two substances are isomorphous. There is perhaps reason to believe that the occurrence of comparatively strong cooperative interaction is a distinctive feature of hydrated chlorides (and possibly other halides) of nickel and cobalt not exhibited by other salts of these metals hydrated to a comparable degree. For example, in $\alpha NiSO_4 \cdot 6H_2O$[10], a Schottky-type specific heat anomaly has been found at liquid helium temperatures but no evidence of cooperative interaction. X-ray analysis has shown[26] that each Ni^{++} ion in this salt is surrounded by an octahedron of six water molecules which apparently help to isolate it rather effectively from its neighbors. While similar octahedra might be expected to surround the metallic ions in $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, recent x-ray studies by Mizuno *et al.*[27] show this not to be the case. They find that each metallic ion is actually surrounded by an octahedron consisting of four water molecules and two chloride ions. The Cl^- ions are at opposite vertices of the octahedron while the H_2O molecules form a square in the plane bisecting the line joining the Cl^-'s and containing the metallic ion. On the basis of preliminary reports of this x-ray work, Haseda and Kanda[3] suggested that the Cl^- ions, replacing as they do water molecules in the usual octahedral coordination scheme, are responsible for the "high" Néel point in $CoCl_2 \cdot 6H_2O$. Presumably they provide paths for the indirect exchange coupling of Co^{++} moments. Our observation of a cooperative transition in $NiCl_2 \cdot 6H_2O$ is certainly consistent with this conjecture. Further speculation as to the mechanism of such coupling should perhaps await the development of a clearer picture of the arrangement of ionic moments in the antiferromagnetic state in both salts.

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[26] C. A. Beevers and H. Lipson, Z. Krist. **83**, 123 (1932).

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Evaluation of Thermal Activation Energies from Glow Curves

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A new method for the evaluation of thermal activation energies from glow curves of excited crystals is described. Use is made of the symmetry of the glow peak, from which the activation energy is calculated by a simple formula: $E=(q/\delta)kT_g^2$, where T_g is the peak temperature, k—Boltzmann's constant, δ—the half-width towards the falloff of the glow peak, and q—a factor which can be computed from the shape of the glow peak. Values of $q \leqslant 1$ were found for monomolecular processes, while $1 \leqslant q \leqslant 2$ correspond to bimolecular ones. The method thus enables to determine the type of kinetics.

INTRODUCTION

THE method of thermoluminescence has been extensively used in the study of trapping states in crystals.[1] In this method energy stored up in the crystal by suitable excitation, is subsequently released with emission of light on warming up the crystal from the low temperature at which it has been excited.

Randall and Wilkins[2] were the first to investigate the thermoluminescence theoretically. They used a model in which electrons in metastable states are raised thermally to an excited state from which they return to the ground state with emission of luminescence. Assuming a uniform rate of heating they obtained an expression for the variation of the thermoluminescence with temperature, but they neglected the bimolecular nature of the process. Later the theory was extended by other investigators,[3–6] who assumed bimolecular kinetics and also allowed for the retrapping of the released electrons.

Computation of activation energies remained still quite complicated, not only for mathematical, but also for physical reasons. The difficulty lies in the fact that in addition to the activation energy, the equations

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[1] For references see: G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, Oxford, 1949); G. F. J. Garlick, *Encyclopedia of Physics*, (Springer-Verlag, Berlin, 1958). Vol. XXVI, pp. 1–28; W. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958).

[2] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

[3] H. E. Klasens and M. E. Wise, Nature **158**, 483 (1946).

[4] V. V. Antonov-Romanovski, Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **10**, 477 (1946).

[5] Ch. B. Lushchik, Doklady Akad. Nauk S.S.S.R. **101**, 641 (1955).

[6] J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).

contained other unknowns; e.g., the so-called frequency factor of the trap, and the probabilities of the transitions involved. Several methods have been proposed in order to overcome this difficulty.[7] These methods are, however, still limited in use. One of the limitations was the assumption of equality of the number of traps and the number of luminescence centers, which does not seem to be always justified.

In the present work, a new method for calculation of activation energies is developed. Use is made in this method of the symmetry properties of the glow peaks. It is to be shown that this symmetry depends not only on the transition probabilities involved (e.g., the amount of retrapping) as has been concluded formerly,[5,7] but is also dependent on the number of traps compared to that of luminescence centers.

The theory developed in the present paper has already been applied successfully to experimental glow curves. Results obtained with alkali-halides are to be described in the following paper.[8]

(1) The Theoretical Model

We start with the physical model shown in Fig. 1, which has already been proposed by various authors.[9] The scheme admits a number of discrete localized levels in the forbidden energy gap between the valence band and the conduction band. In the following it proves convenient to use full formal analogy between electrons and positive holes. We assume several levels of depth E_i below the bottom of the conduction band, which may serve as electron traps. By analogy several trapping levels for positive holes are assumed to be present above the valence band.

Let N_i designate the number per cm^3 of electron traps of depth E_i, and n_i the number of them occupied by electrons. By analogy m_j out of M_j hole traps of "depth" E_j (above the valence band) may be occupied by holes. Such *full* hole traps are often looked at as *empty* luminescence centers.

By excitation of the crystal we understand the process of elevation of electrons from the valence band, or directly from the luminescence centers, into the conduction band, followed by trapping of the electrons in the trapping levels N_i. At the same time holes created in the valence band are trapped in the levels M_j.

The energies E_i and E_j are assumed to be large compared to kT (say, the smallest of E_i, E_j be about 10 kT), where k is Boltzmann's factor, and T the absolute temperature. Under these conditions the number of electrons in the conduction band, and of holes in the valence band will be very small compared to the corresponding numbers in the traps. The condition of charge neutrality of the crystal may then be expressed in the form:

$$\sum n_i = \sum m_j. \qquad (1.1)$$

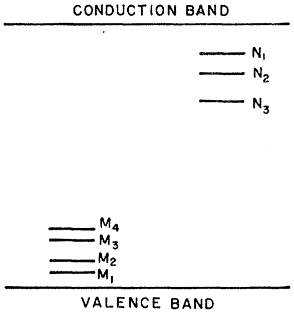

FIG. 1. Energy scheme for a crystal containing electron-trapping levels (N_i) and hole trapping levels (M_j).

On warming up the crystal, trapped carriers may be released from trapping states, and recombine with trapped carriers of the opposite sign. Whether it is electrons or holes that are mainly released will depend on the relative values of E_i and E_j, on the transition probabillties, and on the numbers n_i and m_j involved.

The recombination process may be accompanied by emission of photons when the crystal will exhibit thermoluminescence.

In our model below we shall assume the carriers released thermally to be electrons. The full analogy, however, assures all calculations to fit also the analog case in which holes are released thermally, and recombine with trapped electrons.

We further assume that in the limited temperature range under consideration only one trapping level of depth E (whose concentration is N per cm^3) is effective in releasing the electrons, and recombination takes place at only one type of luminescence center M. This will give rise to an *isolated* glow peak. We shall allow nonradiative transitions. The luminescence yield, however, will be assumed to be constant throughout the considered glow peak.

An important point is that though transitions involving other trapping levels are neglected, such traps exist and may be occupied. This affects the neutrality condition, which can no longer be expressed as $n=m$ as assumed by other investigators.[7] It should now be given in the form:

$$\Delta n = \Delta m, \qquad (1.2)$$

where $\Delta n = n_0 - n$, and $\Delta m = m_0 - m$; n_0, m_0 being the concentrations at the time t_0, and n, m at the time t, of the trapped electrons and trapped holes, respectively.

Two submodels will be discussed:

I. The trapped electron is raised thermally from the ground state of the trap to an excited state *below* the conduction band, from which it may recombine with a trapped hole by a tunneling process.

II. It is raised directly to the conduction band, where it is free to move, and may finally recombine with a trapped hole.

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[7] See, for example, pp. 544–546 of N. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958).

[8] A. Halperin *et al.*, following paper [Phys. Rev. **117**, 416 (1960)].

[9] See, for example, reference 6.

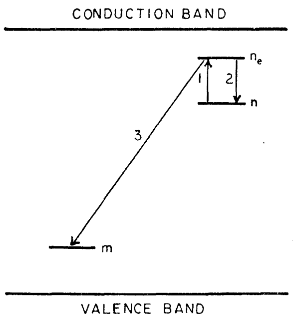

FIG. 2. Energy band model, showing the possible transitions between a single kind of electron traps, their excited states, and one kind of luminescence centers.

We start with submodel I (Fig. 2). In treating this case E will denote the activation energy from the electron trap to the excited state, and is assumed to be large compared to kT (see above). One of the two following transitions are possible for the excited electrons: (a) Return to the ground state of the same trap—transition 2. (b) Recombination with a trapped hole—transition 3.

The probability of retrapping in neighbouring traps of the same type is assumed to be very small, and is therefore neglected in the present model.

The kinetics is formulated in the following equations:

$$\begin{aligned} -dm/dt&=mn_eA_m,\\ -dn/dt&=\gamma n-sn_e,\\ dn_e/dt&=\gamma n-n_e(mA_m+s); \end{aligned} \tag{1.3}$$

where n_e is the concentration of electrons in the excited state; A_m—the probability for recombination; $\gamma=s\times\exp(-E/kT)$—the probability for thermal excitation (transition 1) with s as a frequency factor.

It follows from the principle of detailed balance that s is also the probability (per second) of transition 2.

We assume now that recombination or return to the ground state of the excited electrons is fast enough so that in the last of the Eqs. (1.3) it can be assumed $dn_e/dt=0$, when we obtain:

$$-\frac{dm}{dt}=\gamma n\frac{A_m m}{A_m m+s}. \tag{1.4}$$

In developing an expression for evaluating E we shall treat separately the cases in which the ratio of the initial concentrations of trapped electrons to trapped holes, $\rho=n_0/m_0$, is larger, equal or smaller than unity.

(2) Evaluation of E for the case $\rho>1$

For further simplification of (1.4) we introduce the following dimensionless expressions: $\mu=m/m_0$; $\chi=N/n_0$ ($\geqslant 1$) and the notation:

$$A=A_m;\quad B=s/m_0.$$

From (1.2) we obtain: $n=m_0\ (\mu+\rho-1)$, so that (1.4) takes the form:

$$-\frac{d\mu}{dt}=\frac{\mu(\mu+\rho-1)}{A\mu+B}A\gamma.$$

The thermoluminescence intensity will be proportional to $-dm/dt$ and in suitable units (taking in account also the luminescence yield) it can be written $I=-dm/dt$. In glow experiments carried out with constant warming rates, $dT=\beta dt$, and we obtain:

$$\frac{I}{\beta m_0}=-\frac{d\mu}{dT}=\frac{\mu(\mu+\rho-1)}{A\mu+B}\frac{A\gamma}{\beta}. \tag{2.1}$$

After Lushchik,[5] we introduce the parameter $\delta=T_2-T_g$ (see Fig. 3), T_2 being the temperature at half intensity on the falloff of the peak, and T_g the peak temperature. We obtain then

$$m_g=\int_{t_g}^{\infty}Idt=\frac{1}{\beta}\int_{T_g}^{\infty}IdT\approx\frac{1}{\beta}I_g\delta.$$

Here the subscript g refers to the parameters at the peak of the glow curve, the integration is carried out up to the exhaust of the glow under consideration, and the area under the glow curve to the right of the peak is approximated by a triangle, an approximation experimentally found to be accurate to better than 5%. It follows now that

$$\frac{\mu_g}{\delta}=-\left(\frac{d\mu}{dT}\right)_g=\frac{\mu_g(\mu_g+\rho-1)}{A\mu_g+B}\frac{A}{\beta}\gamma_g. \tag{2.2}$$

Taking the temperature derivative of (2.1), and equating it to zero at the maximum of the glow peak, we obtain with the aid of (2.2):

$$E=qkT_g^2/\delta, \tag{2.3}$$

where

$$q=\frac{\mu_g}{\mu_g+\rho-1}+\frac{B}{A\mu_g+B}.$$

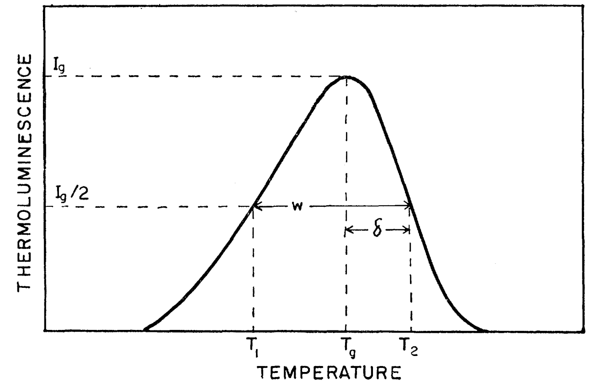

FIG. 3. An isolated glow peak showing the parameters: $\delta=T_2-T_g$; $w=T_2-T_1$, and μ_g, or $\nu_g=\delta/w$.

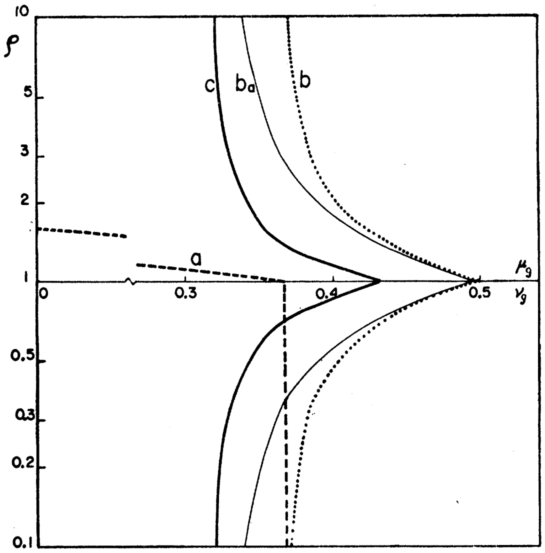

FIG. 4. The ratio of the initial concentrations of trapped electrons to trapped holes ($\rho=n_0/m_0$) as function of μ_g—upper part of the figure and of ν_g—lower part of the figure. Curves *a*, *b*, and *c* correspond to different types of kinetics (see text).

In this equation T_g and δ are readily obtained from the glow curve. The same applies to $\mu_g=m_g/m_0$, which is given by the ratio of the area to the right of the peak to the total area under the glow curve (see Fig. 3). Approximating the glow peak to be triangular we obtain: $\mu_g=\delta/w$, where w is the half-intensity width of the peak. Another expression relating the parameters ρ, A, and B to μ_g is obtained by integration of (2.1) which yields

$$\ln\left[\left(\frac{\mu+\rho-1}{\mu\rho}\right)^{A-B/(\rho-1)}\mu^A\right]=-\frac{As}{\beta}J, \qquad (2.4)$$

where

$$J=\int_{T_0}^{T}\exp(-E/k\vartheta)d\vartheta.$$

As E/kT is large compared to 1, J is given with good approximation[10] by

$$J\approx(kT^2/E)\exp(-E/kT)(1-\Delta);\quad \Delta=2kT/E.$$

Using this approximation and (2.3) in (2.2) yields

$$\ln\left[\left(\frac{\mu_g+\rho-1}{\mu_g\rho}\right)^{A-B/(\rho-1)}\mu_g{}^A\right]=-\frac{(A\mu_g+B)^2(1-\Delta)}{\mu_g(A\mu_g+2B)+(\rho-1)B}. \qquad (2.5)$$

Equations (2.3) and (2.5) will be applied now for the following specific cases:

(a) The dominant process is recombination (more rigorously we assume

$$B/(\rho-1)\ll A,\quad \text{and}\quad B\ll A\mu_g),$$

when by nelgecting second order terms of Δ we get

$$E=q_a kT_g{}^2/\delta\quad\text{with}\quad q_a=\mu_g/(\mu_g+\rho-1), \qquad (2.3a)$$

and

$$\rho=\frac{e}{e-1}(1-\mu_g)\left(1+\frac{\Delta}{e-1}\right)=\rho_0\left(1+\frac{\Delta}{e-1}\right). \qquad (2.5a)$$

Substitution of (2.5a) in the expression for q_a yields

$$q_a=(e-1)\frac{\mu_g}{1-\mu_g}\left(1-\frac{e}{e-1}\Delta\right)=q_{a0}\left(1-\frac{e}{e-1}\Delta\right). \qquad (2.6a)$$

ρ_0 and q_{a0} are plotted against μ_g in curves *a* of Figs. 4 and 5, respectively. Only values corresponding to $\rho<e/(e-1)$ are plotted. For larger values of ρ, μ_g (as well as δ and q) becomes negative, a matter which will be discussed below.

(b) Return to the ground state of the trap is the dominant process, or $B\gg A$ and $B\gg A(\rho-1)$, when we obtain

$$E=q_b kT_g{}^2/\delta;\quad q_b=1+\mu_g/(\mu_g+\rho-1), \qquad (2.3b)$$

$$\ln\left(\frac{\mu_g+\rho-1}{\mu_g\rho}\right)=\frac{(\rho-1)(1-\Delta)}{(2\mu_g+\rho-1)}, \qquad (2.5b)$$

which by substitution of q_b gives

$$(1-2/q_b)(1-\Delta)=\ln[\mu_g-(1-\mu_g)(1-q_b)]. \qquad (2.6b)$$

These transcendental equations were solved numerically. ρ_0 and q_{b0} as functions of μ_g [the subscript 0

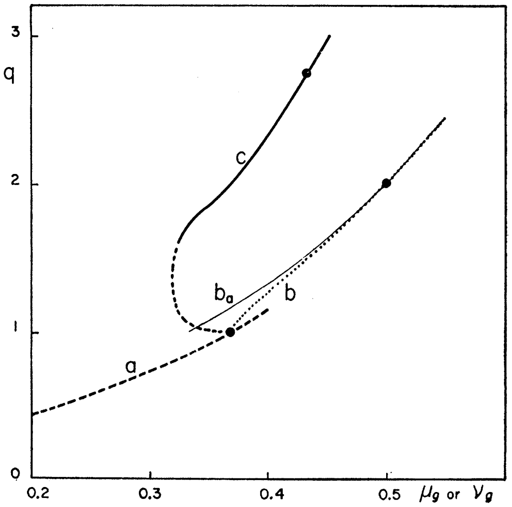

FIG. 5. The factor q [see Eq. (2.3)] as function of μ_g (and ν_g). Curves *a*, *b*, and *c* correspond to different types of kinetics. The black dots indicate the points on the curves at which the initial number of trapped electrons is equal to that of trapped holes ($\rho=1$).

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[10] See, for example, Bonfiglioli, Brovetto, and Cortese, Phys. Rev. **114**, 951, 956 (1959).

indicates the value for $\Delta=0$], are plotted in Figs. 4 and 5, respectively, (curves *b*). An approximate solution is obtained by using the expansion of the logarithmic function:

$$\ln x=2\left[\frac{x-1}{x+1}+\frac{1}{3}\left(\frac{x-1}{x+1}\right)^3+\cdots\right].$$

We take only the first term in the series when (2.5b) and (2.6b) are transformed into

$$\rho=(1-\mu_g)\left[1+\frac{\mu_g}{2\mu_g(1-2\Delta)-(1-\mu_g)}\right]. \qquad (2.7b)$$

$$q_b=\frac{2\mu_g}{1-\mu_g}(1-2\Delta)=q_{b0}(1-2\Delta). \qquad (2.8b)$$

The functions ρ_0 and q_{b0} obtained by this approximation are given by curves b_a in Figs. 4 and 5. It is of interest to point out that Eq. (1.4) takes now the form: $-dm/dt=A_m mn\exp(-E/kT)$, which is just the equation obtained by Hill and Schwed,[6] and by Bonfiglioli *et al.*[10]

(3) Evaluation of E for $\rho=1$

This case is simple and readily obtained. It is treated separately because on integration of (2.1) the case $\rho=1$ turns to be singular (see 2.4). In addition this is the case dealt with by other investigators, and it seems worthwhile to compare our results to others.

Equation (2.3) remains valid but is now reduced to

$$E=q\frac{kT_g^2}{\delta},\quad \text{with}\quad q=1+\frac{B}{A\mu_g+B}; \qquad (3.1)$$

Integration of (2.1) yields for $\rho=1$:

$$A\ln\mu-B\frac{1-\mu}{\mu}=-\frac{AJ}{\beta}, \qquad (3.2)$$

and similar treatment to that in paragraph (2) results in

$$A\ln\mu_g-B\frac{1-\mu_g}{\mu_g}=-\frac{(A\mu_g+B)^2}{(A\mu_g+2B)\mu_g}(1-\Delta). \qquad (3.3)$$

We shall now follow the specific cases as before:

(a) Recombination dominant, when we get

$$E=kT_g^2/\delta, \qquad (3.1a)$$

$$\mu_g=e^{-1}(1+\Delta). \qquad (3.3a)$$

This corresponds to monomolecular type of decay investigated by Randall and Wilkins.[2] Eq. (3.1a) is essentially the same as that developed by Urbach,[11] and was first given in this form by Lushchik,[5] while Eq. (3.3a) has already been developed by Braner.[12]

(b) Return to the ground state of the trap is dominant, when we have

$$E=2kT_g^2/\delta, \qquad (3.1b)$$

$$\mu_g=\tfrac{1}{2}(1+\Delta). \qquad (3.3b)$$

(4) Evaluation of E for $\rho<1$

As long as the number of electrons in the traps is larger or equal to that of the empty luminescence centers ($n_0\geqslant m_0$, or $\rho\geqslant 1$), the luminescence will fall to zero with m. It is somewhat different when $m_0>n_0$, ($\rho<1$). In this case the luminescence will fall to zero with n, and it is convenient to treat this case separately.

From (1.3) we have (for $dn_e/dt=0$): $dm/dt=dn/dt$. Using this in (1.4), and introducing the notations:

$$\nu=\frac{n}{n_0};\quad \varphi=\frac{1}{\rho}=\frac{m_0}{n_0};\quad A=A_m;\quad \bar{B}=\frac{s}{n_0}+A(\varphi-1),$$

we get

$$\frac{I}{\beta n_0}=-\frac{d\nu}{dT}=\frac{\nu(\nu+\varphi-1)}{A\nu+\bar{B}}\frac{\gamma A}{\beta}. \qquad (4.1)$$

This is formally the same as Eq. (2.1) and may be developed in a similar way.

The parameter δ is now obtained from: $n_g=(I_g/\beta)\delta$ and instead of (2.3), (2.5) we have now

$$E=qkT_g^2/\delta,\quad \text{with}\quad q=\frac{\nu_g}{\nu_g+\varphi-1}+\frac{\bar{B}}{A\nu_g+\bar{B}}, \qquad (4.3)$$

$$\ln\left[\left(\frac{\nu_g+\varphi-1}{\nu_g\varphi}\right)^y\nu_g{}^A\right]=-\frac{(A\nu_g+\bar{B})^2(1-\Delta)}{\nu_g(A\nu_g+2\bar{B})+(\varphi-1)\bar{B}}, \qquad (4.5)$$

where $y=A-\bar{B}/(\varphi-1)$.

Specific cases:

(a) Recombination dominant, or $s/n_0\ll A(\varphi-1)$ when we have

$$q_a=1, \qquad (4.3a)$$

$$\nu_g=e^{-1}(1+\Delta), \qquad (4.5a)$$

which is valid for all values of $\varphi>1$ ($\rho<1$). This result is different from that obtained under (a) in paragraph 2, and will be discussed in the conclusions below.

(b) Return to the ground state of the trap is dominant. We get here the same results as in paragraph 2, but with the parameters ν_g and φ replacing μ_g and ρ, respectively. The ρ (or $1/\varphi$) values are plotted in the lower part of Fig. 4. The $q(\nu_g)$ values coincide with the $q(\mu_g)$ values except for curve a (see Fig. 5).

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[11] F. Urbach, *Preparation and Characteristics of Solid Luminescent Materials, Cornell Symposium, 1946* (John Wiley and Sons, Inc., New York, 1948), p. 126.

[12] A. A. Braner, thesis, The Hebrew University, Jerusalem, 1958 (unpublished).

(5) Submodel II. Excitation into the Conduction Band

Once the electron is excited into the conduction band, the trap it left can no longer be distinguished from others of the same type. The kinetics will now be given by the following equations which replace (1.3):

$$\begin{aligned} -dm/dt&=mn_cA_m,\\ -dn/dt&=\gamma n-n_c(N-n)A_n,\\ dn_c/dt&=\gamma n=n_c[mA_m+(N-n)A_n], \end{aligned} \tag{5.1}$$

where n_c is the concentration of electrons in the conduction band, A_n—the probability for retrapping, while other notations remain unchanged.

Equation (1.4) now takes the form

$$-\frac{dm}{dt}=\gamma n\frac{A_mm}{A_mm+A_n(N-n)}. \tag{5.2}$$

In the present model we have to take in account that the effective density of states in the conduction band is temperature dependent. This results in the relation[13]: $s/\sigma_n=HT^2$, where $\sigma_n=A_n/u$ is the cross section for retrapping, and u—the mean velocity of an electron in the conduction band. H depends on the details of the band structure, and includes the effective mass of the electron as a factor.

We shall again treat separately the cases:

$$\rho>1,\quad \rho=1;\quad \rho<1.$$

(6) Evaluation of E for $\zeta>1$.

We introduce the notation

$$A^*=A_m-A_n;\quad B^*=A_n(\rho\chi-\rho+1),$$

with ρ and χ as defined above (paragraph 1).

Following exactly the procedure given in paragraph 2, we obtain now

$$E=q\frac{kT_g^2}{\delta}(1-\Delta);\quad q=\frac{\mu_g}{\mu_g+\rho-1}+\frac{B^*}{\mu_gA^*+B^*}, \tag{6.1}$$

instead of (2.3), while (2.4) is now replaced by

$$\ln\left[\left(\frac{\mu+\rho-1}{\mu\rho}\right)^{A^*-B^*/(\rho-1)}\mu^{A^*}\right]=-\frac{A_m\sigma_nH}{\beta}J^*, \tag{6.2}$$

where

$$J^*=\int_{T_0}^{T}\theta^2\exp(-E/k\theta)d\theta\approx\frac{kT^4}{E}\exp(-E/kT)(1-2\Delta).$$

Using this approximation, and following the procedure described in paragraph 2, yields

$$\ln\left[\left(\frac{\mu_g+\rho-1}{\mu_g\rho}\right)^{A^*-B^*/(\rho-1)}\mu_g^{A^*}\right] =-\frac{(A^*\mu_g+B^*)^2(1-\Delta)}{\mu_g(A^*\mu_g+2B^*)+(\rho-1)B^*}. \tag{6.3}$$

Equations (6.1) and (6.3) are formally the same as (2.3) and (2.5), respectively, except for the correction factor $(1-\Delta)$ in (6.1), which evidently results from the T^2 dependence of s/σ_n. We shall use again these equations for specific cases:

(a) Recombination dominant, or A^* sufficiently large compared to B^* (see paragraph 2), when we have

$$E=q_a(kT_g^2/\delta)(1-\Delta), \tag{6.1a}$$

with q_a exactly the same as given in (2.6a). Similarly ρ is given again by (2.5a).

(b) Equal probabilities for recombination and retrapping, or $A_m=A_n$ $(A^*=0)$. Eqs. (6.1) and (6.3) are reduced to (2.3b) [except for the factor $1-\Delta$] and (2.5b), respectively.

(c) Retrapping dominant, or $A_n\gg A_m$, when Eqs. (6.1) and (6.3) are transformed into

$$E=q_c\frac{kT_g^2}{\delta}(1-\Delta);$$

$$\text{with}\quad q_c=\frac{\mu_g}{\mu_g+\rho-1}+\frac{1}{1-\mu_g/(\rho\chi-\rho+1)} \tag{6.1c}$$

and

$$\ln\left[\left(\frac{\mu_g+\rho-1}{\mu_g\rho}\right)^{\chi\rho/(\rho-1)}\mu_g\right] =\frac{[\chi\rho-(\mu_g+\rho-1)]^2(1-\Delta)}{(\chi\rho-\rho+1)(2\mu_g+\rho-1)-\mu_g^2}. \tag{6.3c}$$

The equations still contain the parameter χ. For weak excitations when only a small percentage of the traps are filled we have $\chi=N/n_0\gg1$, in which case Eqs. (6.1c) and (6.3c) take again the form of (2.3b) [except for the factor $(1-\Delta)$] and (2.5b), respectively. It can easily be shown that in the case $\chi\gg1$ the same equations will also hold for all values of $A_n\geqslant A_m$.

For the other extremity, $\chi=1$, Eqs. (6.1c) and (6.3c) were calculated numerically, and the corresponding functions ρ_0 and q_{c0} are plotted against μ_g in curves c of Figs. 4 and 5, respectively.

It should be noted that the curves for $\chi=2$ are much closer to those for $\chi=\infty$ (curves b) than to those for $\chi=1$.

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[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), p. 108.

(7) Evaluation of E for $\varrho=1$

This is carried out exactly as in paragraph 3, we get now

$$E=q(kT_g^2/\delta)(1-\Delta),\quad \text{with}\quad q=1+\frac{B^*}{A^*\mu_g+B^*},\tag{7.1}$$

and

$$A^*\ln\mu_g-B^*\frac{1-\mu_g}{\mu_g}=-\frac{(A^*\mu_g+B^*)^2}{(A^*\mu_g+2B^*)\mu_g}(1-\Delta).\tag{7.2}$$

For the specific cases we now have:

(a) Recombination dominant, when we get

$$E=(kT_g^2/\delta)(1-\Delta),\tag{7.1a}$$

$$\mu_g=e^{-1}(1+\Delta).\tag{7.2a}$$

(b) $A^*=0$ yields

$$E=2(kT_g^2/\delta)(1-\Delta),\tag{7.1b}$$

$$\mu_g=0.5(1+\Delta).\tag{7.2b}$$

(c) Retrapping dominant. Here for $\chi\gg 1$ we get the same as in (b). The value of E has already been given for this case in the same form by Lushchik[5] (without the correction factor), and the symmetry equation, $\mu_g=0.5$, by Braner.[12] For $\chi=1$ we obtain

$$E=q_c(kT_g^2/\delta)(1-\Delta),\quad \text{with}\quad q_c=1+1/(1-\mu_g),\tag{7.1c}$$

and (for $\Delta=0$)

$$\ln\mu_g=(\mu_g-1)/\mu_g(2-\mu_g),\tag{7.2c}$$

which on calculation (for $\Delta=0$) yields $\mu_g=0.432$, and $q_c=2.76$.

(8) Evaluation of E for $\varrho<1$

We treat this case in a similar way as in paragraph 4. For the specific cases we obtain here essentially the same results as in paragraph 6 except that for the case in which recombination is dominant[14] we have

$$E=(kT_g^2/\delta)(1-\Delta),\tag{8.1a}$$

$$\nu_g=e^{-1}(1+\Delta),\tag{8.2a}$$

which is valid for all values of $\rho<1$.

(9) Conclusions

The treatment of glow curves as proposed in the present work resulted in a simple formula for the evaluation of the thermal activation energies of trapping centers in crystals:

$$E=(q/\delta)kT_g^2.$$

In this formula T_g and δ are obtained directly from the glow curve. The determination of q is somewhat more complicated, nevertheless, it has been calculated for a variety of specific cases, for which q is readily obtained from the symmetry of the glow peak (see Fig. 5). Our model seems to be more general than other treatments reported in literature. For example, our results for $\rho=1$ (paragraphs 3 and 7) include practically all the cases dealt with previously.

Another interesting result in the present work is that the symmetry of the glow peak (given by μ_g or ν_g) was found to be characteristic of the kinetics. Qualitatively this was already known[5,7] for the case $\rho=1$. In the present work it is given quantitatively, and even more, the symmetry is shown to depend on ρ. Monomolecular type of relaxation is indicated by[15] $\mu_g\leqslant e^{-1}$, whereas $\mu_g\geqslant e^{-1}$ corresponds to bimolecular kinetics. There might be some doubt near the common value ($\mu_g=e^{-1}$), in which case the kinetics might be determined from the ρ value which for $\mu_g=e^{-1}$ should be unity for monomolecular kinetics, and infinity for the bimolecular case. Estimation of the value of ρ might in such cases be obtained from the general features of the glow curves, or from information regarding the relative concentrations of traps which might be obtained from the coloration of the crystals or other effects.

The theory assumes a well isolated glow peak. Fortunately this requirement is not critical, which is an important advantage of the method. It is easy to eliminate any interfering glow appearing at lower temperatures by merely keeping the crystal for some time at a temperature somewhat below that of the peak to be measured. The difficulty is to eliminate interfering peaks at the falloff of the peak being measured. Fortunately the error introduced in the calculated value of E by a peak appearing as a shoulder towards higher temperatures is very small. It comes out (as can easily be calculated) that the effects due to the changes in q and δ compensate each other, so that the calculated value of E remains almost unchanged.

We shall now discuss some of the results in more detail. As stated above, a constant value, $\mu_g=e^{-1}$, was obtained for $\rho\leqslant 1$ in the monomolecular case treated under (a) in sections 3, 4, 7, and 8. For $\rho>1$, μ_g was found to decrease, and reaches the value $\mu_g=0$ (and $\delta=q=0$), when $\rho=e/(e-1)\approx 1.58$. For larger values ($\rho>1.58$), μ_g, δ, and q become negative. To explain this we recall that we assumed for this case a very large probability for recombination ($A_m\approx\infty$). This implies that the thermoluminescence should in this case be governed only by the rate at which electrons are released from the traps. This will indeed be the only factor in determining the shape of the glow peak for $\rho\leqslant 1$. For $\rho>1$ the shape should again be given by the rate of release of electrons as long as there are empty centers. The thermoluminescence should, however, stop at the moment at which the centers are completely full. The distribution of electrons between the trapping level

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[14] More rigorously we assume A_m to be large enough so that $A_n\ll A_m$; and $A_n\ll A_m(\varphi-1)$.

[15] Unless otherwise stated, all the values given in this discussion are for $\Delta=0$.

and the excited state (or the conduction band) will then be kept at thermodynamical equilibrium up to a temperature at which recombination in some other centers will become appreciable.

The expected effect of a shortage of luminescence centers on the glow curve is demonstrated in Fig. 6 for a few typical values of ρ. Figure 6 (a) corresponds to the case in which there are empty centers sufficient for all the trapped electrons ($\rho \leqslant 1$), so that there is no interruption in the glow. Figure 6(b) corresponds to $1<\rho<e/(e-1)$, in which case the centers are exhausted somewhere on the falloff of the virtual glow peak determined by the trapped electrons. In this case μ_g, δ, and q are still positive. Figure 6(c) shows the case in which the glow stops just at the maximum [$\rho=e/(e-1)$; μ_g, δ, and q just become zero]. Finally, Fig. 6(d) corresponds to a still larger value of ρ so that the glow stops before reaching the maximum. In this case μ_g and δ should be taken negative.

In practice the probability for recombination is of course finite. Nevertheless, it is enough to have the rate of recombination much faster compared to that of release from the traps. The above given description should not change than, except for some curvature in the still steep falloff of the glow peak. Experimentally values of $\mu_g<e^{-1}$ are very rare, which implies that monomolecular processes with $\rho>1$ occur rarely, if at all. The explanation might be that very large probabilities for recombination are likely only when the traps and centers are very closely related. Such a close relation might be expected in monomolecular reactions in the rigorous meaning of the term, when the number of traps should be equal to that of centers ($\rho=1$).

We turn now to processes of bimolecular character. The formulas (2.3b) and (2.5b) and the corresponding curves in Figs. 4 and 5 hold for the specific case (b) as well as for (c) when $\chi \gg 1$. Even more, they hold for all values of $A_m<A_n$ when $\chi \gg 1$. All these specific cases make the formulas quite general for the bimolecular type of process. It should be noted that experimentally χ is mostly larger than unity. Curves *c* in Figs. 4 and 5 represent therefore a limit which is practically never reached. In the case that 50% of the traps are filled by the excitation ($\chi=2$) the calculated values of q (μ_g) are much closer to curve *b* (Fig. 5) than to curve *c*. Even so, there might be a small effect of filling the traps which will cause some increase in the q values.

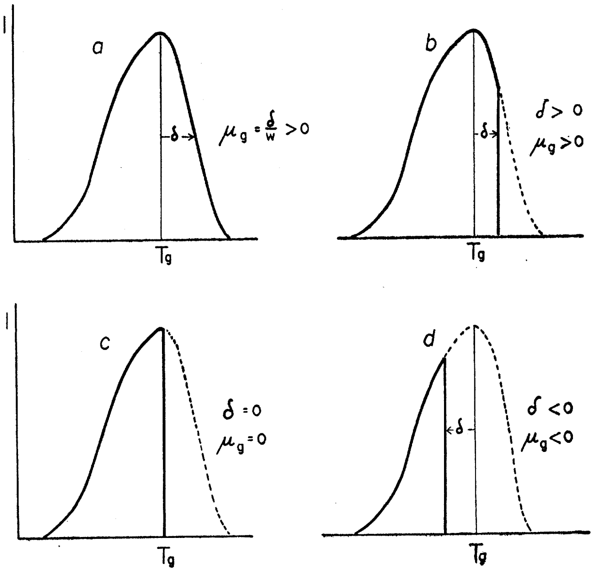

FIG. 6. The theoretical effect of ρ on the shape of the glow peak in case of monomolecular kinetics. (a) $\rho \leq 1$; (b) $1<\rho<e/(e-1)$; (c) $\rho=e/(e-1)$; and (d) $\rho>e/(e-1)$.

As already mentioned in this discussion, all values of μ_g between e^{-1} and 0.5 can be obtained for bimolecular processes. Values of $\mu_g>0.5$ can, however, be obtained and were already observed experimentally in the glow of ZnS:Cu:Cl crystals.[16] The reason for it is to be found in the correction factor Δ. Taking this into account we get as the limiting value $\mu_g=0.5(1+\Delta)$ [see Eq. (3.3b)].

The equation for E remains essentially the same for both the submodels treated in the present work. The main differences are in the correction factor $1-\Delta$ which enters in the equation obtained for submodel II, and in the effect of filling up of the traps which in case of model II should be accompanied by an increase in the q values as stated above.

It has already been pointed out that just the same equations will fit the case in which trapped holes are released and recombine with trapped electrons. The identification of the sign of the released carriers might be established by complementary experiments; e.g., electrical glow curves, thermal bleaching of color centers, etc.

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[16] H. Arbell and A. Halperin Phys. Rev. 117, 45 (1960).