

It is clear from (12) and (13) that for a given element and a fixed 3d electron density, we only have to calculate the quantity which occurs in the braces under the summation sign. We denote these quantities by ν_{at} and ν_{cr}

$$\nu_{at} = \omega_{nl}^{4/3} - 2^{1/3} \cdot (2^{1/3} - 1) \cdot [\omega_{nl}^{\uparrow} \cdot (\omega_{nl}^{\uparrow} - 1) + \omega_{nl}^{\downarrow} \cdot (\omega_{nl}^{\downarrow} - 1)], \quad (16)$$

$$\nu_{cr} = \Delta n^{4/3} + 2^{-1/3} \cdot (\omega_{nl} - \Delta n)^{4/3} - (2^{1/3} - 1) \cdot [\omega_{nl}^{\uparrow} \cdot (\omega_{nl}^{\uparrow} - 1) + \omega_{nl}^{\downarrow} \cdot (\omega_{nl}^{\downarrow} - 1)], \quad (17)$$

where $\Delta n = 2\omega_{nl}^{\uparrow} - \omega_{nl}$ is the number of uncompensated spins. We shall use this quantity to characterize the electron configuration. It is obvious that the smaller ν_{at} or ν_{cr} , the more stable the configuration.

Table 1 lists the results of the analysis for the different values of Δn .

The data show that in an atom (as would be expected) the state with maximum multiplicity is the one which occurs. In crystals, on the other hand, this is only true for Fe, Co, and Ni. It is therefore probable that in these elements, localized spin polarization will occur more easily.

The expressions which we have obtained for the exchange energy density will be used to calculate the physical properties of the 3d metals. This work is currently being carried out.

In conclusion, we may note that since Hund's rule is obeyed for an atom but not for a metal, this might mean that new additions to the energy might occur in a crystal. These terms would be of an exchange - correlation nature and would not be described by the normal expressions from the theory of a quasiuniform electron gas.

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DETERMINATION OF TRAP PARAMETERS BY SIMULTANEOUS MEASUREMENT OF THERMOSTIMULATED LUMINESCENCE AND THERMOSTIMULATED CONDUCTIVITY

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UDC 535.37

A method is proposed for processing of thermostimulated luminescence (TSL) curve in the presence of thermostimulated conductivity (TSC) in which no assumption is made as to the smallness of dn_c/dt (n_c is the conduction electron concentration). Results of the theory are applied to study of ZnS:Ag, Al and ZnS:Cu single crystals, in which elementary traps are revealed, and their activation energy and the value of the frequency factor determined. For ZnS:Cu the radiative transition recombination section is calculated.

The study of thermostimulated conductivity (TSC) and thermostimulated luminescence (TSL) curves is the basic method of studying capture levels in crystallophosphors. The literature describes many methods of analysis of TSL and TSC curves [1-3]. The majority of these methods permit determination of trap depth by

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using geometric parameters of the TSL and TSC peaks such as the maximum temperature T_m and the half-level temperature T' and T'' of the initial and final segments of the curve.

Antonov-Romanovskii [4] proposed a method for processing TSL curves based on analysis of the form of the entire thermoscintillation curve by comparing the experimental curve with the most similar theoretical curve. This method is the most informative one, since it permits determination of recombination kinetics, trap depth, and frequency factor. A shortcoming of the method is the necessity of expressing the luminescence intensity in absolute units, which is often quite difficult in practice.

An original and effective method of TSL curve analysis was proposed by De Muor [5]. The basic kinetic equations are considered for a system of one trap and one recombination center. If the TSL curve is complex and is produced by recombination of electrons freed from several traps, it is necessary to divide the curve into elementary peaks and study each peak individually.

The system of equations is written as follows [5]:

$$\begin{cases} \frac{dn_c}{dt} = \frac{n}{\tau} - \sigma(N-n)n_c - \beta pn_c, \\ \frac{dn}{dt} = \sigma(N-n)n_c - \frac{n}{\tau}, \\ n + n_c = p; \\ J = \eta\beta pn_c. \end{cases} \quad (1)$$

$$J = \eta\beta pn_c. \quad (2)$$

The following notation is used: N and n , the concentration of traps and of electrons within traps; p , the hole concentration at recombination centers; σ and β , the capture and recombination coefficients; n_c , the electron concentration in conduction zone; J , the intensity of luminescence; η , the quantum output; $1/\tau$, the probability of thermal release of an electron from a trap.

$$\sigma = S \cdot v, \quad \beta = \Gamma \cdot v, \quad (3)$$

where S and Γ are capture and recombination sections; v is the thermal velocity of charge carriers.

Solving system (1) with the simplifying assumptions $n_c \ll n$, $dn_c/dt = 0$, the authors obtained for the linear heating case ($T = ut$, where u is the heating rate) the following formulas for the first [Eq. (4)] and second [Eq. (5)] order kinetics:

$$\ln \frac{1}{\tau} = \ln \frac{u J(T)}{\int_T^{T_2} J dT}, \quad (4)$$

$$\ln \frac{1}{\tau} = \ln \frac{u^2 J(T)}{\left(\int_T^{T_2} J(T) dT \right)^2}, \quad (5)$$

where T and T_2 are the current and final values of TSL temperature.

For $1/\tau$ the expression

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(-\frac{E}{\kappa T}\right) \quad (6)$$

is valid, where $1/\tau_0$ is the frequency factor, and E is the trap depth.

The quantities on the right side of Eqs. (4) and (5) are determined experimentally, so that $\ln 1/\tau$ may be constructed as a function of $1/T$, and the slope of the linear portion of the curve may be used to determine trap depth E . In principle, it is sufficient to use only curve (4), since in the region of initial growth, with sufficient filling of traps, TSL does not depend on the character of luminescence kinetics.

Assuming heavy filling of traps ($n \approx N$) from the extension of the straight portion of curve (4) to its intersection with the ordinate axis, we may determine the frequency factor $1/\tau_0$, and with its aid, the electron capture section S in a trap. Using the deviation of the real curve (4) or (5) from the theoretical straight line, we may also determine the recombination section Γ .

The authors applied their method to thermoluminescence of ZnO and obtained satisfactory confirmation of the theory. However, it may occur that TSL is accompanied by TSC, in which case the original simplification $dn_c/dt = 0$ is no longer true.

The present study will obtain a formula for processing of TSL curves in which the assumption of smallness of dn_c/dt is not used.

We take the system of equations (1). Combining the first and second equations of the system, we obtain, with consideration of Eq. (2),

$$J = -\eta \frac{dp}{dt} \quad (7)$$

and after integration

$$p = \frac{1}{\eta} \int_t^{t_2} J dT,$$

where t_2 is the moment of TSL termination.

From the second equation of system (1) for the case of first-order kinetics, we have

$$\frac{dn}{dt} = -\frac{n}{\tau}. \quad (8)$$

Solving this equation with the initial condition $n(0) = N$, we obtain

$$\ln \frac{N}{n} = -\frac{n}{\tau}. \quad (9)$$

At the initial moment of TSL growth, Eq. (9) is valid for any kinetics in view of the smallness of the quantity $\sigma(N - n)n_c$.

Transforming from time to temperature, we obtain from Eq. (9) an expression for $1/\tau$

$$\frac{1}{\tau} = \frac{u \ln \frac{N}{n}}{T}. \quad (10)$$

We cannot determine the quantity n , but, using the third equation of system (1), for the ascending branch of the TSL curve we may take $n = p - n_c \approx p$. Then, with consideration of Eq. (6), we can obtain an expression for determination of E and $1/\tau_0$:

$$\lg \frac{u \lg \frac{N}{p}}{MT} = \lg \frac{1}{\tau_0} - \frac{E}{\kappa T} \cdot M \quad (11)$$

where $M = \log_e$, and N and p are defined by

$$N = \frac{1}{u \eta} \cdot \int_{T_1}^{T_2} J dT, \quad p = \frac{1}{u \eta} \cdot \int_T^{T_2} J dT, \quad (12)$$

where T_1 and T_2 are the temperatures of beginning and end of TSL.

Equation (11) is a solution of system (1) for the case of first-order kinetics with the single assumption $n \approx p$ and is valid for the initial portion of TSL for any kinetics. From Eq. (11) we can determine the activation energy and frequency factor, and with the aid of the latter, the capture section. However, the recombination section cannot yet be determined.

In principle, for weak photoconductors TSL processing by Eqs. (4), (5), and (11) should give identical results, but in practice, differences can be observed in the value of the frequency factor due to the assumptions made in deriving the various equations.

Simultaneous measurement of TSL and TSC may be used to obtain further information on the ratio μ/β . In fact, the photocurrent I is determined by the expression

$$I = A e \mu E n_c, \quad (13)$$

where A is the crystal cross section; e is the charge of an electron; μ is the mobility; E is the electric field intensity.

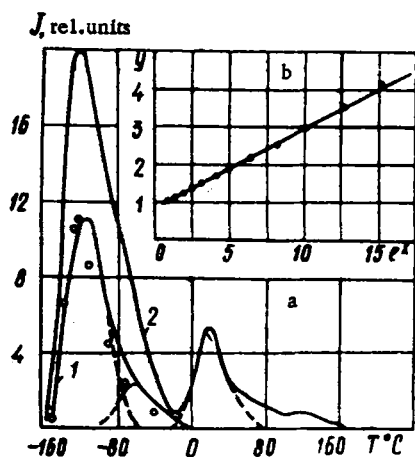


Fig. 1

Fig. 1. a) TSL curves of ZnS:Ag, Al (1) and ZnS:Cu (2) crystals; b) straight line for determination of recombination from TSL peak at -120°C (2).

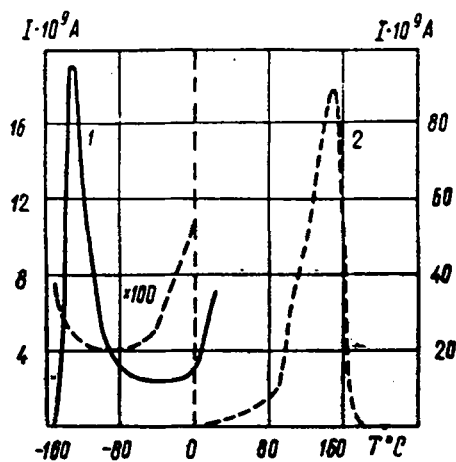


Fig. 2

Fig. 2. Single crystal TSC curves; specimen No. next to curve, right-hand scale for curve 2.

From Eqs. (2) and (13) we obtain

$$p = Q \frac{J}{I}, \quad (14)$$

where $Q = \text{const}$, independent of n , n_c , and p .

$$Q = \frac{AeE}{\eta} \frac{\mu}{\beta} (\text{A}\cdot\text{c}). \quad (15)$$

On the other hand, Q may be determined experimentally

$$Q = \frac{\int_{T_1}^{T_2} JdT}{u\eta J}. \quad (16)$$

The value of Q is a function of temperature. If $\mu(T)$ is known from independent measurements, then $\beta(T)$ may be determined. If the absolute value of η is also known, then the absolute value of β may also be determined. In the general case η also depends on temperature.

RESULTS

Single crystals of ZnS:Ag, Al and ZnS:Cu grown from a melt at the Scientific-Research Institute of Single Crystals (Kharkov) with an activator content of $\sim 10^{-4}$ at. % were studied. Specimens were studied by photoexcitation of the 313 and 365 nm lines by a type PRK-4 mercury lamp and by cathode excitation with an accelerating voltage of 4 kV.

The luminescence spectrum of specimen No. 1 had a maximum at 475 nm, while that of No. 2 showed a maximum at 520 nm. In the spectra of both crystals blue and green bands were present, with the ratio between these colors varying with form of excitation.

TSL and TSC were studied in both specimens with photo- and cathode-excitation for various excitation times and with use of fractional annealing [6]. Such measurements allow determination of all monoenergetic traps and permit resolution of the TSL curve into elementary peaks when necessary [5].

Figure 1 shows TSL curves of both specimens for photoexcitation ($\lambda = 365$ nm), while Fig. 2 gives corresponding TSC curves. The TSC and TSL curves were taken simultaneously under linear heating at a rate of 5 deg/min. It should be noted that use of high heating rates is undesirable, since it leads to a high temperature gradient over specimen thickness. The specimen No. 1 TSL curve was taken in the blue region ($\lambda = 470$ nm); that of specimen No. 2, in the green ($\lambda = 540$ nm). The No. 1 TSL in the green region was identical to

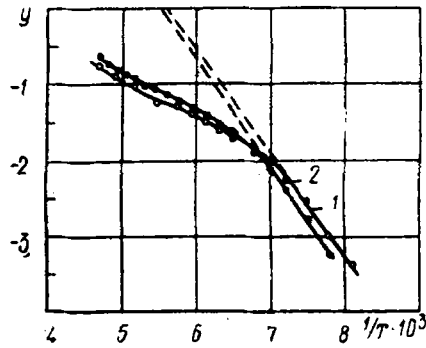


Fig. 3

Fig. 3. Temperature dependence of ZnS:Ag, Al crystal TSL peak at -115°C . 1) $\lambda = 313 \text{ nm}$; 2) $\lambda = 365 \text{ nm}$.

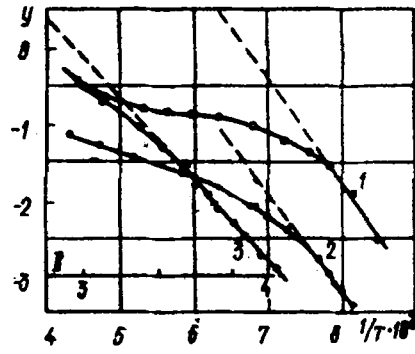


Fig. 4

Fig. 4. Temperature dependence of crystal TSL peak: 1) peak at -120°C , processed by Eq. (4); 2, 3) peaks at -120°C and 25°C processed by Eq. (11), scale II for curve 3.

that in the blue, while for specimen No. 2 in the blue region the peak at 25° was absent, and the low-temperature TSL peak coincided with the peak in the green region.

Comparison of the TSL and TSC curves shows that in the ZnS:Ag, Al single crystal the thermoscintillation peak at -115°C is accompanied by strong TSC, while in the ZnS:Cu single crystal in this region there is only a TSL peak, TSC being absent. This makes it possible to use these specimens for verification of the applicability of Eqs. (4), (5), and (11) for trap parameter determination. Measurement of fractional TSL and TSC revealed that the peak at -115°C in specimen No. 1 was not elementary – its high temperature decay overlaps with the TSL peak at -65°C . The dashed lines of Fig. 1 indicate elementary TSL bands. The TSL peak at -120°C in specimen No. 2 is elementary, since only at 0°C is there insignificant overlapping with the TSL peak at 25°C . Figure 3 shows the temperature dependence of the TSL peak at -115°C in the coordinates

$$y = \lg \frac{u \lg \frac{N}{P}}{MT} = f\left(\frac{1}{T}\right).$$

As is evident from the curve, processing of the TSL curve at $\lambda = 313$ and 365 nm gives good agreement of results. The trap depth, obtained from the slope of the straight segment, comprises $0.28\text{--}0.3 \text{ eV}$, and the frequency factor $1/\tau_0 \approx 5 \cdot 10^6 \text{ sec}^{-1}$. The activation energy, determined by a different method from the initial growth of TSL [1], comprises $0.28\text{--}0.34 \text{ eV}$, which agrees well with the values obtained. Construction of the corresponding curve from Eqs. (4) and (5) gives a value of $E = 0.12 \text{ eV}$ and $1/\tau_0 = 3 \cdot 10^3 \text{ sec}^{-1}$. We see that neglect of dn_0/dt leads to reduced values of activation energy and frequency factor.

Figure 4 shows an analogous TSL curve for specimen No. 2 for the peak at -120°C , and its temperature dependence, calculated with Eq. (4)

$$y = \lg \frac{u J(T)}{\int_f^{T_0} J(T) dT} = f\left(\frac{1}{T}\right);$$

where y has dimensions of min^{-1} .

For this specimen use of the two TSL curves processing methods gives an identical value of activation energy, but there is a divergence in the frequency factor value. The $1/\tau_0$ values can differ by a factor of 10–20, due to the simplifications used in deriving Eqs. (4), (5), and (11). The parameters of this trap in ZnS:Cu are the same as those in the ZnS:Ag, Al single crystal. The same figure shows the processed curve for the TSL peak at 25°C , calculated with Eq. (11). For this trap secondary capture is low, and the TSL peak processing curve coincides with a straight line over practically its entire length. The depth of this trap is $0.55 \pm 0.03 \text{ eV}$, and the frequency factor is $\sim 10^7 \text{ sec}^{-1}$.

As was indicated above, knowing $1/\tau_0$, we may determine the trap capture with the formula [5]

$$\frac{1}{\tau_0 S} = \frac{2\pi m^* (\kappa T)^2 \sqrt{6\pi}}{\hbar^3}, \quad (16)$$

TABLE 1. Trap Energy Depth in ZnS:Ag, Al and ZnS:Cu Single Crystals

Specimen		I	II	III	IV	V
№ 1 ZnS: Ag, Al	T, K	158	208	—	—	—
	E, eV	0,29±0,02	0,38	—	—	—
№ 2 ZnS: Cu	T, K	153	298	333	393	418
	E, eV	0,28±0,02	0,55	0,61	0,73	0,90±0,05

where m^* is the effective mass of an electron, which in ZnS comprises $0.28m_0$ [8]

$$S = \frac{2.19 \cdot 10^{-21}}{\tau_0 (T)^2} \text{ cm}^2.$$

For a temperature $T = 300^\circ\text{K}$ at $1/\tau_0 = 5 \cdot 10^6 \text{ sec}^{-1}$ we obtain for the low-temperature trap in both specimens $S = 10^{-18} \text{ cm}^2$.

Using the De Muor method, one can also determine the recombination section. To do this, we use the deviation of the experimental curve, constructed from Eq. (4) or (5), from its rectilinear extension. For

monomolecular recombination (Fig. 4, curve 1) we construct $y = \frac{\int_{T_0}^{T_1} JdT}{\int_{T_0}^{T_1} JdT}$ as a function of the parameter e^X ,

where X is the difference between the ordinate of the rectilinear extension and the experimental curve. This function must be a straight line in accordance with the formula

$$y = \frac{\Gamma}{S} \exp X - \frac{\Gamma}{S} + 1. \quad (17)$$

The tangent of the slope of this line determines the ratio Γ/S . Figure 1b shows the corresponding graph, constructed for curve 2 of Fig. 1a. It is evident from the graph that the experimental points fit the straight line well.

The ratio $\Gamma/S = 0.2$, whence we find $\Gamma = 2 \cdot 10^{-20} \text{ cm}^2$. For specimen No. 1 the Γ was not determined, since the De Muor method is inapplicable in this case.

For the remaining traps which appear weakly in TSL, the energy depth may be determined by using Urbach's empirical formula [8] $E = T_m/L$, where L is some constant; L can be determined by using the energy and temperature maximum of the low-temperature trap. Urbach gives a value of $L = 500$, while for the specimens studied $L = 545$. The activation energy of the highest-temperature trap, which appears only in TSC, was determined by the initial growth of TSC, which must be exponential.

In order to avoid superposition of TSL from finer traps, the latter were eliminated by fractional annealing to $T = 130^\circ\text{C}$. The E value obtained corresponds to the second constant in the Urbach formula ($L = 465$), which shows its difference from the parameters of trap 1. This is not surprising, since the form of the TSC curve indicates a predominantly monomolecular mechanism of carrier recombination, and trap 1 is characterized by strong secondary capture. Table 1 presents temperature maxima and activation energies of all traps.

The following may be said relative to the nature of the traps. Despite the coincidence of its parameters, trap 1 is of a different nature in the two specimens. In specimen No. 1 it is produced by the presence of Al acting as a coactivator. Measurements were made of TSL in a ZnS:Al single crystal, and the same type of thermoluminescence peak was observed as in specimen No. 1. In Fig. 1 the dots show the TSL curve of the ZnS:Al single crystal. The small shift ($\sim 10^\circ$) of this peak relative to the TSL of the ZnS:Ag, Al single crystal may be explained by the influence of the differing defect surroundings in the two single crystals.

In the ZnS:Cu single crystal the copper was introduced into the original melt in the form of Cu₂S, i.e., without a coactivator, so that charge compensation must be accomplished by intrinsic defects in the ZnS lattice. These defects may be either interstitial zinc Zn_i, or sulfur vacancies V_S. It was shown in [9] that Zn_i produces a TSL peak at 110°K, while for V_S the temperature is 160°K. The TSL peak in specimen No. 1 is located at 153°K, so that it is reasonable to assign it to sulfur vacancies.

Of the other traps, that of greatest interest is the deep trap at 418°K in specimen No. 2 (Fig. 2). Nothing is known of its nature. In its properties it is close to the repulsive traps in CdS described by Bube [10]. Aside from the depth of 0.90 eV, the low-temperature drop gives an additional depth of 0.33 eV, and the emptying process is of a multimolecular character, as in repulsive traps. On the other hand, this trap is filled at all temperatures, and a repulsive trap should be filled only at temperatures above 210°K. More comprehensive studies will be required to clarify the nature and character of this trap in ZnS:Cu.

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PRODUCTION OF e^+e^- PAIRS FROM A VACUUM BY A FREE ELECTROMAGNETIC FIELD OF SPECIAL CONFIGURATION

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UDC 539.12:530.145

This paper considers the production of e^+e^- pairs from a vacuum by a free electromagnetic field which is in the form of a superposition of traveling electric and magnetic fields and a plane wave, all propagating in the same direction. Expressions are obtained for the average and total number of pairs produced.

There have recently been many papers which calculate the probabilities of e^+e^- pair production from a vacuum by external electromagnetic fields [1-6]. The most interesting fields are those which satisfy the free Maxwell equations. This is a result of the prevailing idea that no matter existed in the initial stages of the evolution of the Universe and that particles are generated from a vacuum by free electromagnetic and gravitational fields [7-8].

In this paper, we consider the generation of e^+e^- pairs by a free electromagnetic field which is in the form of a superposition of electric and magnetic fields traveling along the z axis and a plane wave field propagating in the same direction. A special feature of this configuration is that the field which generates the pairs depends only on $ct - z$.

A method of calculating the probabilities for the production of e^+e^- pairs by this type of field has been suggested in [9]; the method is based on the use of the zero-plane formalism [10, 11]. The role of time in this

Lenin Komosomol Teaching Institute, Tomsk. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii*, *Fizika*, No. 6, pp. 101-105, June, 1977. Original article submitted September 20, 1976.

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