Using the isotropy in spin space, we find the values

$$\alpha=1, \quad B/A=2. \tag{A.8}$$

We note that for $T_0 \ll V$ the Hubbard model with repulsion and a half-filled band is equivalent to the Heisenberg model for an antiferromagnet.


[1]E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. 20, 1445 (1968).
[2]J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).
[3]R. B. Griffiths, Phys. Rev. 133, A768 (1964).
[4]A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 64, 342 (1973) [Sov. Phys. JETP 37, 176 (1973)].
[5]K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 69, 764 (1975) [Sov. Phys. JETP 42, 390 (1975)].
[6]M. Takahashi, Progr. Theor. Phys. 43, 1619 (1970); 42, 1098 (1969); 43, 860(E) (1970).
[7]V. G. Vaks, A. I. Larkin and S. A. Pikin, Zh. Eksp. Teor. Fiz. 51, 361 (1966) [Sov. Phys. JETP 24, 240 (1967)].
[8]K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 66, 2290 (1974) [Sov. Phys. JETP 39, 1129 (1974)].
[9]P. A. Lee, T. M. Rice and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).
[10]A. J. Epstein, S. Etemad, A. F. Garito and A. J. Heeger, Phys. Rev. B5, 952 (1972).
[11]L. N. Bulaevskiĭ, A. V. Zvarykina, Yu. S. Karimov, R. B. Lyubovskiĭ and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. 62, 725 (1972) [Sov. Phys. JETP 35, 384 (1972)].
[12]P. Delhaes, F. Aly and P. Dupuis, Sol. State Commun. 12, 1099 (1973).
[13]S. Etemad, A. F. Garito and A. J. Heeger, Phys. Lett. 40A, 45 (1972).
[14]L. N. Bulaevskiĭ, A. A. Gusseĭnov, O. N. Eremenko, V. N. Topnikov and I. F. Schegoiev, Fiz. Tverd. Tela (Leningrad) 17, 781 (1975) [Sov. Phys. Solid State 17, 498].
[15]F. F. Igoshin, A. P. Kir'yanov, V. N. Topnikov and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. 68, 1203 (1975) [Sov. Phys. JETP 41, 597].
[16]H. Shiba, Progr. Theor. Phys. 48, 2171 (1972).



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# On the possibility of controlling surface phenomena by means of laser radiation


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Processes that can be induced by laser radiation on a surface with adsorbed atoms or molecules are considered. The radiation can alter the desorption, increase the surface diffusion, and influence the heterogeneous catalysis in a selective manner (i.e. act on certain types of atoms). Desorption of atoms due to laser irradiation can be used, among other things, to determine the sites of various atomic groups on the surface of the adsorbent. In order to photograph the surface with sufficiently high resolution, a method for obtaining holograms of the adsorbent is proposed, using collimated atomic beams instead of coherent light.



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## INTRODUCTION

Many recent papers have reported the use of laser radiation for selective excitation of vibrational and electronic levels in atoms and molecules.[1–5] Selective excitation uncovers new possibilities of acting on chemical reactions, makes possible mass separation of atoms,[3–5] etc. In the overwhelming number of the considered cases, the laser radiation acts on a homogeneous medium, and for a number of reasons this medium is chosen to be a gas.

In this article we consider the action of laser radiation on heterogeneous systems. We are interested in the new possibilities and effects that may be provided by the presence of the phase-separation surfaces in this case. These include: selective action on the processes of desorption of atoms and molecules adsorbed on a surface with ensuing change of the concentration, mass separation of the atoms via selective desorption (laser chromatography), the effect on the surface diffusion, the change of the catalytic properties of the adsorbents, information on the composition and location of the active groups present on the adsorbent surface (in principle one can hope even to decode the "mosaic" of the molecular groups on the surface of biological objects such as cells, etc.).

Some of these questions have already been considered earlier,[6,7] namely resonant buildup in an adsorption potential with the aid of a set of frequencies, as well as detachment of atoms from a surface. In particular, the possibility was considered of generating hypersound by matched oscillations of the adsorbed atoms in the potential of the wall.[6,7] The possibility of selective heterogeneous separation of vibrationally-excited molecules was considered in[8], but in this variant the selective excitation of the vibrational levels by the laser beam was produced not on the surface but in the volume.

## 1. ACTION OF LASER ON ADSORBATE. ESTIMATES OF THE PROBABILITIES OF EXCITATION AND DESORPTION UNDER THE INFLUENCE OF LASER RADIATION

Depending on the frequency, the mechanisms whereby laser radiation acts on adsorbed particles can be quite different—infrared radiation is capable of inducing par-

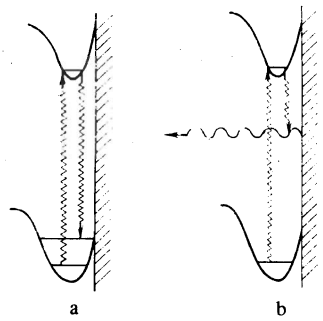


FIG. 1.

ticle vibrations in a given adsorption potential, whereas ultraviolet or visible radiation, by exciting electronic transitions in the adsorbed particles, changes their interaction potential with the surface; in this case the excitation and desorption processes can proceed in accordance with the scheme shown in Fig. 1.

Effective action of infrared radiation on an adsorbate is possible whenever the particles adsorbed on the surface acquire a charge. The Hamiltonian of the interaction with laser radiation takes in this case the form $q_{eff}\mathbf{E}(t)\mathbf{r}$, where $\mathbf{E}(t)$ is the field in the laser wave and $q_{eff}$ is the effective charge of the adsorbed particle. The probability of single-quantum desorption can be represented for this case in the form

$$P_{1d}=2\pi\hbar^{-1}q_{eff}^2 \times|\langle\psi|\mathbf{E}_0\mathbf{r}|\psi_{in'}\rangle|^2\rho(\hbar\omega'-\varepsilon_1); \quad (1)$$

here $\rho(\varepsilon)$ is the density of states in the continuous spectrum, $\varepsilon_1$ is the adsorption energy, $\hbar\omega'$ is the quantum energy, $\mathbf{E}_0$ is the laser-field amplitude, and the prime in $\psi_{in'}$ denotes that this state pertains to the discrete spectrum.

To estimate at least the order of magnitude of $P_{1d}$, we introduce the following simplification: first, we consider a one-dimensional problem, and second, we assume that $\hbar\omega' \gg \varepsilon_1$. In this case we can write

$$\psi=\left(\frac{2}{L}\right)^{1/2}\sin\left[\left(\frac{2M\varepsilon}{\hbar^2}\right)^{1/2}x\right]. \quad (2)$$

$$\rho(\varepsilon)=\frac{L}{\pi\hbar}\left(\frac{M}{2\varepsilon}\right)^{1/2}; \quad (3)$$

Here $L$ is the normalization length, $|\langle\psi_f|x|\psi_{in'}\rangle|^2$ is of the order of magnitude of $\bar{x}^2(\bar{x}/L)$, where $\bar{x}$ is the characteristic dimension over which $\psi_{in'}$ differs from zero. Taking this into account, the estimate for (1) takes the form

$$P_{1d}\sim\frac{q_{eff}^2\bar{x}^3}{\hbar^2}\left(\frac{M}{2\hbar\omega'}\right)^{1/2}E_0^2. \quad (4)$$

Taking $\bar{x}\sim 3\times10^{-9}$ cm, $q_{eff}=4.8\times10^{-10}$ cgs esu, $\hbar\omega'\sim 0.3$ eV, $M\sim10^{-23}$ g, and $E_0\sim 1$–10 cgs esu, we obtain $P_{1d}\sim10^4$–$10^6$ sec$^{-1}$. The desorption cross section, which is connected with $P_{1d}$ by the relation

$$\sigma_{1d}=4\pi P_{1d}\hbar\omega'/E_0^2c, \quad (5)$$

turns out under these conditions to be of the order of $10^{-18}$ cm$^2$.

It should be noted that although the process of direct desorption is strictly speaking not selective, it can be used to change the relative surface concentrations of neutral and charged particles, inasmuch as the radiation acts only on the charged component.

To estimate the probabilities and the cross sections for the excitation of oscillations in the adsorption potential, it is necessary first to estimate the lifetimes of the excited states. Assuming that the lifetime of the excited states $\tau_{1\,exc}$ is determined by the production of acoustic phonons, we obtain in first order perturbation theory

$$\frac{1}{\tau_{1\,exc}}\sim\frac{2\pi}{\hbar^2}\left|\left\langle\psi_f\left|\frac{\partial U}{\partial x}\right|\psi_{in'}\right\rangle\right|^2\delta x_0^2\frac{e^{\hbar\omega/kT}}{e^{\hbar\omega/kT}-1}\frac{2\pi\omega^2}{(2\pi c_s)^3}. \quad (6)$$

Here $U(x)$ is the potential energy of a particle in the adsorption well, $\hbar\omega=\Delta\varepsilon$ ($\Delta\varepsilon$ is the difference between the level energies), $c_s$ is the speed of sound in the adsorbent, $\delta x_0^2$ is the square of the amplitude of the displacement of the surface when the system contains one phonon with frequency $\omega$ ($\delta x_0^2\sim\hbar/\rho\omega$, $\rho$ is the density of the medium), and $T$ is the temperature.

The matrix element in (6) can be represented in the form

$$\left\langle\psi_f\left|\frac{\partial U}{\partial x}\right|\psi_{in'}\right\rangle=\hbar\omega\int\psi_f\frac{\partial\psi_{in'}}{\partial x}dx. \quad (7)$$

To estimate the order of magnitude of the integral in (7) we can take $\psi_{in'}$ and $\psi_{f'}$ to be the wave functions of particles trapped in a rectangular well of dimension $x$. Taking this into account, the estimate for the matrix element takes the form

$$\left\langle\psi_f\left|\frac{\partial U}{\partial x}\right|\psi_{in'}\right\rangle\sim\frac{\hbar\omega}{\bar{x}}\left(\frac{\hbar}{2M\omega}\right)^{1/2}\frac{1}{\bar{x}}.$$

Taking $\bar{x}\sim 3\times10^{-9}$ cm, $T\sim100\,^\circ$K, $M\sim3\times10^{-23}$ g, $c_s\sim5\times10^5$ cm/sec, and $\hbar\omega/kT\sim1$, we obtain $\tau_{1\,exc}^{-1}=10^{11}$ sec$^{-1}$; $\tau_{1\,exc}$ should generally speaking be of the same order as the lifetimes of the vibrationally-excited states in condensed bodies. These times, which are given in[9], lie approximately in the range 5–30 psec. The level widths given in the same paper turn out to be of the order of several reciprocal picoseconds.

The probability of observing a particle in a vibrationally-excited state $|c|^2_{1\,exc}$ can be represented in the form

$$|c|^2_{1\,exc}\sim|\langle\psi_f|x|\psi_{in'}\rangle|^2\hbar^{-2}q_{eff}^2E_0^2\tau_{1\,exc}^2. \quad (8)$$

Accordingly the cross section for the excitation of vibrational levels by resonant quanta can be written in the form

$$\sigma_{1exc}\sim(4\pi\omega/c\hbar)\tau_{1exc}q_{eff}^2|\langle\psi_f|x|\psi_{in'}\rangle|^2, \quad (9)$$

the order of magnitude being $\sigma_{1\,exc}\sim10^{-15}$–$10^{-16}$ cm$^2$.

If the desorption from the excited level is much more intense than from the ground level, then, by using se-

lective excitation, it is possible to increase appreciably the probability of detachment of the particle of a given type. The probability of stimulated desorption of particles of a given sort $i$ can in this case be written in the form

$$P_i=\nu_i\exp\left\{-\frac{\varepsilon_i-\Delta\varepsilon}{kT}\right\}|c|^2_{1\,\mathrm{exc}}\approx\nu_i\exp\left\{-\frac{\varepsilon_i-\Delta\varepsilon}{kT}\right\}\frac{\sigma_{1\,\mathrm{exc}}\tau_{1\,\mathrm{exc}}}{\Delta\varepsilon}W\equiv\frac{\sigma'_{1\,\mathrm{exc}}}{\Delta\varepsilon}W; \tag{10}$$

here $\nu_1\exp[-(\varepsilon_1-\Delta\varepsilon)/kT]$ is the probability of desorption from an excited level in the absence of laser irradiation, $W$ is the power of the laser radiation per unit surface, and $\sigma'_{1\,\mathrm{exc}}$ is a certain effective cross section introduced formally by Eq. (10). At $\nu_1\sim10^{12}$–$10^{13}$ sec$^{-1}$, $\exp[-(\varepsilon_1-\Delta\varepsilon)/kT]\sim0.01$ and $\Delta\varepsilon\sim100$ K, the cross section $\sigma'_{1\,\mathrm{exc}}$ turns out to be of the order of $10^{-17}$–$10^{-18}$ cm$^{-2}$.

### Desorption of atoms by the action of visible or ultraviolet laser radiation on the adsorbate

The probability of observing an atom in an electron-excited state following irradiation can be written in the form

$$|c|^2_{2\,\mathrm{exc}}\sim\left|\frac{d_1E_0}{\hbar\Gamma}\right|^2\left|\int\psi_2^*\psi_1\,dv\right|^2, \tag{11}$$

where $d_1$ is the dipole moment corresponding to the electronic transition, $\Gamma$ is the width of the excited level, and $\psi_1$ and $\psi_2$ are the wave functions describing the vibrational motion in the adsorption potentials in the states shown in Fig. 1. Using as an estimate $d_1\sim10^{-18}$ cgs esu, $\Gamma\sim10^{11}$ sec$^{-1}$, $E_0\sim1$–$10$ cgs esu, and $|\int\psi_2^*\psi_1\,dv|^2\sim0.1$, we obtain $|c|^2_{2\,\mathrm{exc}}\sim10^{-5}$–$10^{-3}$. The corresponding cross section $\sigma_{2\,\mathrm{exc}}$ which is connected with $|c|^2_{2\,\mathrm{exc}}$ by the relation

$$\sigma_{2\,\mathrm{exc}}\sim4\pi\hbar\omega\Gamma|c|^2_{2\,\mathrm{exc}}/E_0^2c,$$

turns out under these conditions to be of the order of $10^{-15}$–$10^{-16}$ cm$^2$.

The probability of an atom or molecule becoming desorbed on going to the ground electronic state is

$$P_d=1-\sum_j\left|\int\psi_j^*\psi_2\,dv\right|^2, \tag{12}$$

where the summation is over all the wave functions of the discrete spectrum. In this case, if the adsorption potentials of the particles in the electron-excited and in the ground states differ significantly from each other, it is possible to put as a rough estimate $P_d\sim1$. The cross section for selective desorption then turns out to be of the order of $\sigma_{2\,\mathrm{exc}}$.

## 2. INFLUENCE OF LASER RADIATION ON SURFACE DIFFUSION

In many cases adsorbed particles on the ground vibrational level of the adsorption potential are unable to move along the surface. However, when they become excited to higher vibrational levels, they turn out to be capable of moving over the surface. For many problems, however, for example mass separation of atoms,

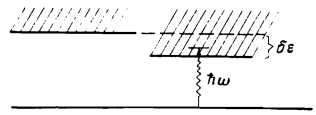

FIG. 2.

it may be of interest to increase the diffusion selectively, namely to increase the diffusion for only the required sort of atoms. This process can be realized by resonantly exciting, with laser light, the vibrations in the adsorption potential.

Inasmuch as we now have infinite motion of the particles along the surface, it follows that in contrast to the excitation problem considered in the preceding section, we are dealing with spreading of energy levels into bands. To obtain a selective increase of the diffusion it is necessary to choose the quantum energy lower than the boundary of the band for one component, but higher than the band boundary for the other component (see Fig. 2). In the case of different isotopes, for example, $\delta\varepsilon$ should be of the order of $\varepsilon\delta M/M$, where $\varepsilon$ is the width of the forbidden band and $\delta M$ is the mass difference. The kinetic energy connected with the particle motion, equal to $M^*V/2$ ($M^*$ is the effective mass and $V$ is the velocity) should be less than $\delta\varepsilon$. Assuming by way of an estimate $M^*\sim M$ and $\delta\varepsilon\sim\varepsilon\delta M/M$, we obtain

$$V\leqslant(2\varepsilon\delta M/M^2)^{1/2}; \tag{13}$$

At $\varepsilon\sim300\,^\circ$K, $M\sim10^{-23}$ g, and $\delta M/M\sim0.1$ we have $V\lesssim3\times10^4$ cm/sec.

The derivation of the estimate for the excitation cross section $\sigma_{3\,\mathrm{exc}}$ in this process is analogous to the method of obtaining $\sigma_{1\,\mathrm{exc}}$ and $\sigma_{1d}$. For $\sigma_{3\,\mathrm{exc}}$ we can write

$$\sigma_{3\,\mathrm{exc}}\sim2\pi\omega Mq^2_{\mathrm{eff}}c^{-1}\hbar^{-2}\bar{x}^2S_0, \tag{14}$$

where $S_0$ is the area on which the particle is localized when in the ground state. At $\omega\sim10^{13}$ sec$^{-1}$, $\bar{x}\sim3\times10^{-9}$ cm, $S_0\sim10^{-16}$ cm$^2$, $M\sim10^{-23}$ g, and $q_{\mathrm{eff}}\sim4.8\times10^{-10}$ cgs esu we obtain $\sigma_{3\,\mathrm{exc}}\sim4\times10^{-18}$ cm$^2$.

The diffusion coefficient $D$ can be represented, using (6) and (14) in the form

$$D\sim\tfrac{1}{3}V^2\tau_{1\,\mathrm{exc}}{}^2\sigma_{3\,\mathrm{exc}}W/\hbar\omega. \tag{15}$$

In the derivation of (15) it is assumed that the particle mean free path $l$ is determined by the relation $l_s\sim V\tau_{1\,\mathrm{exc}}$. Taking $W\sim10^3$ W/cm$^2$ and $V\sim10^4$ cm/sec, we obtain $D\sim10^{-8}$ cm$^2$/sec.

## 3. INFLUENCE OF LASER RADIATION ON HETEROGENEOUS CATALYSIS PROCESSES

The mechanism whereby laser radiation acts on processes occurring in heterogeneous catalysis can be separated into two groups. The first includes methods of changing the concentrations of the reagents in selective desorption, and the second includes the change induced by the laser radiation in the number of active centers on the adsorbent surface.

The equations describing the kinetics of adsorption within the framework of Langmuir's theory,[10] take in the presence of stimulated desorption the form

$$dN_i/dt=\alpha_i Q_i(N_i^*-N_i)-\beta_i N_i, \tag{16}$$

$$\alpha_i=\varkappa_i S_i(2\pi M_i kT)^{-1/2}, \tag{17}$$

$$\beta_i=\nu_i \exp(-\varepsilon_i/kT)+P_i; \tag{18}$$

here $N_i$ is the number of atoms of sort $i$ per unit surface, $Q_i$ is the partial pressure of the $i$-th component, $S_i$ is the effective area of the adsorbed molecule, $N_i^*$ is the number of adsorption centers for molecules of sort $i$ per unit surface, $\varkappa_i$ is the sticking probability, $\nu_i \exp(-\varepsilon_i/kT)$ is the desorption probability in the absence of laser radiation, and $P_i$ is the induced-desorption probability.

The equilibrium surface concentration of the first component is

$$N_i=\frac{\alpha_i Q_i N_i^*}{\alpha_i Q_i+\nu_i \exp(-\varepsilon_i/kT)+P_i}. \tag{19}$$

The concentrations of the adsorbed substances can be controlled if the following conditions are satisfied:

$$P_i>\nu_i \exp(-\varepsilon_i/kT);\ \alpha_i Q_i; \tag{20}$$

$P_i$ is connected with the power $W_i$ of the laser radiation that is resonant with the particles of sort $i$ by the relation

$$P_i=\sigma_i W_i/\hbar\omega_i, \tag{21}$$

where $\sigma_i$ is the cross section of the corresponding desorption process.

Using the estimates made above for $\sigma_i$, and taking by way of example $W_i \sim 10^3$ W/cm$^2$, we obtain $P_i \sim (10^5-10^6)$ sec$^{-1}$. Since $\nu_i \sim 10^{12}-10^{13}$ sec$^{-1}$, satisfaction of (20) calls for satisfaction of the condition $kT \lesssim 0.1\varepsilon_i$.

Let us list, in concluding this section, the requirements that must be satisfied by those heterogeneous chemical reactions for which it is meaningful to use laser stimulation. First, the use of laser radiation is important in those cases when the final product is not removed and the reverse reaction predominates—selective desorption of the final product ensures in this case that the chemical reaction can proceed predominantly in the forward direction. Second, to avoid spontaneous nonselective desorption, the catalyst must operate at relatively low temperatures, such as to satisfy the condition (20).[1)] By way of example, we cite the reaction

$$2H_2C{=}CH{-}CH_3 \rightleftarrows CH_2{=}CH_2+CH_3{-}CH_2{-}CH{=}CH_2$$

(with a rhenium-oxide catalyst at 80 °C) and the reaction

$$3H_2+N_2 \rightleftarrows 2NH_3$$

(with iron at 400 °C).

### Effect of laser irradiation on the adsorbant

It is known[10] that in many cases the illumination of the surface changes its catalytic properties. This effect is explained in[10] as follows: if the adsorption centers are electrons or holes localized on structure defects of the surface, then, by illuminating the surface, it is possible to change the populations of the local levels produced by these defects (to increase or decrease the "degree of ionization" of the structure defects), and by the same token change the concentration of the adsorption centers. Action of laser light can differ from that of ordinary nonmonochromatic illumination in that in this case it becomes possible to populate with electrons (or holes) only those local levels having energies in the range of interest to us. If local levels that differ in energy serve as adsorption centers for different components, then the possibility of controlling the populations of these levels is equivalent to selective control of the surface concentrations of these components.

## 4. USE OF LASER-STIMULATED DESORPTION TO STUDY SURFACE STRUCTURE

The method proposed here is intended for the investigation of complicated surfaces that carry a large number of different atomic groups; it can be used, in principle, to determine the locations and the compositions of these groups.

An investigation of the surface in accordance with the considered method includes the following series of operations: first, the surface must be cooled to temperatures on the order of several degrees Kelvin and placed in a vacuum; the surface is then sprayed with an adsorbent monolayer that does not interact with the surface and adheres to it as a result of physical-adsorption forces (it is convenient to use inert-gas atoms as the adsorbate); the surface is then photographed (this question is dealt with in the next section); the next step is to apply to the surface an infrared laser beam, so that effective desorption of the adhered atoms takes place in the vicinities of the atomic groups whose natural frequencies coincide with the laser frequency. Taking a second photograph and comparing the photographs obtained before and after the laser irradiation, we can determine the locations of these resonant groups. After all this it is possible, by heating the surface, to remove the adsorbents from it and repeat the cycle at a different laser frequency. As a result one can hope to obtain local spectra of the natural oscillations of atomic groups located on the surface, and determine the compositions of these groups from the spectra.

The limitations on the spatial resolution in this method, besides those connected with the photography process, are determined by the dimension of the region in which oscillations of a laser-excited atom groups can build up. If the natural frequencies of the atom groups greatly exceed the limiting Debye frequency (and it is only then that we can count on separating the resonant peaks against the background of the diffuse spectrum), the linear dimensions of the region in which the oscilla-

tions can build up amount to one or two interatomic distances.

Let us estimate the probability of detachment of the atoms adsorbed in the immediate vicinity of the atomic groups that are resonantly excited by the laser. We represent the Hamiltonian describing the vibrations of this atom in the form

$$\hat{H} = -\frac{\hbar^2}{2M_a}\frac{\partial^2}{\partial x^2} + U(x+\delta x(t)) \approx -\frac{\hbar^2}{2M_a}\frac{\partial^2}{\partial x^2} + U(x) + \frac{\partial U}{\partial x}\delta x(t), \tag{22}$$

where $\delta x(t)$ is the displacement of those atoms of the excited group with which the adhered atom is in contact. If $\hbar\omega_1$, where $\omega_1$ is the frequency of the oscillations of the atomic group, exceeds $\varepsilon_1$ ($\varepsilon_1 \sim 0.01-0.1$ eV in the case of physical adsorption), then the probability $P_{2d}$ of detaching an adsorbed particle can be represented in the form

$$P_{2d} = \frac{2\pi}{\hbar}\left|\left\langle \psi_f \left| \frac{\partial U}{\partial x} \right| \psi_{in'} \right\rangle\right|^2 \rho(\hbar\omega_1 - \varepsilon_1)\,\delta x_0^2, \tag{23}$$

where $\delta x_0$ is the amplitude of the oscillations of the molecular group, and $\psi_f$ and $\rho(\varepsilon)$ are given by formulas (2) and (3).

Using the estimate obtained in Sec. 1 for the matrix element of the form $\langle \psi_{f'} | \partial U/\partial x | \psi_{in'} \rangle$, and taking into account the difference between the normalizations of the wave functions pertaining to the discrete and continuous spectra, we obtain

$$P_{2d} \sim \left(\frac{\hbar\omega_1}{M_a}\right)^{1/2} \frac{\delta x_0^2}{\bar{x}^3}. \tag{24}$$

The oscillation amplitude $\delta x_0$ at resonance is of the order of

$$\delta x_0 \approx \frac{\tau E_0}{2M'\omega_1}\frac{\partial d}{\partial x}\Big|_{x=x_0}, \tag{25}$$

where $M'$ is the effective mass, $\tau$ is the damping time, and $\partial d/\partial x$ is the derivative of the dipole moment with respect to the coordinate $x$ taken at the equilibrium point $x_0$ (we assume that the atomic group has an intrinsic or induced dipole moment).

The damping time $\tau$ can be represented in the form

$$\tau^{-1} \approx \tau_2^{-1} + \left(\frac{\hbar\omega_1}{M_a}\right)^{1/2} \frac{\hbar}{M'\omega_1\bar{x}^3}, \tag{26}$$

where $\tau_2$ is the damping time without allowance for the desorption; the second term of (26) determines the damping due to the presence of desorption. Taking, for example, $\partial d/\partial x \sim 10^{-10}$ cgs esu, $\omega_1 \sim 3\times10^{14}$ sec$^{-1}$, $M' \sim M_a \sim 3\times10^{-23}$ g, $\tau_2 \sim 10^{-11}$ sec, $\bar{x} \sim 3\times10^{-9}$ cm, and $E_0 \sim 1$ cgs esu, we obtain $P_{2d} \sim 10^3$ sec$^{-1}$.

In many cases it is preferable not to use $P_{2d}$, but to introduce the cross section $\sigma_{2d}$ for the adsorption of a resonant quantum accompanied by desorption, in the form

$$\sigma_{2d} \approx \left(\frac{\hbar\omega_1}{M_a}\right)^{1/2} \frac{\hbar\tau}{M'\omega_1\bar{x}^3}\sigma_r, \tag{27}$$

where $\sigma_r$ is the cross section for the adsorption of a resonant quantum, and is equal to $\pi\tau(\partial d/\partial x)^2/M'c$. At $\tau_2 \gtrsim 10^{-12}$ sec we have $\sigma_{2d} \sim \sigma_r$. At the parameters indicated above, $\sigma_r$ turns out to be of the order of $10^{-18}$–$10^{-19}$ cm$^2$.

To avoid spontaneous desorption and diffusion of the atoms over the surface, it is necessary to cool the surface to temperatures on the order of several degrees Kelvin. For example, at $\varepsilon_1 = 0.02$ eV and $T \sim 5$ °K, the desorption time amounts to dozens of hours. The question arises whether it is possible to maintain such low temperatures on an intensely heated surface. Assume for example that the laser radiation power is $\sim 10$ W/cm$^2$ ($P_{2d}$ is in this case $\sim 10^2$ sec$^{-1}$). For the cooling efficiency to be maximal, the thickness of the substrate illuminated by the laser must be less than the phonon mean free path, which for quartz glass at $\sim 5$ °K, for example, is of the order of several millimeters. The surface temperature can be obtained in this case from the condition $\sigma_B(c/c_s)^2T^4 = W$, where $\sigma_B$ is the Stefan–Boltzmann constant. Taking $c_s \sim 5\times10^5$ cm/sec we obtain $T \sim 6$ °K. The total power released by the laser on the surface is $W' \sim \pi WR^2$, where $R$ is the dimension of the focus. For $R \sim 10^{-2}$ cm it amounts to $\sim 3$ mW in this case.[2)]

## 5. PHOTOGRAPHY OF SURFACE STRUCTURE

To photograph the surface at a resolution $\sim 1$–$3$ Å and at the same time avoid desorption and destruction of the surface during the course of the photography, it is necessary to use particles of sufficiently low energy, incapable of causing desorption, but having a de Broglie wavelength $\lambda$ not larger than one angstrom. Both requirements can be satisfied in the photography by using low-energy atoms. For example, at an atomic weight $A \sim 20$ and an energy $\sim 30$ °K (which is much less than the value required for desorption) we have $\lambda \sim 1$ Å.

Figure 3 shows schematically one of the possible setups intended for the surface photography. A beam of atoms from source 1 is incident on the object 2 and on the substrate 3, is partially reflected elastically and strikes screen 4, on which it then becomes adsorbed. If the momentum spread $\delta p$ of the atoms leaving the source satisfies the condition

$$\delta p L'/\hbar < 1, \tag{28}$$

where $L'$ is the dimension of the object, then the atoms adsorbed by the screen will form an interference pattern (the role of the reference beam is played here by the stream of atoms elastically reflected by the substrate). The form of the surface can be reconstructed in principle from this picture.

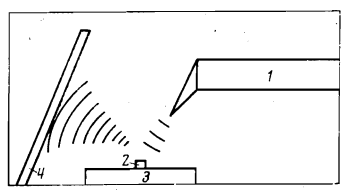


FIG. 3. Diagram of possible experiment: 1—atom source, 2—object, 3—substrate, 4—screen.

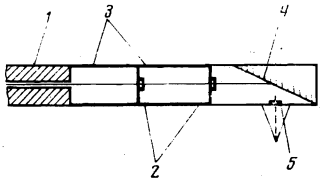


FIG. 4. Diagram of collimator: 1—gas-supply channel, 2—diaphragms, 3—adsorber, 4—crystal, 5—diaphragm.

Strictly speaking, the picture photographed from the screen is a superposition of three pictures—reflection from the substrate, reflection from the object, and interference of these reflections. The contribution of the reflections from the object and from the substrate produces, in the course of reconstruction, certain noises. In some cases, to obtain better reproduction quality, it is meaningful, after taking the photograph, to place alongside the investigated object some fixed object with known structure (reference object) and repeat the photography. Using both photographs it is possible to separate in pure form the interference pattern produced by the atoms that are elastically reflected from the investigated and from the reference objects.

The angle spread $\delta\varphi$ of the atoms and the relative energy spread $\delta\varepsilon/\varepsilon$ turn out to be, taking (28) into account, of the order of $\lambda/L'$. A possible source construction that can deliver atom beams with small angle and energy spreads is shown in Fig. 4. Gas flowing through the channel 1 is collimated by diaphragms 2 and strikes the crystal 4, which reflects the incident atoms at different angles depending on their energies. Diaphragm 5 passes only atoms with given energy. The number of atoms $Q$ injected per unit time from the source should in the optimal case be of the order of $SnV_T(\delta p/p)^3$, where $S$ is the aperture area of the diaphragm 5, $n$ is the concentration of atoms in channel 1, and $V_T$ is the thermal velocity. For example, $Q$ turns out to be of the order of $10^7$ particles/sec at $L' \sim 1000$ Å ($S \sim L'^2$), $\lambda \sim 1$ Å, $n \sim 3\times10^{21}$ cm$^{-3}$ and $V_T \sim 2\times10^4$ cm/sec. The number of atoms needed to obtain a satisfactory interference pattern should be at least one or two orders of magnitude larger than the number of resolved elements $N$ ($N \sim L'^2/\lambda^2$). Assuming that the greater part of the atoms is reflected elastically and strikes the receiving screen at $L' \sim 1000$ Å, $\lambda \sim 1$ Å, and $Q \sim 10^7$ particles/sec we can estimate the exposure duration $\tau_{exp} \sim 1$–$10$ sec.

If we vary the angle of inclination of the crystal from photograph to photograph, then we obtain a series of interference patterns corresponding to different de Broglie wavelengths of the incident particles. Using these interference patterns to reconstruct the form of the object, we can obtain a much more accurate reconstruction than in the case of photographs with one fixed wavelength.

In this system (Fig. 4), the atoms that do not pass through the collimator are adsorbed by the adsorber. More complicated collimator schemes can be proposed, in which these atoms are returned to the gas-supply channel. The multiple utilization of the atoms is particularly important in those cases when radioactive atoms are used, since this makes it possible to decrease appreciably the total number of radioactive material in the injector. The use of radioactive atoms makes it possible to register relatively simply small amounts of adsorbate on the receiving screen.[3)]

Let us estimate the probabilities of adsorption or inelastic reflection of atoms by a surface. The probability of a transition that results in a change of the velocity after the collision of the atom with the wall can be written by using the results of Landau[11] in the form

$$P'\,dv' = \frac{2}{3\pi^2}\frac{m^4 v v'(v^2-v'^2)v'\exp[m(v^2-v'^2)/2kT]}{\rho\hbar^3 c_s^3\,(\exp[m(v^2-v'^2)/2kT]-1)}\,dv', \qquad (29)$$

where $m$ is the mass of the incident atom, $v$ and $v'$ are the velocities before and after the collision. The total inelastic-collision probability $\alpha_{in}$ can be obtained by integrating (29) from zero to $v$. Under the condition $mv^2/2 \gg kT$, we obtain

$$\alpha_{in} = \frac{64}{15}\frac{m}{M'}\left(\frac{\varepsilon}{\Theta_D}\right)^3; \qquad (30)$$

here $M'$ is the mass of the wall atom and $\Theta_D$ is the limiting Debye energy of the wall material. At $m/M' \sim 5$, $\Theta_D \sim 300$ °K, and $\varepsilon \sim 30$ °K, $\alpha_{in}$ turns out to be of the order of 0.02.

The adsorption probability $\varkappa$ in the case when a particle having a kinetic energy that is small in comparison with $\varepsilon_1$ collides with a wall, under the condition $\Theta_D \gg \varepsilon_1$ can be estimated from the formula

$$\varkappa \sim \frac{\varepsilon_1^{3/2}}{2\pi(2m)^{1/2}\rho\bar{x}^2 c_s^3}. \qquad (31)$$

At $\varepsilon_1 \sim 0.03$ eV, $m \sim 3\times10^{-23}$ g, $c_s \sim 5\times10^5$ cm/sec, and $\bar{x} \sim 3\times10^{-9}$ cm we obtain $\varkappa \sim 0.1$.

The foregoing estimates show that most atoms are reflected elastically. This circumstance, on the one hand, is needed to obtain an interference pattern, but on the other hand it is necessary that the atoms striking the screen be adsorbed by the latter. This can be done by using a sufficiently rough screen such that the atoms experience on the average several collisions with the surface before they are reflected from the screen. Approximately ten collisions suffice to make the sticking probability close to unity.

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[1)]Relatively low temperatures ($T \sim 100$–$500$ °C) can be maintained on the surface of a laser-irradiated catalyst at the powers indicated above only in the presence of intense cooling.

[2)]At such low powers the laser can be replaced in principle by a nonmonochromatic light source from which a line of required width is separated with a monochromator or a filter.

[3)]A possible suggestion, for example, is $Ar^{37}$ with an approximate lifetime one month.

[1]S. A. Akhmanov, O. N. Chunaev, V. V. Fadeev, R. V. Khokhlov, D. N. Klyshko, A. I. Kovrigin, and A. S. Piskarscas, Proc. of the Symposium on Modern Optics, New York, March 22–24, 1967.
[2]G. A. Askar'yan, Zh. Eksp. Teor. Fiz. **46**, 403 (1964); **48**, 666 (1965) [Sov. Phys. JETP **19**, 273 (1964); **21**, 439 (1965)].
[3]V. S. Letokov, Science **180**, 451 (1973).
[4]A. N. Oraevskii, Trends in Physics, European Physical Society, Geneva, 1973, p. 95.
[5]N. V. Karlov, Appl. Opt. **13**, 301 (1974).
[6]G. A. Askar'yan and V. A. Namiot, Pis'ma Zh. Eksp. Teor. Fiz. **21**, 646 (1975) [JETP Lett. **21**, 305 (1975)].
[7]G. A. Askar'yan and V. A. Namiot, Zh. Eksp. Teor. Fiz. **69**, 1986 (1975) [Sov. Phys. JETP **42**, 1009 (1975)].
[8]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)].
[9]V. Kaĭzer, Kvantova Elektron. (Moscow) **1**, 2036 (1974) [Sov. J. Quant. Electron. **4**, 1131 (1975)].
[10]F. F. Vol'kenshteĭn, Fiziko-khimiya poverkhnosti poluprovodnikov (Physics and Chemistry of Semiconductor Surfaces), Nauka, 1973.
[11]L. D. Landau, Sobranie trudov (Collected Works) 1, Nauka, 1969, pp. 153–155 [Pergamon].

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# The phenomenological theory of magnetic resonance and of spin waves in antiferromagnetics

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We construct a theory of magnetic resonance in antiferromagnets. The theory contains the maximum possible number of independent phenomenological functions of the temperature that can be determined in principle from dynamic and static experiments. In the high-temperature region the equations of the theory are essentially those of Onsager's theory of thermodynamic fluctuations. At low temperatures, in the so-called spin wave region, several parameters of the Onsager theory turn out to be the same. We describe this situation by new equations for magnetic resonance which are second-order equations in time and which can be derived by means of Lagrange's mechanical principle. As actual cases we consider the most lucid cases of a two-sublattice antiferromagnet in an external field and of the antiferromagnets $CoCO_3$, $MnCO_3$, $FeCO_3$, $CoF_2$, and $MnF_2$.

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## 1. INTRODUCTION

When studying magnetic resonance and spin waves in antiferromagnets theoretically or experimentally it is extremely useful to have general phenomenological expressions for the spectra which contain the maximum number of constants compatible with the symmetry and physical properties of the phenomenon. The first step along this path was the famous Landau–Lifshitz equation[1] which describes ferromagnetic resonance and the essentially long-wavelength spin waves in a ferromagnet. The first phenomenological theory of antiferromagnetic resonance (AFMR) was the theory of Kittel and Keffer[2] (see also[3]) constructed in the molecular field approximation. Borovik-Romanov and Turov (see[4,5] and also[6]) developed a phenomenological theory of AFMR in the large spin approximation for $T=0$. The first attempt to construct a theory of AFMR containing the maximum possible number of constants was undertaken by Gufan.[7]

An essential step in the range of phenomenological theories was the hydrodynamic theory of spin waves constructed by Halperin, Hohenberg, and others.[8] Finally, a complete phenomenological theory of spin waves in the exchange approximation and for the case where there are no external fields was very recently produced by Andreev and Marchenko.[9] Essentially they determined all possible kinds of "acoustic" oscillations in a magnetic system. It turned out that while for oscillations of atoms there are always three and only three acoustic branches, for oscillations of magnetic moments the number of acoustic modes can be both less and more than three. It is determined by the specific exchange group of magnetic symmetry introduced by the authors. Exchange magnetic groups differ from the magnetic groups (including time-reversal) introduced by Landau[10] (see also[11]) in his time and are the same as the so-called color groups.

In the high-temperature range $T \lesssim T_c$ ($T_c$ is the magnetic phase-transition temperature) the theory of AFMR can be constructed in a natural way as a particular case of the general Onsager theory of thermodynamic fluctuations (see, e.g., [12]). In fact, one can write the AFMR equations as Onsager equations for thermodynamic variables:

$$\frac{dq_a}{dt} = -\sum_b \gamma_{ab} \frac{\partial f}{\partial q_b}. \tag{1}$$

Here $f$ is the free energy of a small deviation from equilibrium which is, in general, an arbitrary positive definite quadratic form of the variables $q_a$. The coefficients $\gamma_{ab}$ are the Onsager coefficients; their form is