

theoretical analysis. After emerging from the crystal, the beams diverge rapidly (Fig. 2c).

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EMISSION OF CHARGED PARTICLES FROM A SOLID SURFACE ON WHICH A CHEMICAL REACTION TAKES PLACE

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It is known that when free atoms or radicals recombine from the gas phase on the surface of a solid, the recombination energy leads to different electronic excitations in the solid and is accompanied by luminescence (radical-recombination luminescence - RRL [1]). Effects of this kind include also the excitation of the luminescence of a solid at the expense of the energy released by chemisorption on the surface of molecules or atoms (adsorption luminescence [2]).

The yield of luminescence of this kind (which we shall call heterogeneous chemoluminescence) is low and amounts to 10^{-3} - 10^{-8} photons per elementary chemical act [1, 2]. It is clear that there are energy-release channels other than luminescence. One of them is excitation of phonons, corresponding to heating of the crystal surface. Another possible way is the transfer of chemical energy, particularly the recombination energy of the atoms, to impurities on the surface or in the region adjacent to the surface. This can lead to desorption of these impurities, to dissociation of the adsorbed molecules, and even to detachment of the crystal-lattice components from the surface. If the impurity is on a charged surface, then desorption of ions can be expected. In other words, ion emission can appear during the course of the chemical reaction in this case. The emitted charged particles can also be produced in the elementary chemical-reaction acts themselves.

Finally, as is clear from the existence of heterogeneous chemoluminescence, the chemical can be transferred to the electrons of the solid, and if the transferred energy exceeds the work function of the electron, the appearance of electron emission can be expected.

The present investigation was aimed at experimentally observing the emission of charged particles from a surface during the course of a heterogeneous chemical reaction of atom recombination.

Powdered samples (the luminors ZnS:Mn, CaSO₄:Eu, and others) were deposited in the form of a film on a metallic substrate by precipitation from an alcohol suspension, and placed in an evacuated volume, where their surface could be purified by heating in hydrogen with subsequent outgassing in high vacuum. The free hydrogen or oxygen atmos, with thermal energies, diffused from the region of the high-frequency discharge in the molecular gas towards the sample, on which they recombined (pressure ~0.1 Torr, diffusion path ~0.5 m). A voltage 0 - 25 V of suitable polarity was applied between the sample and the collector. The emission current was registered by a U1-2 dc amplifier (sensitivity 10⁻¹⁴ A). An electric filter prevented the charged particles from passing from the discharge region to the sample. The radical-recombination luminescence was registered with a photomultiplier simultaneously with the emission.

Heating of a freshly deposited sample after turning on the discharge in hydrogen usually led to the appearance of strong currents of negative particles (up to 10⁻¹⁰ A) and positive particles (up to 10⁻¹² A). The heating with the discharge turned off was not accompanied by emission. After the aforementioned surface purification, the emission decreased by several orders of magnitude and the luminescence intensity increased. This initial emission is undoubtedly due to the fact that the atomic hydrogen has chemically removed from the surface the absorbed impurities, particularly oxygen and alcohol. The emitted negative particles can in this case be the ions H₂O⁻. The positive-particle emission may be due to the ions C₆H₅OH⁺.

After treatment in atomic hydrogen and vacuum, emission of both negative and positive particles is observed, but the nature of this emission is different.

Under constant experimental conditions (temperature, pressure), stationary emission persists for a long time. The stationary value of the emission is established several minutes after the atoms are "turned on." The kinetics of the radical-recombination emission (RRE) and of the luminescence (RRL) for the ZnS:Mn sample are shown in Fig. 1. The kinetic behavior of the RRE and RRL is obviously connected with the slow adsorption-caused processes on the surface

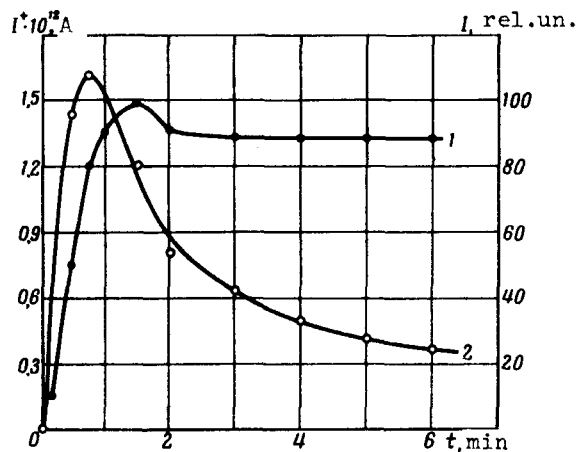


Fig. 1

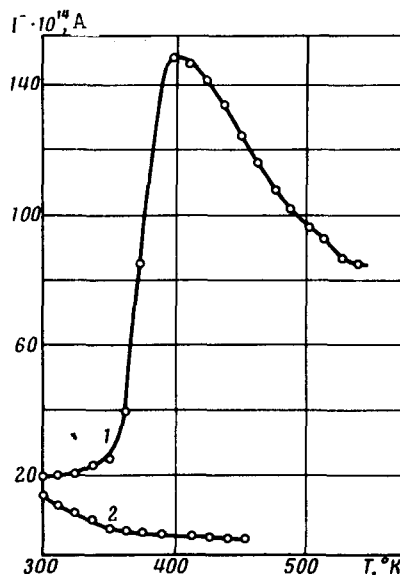


Fig. 2

Fig. 1. Growth kinetics of emission (curve 1) and of luminescence intensity (curve 2) of ZnS:Mn.

Fig. 2. Temperature dependence of the emission of CaSO₄:Eu: 1) discharge turned on, 2) discharge turned off.

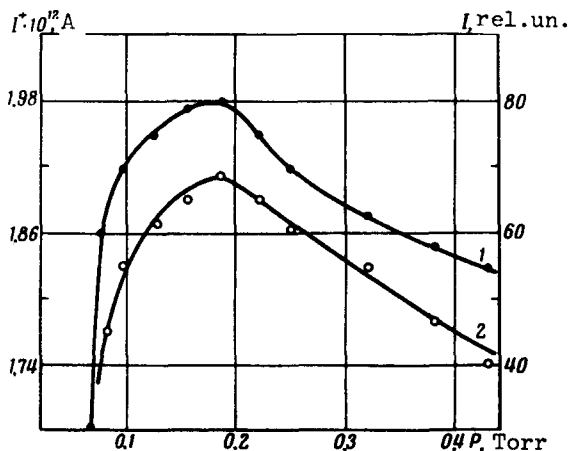


Fig. 3. Dependence of emission (curve 1) and luminescence intensity (curve 2) on the hydrogen pressure for ZnS:Mn.

too small a PPA the RRL intensity is proportional to the PPA [1], it can be concluded that the RRE intensity is also proportional to the PPA. This offers direct evidence that the cause of the RRE is recombination of the atoms on the surface.

The RRE in atomic oxygen is similar in general outline to that in atomic hydrogen, although it has its own distinguishing features.

Summarizing, we can conclude that the totality of the obtained experimental data, viz., the lack of emission when there are no atoms over the sample, the proportionality of the emission intensity to the PPA, the strong dependence of the RRE on the sample temperature, the differences between the RRE characteristics of different solids and even of different impurities in the same solid, and the influence exerted on the RRE by prior processing of the sample, all offer evidence of the existence of emission due to the chemical energy of the reaction occurring on the surface of the solid. It can be assumed that an analogous effect occurs also in the case of adsorption.

The purpose of the present article is not a detailed discussion, but only to report a new physical phenomenon. We note that the positive RRE may be due to impurities of a solid having a low ionization potential. The most probable carriers of the negative emission are electrons.

The RRE carries information concerning the mechanism of energy exchange between gas atoms and the surface. The RRE phenomenon provides a principle for converting chemical energy into electric energy, and is also of interest as a method for investigating surfaces and surface phenomena.

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