % K_2SO_4—and a third sample was grown in a graphite crucible under an inert atmosphere in an effort to produce a purer form of single-crystal KCl than that available commercially.

Crystals were colored at a temperature between 480 and 520°C, in a container with potassium metal held at 300 to 400°C. After attainment of equilibrium (12 to 72 hours), the crystals were brought to room temperature in about 30 seconds, cut, and mounted in the apparatus in total darkness by means of positioning jigs. This precaution was essential because initial rates of fatigue were very high. The sample for measurement was about $5\times2\times1$ mm with the light impinging on the edge and the electric field traversing the smallest dimension.

(b) Photoconductivity Measurements

The crystal was washed in absolute alcohol and placed between electrodes mounted on a Teflon base in an air-tight case containing magnesium perchlorate desiccant. The dark current was negligible. Light of wavelength 560 mμ was provided by a double-prism monochromator with a 300-watt source. The bandwidth was 30 mμ or less for all measurements. A mirror placed behind the crystal returned the light for a second pass, and produced fairly uniform absorption of light throughout the crystal, provided it was not too densely colored. A thermopile, calibrated by means of a carbon filament lamp supplied by the U. S. Bureau of Standards measured the radiant energy impinging upon the crystal. The electric field strength was normally about 3000 volt cm^{-1}. Photocurrents of the order of 10^{-11} ampere were amplified by means of a dc amplifier previously described[2] and recorded by a Brown potentiometer.

Since space-charge polarization is evident for such currents in alkali-halide photoconductors, the recorded photocurrent was extrapolated to the initial time, that is, to the time at which the light was turned on the crystal. To avoid a long delay as the potentiometer came to balance, the recorder indicator was preset to approximately the position anticipated for indication of the photocurrent by means of an auxiliary adjustable voltage; when the light was turned on the crystal, the auxiliary voltage was simultaneously switched off and the photocurrent signal switched on. Thus, the extrapolation could be carried out rather precisely, since the interval was short and the current-time curve was accurately exponential in this region.

After each measurement the crystal was depolarized by illuminating it with the electrodes grounded. The total exposure to light, both during actual measurements and intervening periods, was recorded; and the amount of light absorbed by the crystal was calculated from the absorbance and the crystal size.

(c) Absorbance and Bleaching Measurements

A Beckman Model DU Spectrophotometer was used to measure absorbance; the *F*-center concentration was computed as previously described.[5] Experiments on the initial rate of bleaching were carried out in this instrument. The intensity of the light used for bleaching was determined by means of the thermopile previously described.

THEORY OF FATIGUE

In developing a theory of fatigue of photoconductivity, we make use of certain parts of the description of general photoconductive processes due to Rose.[6] We are concerned here with a system in which the holes arising from the generation of conduction electrons are immobile, being localized at the negative-ion vacancies. We are not concerned with holes in the valence band, as electrons are not removed from the valence band by light of *F*-band energy. The theory to be described preserves the conventional model of the *F* center. One *F* center is ionized, and one conduction electron is produced, for each photon absorbed.[7]

For purposes of simplicity, we assume that conduction electrons are removed from the conduction band by only two kinds of traps: (1) negative-ion vacancies (symbol, *H*) of concentration n_H and cross section s_H, and (2) other traps (symbol, *T*) which retain electrons stably at room temperature, of concentration n_T and assumed to be all of the same cross section s_T. If $s_H>s_T$, the photoconductivity will diminish as n_H increases at the expense of n_T, that is as *F* centers are destroyed and the traps *T* are filled during bleaching.[8]

When the photocurrent attains a steady value (this is accomplished in a time very short compared to times of interest here) the rate of trapping of conduction electrons equals *f*, the rate of production of conduction electrons in unit volume. The rate at which the traps *T* are being replaced by negative-ion vacancies is also the rate at which *F* centers are being destroyed and is given by

$$\frac{dn}{dt}=f\frac{s_Tn_T}{s_Tn_T+s_Hn_H}=f\frac{s_T(n_T{}^0-n+n_c)}{s_T(n_T{}^0-n+n_c)+s_H(n_H{}^0+n)}, \quad (1)$$

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[4] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

[5] A. B. Scott and W. A. Smith, Phys. Rev. **83**, 982 (1951).

[6] A. Rose, RCA Rev. **12**, 362 (1951); see also the *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge et al. (John Wiley and Sons, New York, 1956), p. 3. As far as practicable, the notation of Rose has been used in this paper.

[7] R. W. Pohl, Proc. Phys. Soc. (London) **49**, extra part, 3 (1937).

[8] The traps *T* in an actual crystal when filled probably are to be identified with *M* centers.

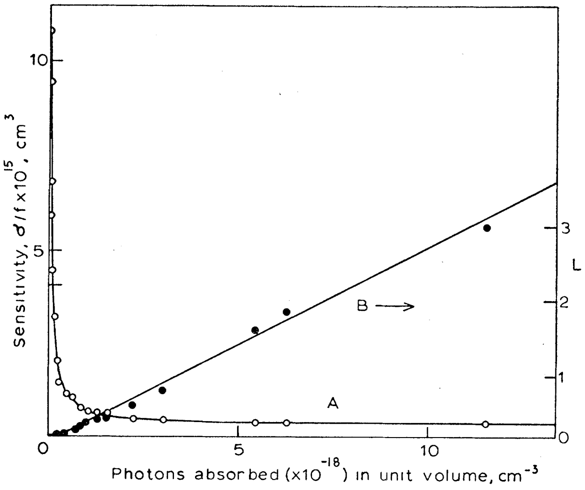

FIG. 1. *A*—fatigue of photoconductivity in colored KCl. *B*—test of Eq. (12).

where the superscript 0 indicates values of concentration at time $t=0$, that is, at the beginning of illumination, n is the concentration of F centers which have been destroyed, or $n_F{}^0-n_F$, n_c is the concentration of conduction electrons, and f is the number of excitations per unit volume per unit time. Since η is unity, f is also the number of quanta absorbed per unit volume per unit time.

Taking n as space independent, f to be both space and time independent[9] and n_c to be negligible with respect to the other concentrations,[10] (1) may be integrated to give

$$\left(1-\frac{s_H}{s_T}\right)n-\frac{s_H}{s_T}(n_H{}^0+n_T{}^0)\ln\left(\frac{n_T{}^0-n}{n_T{}^0}\right)=ft. \quad (2)$$

For the case $s_H \gg s_T$, this result may be simplified to give

$$\ln\left(\frac{n_T{}^0}{n_T{}^0-n}\right)-\frac{n}{n_T{}^0+n_H{}^0}=\frac{s_T}{s_H(n_H{}^0+n_T{}^0)}ft. \quad (3)$$

For short exposures, where n is much smaller than either $n_T{}^0$ or $n_H{}^0$, (1) upon integration leads to

$$n=\frac{s_Tn_T{}^0}{s_Tn_T{}^0+s_Hn_H{}^0}ft. \quad (4)$$

The steady-state concentration of conduction electrons, n_c, is $f\tau$, and the photoconductivity is

$$\sigma=e\mu n_c=e\mu f\tau, \quad (5)$$

where e is the electronic charge and μ is the mobility. The trapping frequency for conduction electrons at the start of illumination is

$$1/\tau^0=v(s_Hn_H{}^0+s_Tn_T{}^0), \quad (6)$$

and after n of the traps T have been replaced by negative ion vacancies, the trapping frequency is

$$\begin{aligned}1/\tau&=v[s_H(n_H{}^0+n)+s_T(n_T{}^0-n)]\\&=1/\tau^0+vn(s_H-s_T). \quad (7)\end{aligned}$$

Here v represents the thermal velocity of a free electron, and n_c has again been considered negligible with respect to the other concentrations.

The sensitivity of a photoconductor may be expressed by σ/f. When conductivity is measured in reciprocal time[11] and f in photons absorbed in unit volume per unit time, σ/f has the dimensions of volume. For expressing the fatigue of photoconductivity, the most convenient variable is the reciprocal sensitivity, or $f/\sigma=R$. Then, from (5) and (7)

$$R=R^0+(vn/e\mu)(s_H-s_T). \quad (8)$$

At $t=\infty$, $n=n_T{}^0$, that is, all the traps are filled; so that

$$R^\infty=R^0+(vn_T{}^0/e\mu)(s_H-s_T). \quad (9)$$

Eliminating n from (4) and (8),

$$R=R^0+\frac{v}{e\mu}(s_H-s_T)\left(\frac{s_Tn_T{}^0}{s_Tn_T{}^0+s_Hn_H{}^0}\right)ft. \quad (10)$$

That is, for short exposures, the reciprocal sensitivity is linear in the total number of excitations that have occurred in unit volume, ft. For longer exposures, and for simplicity making the assumption that $s_H \gg s_T$, (3), (8), and (9) give

$$\frac{R^0-R}{R^\infty-R^0+vs_Hn_H{}^0/e\mu}+\ln\left(\frac{R^\infty-R^0}{R^\infty-R}\right)=\frac{s_T}{s_H(n_H{}^0+n_T{}^0)}ft. \quad (11)$$

The term $vs_Hn_H{}^0/e\mu$ represents a contribution to the reciprocal sensitivity due to the negative-ion vacancies originally present in the crystal. Generally $vs_Hn_H{}^0/$

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[9] Use of a double-pass of the light beam, together with fairly low F-center concentrations, produces a moderately uniform excitation rate, f, and therefore also a uniform n, throughout the volume of the crystal. Regarding the time independency of f, a somewhat more serious problem is encountered, since with a constant illumination, f continually decreases as the F centers are bleached. Nevertheless, the relative decrease in f was generally less than 12% of the relative photocurrent fatigue in the exposure region of interest. As a refinement, the variation in f was taken into account in the actual computations.

f can actually be expressed as a function of n, provided n is space independent; use of this function in (1) furnishes an integrable equation which is, however, extremely cumbersome in the integrated form.

[10] From the observed photoconductivity, and an estimated mobility of 10 cm^2 volt^{-1} sec^{-1}, n_c was less than 10^6 cm^{-3} in all experiments. The n^0's are not likely to be less than 10^{15} cm^{-3} and n exceeded 10^{15} cm^{-3} very shortly after illumination was started.

[11] This is equivalent to the use of cgs units, with permittivity dimensionless. 1 ohm^{-1} cm^{-1}$=9\times10^{11}$ sec^{-1}.

$e\mu-R^0$ was small compared to R^∞, so that the quantity

$$\frac{R^0-R}{R^\infty}+\ln\left(\frac{R^\infty-R^0}{R^\infty-R}\right)=L \qquad (12)$$

should be linear with ft over the entire exposure range.

RESULTS AND DISCUSSION

(a) Fatigue of Photoconductivity

Six samples from two different additively colored KCl crystals were studied, having $n_F{}^0$ between 2 and 7×10^{16} cm^{-3}. As the crystals were exposed to light the sensitivity σ/f fell very rapidly initially but approached a limiting nonzero value after the absorption of a number of quanta in the neighborhood of 10^{19} cm^{-3}. f was calculated from the initial light intensity and the measured absorbance of the crystal. As the absorbance changed gradually during bleaching, the value of f was recomputed at several points and ft actually represents an integrated product. In Fig. 1, Curve A illustrates the behavior of sensitivity upon irradiation for one of the samples. All samples displayed essentially the same behavior although the initial sensitivities were somewhat variable, the range being from 7 to 14×10^{-16} cm^3, and the sensitivities after very long exposure ranged from 0.38 to 0.65×10^{-16} cm^3. Since these numbers are dependent upon the initial trap concentrations, some variation is to be expected not only for crystals colored and quenched separately but for samples taken from different parts of the same crystal, as the trap concentration is expected to be dependent on local cooling rate and strains produced by cooling.

Curve B of Fig. 1 is a plot of L from (12) against ft, for the same crystal. R^∞ was taken to be 2.65×10^{16} cm^{-3}. The curves for all of the samples were similar, though some numerical variation appeared. The curve is reasonably linear over the greater part of its range, indicating that the error introduced by neglecting s_T in comparison to s_H was not serious and that s_T can be taken to be constant for most of the range. However, the curve departs from linearity below $ft=5\times10^{17}$ cm^{-3}, the departure arising from the failure of R to increase initially as rapidly with ft as it should. The presence of a small concentration of traps of about the same cross section as that of the negative-ion vacancy and which thus fill up rapidly is probably reponsible for this result. After these traps are full, the only other traps of importance are the traps H and T.

The existence of a finite residual sensitivity after long exposure is consistent with the trap-filling postulate, whereas the "soft" *F*-center proposal would require the sensitivity to go to zero exponentially. As a test of the reality of the residual sensitivity, one of the crystals which had already been exposed until $ft=2.5\times10^{19}$ cm^{-3} was given an equal additional exposure; no further measureable change in sensitivity occurred.

(b) Bleaching

The trapping of photoelectrons at sites other than negative-ion vacancies may also be investigated by means of studies on the bleaching of the *F* band. There is an important difference, however, in the two experiments. If these other trapping sites have the same cross section as negative-ion vacancies, bleaching would occur with no change in the photoconductivity; if their cross section is greater than that of the negative-ion vacancy (an unlikely possibility) the photoconductivity would increase as bleaching proceeded.

Ueta and Känzig[12] observed that the *F* band in colored KCl was bleached in two stages; (a) a rapid initial stage during which, they proposed, traps originally present in the crystal were filled with electrons liberated from the *F* centers, and (b) a slow stage during which, they proposed, new traps must be formed by migration processes. They were able to estimate the concentration of traps originally present by the decrease in *F*-center concentration during the first stage. We have utilized the same experiment in order to find $n_T{}^0$.

Ueta and Känzig suggested that the traps formed during the slow bleaching stage were vacancy quartets. If a quartet were made from a negative-ion vacancy produced by bleaching, a positive-ion vacancy previously ejected from a quartet, and a vacancy pair already present, R would remain constant during that slow bleaching stage, as one negative-ion vacancy would be incorporated in the new trap for each one produced in bleaching. This agrees with the result that R attains a definite limit, R^∞, even though bleaching progresses indefinitely.

(c) Trap Concentrations and Cross Sections

We now proceed to the estimation of the constants of the equations. $n_T{}^0$ was found as described above. $v/e\mu$ was taken to be 7.0×10^{12} cm^{-2} as a representative value for a polar crystal.[13] For the example shown in Fig. 1, n_F was originally 6.9×10^{16} cm^{-3}, R^0 was 8.5×10^{14} cm^{-3}, R^∞ was 26.5×10^{15} cm^3, and the slope L/ft was 2.6×10^{-19} cm^3. Since, assuming $s_T\ll s_H$,

$$R^0=(v/e\mu)(s_Hn_H{}^0+s_Tn_T{}^0),$$

$$R^\infty=R^0+(v/e\mu)s_Hn_T{}^0,$$

$$L/ft=s_T/s_H(n_H{}^0+n_T{}^0),$$

the cross sections and concentrations of both the traps H and T can be estimated. These results are tabulated for two crystals of different original *F*-center concentration in Table I.

These results justify the previous assumption that $s_T\ll s_H$. Further, the cross section found for the negative-ion vacancy is of the expected order of magnitude. Ueta and Känzig reported $n_T{}^0$ to be about 2.8×10^{16}

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[12] M. Ueta and W. Känzig, Phys. Rev. **97**, 1591 (1955).

[13] Based on $v=10^7$ cm/sec and $\mu=10$ cm^2 volt^{-1} sec^{-1}.

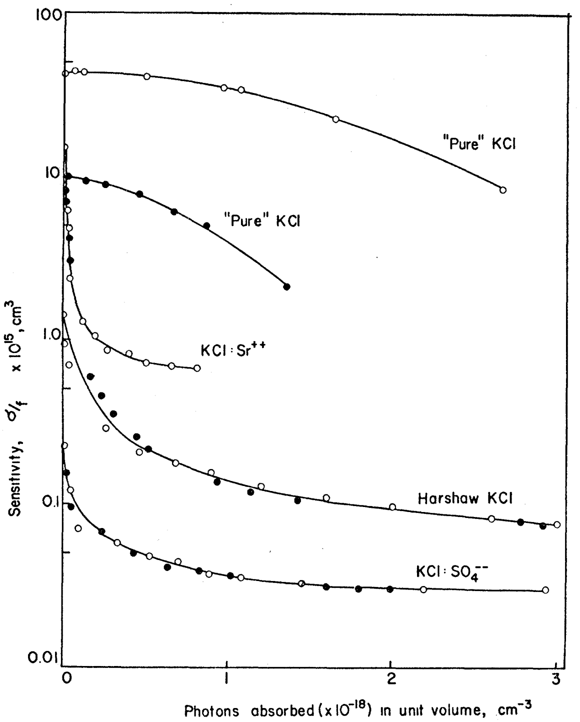

FIG. 2. Fatigue of photoconductivity in pure and impure colored KCl. Shaded circles: measurements made after one year.

cm^{-3} in their experiments; our results seem to indicate that $n_T{}^0$ is related to the density of coloration.

(d) Impurity Effects

Divalent impurity ions may be expected to effect the photoconductivity markedly through their influence on the concentration of traps. Positive divalent ions increase the positive-ion vacancy concentration and consequently, by mass action, negative-ion vacancies are removed to form vacancy pairs and clusters or are deposited at surfaces. $n_H{}^0$ should thus be depressed in KCl containing SrCl$_2$. Sr^{++} ions themselves are traps of cross section probably about the same as s_H; however, at room temperature a large fraction of Sr^{++} ions are associated with positive-ion vacancies to give traps resembling the vacancy-pair with respect to cross section.

Negative divalent ions, such as SO$_4{}^{--}$, increase the negative-ion vacancy concentration. A considerable part of the negative-ion vacancies are probably associated with SO$_4{}^{--}$ to give traps of about the cross section of a vacancy pair.

Because of the association equilibria involving the impurity ions and vacancies, it is not likely that the sensitivity of doped crystals would follow the foregoing equations developed for a simpler model; however, the photoconductivity of such crystals provides some interesting and useful information.

Figure 2 illustrates the variation in sensitivity (presented on a logarithmic scale), with exposure of four crystals of differing purity, all colored and brought to room temperature in the same manner. All except the crystal which was grown under conditions favoring a greater degree of purity displayed the usual fatigue upon bleaching; the decrease of sensitivity of the "pure" crystal was slight compared to the others.

TABLE I. Concentrations and cross sections of traps in additively colored KCl, assuming $v/e\mu = 7.0\times10^{12}$ cm^{-2}.

$n_F{}^0$, cm^{-3}	$n_H{}^0$, cm^{-3}	s_H, cm^2	$n_T{}^0$, cm^{-3}	s_T, cm^2
6.9×10^{16}	5.9×10^{14}	1.7×10^{-13}	2.1×10^{16}	1.0×10^{-15}
2.8×10^{16}	6.2×10^{14}	2.3×10^{-13}	9.3×10^{15}	1.2×10^{-15}

The variation in initial sensitivity between samples was remarkable. Compared to the Harshaw crystal, addition of SO$_4{}^{--}$ depressed the initial sensitivity eightfold; addition of Sr^{++} increased it tenfold and that of one sample of the "pure" crystals was increased about 30 times. Trap concentrations and cross sections cannot be evaluated in the doped crystals in the same way as before, since the initial decrease of F-center concentration on bleaching will not yield $n_T{}^0$ as before. For example, in KCl:Sr^{++}, bare Sr^{++} ions and Sr^{++}-vacancy complexes and other traps T all may trap electrons to produce bleaching, (with the formation of Z_1 centers among others) but the cross section of Sr^{++} ions is such that their concentration cannot be included in $n_T{}^0$. However, a rough indication of the effect of impurities may be obtained by taking $n_T{}^0$ from the bleaching result, neglecting the concentration of Sr^{++} and including the cross section and concentration of complexes in s_T and $n_T{}^0$. Taking s_H and s_T from Table I as 2×10^{-13} cm^2 and 1×10^{-15} cm^2, respectively, $n_H{}^0$ in KCl:Sr^{++}, computed from R^0, is 5×10^{12} cm^{-3}. Similarly, $n_H{}^0$ in KCl:SO$_4{}^{--}$ was calculated to be 4×10^{15} cm^{-3}. It is seen that the negative-ion vacancy concentration was indeed markedly altered, in the expected directions, by the addition of divalent impurities. This result is in contrast to that of Rabin[14] who found that NaCl containing CaCl$_2$ colored more rapidly under x irradiation than pure NaCl and concluded that the presence of Ca^{++} ions increased the negative-ion vacancy concentration. However, Rabin's estimate includes both free negative-ion vacancies and those in pairs and clusters.

The KCl:Sr^{++} crystal was unusual in another respect, namely, recovery from fatigue occurred rapidly. An hour's standing after bleaching served to restore most of the initial sensitivity, whereas practically no recovery from fatigue was observed in several hours following the bleaching of the other crystals. The high positive-ion vacancy concentration undoubtedly accelerates the rate of vacancy-pair formation, thus removing negative-ion vacancies with appreciable speed after their formation by bleaching. Thus the slope of a

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[14] H. Rabin, Bull. Am. Phys. Soc. 3, 126 (1958).

curve such as that in Fig. 2 is dependent upon the rapidity with which the measurements are carried out in the case of crystals doped with divalent cations.

The behavior of the "pure" crystal showed that both $n_H{}^0$ and $n_T{}^0$ were very low. This result agrees with that of Kawamura[15] who observed very little bleaching and consequently practically no *M*-center formation with specially purified colored KBr.

All measurements on these crystals were repeated upon adjacent pieces after one year. Considerable decrease in sensitivity occurred in the "pure" crystal, which may be ascribed either to inhomogeneity of the crystal or to aging. In the others there was no appreciable change. It does not appear that sensitivity decreases with time at room temperature, as previously reported,[2] as a usual occurrence, provided storage and handling are in total darkness.

(e) Additional Observations

An interesting observation was made during the course of this study, which merits remark and further experimentation. The sensitivity of a given crystal was higher if measured immediately after depolarization (illumination with zero field) then if the crystal remained in the dark for a minute or so before measurement. There seems to be a decay time associated with the presence of shallow traps which, during illumination, contain electrons in equilibrium with the conduction electrons. The half-time for attainment of equilibrium, or emptying of the traps, was found to be about 40 seconds. Polarization entirely obscures the effect of such shallow traps upon the rise-time of photoconductivity, when dc measurements are made; the effect should be apparent when an ac method is used, but does not seem to have been previously noted in pure alkali halides containing *F* centers. MacDonald,[16] however, using ac of frequency 20 sec^{-1} observed an even slower photocurrent decay in KBr containing both *F* and *U* centers, which he attributed to the presence of shallow traps, possibly interstitial hydrogen atoms.

In order to eliminate the effects of shallow traps on the sensitivity reported, all measurements were made after a 20-second dark interval following depolarization. This standardized procedure rendered successive measurements reproducible.

ACKNOWLEDGMENT

The assistance of E. H. Coker and P. M. Gruzensky, who prepared some of the crystals used in this study, is acknowledged with thanks.

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[15] H. Kawamura, J. Phys. Chem. Solids **8**, 161 (1959).

[16] J. R. MacDonald, J. Chem. Phys. **23**, 275 (1955).

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Interpretation of Relative Thermoelectric Phenomena at Low Temperatures with Special Consideration of the Effects of Cold-Work on Copper

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Formulas first derived by Kohler and more recently discussed by MacDonald are used to account for relative thermoelectric effects at low temperatures in pure metals, dilute alloys, and in cold-worked copper. Since calculations based on these formulas give diffusion thermoelectricity, phonon drag contributions to thermoelectricity should appear as differences between the calculated and measured curves of thermoelectric power as a function of temperature.

I. INTRODUCTION

THE thermoelectric behavior of relatively pure metals at low temperatures (say below $\theta/15$) is often puzzling since it is possible to obtain absolute thermoelectric powers from different samples which may differ not only in sign but by as much as two orders in magnitude, although residual resistivity measurements indicate that there is but little difference in the overall purity of the samples. Kohler[1] (see also Nordheim and Gorter[2]) first derived expressions from formal electron transport theory which have been deduced again more recently by MacDonald directly from simple thermal circuit theory.[3] These, as we shall show, can be applied to account for relative thermoelectric phenomena in pure metals and dilute alloys at low temperatures. The theorem which considers the influence of competing scattering mechanisms on the thermoelectricity of a homogeneous conductor containing only one type of charge carrier by treating them independently in series, can be expressed as follows

$$S=\sum W_iS_i/\sum W_i. \tag{1}$$

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[1] M. Kohler, Z. Physik **126**, 481 (1949).

[2] L. Nordheim and C. J. Gorter, Physica **2**, 383 (1935).

[3] A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. (to be published).