THE MECHANISM OF DISINTEGRATION OF COLOR CENTERS AND THE NON-STATIONARY RECOMBINATION LUMINESCENCE OF NaCl-Ag PHOSPHOR CRYSTAL. I

V. P. Chernenko, Yu. L. Lukantsever, and F. N. Zaitov

A combined method has been used to study the disintegration processes of the 355, 465, and 720 color centers of NaCl-Ag phosphor in the temperature range 100-550° K. The emission spectra of thermostimulated and photostimulated recombination luminescence of NaCl-Ag excited by X-rays at various temperatures were also studied. The possibility of ion-electron and ion-hole disintegration mechanisms of the color centers in the phosphor crystal at low temperatures is examined.

INTRODUCTION

The study of recombination processes in activated alkali-halide crystals over a sufficiently wide temperature range can give important information about the mechanism of recombination luminescence in these crystals. In particular, the combined study of the processes of integral thermo- or photoluminescence and decoloration of phosphors in various excited-absorption bands is a valuable source of information on the mechanism of the creation and disintegration of color centers and the accompanying transformations of the energy absorbed by the crystal.

In recent years, a number of authors have used this approach to study the detailed mechanism of recombination luminescence and to investigate emission spectra during thermoluminescence [1-3, 9], and they have established that these spectra change substantially during relaxation.

Earlier [3], we elucidated the origin of the integral thermoluminescence peaks in synthetic NaCl-Ag phosphor and determined that such capture and emission centers were responsible for luminescence at various stages of thermoluminescence.

The present paper continues the study of the emission spectra of nonstationary luminescence, and also the processes of thermoluminescence and thermodecoloration over a wider range of temperatures (from 100 to 550° K).

EXPERIMENTAL

The NaCl-Ag phosphor studied in the present work was grown from a melt of natural rock salt (Toktogul'-skoe deposit) and an Ag activator, which was introduced into the melt as AgNO$_3$ (0.2 mole-% in mixture).

We studied thermoluminescence, thermodecoloration, and also the emission spectra in thermo- and photostimulated recombination luminescence after excitation of the NaCl-Ag phosphor crystal with X-rays at 130 and 290° K. The phosphor was excited by X-rays from a URS-55a apparatus (BSV-Cu tube, I = 15 ma, V = 50 kV). The excitation time varied, depending upon the nature of the experiment, from 30 to 240 min (radiation doses of 75-600 R).

For the low-temperature studies, the phosphor was placed in a cryostat made of molybdenum glass, which was filled with liquid oxygen. The design of the cryostat [4] made it possible to place a heater directly in the liquid oxygen and to effect a continuous transition from low (100° K) to high (600° K) temperatures at a given rate of heating. In most of the tests this rate was 0.3°/sec.

The absorption spectra of the phosphor at both low and room temperatures, and also the curves of integral thermoluminescence (TL) and thermodecoloration (TD) of crystals at various temperatures, were recorded by means of a photometer, which consisted of a FEU-29 photomultiplier, a dc amplifier, and a EPP-09 electronic recording potentiometer. The emission spectra of the photo- and thermostimulated luminescence were recorded with a photometer, which consisted of a FEU-29 photomultiplier, a dc amplifier, and a N-102 loop oscillograph [3]. In all cases, the emission spectra were corrected for the spectral sensitivity of the FEU-29, and also for the nonlinearity of the frequency ν sweep of the spectrum. The sweep time of the emission spectrum of the thermoluminescence and of the photostimulated luminescence from 6 to 2 eV was 15 sec.

RESULTS AND DISCUSSION

Study of the absorption spectra of this phosphor showed that the form of the spectrum varied substantially with the X-ray dosage (X-irradiation time), and also after preliminary heat treatment of the crystal before excitation.

Table 1 shows the positions of the peaks of the excited-absorption bands of the NaCl-Ag phosphor under study at 180° and 290° K in the spectrum region

Table 1

No. of excited-absorption bands	T_{ex} = 180 K							T_{ex} = 290 K						
	1	2	3	4	5	6	7	1	2	3	4	5	6	7
λ_m of excited-absorption bands (in mμ)	*	*	*	355	455	620	720	210	240	275	355	465	620	720

*Study of bands 1-3 at low temperatures was difficult owing to considerable absorption by the cryostat material in the spectrum region concerned.

from 1.6 to 6 eV after X-irradiation of the crystal for 1 hr (X-irradiation dose 150 R).

Comparison of the absorption coefficients in the various excited-absorption bands given in Table 1 showed that absorption is greatest in the bands with λ_{max} = 355 and 465 mμ. Most attention was therefore given to the study of these absorption bands. It should be noted that the data in Table 1, referring to T_{ex} = = 290° K, differ somewhat from the results cited in our earlier paper [3] for synthetic NaCl-Ag; this discrepancy may be caused by differences in the origin of the phosphors.

Figure 1 shows integral curves of TL for NaCl-Ag excited at 130 and 290° K, and also TD curves of the absorption bands of this phosphor with λ_{max} = 355, 465, and 720 mμ.

The TL curve of the phosphor excited at 130° K (see curve 1, Fig. 1a) has two strong low-temperature peaks I (T_m = 190° K) and II (T_m = 250° K) and two comparatively weak high-temperature peaks, III(T_m = = 310° K) and IV (T_m = 380° K). Peak IV, at T_m = = 380° K, was preserved when the phosphor was excited at room temperature (curve 2, Fig. 1a). Thermodecoloration of the 355 mμ absorption band occurs in several stages (curve 1, Fig. 1b). The maximum disintegration rates of the corresponding absorption centers occur at temperatures of 190, 225, 265, and 400° K (curve 1', Fig. 1b).

Low-temperature decoloration of the 465 mμ band occurs somewhat differently: as can be seen from Fig. 1c (curve 1), the TD curve rises at first, and then falls in several stages; the highest rates of disintegration of the 465 color centers occur at 225 and 265° K. Similarly, the absorption band with λ_m = 720 mμ (curve 1, Fig. 1d) is decolored upon low-temperature excitation (T_{ex} = 150° K).

The data indicate that for low-temperature excitation (T_{ex} = 150° K), the maximum rates of formation of the 465 and 720 absorption bands lie in the same temperature range, ~190° K, the TD curves of the 355 and 465 absorption bands have a simpler form (curves 2, Fig. 1b and c), and the maximum rates of disintegration of absorption centers of these two types are at T_m = 370 and 410° K and T_m = 370, 390, and 450° K, respectively.

The above results make it possible, to a certain extent, to elucidate the disintegration mechanism of color centers, and to determine the color centers whose disintegration is responsible for the various thermoluminescence peaks of the phosphor.

In the temperature range where peak I appears (190° K, Fig. 1a–d, curves 1), there is partial disintegration of the 355 centers and growth of the 465 and 720 color centers. The processes that occur in this temperature range can be interpreted in two ways.

1. If it is assumed that the 355 band is of the hole type, then the reduction in the number of 355 centers in the range 180–200° K (see Fig. 1b) and the simultaneous increase in the number of the electron centers 465 and 720 in this range (see Fig. 1c and d) could be due to disintegration of electron centers of a hitherto unknown type, localization of the liberated electrons

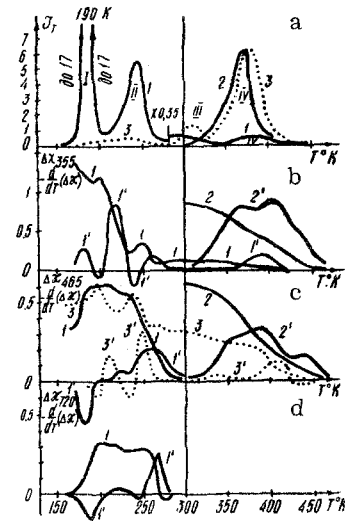at the F and M trapping centers, and recombination of a part of these electrons with the holes of the 355 centers.

Fig. 1. Relaxation curves of NaCl-Ag phosphor: a) thermoluminescence $I_T(T)$: 1—T_{ex} = = 130° K; 2—T_{ex} = 290° K; 3— T_{ex} = 290° K followed by cooling to 150° K before measurement; b) $\Delta\varkappa_{355}(T)$: 1—T_{ex} = 180° K, 1'—$(\partial/\partial T)(\Delta\varkappa_{355})$; 2—$T_{ex}$ = = 290° K; 2'— $-(\partial/\partial T)(\Delta\varkappa_{355})$; c) $\Delta\varkappa_{465}(T)$: 1—T_{ex} = 180° K, 1'— $-(\partial/\partial T)(\Delta\varkappa_{465})$, 2—$T_{ex}$ = 290° K, 2'— $-(\partial/\partial T)(\Delta\varkappa_{465})$, 3—$T_{ex}$ = = 150° K for heat- and radiation-treated phosphor; 3'—$(\partial/\partial T)\cdot$ $\cdot(\Delta\varkappa_{465})$ for conditions of 3; d) $\Delta\varkappa_{720}(T)$: 1—T_{ex} = 150° K, 1'— $-(\partial/\partial T)(\Delta\varkappa_{720})$.

2. But if the 355 band is of the electron type, then the processes that occur in the region of TL peak I could be regarded as the result of the release of electrons from the 355 centers and their capture by the F and M centers.

In order to obtain a better insight into the nature of the 355 absorption band and the character of the relaxation process in the temperature range concerned, we studied the behavior of the 355 band during photothermal disintegration of the F color centers and release of electrons. Parallel disintegration of the 355 color centers was also observed.

In our opinion, this test confirms the hole nature of the 355 absorption band, since if it were of electron type, with luminescence of the F band, the 355 band would have increased or, at least, remained unchanged, as was observed in the same experiment on the electron 275 band.

In view of this, we are inclined to think that, in the temperature range 180–200° K, the first of the above-mentioned possible mechanisms of the relaxation process is operative and that the first TL peak is of electron type.

In the temperature range 220–270° K, where TL peak II appears, disintegration of the 355 centers as well as of the 465 and 720 color centers occurs. If it is assumed that the 355 band corresponds to hole color centers, then the processes occurring in the temperature range indicated can be described in at least one of the following ways:

1. During thermal disintegration of the F and M electron centers, the electrons liberated recombine with the holes that are localized at the 355 centers, and this leads also to a reduction in the absorption in the 355 band.

2. During thermal disintegration of the 355 hole centers, the free holes that are formed recombine with the electrons localized at the F and M centers, and this leads to a reduction of the F and M bands in the same temperature range (see also [10]).

A final decision as to which of the two mechanisms is operative in the crystal in the temperature range in question requires additional, more direct experiments to be made to determine the sign of the free charges that participate in the recombination process (for example, by the method of exoelectron emission).

The above facts can be interpreted from the point of view of the concepts of an ion mechanism of disintegration of color centers that have recently been developed by the authors [5, 6, 11, 12, 16].

The concept of an ion type of disintegration of the F, M, and 355 color centers in the temperature range where the thermoluminescence peaks I and II appear agrees also with certain other experimental data of ours.

If the NaCl-Ag crystal is irradiated with X-rays at 290° K, absorption bands with λ_m = 355, 465, 620, and 720 mμ appear in the spectral region 300–800 mμ. If, then, after irradiation has ended, the excited crystal is cooled to 150° K, the absorption spectrum is essentially unchanged. This points to the fact that when the crystal is cooled, the properties of the color centers remain as before. The TL curve of such a crystal, however, as compared with the TL curve of a crystal excited at T_{ex} = 130° K, is markedly changed (Fig. 1a, curve 3): peaks I and II at T_m = 190 and 250° K are greatly reduced in size relative to high-temperature peaks III and IV, while with ordinary plotting of the TL curve (Fig. 1a, curve 1), the strengths of the peaks are inversely proportional. The absolute values of the strengths of TL peaks I and II are also sharply reduced (see curves 1 and 3).

The TD curve for the F centers of a crystal that has been subjected to repeated preliminary heat and radiation treatment and excited at 150° K differs greatly (see curve 3, Fig. 1c) from the corresponding TD curve for a freshly cut crystal (curve 1, Fig. 1c). The rise in the 190° K range and also the fall in the 250° K range are much less marked in curve 3 than in curve 1. The principal decay $\Delta\chi_{465}(T)$ in this case occurs at 410° K.

The excited-absorption spectra in the region of the F, M, and 355 bands with excitation of the NaCl-Ag phosphor at 150° K and 290° K were identical. This indicates that the color centers of each type are the same for high-temperature and low-temperature excitation. Moreover, the disintegration of these centers, as can be seen from Fig. 1b and c (curves 1 and 2), occurs in quite different temperature ranges, depending upon the excitation temperature of the phosphor.

Thermal disintegration of the F and 355 color centers created at 290° K, just as of those created at 130° K, is accompanied by luminescence (Fig. 1a, TL peak IV, curve 2).

The experimental material presented above indicates that, over a wide temperature range (150–500° K), such factors as the stability of the color centers and the temperature ranges in which the color centers participate most actively in the relaxation processes (in particular, in the generation of luminescence) are determined chiefly not by the nature of the centers themselves, but by the nature of the crystal lattice as a whole and especially by that of the ion environment near these centers [17, 18]. Depending upon the excitation conditions, color centers of the same nature can participate in relaxation processes at different temperatures.

Comparison of the results examined above with the thermoluminescence emission spectra in Fig. 2 makes it possible to obtain additional information about the mechanism of formation of recombination luminescence. As is apparent from Fig. 2, the emission spectrum in thermoluminescence varies in the NaCl-Ag phosphor after both low-temperature and high-temperature excitation. This variation consists of the spectrum becoming more complex as the temperature rises and also of a certain redistribution of the intensities among the emission bands during the relaxation process. The intensity redistribution in the thermoluminescence emission spectra can be studied in more detail by investigating the "flare up" of certain emission bands from the data in Fig. 2. Figure 3 shows the spectral curves of thermoluminescence obtained in this way for various spectral emission ranges: 515, 440, 410, 375, and 325 mμ.

From the data presented, it can be seen that the ratio of the strengths of the emission bands at each TL peak differs after both low-temperature and high-temperature excitation of the phosphor crystal.

Data characteristic of the various relative strengths of the emission bands at different stages of thermoluminescence after excitation of the crystal at 90° K are shown in Table 2.

From the table, it is apparent that within the limits of each of the four TL peaks, the "contribution" to emission introduced by each band is different; this "contribution" varies on passing from one peak to another. The results indicate that several types of emission centers take part in recombination luminescence in this particular phosphor. In each temperature range, these centers are characterized by a different relative number of emitted quanta (see Table 2), and also by a different radiation efficiency at various stages of thermoluminescence (see Fig. 3).
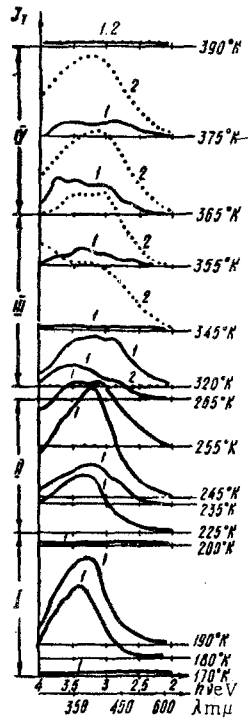
Fig. 2. Emission spectra
for thermoluminescence of
NaCl-Ag phosphor excited
at: 1) $T_{ex} = 0°$ K, 2) $T_{ex} =$
$= 290°$ K. Measurement of
the spectra was begun from
the excitation temperature
of the phosphor. Designa-
tions I–IV correspond to the
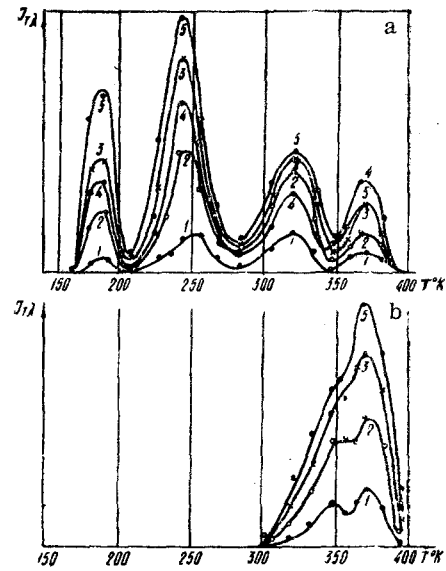numbering of the thermolumi-
nescence peaks in Fig. 1.

Fig. 3. Thermoluminescence of
NaCl-Ag phosphor for various
spectral intervals of emission at
various excitation temperatures:
a) $T_{ex} = 90°$ K, b) $T_{ex} = 290°$ K;
1) 515 mμ, 2) 440 mμ, 3) 410 mμ,
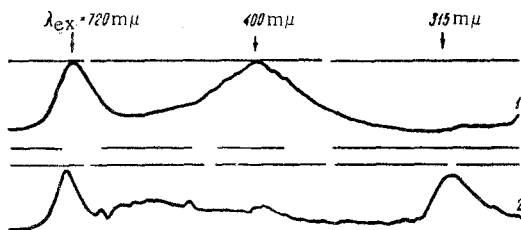4) 325 mμ, 5) 375 mμ.

Fig. 4. Oscillogram of emission spectrum
of NaCl-Ag phosphor photostimulated in
the M band ($\lambda_m = 720$ mμ) at various exci-
tation temperatures: 1) $T_{ex} = 180°$ K, 2)
$T_{ex} = 290°$ K. Measurements of spectra of
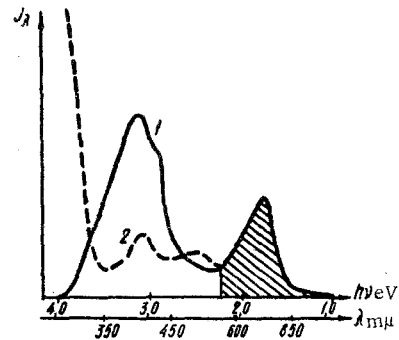were made at the corresponding excitation
temperature.

Fig. 5. Emission spectra of NaCl-Ag
phosphor on photostimulation of emis-
sion in the M band (720 mμ): $T_{ex} =$
$= 180°$ K, $T_{ex} = 290°$ K. The shaded
area corresponds to the stimulated light
from the spectral region of the M band
that has disintegrated into the spectrum.

It is interesting to compare the emission spectra of photostimulated luminescence with the above thermoluminescence emission spectra. Emission spectra of photostimulated luminescence taken at T_{ex} = 180 and 290° K and measured with a recording spectrophotometer are shown in Fig. 4. Figure 5 shows the same spectra after corrections had been made for the dispersion of the monochromator and the spectral sensitivity of the photomultiplier.

Table 2

$T°$ K	$\dfrac{I_{515}}{I_{373}}$ %	$\dfrac{I_{510}}{I_{375}}$ %	$\dfrac{I_{410}}{I_{375}}$ %	$\dfrac{I_{375}}{I_{375}}$ %	$\dfrac{I_{325}}{I_{375}}$ %
190	8 0	32.5	61.0	100	48.5
245	1.5	46.5	83.5	100	67.5
320	32.5	82.5	95	100	65
370	22	56.5	100	100	136

From Fig. 5 (1), it can be seen that, with low-temperature excitation of the crystal, at the maximum of the M band, luminescence is generated in the spectral range 500–300 mμ with the principal maximum at λ_m = 400 mμ. The emission is of the recombination kind and of an electron nature, since it is due to the photothermal release of electrons from the M centers. Comparison of the emission spectrum of photostimulated luminescence with the thermoluminescence emission spectrum at the same temperature of 180° K (see Fig. 2) shows good agreement. Such agreement of the emission spectra confirms the conclusion reached above about the electron nature of the relaxation processes during thermoluminescence in the region of TL peak I (180–200° K). Similar agreement between the form of the emission spectrum of photostimulated luminescence in the electron M band and the thermoluminescence emission spectrum at ~300°K (Fig. 5, curve 2, and Fig. 2) points to the electron nature of thermoluminescence at room temperatures as well. Since the disintegration of various color centers in the low-temperature range evidently takes place by an ion mechanism, as was indicated above, recombination luminescence caused by this disintegration, over a wide temperature range, is due to ion-electron and also probably to ion-hole processes that occur in the lattice of the phosphor crystal.

The material of the present paper again confirms (see also [13–15]) the necessity and importance of taking into account ion processes in studying the mechanism of recombination luminescence of alkali-halide phosphor crystals over a rather wide temperature range, including comparatively low temperatures.

REFERENCES

1. A. Halperin, N. Kristianpoller, and A. Ben-Zvi, Phys. Rev., 116, 1081, 1959.
2. I. K. Vitol, Ch. B. Lushchik, and I. V. Yaek, Trudy IFA AN EstSSR, 12, 175, 1960.
3. V. P. Chernenko, F. N. Zaitov, and Yu. L. Lukantsever, Optika i spektroskopiya, 15, 86, 1963.
4. Yu. L. Lukantsever, Dissertation, Tomsk, 1959.
5. F. N. Zaitov, Trudy IFA AN EstSSR, 15, 138, 1961.
6. Yu. L. Lukantsever and F. N. Zaitov, Izv. AN SSSR, ser. fiz., 25, 473, 1961.
7. W. Dnerig and I. Markham, Phys. Rev., 88, 1043, 1952.
8. I. Markham and R. Platt, Phys. Rev., 92, 597, 1953.
9. I. V. Yaek and M. F. Okk, Trudy IFA AN Est. SSR, 21, 96, 1962.
10. P. A. Khellenurme, Author's abstract of dissertation, Tartu, 1961.
11. F. N. Zaitov and V. Ya. Kark, Trudy IFA, AN EstSSR, no. 6, 82, 1957.
12. F. N. Zaitov and Yu. L. Lukantsever, collection: Physics of Alkali-Halide Crystals [in Russian], Riga, 216, 1961.
13. M. A. Elango, Trudy IFA AN EstSSR, 21, 215, 1962.
14. Yu. L. Lukantsever and F. N. Zaitov, Izv. AN SSSR, ser. fiz., 25, 47, 1961.
15. I. A. Parfianovich, E. N. Shuraleva, and. V. G. Krongauz, Optika i spektroskopiya, 14, 513, 1963.
16. F. N. Zaitov, Uchenye zapiski Oshskogo gospedinstituta, no. 5, 1963.
17. V. I. Sidlyarenko, F. N. Zaitov, and Yu. L. Lukantsever, Optika i spektroskopiya, 13, 143, 1962.
18. V. I. Sidlyarenko, Yu. L. Lukantsever, and F. N. Zaitov, Izv. vuzov SSSR, Fizika, no. 2, 109, 1963.