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The Problem of the Position of the Copper Activator in Zinc-Sulfide Scintillators

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An outline of the implanting process of an activator is presented, based upon investigation of the luminescent properties of ZnSCu-scintillators, obtained by thermal treatment at low temperatures (up to 600 °C) and by repeated firing. This outline is in agreement with the assumption of the dispersed position of copper in the scintillator system.

1. Two ways were used to obtain the characteristics of the behavior of the copper activator in ZnS-scintillators: a) preparation of the ZnSCu-scintillators according to the typical technological method, but applying low temperatures (below 600 °C), and b) investigation of the penetration of copper into an already formed crystalline ZnS structure that was obtained by heat treatment.

The scintillators were prepared from dry amorphous zinc sulfide powder, obtained by precipitating the sulfate in warm weak acid solution with hydrogen sulfide. The aqueous solution of the activator was introduced to the sulfide. After drying, addition of the crystalline flux, and careful mixing, the mixture was put in a quartz crucible, the cover of which was coated with kaolin paste. Crucibles and contents were heated up to 300-320 °C, then placed in the furnace that was heated up to the required temperature, and maintained at temperature. The luminescence was investigated at room temperature, with the exciting light $\lambda = 365 \mathrm{m}\mu$ of the mercury lamp at the distance of 25cm (lamp PRK4 with filter UFS); the brightness was measured with the Pulfrich photometer, spectra were studied with the visual spectrophotometer.

2. In thermal treatment of the amorphous sulfide[1], the formation of crystals and the incorporation of the activator can take place at comparatively low temperature (in range of 400 °C), however, the indicated processes, under these conditions, are slow and require many hours. When ZnS is heated, with NaCl flux at 400 °C during 1 hour period without addition of copper, the mixture is obtained without notable luminescence, but at 450 °C a yellow fluorescence shows up (possibly, from ZnO[2]). At 500 °C a bluish luminescence occurs, which develops to a bright one at 600 °C when, the sample heated for 1 hour.

When ZnS is heated with Cu (10^{-4}g/g) and with NaCl flux (5%) at 350 °C for a long time (up to 30 hrs.) specimens are obtained with a rather weak orange-yellow luminescence, the intensity of which increases constantly with time of heating. The rise in temperature of the thermal treatment up to 400 °C produces remarkable intensities of the orange luminescence which is apparently connected with the formation of Cu_2S[3] or double sulfides of zinc and copper. The intensity of the luminescence increases with the increasing heating time (Table 1); the color changes from dark orange to yellow and even to yellow-green (Fig. 1). The after-glow also increases. When the firing temperature is raised, the increase of brightness and occurrence of yellow-green fluorescence are observed: after 4-hour heating at 450 °C, specimens with yellow-green luminescence with after-glowing are obtained. At 600 °C this event develops to full scale and upon further rise in temperature, typical ZnSCu-scintillators are formed, Table 1.

In case of H_3BO_3 flux the occurrence of luminescent properties is much weaker and slower. In the absence of copper, pale luminescence is first observed at 600 °C, and blue light-at 700 °C. In the presence of copper (10^{-4} g/g) at 400 °C, dark orange luminescence takes place, while a constant increase of brightness with the heating time is observed. At 600 °C the yellow-green luminescence does not appear at once, and remarkable intensities are obtained after prolongued period of time (Table 2 and Fig. 2). Samples obtained at 700 °C firing temperature (in 30 min. period) exhibit a pale-yellow luminescence, the after-glowing being faint; at the firing temperature of 800 °C (30 min) blue luminescence shows up and the after-glowing almost disappears.

In order to explain the nature of the orange

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[1] F. Tiede and F. Weiss, Chem. Ber. **65**, 364 (1932)

[2] N. F. Zhirov, *Luminophors*, Defense J., 1941, p. 307; F. A. Kroeger and J. A. M. Dikhoff, Electrochem. Soc., **99**, 144 (1952)

[3] Ia. I. Gerasimov and A. N. Krestovnikov, *The Chemical Themodynamics in Color Metallurgy*, ONTI, 1933, Vol. 1, p. 163; Vol.2, p. 40

luminescence of ZnSCu, two series of samples were prepared at various temperatures with one-and two-valent chlorides of copper and with a great excess of the activator (calculated as 5% Cu). In case of Cu^{++},where, in the first place, CuS being already dissociated[3] is formed; the process takes place more slowly than with Cu^{+}, where Cu_2S appears at once, and therefore the sample, obtained by firing at 400 °C, in 30 minutes, shows, in case of univalent copper, more intensive luminosity (red color). At 500 °C the mixture with univalent copper exhibits yellow-green luminescence, whereas the mixture with bivalent copper--the yellow one. In Fig. 3, spectral characteristics of the luminescence of the two samples prepared at 600 °C (firing time 30 min) are presented. At still higher firing temperature luminescence almost disappears.

TABLE I

Dependence of the Brightness of the Luminescent Light of ZnSCu-system on Heating Time at 400 °C

Time in hrs.	1	2	4	6	8	10	14	18	22
$I_{relative}$	2.4	6	22	42	57	71	83	90	100

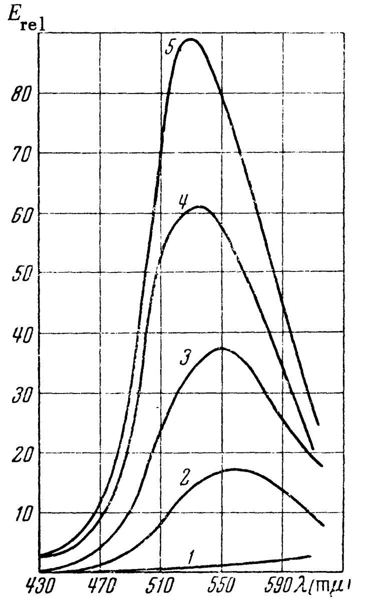

Fig. 1. Spectra of luminescent light of ZnSCu-NaCl scintillators for various heating periods at 400 °C; 1 = 1, 2 = 4, 3 = 8, 4 = 18, 5 = 22 hours.

A similar picture is observed by heating with the addition of separately prepared CuS and Cu_2S.

3. For the purpose of investigating the processes taking place in the crystalline ZnS, three series of experiments were carried out.

a) In the first experiment a typical ZnSCu-scintillator with the green luminescence was used, prepared with 10^{-4} g/g Cu and chloride flux washed out after firing; it was heated for the second time with H_3BO_3 flux. After a half an hour firing at 1100 °C, blue fluorescence shows up while the phosphorescence remains still green. By prolonging the second firing time, the after-glowing disappears and blue fluorescence stays.

TABLE II

The relative intensities of the luminescent light of ZnSCu-systems, fired for various periods of time at 450 ° and 600 °C with NaCl and H_3BO_3 fluxes

Firing Time	450 °C		600 °C	
	NaCl	H_3BO_3	NaCl	H_3BO_3
30 min	—	—	84	0.36
1 hr	11	0.15	100	0.48
2 hrs	21	0.18	106	0.60
4 hrs	31	0.20	—	0.72
8 hrs	—	—	—	1.02
12 hrs	—	—	—	1.64
16 hrs	—	—	—	2.34

b) A ZnSCu mixture was used as the initial sample, and was prepared with an excess of activator (10^{-4} g/g Cu) and H_3BO_3 flux,i.e., with a blue fluorescence[4] . When heated with NH_4Cl (10%) for 1 hour at 500 °C it shows green luminescence. In case of NaCl flux (10%) at 500 °C, even 4 hour heating does not produce mixture with the green luminescence; however, heated at 600 °C for 1 hour, the mixture shows green luminescence.

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[4] A. A. Cherepnev and T. S. Dobroliubskaia, Doklady Akad. Nauk SSSR 66, 621 (1949)

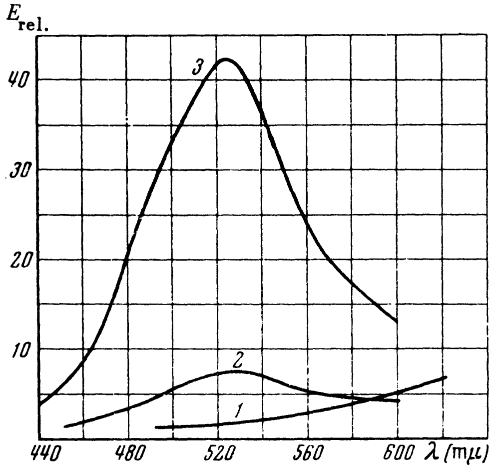

Fig. 2. Luminescence spectra of ZnSCu - H_3BO_3-scintillators with various firing time at 600 °C : 1=30 min, 2=4, 3=16 hours.

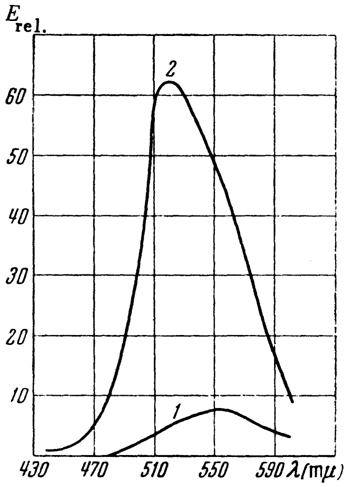

Fig. 3. Luminescence spectra of ZnS-scintillators, fired at 600 °C with the additions: 1=$CuCl_2$, 2=CuCl.

c) The method of references 5,6 of activating, by subsequent heating, pure ZnS which was already fired was applied. ZnSZn-specimens were prepared by firing amorphous ZnS at 900 ° and 1100 °C for 30 min period: two of them were with NaCl flux, the other two with high H_3BO_3, 5% each. Mixtures fired at 900 °C had bright-blue luminescence, whereas mixtures fired at 1100 °C showed faint bluish luminescence with a green phosphorescence not greater than that of residual, hardly removable copper. These mixtures were heated secondarily for 30 minutes with the copper activator added (10^{-4} and 10^{-5} g/g) and with the same flux (5%) which was used during the first firing operation. A series of new luminescent specimens were obtained, which are illustrated in Table 3 with the characteristics of color of their luminescence.

As it is seen from the table, the fluxes have an effect upon the final result. With the increased time of secondary heating, the NaCl flux produces the yellow-green luminescence, of characteristic copper, and after glowing, and the H_3BO_3 flux shows the same luminescence only with small amounts of activator. With its larger concentration, the flux produces a blue fluorescence without after glowing.

4. To explain the reported experimental data, the following suppositions are made[4,7,8]. During the formation of ZnS-scintillators in the system being subjected to the thermal treatment, a series of chemical reactions of separation of metals is possible through the mutual action of the sulfides and the oxidized compounds [3,8]. The sources of oxygen are oxygen compounds decomposing in the technological process (ZnO, $ZnSO_4$), fluxes containing oxygen, moisture, atmospheric oxygen, absorbed or penetrated into the system from the outside (explanation of experiments of Grillot [9]). The fluxes facilitate the course of the reactions and the formation of metals in the dispersed phase (the molten chlorides help in dispersion of metals [10]). The experimental fact of activation by copper at low temperatures can be explained by the electrolytic displacement by the diffusing copper of zinc that is stoichiometrically in excess, the formation of which can be explained by the indicated reactions (mainly between the oxide and sulfide [11]), or by the removal of sulfur as a result of dissociation[12]. It is natural to assume that copper can

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[6] F. A. Kroeger, J. E. Hellingman and N. W. Smith, Physica 15, 990(1949); F. N. Garlick, *Luminescent Materials*, Oxford 1949, p. 65

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[9] E. Grillot and M. Bancie-Grillot, C. R., 231, 966 (1950)

[10] R. Lorenz and W. Eitel, *Pyrosole*, Leipzig, 1926

[11] B. M. Gugel, Zh. Ob. Khim. 20, 1376(1950)

[12] A. A. Bundel' and A. I. Russanova, Izv. Akad. Nauk SSSR, Ser. Fiz. 13, 173 (1949)

TABLE III

Color of the luminescence of the ZnS-Scintillators with NaCl and H_3BO_3 fluxes, activated twice by copper and heated twice

Temperature of the first firing		900 °C								1100 °C							
Concentration of the activator g/g		10^{-5}				10^{-4}				10^{-5}				10^{-4}			
Flux		NaCl		H_3BO_3		NaCl		H_3BO_3		NaCl		H_3BO_3		NaCl		H_3BO_3	
Temperature of the second heating	300°	lb	ph	lb	ph	plb	ph	lb	-	plb	ph	plb	ph	gr-lb	ph	gr-lb	ph
	350°	lb	ph	lb	ph	pl	ph	lb	-	plb	ph	plb	ph	lb	ph	lb	ph
	400°	pl	ph	pl	strong ph	pl	ph	plb	strong ph	plb	ph	plb	ph	lb	ph	plb	ph
	500°	pl-ye	ph	ye	strong ph	ye	ph	w	n-ag	lb-ye	ph	plb	ph	lb	ph	pl	ph
	600°	ye	ph	ye	bright ph	ye-grn	ph	b	n-ag	ye	ph	y-grn	ph	ye-grn	strong ph	b	n-ag

CODE: ph-phpsphorescence, n-ag- no after glowing, lb-light blue, b-blue, gr-gray, pl-pale, w-white, ye-yellow, grn-green.

show up in various dispersed conditions; fine, almost atomic, dispersion, is the cause of green luminescence and also of after glowing, because of the creation of structures connected with the occurrence of the "trap sites" of electrons. When particle of copper grows up to the colloidal size, the luminescent properties of copper disappear. The degree of dispersion of copper metal can change under influence of the secondary action of the chlorides. Thus, the fluxes can play a great but auxiliary role.

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The Theory of Scattering in the Semi-Classical Approximation

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A method is given for finding the wave function and the Green's function for a three-dimensional problem in the semi-classical approximation. The idea of the method is illustrated by the problem of reflection from a barrier.

1. INTRODUCTION

IN scattering problems the semi-classical approximation is usually applied to the calculation of the phase shifts corresponding to the different angular momenta of the particle. This method is applied only in the case of a central field.

In the present work it is shown that the wave function can be found without the assumption of the central character of the potential field, if the trajectories of the classical problem are known.

As is well known, the semi-classical approximation, which has been thoroughly studied in the one-dimensional case, does not give the exact solution, but an asymptotic series in the semi-classical parameter ξ ($\xi = \lambdabar / l$ where $\lambdabar$ is the wave-length of the particle, l, is a length characterizing the variation of the potential). Quantum effects, which decrease exponentially with diminishing ξ, cannot be determined in any approximation of this asymptotic series, because the error of the asymptotic representation exceeds the effect sought.

Let us consider, for example, the problem of the calculation of the reflection coefficient from a potential barrier V, when the conditions of the semi-classical approximation are fulfilled in the entire space (i.e., the kinetic energy is nowhere reduced to zero). It is not difficult to see that neither the first nor the succeeding approximations in ξ contain terms corresponding to the reflected wave. Analogous questions arise in the three-dimensional problem also. For example, in the case in which the deflection into large angles is forbidden in classical mechanics, the scattering into these angles decreases exponentially with diminishing ξ, and cannot be found with the aid of an asymptotic expansion in ξ.

In the present work a method is given for improving the semi-classical approximation, which enables us to find the solution of the above-mentioned problems. This method consists of the following: the wave function of the problem is written in the form $\psi = \psi_0 + \psi_1$, whereby ψ_0 is the ordinary semi-classical solution; for ψ_1 an inhomogeneous equation is obtained, the solution of which is found by the use of the Green's function. In this work it is shown how one can obtain an approximate Green's function, if the trajectories of the classical problem is known.

2. ONE-DIMENSIONAL PROBLEM

1. It is required to find the solution of the Schrödinger equation

$$\begin{gathered}\psi'' + k^2(x)\psi = 0, \\ k^2 = 2[E - V(x)], \quad m = \hbar = 1,\end{gathered} \tag{1}$$

describing the reflection from a potential barrier $V(x)$ under conditions such that the condition for