CONFERENCES AND SYMPOSIA

Scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (28 January 1998)

A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences was held on 28th January 1998 at the P L Kapitza Institute for Physical Problems, RAS. The following reports were presented at the session:

(1) **Nagaev E L** (Institute for High-Pressure Physics of RAS) "Magnetoimpurity theory of colossal magnetoresistance materials";

(2) **Bonch-Bruevich A M, Vartanyan T A, Przhibel'skiĭ S G, Khromov V V** (S I Vavilov State Optics Institute, RAS, St. Petersburg) "Photodetachment of surface atoms of metals".

Brief presentations of both reports are given below.

Magnetoimpurity theory of colossal magnetoresistance materials

E L Nagaev

I. A specific feature of ferromagnetic semiconductors is the peak of the resistivity ρ close to the Curie point T_C. The ρ peak is suppressed by an external magnetic field which leads to negative isotropic colossal magnetoresistance (CMR). These correlated properties are common for all ferromagnetic semiconductors, both degenerate and nondegenerate and independently of the charge carrier sign, of which there are several dozen. It also manifests itself in initially antiferromagnetic semiconductors if, as a result of doping, they become ferromagnetic semiconductors [1].

At present a special interest of investigators is attached to the ferromagnetic semiconductors $La_{1-x}Di_xMnO_3$, obtained from the antiferromagnetic insulator $LaMnO_3$ by doping with the divalent ions Di = Ca, Sr and so on, which injects holes into the crystal $(0.6 > x > 0.25)$. One would be wrong in assuming that this interest be related to the fact that the ρ peak and CMR are pronounced in manganites especially strongly. On the contrary, these effects are pronounced much more weakly than in many other ferromagnetic semiconductors. For example, the ρ peak does not exceed 2 to 3 orders of magnitude [2], whereas in some doped EuO samples, approaching T_C from the low-temperature side, the transition from the high-conductive state to the insulating state takes place with a record resistivity jump of 19 orders of magnitude [3]. But in manganites, unlike other ferromagnetic

semiconductors, the CMR peak is achieved at room temperatures, which makes them especially promising for practical applications.

2. Many physicists engaged in investigations of manganites ignore the fact that, qualitatively, the properties of the manganites with complete ferromagnetic ordering are quite similar to those of other ferromagnetic semiconductors and try to relate them to concrete specific features of the manganites, first of all, to the presence of the Jahn – Teller Mn^{3+} ions in them. In addition, the erroneous opinion that not only the Jahn – Teller effect but also the so-called double exchange is necessary for appearance of the ρ peak is very popular (both these statements were made in Ref. [4]).

As for the Jahn – Teller effect, it can influence the manganite transport properties to some extent. But both the resistivity peak and CMR are observed in all ferromagnetic semiconductors without Jahn – Teller ions (all 30 ferromagnetic semiconductors listed in Ref. [1] are of this type). This fact indicates unequivocally that the Jahn – Teller effect cannot be the origin of these peculiar features and only accompanies them in manganites. It is sufficient to mention the fact that EuO, incorporating the properties of the ferromagnetic semiconductors to the maximal degree, by no means is a Jahn – Teller material.

One should carry out much more attentive analysis to elucidate the role of the exchange interaction between the charge carriers and localized d- or f-spins peculiar to magnetic conductors and semiconductors. Its intensity AS, where A is the exchange integral between the localized d- (or f-) spin and charge carrier, and S is the d-(f-) spin magnitude, should be compared to the carrier energy band width W. The not very transparent term 'double exchange', introduced in Ref. [5], means the usual exchange interaction between the charge carrier and localized spin, when it is so strong that its energy exceeds the carrier energy band width $(W \ll AS)$. Physically, such a situation is realized in transition metal compounds, if the electrons or holes move over their partially filled d-levels. For example, in manganites it should be realized if the holes move over the Mn^{3+} ions , converting each of them into a Mn^{4+} ion when dwelling at it. There is experimental evidence in favor of this scenario, but in favor of the opposite scenario, too. In the latter case the holes move over the O^{2-} ions, and then the inequality $W \gg AS$ should be met (e.g., Ref. [6]). Thus, this problem is not yet solved conclusively. It should also be noted that, generally speaking, the number of holes is less than the number of divalent impurity atoms as the impurity can form electrically nonactive clusters.

But the double exchange is, certainly, absent from the rare earth compounds where the electrons do not move over the partially filled f-shells but over the empty s- or d-shells. Under typical conditions, in the rare-earth metals and their com-

pounds W exceeds AS by an order of magnitude. For example, in EuO W amounts to 4 eV, and AS only to 0.25 eV [1]. Nevertheless, EuO displays specific properties of ferromagnetic semiconductors to a maximal degree.

Similar properties are displayed by dozens of other ferromagnetic semiconductors without the double exchange, in particular, EuS, CdCr$_2$Se$_4$, CdCr$_2$S$_4$ and so on [1]. Hence, one cannot consider the double exchange as a necessary condition for the resistivity peak and related CMR. But one can state that both these features manifest themselves at any strength of the exchange interaction between the charge carriers and localized spins.

Probably, the incorrect conclusions made in Ref. [4] are a consequence of the incorrect procedure for calculation of the conductivity: it is calculated from the Kubo formula within a high-frequency approximation, and then in the final result the frequency is put equal to zero. Meanwhile, both these limiting cases are mutually exclusive.

3. Now we will discuss the real mechanism for appearance of the resistivity peak and CMR in the ferromagnets. First of all, it should be mentioned that resistivity peak of ferromagnetic semiconductors is necessarily related to imperfections of the crystal lattice. For example, in the perfect Ni crystals at the Curie point only a break in the resistivity vs. temperature curve is observed, and only the temperature derivative of the resistivity is peaked. But if one makes the same crystal imperfect in some manner, then it will display a resistivity peak in the vicinity of the Curie point. In degenerate magnetic semiconductors the part of imperfections is played by the ionized donor or acceptor impurity.

Along with this, there is no question that the magnetic state of the crystal influences the charge transport. In the theory, stated below and called the magnetoimpurity theory [7], both these factors are united in the following manner. On increasing the temperature, the nonmagnetic impurity atoms acquire effective magnetic moments which increase the interaction of charge carriers with impurity atoms. These effective moments are maximal in the vicinity of T_C, just where the resistivity of the crystal is maximal.

In detail more: in degenerate semiconductors, both magnetic and nonmagnetic, the electrons of the donors (or the holes of the acceptors) are delocalized, and the donors are ionized. But the delocalized electrons continue to interact with randomly located ionized donors. This randomness causes two main effects: a fraction of the charge carriers go over to localized states, but they are not localized at separated donors but at groups of them arising as a result of the impurity density fluctuations. One talks about these carriers as about the carriers in the band-tail states. Those carriers which have higher energies are delocalized but are scattered by the impurity, which leads to their finite mobility. In addition, they screen the electrostatic field of the ionized impurity which results in an enhanced density in the vicinity of the impurity atoms.

The peculiarities of degenerate ferromagnetic semiconductors are determined by the fact that the charge carriers tend to support the ferromagnetic ordering in them, as the latter ensures their minimal energy [1]. With increasing temperature the ferromagnetic ordering in the crystal becomes destroyed. But its destruction in the vicinity of the impurities occurs more slowly than in the rest of the crystal, as in this vicinity the density of the charge carriers is higher. Hence, the degree of ferromagnetic order is also higher there.

For this reason an excessive magnetic moment arises close to the impurities, on increasing temperature. The charge carrier scattering by this excessive moment is combined with its scattering by the screened Coulomb potential. Hence, the total scattering increases with temperature. Correspondingly, the scattering of the delocalized electrons and the number of electrons localized in the band-tail increase, too. The resistivity grows. It can even occur that, due to the increased attraction of the electrons to donors, these electrons will completely localize at them, i.e., the Mott transition to an insulating state will take place.

On a further increase of temperature, the excessive magnetization close to the impurities becomes destroyed, too, and the crystal becomes highly conductive again. The same occurs under the magnetic field, which tends to establish complete ferromagnetic ordering and, hence, diminishes the difference in the magnetization close to the impurities and far from them. This is the origin of CMR.

An analysis of the interaction of the charge carriers with the impurity is carried out using the condition of the constant electrochemical potential and the Poisson equation. The difference from the standard approach to nonmagnetic systems consists in the fact that the dependence of the electron energy on the magnetization is taken into account. In the Born–Oppenheimer approximation, it is assumed that the magnetization $M(r) = M[n(r)]$ is a smooth function of coordinates as the typical length for its change, i.e. the screening length, is large in semiconductors [8]. For this reason, for example, at $W \gg AS$ in the spin-wave approximation the corresponding contribution to the electron energy is equal to $(-AM[n(r)]/2)$, if the conduction electrons are completely spin-polarized.

As a result, one finds that the total interaction of the conduction electron with the electrostatic field of the ionized donor and the excess magnetization in its vicinity is given by a screened Coulomb-like potential, in which the true electron charge e is replaced with the effective charge $e_{ef} = e(\varepsilon/\zeta)^{1/2}$, exceeding the former. The effective dielectric constant ζ is related to the true dielectric constant ε by $\zeta = \varepsilon(1 - \Gamma)$, where at $W \gg AS$ the magnetoelectric constant Γ, accounting for dependence of the local magnetic ordering on the electron density, is given [1, 9, 10] by expressions

$$\Gamma = \frac{A}{2}\frac{dM}{dn}\frac{dn}{d\mu} \propto \frac{A^2 T}{(H + T_C/S)^2}\frac{dv}{d\mu} \quad \text{where} \quad \frac{T_C}{S} \ll T \ll T_C,$$

$$\Gamma \propto \frac{A^4 S^2 (S+1)^2 ma^3 k_F v}{\mu^2 T} \quad \text{where} \quad T \gg T_C, \quad H = 0 \ (v = na^2),$$

$$\Gamma \propto \frac{A^2}{T}\frac{dv}{d\mu}\exp\left\{-\frac{(H + Av/2)S}{T}\right\} \quad \text{where} \quad T \gg T_C, \quad H \to \infty,$$

$$(1)$$

where n is the electron density, μ their Fermi energy, and a the lattice constant. In the opposite limiting case of the double exchange, $W \ll AS$, an explicit expression for the magnetoelectric constant was obtained only for the spin-wave region [1, 11]:

$$\Gamma \propto \frac{n^{1/3} atT}{S^2 (H + T_C/S)^2},$$

$$(2)$$

where t is the electron hopping integral.

4. As is seen from Eqns (1), (2), on increasing the temperature, the effective charge e_{ef} of an impurity atom increases in the spin-wave region and decreases in the paramagnetic region. Thus, it is maximal in the vicinity of T_{C}, where the resistivity maximum should be located. The magnetic field decreases e_{ef}, making it approach e.

For relatively small changes in ρ, using an expression for the density of states in the band tail presented in Ref. [8], and replacing in it e by e_{ef}, one obtains formulae

$$n_l \propto \left(\frac{me^2 n^{1/2} r_s^{1/2}}{\varsigma} \right)^{3/2}; \quad r_s = \sqrt{\frac{\zeta}{\varepsilon}} r_s^0; \quad \frac{1}{r_s^0} = \sqrt{\frac{4\pi e^2}{\varepsilon} \frac{\mathrm{d}n}{\mathrm{d}\mu}} \tag{3}$$

for the total number of electrons localized in the tail, where m is the conduction electron effective mass. According to Eqn (3), $n_l \propto e_{\text{ef}}^{9/4}$ i.e., the number of electrons localized in the tail is maximal, and the number of delocalized electrons is minimal at the temperature at which e_{ef} is maximal.

Similarly, at this temperature the relaxation time for the scattering of delocalized electrons by the impurity is minimal. It is seen from the Brooks–Herring expression for the scattering of conduction electrons by ionized impurities modified in the same manner as (3):

$$\tau_k^{-1} \propto \frac{e^4 n m}{k^3 \zeta^2} \left[\ln(1 + \eta) - \frac{\eta}{1 + \eta} \right], \quad \eta = 4k^2 r_s^2 . \tag{4}$$

As for semiconductors $\eta \gg 1$, the relaxation time is proportional to $1 / \left[e_{\text{ef}}^4 \ln(e/e_{\text{ef}}) \right]$.

On increasing e_{ef}, the growth of the attraction of the electron to the donor can become so strong that a Mott transition from the high-conductive state to the insulating state can take place. Obviously, for this aim the effective radius $a_{\text{B}} = \hbar^2 / m e_{\text{ef}}^2$ of the Bohr orbit should become of the order of the mean distance $n^{-1/3}$ between the impurity atoms. For semiqualitative estimates of the metal-insulator transition temperature one may use the Mott criterion in its standard form, $a_{\text{B}} n^{1/3} = 0.25$, and use Eqns (1), (2).

5. At $x < 0.25$ the manganites are in a state with spontaneous magnetization which is below the saturation magnetization. Neutron scattering studies [12] display the presence of both antiferromagnetic and ferromagnetic scattering peaks. This picture might correspond either to canted antiferromagnetic ordering or to a mixture of the collinear ferromagnetic and antiferromagnetic phases. A choice in the favor of the second version was made in Ref. [12] as a result of scattering in the magnetic field which influenced the ferromagnetic peaks and did not influence the antiferromagnetic peaks.

Nevertheless, in Ref.[13] the results of Ref. [12] were interpreted as evidence of canted antiferromagnetic ordering which is established as a result of competition between direct antiferromagnetic exchange and indirect exchange between d-spins via the holes. The double exchange ($W \ll AS$) was assumed. In principle, if the isotropic exchange interaction cannot be described by an effective Heisenberg Hamiltonian and includes terms of higher orders in spins, then canted antiferromagnetic ordering in possible even in the absence of the Dzyaloshinskii anisotropy [14]. If one tries to construct such an effective Hamiltonian at $W \ll AS$, one finds that it should have such a non-Heisenbergian structure. If one limits oneself to uniform states of the crystal, then, really, for a certain range of hole densities canted antiferromagnetic ordering is more energetically favored than collinear antiferromagnetic and ferromagnetic orderings.

But uniform canted antiferromagnetic ordering turns out to be unstable with respect to fluctuating static fields of ionized impurity. To make sure of this, it is sufficient to note that for canted antiferromagnetic ordering the magnetoelectic constant Γ is nonzero and rather large. In the case of the double exchange and the staggered antiferromagnetic ordering at $W \ll AS$ one obtains for it [1, 9]

$$\Gamma = \frac{0.3}{v^{2/3} v_{\text{F}}} \left(\frac{v}{v_{\text{F}}} \right)^{1/3}, \quad v_{\text{F}} \propto \frac{T_{\text{C}}}{W} \ll 1 , \tag{5}$$

where v_{F} is the number of the charge carriers per atom at which the ferromagnetic ordering becomes stable ($v < v_{\text{F}}$). Obviously, for not very small v (for example, for comparable with v_{F}) the quantity Γ is sufficiently close to 1 or can even exceed 1. In the former case this means a Mott transition to the insulating state contrary to the initial assumption about the metallic-like conductivity of the system. In the latter case the effective dielectric constant ζ becomes negative, and the effective charge imaginary, which also points to the instability of the uniform highly conductive state and to the tendency of the system to transition into the nonuniform state.

It is worth mentioning, that the hypothesis [13] about the canted antiferromagnetic ordering contradicts not only the neutronographic data [12], but also the electric data, according to which in the region of non-saturated ferromagnetism manganite samples with $x < 0.18$ do not exhibit the metallic-like conductivity assumed in Ref. [13].

But the semiconducting conductivity is compatible with the electronic phase separation proposed in Ref. [15] (see also Ref. [1]). In this theory all the charge carriers are concentrated in the ferromagnetic phase, and the antiferromagnetic phase is insulating. If the volume of the former is less than the latter, the ferromagnetic phase forms highly conductive inclusions inside the antiferromagnetic host. As they do not contact each other, the sample as a whole is insulating. But under the magnetic field the volume of the ferromagnetic phase increases, and the inclusions begin to contact. Hence, the sample as a whole becomes highly conductive. This is a different mechanism of CMR from that in the completely ferromagnetic region.

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Photodetachment of surface atoms of metals

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Nonthermal photodetachment of adatoms occupies a special place among the processes induced by the action of a photon flux on a solid surface. This essentially quantum mechanical phenomenon is related to a number of fundamental problems of the light–matter interaction and to the mechanism of nonradiative processes. The study of these processes is of interest for a number of applications.

The mechanisms of light excitation of the motion of adatoms for insulators, semiconductors, and metals are different. The study of photostimulated processes on metal surfaces has a complex history.

On the one hand, metal surfaces have been studied more thoroughly than insulator surfaces, since many methods of investigation, such as low-energy electron diffraction, tunneling microscopy, and the method of photoemission with high energy and angular resolutions, can be applied only in studies of conducting surfaces. At the same time it is obvious that many photon- and electron-stimulated processes on metal surfaces are inhibited for at least two reasons.

First, the electronic states in a metal (and on the metal surface) are highly delocalized, so that excitation of local electron bonds in the atom (molecule)–metal adsorption is improbable.

Second, the strong bond that exists between the surface states and the electrons in the bulk of the metal results in a situation in which the excited electronic states rapidly decay due to the existence of a large number of channels of dissipation of the excitation energy into the bulk of the metal. The typical lifetimes of the electronic states on the metal surface related to charge transfer amount to $\tau = 10^{-15} - 10^{-16}$ s, which is much shorter than the periods of atomic movements in the lattice, $\Omega = 10^{12} - 10^{13}$ s^{-1}. The estimate $\exp(-\Omega\tau) \sim 10^{-40} - 10^{-400}$ gives the probability (or, to be more exact, the improbability) of photodetachment of adsorbed atoms or molecules from the metal.

However, as early as in the 1950s, it was discovered that when the metal walls of a vacuum chamber are bombarded by electrons whose energies range from several tens to several hundreds electronvolts, the vacuum deteriorates because of electron-stimulated desorption of the submonolayer of the walls. In the 1960s, Menzel and Gomer [1] proposed that this process occurs because of the electronic excitation of the inner shells of the adsorption complex. According to the Menzel–Gomer–Readhead (MGR) model [2, 3], the excitation is a transition between the terms of the different electronic and often ionic states of the adsorption complex. The relaxation of this localized excitation is not accompanied by the departure of electrons from the excitation region and, there-fore, is not very rapid. The transitions between the terms of the adsorption complex are accompanied by a transfer of energy to the translational motion of molecules and to electrons in the bulk of the metal.

Subsequent research into such processes, which are caused by x-ray photons, corroborated this model. For instance, it was found that the efficiency of photodetachment rapidly decreases with increasing wavelength of the radiation and disappears at energies below $5 - 10$ eV, despite the fact that the adsorption energy is approximately ten times lower. Thus, it seemed that radiation that does excite the inner shells of adsorbed particles cannot initiate substantial motion on metal surfaces. The observed cases of desorption from metals were explained either by the heating of the surface by the radiation and thermal desorption or by photoprocesses involving the nonuniformities of the surface, e.g. on a section of an oxidized metal surface.

In the 1980s the situation changed dramatically. Two new phenomena were discovered independently and almost simultaneously. The first was laser-induced desorption of electron-donor molecules from a metal surface (NO from Pt) [4]. The mechanism of this process is similar to that of photodetachment from the surface of semiconductors, i.e. low-energy photons ($1 - 3$ eV in the case of NO) excite electrons in the surface layer of the metal. The diffusion of these electrons and their adhesion to an adsorbed molecule leads to the formation of a surface complex, whose de-excitation is the cause of desorption of the molecule. This mechanism differs from the MGR model in that the laser light excites not the adsorption complex proper but an electron in the bulk of the metal.

The other phenomenon, to which this report is devoted, also belongs to the class of photodetachment phenomena, but is much more exotic and in the light of the above ideas is, at first glance, entirely impossible. In 1984 photodetachment of Na atoms from the surface of a pure intrinsic metal was discovered [5]. Note that here were are speaking of photodetachment of atoms initially belonging to the sur-face, rather than of foreign atoms or molecules, as was discussed above. The phenomenon, which may be called the photoemission of atoms, was observed by different researchers and involved different objects. This effect has been identified in all alkali atoms and in silver, gold, and aluminum. However, there is still not enough experimental data to provide an exhaustive description of the pheno-menon.

First we will discuss the main laws governing this phenomenon, with reasoning based on the results of our own work [5–11]. The experimental devices used in photodetachment studies are basically the same. They consist of a vacuum chamber with a vacuum of $10^{-10} - 10^{-11}$ Torr into which a metal film, primarily a sodium film, is placed. The results for sodium are the most reliable and exhaustive. Various types of film were used: islet films on insulator substrates (quartz, lithium fluoride, sapphire) with islet diameters ranging from 10 to 100 nm, and solid films with a thickness of $100 - 200$ μm on insulator or metal films. The photodetachment was initiated by the pulsed or continuous light of a laser or a powerful lamp in the visible and UV parts of the spectrum. The atoms that had left the film were registered either by ionizing these atoms with an electron beam or additional high-powered laser light with subsequent detection of the ions [12–15], or by the absorption or fluorescence spectroscopy method that uses

cw laser radiation in resonance with an electron transition of the sodium atom [7]. The recording sensitivity of the latter method was the highest and amounted to $10^3 – 10^4$ atoms per cubic centimeter, with a time resolution of order 10^{-6} s. Note that in all the variants the devices allowed measurement, among other things, of the energy distribution of the atoms detached from the surfaces by their times of flight from the surface to the recording area.

The main results of these experiments consist in the following:

(1) Within a broad range of laser-light fluxes, $10^2 – 10^5$ W cm^{-2}, the number of photodetached atoms is linear in the intensity of the light. This fact, combined with the low quantum yield of the process, entirely excludes the possibility of ordinary thermal evaporation, since this would require the evaporation rate to be an exponential function of the intensity. The quantum efficiency of the photodetachment process proved to be extremely low, of the order of $10^{-7} – 10^{-10}$ atoms per photon.

(2) The photodetachment spectrum for metallic sodium atoms (Fig. 1) is determined primarily by the optical characteristics of the film (more precisely, by the dependence of the strength of the light's electric field at the metal surface on the light's wavelength). The value of the electric field strength at the metal surface increases dramatically as the frequency of the incident light approaches the frequency of
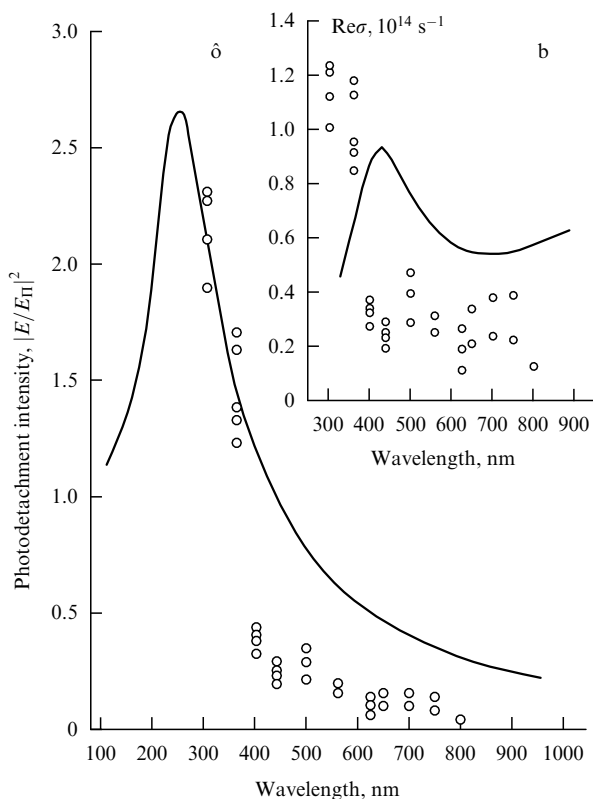
the plasma modes of the film. Here the photodetachment spectrum normalized to the square of the field's amplitude at the surface does not coincide with the spectrum of the real part of the high-frequency conductivity. This means that the photodetachment is not caused by absorption of light in the bulk of the metal. Note that the photoemission spectra of the atoms are determined by the size of the islets, as discovered by Hoheisel et al. [13], who found that the action spectrum is directly correlated with the excitation spectrum of plasmons in the metallic clusters (Mie resonances). The detected effect makes it possible, at least in principle, to selectively 'photoevaporate' clusters of definite shapes and sizes and to enhance the uniformity of their distribution [14].

(3) The efficiency of photoemission of atoms was found to be higher the greater the number of structural defects on the surface. The conclusion was drawn on the basis of two experiments [6, 7]. In the first the temperature dependence of the efficiency of photodetachment of atoms was determined. This dependence is of an activation nature, $\exp(-E/kT)$, with $E = 1000$ cm^{-1}. In the second experiment it was found that there is a gradual decrease in the efficiency of photoemission of atoms by the surface of a film prepared by rapid cooling (over the course of a few seconds) from room temperature to liquid nitrogen temperatures. The number of atoms leaving such a surface was found to monotonically decrease when a sequence of laser pulses was applied to the surface. The signal intensity was found to fall below the level at room temperature to the zero level, determined by the noise of the registering devices. The results of these experiments can be explained by the photodetachment of only those atoms that are in structurally defective states. The adatoms 'frozen' in the rapid cooling process are photodesorbed, with the surface becoming polished. Here, for reasons discussed earlier, the general-position atoms cannot be detached by laser light. With allowance for the entropy factor, the formation energy of structural defects is $2E = 2000$ cm^{-1}. At room temperature, the corresponding surface defect concentration corresponding to this value is 10^{13} cm^{-2}. The nature of the structural defects has yet to be established. Most likely, these defects are single atoms at steps on flat sections of the surface.

(4) It was found that the increase in the number of structural defects due to sputtering of atoms on a metallic field cooled to liquid nitrogen temperatures leads not only to an appreciable increase in atomic emission but also to an increase of the quantum yield of electron emission and an increase in the work function for the electrons of the metal from 2.31 to 2.36 eV [8]. The latter effect suggests that the structural defects form an electric double layer at the layer. Estimates of the charge of an elementary dipole of this layer yield $0.03e$. Thus, in contrast to general-position atoms at the surface, the electronic states of the structural defects capable of photodesorption are of a more localized and ionic nature.

(5) The energy spectrum of the photodesorbed atom differs substantially from the Maxwellian spectrum [7, 13, 16]. At the same time, the spectrum derived from the experimental data is found to be in good agreement [7] with the calculated spectrum if one assumes that the Maxwellian spectrum is deformed because of damping of excitation, whose lifetime differs little from the time of atomic detachment. This lifetime rapidly grows with the distance from the surface:

$$\tau = \tau_0 \exp \frac{x}{a}, \tag{1}$$

Figure 1. (a) Open circles stand for the sodium-atom photodetachment spectrum normalized to the power of the incident light, and the solid curve represents the wavelength dependence of the ratio of the square of the field amplitude at the metal surface to the square of field amplitude in the incident light. (b) Open circles stand for the sodium-atom photodetachment spectrum normalized to the square of the field amplitude at the surface, and the solid curve represents the wavelength dependence of the real part of the high-frequency conductivity of metallic sodium.

where τ_0 is the excitation lifetime at the surface, and a is the characteristic size of the region in which the atom interacts with the surface. Because the photodetachment quantum yield exponentially depends on the time the desorbed atom stays in the region with the surface potential, which in turn is inversely proportional to the velocity of the atom, the time-of-flight spectrum has the form

$$S(t) = t^{-3} \exp\left(-\frac{ml^2}{2kTt^2} - \frac{ta}{\tau_0 l} \right), \qquad (2)$$

where m is the mass of a sodium atom, and l is the distance between the metallic field and the place where the atom is detected. The number of slowly moving atoms detached from the surface is small in this spectrum, since at an effective temperature of 700 K for the outgoing flux the most probable energy is 0.2 eV. The best agreement between the calculated and experimental spectra is achieved at $a = 1\,\text{Å}$ and $\tau_0 = 3 \times 10^{-14}$ s (Fig. 2). The latter value is much larger than the time of decay of an electron excitation in the bulk of the metal.
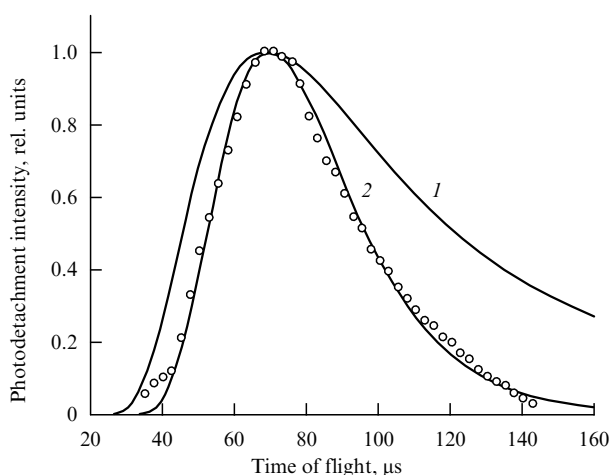

Figure 2. Open circles stand for the time-of-flight spectrum of sodium atoms ejected by the metal surface because of a pulse of laser light [$\lambda = 530$ nm] incident on the surface; curve *1* stands for a Maxwellian velocity distribution of the atoms with the peak coinciding with the experimentally measured spectrum; and curve *2* was calculated via Eqn (2) with allowance for the lifetime of excitations at the metal surface.

Note that it is difficult to study the above phenomenon experimentally because of its low efficiency ($10^{-7} - 10^{-10}$) and the complexity of detecting neutral particles. A partial explanation of this probably lies in the fact that the results achieved by different groups of experimenters differ. This is true, in particular, of time-of-flight spectra, measurements of the average energies of the outgoing particles, and measurements of the action spectrum [7, 15, 16]. For instance, it was found that the time-of-flight spectrum of atoms desorbed by pulsed ultraviolet 353-nm radiation is bimodal [16] with the most probable energies at 0.2 and 0.32 eV. The same researchers also detected [17] that as a result of illumination of an islet film formed by atom sputtering onto a surface cooled to liquid nitrogen temperatures, not only individual nitrogen atoms but also Na_2 molecules become detached, with the number of the latter exceeding the thermodynamic equilibrium number by many orders of magnitude.

There is still no well-developed theory of this phenomenon. The reason is that the processes are complex and photoatomic emission may follow many paths. A qualitative interpretation of the phenomenon can be achieved if one uses the spectral-term approach and allows for relaxation in the motion of atoms. Here two photodetachment mechanisms are possible. The first is the direct mechanism, similar to that of photodissociation of molecules, is realized by exciting a complex to a separation state. In the second mechanism, the excitation energy of an adsorption complex is transferred to a desorbed atom in the process of electron de-excitation in the adsorption complex. Since the photodesorbed adsorption atoms are bound to the surface more weakly than the general-position atoms, they act as foreign atoms. This suggests that their electronic states are partially localized, with the result that here electron excitations live longer than ordinary electron excitations in a metal.

Since the energy spectrum of the atoms leaving the surface can be satisfactorily approximated by a Maxwellian spectrum deformed in the ejection process, photodetachment can be visualized as follows. After an adsorption atom has been transferred to an excited state, it moves away from the metal surface. A nonradiative process, related most probably to plasmon modes, transfers (in 3×10^{-14} s) the adsorption complex from the excited state to the ground electron state, so that only the atoms that are able to leave the region of surface attraction during that time interval are desorbed.

The photodetachment cross sections of atoms are estimated by experiments at 10^{-23} cm^2. If we assume that the cross section of the initial act of photon absorption is of the order of $10^{-16} - 10^{-17}$ cm^2, which is typical of molecular absorption, and that the smallness of the photodetachment cross section is determined only by the quenching of the electron excitation near the surface, the size of the region in which quenching takes place estimated in this manner amounts to a realistic value of $2 - 4\,\text{Å}$. The 'overheating' of the atomic flux in comparison to the substrate temperature can be explained by the fact that a fraction of the energy of electron excitation of the adsorption atoms is transformed into the kinetic energy of these atoms.

The theoretical description of the detected phenomenon is fraught with difficulties because of the insufficient volume of experimental data and because of the need to step outside the scope of the band-structure model of metals if one wishes to build such a theory. Questions of charge transfer and the applicability of the spectral-term model have been ignored in our interpretation. However, the proposed approach is justified by the fact that the experimental data agree with the estimates of the parameters of the process. We believe that further studies of this phenomenon are very important not only for understanding the electronic properties of metal surfaces but also for possible practical applications.

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