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TRANSFER OF EXCITATION FROM THE CRYSTAL LATTICE TO RARE EARTH IONS

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We have experimentally confirmed the possibility of efficient transfer of excitation energy from the crystal lattice to activator ions. We present the results of a study of energy transfer from the uranyl cesium tetrachloride lattice to rare earth ions. It is shown that an essential role in this transfer is played by migration of uranyl ion excitation along the crystal lattice.

ONE of the means of sensitizing luminescence is the transfer to activator ions of energy absorbed by the crystal lattice. This type of sensitization is extremely important in crystalline phosphors, where the energy transfer is accompanied by transfer of charge.

In the case of rare earth activators, where the luminescence is due to f-electrons, this energy transfer mechanism is impossible and therefore the process of energy transfer without charge transfer—nonradiative transfer and reabsorption of luminescence—is important.

A number of papers have been published, devoted to luminescence of rare earths in tungstates and molybdates,[1] in which the authors observed radiationless energy transfer from the lattice to activator ions in excitation of the lattice in the fundamental absorption band in the ultraviolet part of the spectrum. However, a detailed study of this phenomenon has not been carried out.

We can compare the efficiency of sensitization from the lattice with the sensitization of the ion-ion type, assuming that the activator-lattice interaction is equivalent to interaction of a sensitizer-activator pair with increase of the sensitizer concentration to 100 mol. %. This is an extremely crude approximation, which neglects the collective properties of the ions in the lattice.

The energy transferred in interaction of a pair of ions, according to Dexter,[2] is

$$E_{\mathrm{tr}} = E_{\mathrm{abs.sen}} \eta_{\mathrm{sen}} P_{\mathrm{tr}} ,$$

where the energy transfer probability P_{tr} is written in the semiclassical approximation as

$$P_{\mathrm{tr}} \sim \frac{\Omega' M_{\mathrm{sen}} M_{\mathrm{act}}}{\Omega_{\mathrm{sen}} \Omega_{\mathrm{act}} \hbar^2 R^m} .$$

Here η_{sen} is the quantum yield of the sensitizer; M_{sen} and M_{act} are the dipole moments of the ions; for a dipole-dipole interaction $m = 6$; for a dipole-quadrupole interaction $m = 8$; Ω_{sen} is the width of the luminescence line of the sensitizer; Ω_{act} is the width of the absorption line of the activator; Ω' is the amount of overlap of the spectra Ω_{sen} and Ω_{act}; and R is the average distance between ions.

For sensitization from the lattice $R = R_{\mathrm{min}}$, which is determined by the lattice constants, and the ratio $\Omega'/\Omega_{\mathrm{sen}}\Omega_{\mathrm{act}}$ approaches a maximum, since the luminescence of the lattice is broad-band. If the absorption bands of the sensitizer ion are weak, the increase of concentration also has a favorable effect on the absorption depth.

To study energy transfer from the lattice it is convenient to select luminescent crystals with their fundamental absorption in the visible region. We expected that crystals of the compounds of hexavalent uranium would be suitable subjects for study of lattice sensitization, since in the energy spectrum (see Fig. 1) of the uranyl complex $[\mathrm{UO}]^{2+}$,

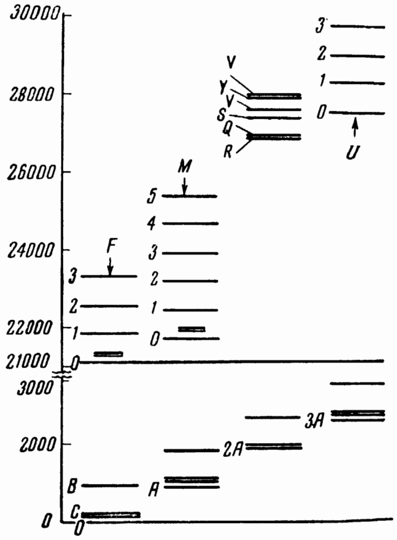

FIG. 1. Energy spectrum of the uranyl complex in the crystal $Cs_2[UO_2(NO_3)_3]$ according to Dieke and Duncan.[7]

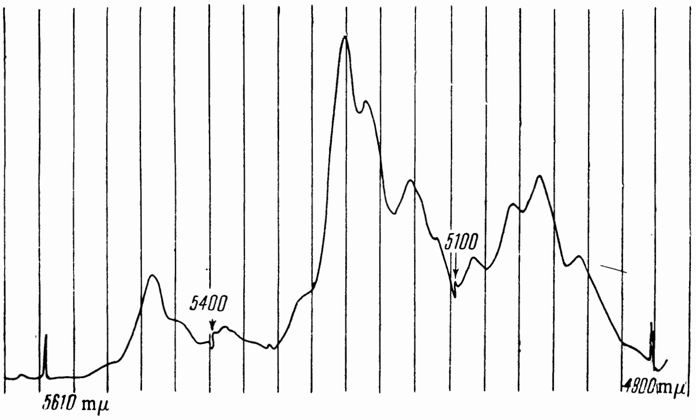

FIG. 2. Luminescence spectrum of $Cs_2[UO_2Cl_4]$ crystal.

beginning at 5000 Å, dense, wide bands of excited states are observed, connected with electronic transitions.

The luminescence of uranyl is well known to be very broad-band and lies in the convenient yellow-green region.

The nature of the absorption and luminescence spectra of uranyl compounds is such that we would expect energy transfer to ions of most rare earths, in which the pumping levels are located above 5600 Å (the red limit of the intense luminescence bands of $[UO_2]^{2+}$) and the metastable levels do not fall in the uranyl absorption band.

According to the quantum theory of solids, for crystals in which the uranyl complexes are sufficiently close together, we would expect overlapping of the molecular wave functions and the possibility of energy migration in the form of Frenkel excitons. The more compact the crystal structure, the greater the number of allowed directions of migration.[3,4] It is obvious that in such crystals the absorption and luminescence bands must be broadened.

For the investigations we selected anhydrous crystals of the compound $Cs_2[UO_2Cl_4]$, whose structure, according to preliminary data, is identical to the structure of $Cs_2[UO_2Br_4]$, which was studied by Mikhaĭlov et al.[5]

The luminescence and absorption spectra of these compounds measured by us (Fig. 2) do not differ appreciably from those given in the monographs of Levshin[6] and Dieke and Duncan.[7] The excitation spectrum of lattice luminescence corresponds to the structureless absorption spectrum observed in samples thicker than 2—3 mm.

The sensitization of rare earth ions by the lattice was studied in polycrystalline samples of uranyl cesium tetrachloride activated by rare earths (not including Ce and Gd) with a concentration of 0.1—0.5 mol. %. We have recorded the luminescence spectra and the excitation spectra, and measured the lifetimes.

Similar observations made on single crystals with Nd and Eu additives showed that they were completely identical to the luminescence in monocrystalline samples.

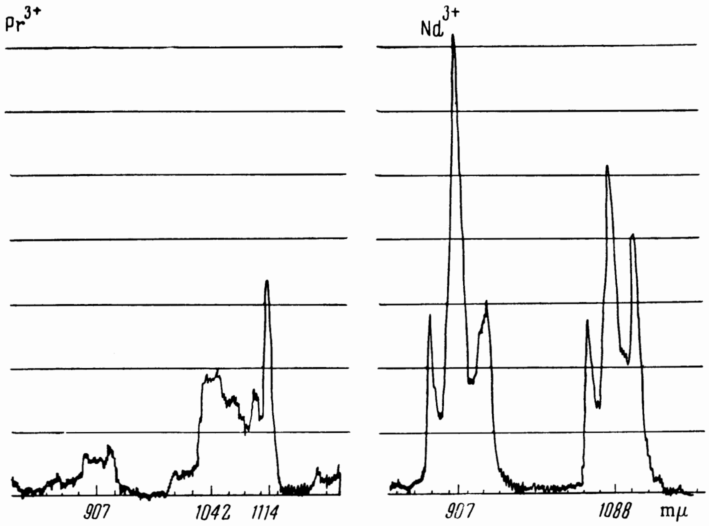

FIG. 3. Luminescence spectrum of Pr^{3+} and Nd^{3+} in a $Cs_2[UO_2Cl_4]$ crystal.

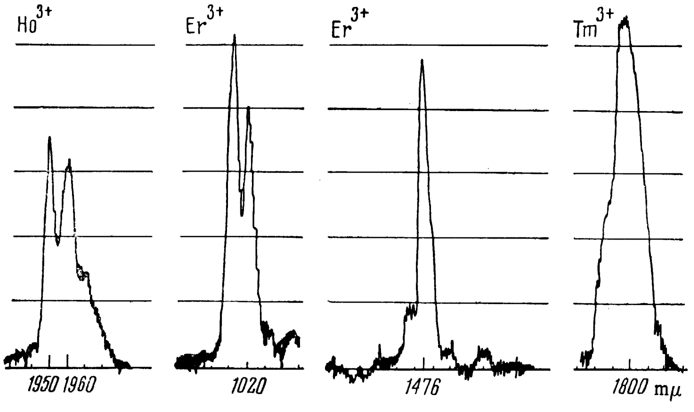

FIG. 4. Luminescence spectrum of Ho^{3+}, Er^{3+}, and Tm in a $Cs_2[UO_2Cl_4]$ crystal.

The luminescence was excited both directly in the excitation bands of the ions themselves and through excitation of the lattice. The luminescence spectra (Figs. 3—5) correspond to the spectra of triply charged rare earth ions.

Pr, Nd, Eu, Ho, Er, and Tm luminesce strongly; Sm is somewhat weaker; no luminescence of Tb and Dy was observed. Luminescence of Yb in the IR region is observed only on pumping in the ion absorption band (910-980 mμ).

It should be noted that the yellow-orange lines of Sm and Eu overlap the broad-band luminescence of uranyl, and are separated on the basis of the shape and width of the lines.

The excitation spectra of Pr, Nd, and Eu (Fig. 6) are identical in nature and differ only in the fine structure due to the absorption lines of the activator ions.

The structure in the excitation spectrum of Sm is not resolved, as the result of the weak luminescence of the sample.

The excitation spectra of Er, Ho, and Tm were not recorded. However, the presence of bright luminescence on excitation through interference filters at wavelengths of 410, 440, and 460 mμ and the absence of luminescence on excitation through filters at 520 and 588 mμ gives a basis for suggesting that the excitation spectra of Er, Ho, and Tm do not differ from those measured.

The excitation spectra show the existence of efficient energy transfer from the lattice to the activator ions. Luminescence excited indirectly through lattice pumping is much more intense than in pumping directly in the absorption band of the ions.

The energy transfer is accompanied by appreciable shortening of the lifetime of the excited state of uranyl, which indicates a radiationless transfer mechanism. Thus, while the lifetime of a pure single crystal is 4.5×10^{-4} sec, on introducing 0.5% of $EuCl_2$ into the crystal it falls to 2×10^{-4} sec. $NdCl_3$ concentrations of 0.05, 0.1, and 0.15% result in uranyl lifetimes (in units of 10^{-4} sec) of 3.4 ± 0.1, 2.4 ± 0.1, and 1.8 ± 0.1.

In explaining the transfer mechanism we must take into account that: 1) the shortening of the uranyl excited state lifetime indicates the radiationless nature of the transfer; 2) the lifetimes of

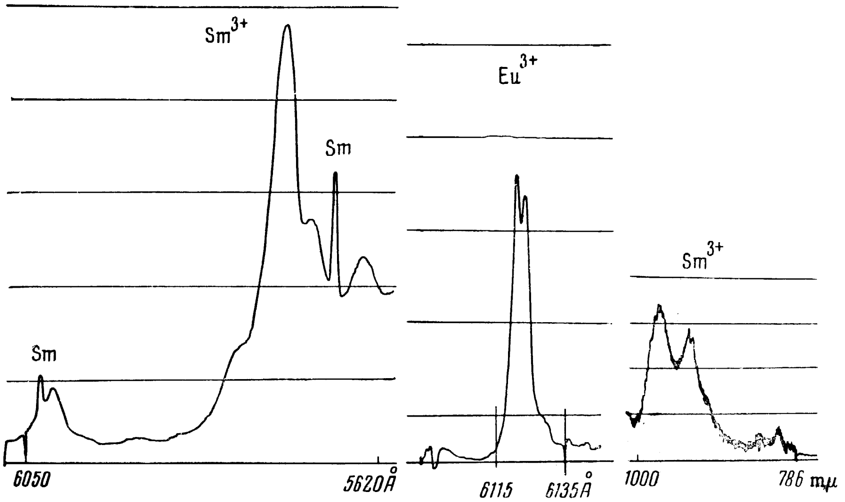

FIG. 5. Luminescence spectra of Sm^{3+} and Eu^{3+} in a $Cs_2[UO_2Cl_4]$ crystal.

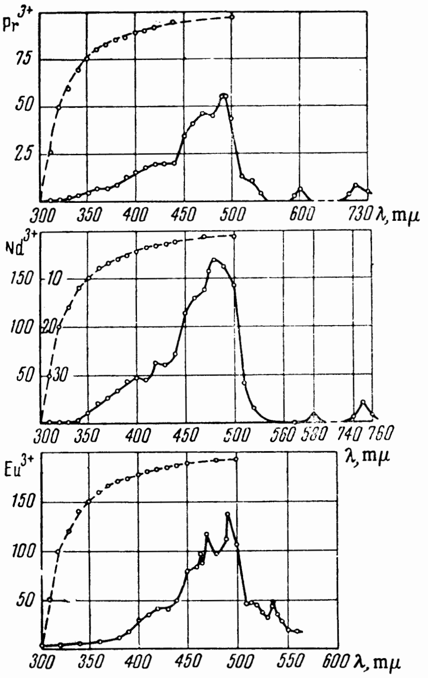

FIG. 6. Excitation spectra of Pr^{3+}, Nd^{3+}, and Eu^{3+} in a $Cs_2[UO_2Cl_4]$ crystal; the dashed line shows the intensity of the exciting radiation.

the excited state of the activators being discussed are roughly an order of magnitude larger than for uranyl and do not depend on the means of excitation of the activator (experimental accuracy 10%);

3) the excitation transfer time between neighboring uranyl complexes, determined by Dexter[8] for weakly resolved dipole transitions without inclusion of collective effects, is of the order of 10^{-11} sec;

4) the lifetime of the uranyl excited state is 4.5×10^{-4} sec, and radiationless transitions inside the uranyl absorption bands occur in a time not greater than 10^{-7} sec.

It follows from (3) and (4) that the range of an exciton, before equilibrium is reached with the lattice, can reach 10^4 lattice constants.

Energy transfer to the activator occurs in the scattering of the exciton by the activator. The high mobility and large mean free path of the exciton provide efficient sensitization. Some contribution to the sensitization can also be given by other effects (for example, reabsorption of radiation).

The identical nature of the excitation spectra of the activators and the absence of energy transfer to Yb are obtained as consequences of the sensitization mechanism proposed.

Thus, in the example considered we have shown a high efficiency of energy transfer from the lattice to the activator.

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[1] L. G. Van Uitert, R. R. Soden, and R. C. Linares, J. Chem. Phys. **36**, 1793 (1962).

[2] C. C. Klick and J. H. Schulman, Solid State Phys. **5**, 130 (1957).

[3] C. Kittel, Introduction to Solid State Physics, 2d ed., New York, Wiley, 1956. Russian translation, 1963.

[4] A. I. Ansel'm, Vvedenie v teoriyu poluprovodnikov (Introduction to the Theory of Semiconductors), Moscow, 1962.

[5] Yu. M. Mikhaĭlov, V. G. Kuznetsov, and E. G. Kovaleva, Zhurnal strukturnoĭ khimii **6**, 787 (1965).

[6] V. L. Levshin, Fotolyuminestsentsiya zhidkikh i tverdykh veshchestv (Photoluminescence of Liquid and Solid Materials), Gostekhizdat, 1951.

[7] G. H. Dieke and A. B. Duncan, Spectroscopic Properties of Uranium Compounds, McGraw Hill, New York, 1949.

[8] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

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