Electron accommodation during hydrogen atom adsorption on a juvenile surface of a zinc sulfide single crystal

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"Electron accommodation" during the adsorption of hydrogen atoms on a juvenile surface of a cleaved zinc sulfide single crystal has been discovered and studied. This accommodation is manifested in adsorption events by an emission of photons in the visible range during the adsorption of the atoms. The basic characteristics of this adsorption emission have been studied. The elementary mechanism for the phenomenon is analyzed.

1. INTRODUCTION

When an atomic particle collides with a solid surface and enters the adsorption potential of the surface, it vibrates one or more times, transferring its excess energy to the solid. Most studies of the relaxation of an excited adsorption bond have considered the energy transfer (accommodation) only to vibrational degrees of freedom of the crystal (e.g., Refs. 1 and 2). If the heat of adsorption is large (on the order of 1 eV), however, and for solids with ordinary Debye temperatures, the amount of energy released is large in comparison with the energy of even the highest-frequency phonons (which is on the order of 10^{-2} eV), so that the exchange of the heat of adsorption with phonons is extremely difficult. In recent years it has been found that the relaxation of the adsorption bond at the surface of a metal[3] and also the accommodation of molecules in the first vibrational level[4,5] occur predominantly by means of conduction electrons rather than phonons. The excitation of these electrons is accompanied by the production of electron-hole pairs in the metal. In insulators and semiconductors, this mechanism is regarded as unlikely because of the low density of conduction electrons. However, recent results have shown that an "electron accommodation mechanism" can compete with the phonon accommodation mechanism at the surfaces of insulators and semiconductors. The relaxation from vibrational states with large quantum numbers in this case involves strongly bound electrons of the crystal, in filled energy bands or at local levels of impurity centers.

Electron accommodation is manifested by the excitation of a nonequilibrium conductivity of the solid during adsorption and by other nonequilibrium electronic effects associated with the production of impurity excitations or electron-hole pairs in the solid (see Refs. 6–8 and the bibliographies there). In luminescent crystals an electronic excitation may lose its energy radiatively, i.e., in an event accompanied by luminescence. Emission in the visible part of the spectrum would require an adsorption energy ~2 eV. The largest heat of adsorption is exhibited by gas particles with unsaturated valence bonds, free radicals. Only one molecular species, the O_2 molecule, with two unpaired electrons (a biradical), is known to be capable of exciting visible luminescence during adsorption.[9] This luminescence, however, is interpreted not as a consequence of the conversion of the heat of adsorption into light but as a result of a radiative release of energy (through adsorption) previously stored in the defective solid.[9] In this case the adsorption serves as the trigger mechanism for relaxation of the solid with the adsorbate from a metastable electronic state to the ground state. Luminescence of this sort might be called "adsorption-stimulated luminescence," to distinguish it from "true" adsorboluminescence, which is due to the heat of adsorption (compare with the photostimulated release of stored light and photoluminescence).

Electron accommodation during adsorption on insulators, possibly accompanied by the emission of photons in the course of the relaxation of an excited adsorption bond, has thus not been discussed in the literature. This problem may be of extremely general importance, since energy dissipation plays an important role in heterogeneous processes (condensation, crystal growth and epitaxy, catalysis, two-dimensional phase transitions, the plasma etching of semiconductors, etc.), and this problem has recently attracted interest in connection with the use of lasers for selectively activating surface processes and in adsorption isotope separation.[2,10]

In this paper we report an attempt to find a new atomic system (other than oxygen) which is capable of exciting visible luminescence upon adsorption, with the ultimate goal of determining how many systems exhibit this accommodation from a deep adsorption potential through electronic degrees of freedom of a crystal which are capable of acquiring much energy. An understanding of the situation would make it possible to choose between the two hypotheses outlined above regarding the nature of the adsorption emission, since the stimulation mechanism would have an obvious "oxygen" nature. At the same time, we would be able to find an answer to the fundamental question of whether a direct conversion of adsorption energy into optical radiation is possible.

2. EXPERIMENTAL RESULTS

Our search for an atomic particle active in adsorboluminescence began with the observation that the gases which exhibit the highest adsorption activity are those which are in a nonequilibrium state, e.g., disassociated gases. From this group we selected atomic hydrogen. The H atom has a single unpaired electron and should be adsorbed particularly tight-

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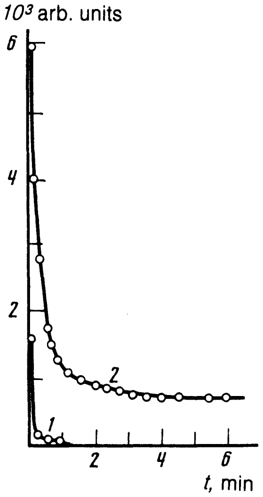

FIG. 1. Kinetics of the emission from the surface from a ZnS–Mn single crystal during cleavage in (1) molecular hydrogen and (2) atomic hydrogen.

ly. To optimize the conditions for adsorption, we "disassociated" not only the gas but also the solid itself, cleaving the crystal in the corresponding gaseous atmosphere.

During the cleavage of ZnS, ZnS–Cu, Zn–Cl, ZnS–Mn, and ZnSe single crystals [the (011) plane] and CdS single crystals (the $11\bar{2}0$ plane) in vacuum or in molecular hydrogen, we observe only a faint glow, which decays rapidly (in 5–10 s; Fig. 1). When the same crystals are cleaved in atomic hydrogen,[1)] in contrast, an intense emission of light is observed, up to 10^{12} photons/(cm^2·s) at a flux density of $j < 10^{18}$ cm^{-2}·s^{-1} to the sample ($100 < T < 380$ K; Fig. 1). The emission then decays comparatively slowly, reaching a steady state after more than 100 s. At the temperature $T = 150$ K, we observe emission from ZnS–Mn with atoms on its surface for more than 6 h, without any sort of decrease in intensity.

A particularly intense yellow-orange glow, in the region 500–800 nm, occurs when the ZnS–Mn single crystal is cleaved in atomic hydrogen. Figure 2 shows the spectrum of this glow. The glow spectra of the other zinc sulfide samples depend on the impurities (Cu^+, Cl^-) or intrinsic defects in them. Cadmium sulfide emits in the orange region. The intensity of the initial flash and of the subsequent decay of these samples was five or ten times lower than that of ZnS–Mn.

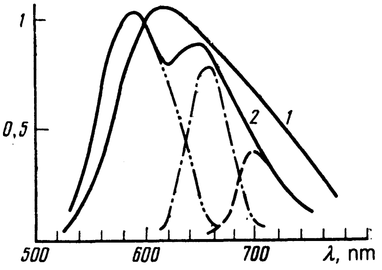

FIG. 2. Emission spectrum of a cleaved ZnS–Mn surface in atomic hydrogen at (1) 100 K and (2) 353 K (the broken lines show a resolution of curve 2 into the elementary bands).

The emission flash and slow decay of the single crystals in atomic hydrogen cannot be explained on the basis of triboluminescence, since the characteristics of the emission in vacuum (or in molecular hydrogen) differ sharply from those during cleavage in atomic hydrogen. Triboluminescence does contribute somewhat to the emission, but only directly during the cleavage and just after (< 1 s); the corresponding points have not been included in the curves shown here.

The kinetics of the emission of the surface, in the form of a flash without a buildup stage (at the macroscopic time scale), which is observed when the surface makes contact with hydrogen atoms, and which is the same for all the samples, shows that this emission is not the adsorboluminescence in atomic hydrogen, AL_H, which has been identified previously. The intensity of the AL_H, which is proportional to the adsorption rate, reaches a maximum at the time $t = 0$, when the surface holds the maximum number of free adsorption electrons. The luminescence is excited as a result of the release of the energy q_1 when hydrogen atoms are adsorbed at vacant centers which appear when the surface is cleaved. According to the data of Ref. 11, the heat of adsorption of the hydrogen atom on ZnO (a compound with properties similar to those of ZnS) is 2.1 eV. At surface defects we could expect an even higher heat of adsorption.

A steady-state glow may occur when chemisorbed atoms recombine with atoms which are incident from the gas phase; this is radical recombination luminescence (RRL_H). The energy release q during the recombination of atoms can be found from the formula $q = D_{H\text{-}H} - q_1 + q_2$, where $D_{H\text{-}H} = 4.48$ eV is the binding energy of the atoms in the free molecule, and q_2 is the heat of adsorption of the H_2 molecule at the center (about 0.3 eV for H_2 on ZnS; Ref. 12). We thus see that q decreases with increasing q_1, so that the AL_H and RRL_H should generally be excited as a result of the energy released at centers of different types, although the same centers (Mn^{2+} in ZnS) may be emitting, as a result of energy transferred to them. Because of the low heat of adsorption of the molecules, after they become adsorbed from the gas phase they will spend only a short time on the surface before they are desorbed; they cannot block the entire surface. The recombination reaction accordingly occurs in a steady state, and the luminescence is observed even at low temperatures (as low as 100 K). The atomic adsorboluminescence, which dominates the emission in the initial stage of the kinetics (during the "flash"), does not disappear even during the steady-state emission, since the recombination reaction continually frees centers for new atomic adsorption events. As a result, when recombinational "cleansing" of the centers takes place, a sort of "prolonged" atomic adsorboluminescence can occur in a steady state[5] (the steady-state value of the ordinary "molecular" adsorboluminescence is obviously zero). The intensity of this prolonged adsorboluminescence is proportional to the number of recombination events per unit time at adsorboluminescence excitation centers.

To determine the mechanisms by which AL_H and RRL_H are excited, we used a time-varying method to study

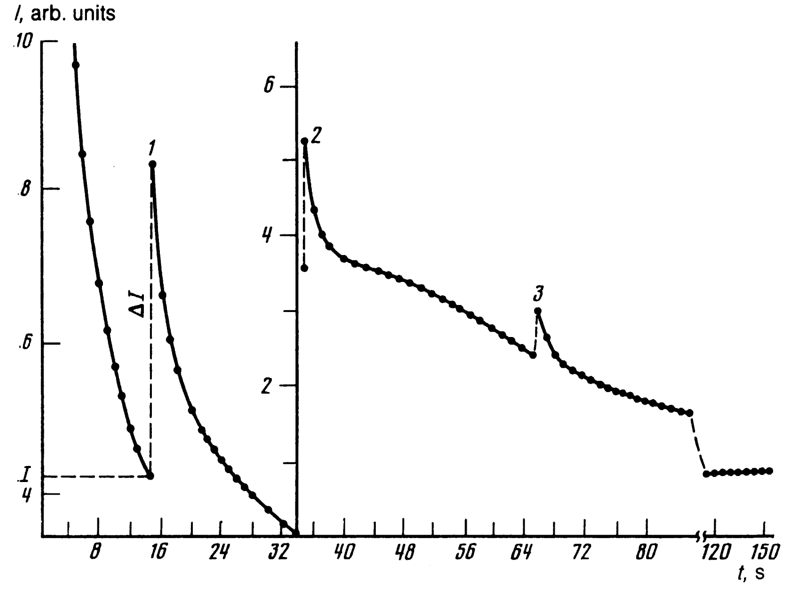

FIG. 3. Relaxation responses of the intensity of the emission from a ZnS-Mn single crystal to abrupt changes in the flux density j of hydrogen atoms during the decay of the emission after the cleavage. 1, 2, 3—flashes corresponding to increases in j by factors of 2, 1.5, and 1.2 ($T = 105$ K).

the responses of this system to sudden changes in the atomic flux density j by an amount Δj. This response is a characteristic of the relaxation of the system to new excitation conditions.

In the study of the AL_H, the jumps Δj were introduced on the descending part of the emission kinetics (Fig. 3), where the AL_H is predominant. When j was increased Δj we observed a luminescence flash of magnitude ΔI above the initial level I, followed by a characteristic decay (with an initial rate higher than before the jump Δj). This unsteady variation in j can be repeated again and again during the decay of the emission after cleavage. For any flash we find $\Delta I/I = \Delta j/j$, and the initial rate of decay of the emission after each flash increases along with an increase in $(dI/dt)_0 \sim j$. These results can be understood quite easily by noting that the intensity of the adsorboluminescence is related to the flux of atoms and to the concentration N of vacant surface centers by the simple relation $I = \alpha jN$ (α is a coefficient), which will be derived in Subsection 3B [see expression (1)].

To obtain information on the mechanism for the RRL_H, we introduce a jump Δj in the steady stage of the kinetics, where we would expect the RRL_H to be present. What we have in mind here is that the RRL_H intensity is related to the atomic flux density j and the surface concentration N_1 of adsorption centers occupied by atoms (not the concentration of vacant centers, as in the case of the adsorboluminescence) by the relation $I = \beta jN_1$ (β is a coefficient), which will be derived in Subsection 4B. For $\Delta j > 0$ (an increase in j), we observe an abrupt increase in the emission, and we find $\Delta I/I = \Delta j/j$ (Fig. 4); this relation holds for both the radical-recombination luminescence and the adsorboluminescence. For a certain time, the emission then decays linearly in time; this linear decay cannot be attributed to radical-recombination luminescence (Subsections 3C and 4C). The decay is a consequence of AL_H and is attributed to

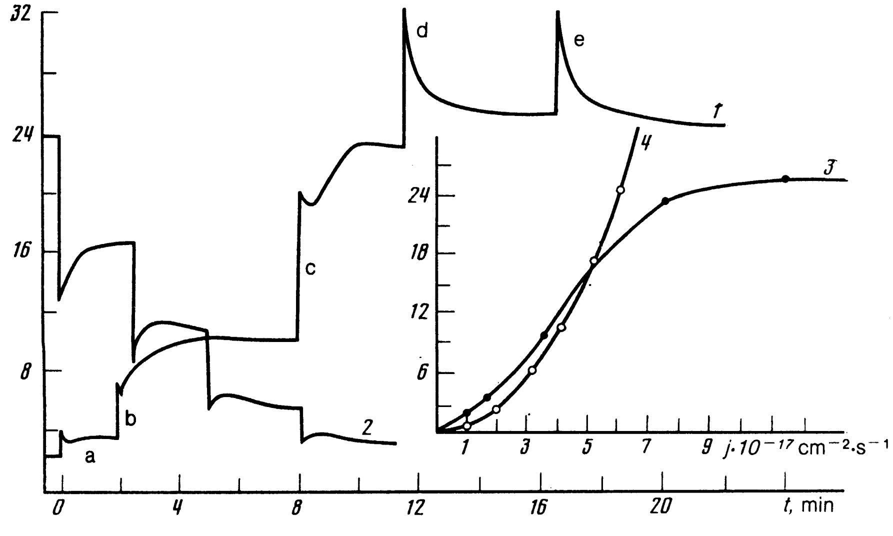

FIG. 4. Relaxation responses of the intensity of the emission from a ZnS-Mn single crystal to an abrupt change in the flux density j of hydrogen atoms, by an amount Δj, when steady-state luminescence is reached after cleavage (at 140 K). 1—$\Delta j > 0$; 2—$\Delta j < 0$. The inset shows the j dependence of the intensity of the steady-state emission at a low temperature (140 K; curve 3) and a high temperature (370 K; curve 4).

a decrease in the number of vacant centers because of an increase in the coverage of the surface by atoms, i.e., a decrease in the rate of adsorption of hydrogen atoms. After the linear decay, the intensity goes through a minimum and increases again or continues to fall off in a nonlinear fashion depending on the value of j. At sufficiently small values of j, the overall increase in the intensity upon the attainment of a new steady-state value (after an increase in j by Δj) exceeds the initial intensity I by a factor of more than $1 + \Delta j/j$. This result is due to an increase in the equilibrium surface coverage by atoms with increasing j and is unambiguous evidence for a contribution of the recombination component $\mathrm{RRL_H}$ in addition to $\mathrm{AL_H}$ to the overall intensity of the steady-state luminescence. The relaxation curves thus show that the steady-state and time-varying emission from juvenile surfaces of ZnS–Mn (and of other crystals) in atomic hydrogen is excited simultaneously both in recombination events and in events of the adsorption of hydrogen atoms. In the initial stage of the kinetics, the adsorption emission makes by far the greater contribution.

At small values of j we can clearly see two extrema (a minimum and a maximum) on the relaxation curves (Fig. 4). This result is evidence that there are two types of surface centers, one responsible for the excitation of the $\mathrm{AL_H}$ and the other for the excitation of the $\mathrm{RRL_H}$. With centers of a single type and with two forms of adsorbed hydrogen $(\mathrm{H})_{\mathrm{ads}}$ and $(\mathrm{H_2})_{\mathrm{ads}}$ (at least at low temperatures, $T < 100$–170 K, where the third charged adsorption form, $(\mathrm{H^+})_{\mathrm{ads}}$, is not present[6]), the kinetic curve is described by the theory as a linear combination of two exponential functions (more on this below). This combination, however, is capable of describing only a single extremum on the kinetic curve. The conclusion that there are two types of centers, responsible for the excitation of the $\mathrm{AL_H}$ and the $\mathrm{RRL_H}$, was reached above on the basis of energetic considerations.

In the case $\Delta j < 0$ (a decrease in j), the relaxation curves (curve 2 in Fig. 4) measured when a steady-state emission is achieved are a complete inversion of the curves for the case $\Delta j > 0$, described above; they can be explained by precisely the same processes (curves 1 and 2).

At large values of j, jumps $\Delta j > 0$ lead to an increase in the steady-state emission intensity: The relaxation curves go to the same initial intensities that prevailed before the jump (Fig. 4, parts d and e of curve 1). This nontrivial fact can be explained on the basis that at the large values of j there is a high rate of formation of $\mathrm{H_2}$ molecules at the surface; spending a finite time on the surface before desorption, they block the surface centers (recombinational blocking of centers). The effect is to saturate the emission intensity at large values of j, especially at low temperatures (curve 3 in Fig. 4). The curves of $I(j)$ plotted from the steady-state relaxation curves found at moderate temperatures are quadratic at small values of j (a bimolecular recombination reaction), while at large values of j they again reach saturation, because of recombinational blocking of centers (in this case, the recombination reaction goes in zeroth order). At sufficiently high temperatures, the blocking is inconsequential, and the $I(j)$ curves show only a hint of saturation (curve 4 in Fig. 4). At low temperatures, in contrast, the quadratic initial part of the $I(j)$ curve either is poorly expressed or gives way to a linear region because of the obvious blocking.

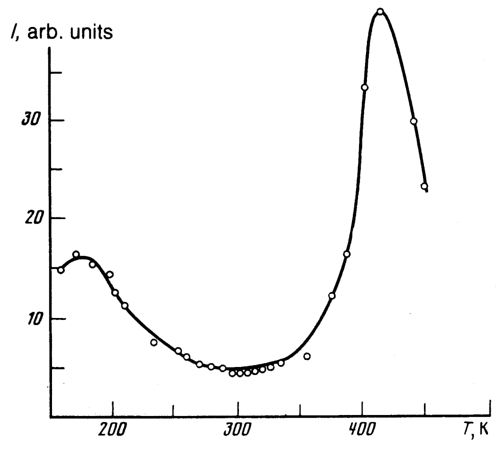

FIG. 5. Temperature dependence of the steady-state luminescence of a cleaved ZnS–Mn surface in atomic hydrogen.

The temperature dependence of the steady-state luminescence $I(T)$, has two maxima for the ZnS–Mn sample, at 170 and 420 K (Fig. 5). This result is yet one more piece of evidence for the two-center nature of the excitation of the emission in this sample.

3. KINETIC MECHANISM FOR THE PROLONGED ADSORBOLUMINESCENCE

We will derive a phenomenological theory for the heterogeneous processes which occur during excitation of the luminescence.

A. Model for the excitation of adsorboluminescence and radical-recombination luminescence with adsorption centers of a single type

Let us assume that the luminescence is excited as a result of adsorption and recombination events at centers M (from which energy is transferred to emission centers of one type). The kinetic mechanism can then be described by

$$R + M \underset{\nu_1'}{\overset{\nu_1}{\rightleftarrows}} RM + h\nu \quad (\mathrm{AL_H} \text{ and prolonged } \mathrm{AL_H}), \tag{I}$$

$$R + RM \xrightarrow{\nu_2} R_2M + h\nu \ (\mathrm{RRL_H}), \tag{II}$$

$$R_2 + M \underset{\nu_3'}{\overset{\nu_3}{\rightleftarrows}} R_2M. \tag{III}$$

Here R is a free atom (radical), R_2 is a molecule, RM and R_2M represent adsorption states, and the probabilities per unit time of the corresponding reactions are written above the arrows. Since the heat of adsorption is $q_1 > h\nu = 2.1$ eV (the yellow-orange emission of ZnS–Mn), we can write

$$\nu_1' = \nu_{10}' \exp(-q_1/kT) \approx 0 \quad (\nu_{10}' \approx 10^{12}\ \mathrm{s}^{-1})$$

for temperatures up to ~ 1000 K. In other words, hydrogen atoms are not desorbed from the M centers by a thermal mechanism.

B. Kinetic and steady-state characteristics of the prolonged adsorboluminescence

According to the 3A model, the intensity of the adsorboluminescence is

$$I=\eta_1\nu_1 N, \tag{1}$$

where η_1 is the elementary quantum yield of the adsorboluminescence, $\nu_1=\sigma_1 j$ is the probability for the adsorption of an atom R at a center M per unit time, σ_1 is the cross section for the adsorption of an atom, and N is the concentration of free centers M (in units of cm^{-2}).

The concentration N can be found as a function of the time, the temperature T, and j by solving the system of kinetic equations

$$\begin{gathered}\dot{N}=-\nu_1 N-\nu_3 N+\nu_3' N_2,\\ \dot{N}_1=\nu_1 N-\nu_2 N_1, \quad \dot{N}_2=\nu_2 N_1+\nu_3 N-\nu_3' N_2.\end{gathered} \tag{2}$$

Here N_1 and N_2 are the surface concentrations of RM and R_2M; $\nu_2=\sigma_2 j$ (σ_2 is the recombination cross section); $\nu_3=\sigma_3 j_1$ (σ_3 is the cross section for the adsorption of the molecules, and j_1 is the flux density of molecules); and $\nu_3'=\nu_{30}'\exp(-q_3/kT)$, where ν_{30}' is the desorption frequency factor and q_3 is the activation energy for the desorption of a molecule.

The kinetics of the prolonged adsorboluminescence when atoms strike a surface without an absorbate (at the instant of cleavage) can be found by solving system (2) with homogeneous initial conditions at $t=0$ ($N=N_0$, $N_1=0$, $N_2=0$):

$$\begin{aligned}I(t)=\frac{\eta_1 N_0\nu_1}{r_1-r_2}\Big[&\Big(1+\frac{\nu_3'}{r_1}\Big)(r_1+\nu_2)(e^{r_1 t}-1)\\ &-\Big(1+\frac{\nu_3'}{r_2}\Big)(r_2+\nu_2)(e^{r_2 t}-1)\Big]+\eta_1\nu_1 N_0,\end{aligned}$$

where

$$\begin{gathered}r_{1,2}=-\lambda[1\mp(1-\varkappa/\lambda^2)^{1/2}], \quad 2\lambda=\nu_1+\nu_2+\nu_3+\nu_3',\\ =\nu_1\nu_2+\nu_3'(\nu_1+\nu_2)+\nu_3\nu_2.\end{gathered}$$

At small values of t ($|r_{1,2}t|\ll 1$) we have

$$I(t)=I[1-(\sigma_3 j_1+\sigma_1 j)t]; \tag{3}$$

i.e., the adsorboluminescence decays linearly, as is observed experimentally (Fig. 1). In general (for arbitrary excitation parameters j_1, j, and T), the time dependence $I(t)$ is not monotonic: The intensity goes through a minimum at

$$t=\frac{1}{r_1-r_2}\ln\frac{(r_2+\nu_3')(r_2+\nu_2)}{(r_1+\nu_3')(r_1+\nu_2)}.$$

The steady-state prolonged adsorboluminescence is described as a function of the atomic flux density by

$$I(j)=\frac{\eta_1\nu_1\nu_2\nu_3' N_0}{\nu_1\nu_2+\nu_3'(\nu_1+\nu_2)+\nu_3\nu_2},$$

or

$$I(j)=\frac{\eta_1\sigma_1\sigma_2\nu_3' N_0 j}{\sigma_1\sigma_2 j+\nu_3'(\sigma_1+\sigma_2)+\nu_3\sigma_2}. \tag{4}$$

At small values of j, in contrast with the behavior of the radical-recombination luminescence, the intensity of the adsorboluminescence increases linearly with j (the adsorption reaction is monomolecular), but at large values of j it is similar to the radical-recombination luminescence in exhibiting saturation (a recombinational blocking of centers).

The quadratic increase in the luminescence intensity with j which is found experimentally at values of T which are not too low (curve 4 in Fig. 4) implies that radical-recombination luminescence is contributing along with the adsorboluminescence to the emission.

C. Relaxation responses of the prolonged adsorboluminescence

Let us assume that we have abruptly changed j by an amount Δj on the descending part of the $I(t)$ curve (Fig. 1). From (1) we find $\Delta I=I(\Delta j/j)$, in this situation, in agreement with experiment. From the solution of system (2) with inhomogeneous initial conditions, we find the following result for the initial part of the kinetics of the response of the system:

$$\begin{aligned}&I(0+t)\\ &=(I\pm\Delta I)\Big\{1-\Big[\sigma_3 j_1+\sigma_1(j\pm\Delta j)-\nu_3'\frac{N_{20}}{N_0-N_{10}-N_{20}}\Big]t\Big\}.\end{aligned}$$

In the initial stage we usually have $N_{20}/(N_0-N_{10}-N_{20})\ll 1$. We can therefore write the final result

$$I(0+t)=(I\pm\Delta I)\{1-[\sigma_3 j_1+\sigma_1(j\pm\Delta j)]t\}. \tag{5}$$

From the slope of the initial part of the relaxation curves of the response $dI(0+t)/dt$, and the known flux density of exciting atoms $j\pm\Delta j$, we can find a quantitative estimate of the adsorption cross sections for H atoms (σ_1) and H_2 molecules (σ_3) on the surface after the cleavage.[2)] From (5) we find

$$\sigma_1(j\pm\Delta j)+\sigma_3 j=-\frac{1}{I\pm\Delta I}\frac{dI(0+t)}{dt}.$$

For ZnS–Mn with $j\approx 10^{17}\ \mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$, we find the cross sections listed in Table I. We see from this table that the cross section for the adsorption of atoms at the centers which are responsible for the $\mathrm{AL_H}$ increases slightly with the temperature.

We now consider the nature of the relaxation responses when j is changed abruptly by $\pm\Delta j$—in this case after the luminescence intensity reaches a steady state (at the time t', which we will take as the origin of the time scale). In this case we find the following expression from the solution of system (2) with initial conditions determined by the steady-state surface coverage at the flux density j:

$$\begin{aligned}I(0+t)=(I\pm\Delta I)\Big[&1-\sigma_1\Delta j\\ &\times\frac{(\exp R_1 t-1)(1+\nu_2/R_1)-(\exp R_1 t-1)(1+\nu_2/R_2)}{R_1-R_2}\Big].\end{aligned}$$

Expressions for R_1 and R_2 in terms of the parameters ν_i, and $\Delta\nu_i$ are given in Ref. 13. In the initial region we have

$$I(0+t)=(I\pm\Delta I)[1\mp\sigma_1\Delta j t\pm(\nu_1+\nu_3+\nu_3')\sigma_1\Delta j(t^2/2)]. \tag{6}$$

TABLE I. Parameters of the interaction of hydrogen atoms and molecules with the ZnS–Mn (1%) surface.

T, K	$\sigma_1\cdot 10^{19}$, cm^2	$\sigma_1 j$, s^{-1}	$\sigma_3\cdot 10^{22}$, cm^2
105	9±2	0.085±0.015	<7
300	18±2	0.18±0.02	–
373	30±5	0.30±0.05	<30

The new steady-state intensity is

$$I(0+\infty)=(I\pm\Delta I)\left[1\mp\sigma_1\Delta j\frac{(j\pm\Delta j)\sigma_2}{R_1R_2}\right], \tag{7}$$

$$I(0+\infty)<I+\Delta I \text{ for } \Delta j>0,$$
$$I(0+\infty)>I-\Delta I \text{ for } \Delta j<0.$$

Experimentally, in contradiction of this result, we observe $I(0+\infty)>I+\Delta I$ at $\Delta j>0$; i.e., the steady-state intensity is higher by a factor of more than $1+\Delta j/j$ than the initial intensity (before the jump). This result means that in the steady-state stage of the emission the overall luminescence intensity has a component from some mechanism other than the prolonged adsorbable luminescence. As follows from the results given above, this other mechanism is RRL$_H$.

We can use the relaxation curves (6) to calculate the cross section σ_1 for the adsorption of atoms at the centers which are responsible for the excitation of AL$_H$:

$$\sigma_1\Delta j=\mp\frac{1}{I\pm\Delta I}\frac{dI(0+t)}{dt}.$$

For ZnS–Mn, the calculations yield

$$\sigma_1=(10\pm4)\cdot10^{-19}\text{ cm}^2,\quad T=150\text{ K},$$
$$\sigma_2=(26\pm9)\cdot10^{-19}\text{ cm}^2,\quad T=300\text{ K}.$$

These results agree fairly well with the values found above from the relaxation responses on the time-varying part of the $I(t)$ kinetics.

D. Radical-recombination luminescence excited at the same centers as for the AL$_H$ (*M* centers)

For these centers, as we have already mentioned we have $\nu_1'=0$. The *M* centers, which participate in the excitation of the prolonged AL$_H$, can, generally speaking, also serve as centers for the excitation of RRL$_H$, if the energy conditions are appropriate. This circumstance is incorporated through reaction (II) in the model of Subsection 3A. This case also requires analysis, since it clearly cannot be ignored.

For homogeneous initial conditions, the RRL kinetics is described by

$$I(t)=\frac{\eta_2N_0\nu_1\nu_2}{r_1-r_2}\left[\left(1+\frac{\nu_3'}{r_1}\right)(e^{r_1t}-1)-\left(1+\frac{\nu_3'}{r_2}\right)(e^{r_2t}-1)\right], \tag{8}$$

where η_2 is the elementary quantum yield of the RRL$_H$. At small values of t ($|r_{1,2}t|\ll1$) we have

$$I(t)=\eta_2N_0\sigma_1\sigma_2j^2t;$$

i.e., the RRL$_H$ increases linearly with the time.

The steady-state RRL intensity with $\nu_1'=0$ is determined by expression (4) for the prolonged adsorboluminescence, with η_1 replaced by η_2, since in the steady state the number of events per second in which an atom is adsorbed at an *M* center is equal to the number of atomic recombination events: $\nu_1N=\nu_2N_1$ [see the second equation in (2)]. For this reason, it would be impossible to devise any steady-state experiment which would be capable of distinguishing prolonged adsorboluminescence from radical-recombination luminescence, if the two are excited at centers of the same type. The only way to distinguish between them would be to use a time-varying response method.

The RRL response to a jump Δj before the attainment of a steady-state intensity is described by

$$I(0+t)=(I+\Delta I)\,[1+\sigma_1(j+\Delta j)\,(N_0/N_{10}-1-N_{20}/N_{10}-\sigma_2/\sigma_1)\,t]. \tag{9}$$

According to (9), after the initial jump ΔI we should observe a further increase in the radical-recombination luminescence by virtue of the relation $N_0/N_{10}>1$ (so that there would be a further increase in the surface coverage by atoms with increasing j). Experimentally, however, on the initial parts of the response curves, after the jump ΔI, we observe a decay, rather than an increase, in the intensity (Fig. 3). In other words, the emission associated with low surface coverage by atoms (the descending part of the kinetics; Fig. 1) cannot be radical-recombination luminescence. It is adsorboluminescence.

The response of the radical-recombination luminescence to a jump Δj after the attainment of a steady-state emission, as we go to $t'=\infty$, which we adopt as the origin of our new time scale, is described by

$$I(0+t)=(I\pm\Delta I)\left[1\mp\sigma_1\sigma_2(j\pm\Delta j)\times\Delta j\,\frac{(e^{R_1t}-1)R_2-(e^{R_2t}-1)R_1}{R_1R_2(R_1-R_2)}\right]. \tag{10}$$

In the initial part of the response we have

$$I(0+t)=(I\pm\Delta I)\,[1\mp\sigma_1\sigma_2(j\pm\Delta j)\Delta j(t^2/2)]; \tag{11}$$

i.e., the intensity of the radical-recombination luminescence falls off quadratically over time (with $\Delta j>0$), in contrast with the linear decay observed experimentally. This linear decay, as we found above, occurs because only the adsorboluminescence, not the radical-recombination luminescence, is excited at the *M* centers. The intensity of the radical-recombination luminescence in this model tends monotonically toward a new steady-state level at the end of the response:

$$I(0+\infty)=(I\pm\Delta I)\left[1\mp\frac{\sigma_1\sigma_2(j\pm\Delta j)}{R_1R_2}\right], \tag{12}$$

$$I(0+\infty)<I+\Delta I \text{ for } \Delta j>0,$$
$$I(0+\infty)>I-\Delta I \text{ for } \Delta j<0.$$

In other words, in the case $\Delta j > 0$ the quantity $I(0+\infty)$ must be lower than the initial intensity (at the instant of the jump), $I+\Delta I$ again contradicting experiment (parts b and c of curve 1 in Fig. 4). Furthermore, expression (12) does not describe the quadratic increase in $I(j)$ at elevated temperatures ($T > 173$ K), which is observed experimentally (curve 4 in Fig. 4).

This analysis shows that the M centers which are responsible for the excitation of AL_H cannot simultaneously be the centers for the excitation of the RRL_H in the ZnS–Mn crystal.

In summary, a complete description of the experimental results available requires postulating centers of yet another type: L centers, which are responsible for the excitation of the radical-recombination luminescence. These centers must have a relatively low binding energy (q_1) with the H atom, so that the energy released during a recombination event, $q = D - q_1 + q_2$, will be sufficient to excite the radical-recombination luminescence.

4. KINETIC MECHANISM FOR RADICAL-RECOMBINATION LUMINESCENCE AT *L* CENTERS

A. Model for the excitation of radical-recombination luminescence

Let us assume that the luminescence is excited in events in which atoms of species R recombine at L centers on a surface. The simplest excitation model which still reflects the most important aspects of the phenomenon is

$$R + L \underset{\mu_1'}{\overset{\mu_1}{\rightleftarrows}} RL, \tag{I}$$

$$R+RL \xrightarrow{\mu_2} R_2L+h\nu, \tag{II}$$

$$R_2 + L \underset{\mu_3'}{\overset{\mu_3}{\rightleftarrows}} R_2L. \tag{III}$$

B. Kinetic and steady-state characteristics of the radical-recombination luminescence

At a zero initial surface coverage, the time evolution $I(t)$ is again described by expression (8), derived above, but the relative probabilities ν_i, ν_i' must be replaced by the corresponding probabilities μ_i, μ_i' for the new centers, the L centers. The steady-state intensity is described as a function of j by

$$I(j)=\frac{\eta_2\sigma_2\sigma_1\mu_3' N_0{}^L j^2}{\sigma_1\sigma_2 j^2+[\mu_3'(\sigma_1+\sigma_2)+\mu_3\sigma_2]j+\mu_1'(\mu_3+\mu_3')}. \tag{13}$$

At low values of j and at high temperatures, for which desorption is predominant, the term $\mu_1'(\mu_3+\mu_3')$ is predominant in the denominator:

$$I(j)=\frac{\eta_2\sigma_1\sigma_2\mu_3' N_0{}^L}{\mu_1'(\mu_3+\mu_3')} j^2.$$

The intensity increases quadratically with j_2. At "high" values of j and "low" values of T, the term $\sigma_1\sigma_2 j^2$ dominates the denominator in (13); the intensity $I(j)$ tends toward saturation (curve 3 in Fig. 4) and is independent of j:

$$I(j)=\eta_2\mu_3' N_0{}^L.$$

C. Relaxation responses

If the flux density of atoms is changed abruptly by Δj before the intensity reaches a steady level, the behavior of the intensity of the radical-recombination luminescence at "small" values of t is described by

$$I(0+t)=(I+\Delta I)\{1+[\sigma_1(j+\Delta j)(N_0/N_{10}-1-N_{20}/N_{10}) -\mu_1+\sigma_2(j+\Delta j)]t\}. \tag{14}$$

At low surface coverages, the intensity of the radical-recombination luminescence continues to increase linearly with t after the jump, but faster.

If the jump in the atomic flux density occurs after the radical-recombination luminescence has reached a steady intensity, the behavior of the intensity is determined by[13]

$$I(0+t)=(I+\Delta I)\left[1+\mu_1'\frac{\Delta j}{j}\frac{e^{R_1t}+e^{R_2t}}{R_1-R_2} -\frac{f\Delta j}{R_1R_2j}\frac{R_1(1-e^{R_2t})-R_2(1-e^{R_1t})}{R_1-R_2}\right], \tag{15}$$

$$f=\mu_1\mu_2(1+\Delta j/j)-\mu_1'(\mu_3+\mu_3').$$

At "small" values of t we have

$$I(0+t)=(I+\Delta I)\left\{1+\frac{\Delta j}{j}\mu_1't-\left[\mu_1\mu_2\left(1+\frac{\Delta j}{j}\right)+(\mu_1')^2 +\mu_1'(\mu_1+\mu_2)\left(1+\frac{\Delta j}{j}\right)\right]\frac{\Delta j}{j}\frac{t^2}{2}\right\}. \tag{16}$$

At "small" values of j and "high" values of T, the intensity increases after the jump according to (15), and then it approaches a new steady-state value either monotonically or after going through a maximum. This new steady-state value is $I(0+\infty)$, which satisfies $I(0+\infty) > I+\Delta I$. At "large" values of j and "low" temperatures the intensity of the response of the radical-recombination luminescence after the jump decreases in proportion to t^2. Experimentally, a dependence $\sim t^2$ is not observed in its pure form, since the adsorboluminescence is superimposed on the radical-recombination luminescence. On the response curves, however, we see a transition from a linear region to a quadratic one (curve 2 in Fig. 3). The response curve tends toward a steady-state value $I(0+\infty) = I$; i.e., the intensity remains at a steady level, because of the recombinational blocking of the centers (parts d and e of curve 1 in Fig. 4).

For an arbitrary atomic flux density $j+\Delta j$, the steady-state intensity is

$$I(0+\infty)=(I+\Delta I)\left(1-\frac{f}{R_1R_2}\frac{\Delta j}{j}\right). \tag{17}$$

For small values of j we have

$$I(0+\infty)=I(1+\Delta j/j)^2.$$

For large values of j we have

$$I(0+\infty)=I.$$

Radical-recombination luminescence in the absence of adsorboluminescence therefore does not describe the change in the luminescence intensity which is linear in t on the parts of the response curves just after a change in j, but it does give a good description of the subsequent behavior and of the transition to a new steady state: the increase to an intensity above $I + \Delta I$, the maxima in the relaxation responses, and the nonlinear decays at "large" values of j and "low" values of T (parts b and c in curve 1 in Fig. 4).

5. SIMULTANEOUS EXCITATION OF AL$_H$ AND RRL$_H$ AT ADSORPTION CENTERS OF TWO TYPES

All of the experimental results which have been obtained can be explained on the basis of the existence of two distinct types of adsorption centers, if one type is responsible for the excitation of the AL$_H$ (these are probably Mn^{2+} centers), while the other type is responsible for the RRL$_H$ (these are probably Zn^{2+} centers) at the surface of the ZnS–Mn.

In this case the model of the surface processes includes reactions (I)–(III) of the models in Subsection 3A, where $\nu_1' = 0$ and $\eta_2 = 0$, and also reactions (I)–(III) of the models of Subsection 4A.

When there are centers of two types which are responsible for the excitation of the luminescence, the responses are described by the following expressions.

a) The relaxation responses during the decay of the emission after cleavage are described by

$$I_\Sigma(0+t) = I_{\mathrm{RRL}}(0+t) + I_{\mathrm{AL}}(0+t)$$
$$= (I_{\mathrm{AL}} + \Delta I_{\mathrm{AL}})[1 - \sigma_3 j_1 t - \sigma_1 (j+\Delta j)t]$$
$$+ (I_{\mathrm{RRL}} + \Delta I_{\mathrm{RRL}})\{1 + [\sigma_1 (j+\Delta j)(N_0/N_{10} - 1 - N_{20}/N_{10})$$
$$-\mu_1' + \sigma_2 (j+\Delta j)]t\}. \tag{18}$$

Since the condition $I_{\mathrm{RRL}} < I_{\mathrm{AL}}$ holds at small values of t, we can ignore everything except the first term in (18).

b) The relaxation responses when steady-state luminescence is reached after the cleavage are described by

$$I_\Sigma(0+t) = I_\Sigma \Big\{ 1 - \Big(\frac{I_{\mathrm{AL}}}{I_\Sigma} \sigma_1 \Delta j - \frac{\Delta j}{j} \mu_1' \frac{I_{\mathrm{RRL}}}{I_\Sigma} \Big) t$$
$$+ \Big[\frac{I_{\mathrm{Al}}}{I_\Sigma} \nu_1 (\nu_1 + \nu_3 + \nu_3')$$
$$- \frac{I_{\mathrm{RRL}}}{I_\Sigma} \mu_1 \mu_2 \Big(1 + \frac{\Delta j}{j}\Big) + (\mu_1')^2$$
$$+ \mu_1' (\mu_1 + \mu_2) \Big(1 + \frac{\Delta j}{j}\Big)\Big] \frac{\Delta j}{j} \frac{t^2}{2} \Big\}. \tag{19}$$

Here $I_\Sigma = I_{\mathrm{AL}} + \Delta I_{\mathrm{AL}} + I_{\mathrm{RRL}} + \Delta I_{\mathrm{RRL}}$.

The initial regions are described well by expression (19). With $T = 300$ K and $P_H = 7 \cdot 10^{-2}$ torr, for example, we have

$$I_\Sigma(0+t) = 500(1 - 7 \cdot 10^{-2} t + 4{,}35 \cdot 10^{-3} t^2).$$

This expression shows, in particular, that the adsorboluminescence outweighs the radical-recombination luminescence during the initial stage of the emission after the cleavage [cf. the signs on t and t^2 and the signs in expression (19)]. It follows from (19) that as ν_3 is increased, i.e., as the flux density of molecules is increased, the decay on the response curves becomes less obvious, again in accordance with the experimental data. At $j_1 = 10^{20}$ cm$^{-2}\cdot$s^{-1}, the maximum is clearly observed while at $j_1 = 10^{22}$ cm$^{-2}\cdot$s^{-1} it is essentially absent.

Let us find equations relating the new values of the steady-state intensity after a jump Δj in j and the intensity before the jump.

1) For "small" values of j (in the present experiments, for $j < 10^{17}$ cm$^{-2}\cdot$s^{-1}) at which adsorption processes predominate, and at which recombinational blocking of the surface is not observed, we have

$$I_\Sigma(0+\infty) = I_\Sigma \Big[1 - \frac{I_{\mathrm{AL}}}{I_\Sigma} \frac{\sigma_1 \sigma_2 \Delta j}{\nu_1'(\sigma_1 + \sigma_2) + \nu_3 \sigma_2} + \frac{I_{\mathrm{RRL}}}{I_\Sigma} \frac{\Delta j}{j} \Big]. \tag{20}$$

We see that any increment in the steady-state intensity $I_\Sigma(0+\infty)$ above the luminescence intensity during the flash $I_\Sigma(0+t)$ could result only from radical-recombination luminescence. These increments can be used to estimate the separate contributions of the radical-recombination luminescence and the adsorption luminescence to the overall luminescence intensity, making use of the increments in the new steady-state luminescence level $I_\Sigma(0+\infty)$ above the intensity in the flash:

$$I_\Sigma(0+\infty) - I_\Sigma(0+t) \leqslant I_{\mathrm{RRL}}(\Delta j/j).$$

For the adsorboluminescence and radical-recombination components of the steady-state luminescence we find the following estimates:

j, 10^{17} cm$^{-2}\cdot$s^{-1}:	1.44	2.16	3.45	4.37	6.6
$I_{\mathrm{AL}}/I_{\mathrm{RRL}}$:	0.38	0.52	2.63	3.8	3.8.

We see that adsorboluminescence and radical-recombination luminescence are comparable in intensity. On a juvenile surface created by cleavage, the adsorboluminescence component is larger than in repeated experiments on a surface cleansed by thermal desorption. The j dependence of the ratio $I_{\mathrm{AL}}/I_{\mathrm{RRL}}$ is evidence that the adsorboluminescence and the radical-recombination luminescence are excited at different centers (otherwise, this ratio would be independent of j, by virtue of the relation $\nu_1 N = \nu_2 N_1$ for arbitrary j).

2) For "large" values of j ($j > 5 \cdot 10^{17}$ cm$^{-2}\cdot$s^{-1}), for which the blocking of the surface by molecules is predominant, and the adsorption and recombination rates are higher than the desorption rate, we have

$$I_\Sigma(0+\infty) = I_\Sigma(-0),$$

In other words, the new steady-state luminescence intensity is equal to the intensity of the luminescence before the flash, again as observed experimentally (regions d and e on curve 1 in Fig. 4).

The kinetics of the responses can be used to experimentally find the behavior of the steady-state luminescence intensity I as a function of the flux density of exciting atoms, j. At "high" sample temperatures and "low" flux densities of the exciting atoms this behavior is, according to (4) and (13),

$$I_\Sigma(j)=\frac{\eta N_0{}^M\sigma_1\sigma_2}{\sigma_1+\sigma_2}j+\frac{\eta_2\sigma_1\sigma_2\mu_3{}'N_0{}^L}{\mu_1{}'(\mu_3+\mu_3{}')}j^2. \tag{21}$$

At "low" temperature and "high" excitation levels, a saturation sets in:

$$I_\Sigma=\eta_1\nu_3{}'N_0{}^M+\eta_2\mu_3{}'N_0{}^L.$$

Experimentally, one can clearly observe the onset of saturation in the $I_\Sigma(j)$ dependents at $j>5\cdot10^{17}$ cm$^{-2}\cdot$s^{-1} at temperatures $T<173$ K, while at relatively high temperatures (>370 K) a quadratic increase in the intensity predominates (curves 3 and 4 in Fig. 4).

6. ELEMENTARY MECHANISMS FOR THE EXCITATION OF EMISSION AT THE SURFACE OF ZINC SULFIDE SINGLE CRYSTALS BY ATOMIC HYDROGEN

The emission spectra of ZnS–Mn excited by hydrogen atoms contain, in addition to the fundamental band (i.e., that which is also seen in the photoluminescence spectrum) at $\lambda=590$ nm, two additional bands, at $\lambda_1=655$ nm and $\lambda_2=705$ nm, which are not observed during photoexcitation (Fig. 2). All three bands undergo a short-wave shift with increasing temperature, as is characteristic of the Mn^{2+} ion with an unfilled $3d^5$ shell. All of the bands are therefore emitted by manganese centers, but these centers differ in structure. Analysis of the change in the width of the 590-nm band with increasing temperature shows that its width is determined by high-frequency local vibrations of adsorbed hydrogen (probably molecular hydrogen) with an energy $\hbar\omega_S=0.09$ eV. During photoluminescence in the same band, the energy of the vibrations which are interacting with the electron neck transition is determined by lattice vibrations and has the value $\hbar\omega=0.04$ eV. Together, these results suggest that the fundamental band is emitted by Mn^{2+} ions, as in the photoluminescence, but these ions are two or three atomic layers below the surface, where the local vibrations of the adsorbed hydrogen still have an effect. The band at 705 nm is probably due to an Mn^{2+} ion in the first atomic layer of the lattice, on which the H_2 molecule is adsorbed (according to the data of Ref. 14, the center also includes a sulfur vacancy). The other red band at 655 nm seems to be due to associative centers of some sort on the surface.

That local vibrations of adsorbed hydrogen have manifestations in the emission spectrum implies a vibrational-electronic interaction of adsorption bonds with emission centers (either directly or through intermediate adsorption centers). In the case of ZnS–Mn, these adsorption centers might be Zn^{2+} and Mn^{2+} ions, which are responsible for the excitation of the luminescence.

An interaction which is described in quantum mechanics by a nonadiabaticity operator (an electronic-vibrational interaction) occurs between vibrational and electronic degrees of freedom of a crystal. Consequently, during the formation of vibrational excitations in the course of a reaction, nonadiabatic transitions may occur between adiabatic terms. This event would mean that the Born-Oppenheimer approximation is not applicable under these conditions. For example, a nonadiabatic excitation of Mn^{2+} ions at or near the surface may result from the incidence of a hydrogen atom from the gas phase on an Mn^{2+} ion. This mechanism would require that the terms of the ground and electronically excited states come sufficiently close together in configuration space (a small Landau-Zener splitting). (If there is a favorable term structure, there could also be an adiabatic transition of the system consisting of an adsorbed atom and a crystal ion into an electronically excited state.)

There is, however, a mechanism whose operation does not require special assumptions regarding the structure and shape of the terms. This mechanism involves the interaction between the electronic system of a center of the solid (in our case, the Mn^{2+} ion) and a vibrating electric dipole which is formed at the surface during the adsorption (or recombination) of atoms. By virtue of its "long-range" nature, this mechanism explains the excitation of ions below the surface (spectral data).

The largest dipole moment would probably be that of the heteronuclear $(H\text{-}Mn^{2+})_S$ bond, where there is the possibility of a partial charge transfer from the hydrogen atom to the $4S$ level of the Mn^{2+} ion. The energy released during the adsorption $(H+Mn^{2+})$ and recombination $(H+H\text{–}Zn^{2+})$ of atoms is concentrated in the vibrational degrees of freedom of the newly formed bond. Relaxation through a many-phonon process of the energy of the high-frequency vibrations, which are local (the large $H\text{–}Mn^{2+}$ binding energy, and the small mass of the hydrogen atom), would be extremely difficult because of the large energy of the local vibrations in the $(H\text{–}Mn^{2+})^v$ and $(H\text{–}H)^v\text{–}Zn^{2+}$ bonds (v represents vibrational excitation, and S represents the surface). The latter energy is nearly an order of magnitude greater than the energy of longitudinal optical phonons in the ZnS lattice ($\hbar\omega=0.04$ eV). Under these conditions a multiquantum vibrational-electronic transition, i.e., a multiquantum transition between vibrational levels $m\rightarrow n$ $(m>n+1)$ in an excited bond, can take place, accompanied by a simultaneous transition of an electron to an excited level in the $3d^5$ shell of the Mn^{2+} ion (the transition $^6S\rightarrow{}^4G$). Such a transition would be possible because of the pronounced anharmonicity of the vibrations in the high-lying vibrational states of adsorption bonds. In contrast with radiationless transitions involving a conversion of electronic energy into vibrational energy, what is involved here is the inverse process, of conversion of vibrational energy into electronic. The effect is reminescent of an "inverse radiationless transition."[15]

The operator describing the interaction between the electric field of the dipole ($H\text{–}Mn^{2+}$ bond), E and an electron of the emission center (a dipole-dipole interaction) is written as follows in the static region of the dipole:

$$\hat{L}_{dd}=-\frac{ie}{m_e\omega}(\mathbf{E},\hat{\mathbf{p}})=-\frac{ie(\varepsilon+2)}{3\varepsilon m_e\omega b^3}\left[\frac{3(\boldsymbol{\mu},\mathbf{b})(\mathbf{b},\mathbf{p})}{b^2}-(\boldsymbol{\mu},\hat{\mathbf{p}})\right].$$

Here e and m_e have the charge and mass of the electron, ω is the transition frequency, b is the energy-transfer distance, ε is the dielectric constant of the crystal at the transition frequency, $\boldsymbol{\mu}$ is the dipole moment of the excited bond, and the operator $\hat{\mathbf{P}}$ represents the electron momentum.

In the case of a quadrupole-dipole interaction, which occurs in the case of adsorbed homonuclear molecules which are not polarized by an adsorption center, the operator $\hat{L}$ is

$$\hat{L}_{kd} = -\frac{ie}{m_e \omega b^4 \varepsilon}\left[\frac{5}{2} D_{\alpha\beta} l_\alpha l_\beta \hat{p}_\gamma l_\gamma - D_{\alpha\beta} \hat{p}_\beta l_\alpha\right].$$

Here $D_{\alpha\beta}$ is the symmetric quadrupole-moment tensor; the $l_{\alpha,\beta,\gamma}$ are the components of the vector $\mathbf{l} = \mathbf{b}/b$; and a repeated index means a summation.

For anharmonic vibrations, a multiquantum vibrational transition is possible in first order in the expansion of the dipole moment $\boldsymbol{\mu}$ (or of the quadrupole moment D) in the internuclear coordinates:

$$\boldsymbol{\mu} = \boldsymbol{\mu}(\mathbf{r}_0) + \exp\left[i\mathbf{k}(\mathbf{b}+\mathbf{r}_e) - i\omega t - (\Gamma/2)t\right](\mathbf{r}-\mathbf{r}_0, \nabla_r)\boldsymbol{\mu}(\mathbf{r}_0).$$

Here $\mathbf{r}_0$ is the equilibrium position of the nuclei, $\mathbf{r}_e$ is the electron coordinate, and Γ is the rate of vibrational relaxation.

In first-order perturbation theory, the transition probability per unit time is

$$K_{dd,kd} = \frac{\pi^{1/2}\hbar^2 f_{if}}{2m_e M \omega_0 \varepsilon_{fi}} z_{dd,kd}^2 \Psi\left(\frac{q_1}{\varepsilon_{fi}}\right)\exp\left(-\frac{\varepsilon_{fi}}{\hbar\omega_0}p\right)\Delta(\varepsilon_{mn}-\varepsilon_{fi}). \tag{22}$$

The function $\Delta(x)$ is determined by the overlap of the energy spectra of the donor (1) and the acceptor (2), i.e., of the vibrationally excited dipole (in the overtone region) and the emission center.

$$\Delta(x) = \begin{cases} (\sigma_1^2+\sigma_2^2)^{-1}\exp\left(-\dfrac{x^2}{4\sigma_1^2+4\sigma_2^2}\right), & \Gamma\hbar \ll 2^{1/2}\sigma_1, \\ \pi\Gamma\hbar(x^2+\Gamma^2\hbar^2/4)^{-1}, & \Gamma\hbar > 2^{1/2}\sigma_1, \end{cases}$$

$$\sigma_{1,2}^2 = \frac{\hbar^2}{2}\sum_{\varkappa_{1,2}} \dot{\xi}_{1,2}^2 \omega_{1,2}^2 \operatorname{cth}(\hbar\omega_{1,2}/2kT),$$

$$\Psi(x) = x^2(1-x^{1/2})^2[1+(x/2)^{1/2}].$$

In (22), f_{if} is the oscillator strength at the frequency of the transition, $\varepsilon_{fi}/\hbar$, at the emission center; M is the reduced mass of the oscillator; $\omega_0 = \alpha(2q_1/m)^{1/2}$, q_1 is the energy of the newly formed $(R\text{–}M)_S$ and $(R\text{–}R)_S\text{–}L$ bonds; and α is the parameter of the anharmonic Morse potential $V(r) = -q_1 + q_1[1-e^{-\alpha(r-r_0)}]^2$. For the dipole-dipole and quadrupole-dipole interactions, the respective expressions for $z_{dd,kd}$ are ($\theta^2 = 2/3$, $\bar{\chi}^2 = 1/4$)

$$z_{dd}^2 = \overline{\theta^2}\left[\frac{e(\varepsilon+2)}{3\varepsilon b^3}\dot{\mu}(r_0)\right]^2, \quad z_{kd}^2 = \overline{\chi^2}\left[\frac{e}{\varepsilon b^4}\dot{D}(r_0)\right]^2.$$

The ratio of transition rates K_{dd}/K_{kd} is equal to $(b/a)^2$ where a represents the molecular dimensions of the excited complex. At large distances ($b > a$), the dipole-dipole mechanism for energy transfer is predominant, but at small values of b ($b < a$) the two mechanisms make comparable contributions; in fact the dipole-quadrupole interaction may be predominant.

For an allowed dipole transition at a center of emission caused by a polarized $(\mathrm{H}^{+\delta}\text{–}\mathrm{H}^{-\delta}\text{–}\mathrm{Me}^{+n})_S$ bond, we have the following estimates of the quantities in (22):

$$f_{if} = 1, \quad \hbar\omega_0 = 0.3\ \text{eV}, \quad \varepsilon_{fi} = 2.1\ \text{eV}, \quad q_1 = 2.5\ \text{eV},$$

$$\dot{\mu}(r_0) = 1\,\frac{\mathrm{D}}{\text{Å}}, \quad \varepsilon = 1, \quad b = 3\text{Å},$$

$$p = \frac{x\ln x}{x-1} = 1{,}9, \quad x = \frac{4q_1+\hbar\omega_0}{\varepsilon_{mn}+\hbar\omega_0} = 3.7, \tag{23}$$

$$K_{dd} = 10^{13}\exp\left(-\frac{\varepsilon_{fi}}{\hbar\omega_0}p\right) \times(\sigma_1^2+\sigma_2^2)^{1/2}\Delta(\varepsilon_{mn}-\varepsilon_{fi}) \leqslant 10^7\text{–}10^8\ \text{s}^{-1}.$$

For an unpolarized hydrogen bond we have $\dot{D}(r_0) = 2.9\ D$, and at $b < 3$ Å the dipole-quadrupole and dipole-dipole mechanisms for the energy transfer make comparable contributions.

The emission yield of electronically excited states in a multiquantum mechanism is

$$\eta^* = \frac{K_{dd,kd}}{K_{dd,kd}+\Gamma}\frac{g_n}{g}\exp\left(-\frac{E_n}{kT}\right). \tag{24}$$

The second and third factors here are the probability for an adiabatic transition of a complex into the vibrationally excited ground state, and the g_n is the statistical weight of the state.

The relaxation rate is determined not only by the exchange of a local vibration $\hbar\omega_0$ for phonons $\Gamma_{vph} \leqslant 10^7\text{–}10^9\ \text{s}^{-1}$) and in the adsorbed layer ($\Gamma_{vv} < 10^{10}\text{–}10^{12}\ \text{s}^{-2}$) but also by the nonequilibrium desorption of a vibrationally excited molecule[16] $\Gamma^* = 10^9\text{–}10^{11}\ \text{s}^{-1}$): $\Gamma = \Gamma_{vph} + \Gamma^*$. The excitation yield is $\eta^* = 10^{-4}\text{–}10^{-1}$, in agreement with the observed emission intensities.

Taking into account the radiationless energy transfer between a vibrationally excited complex and emission centers at the surface (S) and in the volume (V) of the crystal over a distance b_S and b_V, we find the luminescence yield for the case of excitation by hydrogen atoms from the expression

$$\eta_{1,2} = \frac{B\eta_{1,2}^*}{1+\tau W}\left\{1+\frac{B_V}{1+\tau_1 W_1}\left[\left(\frac{r_0}{r_0+b_V}\right)^n \times(1+\tau W)+K_V(b_V)\tau_u\right] + \frac{B_S}{1+\tau_2 W_2}\left[\left(\frac{b_0}{b_0+b_S}\right)^n(1+\tau W)+K_S(b_S)\tau_u\right]\right\}. \tag{25}$$

Here B, B_v, and B_S are the quantum yields of the emission of an electronically excited complex with an absorbed molecule or atom (B) and of emission centers in the volume of the sample (B_v) and at its surface (B_S). The factors $(1+\tau W)^{-1}$, $(1+\tau_{1,2}W_{1,2})^{-1}$ allow for concentration quenching; $K_V\tau_u$, $K_S\tau_u$ are the probabilities for the exchange of electronic-excitation energy between a center excited during adsorption (or recombination) and volume and surface emission centers. Expression (25), which reflects the possibility of the excitation by atoms of not only volume centers but also surface centers, including centers containing adsorbate atoms or molecules, shows why the adsorboluminescence and radical-recombination-luminescence spectra are richer than the photoluminescence spectra (Fig. 2).

7. CONCLUSION

It can thus be regarded as an established fact that radiative adsorption of hydrogen atoms does indeed occur on zinc sulfide and other chalcogenides. The observed effect proves unambiguously that, at least in the systems which have been studied, direct conversion of the chemical energy of adsorption into radiant energy occurs. In other words, the effect stems from "electron accommodation" in adsorption events. Systems have already been identified in which the electron mechanism for accommodation operates with a surprisingly high efficiency (0.6 per reaction event[7]), raising the hope that it may be possible to develop a chemically pumped solid-state laser.[17] The observation of emission during the adsorption of hydrogen atoms, along with the well-known emission when atoms recombine, means that we can seek systems in which both of these events are radiative and in which the total emission yield over a recombination cycle can exceed unity (a two-step recombination reaction would thus be particularly promising for pumping). The results reported here furnish some principles for searching for optically active adsorption systems.

[1)] The $H + H_2$ mixture is supplied to the reaction chamber from an rf discharge. The hydrogen which we used was purified with a nickel filter. The emission was detected by a photomultiplier and recorded by a potentiometer with digital readout.

[2)] The product of σ_1 and η_1, where η_1 is the elementary quantum yield of the adsorboluminescence, serves as a measure of the overall efficiency of the excitation of the adsorboluminescence centers.

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