where v is the velocity of the incident proton, p is the momentum of the π-meson, M and m are the masses of nucleon and π-meson respectively, W is the kinetic energy of two nucleons in the center of mass system. To derive this formula the relation between energy and momentum for the π-meson was taken as $\mathcal{E}_\pi = \sqrt{p^2 + m^2}$, and for the nucleon as $\mathcal{E}_N - M = p_n^2/2M$. The choice of the last relation is justified by the fact that the maximum nucleon energy in the region considered does not exceed 75 mev.

In the energy region studied in this experiment the dependence shown in (5) can be approximated by a power law of the form: $\sigma_{pp}^{\pi^\circ} = \text{const}\ \eta_{\max}^{3.6}$. As is known, in the region $\eta \ll 1$, the statistical factor is proportional to $\eta_{\max}^4$.

Through comparison of this calculated dependence (power equal to 3.6) with the given experiments (power of approximately 4) it can be concluded that the energy dependence of the transition matrix element for (1) is small.

In conclusion the author expresses his gratitude to M. G. Meshcheriakov, L. I. Lapidus and S. M. Bilen'kii for discussion of experimental results, and also to A. S. Kuznetsov who took part in the construction of the electronic apparatus.

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The Possibility of a Two-Step Excitation Mechanism in Sulfide Phosphors

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Experimental data on the kinetics of luminescence in strongly quenched phosphors indicate that in spite of widely held ideas to the contrary, the bimolecular theory is not applicable. An interpretation of the experiments in terms of a two-step phosphorescence excitation mechanism is presented. It is shown that a two-step excitation process is responsible for photoconductivity in CdS (Cu) having high copper concentrations. Moreover luminescence in this material exhibits properties typical of strong quenching.

1. The kinetics of "fast" luminescence in sulfide phosphors (for example, ZnS, CdS, etc.) has been studied in a number of investigations[1] in which the tau-meter method[2] was employed. At temperatures far below the temperature at which quenching occurs, the growth and decay curves are approximated by functions which do not satisfy any simple kinetic equations. The possibility of interpreting these relaxation curves or of drawing even qualitative conclusions concerning processes in these phosphors is very remote. The expression which approximates the decay curve

$$I \sim (1 + at)^{-\alpha}. \qquad (1)$$

(where, for ZnS-Cu at room temperature, α has a value of the order of 0.7) cannot be correct *a priori* if the time is allowed to increase without limit because of the infinity which appears in the stored light-sum. Moreover, Eq. (1) is not valid at the very beginning of the decay curve (for example in the region of 100-90 per cent of the steady-state luminescence); using a method developed by the author[3] in which the relaxation curves are electrically differentiated, it has been shown that the curve in (1) is affected by the intensity of excitation E in a manner which is given by the expres-

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[1] V. A. Arkhangel'skaia, A. M. Bonch-Bruevich, N. A. Tolstoi and P. P. Feofilov, Dokl. Akad. Nauk SSSR 64, 187, (1949); J. Exptl. Theoret. Phys. U.S.S.R. 21, 290 (1951). D. B. Gurevich, N. A. Tolstoi and P. P. Feofilov, Dokl. Akad. Nauk SSSR 71, 29 (1950). V. A. Arkhangel'skaia, A. M. Bonch-Bruevich and N. A. Tolstoi, Izv. Akad. Nauk SSSR Ser. Fiz. 15, 695 (1951).

[2] N. A. Tolstoi and P. P. Feofilov, Usp. Fiz. Nauk 41, 44, (1950).

[3] N. A. Tolstoi, Izv. Akad. Nauk SSSR Ser. Fiz. 15, 712 (1951).

sion[1] $a\sim E^p$ (where for ZnS-Cu at $t=20°$C, d is 0.6-0.7) and that the dependence on E is very much weaker in the initial relaxation stages. In the limit (of increasing E) the initial slope of the decay curve, in general, tends toward a constant value. Hence, a single approximation cannot be used to describe the entire decay curve. From the point of view of methodology, the matter is further complicated by the fact that in the phosphors in question there occur slow processes which do not have time to reach completion when undergoing excitation by rectangular light pulses. This situation introduces additional difficulties in the interpretation of the relaxation curves.

2. We shall use an approach which offers the possibility of great simplification in the interpretation of the relaxation curves[4]. Consider the general symbolic kinetic equation

$$dn/dt = -I - T + \gamma E, \tag{2}$$

where n is the number of excited centers, I is the number of electrons which return to the initial state per second with radiation, and T is the same quantity without radiation, and γE is the number of electrons excited per second by light with an intensity E. For brevity we will call I the luminescence, T the quenching, and E the excitation.

Suppose the phosphor to be in a state of strong concentration or temperature quenching. Then, obviously, $I \ll T$ and we can write as a first approximation

$$dn/dt = -T + \gamma E, \tag{3}$$

i.e., the net number of electrons depends only on the quenching and the excitation. In general it will be assumed that

$$T = \beta n \tag{4}$$

(physically, Eq. (4) is connected with the fact that the interaction between a finite number of excited electrons or centers and the virtually infinite number of thermal fluctuations is a process of the first type or "pseudo-monomolecular" process). Then

$$dn/dt = -\beta n + \gamma E, \tag{5}$$

whence

$$n_\infty = \gamma E/\beta \qquad \text{(steady-state);} \tag{6}$$

$$n = n_\infty e^{-\beta t} \qquad \text{(decay);} \tag{7}$$

$$n = n_\infty (1 - e^{-\beta t}) \qquad \text{(growth).} \tag{8}$$

Thus the number of excited electrons n is given by the simplest kind of exponential kinetics. The form of the relaxation curves does not depend on E and $n_\infty \sim E$. Formulas (6)-(8) are called the "quenching kinetics" formulas.

We now consider the second approximation and will assume that $I \neq 0$ although $I \ll T$. Then, whatever the algebraic dependence of $I(n)$, the kinetics of luminescence will be algebraically connected with the exponential quenching kinetics which are already known. For example, if the luminescence is monomolecular or pseudo-monomolecular (recombination) in character, i.e., $I = \alpha n$, then

$$I_\infty = \alpha\gamma E/\beta, \tag{9}$$

$$I = I_\infty e^{-\beta t} \qquad \text{(decay);} \tag{10}$$

$$I = I_\infty (1 - e^{-\beta t}) \qquad \text{(growth);} \tag{11}$$

while if the luminescence is bimolecular, i.e., $I = \alpha n^2$, then

$$I_\infty = \alpha\gamma^2 E^2/\beta^2, \tag{12}$$

$$I = I_\infty e^{-2\beta t} \qquad \text{(decay);} \tag{13}$$

$$I = I_\infty (1 - e^{-\beta t})^2 \qquad \text{(growth).} \tag{14}$$

Hence, under conditions of strong quenching, the luminescence mechanism emerges, so to speak, in "bare" form. It has been assumed that I is a function only of the number n and does not depend, for example, on the distribution of excited electrons over trap levels at different depths (in such a case I, in general, would not be determined uniquely by the quantity n). Generally speaking, I is not a unique function of n, but this assumption is justified under conditions of strong quenching, especially when the quenching is due to high temperatures. The exponential behavior of the decay of luminescence or the falling-off of photoconductivity appears, in this case, as a criterion of the validity of an assumed dependence of the type $I = \alpha n^m$ (m= const).

Finally we may note that when there is strong quenching the methodological difficulties connected with the existence of slow relaxation processes are avoided.

3. We now recapitulate certain experimental data relating to relaxation in strongly quenched phosphors.

a) The steady-state luminescence shows superlinearity as a function of the intensity of the exciting light E. In a number of cases the function

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[4] N. A. Tolstoi, Dokl. Akad. Nauk SSSR **95**, 249 (1954).

$I_\infty(E)$ tends toward $I_\infty \sim E^2$.

b) The decay curve is found to be exponential or very close to exponential; τ is independent of E but falls off with increasing temperature.

c) The growth curve starts with a parabolic dependence ($I \sim t^2$) and then after inflection goes considerably slower than the decay curve. The form of the curve depends markedly on E. Schematic curves of growth and decay are shown in Fig. 1.

d) The area above the growth curve L_g (Fig. 1) is much greater than the area under the decay curve L_d. The ratio L_g/L_d, which we call s below, decreases with an increase in E; this however may be seen from *b* and *c*. A typical ratio $s=10$*.

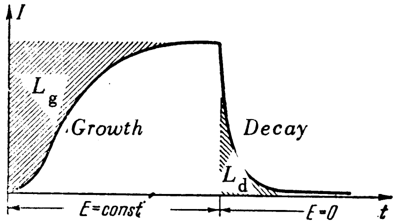

FIG. 1.

e) The maximum slope of the growth curve (at the inflection point) I'_{max} is much smaller than the maximum slope of the decay curve (at the beginning of the latter).**

4. We now examine the extent to which the considerations developed in Sec. 2 are useful in explaining the experimental data given in Sec. 3. At first glance it would seem that the formulas given in (12)-(14) (bimolecular luminescence) are in agreement with the experimental data (the quadratic dependence of $I_\infty(E)$, the exponential behavior of decay and the parabolic nature and the inflection of the growth curve). However, the experimental results contradict the theory in one essential point: according to (14) the form of the growth curve is independent of E; actually, however, such a dependence exists. The only approach which reconciles theory and experiment lies in assuming a strong dependence of the quenching probability β on E [since the form of the growth curve depends only on the time coefficient in (14)]. Physically this means taking cognizance of the strong quenching property of the exciting light (QPEL). When this is taken into account the quenching probability appears in the form

$$\beta = \beta_T + \beta_0 E, \tag{15}$$

where β_T is the probability for purely thermal quenching, and $\beta_0 E$ is the optical quenching probability. Then we should write in place of (12)-(14)

$$I_\infty = \alpha\gamma^2 E^2 (\beta_T + \beta_0 E)^{-2}, \tag{16}$$

$$I = I_\infty \exp\{-2\beta_T t\} \qquad \text{(decay)}; \tag{17}$$

$$I = I_\infty (1 - \exp\{(\beta_T + \beta_0 E)t\})^2 \quad \text{(growth)}, \tag{18}$$

The assumption of (QPEL) appears to be unavoidable if one starts from the considerations developed in Sec. 2 and the experimental dependence of the growth on E. We shall find, however, that even the modified equations are found to be in quantitative disagreement with the experiments.

Having calculated L_g and L_d (Fig. 1) starting from formulas (13) and (14), we obtain $L_d = I_\infty/2\beta$ and $L_g = 3I_\infty/2B$ so that*** $s=3$. If, however, we use the modified formulas (17) and (18), i.e., if (QPEL) is taken into account, then

$$s = 3\beta_T/(\beta_T + \beta_0 E) \leqslant 3. \tag{19}$$

The ratio s falls off with an increase in E and for $\beta_0 E > 2\beta_T$ it becomes less than unity. Thus the ratio s can never have a value greater than 3; with sufficient intensity of the exciting light, moreover, (QPEL) can bring about a situation in which the area above the growth curve becomes smaller than the area under the decay curve.+ The experiments, as we have seen, yield $s > 3$; for large E, $s \approx 10$ is observed and with a reduction in E this ratio grows still larger. The disagreement between experiment and Eq. (19) indicates that the growth curve (18) cannot be brought into quantitative agreement with experiment for any value of the exponent $\beta = \beta_T + \beta_0 E$ in the exponential term. Actually $\beta > \beta_T$, but for agreement with experiment we require at least that $\beta < \beta_T$, i.e., that $\beta_0 E > 0$. If one

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* This ratio can be determined by an objective method for measuring L_g and L_d, (the "L-meter") developed by the author in conjunction with I. A. Litvinenko.[5]

** This can be determined by electrical differentiation.[3]

[5] N. A. Tolstoi and I. A. Litvenenko, J. Exptl. Theoret. Phys. (U.S.S.R.) 29, 507 (1955).

*** For a nonquenched "pure bimolecular" phosphor ($dn/dt = -\alpha n^2 + \gamma E$) s may be taken equal to unity.

+It has been shown in a paper by Tolstoi and Shatilov[6] that the limit on the values of s, $s \leq 3$, is valid under more general assumptions as to the recombination mechanism.

[6] N. A. Tolstoi and A. V. Shatilov, J. Exptl. Theoret. Phys. U.S.S.R. 30, 109 (1956).

allows the possibility, even formally, that $\beta_0 E < 0$ (negative QPEL) then one is quickly brought into another contradiction with experiment: with an increase of the exciting light intensity a slower growth curve is obtained and not a faster one as is actually observed. Furthermore, the dependence of the steady-state luminescence on the intensity of excitation is found to be greater than quadratic [cf Eq. (16)] . Although such a dependence has been mentioned in the literature, it is not appropriate for those phosphors and those experimental conditions which are under discussion here.

Thus we are confronted by a serious difficulty: not making any assumptions of an arbitrary nature as to the mechanism of luminescence and quenching we obtain theoretical curves which are found to be in strong disagreement with experiment. We may point out the fact that the growth curve is the "corner stone" of our analysis. It is obvious that in general the growth kinetics will be more sensitive to the luminescence mechanism, but strangely enough only a small amount of work in the literature is devoted to a study of growth phenomena.

To show the necessity for the assumptions $T=\beta n$ and $I=\alpha n^2$ which were made in Sec. 2 we point out that violating the first of these would lead to a non-exponential decay, i.e., to a stronger disagreement with experiment (for example $T=\beta n^2$ would indicate a hyperbolic decay). Violation of the requirement $I=\alpha n^2$ would mean a nonparabolic dependence at the beginning of growth, i.e., it would also contradict experiment (for example $I=\alpha n$ would indicate a linear dependence at the beginning of the growth curve). Departure from the idea of a single-valued dependence of $I(n)$ would also lead to a non-exponential decay and could lead to a dependence of the form of the decay curve on E. The notion that the indicated assumptions are in fact violated but are "compensated" in such a way as to lead to the required results is so artificial as not to warrant discussion.

The only alternative which remains is to investigate the admissibility of one tacitly made assumption which has not been mentioned up to this point and which is usually considered indisputable: the number of electrons excited by the light is proportional to its intensity (γE). This relation can be violated in two ways.

1) Absorption of light causes an impoverishment of the phosphor due to electrons which are not yet excited, i.e., γ depends on E, becoming smaller with an increase in the latter. Obviously this effect would be of most importance in non-quenched phosphors, which store large light-sums, where it should tend to make the functional dependence of $I(n)$ less than linear. Aside from the fact that this is not found in our case, (thus strengthening the idea that it does not occur in quenched phosphors), such an assumption would only worsen the difficulty since, as is easily shown, it can lead only to a lower value for s.

2) The excitation of electrons in the phosphor is not a one-step process. In the first stage the excited electrons are trapped and form the "first light-sum". A second excitation of these electrons forces them into other states in which they constitute the "second light-sum" which can be dissipated both by radiative and nonradiative transitions. Although this picture of the phosphor mechanism may seem strange, as we shall show below, it favors many experimental facts associated with photoconductivity.[8] The theory based on these ideas is found to be in good agreement with the experimental material we have presented above.

5. We begin with a consideration of a simple formal scheme for a two-step phosphor mechanism (Fig. 2). Let n_0 be the number of electrons in the unexcited state, n_1 the number at an "intermediate" trapping level from which (in the particular case under consideration) radiative transitions cannot be performed (n_1 is the "first light-sum"), and n_2 the number of electrons in the "excited" levels from which radiative transitions to the "ground" states are possible (n_2 is the "second light-sum"). We shall take n_0 to be infinite. Then the kinetic equations, under the assumption that *all transitions in the scheme are of pseudo-momomolecular nature*, take on the form

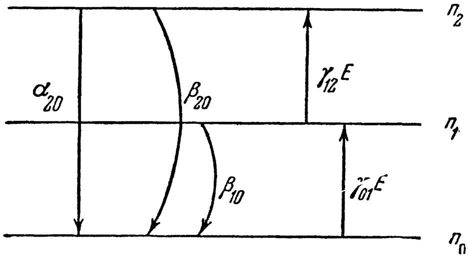

FIG. 2.

$$dn_2/dt = -(\alpha_{20} + \beta_{20})n_2 + \gamma_{12}En_1, \qquad (20)$$
$$dn_1/dt = -(\beta_{10} + \gamma_{12}E)n_1 + \gamma_{01}En_0.$$

The quantities β_{20}, β_{10} express the probabilities for the respective nonradiative transitions,

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[8] V. E. Lashkarev and G. A. Fedorus, Izv. Akad. Nauk SSSR Ser. Fiz. **16**, 81 (1952).

α_{20} is the probability for a radiative transition, $\gamma_{12}E$ is the probability for secondary excitation, and $\gamma_{01}En_0$ is the probability for primary excitation. Then in the simplified theory, the solution of equations (20) will have for the first light-sum the form

$$n_{1\infty} = \gamma_{01}En_0/(\beta_{10} + \gamma_{12}E) \quad (21)$$

(stationary light sum)

$$n_1 = n_{1\infty}e^{-\beta_{10}t} \text{ (decay)} \quad (22)$$

$$n_1 = n_{1\infty}(1 - e^{-(\beta_{10}+\gamma_{12}E)t}) \text{ (growth)} \quad (23)$$

and for the second light-sum

$$n_{2\infty} = \gamma_{01}\gamma_{12}E^2n_0/AB \quad (24)$$

(stationary light sum)

$$n_2 = n_{2\infty}e^{-At} \text{ (decay)} \quad (25)$$

$$n_2 = n_{2\infty}\left(1 - \frac{A}{A-B}e^{-Bt} + \frac{B}{A-B}e^{-At}\right) \text{ (growth)} \quad (26)$$

where A and B indicate:

$$A = \alpha_{20} + \beta_{20}, \quad B = \beta_{10} + \gamma_{12}E. \quad (27)$$

If, in place of the quantities A and B, we introduce the quantities $\tau_A = 1/A$ and $\tau_B = 1/B$ and make use of Eq. (24), then the expressions for decay and growth of luminescence take on the following forms:

$$n_2 = n_{2\infty}e^{-t/\tau_A}, \quad (25')$$

$$n_2 = \frac{n_{2\infty}}{\tau_B - \tau_A}[\tau_B(1 - e^{-t/\tau_B}) - \tau_A(1 - e^{-t/\tau_A})]. \quad (26')$$

We now consider the extent to which the expressions (24)-(27) are capable of describing the kinetics of luminescence in the quenched phosphors which are of interest here. From (24)-(27) it is apparent that the second light-sum n_{200} increases more rapidly than linear with respect to E if β_{10} is comparable with $\gamma_{12}E$. Inasmuch as we are considering the luminescence to be pseudo-monomolecular, the intensity of luminescence $I = \alpha_{20}n_2$ depends on E in exactly the same fashion. The decay (25) is exponential and its rate does not depend on E. On the other hand, the form of the growth curve (26) depends on E through the quantity B. As is shown by (26′), the growth is given by the sum of two increasing exponential terms of different sign and with time constants proportional to their amplitudes. It is not difficult to show that the growth curve behaves parabolically at the beginning. Expressing (26) as a series with respect to t and limiting ourselves to terms up to t^2, we have

$$I = \alpha_{20}n_2 = {}^1/_2\,\alpha_{20}\gamma_{01}\gamma_{12}E^2t^2.$$

It is apparent that the growth behavior in the parabolic region is independent of A and B.

We now form the ratio s. From Eqs. (25) and (26) we obtain (after integration)

$$L_P = \frac{\alpha_{20}n_{2\infty}}{A}\left(1 + \frac{A}{B}\right); \quad L_3 = \frac{\alpha_{20}n_{2\infty}}{A}; \quad (28)$$
$$s = 1 + A/B.$$

It is obvious that the quantity s can assume values greater than unity. The increase in the magnitude of s with increasing temperature, which is observed experimentally, can be interpreted, for example, by assuming that the quenching probability for the second light-sum $n_{2\infty}$ increases faster than the quenching probability for the first light-sum $n_{1\infty}$. Thus the notion of a two-step excitation process yields a possible explanation of all the characteristics of the kinetics of quenched phosphors which were indicated earlier: the more-than-linearity of the steady-state luminescence, the dependence of the form of the growth curve on E, the parabolic behavior at the beginning of the growth curve, the exponential decay, and the large value of the ratio s. We emphasize once again that these results are obtained on the basis of a pseudo-monomolecular recombination mechanism.

6. The hypothesis of a two-step excitation mechanism in phosphors, which brings the theory into agreement with experiment for strongly quenched phosphors (high temperatures) cannot be disregarded when considering unquenched phosphors (the same materials at ordinary temperatures). In fact, the number of electrons in the 1-levels (Fig.2) must be larger for unquenched phosphors and their trapping "stability" (in the thermal sense) greater. Direct optical excitation 0→2, which is considered virtually impossible at high temperatures (this is one of the fundamental hypotheses of the proposed theory), should be still less probable at low temperatures (since the thermally introduced energy, which, in general, might "free" excited electrons from the initial fast trapping at the 1-level will be smaller at low temperatures). Thus,

in any case, we must show that the two-step excitation does not contradict the experimental data on the properties of the phosphors at low temperatures.

We now give a more exact system of equations for the two-step mechanism which takes into account an effect which we have neglected in forming system (20). We have in mind the fact that the additional absorption at the 1-level reduces the absorption at the ground 0-level so that E, the total number of light quanta incident in one second on the phosphor, can be divided into two parts:

$$\frac{\gamma_{01}n_0}{\gamma_{01}n_0+\gamma_{12}n_1}E \quad \text{and} \quad \frac{\gamma_{12}n_1}{\gamma_{01}n_0+\gamma_{12}n_1}E, \qquad (29)$$

which are absorbed respectively at the 0-level and the 1-level. In this connection we assume that the number of electrons in the 0-level is virtually infinite so that a reduction of their absorption is to be associated not with a smaller number, but rather with the fact that electrons in the 1-levels, as though shielding the electrons in the 0-levels, tend to intercept the exciting-light quanta. Hence our more exact equations assume the form

$$\frac{dn_2}{dt}=\frac{E\gamma_{12}}{\gamma_{01}n_0+\gamma_{12}n_1}n_1-(\alpha_{20}+\beta_{20})n_2; \qquad (30)$$

$$(31)$$

$$+\frac{E\gamma_{01}n_0}{\gamma_{01}n_0+\gamma_{12}n_1}.$$

We solve these for the case in which there is no quenching: $\beta_{20}=\beta_{10}=0$. Calling $\gamma_{12}/\gamma_{01}n_0=\gamma$ and $\gamma n_1=\varphi$ we have, in place of (31),

$$(1/E\gamma)\,d\varphi/dt=(1-\varphi)/(1+\varphi). \qquad (32)$$

the solution of which is

$$(1-\varphi)^2e^{\varphi}=Ce^{-E\gamma t}. \qquad (33)$$

The constant C is determined from the condition $n_1=0$, whence $\varphi=0$ at $t=0$. Then from (33) we have $C=1$. The steady-state value of φ (for $t\to\infty$) is obviously equal to unity. Thus the steady state value for n_1 will be

$$n_{1\infty}=1/\gamma=\gamma_{01}n_0/\gamma_{12}. \qquad (34)$$

Whence, taking (29) into account, we obtain the following results: in the steady state (no quenching!) half of the quanta are absorbed in the 0-level and the other half at the 1-level. It will be seen that the result does not contradict our assumption of no "impoverishment" of the 0-levels if it is assumed that $\gamma_{12}\gg\gamma_{01}$, i.e., if it is assumed that the absorption probability in the 1-levels is much greater than the absorption probability in the 0-levels. We call attention to the fact that the expression for $n_{1\infty}$ (34) coincides with formula (21), which is obtained by the quenching case, if we set $\beta_{10}=0$ in the latter. As is apparent, $n_{1\infty}$ =const and is also independent of E. Physically, this result is similar to the well known discovery due to Antonov-Romanovskii concerning the light-sum storage limit as a function of the stimulation properties of the exciting light (cf. reference 7).

We now consider the quantity n_2. Formula (31) can be rewritten in the form

$$dn_2/dt=E\varphi/(1+\varphi)=-\alpha_{20}n_2, \qquad (35)$$

whence, by (33) we have for the steady-state luminescence

$$I_\infty=\alpha_{20}n_{2\infty}=E\left.\frac{1-e^{-(\varphi+E\gamma t)/2}}{2-e^{-(\varphi+E\gamma t)/2}}\right|_{t\to\infty}=\frac{E}{2}. \qquad (36).$$

Thus the steady-state luminescence is proportional to the intensity of the exciting light and has a quantum yield equal to 0.5.

We now show that the quantity $n_2(t)$ increases initially according to a quadratic law. Considering (33) at small t we have $\varphi=E\gamma t$, whence, to the same accuracy, Eq. (35) yields

$$I=\alpha_{20}n_2=\frac{\alpha_{20}\gamma E^2t^2}{2}=\frac{\alpha_{20}\gamma_{12}}{2\gamma_{01}n_0}E^2t^2. \qquad (37).$$

Thus our scheme predicts two well known properties of the nonquenching case: the linearity of the steady-state luminescence and the quadratic dependence of the luminescence intensity of the phosphor for "pulse excitation" (Antonov-Romanovskii, Levshin). It is worthy of note that the latter result has been obtained under the assumption that recombination takes place not according to a bimolecular law, but rather according to a pseudo-monomolecular relation ($I\sim\propto n$ and not $I\sim\propto n^2$). As in the strong quenching case the decay exhibits an exponential dependence on the time

$$I=I_\infty e^{-\alpha_{20}t}. \qquad (38).$$

This result does not agree with experiment[1] but may perhaps be explained by the crude nature of the scheme under consideration here (in particular the

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[7] V. V. Antonov-Romanovskii, Izv. Akad. Nauk SSSR Ser. Fiz. 15, 637 (1951).

existence of levels at only one depth).

7. We have considered the possibility of a two-step luminescence excitation mechanism inasmuch as we are convinced of the impossibility of satisfying the experimental data on quenched phosphors through the use of a one-step theory. There are, however, other facts which give much more direct evidence for the validity of a two-step mechanism. Lashkarev and Fedorus[8] have observed photoconductivity in certain single-crystals of CdS in which the steady-state value $\Delta\sigma_0$ as a function of the intensity of the exciting light is given by the relation $\Delta\sigma_0 \sim E^{3/2}$ (over a particular intensity range). The existence of such a "more-than-linear" dependence for $\Delta\sigma_0$ can be explained only by a two-step excitation mechanism, although the possibility exists that a one-step mechanism may also be playing a role. A two-step mechanism for the excitation of photoconductivity was also postulated by Lashkarev. We have also observed[++] a marked "more-than-linear" dependence for $\Delta\sigma_0$ in copper-activated polycrystalline cadmium-sulfide. In certain cases this dependence is found to be purely quadratic $\Delta\sigma_0 \sim E^2$ (see Fig. 3a and 3b). This semiconductor exhibits phosphorescence in the red-infrared region of the spectrum; the dependence of the steady-state luminescence I_∞ on the intensity of excitation E is found, in certain cases, to be close to quadratic. The growth curve has an inflection at its beginning and goes much slower than the decay curve ($L_g \gg L_d$). In other words the luminescence in this material displays all the characteristic properties mentioned above in connection with quenched sulfide phosphors. Consequently, if one assumes that the photoconduction and luminescence mechanisms in CdS-Cu are not separate and independent, it is reasonable to assume that the two-step excitation which is responsible for the "quadratic" photoconductivity in this material is also responsible for the "quadratic" luminescence. If this is so, it would seem that the origin of the "quadratic" behavior of luminescence in quenched ZnS-Cu and similar phosphors (exhibiting the same characteristics as CdS-Cu) lies in a two-step mechanism and that it is unnecessary to look for any other explanation; this reasoning is even more compelling when one considers that the alternative bimolecular scheme, as we have shown, is in disagreement with a large number of experimental criteria. For these reasons it deems desirable to analyze in detail the results which can be obtained from a more complete theory of phosphorescence and photoconductivity based on a two-step excitation mechanism and to compare these results with experiment. This project will be the subject of a forthcoming paper.

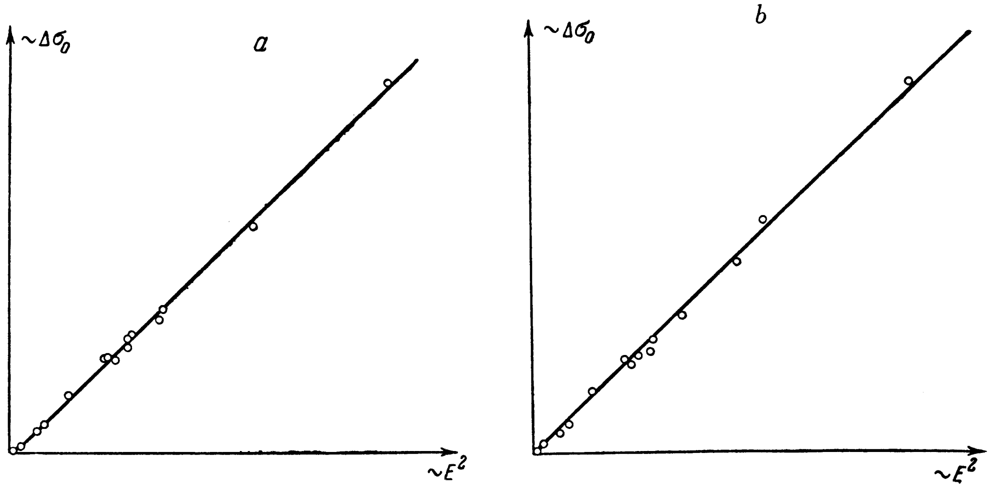

FIG. 3. CdS—Cu, crystal; a-γ=546 mμ, b-γ=578 mμ

[++] This work was carried out in conjunction with B. T. Kolomiits.

Translated by H. Lashinsky