- <sup>17</sup>L. M. Blinov, V. A. Kizel', V. G. Rumyantsev, and V. V. Titov, Kristallografiya 20, 1245 (1975) [Sov. Phys. Crystallogr. 20, 750 (1975)].
- <sup>18</sup>E. M. Aver'yanov, A. Vaitkyavichyus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin, and V. F. Shabanov, Preprint Institute of Physics, Siberian Branch, Academy of Sciences, USSR, No. 88F, Krasnoyarsk, 1978.
- <sup>19</sup>G. Labrunie and M. Bresse, C. R. Acad. Sci. B **276**, 647 (1973).
- <sup>20</sup>E. M. Aver'yanov and V. F. Shabanov, Kristallografiya 23, 320 (1978) [Sov. Phys. Crystallogr. 23, 177 (1978)].
- <sup>21</sup>E. M. Aver'yanov, K. S. Aleksandrov, and V. F. Shabanov, Dokl. Acad. Nauk SSSR **242**, 84 (1978) [Sov. Phys. Doklady **23**, 665 (1978)].

- <sup>22</sup>V. F. Shabanov, E. M. Aver'yanov, P. V. Adomenas, and V. P. Spiridonov, Zh. Eksp. Teor. Fiz. 75, 1926 (1978)
   [Sov. Phys. JETP 48, 970 (1978)].
- <sup>23</sup>E. Sackmann, P. Krebs, H. U. Rega, J. Voss, and H. Möhwald, Mol. Cryst. Liq. Cryst. 24, 283 (1973).
- <sup>24</sup>A. L. Tsykalo and A. D. Bagmet, Fiz. Tverd. Tela 20, 1326 (1978) [Sov. Phys. Solid State 20, 762 (1978)].
- <sup>25</sup>V. G. Podoprigora and V. F. Shabanov, Kristallografiya 20, 1109 (1975) [Sov. Phys. Crystallogr. 20, 677 (1975)].
- <sup>26</sup>F. Volino, A. J. Dianoux, and H. Hervet, Mol. Cryst. Liq. Cryst. 38, 125 (1977).

Translated by W. F. Brown, Jr.

# High-efficiency electronic accomodation in the interaction of atomic hydrogen with single-crystal germanium

A. E. Kabanskii and V. V. Styrov

Tomsk Institute of Automatic Control Systems and Radio Electronics (Submitted 26 December 1978) Zh. Eksp. Teor. Fiz. **76**, 1803–1811 (May 1979)

We describe an original experimental procedure for determining the probability of electronic excitation of a crystal  $\eta_e$ , with formation of dissociated electron-hole pairs, and of the coefficient  $\beta_e$  of electronic accommodation in the acts of chemical excitation of atomic hydrogen with the (111) surface of single-crystal germanium. The results  $\eta_e = 0.6 \pm 0.1$  and  $\beta_e > 0.10 \pm 0.02$  attest to effective conversion of chemical energy into energy of electronic excitation of the crystal. The surface quasimolecule approximation is used to construct a theoretical model that describes the production and transport of electronic excitation in a crystal in the elementary chemical act. It is concluded that the electron accommodation must be taken into account in addition to the phonon accommodation in processes of chemical energy relaxation on a surface.

PACS numbers: 82.65.My

### **1. INTRODUCTION**

Interest has increased lately in the problem of energy exchange on the interface between a gas and a solid, in connection with the study of the possible use of lasers for selective activation of adsorption and catalytic processes<sup>1-3</sup> and adsorption isotope separation.<sup>4,5</sup> This is a vital problem from many points of view, inasmuch as energy dissipation processes play an important role in many heterogeneous processes (plasma etching of semiconductors, crystal growth, formation of molecular coatings and layers, two-dimensional phase transitions, and others).

Energy exchange between solids and gas molecules (atoms) that have in the general case translational, rotational, and vibrational energies, are usually treated in terms of Knudsen thermal accomodation coefficients (see Ref. 6). Wood, Mills, and Wise<sup>7</sup> introduced the concept of the accomodation coefficient for a chemically reacting gas consisting of free atoms (radicals). Since the main contribution to energy exchange is made in this case by chemical energy, compared with which the energy of thermal motion can be neglected, we take the accomodation coefficient  $\beta$  to mean that part of the released chemical energy which is transferred in the mean to the solid in the elementary reaction act:  $\beta = Q/q$ (Q is the energy transferred to the body and q is the thermal effect of the reaction event). It is assumed here that the accomodating energy is received by the solid in the form of vibrational energy, and just as in the case of Knudsen accomodation, it leads in final analysis only to thermal effects.

It has been recognized of late, however, that the accomodation of chemical energy in heterogeneous reactions can lead to substantial disruption of the equilibrium in the electronic system of the crystal, and is accompanied by crystal luminescence, by electron emission,<sup>8</sup> and by other nonequilibrium effects<sup>9-11</sup> that are the surface analogs of the corresponding effects in optical excitation. Thus, besides the vibrational mechanism one can speak of an electronic accomodation mechanism, i.e.,

$$\beta = \beta_e + \beta_v = \eta_e E_e/q + \eta_v E_v/q. \tag{1}$$

Here  $\eta_e$  and  $\eta_v$  are the probabilities of the electronic (e) and vibrational (v) excitations of the surface of the solid in the course of the reaction  $(\eta_e + \eta_v = 1)$ ,  $E_e$  is the energy of the excited electronic state,  $E_v$  is the energy transferred to the vibrational degrees of freedom ( $E_e + E_v = Q$ ),  $\beta_e$  and  $\beta_v$  are the partial accomodation coefficients in the electronic and vibrational mechanisms.

If we imagine a gas + solid system in which  $\eta_e \approx 1 > \eta_v$ and  $E_e \gg E_v$ , such that the electronic excitations relax predominantly by radiation (a good luminor), then the accomodation of the chemical energy in such a system will not be accompanied by heating. In systems with large  $\eta_e$  it might be possible to produce chemical pumping of a solid-state laser.<sup>12</sup> Until now, however, it has been assumed that for heterogeneous processes in which solids with large vibrational degrees of freedom participate, such a situation is quite improbable, and the electronic accomodation channel is ineffective compared with the vibrational one  $(\eta_e \ll \eta_v, \beta_e \ll \beta_v)$ .

The purpose of the present paper is to demonstrate that this widely held viewpoint is unfounded and to report a hitherto unknown effect, namely, high probability  $(\eta_e > \eta_v)$  of electronic excitation of a semiconductor (germanium) on whose surface simple reactions take place (adsorption and heterogeneous recombination of atomic hydrogen):  $H + H + Ge \rightarrow H_2 + (Ge)^e$ . It is known that for some gas-phase analogs of this reaction, i.e., for reactions of the type  $A + A + M \rightarrow A_2 + M^e$ , electronic excitation takes place of the atom (molecule) M with a probability close to unity.<sup>13</sup>

### 2. EXPERIMENT

The experimental setup is shown in Fig. 1a. The germanium crystal, cut along the (111) plane in the form of a plate and provided with ohmic contacts, was placed in a vacuum chamber between the poles of an electromagnet. Hydrogen atoms having thermal energy diffused towards the sample from an atom source (high-frequency discharge in spactrally pure  $H_2$ ) and interacted with its surface. This led to nonequilibrium generation of electron-hole pairs in the germaium (chemo-injection). The flux of the e - p pair from the surface into the volume was revealed by the chemomagnetic emf  $E_{cm}$  (Ref. 10) (the analog of the photomagnetic emf in the Kimoin-Noskov effect). We measured simultaneously the heat power released in the crystal in the acts of heterogeneous recombination of the H atoms. The efficiency  $\eta_e$ was calculated as the ratio of the flux  $\Phi_e$  of the generated pairs to the flux  $\Phi_r$  of the recombination acts of the hydrogen atoms on the germanium:  $\eta_e = \Phi_e / \Phi_r$ . The flux  $\Phi_e$  was calculated  $as^{10}$ 

$$\Phi_{e} = E_{cm} \sigma_{0} \left( 1 + \frac{S_{1}}{S_{2}} \right) / e(\mu_{n} + \mu_{p}) \times Bhd.$$
<sup>(2)</sup>

Here e is the elementary charge,  $\varkappa$  is the Hall factor, B is the magnetic-field induction,  $\mu_n$  and  $\mu_p$  are the



FIG. 1. Experimental setup for the determination of the probability of electronic chemo-excitation of germanium: a—the method of the chemomagnetoelectric effect (1—investigated germanium sample, 2—germanium microcalorimeter, 3—insulation layer (organic lacquer); b—rectification chemo-effect method ( $I_{sc}$  short-circuit-current meter).

carrier mobilities, h is the width of the sample, d is its thickness,  $\sigma_0$  is the conductivity of the sample under chemo-excitation, and  $S_1$  and  $S_2$  are the effective rates of surface recombination of the carriers on the front (active) and rear (passive) sides of the germanium plate. The quantity  $1 + S_1/S_2$  was determined from a formula similar to (2) on the basis of measurements of the photomagnetic emf (in the course of the chemo-excitation) and of a determination of the flux of the absorbed optical quanta by a calorimetric procedure (see below). The photoexcitation source was a light-emitting GaAs diode with  $\lambda_{max} \approx 0.95 \mu$  m.

To determine the flux  $\Phi_r$ , we used an isothermal microcalorimeter with sensitivity  $\sim 10^{-6}$  W, constituting a germanium plate mounted under the sample in thermal contact with the latter (see Fig. 1a). The thermal power released by the investigated sample as a result of recombination of the hydrogen atom was obtained from the equivalent heating of the calorimeter by the Joule power  $\Delta P$ , on account of the current flowing through the sample. The flux  $\Phi_r$  was defined as  $\Phi_r = \Delta P/sQ$ . Here s is the surface area of the investigated sample and Q is the energy transferred to the solid in the cycle of the heterogeneous recombination of the hydrogen atoms on the surface of the germanium:

$$H+H+Ge \rightarrow H+HGe \rightarrow H_2+Ge$$

(the quantities above the arrows are the thermal effects of corresponding reaction acts).

The value of  $\eta_e$  determined in this manner pertains not to the elementary act, but to the entire atom recombination cycle (I) for which  $Q \approx D_v = q_1 + q_2$ , where  $D_{gas}$  is the heat of dissociation of  $H_2$  in the gas phase ( $\approx 4.48 \text{ eV}$ ).<sup>1)</sup>

Figure 2a shows the values of  $\eta_e$  obtained by varying 'the hydrogen concentration in the gas  $(n_H)$ . With increasing temperature of the sample in the 295-360 K range, the values of  $\Phi_e$  and  $\Phi_r$  measured by the independent methods described above increase at equal activation energy  $\approx 0.21$  eV (Fig. 2b). This means that  $\eta_e$  is practically independent of  $n_H$  and T in the investigated range of variation of these parameters and is equal to  $0.6 \pm 0.1$ 

The detection of the excited carriers of opposite signs can be effected also with the aid of an n-p junction on



FIG. 2. a) Dependence of probability of electronic chemoexcitation of germanium on the concentration  $n_{\rm H}$  of the hydrogen atoms in the gas phase. b) Dependence (in logarithmic scale) of the flux of electron-hole pairs  $\Phi_e$  (1) and of the flux of recombination acts  $\Phi_r$  (2) of hydrogen atoms on germanium on the reciprocal temperature.

the basis of the rectification effect. We used in the experiment a planar Ge junction with a facing *n*-layer less than 5  $\mu$ m thick (Fig. 1b). At  $n_{\rm H} = 2 \times 10^{19}$  m<sup>-3</sup> the measured short-circuit current was  $10^{-8}$  A. We determine the coefficient of gathering of the generated carriers by the junction region, and the fluxes  $\Phi_e$  and  $\Phi_r$ . The probability  $\eta_e$  of electronic chemo-excitation of the *n*-Ge surface turned out to be  $0.5 \pm 0.1$ , which practically coincides with the value obtained above by measuring the chemomagnetic emf.

The results enable us to estimate the coefficient  $\beta_e$ of electronic accomodation, namely  $\beta_e = \eta_e E_e/Q \ge \eta_e E_g/D_{gas} \approx 0.10 \pm 0.02$ , where  $E_g \approx 0.7$  eV is the width of the forbidden band of germanium. Consequently, even in the relatively unfavorable case when  $E_g$  is much less than  $D_{gas}$  (germanium-hydrogen), more than 10% of the energy released in the reaction is converted into energy of electronic excitation of the crystal. The electronic accomodation must thus be taken into account, alongside the phonon accomodation, when the relaxation of chemical energy on a surface is considered.

# 3. DISCUSSION OF RESULTS AND CHEMO-EXCITATION MODEL

Electron-hole excitation of a germanium surface by hydrogen atoms will be discussed below within the framework of the model of potential surfaces. This model explains well the course of gas-phase reactions within the limits of one potential-energy surface (the adiabatic reaction channel), as well as in the configuration-space region that includes more than one surface (nonadiabatic reaction channel). To describe a concrete chemical process in which electron-excited states take part, it is necessary to know the detailed structure and the properties of the electron terms: the region of crossing (or quasicrossing), the multiplicity of the symmetry, etc. These characteristics determine the probabilities of various reaction channels, and the lifetimes of the excited states.

For heterogeneous reactions with participation of a solid, the applicability of the potential-surface model is not obvious, at least because of the exceptional complexity of calculating the adiabatic term, and the multidimensionality of the possible nonadiabatic transitions. Only if the complex motion of the representative point can be reduced to one-dimensional can the probabilities of transitions of the system into an electron-excited state be calculated by using the well-developed theory of nonadiabatic transitions in diatomic molecules. $^{14}$  We shall therefore describe the adsorption in the approximation of the surface quasimolecule (GeH)<sub>s</sub>. This can be done in our problem for the following reasons: (1) The binding energy in the quasimolecule is much higher than the binding energy of two neighboring germanium atoms on the surface:  $D(H-Ge) \approx 3.3 \text{ eV}$ , whereas  $D(Ge_s - Ge_s)$  $\leq 1.0 \text{ eV.}^{15}$  Furthermore, according to calculations,<sup>16</sup> when hydrogen is adsorbed the population of the bonds of the attacked germanium atom with the other lattice atoms by the electrons becomes lower, meaning that they are greatly weakened. It is these arguments which allow us to separate on the surface a quasi-isolated

structural unit in the form of the quasimolecule (GeH)<sub>s</sub>. (2) The vibrational and electronic forms of the motion in the (GeH)<sub>s</sub> molecule are quasi-isolated from the substrate crystal. In fact, when a light hydrogen atom is adsorbed on the surface of germanium, adsorption frequencies  $\omega_a$  appear in the vibrational spectrum of the crystal and lie below the quasicontinuous phonon spectrum:  $\hbar \omega_a > k_B \Theta_D$ .<sup>3</sup> This weakens greatly the external channel of the vibrational relaxation.<sup>3</sup> The quasi-isolated status of the electronic forms of motion in (GeH)<sub>s</sub> follows from the fact that the structure of its electronic terms are determined by the local covalent H-Ge bond, and the influence of the surrounding atoms manifests itself as a relatively weak perturbation of the quasimolecule terms.

The solution of the problem of constructing a model of electronic chemo-excitation of germanium following adsorption of hydrogen atoms breaks up into three stages: the first is to find the adiabatic electronic terms of the (GeH)<sub>s</sub> molecule; the second is to ascertain the channels of the chemosorption of the hydrogen atom on the germanium in configuration space and to calculate the probability that the representative point of the system will land on a term of an electron-excited state of (GeH)<sub>s</sub>; the third is the estimate of the probability of delocalization of the excitation from the quasimolecule in the crystal, with formation of an electronhole pair.

1. Figure 3 shows the potential energy curves for three states  $(X^2\Pi, a^4\Sigma^-, B^2\Sigma^-)$  of the (GeH)<sub>s</sub> molecule, constructed in analogy with the potential curve of carbon monohydride CH,<sup>17</sup> the homolog of which is germanium. The minima of the electron-excited terms  $a^4\Sigma^-$  and  $B^2\Sigma^-$  are located on the energy scale in accordance with the known electron-energy level scheme of the GeH molecule.<sup>18</sup> The ground state of the surface atom of the germanium that reacts with the hydrogen atom is assigned to the electron configuration  $sp^3$ , which corresponds to hybrid tetrahedral orbitals. In this case it is natural to speak of a surface radical of the type

("dangling bond").

2. It is seen from Fig. 3 that the term  $Ge(sp^3) + H(^2S)$ , which corresponds to the reagents as  $r \to \infty$ , is split when they come closer together into three adiabatic terms corresponding to the ground  $(X^2\Pi)$ , first  $(a^4\Sigma^-)$  and third  $(B^2\Sigma^-)$  electron-excited states. Thus, there exist two reaction channels with formation of an electron-excited quasimolecule  $(GeH)_{s}^{e}$ : adiabatic, when the system rolls



down without activation to the  $a^{4}\Sigma^{-}$  state or lands in the  $B^{2}\Sigma^{-}$  state after overcoming an activation barrier ( $E_{0} \approx 1 \text{ eV}$ ), and nonadiabatic, due to the interaction of the  $X^{2}\Pi$  and  $a^{4}\Sigma^{-}$  terms in the region of their crossing (the  $K_{12}$  region).

The probability  $P_e^{(n)}$  that a surface quasimolecule (GeH)<sub>s</sub> will land in the first excited state  $a^4\Sigma^-$  after multiple passage of the representative point through the region  $K_{12}$  in the course of the vibrational relaxation takes the form

$$P_{\bullet}^{(n)} = \frac{\frac{1}{2} (g_1 + g_2) + \frac{1}{2} (g_2 - g_1) (1 - 2P_{12})^{2n}}{g_1 + g_2 + g_2 \exp(-E_0/k_BT)},$$
(3)

where  $g_1$ ,  $g_2$ , and  $g_3$  are the statistical weights of the states  $X^2\Pi$ ,  $a^4\Sigma^-$ , and  $B^2\Sigma^-$ , respectively, 2n is the number of passages of the representative point through the region  $K_{12}$ , and  $P_{12}$  is the Landau-Zener probability of transition between terms 1 and 2 (see Fig. 3) in a single passage. It follows from (3) that at  $g_2 > g_1$  the probability  $P_e^{(n)}$  takes on values from 1 to  $\frac{1}{2}$ , at  $g_2 > g_1$  we have  $P_e^{(n)} < \frac{1}{2}$ , and in the case  $g_2 = g_1$  we get  $P_e^{(n)} = \frac{1}{2}$  (it is assumed here that  $E_0 \gg k_B T$ ).

3. The delocalization of the electronic excitation from the molecule and the appearance of a free electron+free hole pair in the crystal can be effected by an energy transport mechanism or by a charge transport mechanism. The highest energy-transport probability corresponds to the resonant case, when the energy of the electron-excited state of the quasimolecule lands among the energies of the exciton band of the crystal or in the continuum region corresponding to formation in the matrix of dissociated electron-hole pairs. The configuration interaction of the discrete state of the molecule with the states of the continuum of the crystal leads to a broadening of the quasimolecule level, with a smearing  $\Gamma_1$ , which is equivalent to a finite time  $\tau_1 \approx \hbar/\Gamma_1$  of the electron-excited state of the surface donor of energy relative to its delocalization in the continuum of the crystal<sup>19</sup> with production of an electron-hole pair. A similar mechanism was postulated by Frank and Teller as the mechanism of sensitization of the photosensitivity of solver halide by adsorbed dyes (see Ref. 20).

The charge-transport mechanism was proposed in connection with the same problem by Gurney and Mott.<sup>20</sup> The transition of an electron from an excited level of a surface molecule into the *C* band of a crystal is via isoenergetic tunneling followed by tunneling of the electron from the *V* band of the crystal to a vacancy ground level of the molecule. This mechanism leads also to the formation of an e-p pair in the crystal and is characterized by an effective time  $\tau_2 \approx \hbar / \Gamma_2$  ( $\Gamma_2$  is the broadening of the surface-molecule level broadening not connected with dissipative processes).

It follows from the analysis of the energy scheme of the crystal and of the molecule that both excitation-localization processes are possible in the considered system if the nuclei are in equilibrium positions. A substantial feature of the process of electron-excitation transport in a crystal in the course of heterogeneous chemical reaction is that it can proceed from the "hot" vibrational state of the produced molecule to the electron-excited or ground state. In contrast to the hot transport (HT) in photoexcitation,<sup>21</sup> which calls for Franck-Condon transitions with appreciable Stokes shift, the condition for the HT in chemo-excitation come about automatically, since the energy released in the chemical reaction at the initial instant is fully (ground term) or partially (electron-excited term) concentrated in the form of nonequilibrium vibrations on the produced bond, e.g., the bond

→Ge-H,

In order for the HT to have an appreciable probability, it is necessary to satisfy the relations  $\tau_1, \tau_2 < \tau_{rel}$  ( $\tau_{rel}$ is the time of vibrational relaxation of the molecule). It is known<sup>3, 22</sup> that the processes of vibrational relaxation are more difficult on the crystal surface than in its interior, and frequency  $\tau_{\rm rel} \gg \tau_v,$  where  $\tau_v = 10^{-12}$  $-10^{-13}$  sec is the time of one vibration (in the case of the hydrogen-germanium system the reason is that  $\omega_a$  $>\omega_{\rm p}$ , i.e., the adsorption frequency greatly exceeds the crystal vibration frequency). The slowing down of the vibrational relaxation on the surface increases additionally the probability of the HT in chemo-excitation compared with photo-excitation. Finally, the quasimolecule electronic-level displacements induced by the vibrational motion of the nuclei relax the rather stringent "resonance" requirements in the energy transport, or the requirements that the levels be of equal energy in charge transport. Thus, in vibrational motion of the nuclei. the electron level corresponding to the ground term of the quasimolecule can shift into the region of energies that coincide with the C band of the semiconductor. This leads to tunneling of the electron into the crystal, and the subsequent capture of the electron from the Vband by a vacant level of the molecule will complete the process of e - p pair production in the cyrstal on acacount of the vibrational energy in the electronic ground state. This process has no analogs in the traditional methods of crystal excitation (light, electrons, etc.), since these methods cannot ensure such a large vibrational disequilibrium.

The total probability  $\eta_e^a$  of electron-hole excitation of germanium in the chemosorption act, with allowance for the arguments advanced above, is

$$\eta_{e}^{a} = 1 - (1 - P_{e}^{(n)}) (1 - P_{i})^{m} - P_{e}^{(n)} (1 - P_{i})^{k}.$$
(4)

Here *m* and *k* are the numbers of oscillations in the relaxation process, for which energy consideration permit transport of excitation in the crystal from terms 1 and 2 of the molecule;  $P_i$  is the transport probability per oscillation and is assumed here to be the same for the ground and excited states of the quasimolecule. To calculate  $\eta_e^a$ , we estimate the value of  $P_1$  from the expression

$$P_{i} = \tau^{-i} / (\tau^{-i} + \tau_{v}^{-i}), \qquad (5)$$

where  $\tau$  is the effective time of excitation delocalization:

$$\tau = \tau_1 \tau_2 / (\tau_1 + \tau_2). \tag{6}$$

Let the production of the electron-hole pairs proceed only in accord with one mechanism, say the energytransport mechanism, i.e.,  $\tau = \tau_1$ . According to Tekhver and Khizhnyakov<sup>21</sup> the donor-acceptor interaction that ensures the HT leads to a level broadening  $\Gamma_1 \sim 10^{-2}$ eV. Hence  $\tau_1 \approx \hbar/\Gamma_1 \sim 10^{-13}$  sec, i.e., a value on the order of  $\tau_v$ . This corresponds to a highprobability of excitation transfer in the crystal:  $P_1 \sim 1-0.5$ . It can be shown that similar estimates follow for  $P_1$  from the tunnel mechanism of the charge transport. In (4), usually  $k \gg m$ , and therefore

$$\eta_{e}^{a} \cong 1 - (1 - P_{e}^{(n)}) (1 - P_{i})^{m} .$$
(4')

Since in our case we must put in (3), when calculating  $P_e(n)$ ,  $g_1 = g_2 = 4$  and  $\exp(-E_0/k_BT) \ll 1$ , we get

$$1 > \eta_e^a \approx 1 - \frac{1}{2} (1 - P_1)^m > \frac{1}{2}.$$

(1")

The experimentally obtained  $\eta_e$  agrees with this theoretical estimate. It can be assumed on this basis that the chemo-excitation in the reaction (I) is due mainly to the first most energetic stage, i.e., the adsorption stage. This does not exclude, however, the possibility that a definite (but much smaller) contribution to the generation of the nonequilibrium carriers is made also by the second stage (recombination proper).

We note that in the considered model of chemo-excitation all the activation barriers were overcome either on account of the chemical energy released on the Ge-H bond, or via tunnel and below—the barrier transitions, which do not depend (or depend weakly) on the temperature. Thus, the considered model explains not only the value of  $\eta_e$  but also its temperature behavior (independence of temperature).

## 4. CONCLUSION

We have experimentally determined here the elementary probability  $\eta_e$  of electronic chemo-excitation, for the atomic hydrogen+germanium system. Knowledge of  $\eta_e$  and of its dependence on the system parameters (atom concentration, temperature) is exceedingly important for the construction of a microscopic theory of chemo-excitation of crystal. The result shows that under certain condition the energy of a heterogeneous chemical reaction on the crystal-gas interface is transformed with high efficiency into energy of electronic excitations of the crystal. This new result can significantly alter the existing notions concerning the course of heterogeneous processes and the mechanisms of energy scattering by a surface.

An electron or hole thrown in the chemical reaction into "its own" band from an impurity or proper level of a crystal can be captured by a trap (defect) and live there for a long time prior to recombination; this corresponds to storage and prolonged preservation of chemical energy by the crystal. This energy can subsequently be used to activate succeeding chemical acts; this provides a new approach to the old problem of energy recuperation in catalysis, and to the understanding of the mechanism whereby energy chains are produced in heterogeneous reactions. So prolonged a preservation of energy is impossible on vibrational degrees of freedom.

The existing theories of the recombination coefficients

of atoms<sup>23</sup> and of the accomodation coefficient<sup>6</sup> are based on vibrational relaxation. This may turn out to be insufficient or even incorrect, if the electronic relaxation channel, which ensures a different rate of energy diversion and generally speaking a different value of the recombination (accomodation<sup>24</sup>) coefficient, predominates. The electronic relaxation channel must also be kept in mind when the problem of initiation of heterogeneous processes by a laser is considered.<sup>1-5</sup>

We note that the phenomenon investigated in this paper, that of high-efficiency generation of electron-hole pairs in a germanium crystal interacting with atomic hydrogen, which was experimentally observed in chemomagnetic and chemo-rectification effects, provides a new principle of conversion of chemical energy into electricity. The discovery of this phenomenon is an important step towards the realization of a method for chemical pumping a solid-state laser<sup>12</sup> and thus converting chemical energy into coherent optical radiation (all the presently existing chemical lasers use gases). The energy yield of heterogeneous chemoluminescence amounting to 1% (Ref. 25), already obtained in the ZnS + Tm + atomic hydrogen system,<sup>25</sup> seems promising.

In conclusion, the authors thank A. A. Ovchinnikov for stimulating discussions and interest in the work and Yu. I. Tyurin for helpful remarks in the discussion of the results.

- <sup>1)</sup>The energy Q is not exactly equal to  $D_{gas}$ , since some of the energy can be carried away into the gas pase by the vibrationally excited  $H_2$  molecule produced in (I). This part is small, inasmuch as in the system under consideration  $q_1$  (3.3 eV) is much larger than  $q_2$  (4.48 3.3 = 1.18 eV). Substitution of  $D_{gas}$  for Q leads to a systematic error that does not exceed 20% in any case.
- <sup>1</sup>K. S. Gochelashvili, N. V. Karlov, A. I. Ovchenkov, A. N. Orlov, R. P. Petrov, Yu. N. Petrov, and A. M. Prokhorov, Zh. Eksp. Teor. Fiz. 70, 531 (1976) [Sov. Phys. JETP 43, 274 (1976)].
- <sup>2</sup>M. S. Djidjoev, R. V. Khoklov, A. V. Kiselev, V. J. Lygin, V. A. Namiot, A. J. Osipov, V. I. Panchenko, and B. J. Provotorov, Proc. Conf. Tunable Lasers and Applications, Loen-Nordfjord, Norway, M.I.T. Press, Cambridge, Mass., 1975.
- <sup>3</sup>M. S. Dzhidzhoev, A. I. Osipov, V. Ya. Panchenko, V. T. Platonenko, R. V. Khokhlov, and K. V. Shaitan, Zh. Eksp. Teor. Fiz. 74, 1307 (1978) [Sov. Phys. JETP 47, 684 (1978)].
- <sup>4</sup>K. S. Gochelashvili, N. V. Karlov, A. N. Orlov, R. P. Petrov, Yu. N. Petrov, and A. M. Prokhorov, Pis'ma Zh. Eksp. Teor. Fiz. 21, 640 (1975) [JETP Lett. 21, 302 (1975)].
- <sup>5</sup>N. V. Karlov and K. V. Shaitan, Zh. Eksp. Teor. Fiz. 71, 464 (1976) [Sov. Phys. JETP 44, 244 (1976)].
- <sup>6</sup>L. D. Landau, Sobranie trudov (Collected Works), pt. 1, Nauka, 1969, p. 146.
- <sup>7</sup>B. J. Wood, J. S. Mills, and H. Wise, J. Phys. Chem. 67, 1462 (1963).
- <sup>8</sup>V. V. Styrov, Pis'ma Zh. Eksp. Teor. Fiz. 15, 242 (1972) [JETP Lett. 15, 168 (1972)].
- <sup>9</sup>V. V. Styrov and V. M. Tolmachev, Dokl. Akad. Nauk SSSR 218, 1150 (1974).
- <sup>10</sup>V. V. Styrov, Yu. I. Gyurin, and A. E. Kabanskii, Fiz. Tekh. Poluprovodn. 11, 2164 (1977) [Sov. Phys. Semicond. 11, 1271 (1977)].

- <sup>11</sup>V. G. Kornich, V. K. Man'ko, and A. N. Gorban', Pis'ma Zh. Eksp. Teor. Fiz. 27, 489 (1978) [JETP Lett. 27, 460 (1978)].
- <sup>12</sup>V. V. Styrov, Pis'ma Zh. Tekh. Fiz. 2, 540 (1976) [Sov. Tech. Phys. Lett. 2, 211 (1976)].
- <sup>13</sup>T. Carrington and D. Garvin, transl. in: Vozbuzhdennye chastitsy v khimicheskoi kinetike (Excited Particles in Chemical Kinetics), Mir, 1973, p. 123.
- <sup>14</sup>E. E. Nikitin, Teoriya elementarnykh atomno-molekulyarnykh protsessov v gazakh (Theory of Elementary Atomic-Molecular Processes in Gases), Khimiya, 1970.
- <sup>15</sup>M. Green and M. J. Lee in: Solid State Surface Science (M. Green, ed.) Kekker. Russ. transl. Mir, 1972, p. 155.
- <sup>16</sup>S. G. Gagarin, Yu. A. Kolbanovskii, and L. S. Polak, Teor. Eksp. Khim 8, 217 (1972).
- <sup>17</sup>J. C. Lie, J. Hinze, and B. Liu, J. Chem. Phys. 59, 1872 (1973).
- <sup>18</sup>L. Veseth, J. Mol. Spectrosc. 48, 283 (1973).
- <sup>19</sup>V. M. Agranovich and M. D. Galanin, Perenos energii elek-

tronnogo vozbuzdeniya v kondensirovannykh sredakh (Electron-Excitation Energy Transport in Condensed Media), Nauka, 1978.

- <sup>20</sup>N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Dover, 1948.
- <sup>21</sup>I. Yu. Tekhver and V. V. Khizhnyakov, Zh. Eksp. Teor. Fiz. **69**, 599 (1975) [Sov. Phys. JETP **42**, 305 (1975)].
- <sup>22</sup>A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 57, 263 (1969) [Sov. Phys. JETP 30, 147 (1970)].
- <sup>23</sup>K. V. Shaitan, Vestn. Mosk. Univ., No. 1, 42 (1976).
- <sup>24</sup>M. A. Kozhushner, V. G. Kustarev, and B. R. Shub, Dokl. Akad. Nauk SSSR 237, 841 (1977).
- <sup>25</sup>V. G. Krongauz and B. P. Dmitriev, Lyuminestsentnye materialy i osobo chistye veshchestva (Luminescent Materials and Highly Purified Substances), No. 8, Stavropol', 1973, p. 121.

Translated by J. G. Adashko

# Resonance excitation of hypersound by two-dimensional plasmons

M. A. Krasheninnikov and A. V. Chaplik

Institute of Semiconductors, Siberian Division, USSR Academy of Sciences (Submitted 28 December 1978) Zh. Eksp. Teor. Fiz. 76, 1812–1815 (May 1979)

The feasibility of exciting superhigh-frequency acoustic waves by means of piezoelectric coupling to twodimensional plasma waves is demonstrated. The cases of two-dimensional plasmons on the free boundary of a crystal and in the inversion layer of a metal-dielectric-semiconductor structure are considered. The effect of a magnetic field on plasmon damping and hypersound generation is elucidated.

PACS numbers: 72.30. + q, 71.45.Gm

In our previous paper,<sup>1</sup> we drew attention to the possibility of resonance interaction between a two-dimensional plasma wave and a surface piezoacoustic wave if the plasma layer is organized on the surface of the piezocrystal. This may be a metal-dielectric-semiconductor (MDS) structure on a piezoelectric semiconductor, or a thin film of a semimetal or a semiconductor sputtered onto a piezocrystalline substrate.<sup>1)</sup> It was shown that there exists in the system in question a specific two-dimensional-plasmon damping mechanism (besides the collision and Landau-damping mechanisms) stemming from the emission of acoustic waves into the body of the piezoelectric substrate. Thus, a two-dimensional plasma wave can serve as a source for the generation of sound with frequency equal to the plasma frequency  $\omega_{b}$ . This quantity is determined by the formula<sup>5</sup>

$$\omega_p^2 = 4\pi e^2 N_* k/m (\varepsilon + \varepsilon_D \operatorname{cth} k\Delta), \quad \omega_p \gg k v_0, \tag{1}$$

where  $N_s$  is the surface charge density in the inversion layer; k is the plasmon wave vector;  $\varepsilon_{,}\varepsilon_{D}$  are the permittivities of the semiconductor and the dielectric of the MDS structure;  $\Delta$  is the thickness of the dielectric,  $e, m, v_0$  are the charge, effective mass, and Fermi velocity of the electron. In the cited experiments,<sup>2-4</sup>  $N_s$ ~10<sup>12</sup> cm<sup>-2</sup>,  $m = 0.2m_0$ , and  $k \sim 2 \times 10^4$  cm<sup>-1</sup>; then  $\omega_p$ ~6×10<sup>12</sup> sec<sup>-1</sup>.

In the present paper we present the results of the solu-

acoustic vibrations, i.e., we find the acoustic field in the piezocrystal for a given "extraneous" electric field on its surface. Such a formulation corresponds to the scheme of the experiments described in Refs. 2-4: onto the metallic electrode of the MDS structure falls electromagnetic radiation of frequency  $\omega$ , and the transmittance of the electrode is modulated with a spatial period of  $2\pi/k$ . If the quantities  $\omega, k$ , and  $N_s$  are connected by the relation (1), then a two-dimensional plasma wave arises in the system. For the indicated values of  $N_s$  and k, the phase velocity of the plasmon is much greater than the velocity, s, of sound. Therefore, it follows from the phase-matching conditions that the wave vector, q, of the emitted wave is almost perpendicular to the surface, so that its component along the direction of propagation of the plasmon is equal to k (see Fig. 1). We also investigate the effect of a magnetic field, and show that, besides the obvious change in the dispersion law, the value of the decrement of the plasma waves becomes appreciably magnetic-field dependent.

tion of the nonhomogeneous problem of coupled plasma-

Let us first consider the simplest case:  $\varepsilon_D = 1$ ,  $k\Delta \rightarrow \infty$ , i.e., the plasma layer is located on the free surface of a piezocrystal. The crystal has the symmetry  $C_{6\nu}$ , the hexagonal axis lies in the plane of the surface, the plasmon wave vector is perpendicular to the  $C_6$