COOPERATIVE SENSITIZATION OF THE LUMINESCENCE OF SILVER-HALIDE SALTS AND SPECTRAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

PHYSICS

1967

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

UDC 535.37:548.0

PHYSICS

V. V. OVSYANKIN, Corresponding Member of the Academy of Sciences of the USSR P. P. FEOFILOV

COOPERATIVE SENSITIZATION OF THE LUMINESCENCE OF SILVER-HALIDE SALTS AND SPECTRAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

The phenomenon of cooperative sensitization of luminescence, which we recently discovered in crystalline systems with rare-earth activators ([1]), consists in the possibility of observing the emission of acceptor ions upon excitation in substantially longer-wavelength absorption bands of donor ions. The phenomenon was interpreted as the result of accumulation of the excitation energy of two (or more) donor ions on one acceptor ion, it being assumed that the donor and acceptor ions are in strong interaction caused by overlap of the wave functions of the three (or more) ions participating in the process.

An analogous phenomenon, also apparently connected with accumulation of the energy of electronic excitations, was found by us in observing the action of long-wavelength (red and infrared) light on silver-halide salts and photographic emulsions.

Intense luminescence of silver-halide salts (AgHal), excited in the region of their intrinsic absorption bands and observed at low temperatures, has long been known and has repeatedly been the object of investigation ([2–5]). It turned out that if a layer of dye from among those used as optical sensitizers is adsorbed on the surface of AgHal microcrystals, then, in sharp contradiction to Stokes' law, the luminescence of such a system can be excited not only in the intrinsic absorption bands of AgHal, but also by considerably longer-wavelength light in the sensitizer bands.

Fig. 1. Excitation spectra of AgI luminescence in the region of sensitization by panchromatic dyes giving maxima of optical sensitization of photographic emulsions near 633 mμ (1) and 690 mμ (2). Temperature 77°K.

To obtain the excitation spectrum of the luminescence, the light of an incandescent lamp (ribbon lamp, 200 W) was passed through a red light filter (OS-14 glass) and an MDR-2 monochromator and fell on the sample (a thin powder layer or emulsion layer) placed in a Dewar vessel with liquid nitrogen. The glow was recorded by an FEU-38 photomultiplier through a light filter that eliminated the scattered exciting light and transmitted the short-wavelength bands of luminescence.

In Fig. 1, as an example, are shown the excitation spectra of the luminescence of silver iodide obtained by mixing one-normal solutions of $AgNO_3$ and KI followed by washing with distilled water. Sensitization was carried out by wetting the moist precipitate with alcoholic solutions of panchromatic dyes giving maxima of optical sensitization of photographic emulsions near 633 and 690 mμ. As can be seen, the excitation spectra in the ob–

regions of sensitization are comparatively narrow bands, whose position and shape correspond to the absorption of the dyes used in the adsorbed state. Similar excitation spectra are found for crystals of other AgHal sensitized with the same dyes, in particular for brightly luminescent mixed AgBr–AgI crystals, as well as for panchromatic emulsions (Panchrom-10).

The coincidence of the excitation spectra of the sensitized luminescence with the absorption spectra of the sensitizer indicates that the primary act in the excitation of luminescence by long-wavelength light should be considered the absorption of light by dye molecules adsorbed on the surface of AgHal microcrystals. Rapid migration of the excitation energy through the system of adsorbed molecules makes probable the encounter of two excited states at a distance that ensures the interaction necessary for the cumulation of the energy of electronic excitations with its transfer to levels corresponding to the intrinsic absorption bands of AgHal. Relaxation along these levels rapidly brings the crystal into the lowest excited state, which makes impossible the reverse process—envisaged by Dexter’ s theory (^{6})—of the decay of one excited state into two.

As is known, the intensity of the short-wavelength luminescence bands of AgHal excited in the bands of intrinsic absorption, as also in many other “pure” salts (^{4}), depends nonlinearly on the excitation density ρ, and this dependence can be approximated by the law

$$I \sim \rho^{\gamma},$$

where $1.0 < \gamma < 1.5$. In the case of the samples we studied, AgI + sensitizer, $\gamma = 1.23$. The luminescence intensity of the same samples upon excitation in the absorption band of the sensitizer, over a broad interval of variation of the excitation density, can be described by the same law, with γ changing from 1.45 at small ρ to 1.37 when ρ increases by 2 orders of magnitude.

The closeness of γ for different methods of excitation shows that the mechanism of summation of excitations does not introduce substantial changes into the dependence $I(\rho)$, which is determined primarily by semiconductor processes involving electrons entering the conduction band. In other words, upon excitation through the sensitizer, just as upon direct excitation, the number of electrons entering the conduction band is practically proportional to ρ. It is easy to see that this may be a consequence of the high probability of cumulation of the excitation energy of donors (dye molecules) on the acceptor (AgHal). Indeed, the balance equation for the number of excited states of donors (Fig. 2a) has the form

$$dn_2/dt = B_{12}\rho_{12}n_1 - \tau_2^{-1}n_2 - 2an_2^2.$$

If the number of acts of cumulation of donor energy is much greater than the number of acts of spontaneous deactivation ($an_2^2 \gg \tau_2^{-1}n_2$), then under stationary conditions the number of excitations created in the AgHal lattice per unit time will be equal to $an_2^2 = \frac{1}{2}B_{12}\rho_{12}N$ ($N \approx n_1$), i.e., will depend linearly on the excitation intensity. Conversely, if $\tau_2^{-1}n_2 \gg an_2^2$, then $an_2^2 = aB_{12}^2\rho_{12}^2N^2\tau_2^2$, i.e., the dependence proves to be quadratic.

On the other hand, one may assume that the linearity of the processes leading to excitation of the AgHal crystal lattice is fundamental in character, and attempt to explain the phenomenon of excitation with an anomalously large Stokes shift in a manner similar to that done in (7) to explain the mechanism of optical sensitization of photographic emulsions, assuming that the deficiency of the energy of the absorbed

the quantum is compensated by the vibrational energy of the molecule. One could also make use of the mechanism of optical sensitization proposed in (8) or (9), and assume that the deficiency of energy is borrowed from the AgHal lattice. Temperature experiments may serve as a criterion for the admissibility of these assumptions. Deep cooling of the specimens should completely suppress the effects in the case where the missing energy is drawn from thermal energy. The experiments we carried out showed that at 4.2°K the intensity of the glow of specimens (AgJ+ panchromatic sensitizer, Infrachrome-920 film, etc.) not only does not decrease but, on the contrary, increases, in some cases by several orders of magnitude (Infrachrome-920). This result unequivocally testifies to the untenability of assumptions about the thermal nature of the coverage of the energy deficit.

Fig. 2. Schemes of accumulation of excitation energy of the donor D (dye-sensitizer) in the conduction band of AgHal. *a*—direct transfer of excitation into the band; *b*—transfer of energy to intermediate AgHal levels with subsequent accumulation.

Accumulation of the excitation energy of donor-sensitizers, with its transfer to the conduction band of the acceptor (AgHal), can evidently explain not only the completely reversible luminescence process observed upon excitation in the

Fig. 2. Schemes of accumulation of excitation energy of donor D (dye-sensitizer) in the conduction band of AgHal. *a*—direct transfer of excitation to the band, *b*—transfer of energy to intermediate AgHal levels with subsequent accumulation

Figure 2: Fig. 2. Schemes of accumulation of excitation energy of donor D (dye-sensitizer) in the conduction band of AgHal. *a*—direct transfer of excitation to the band, *b*—transfer of energy to intermediate AgHal levels with subsequent accumulation

absorption bands of the sensitizer, but also the phenomenon of optical sensitization of photographic emulsions (see, for example, (10)), since luminescence and photolysis of silver halide may be regarded, to a certain extent, as alternative processes. Lowering the temperature sharply decreases the photosensitivity of emulsions, while luminescence flares up. The phenomenon of sensitization of photoconductivity upon adsorption of dye molecules (see, for example, (11)), as well as, possibly, other photophysical and photochemical processes associated with sensitization, may be explained just as naturally.

We were able to observe the visible glow of silver-halide salts and photographic emulsions, excited by long-wavelength light, also in the case where they contained no sensitizer; however, in these cases the glow was several orders of magnitude weaker. This is in full agreement with the presence of weak photosensitivity in unsensitized emulsions in a region far from the maximum of their intrinsic sensitivity. The possibility of two-quantum excitation of the luminescence of "pure" AgHal and the presence of intrinsic long-wavelength sensitivity make it possible to propose another variant of the mechanism of accumulation of donor-

···(Fig. 2b), differing from the one considered in that the accumulation of energy occurs through the interaction not of the levels of sensitizer molecules, but of hypothetical levels responsible for the long-wavelength photosensitivity of AgHal and populated by ordinary sensitization.*

It should be noted that analogous phenomena of cooperative sensitization of luminescence were observed by us not only in silver halide salts, but also in a number of others (TlCl, HgJ_2, PbJ_2). When treated with a solution of the sensitizing dye, these salts acquire the ability to luminesce upon excitation in the region of the dye absorption bands, substantially more long-wavelength than the edge of their own absorption.

Received
4 II 1967

References Cited

[1] V. V. Ovsyankin, P. P. Feofilov, *Pis' ma ZhETF*, **4**, 471 (1966).
[2] J. T. Randall, *Nature*, **142**, 113 (1938); *Proc. Roy. Soc.*, **170**, 272 (1939).

[3] V. A. Arkhangel' skaya, P. P. Feofilov, *DAN*, **91**, 1055 (1953).

[4] V. A. Arkhangel' skaya, P. P. Feofilov, *DAN*, **108**, 803 (1956); *J. Phys. et Radium*, **17**, 824 (1956); *Optics and Spectroscopy*, **2**, 107 (1957).

[5] S. I. Golub, *Luminescence of Silver Halides*, Doctoral dissertation, Odessa, 1965.

[6] D. L. Dexter, *Phys. Rev.*, **108**, 630 (1957); **126**, 1962 (1962).

[7] P. V. Meyklyar, B. I. Stepanov, *DAN*, **54**, 799 (1946); *ZhFKh*, **20**, 17 (1947).

[8] J. Frank, E. Teller, *J. Chem. Phys.*, **6**, 861 (1938).

[9] R. W. Gurney, N. F. Mott, *Proc. Roy. Soc.*, **1964**, 151 (1938).

[10] K. Mees, *The Theory of the Photographic Process*, Moscow–Leningrad, 1949; A. N. Terenin, *Photochemistry of Dyes*, Izd. AN SSSR, 1947; Yu. N. Gorokhovskii, *Spectral Studies of the Photographic Process*, Moscow, 1960; E. Klein, R. Matejec, *Agfa Mitt.*, **4**, 16 (1965).

[11] I. A. Akimov, in: *Elementary Photoprocesses in Molecules*, "Nauka," 1966, p. 397.

[12] D. L. Rousseau, G. E. Leroi, G. L. Link, *J. Chem. Phys.*, **42**, 4048 (1965).

* Apparently, the decomposition of AgCl under the action of ruby-laser radiation observed in [12] should also be regarded as the result of energy accumulation on real, and not virtual, levels, as the authors assume.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.