

## The Investigation of Trapping Centers in Crystals by the Method of Thermal Bleaching

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A method of investigating trapping centers in crystals is discussed which consists of measuring the temperature dependence of the absorption coefficient at the maximum of an absorption band of a color center as the excited crystal is warmed up at a constant rate (the method of thermal bleaching). The theory of the method is given for both the case of a single kind of trapping center and for the case of several types of traps of appreciably different depth. The possibilities of the method are illustrated with data obtained in thermal bleaching of single crystals of KCl, KCl·CaCl<sub>2</sub>, and KCl·SrCl<sub>2</sub>.

### INTRODUCTION

At the present time the method of thermal luminescence is widely used in the study of trapping centers in crystals. This method consists of measuring the luminescence intensity  $I$  from an excited phosphor as it is warmed up at a constant rate. In the past ten years a series of significant results on trapping centers in different crystal phosphors has been obtained with this method. However, at the same time some unsatisfactory features of this method have also been found. Because this method is essentially connected with observing light intensity, it cannot be applied in the investigation of trapping centers of nonluminescent crystals. Temperature quenching of the luminescence often does not permit the use of this method for the study of deep traps in typical crystal phosphors.<sup>1</sup> Thus it is necessary in many cases to measure some quantity other than the intensity of the emitted light. In several investigations<sup>2</sup> attempts were made to measure the amount of conductivity  $i$  as the temperature is raised at a constant rate in excited crystals. However, obtaining the dependence of  $i$  on  $T$  involves a number of experimental difficulties and the theoretical dependence is not yet known so that the method of thermal release of trapped charge has not received widespread application.

It therefore seems most suitable to use the well-known phenomenon of thermal bleaching to study traps in nonluminescent crystals. This

bleaching is caused by the thermal release of electrons or holes from the traps. If the absorption coefficient  $\Delta\kappa$  for traps of a given type is measured as a function of temperature on uniform warming, then the curve  $\Delta\kappa(T)$  will have a rapid drop in some rather narrow temperature interval. This temperature will characterize the depth of the corresponding trapping level. A suitable method based on the temperature dependence of  $\Delta\kappa$  will be called in the following the method of thermal bleaching.\*

### THEORY OF THE METHOD

Since the coefficient of the additional absorption produced by exciting the crystal is proportional to the number  $n_i$  of electrons trapped at centers of a given type, then determining the theoretical dependence of  $\Delta\kappa(T)$  leads directly to  $n_i(T)$ . The latter may easily be determined analogously to the determination of  $I(T)$  by Randall<sup>3</sup> and Antonov-Romanovskii.<sup>4</sup> It will be seen that  $n_i(T)$  is in many cases much simpler than  $I(T)$ .

If the phosphor contains traps of one depth only and if the kinetics are of bimolecular character, then the decrease per unit time in the number of trapped electrons is given by the expression

$$-\frac{dn_i}{dt} = p_i n_i \frac{\sigma_r n}{\sigma_r n + \sigma_t (N_i - n_i)} \quad (1)$$

\*The absorption associated with trapping centers in many cases, if not in all, lies in the visible region and leads to a coloring of the crystal. A decrease of  $\Delta\kappa$  corresponds to bleaching of the crystal.

<sup>1</sup>I. A. Farfianovich, J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 314 (1951). M. Schön, Naturwiss. 38, 235 (1951).

<sup>2</sup>G. Garlick and F. Gibson, Proc. Roy. Soc. (London) 188A, 485 (1947). R. Bube, Phys. Rev. 83, 393 (1951). N. P. Kalabuchov, Izv. Akad. Nauk SSSR, Fiz. Ser. 16, 130 (1952). D. Dutton and R. Maurer, Phys. Rev. 90, 126 (1953).

<sup>3</sup>J. Randall and M. Wilkins, Proc. Roy. Soc. (London) 184A, 366 (1945).

<sup>4</sup>V. V. Antonov-Romanovskii, Izv. Akad. Nauk SSSR, Fiz. Ser. 10, 477 (1946).

$\sigma_r$  is the effective recombination cross section;  $\sigma_t$  is the effective capture cross section;  $N_i$ , the number of absorption centers;  $n$ , the number of ionized luminescence centers;  $p_i$ , the probability of thermal release of the electrons. According to Ref. 5,

$$p_i = p_{i0} \exp(-E_T/kT). \quad (2)$$

The quantity  $E_T$  will be called the thermal ionization energy of the absorption center.

Since the lifetime of an electron in a conduction band is much smaller than the lifetime of an electron in a level of the trap, then we may consider that  $n_i$  is equal to  $n$ . In most practical cases the excitation does not produce a complete filling of the traps<sup>6</sup> so that  $n_i \ll N_i$ . Eq. (1) can be rewritten in the form

$$-\frac{dn_i}{dt} = p_i n_i \frac{\sigma_r n_i}{\sigma_r n_i + \sigma_t N_i}. \quad (3)$$

If the probability of retrapping  $A_t$  is significantly larger than the probability of recombination  $A_r$ , then

$$-dn_i/dt = p_i n_i^2 \sigma_r / \sigma_t N_i. \quad (4)$$

Using the fact that, experimentally, the temperature is raised at a constant rate,  $dT/dt = \beta_0$ , Eq. (4) becomes

$$-dn_i/dT = p_i n_i^2 \sigma_r / \sigma_t N_i \beta_0. \quad (5)$$

Integrating this expression with the condition  $N = n_{i0}$  for  $T = T_0$  gives

$$n_i = n_{i0} \left\{ 1 + \frac{\sigma_r n_{i0} p_0}{\sigma_t N_i \beta_0} \int_{T_0}^T [\exp(-E_T/kT)] dT \right\}^{-1}. \quad (6)$$

If the probability of retrapping is much smaller than the recombination probability, then

$$-dn_i/dt = p_i n_i \quad (7)$$

whereupon

$$n_i = n_{i0} \exp \left\{ -\frac{p_0}{\beta_0} \int_{T_0}^T [\exp(-E_T/kT)] dT \right\}. \quad (8)$$

The theoretical dependence  $n_i(T)$  has a much more complicated character if  $A_t \approx A_r$ .

Figures 1 and 2 show the theoretical dependence calculated from Eqs. (6) and (8) for trapping levels of different depths. In the calculations, it was assumed that  $p_0 = 10^{10} \text{ sec}^{-1}$ ;  $\beta_0 = 0.15^\circ \text{ K/sec}$ .

In addition for the case  $A_t \gg A_r$  we took

$\sigma_r n_{i0} / \sigma_t N_i = 10^{-2}$ . The characteristic parameter of the curves  $n_i(T)$  is the temperature  $T_k$  at which  $n_i = 0.5 n_{i0}$ . From Figures 1 and 2 it follows that the following relationship holds with considerable accuracy:

$$E_T = \alpha T_k. \quad (9)$$

The coefficient  $\alpha$  depends essentially on the quantities  $p_0$  and  $\beta_0$  and for the case  $A_t \gg A_r$ ,

also on  $n_{i0} / N_i$ . In Fig. 3 it is seen that upon

decreasing  $\beta_0$  the region of rapid fall-off of  $n_i(T)$  is displaced toward lower temperatures. We notice

that the form of Eq. (8) does not depend upon the number of trapped electrons, but that the form of Eq. (6) is significantly affected by it. Fig. 4

shows two curves of  $n_i(T)$  for the case  $A_t \gg A_r$ ,

calculated for different numbers of trapped electrons,  $\sigma_r n_{i0} / \sigma_t N_i = 10^{-2}$  and  $10^{-3}$ .

It is seen that decreasing  $n_{i0}$  displaces the region of rapid fall-off toward higher temperatures. As is seen in Fig. 4,  $\Delta T_k \approx 30^\circ \text{ K}$ , which means that this effect can easily be detected experimentally. For

the case  $A_t \ll A_r$  the form of  $n_i(T)$  does not

depend on the number of trapped electrons. Consequently, studying the dependence of the curves  $n_i(T)$  on the number of trapped electrons may provide a suitable criterion for the character of the kinetics of the decay. Analogous criteria permitting distinguishing between the cases  $A_t \gg A_r$

and  $A_t \ll A_r$  by the variation of  $I(T)$  with  $n_{i0}$

were proposed by Antonov-Romanovskii.

We note that

$$-dn_i/dt = \gamma I. \quad (10)$$

<sup>5</sup>R. Kubo, Phys. Rev. **86**, 929 (1952). M. A. Krivolgaz, J. Exptl. Theoret. Phys. (U.S.S.R.) **25**, 191 (1953).

<sup>6</sup>V. V. Antonov-Romanovskii, Izv. Akad. Nauk SSSR Fiz. Ser. **15**, 637 (1951).

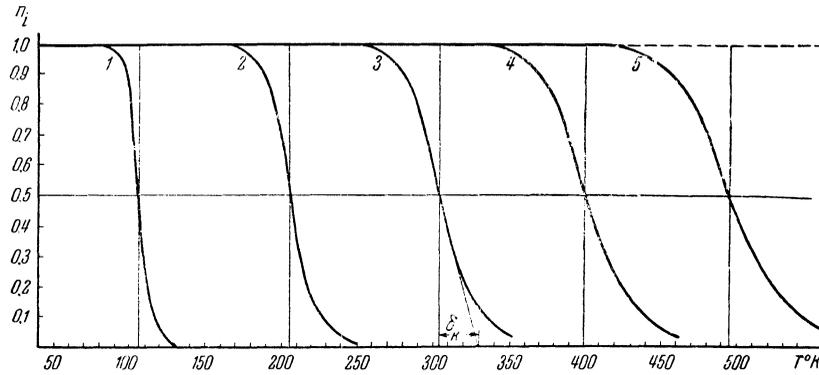


FIG. 1. Theoretical thermal bleaching curves for the case of large retrapping probability.

$p_0 = 10^{10} \text{ sec}^{-1}$ ;  $\beta_0 = 0.15 \text{ }^\circ\text{K/sec}$ ;  $\sigma_r n_{i0} / \sigma_t N_i = 10^{-2}$ ;  
 Curve 1,  $E_T = 0.2$ ; Curve 2,  $E_T = 0.4$ ; Curve 3,  $E_T = 0.6$ ;  
 Curve 4,  $E_T = 0.8$ ; Curve 5,  $E_T = 1.0 \text{ ev}$ .

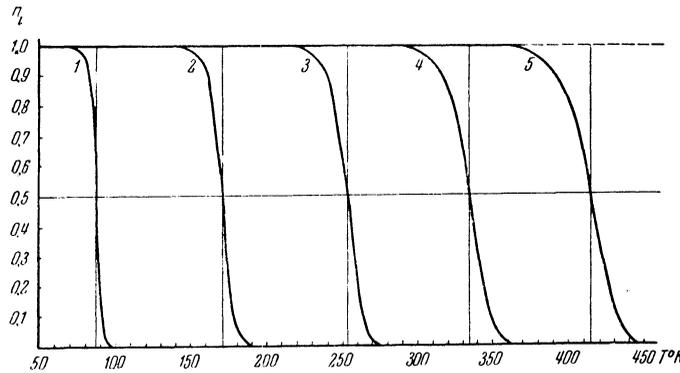


FIG. 2. Theoretical thermal bleaching curves for the case of small retrapping probability.

$p_0 = 10^{10} \text{ sec}^{-1}$ ;  $\beta_0 = 0.15 \text{ }^\circ\text{K/sec}$ ;  $E_T$  values same as in Fig. 1.

In the absence of any temperature quenching,  $n$  is a constant and the derivative of  $n_i(T)$  should give a curve which has the same form as the thermal luminescence curve of the given phosphor. If there is temperature quenching then a comparison of  $n_i(T)$  and  $I(T)$  may give the temperature dependence of the "quantum efficiency of the phosphorescence",  $n$ . If there are traps of several different sorts in the phosphor with significantly different depths, then in that temperature region in which the electrons are being released from levels  $i$

$$-\frac{dn_i}{dt} = p_i n_i \frac{\sigma_r n + \sum_{j>i} \sigma_{tj} (N_j - n_j)}{\sigma_r n + \sigma_{ti} (N_i - n_i) + \sum_{j>i} \sigma_{tj} (N_j - n_j)} \quad (11)$$

Again considering that the lifetime of the electrons in the conduction band is short and that  $n_i$  is much less than  $N_i$  we have

$$-\frac{dn_i}{dt} = p_i n_i \frac{\sigma_r n + \sum_{j>i} \sigma_{tj} N_j}{\sigma_r n + \sigma_{ti} N_i + \sum_{j>i} \sigma_{tj} N_j} \quad (12)$$

For the deepest levels,  $\sum_{j>i} \sigma_{tj} N_j = 0$ , and Eq. (12) is equivalent to Eq. (3), i.e., for the deepest traps relations hold which correspond to those found for a single level only. For shallower traps,

$\sum_{j>i} \sigma_{tj} N_j \neq 0$ . If  $A_t \gg A_r$  then

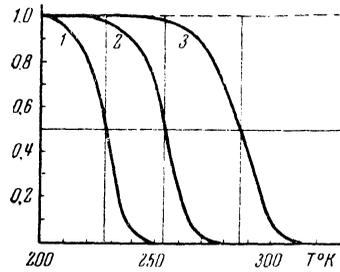


FIG. 3

FIG. 3. Theoretical dependence of the thermal bleaching curves on rate of warm-up for the case of small retrapping probability  $E_T = 0.6$  eV;  $p_0 = 10^{10}$  sec $^{-1}$ ; Curve 1,  $\beta_0 = 0.005$ , Curve 2,  $\beta_0 = 0.15$ , Curve 3,  $\beta = 4.5^\circ$  K/sec.

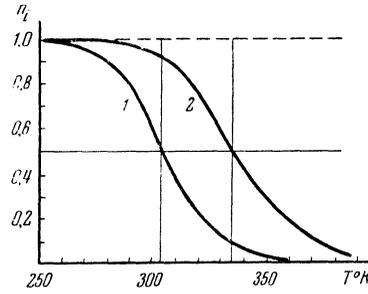


FIG. 4

FIG. 4. Theoretical dependence of the thermal bleaching curves on the number of trapped electrons for the use of large retrapping probability.  $E_T = 0.6$  eV;  $p_0 = 10^{10}$  sec $^{-1}$ ;  $\beta_0 = 0.15^\circ$  K/sec; Curve 1,  $\sigma_r N_{i0} / \sigma_t N_i = 10^{-2}$ ; Curve 2,  $\sigma_r N_{i0} / \sigma_t N_i = 10^{-3}$ .

$$-\frac{dn_i}{dt} = p_i n_i \frac{\sum_{j>i} \sigma_{tj} N_j}{\sigma_{ti} N_i + \sum_{j>i} \sigma_{tj} N_j} = C p_i n_i. \quad (13)$$

From this we get

$$n_i = n_{i0} \exp \left\{ -C \frac{p_0}{\beta_0} \int_{T_0}^T [\exp(-E_T/kT)] dT \right\}. \quad (14)$$

If  $A_t \ll A_r$  then

$$-dn_i/dt = p_i n_i \quad (15)$$

and

$$n_i = n_{i0} \exp \left\{ -\frac{p_0}{\beta_0} \int_{T_0}^T [\exp(-E_T/kT)] dT \right\}. \quad (16)$$

Thus for shallow traps, both cases  $A_t \gg A_r$  and  $A_t \ll A_r$  give identical behaviors for  $n_i(T)$ . The only difference is the presence of the coefficient  $C$  in Eq. (14). We note that for all trapping levels other than the deepest in both limiting cases the form of  $n_i(T)$  does not depend on the trapped light sum. Thus

$$I = -\frac{dn}{dt} = p_i n_i \frac{\sigma_r n}{\sigma_r n + \sigma_{ti} N_i + \sum_{j>i} \sigma_{tj} N_j}, \quad (17)$$

so that the curve determined by differentiating  $n_i(T)$  will be similar to  $I(T)$  only in the case of small probability of retrapping, in which case

$$I = p_i n_i. \quad (18)$$

If the probability of a retrapping is large, then

$$I = \frac{\sigma_r}{\sigma_{ri} N_i + \sum_{j>i} \sigma_{tj} N_j} p_i n_i n \quad (19)$$

and  $-dn_i/dt$  will not coincide in general with  $I$ .

Only if  $n_i \ll n$  and consequently a release of electrons from levels  $i$  does not change the light sum  $n$  very much,

$$I = B p_i n_i \quad (20)$$

and  $-dn_i/dt$  coincide in form with  $I$  in the absence of temperature quenching.

Therefore for other than the deepest traps, the theoretical dependence of  $n_i(T)$  is much simpler than that of  $I(T)$ . The variation of  $n_i(T)$  is also appreciably simpler than that of  $i(T)$ .

We now consider some methods for determining the thermal ionization energy of trapping centers from the parameters of the thermal quenching curves. Some such parameters are: 1) the temperature  $T_k$  of which  $n_i = 0.5 n_{i0}$ ; the "halfwidth of the fall-off"  $\delta_k = -n_{ik} / (dn_i/dT) T_k$ ;  $\delta_k$  is shown graphically in Fig. 1.

The relation between  $E_T$  and  $p_0$  of the traps with the above parameters and with the warming rate

$\beta_0$  also may easily be found. For the case where

$$-\frac{dn_i}{dT} = \frac{p_0}{\beta_0} \left[ \exp\left(-\frac{E_T}{kT}\right) \right] \frac{\sigma_r n_i^2}{\sigma_r n_i + \sigma_{ti} N_i}, \quad (21)$$

then for  $T = T_k$

$$-\left(\frac{dn_i}{dT}\right)_{T_k} = \frac{p_0}{\beta_0} \left[ \exp\left(-\frac{E_T}{kT}\right) \right] \frac{\sigma_r n_{ik}^2}{\sigma_r n_{ik} + \sigma_{ti} N_i}. \quad (22)$$

from which

$$E_T = kT_k \ln \left[ \frac{p_0}{\beta_0} \delta_k \left(1 + \frac{2\sigma_{ti} N_i}{\sigma_r n_{i0}}\right)^{-1} \right]. \quad (23)$$

If  $A_t \gg A_r$ , Eq. (23) becomes

$$E_T = kT_k \ln \left[ \frac{p_0}{\beta_0} \delta_k \frac{\sigma_r n_{i0}}{2\sigma_{ti} N_i} \right]. \quad (24)$$

If  $A_t \ll A_r$ , then

$$E_T = kT_k \ln \left[ \frac{p_0}{\beta_0} \delta_k \right]. \quad (25)$$

On the other hand, from the condition  $n_i|_{T=T_k} = 0.5 n_{i0}$ , we get for the case  $A_t \gg A_r$

$$E_T = kT_k \ln \left[ \frac{p_0 \sigma_r n_{i0} k T_k^2}{\beta_0 \sigma_{ti} N_i E_T} \right]; \quad (26)$$

and for the case  $A_t \ll A_r$

$$E_T = kT_k \ln \left[ \frac{p_0 k T_k^2}{\beta_0 E_T} \right]. \quad (27)$$

[ Eqs. (26) and (27) come from an approximate integration of the exponential in (6) using the approximation,  $1/T - 1/T_k \approx (T_k - T)/(T_k^2)$ , in the region

where the integrand is not very small.) From (24) and (26), for  $A_t \gg A_r$ ,

$$E_T = 2kT_k^2 / \delta_k. \quad (28)$$

Similarly for  $A_t \ll A_r$ , from (25) and (27),

$$E_T = kT_k^2 / \delta_k \ln 2. \quad (29)$$

From what has been said before, it is evident that relations similar to (25) and (29) hold for other than the deepest traps. For this case a factor  $C \leq 1$  must be inserted in (25). In Tables 1 and 2 are given the quantities  $T_k$  and  $\delta_k$  determined from the data in Figs. 1 and 2 respectively. Also given are  $E_T$  calculated using (28) and (29). Comparing the first and fourth columns shows that (28) and (29) give somewhat too high values of  $E_T$ . The error never exceeds 7 per cent. Thus the expressions obtained above may be used to determine  $E_T$  for trapping centers. We note that the derivative curve  $n'_i(T)$  also provides parameters (such as the position of the maximum  $T_m$  and the halfwidth of the peak  $\delta$ ) depending on  $E_T$  and  $p_0$

and from which the latter may be calculated.<sup>7,8</sup>

However, the graphical differentiation can be difficult and the determination of  $E_T$  using (23) - (29) seems more convenient to us.

TABLE I

$E_T$ , ev	$T_k$ , °K	$\delta_k$ , °K	$E_T$ from Eq. (28)
0.2	106	9	0.215
0.4	206	17	0.430
0.6	304	26	0.620
0.8	400	33	0.830
1.0	496	41	1.060

TABLE II

$E_T$ , ev	$T_k$ , °K	$\delta_k$ , °K	$E_T$ from Eq. (29)
0.2	88	4.5	0.217
0.4	171	8.5	0.425
0.6	254	12.5	0.635
0.8	335	17	0.820
1.0	415	20	1.070

It is easy to show that  $T_k$  differs little from  $T_m$ . If  $A_t \gg A_r$ ,  $T_k$  is a few degrees higher than  $T_m$ ; if  $A_T \ll A_r$ ,  $T_k$  is a few degrees lower than  $T_m$ . In the latter case

$$T_k - T_m \approx T_m \ln \ln 2 / \ln \left[ \frac{p_0}{\beta_0} \delta_k \right]. \quad (30)$$

If the kinetics of the afterglow are monomolecular<sup>9</sup> then for the deepest as well as for the shallower traps,

$$n_i = n_{i0} \exp \left\{ -C \frac{p_0}{\beta_0} \int_{T_0}^T \left[ \exp\left(-\frac{E_T}{kT}\right) \right] dT \right\}. \quad (31)$$

<sup>7</sup>Ch. B. Lushchik, Dokl. Akad. Nauk SSSR, 101, 641 (1955).

<sup>8</sup>I. A. Farfianovich, J. Exptl. Theoret. Phys. (U.S.S.R.) 26, 696 (1954).

<sup>9</sup>V. V. Antonov-Romanovskii, Works (Trudy) of the Physical Institute, Academy of Sciences USSR, 24, 430 (1939).

For the case  $A_t \ll A_r$ ,  $C < 1$  and for  $A_t \gg A$   $C = 1$ . The form of  $n_i(T)$  does not now depend on the number of trapped electrons. The thermal ionization energies of the traps may be determined using (25) and (29).

Until now we have been assuming that the number of electrons in certain trapping levels decreases as a result of releasing them to the conduction band where they subsequently recombine with holes in empty trapping centers or sometimes with ionized luminescence centers. However, it can also proceed through thermal ionization of the holes in "empty" trapping centers which recombine with trapped electrons. In this case  $n_i(T)$  will be determined by the thermal ionization energy of the "empty" trapping centers. The theory developed above may be generalized to the case where both holes and electrons can be released thermally.

We consider a crystal containing electron traps of depth  $E_T$  and hole traps of depth  $Q_T$ . We will devote all quantities pertaining to electrons with the index "e" and those pertaining to holes with "h". Assuming that the lifetimes of electrons in the conduction band and of holes in the filled band are small compared with  $p_e^{-1}$  and  $p_h^{-1}$  and also that  $n_e \ll N_e$ ,  $n_h \ll N_h$ , we may write

$$-\frac{dn_i}{dt} = p_e n_i \frac{\sigma_{re} n_i}{\sigma_{re} n_i + \sigma_{te} N_e} + p_h n_i \frac{\sigma_{rh} n_i}{\sigma_{rh} n_i + \sigma_{th} N_h} \quad (32)$$

(The number of recombinations of free holes with free electrons will be significantly smaller, because of their small concentrations, than the recombinations with trapped charges and is therefore neglected.) If  $Q_T > E_T$  then  $p_e \gg p_h$  and

$$-\frac{dn_i}{dt} = p_e n_i \frac{\sigma_{re} n_i}{\sigma_{re} n_i + \sigma_{te} N_e} \quad (33)$$

If  $Q_T < E_T$  then  $p_e \ll p_h$  and

$$-\frac{dn_i}{dt} = p_h n_i \frac{\sigma_{rh} n_i}{\sigma_{rh} n_i + \sigma_{th} N_h} \quad (34)$$

We emphasize that the law of variation of the number of electron traps and of hole traps are identical. However, for  $Q_T > E_T$ ,  $n_i(T)$  leads to a determination of the thermal ionization energy of

electron traps and for  $Q_T < E_T$  - hole traps. Thus only the smaller of  $E_T$  and  $Q_T$  can be determined from  $n_i(T)$  and not the larger.

The case  $Q_T < E_T$  corresponds to the presence of high temperature quenching.<sup>9a</sup> Equation (32) represents a generalization of a relation found by Antonov-Romanovskii for the decay of a bimolecular afterglow process with a monomolecular quenching<sup>9a</sup> (see also Ref. 10). We note that the lower temperature quenching (which occurs after recombination of an electron with a luminescence center) does not affect the behavior of  $n_i(T)$  but may greatly change  $I(T)$ .

Consequently, even for luminescent crystals, the thermal-bleach method has wider applicability than the thermal luminescence method.

#### EXPERIMENTAL DETERMINATION OF THERMAL BLEACHING CURVES

To determine  $n_i(T)$  it is necessary to measure some quantity proportional to  $n_i$  while the crystal is being warmed up at a constant rate. One such quantity is the absorption coefficient in the maximum of the band of the additional absorption  $\Delta \kappa_{mi}$

$$\Delta \kappa_{mi} = B n_i.$$

It should be remarked that even for the case  $n_i = \text{const}$ . there is some dependence of  $\Delta \kappa_{mi}$  on temperature because of the change in shape of the absorption band, so that strictly speaking  $B = B(T)$ . However, as has been shown in a number of experimental investigations and as follows also from the calculations of Pekar<sup>11</sup> when  $n_i = \text{const}$   $\Delta \kappa_{mi} \sim T^{-1/2}$  so that the coefficient  $B$  depends very weakly on temperature. The dependence  $B(T)$  may be entirely neglected in comparison with the extremely rapid variation of  $n_i(T)$ . For this reason in the following, we will assume that

$$\Delta \kappa_{mi} = B n_i \text{ and } B \neq B(T). \quad (35)$$

We note that the increase in dielectric constant of a crystal with excitation  $\Delta \epsilon$  is also proportional to  $n$

<sup>10</sup> N. A. Tolstoi, Dokl. Akad. Nauk SSSR 95, 249 (1954).

<sup>11</sup> S. I. Pekar, *Investigations of the Electron Theory of Crystals*, GTTI, 1951 (Translated into German, Akademie Verlag, Berlin, 1954).

$$\Delta\epsilon = B' n$$

However in this case, as has been observed by Garlick<sup>12</sup> the coefficient  $B'$  is extremely sensitive (exponentially) to temperature. Thus  $\Delta\epsilon(T)$  does not permit a determination of  $n_i(T)$ . Consequently, the measurement of  $\Delta\kappa_{mi}(T)$  seems most suitable for the determination of  $n_i(T)$ .

In order that the process of measuring  $\Delta\kappa_{mi}$  does not decrease the number of trapped electrons through optical excitation it is necessary to work with weak light intensity. It is evident that this restriction is determined only by the sensitivity of the radiation detector being used and may always be satisfied. For the crystals studied by us using a SF-4 spectrophotometer the number of optically released electrons was determined to be not greater than 1% of the number of electrons thermally released during the measurement.

The most suitable objects for measurement are single crystals which permit precision determinations of the absorption coefficient. Since the determination of the curve  $\Delta\kappa_{mi}(T)$  is made using a single wavelength, the method may also be used with thin polycrystalline layers in which light scattering takes place. For this the most suitable material is evidently the so-called sublimate phosphors.<sup>13</sup>

We have tested the thermal bleach method on single crystals of alkali halides of highest purity. The  $\Delta\kappa_{mi}(T)$  curves were determined using a special adaptation for this purpose of a SF-4 spectrophotometer. The rate of warmup was 0.15°K per second, i.e., the same magnitude that was used in the previous calculations. Since the crystals that were investigated emit a weak thermal luminescence upon being warmed up, we put a filter before the window of the photo element which passed only the "operating wavelength" corresponding to the maximum of the band of the additional absorption.

It should be remarked that the sensitivity of the thermal bleach method is significantly less than that of the method of thermal luminescence. The latter method permits the investigation of traps in

phosphors which do not have sufficient absorption to be detected.

#### APPLICATION OF THE METHOD TO THE STUDY OF TRAPPING CENTERS

The method of thermal bleach has been applied by us to the study of several trapping centers in alkali halide crystals. We studied single crystals KCl with small additions of bivalent ions of metals in the second group. The single crystals were grown by the method of Kyropoulos. The concentration of the additive corresponds to the amount introduced in the melt.

The single crystals which were grown from KCl marked cp were very weakly colored by a condensed aluminum spark. Irradiation with x-rays produced an intense violet color. The spectrum of the additional absorption in an x-irradiated single crystal of KCl which was measured on the SF-4 spectrophotometer is shown in Fig. 5 (curve a). It

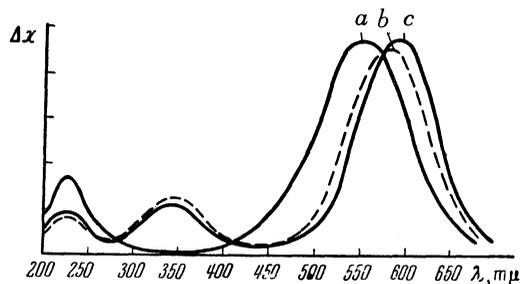


FIG. 5. Spectra of the additional absorption: a-KCl, x-rayed; b-KCl·SrCl<sub>2</sub>·0.5 mol %, excited by spark; c-KCl·CaCl<sub>2</sub>·0.5 mol %, excited by spark.

consists of two widely separated bands at 555 and 225  $\mu$ . The first band corresponds to the so-called  $F$ -color centers (electrons), the second to  $V$ -color centers (holes). Single crystal KCl containing a small quantity (0.5 mole per cent) CaCl<sub>2</sub> and SrCl<sub>2</sub> are colored very much more easily than the single crystals of pure KCl. Illumination by an aluminum spark for a period of one hour produced about  $10^{16}$  color centers per cm<sup>3</sup>\*. The spectra of the additional absorption produced by the aluminum arc in the crystals of KCl·CaCl<sub>2</sub> and KCl·SrCl<sub>2</sub> are shown in Fig. 5 (curves b and c).

\*The number of Ca<sup>++</sup> and Sr<sup>++</sup> ions present in the crystal and acting as electron traps is not less than  $5 \cdot 10^{17}$  per cm<sup>3</sup>. Thus the relationship  $n_i \ll N_i$  is very well satisfied in our case.

<sup>12</sup>G. Garlick, *Luminescent Materials*, Oxford, 1949.

<sup>13</sup>F. D. Klement, *Izv. Akad. Nauk SSSR, Fiz. Ser.* 9, 411 (1945).

For  $\text{KCl} \cdot \text{CaCl}_2$ , there are bands at 580, 350, and 225  $m\mu$ . For  $\text{KCl} \cdot \text{SrCl}_2$  there are bands at 590, 350, and 225  $m\mu$ . The bands at 580 and 590  $m\mu$  coincide well with the so-called  $Z_1$ -bands in additively colored crystals of  $\text{KCl} \cdot \text{CaCl}_2$  and  $\text{KCl} \cdot \text{SrCl}_2$  studied by Pick.<sup>14</sup>

Similar bands have been found by Etzel<sup>15</sup> in  $x$ -irradiated crystals of  $\text{NaCl}_2$  -  $\text{CaCl}_2$ . According to the hypothesis of Seitz<sup>16</sup> these bands correspond to electrons that are trapped at bivalent alkaline earth ions. The bands at 225  $m\mu$ , which are present also in pure  $\text{KCl}$  as well as in  $\text{KCl}$  containing  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$ , Seitz attributes to a complex of vacancies which has trapped holes.<sup>17</sup>

It is of interest to study the 350  $m\mu$  band which is present in  $\text{KCl} \cdot \text{CaCl}_2$  and  $\text{KCl} \cdot \text{SrCl}_2$  but which is absent in pure  $\text{KCl}$ . As is known<sup>18</sup> in pure  $\text{KCl}$  at 78° K there is a band of additional absorption at 335  $m\mu$  which disappears at room temperature and which Seitz attributes to holes trapped at single cation vacancy sites.<sup>17</sup> Since in crystals containing bivalent positive ions there must also be an equal number of cation vacancy sites, it is not surprising that similar bands appear in crystals of  $\text{KCl} \cdot \text{CaCl}_2$  and  $\text{KCl} \cdot \text{SrCl}_2$ .

We note that in correspondence with the data of Etzel for  $\text{NaCl} \cdot \text{CaCl}_2$ <sup>15</sup> we have also found that the addition of  $\text{CdCl}_2$  to  $\text{KCl}$  does not lead to strong coloring. Apparently the  $\text{Cd}^{++}$  ions form complexes with the cation vacancy at room temperature in contrast to  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$ . This is not surprising since it is more electropositive than  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  because of the special electronic shell structure of  $\text{Cd}^{++}$ .\*

From Fig. 5 it follows that the optical activation energy  $E_\lambda$  of the trapping centers in the impure crystals is less than  $E_\lambda$  for  $F$ -centers and that  $E_\lambda$  for  $\text{Sr}^{++}$  is less than for  $\text{Ca}^{++}$ . It is of interest to see whether there is a correspondingly similar behavior

for the thermal ionization energies also. In order to determine  $E_T$  we used the method of thermal bleaching. The curve of  $\Delta \kappa_{mi}(T)$  so obtained for the electron traps is given in Fig. 6. From the figure it is immediately clear that the thermal ionization energies of the traps in the impure crystals is less than  $E_T$  for  $F$ -centers and that  $E_T$  for  $\text{Sr}^{++}$  is less than for  $\text{Ca}^{++}$ .

In order to obtain quantitative data about  $E_T$  of the corresponding traps it was necessary first to consider the question of the applicability to the present case of the different formulas introduced earlier. Since we experimented with crystals in which there were practically only traps of a single depth, then by studying the dependence of the shape of the curve  $\Delta \kappa_{mi}(T)$  on the number of trapped electrons it was possible to give a direct experimental answer to the question of which one of the various formulas derived earlier is applicable to the present case. We measured the curves  $\Delta \kappa_{mi}(T)$  for two values of the trapped light sum ( $n_{01} : n_{02} = 8.1$ ). As is seen in Fig. 7, the shape of  $\Delta \kappa_{mi}(T)$  is practically independent of  $n_{i0}$  (in particular  $T_k$  does not depend on  $n_{i0}$ ). The data presented justify the conclusion that there is small probability of retrapping in phosphors of this type which was made by us in an earlier work.<sup>7</sup>

In Fig. 8 are given curves of thermal bleaching of the phosphor  $\text{KCl} \cdot \text{TlCl}$  which were obtained under the same conditions as the curve  $\Delta \kappa_{mi}(T)$  for  $\text{KCl}$ .\* Comparing  $T_k$  of the curve  $\Delta \kappa_{mi}(T)$  for  $F$ -centers in  $\text{KCl}$  and  $T_m$  of the corresponding thermal luminescence peak shows that  $T_m > T_k$ .

This also affirms the conclusions of the theory which assumes small probability of retrapping. We note that graphical differentiation of the curve  $\Delta \kappa_{mi}(T)$  gives a curve which almost coincides in form with the curve  $I(T)$  (Fig. 8, curves 2 and 3).

On the basis of these experiments we used formulas (25) and (29) to calculate the thermal ionization energy. In using (25) we assumed in accordance with the result of earlier work<sup>20</sup> that  $p_0 = 10^{10}$   $\text{sec}^{-1}$ . The quantities obtained by the different methods differed from each other by no more than

\*The curve  $I(T)$  was obtained after a preliminary warming to 380° K and subsequent cooling to room temperature.

<sup>20</sup>Ch. B. Lushchik, Dokl. Akad. Nauk SSSR 101, 833 (1955).

\*Shamovskii and Gosteva<sup>19</sup> have given another interpretation to this observation.

<sup>14</sup>H. Pick, Ann. d. Phys. 5, 35 (1939).

<sup>15</sup>H. Etzel, Phys. Rev. 87, 906 (1952).

<sup>16</sup>F. Seitz, Phys. Rev. 83, 134 (1951).

<sup>17</sup>F. Seitz, Phys. Rev. 79, 529 (1950).

<sup>18</sup>P. Pringsheim, R. Casler, P. Yuster, J. Chem. Phys. 18, 1564 (1950).

<sup>19</sup>L. M. Shamovskii and M. I. Gosteva, Zh. Fiz. Khim. 28, 1266 (1954).

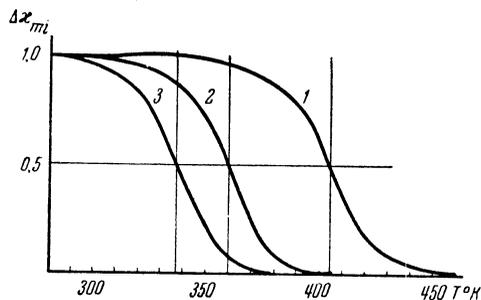


FIG. 6

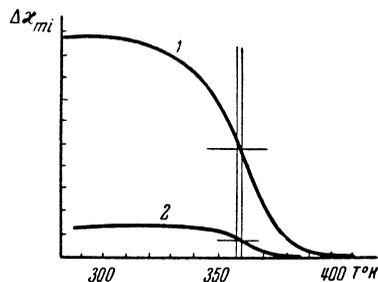


FIG. 7

FIG. 6. Thermal bleaching curves for electron traps: 1-KCL,  $\lambda_m = 555 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ ; 2-KCl·CaCl<sub>2</sub>,  $\lambda_m = 580 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ ; 3-KCL·SrCl<sub>2</sub>,  $\lambda_m = 590 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ .

FIG. 7. Dependence of the thermal quenching curves on the number of trapped electrons.  $\lambda_m = 580 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ ; 2-KCl·CaCl<sub>2</sub> spark excited 3 hours; 2-KC·CaCl<sub>2</sub> spark excited 15 minutes.

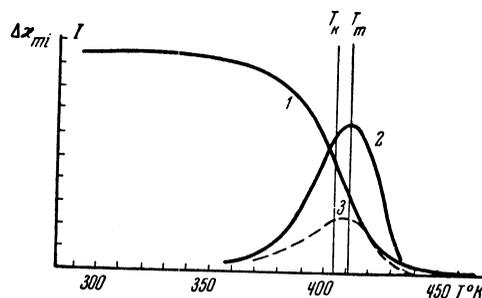


FIG. 8. Comparison of the thermal bleaching and thermal luminescence curves.  $\beta_0 = 0.15^\circ \text{ K/sec}$ ; 1- $\Delta x_{mi}(T)$  for the *F*-band of  $\alpha$ -irradiated KCl; 2- $I(T)$  for spark excited KCl·TiCl 0.01 mol %; 3-the graphical differentiation of  $\Delta x_{mi}(T)$ .

5%. The calculated values of  $E_T$  are given in Table 3. The values of  $E_\lambda$  are given also for comparison. From the values in the table it follows that  $E_T$  and  $E_\lambda$  are larger for *F*-centers than for the centers which are produced by adding  $\text{Ca}^{++}$  and that  $E_\lambda$  and  $E_T$  are larger for the impurity centers in  $\text{KCl}\cdot\text{CaCl}_2$  than for the traps in  $\text{KCl}\cdot\text{SrCl}_2$ . This agrees with the fact that the ionization potentials of a hydrogen atom (analog of an *F*-center) is greater than the ionization potential of  $\text{Ca}^+$  but that the latter is greater than the ionization potential of Sr. +

We also measured the curves of thermal bleaching of the trapping centers for holes ( $\lambda_m = 350 \text{ m}\mu$ )

in  $\text{KCl}\cdot\text{CaCl}_2$  and  $\text{KCl}\cdot\text{SrCl}_2$ . Comparing  $\Delta x_{mi}(T)$  for the hole traps (Fig. 9) and  $\Delta x_{mi}(T)$  for the electron traps (Fig. 6) shows that the de-

TABLE III

	$E_\lambda$ in ev	$E_T$ from Eq. (25) in ev	$E_T$ from Eq. (29) in ev
KCl	2.22	0.97	1.02
KCl·CaCl <sub>2</sub>	2.12	0.85	0.86
KCl·SrCl <sub>2</sub>	2.08	0.80	0.80

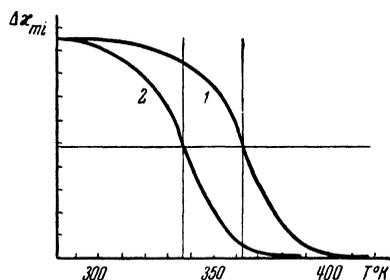


FIG. 9. The thermal bleaching curves for hole traps. 1-KCl·CaCl<sub>2</sub>,  $\lambda_m = 350 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ ; 2-KCl·SrCl<sub>2</sub>,  $\lambda_m = 350 \text{ m}\mu$ ,  $\beta_0 = 0.15^\circ \text{ K/sec}$ .

crease in the number of electrons and in the number of holes follows the same law just as one should expect. In connection with this result the question arises: Which are freed by the warming up, electrons or holes? We assume that the electrons are released. This assumption is based on the following facts:

1. The peak of the thermal luminescence in the phosphor KCl·TlCl which is associated with recombination of electrons (!) with ionized luminescence centers agrees well with the region of

rapid fall-off of the curve  $\Delta \kappa_{mi}(T)$  (see Fig. 8).

2. For electron traps  $E_\lambda$  depends on the type of impurity, for hole traps it is independent of the impurity. Since the data from the thermal quenching shows clearly a dependence of  $E_T$  on the type of impurity it is natural to consider that warming the crystal releases electrons. Then the temperature dependence of the absorption coefficient associated with the hole traps is determined by the thermal ionization energy of the trapped electrons.

The data given here, notwithstanding its illustrative character, serve in our opinion as evidence for the potential usefulness of the method of thermal quenching for the investigation of trapping centers in crystals. The application of this method in conjunction with the thermal luminescence method and the method of additional absorption will permit extending our knowledge of trapping centers in crystalline materials.

The present work was carried out in the laboratory of luminescence under the guidance of Prof. F. D. Klement to whom the author offers his deep thanks for the interpretation of the results. An author is very much indebted also to N. Lushchik and E. Vil'per for their help in this work.

Translated by B. Goodman