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EXCITATION OF ELECTRONS IN SOLIDS BY RELATIVELY SLOW ATOMIC PARTICLES

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CONTENTS

I. INTRODUCTION

WHEN relatively slow atomic particles (we shall take these to mean in general ions and atoms with energies from several eV to several dozen keV) interact with a solid, they lose their kinetic energy and to over to a stationary charged state via a number of different processes. These processes are customarily subdivided into two classes: processes connected with an increase in the kinetic energy of the atoms of the solid (so-called "elastic interactions"), and processes connected with the excitation of the electrons of the solid, both by intraband and interband transitions ("inelastic interactions"). Until recently, in theoretical analysis of the deceleration of atomic particles in solids, it was assumed, following Bohr [1], that the role of inelastic interactions at particle energies of the order of 1 keV or less is small, and the excitation of the elctrons was disregarded (see, for example, [2]). Yet the experimental data show that an appreciable number of excited electrons is observed in the solid even at particle energies lower than 1 keV. These are due to the appearance of ion-electronic emission, radiative (induced) conductivity, ionoluminescence, etc.

Unfortunately, there are at present no systematic surveys summarizing the information on the excitation of electrons of the solid by bombardment with atomic particles. Several monographs [3-6] consider only ion-electronic emission of polycrystalline metallic samples. Yet presently available information indicates that emission of this type takes place from semiconductors and dielectrics, and also from single-crystal targets; this information greatly supplements the available data on this phenomenon.* In addition, data have been obtained on the radiative conductivity of germanium and on ionoluminescence, which from our point of view are of great interest for the problem under consideration, since they make it possible to estimate the total number of excited electrons. In this review we have attempted to gather the recently published data on the excitation of electrons in solids by relatively slow atomic particles.

*Secondary phenomena due to ion bombardment of solids are considered in [183]. Certain data on kinetic ejection of electrons are given in a recently published review [184].

II. EXCITATION OF ELECTRONS DUE TO THE INTERNAL ENERGY OF THE ATOMIC PARTICLE-PLUS-SOLID SYSTEM AND POTENTIAL EJECTION OF ELECTRONS

1. Basic Ideas on the Mechanism of the Phenomenon

The interaction between an approaching atomic particle and a solid induces different electronic transitions. If we confine ourselves to the case when an ion or an excited atom having sufficiently large internal energy and moving with faster than thermal velocity (for example, $E_0 \gtrsim 5$—10 eV) approaches the surface of the body, then the main transitions should be resonance and Auger transitions. (The probability of radiative transitions occurring within a time $\sim 10^{-8}$ sec is small for this case, since the time of interaction between the particle and the surface is smaller by several orders of magnitude [7].) If the bombarding particle has an unoccupied energy level lying lower than the Fermi level in the metal, it is possible to regard the particle-plus-metal system as excited, and the excitation can be replaced by means of the Auger effect (Fig. 1). In this case one of the electrons will go over to the vacant ground-state level of the particle, and the released energy will be transferred to another electron. This may be either another electron of the metal, or an electron hitherto at the excited level of the particle. The latter is possible in the case when an excited atom

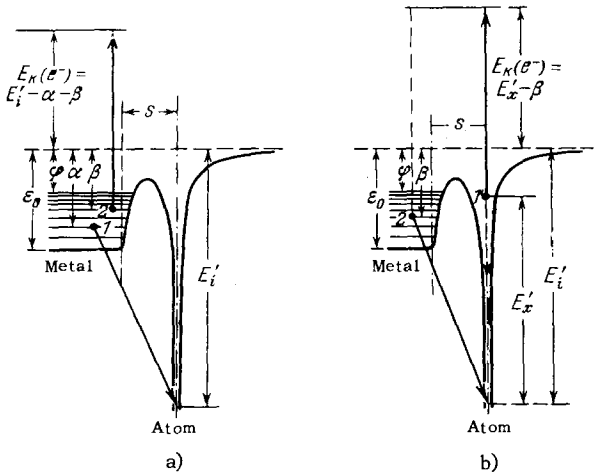

FIG. 1. a. Auger-neutralization of a positive ion on a metallic surface. The electron (1) neutralizes the bombarding particle, and the energy $E_i' - a$ released thereby is transferred to the electron (2). E_i' is the ionization energy of the atom located at a distance s from the surface; $E_k(e^-)$ is the kinetic energy of electron (2) is vacuum; φ is the work function of the metal; ε_0 is the energy of the bottom of the conduction band relative to the vacuum level. b. Auger-deactivation of an excited atom on a metal surface. The process with electron exchange is shown by the solid lines, and the process without exchange by the dashed lines. E_x' is the excitation energy of the atom located at a distance s from the surface.

approaches the surface, and also when the bombarding particle is an ion capable of first becoming neutralized (resonant transitions in the presence of the corresponding levels are more probable).

Thus, the Auger processes are responsible for the appearance of excited electrons in this case [7-8]. In the case of direct neutralization of the ion by the metal electron, one speaks of Auger neutralization. On the other hand, if the ion is first resonantly neutralized and its electron then acquires energy as a result of the Auger transition of another electron to the ground level of the particle, one speaks of a two-stage mechanism, the second stage of which is Auger-deactivation.* Some of the excited electrons can escape to the vacuum under favorable conditions. This phenomenon is called potential ion-electronic emission. We note that the electronic transitions under consideration are qualitatively the same for all solids (metals, dielectrics, and semiconductors).

2. Experimental Data on Potential Ejection of Electrons from Metals

In accordance with the concepts indicated above, at least one fast electron is produced upon neutralization of a singly-charged ion or upon deactivation of a metastable atom by the Auger effect. Of course, it can further lose its energy by interacting with other electrons of the metal, as a result of which the total number of excited electrons per bombarding particle may increase appreciably. The excitation of the electrons was studied only by investigating the electron emission in vacuum.

2.1. Characteristic features of emission. Potential ejection of electrons is customarily characterized by a coefficient γ_p, which is the average number of electrons escaping to the vacuum per unit incident particle with specified energy E_0, and by the distribution $N_0(E_k)$ of these electrons with respect to the kinetic energies E_k outside the solid. Both these characteristics depend on the properties of the bombarded object and of the particles incident on it, and also on their kinetic energy. It is essential to note that the electrons acquiring energy as a result of Auger transitions are as a rule quite fast. It is easy to understand (see Fig. 1) that the maximum energy of the electrons acquiring energy as a result of Auger neutralization of an ion or of Auger deactivation of an excited atom will be equal inside the metal to $E_i - \varphi$ or to E_x respectively, where E_i is the ionization energy and E_x is the excitation energy of the atoms incident on a metal having a work function φ. (For simplicity we assume that there are no electrons at levels higher than the Fermi level.) Consequently, the maximum energies of the electron outside the solid should be $E_i - 2\varphi$ and $E_x - \varphi$ for the ions and atoms, respectively.

Greatest attention was paid to the study of potential detachment of electrons by inert-gas ions. The atoms of these elements have large ionization potentials V_i (from 24.6 V for helium to 12.1 V for xenon), thus ensuring that an appreciable fraction of the total number of excited electrons go into the vacuum.

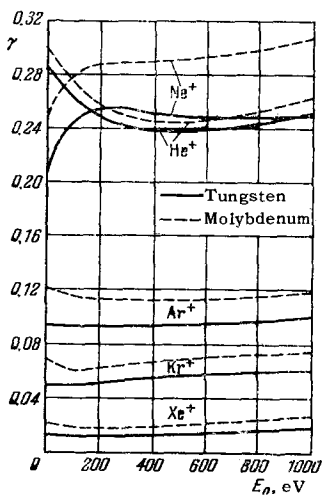

FIG. 2. Ejection of electrons from tungsten and molybdenum by inert-gas ions [10]. Solid lines – W, dashed – Mo.

*These electronic processes are described in greater detail by Hagstrum in [8]. This and his earlier papers are considered in the review [9], in which the latter process was called, in our opinion less appropriately, Auger relaxation.

Figure 2 shows the dependence of the coefficient* γ on the energy of singly-charged ions of all the inert gases bombarding pure polycrystalline tungsten and molybdenum targets [10]. We see that in first approximation the emission does not depend on the ion energy. Figure 3 shows the energy distributions of the knocked-out electrons for a molybdenum target bombarded by different ions with $E_0 = 10$ eV.[10] We see that the absolute values of the electron emission to the vacuum is quite large, reaching in the limit three electrons for each ten bombarding ions of helium, the energies of some of these electrons being as high as 12—15 eV. When multiply-charged ions are used, the number of excited electrons and their energies increase still further.[9,11]

2.2. Influence of the nature of the bombarding particles. Inasmuch as the maximum (and consequently also the average) energy of the excited electrons is determined by the internal energy of the particle-plus-solid system, the phenomenon of potential ejection of electrons from a given metal is determined primarily by the ionization and excitation potentials of the atoms incident on the target. At the present time, data have been obtained on electron ejection from refractory metals by the ions H_2^+, N_2^+, O_2^+ [12], He^+, Ne^+, Ar^+, Kr^+, Xe^+ (see, for example[10]), Zn^+, Cd^+ [13], and Hg^+ (see, for example,[14]).† Figure 4 shows a summary of these data, taken from [16] and supplemented by the results of the latest investiga-

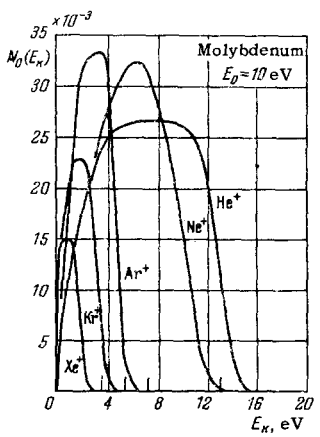

FIG. 3. Energy distribution of electrons ejected from molybdenum by inert-gas ions with energy $E_0 = 10$ eV [10]. The vertical lines at the abscissa axis denote the value of $E_i - 2\varphi$.

tions. In the first approximation, the coefficient γ_p increases linearly with increasing $eV_i - 2\varphi$. This relation does not hold for the molecular ions H_2^+, N_2^+, and O_2^+, which have approximately the same energy as the Ar^+ ion. The authors of [12] propose that this is due to transfer of part of the energy released upon neutralization to the excitation of oscillations of the particles in the molecule.

The variation of γ_p with the type of bombarding particle is uniquely connected with the character of the electron-energy distribution curve (see Fig. 3). The maximum kinetic energy of the electrons ejected by slow ions ($E_0 \lesssim 10$ eV) usually does not exceed ($eV_i - 2\varphi$), in agreement with the predictions for the Auger-neutralization process.

Experiments with neon isotopes [11] have shown that the mass of the bombarding particle has practically no effect on the values of γ_p.

Naturally, an increase in the multiplicity of the charge of the bombarding particle increases the values of the coefficient γ_p. An analysis of the experimental data [11] show that the average number of electrons per multiply-charged ion can greatly exceed unity (for example, $\gamma_p \approx 2.8$ for Xe^{5+} with energy $E_0 = 200$ eV). Obviously the number of electrons excited by an ion is even larger, i.e., in this case the neutralization of the ion takes place in several stages, each of which provides a fast electron. This information is confirmed by the form of the electron-energy distribution curves: In spite of the large growth of the values of γ_p on going from singly- to multiply-charged ions, the maximum electron energy increases relatively little and never reaches values close to the energy released when the particle is fully neutralized.

2.3. Influence of the nature of the bombarded object, the state of its surface, and the temperature. The potential ejection of electrons depends on the properties of the metal bombarded by the ions. The presently available data still do not permit an evaluation of the differences in the ejection of electrons by this mechanism from different faces of a metallic single crystal (only one paper has been published in

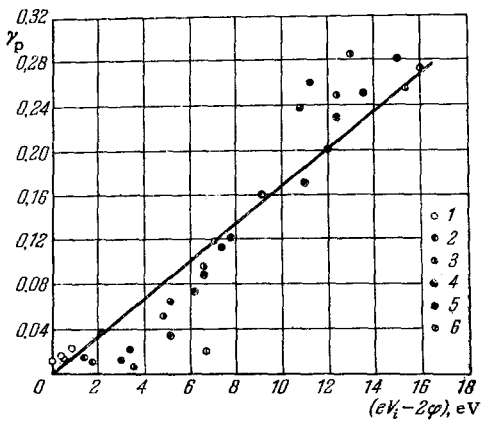

FIG. 4. Coefficient γ_p vs. $(eV_i - 2\varphi)$ as given by different authors: 1 – [13], 2 – [14], 3 – [10], 4 – [60], 5 – [18], 6 – [12].

*The ion-electronic emission characterized by the coefficient γ can be due either to potential or to kinetic energy, so that the experimental values are $\gamma = \gamma_p + \gamma_k$. An analysis of the data shows that under the conditions of Hagstrum's investigation $\gamma \approx \gamma_p$, since $\gamma_p \neq 0$ only when the targets are bombarded with He^+ ions with $E_0 > 400$ eV.

†Comparing the ejection of electrons by ions and by atoms of sodium from a molybdenum target during the course of deposition of a potassium coating on it, the authors of [15] attributed the observed differences to potential ejection of electrons by the Na^+ ions from a film having a minimum work function ($\gamma_p \approx 2\%$).

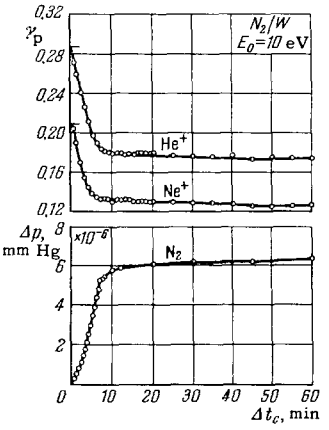

FIG. 5. The coefficient γ_p for tungsten bombarded by He^+ and Ne^+ with E_0 = 10 eV, and the increase of the pressure Δp in the instrument after flashing of the target, as a function of the time of exposure of the metal to nitrogen Δt_c [19]. The gas pressure is such that a monatomic coating of tungsten by nitrogen is obtained after approximately 10 min.

which emission from the (111) face of Ni crystal is described [17]). The differences between the emissions from different metals are connected primarily with the differences in their work functions. An example is afforded by the curves shown in Fig. 2 for tungsten and molybdenum targets. Experiments with different metallic targets has made it possible to establish that γ_p increases linearly with decreasing work function of the metal [18].

When molecules of nitrogen, oxygen, or hydrogen [19] are adsorbed on a pure metal, the potential ejection of the electrons decreases (Fig. 5). It has been shown [19] that the reduction of the emission cannot be due only to changes in the work function of the sample as a result of the formation of the adsorbed coating. The number of fast particles in the spectrum of the secondary electrons is greatly reduced.

Variation of the temperature of the target over a wide range does not influence the emission current due to the inert-gas ions, provided no change takes place in this case of the state of the surface layer of the metal as a result of adsorption or desorption [4]. It is shown in [14] that for Ar^+ ions bombarding targets of tungsten and molybdenum, γ_p does not depend on the temperature T of the metal up to 2000°K (Fig. 6). At the same time, γ_p increases noticeably when T increases if Hg^+ is the bombarding ion. When the temperature of a tungsten target is increased from 1000°K to 2100°K, the values of γ_p more than double. There is no doubt that if eV_i is close to double the work function of the metal and the probability of excitation of the electrons at levels higher than vacuum is small, then the presence of thermal smearing of the electrons above the Fermi level assumes an important role [14].

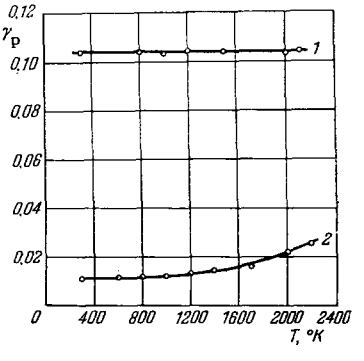

FIG. 6. Dependence of the coefficient γ_p of tungsten on the target temperature [14]. The bombarding ions were Ar^+ (curve 1) and Hg^+ (curve 2) with E_0 = 1 keV.

2.4. Dependence on the ion kinetic energy E_0. In the zeroth approximation it can be assumed that γ_p does not depend on the kinetic energy of the ions [4,11,14,16]. More careful measurements, however, performed so far only with inert-gas ions [10,11], have established a number of regularities which call for an explanation. As seen from Fig. 2, when the energy of He^+ ions is increased, the values of γ decrease, giving way to an increase in γ when $E_0 > 400$ eV. There are grounds for assuming [10,11] that this growth is due to the appearance of kinetic ejection electrons by He^+ ions (experimental values $\gamma = \gamma_p + \gamma_k$) and that the coefficient of potential ejection of the electrons γ_p will decrease for He^+ in the entire interval of energies E_0 used in these investigations. At the same time, it has been observed for Ne^+ that γ_p increases with E_0. For heavy ions of inert gases, the changes of $\gamma(E_0)$ are small.

The changes of the energy of the primary particles affect also the form of the electron-energy distribution curve. For all the ions except Ne^+, a monotonic broadening of the distribution curve is observed with increasing length of the "tail" (Fig. 7), and only for He^+ with $E_0 > 400$ eV is there a sharp increase of the group of slow electrons due to the kinetic ejection.

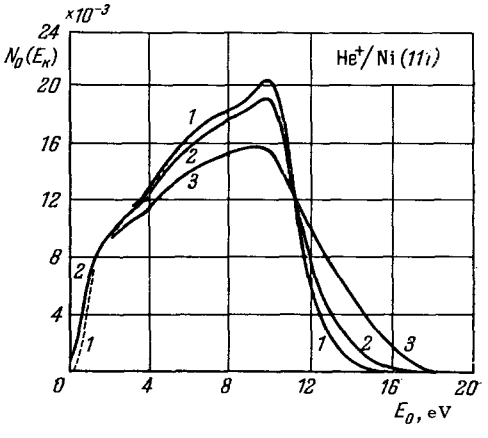

FIG. 7. Energy distribution of the electrons ejected from the (111) face of nickel by helium ions [17]. The ions energies are: 1 – 4 eV, 2 – 10 eV, 3 – 100 eV.

When targets are bombarded with neon ions, a much sharper increase is observed in the distribution "tail," so that the limiting electron energies can greatly exceed the limit $eV_i - 2\varphi$ even for relatively small values of E_0.

At primary-ion energies on the order of several keV (and even before that for hydrogen and helium ions), electrons knocked out directly as a result of the kinetic energy of the ions appear. This makes it difficult to study the potential ejection of the electrons when $E_0 \gtrsim 1$ keV. Nonetheless, attempts have been made to estimate the contribution of the electrons acquiring energy as a result of ion neutralization to the total ion-electron emission. To this end, the electron emissions due to ions and due to neutral atoms of the same element are compared. According to [20], the plots of γ for the pairs $He^+ - He$, $Ne^+ - Ne$, and $Ar^+ - Ar$ are simply shifted relative to one another by an amount γ_p, which does not depend on E_0, the latter not exceeding 5 keV in these experiments. At the same time, according to [21], the $\gamma(E_0)$ curve for Ar^+ ions is steeper than the curve for Ar, thus indicating apparently that potential ejection of electrons by ions increases with increasing E_0. It is possible, however, that this result is connected with imperfections in the method used to register the primary beam of neutral atoms (see [22,23]).

At ion energies exceeding several keV, the potential ejection of the electrons by ions, if it takes place at all, is as a rule much smaller than the kinetic detachment, and is difficult to observe. The change in the values of γ was observed in [24] when the multiplicity of the charge of the bombarding particles was changed; this is attributed by the author to potential ejection of electrons, whereas in [25] and [26] the total electron emission caused by ions of a given element with the same energy E_0 did not depend on charge multiplicity. We shall return to a discussion of the dependence of γ_p on the ion energy in Sec. 4 of the present chapter.

3. Emission of Electrons from Semiconductors and Dielectrics Bombarded by Slow Ions

A study of potential ejection from semiconductors (inert-gas ions were used to bombard the (111) and (100) faces of single crystals of silicon and germanium [27,28], and also the faces (111), $(\bar{1}\bar{1}\bar{1})$, and (110) of crystalline gallium arsenide [29]) has shown that the main features of the phenomenon are the same for semiconductors and metals. Nonetheless, the values of γ_p for semiconductors are as a rule somewhat smaller: Whereas for W and Mo bombarded with He^+ ions with $E_0 = 10$ eV the values of γ_p are respectively 0.29 and 0.30, for the (111) faces of Ge and Si we have $\gamma_p \approx 0.19$. This difference between the absolute values increases on going to heavier ions, and for Xe^+ the values of γ_p differ from those indicated above by an entire order of magnitude. The author attributes this to resonant neutralization of the heavy ions of the inert gases directly to the ground state.

The electron energy-distribution curves also have a somewhat different form (Fig 8). When Ge and Si crystals are bombarded with He^+ and Ne^+ ions, the curve has two maxima, due to the character of the energy distribution of the electrons in the valence band of semiconductors with a diamond-type lattice [30]. When the ion energy is increased, the distribution curve broadens and the singularities of its structure become smoothed out (a similar behavior takes place also for metals).

No qualitative differences are observed in the electron energy distribution for different faces of a single crystal, although small quantitative changes do occur. It is interesting that damage to the crystalline structure of the surface layer of the semiconductor likewise does not lead to essential changes in the electron energy distribution curve, although the pattern of the diffraction of slow electrons from the bombarded section of the surface becomes completely smoothed out [31]. On the other hand, the adsorption of foreign atoms greatly influences the character of the distribution curve: Whereas adsorption of CO causes only a slight lowering of the second maximum of the curve, adsorption of O_2 annihilates this maximum completely [31]

The changes occurring in the spectrum of fast electrons knocked out from the indicated semiconductor targets, as well as from metallic targets Ni (111), Cu (110)) by inert-gas ions were analyzed in [32,33]. It was shown that the broadening of the high-energy part of the spectrum (similar to that shown in Fig. 7 for Ni) is proportional to the velocity of the bombarding particles [32], and at equal velocities it is the same for He_3^+ and for He_4^+ [33]

Information on the ejection of electrons by slow

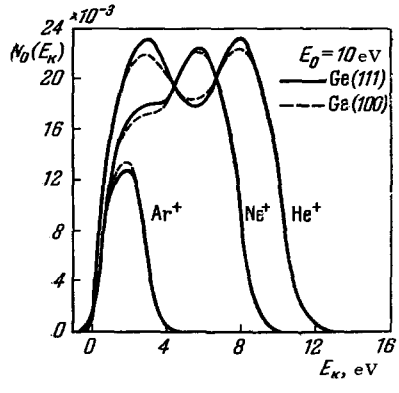

FIG. 8. Energy distribution of electrons ejected from the (111) and (100) faces of germanium by He^+, Ne^+, and Ar^+ ions with $E_0 = 10$ eV [26].

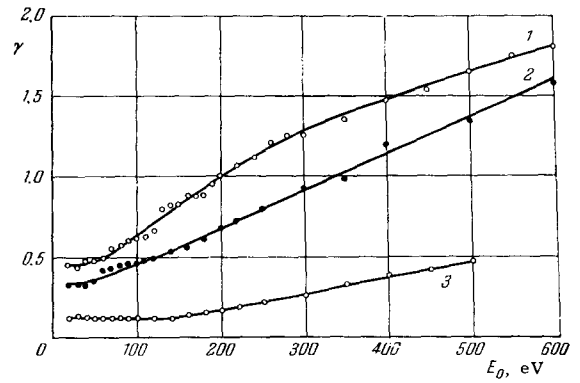

FIG. 9. The coefficient γ of alkali-halide single crystals vs. the energy of the helium ions.[37]. 1 – KBr; 2 – NaCl; 3 – LiF.

ions of inert gases from barium oxide is reported in [34].

The existence of potential ejection from dielectrics was demonstrated in an experiment [35] in which a glass target was bombarded with He^+ ions. Subsequent studies concerned only ion-electron emission from alkali-halide compounds heated enough to produce a conductivity sufficient for current to flow through the sample [36-38,185,186]. Figure 9 shows data [37] for single-crystal KBr, NaCl, and LiF bombarded with He^+ ions. There is no doubt that ejection of electrons, connected with release of energy upon neutralization of the bombarding particles, has been observed. However, unlike metallic targets, there is no broad section on which the electron ejection is exclusively potential. It can be assumed that in this case it is difficult to effect a simple distinction between potential and kinetic emission.[39]

Kondrashev and Petrov [4] report data on the energy spectrum of electrons leaving the (100) face of single-crystal KCl bombarded by He^+ ions (Fig. 10).

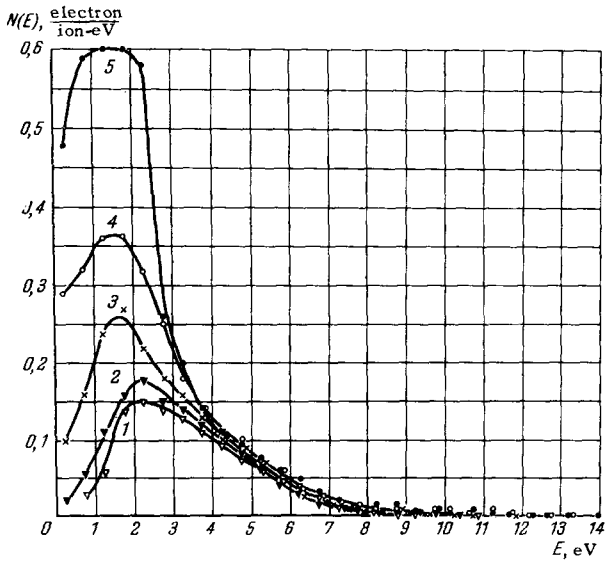

FIG. 10. Energy distribution of electrons knocked out of the (100) face of single-crystal KCl by helium ions [38]. 1 – E_0 = 20 eV; 2 – 40 eV; 3 – 100 eV; 4 – 200 eV; 5 – 400 eV.

The presence of electrons whose excitation is accompanied by transfer to them of the potential energy from the crystal ions is not subject to any doubt. At the same time, the shape of the distribution curve, even for minimal E_0, differs greatly from that expected on the basis of simple considerations used to explain the energy spectra of electrons from metals and semiconductors. Experimental results [37,38] show that the values of γ at minimal ion energies decrease when the width ΔE of the forbidden gap of the crystals increases. It must be borne in mind that an appreciable role can also be played by the electron affinity of the crystal: at a constant number of excited electrons, the yield will increase with decreasing affinity. It is probable that the large values of the coefficient γ for alkali-halide crystals are due in part to their small electron affinity (unlike Ge and Si, for which it is large). The Ne^+ and Ar^+ ions produce a smaller ion-electron emission [38] at small values of E_0 than He^+. No electron emission is observed at all from LiF bombarded with Ar^+ ions having $E_0 < 100$ eV. It must be kept in mind that in this case $eV_i < 2\Delta E$, so that there can be no neutralization of the ion by the ordinary Auger process at all.

4. Neutralization of Ions on a Surface and Potential Ejection of Electrons (Theoretical Concepts)

There is no doubt that direct potential ejection of electrons is connected either with direct Auger-neutralization of the ion, or with Auger deactivation of the excited atom, both of which can be preceded by resonance processes. One can attempt, following Oliphant and Moon [41], to regard the process as tunnel emission of an electron to the bombarding particle (see, for example, [42]). More promising, however, although also more complicated, is the quantum-mechanical analysis used by Sh. Sh. Shekhter [7] and developed by Hagstrum [8,43]. To perform a consistent calculation it is necessary to know the matrix elements of the transitions, from the initial to the final state, of the electrons that take part in the act under consideration. This problem has not yet been solved completely, and the author of [8,43] approximates the matrix element by a product of functions that introduce an explicit dependence of the element on the angle between the velocity vector of the excited electron and the normal to the surface of the solid, and also a dependence on the energy of the electron in the initial state within the band (for semiconductors, the last function is $q(\epsilon)$, where ϵ is the electron energy reckoned from the bottom of the band, and is chosen on the basis of certain considerations regarding the character of the wave functions of the electrons in the band; for metals $q(\epsilon)$ is a constant).

The total probability per unit time of the electron transition, at a fixed distance s from the particle to the surface of the metal, is then given by

$$R_t(s) = C \int\int\int\int\int\int N_c(\varepsilon_f)\, I(\Delta\varepsilon_f, s)\, N'_v(\varepsilon')\, N'_v(\varepsilon'') \times \delta(\varepsilon' + \varepsilon'' + E'_i - \varepsilon_0 - \varepsilon_f - \Delta\varepsilon_f)\, P_\Omega(\theta, \varepsilon_f, s_m) \times d\Omega\, d\varepsilon'\, d\varepsilon''\, d(\Delta\varepsilon_f)\, d\varepsilon_f. \quad (1)$$

In this expression C is a constant, $N_c(\epsilon_f)$ is the density of the final states for an excited electron with energy ϵ_f (in the conduction band), $N'_V(\epsilon) = q(\epsilon) N_V(\epsilon)$, where $N_V(\epsilon)$ is the density of the initial states of the electrons (for a semiconductor—in the valence band); the Dirac δ-function ensures satisfaction of the energy conservation law; $I(\Delta\epsilon_f, s)\, d(\Delta\epsilon_f)$ is the probability that the energy of the excited electron produced as a result of a process that has occurred when the particle was at a distance s from the surface will have an uncertainty $\Delta\epsilon_f$ in accord with the Heisenberg principle; $P_\Omega(\theta, \epsilon_f, s_m)\, d\Omega$ is the probability that an excited electron with energy ϵ_f, produced during the time of the transition occurring at a distance $s = s_m$, will have a velocity in the angle interval $d\Omega = \sin\theta\, d\theta\, d\varphi$, where θ is the angle to the normal to the surface (in general P_Ω depends on s; for simplicity one uses in the calculation the probability P_Ω for $s = s_m$, where s_m corresponds to that distance between the particle and the surface at which the maximum number of Auger transitions takes place; see below); E'_i is the ionization energy of the atom situated at a distance s from the surface ($s = \infty$, $E'_i = E_i$). The remaining symbols are the same as in Fig. 1.

Using expression (1) and introducing certain parameters in the subsequent calculation, we can obtain qualitative results which describe the experimental data quite well. This allows us to regard the theory as correct in principle. It is possible further to use the experimental results to refine the previously introduced parameters, by matching theory to experiment, and by the same token obtain additional information on certain properties of the electrons in a solid, particularly the energy structure of the valence band of the semiconductor. An analysis [43] shows that the choice of parameters such as to match the theory to the experimental data is sufficiently unique.

Let us consider the main elements of the calculation. It is convenient to use for this purpose the diagram shown in Fig. 11 [43]. The lower left corner of this diagram shows the energy structure of a semiconductor such as germanium or silicon. The bottom of the valence band corresponds to an energy $\epsilon = 0$; at the top of the valence band we have $\epsilon = \epsilon_V$; at the bottom of the conduction band $\epsilon = \epsilon_c$; to transfer the electron from the bottom of the valence band to the vacuum level with zero kinetic energy it is necessary to perform work $\epsilon = \epsilon_0$. The electron energies in vacuum are reckoned from this level and are denoted E_f (see the upper right corner of the diagram). The valence band of a semiconductor with diamond structure, similar to Ge and Si, is made up of four overlapping bands. The energy-state density in each of the band is described by the author of [43] by segments of parabolas. Thus, the real density of states (which is not known exactly) is approximated by the curve $N_V(\epsilon)$ shown in Fig. 11. Two parameters are introduced here: the total width ϵ_V of the valence band, and the width of the narrower two degenerate bands $(1 - p)\epsilon_V$, where $p < 1$. The area under the curve is determined from the normalization condition. Inasmuch as the probability of the Auger process depends on the character of the wave functions (s- and p-), it is assumed that the probability of the process in which p-electrons take part is smaller than that with s-electrons, and differs from the latter by a factor $r (r < 1)$. This is the third parameter. Its introduction makes it possible to construct $q(\epsilon)$ for the different bands making up the valence band, and to introduce in lieu of the normal density $N_V(\epsilon)$ of the electron states in the band the effective density $N'_V(\epsilon) = q(\epsilon) N_V(\epsilon)$, in which account is taken of the dependence of the interaction probability on the character of the electron wave function. At the same time, a parameter σ is introduced, which makes it possible to take into account the smearing of the distribution as a result of the Heisenberg uncertainty principle (as a first approximation one can put $\sigma = 0$ and disregard this smearing).

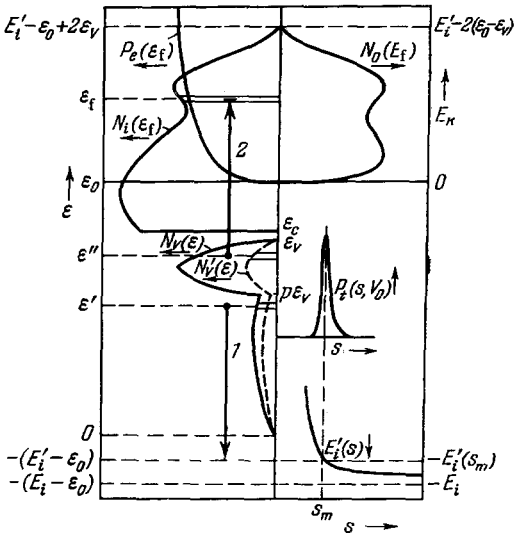

FIG. 11. Energy diagram showing the most important functions and parameters used in the theory [43]. The energies marked ε are reckoned from the bottom of the valence band, whereas those marked E are measured from the vacuum level. The symbols are defined in the text.

Of great important is the next parameter E'_i, which was already mentioned. The interaction of the approaching atomic particle with the surface affects the position of the energy levels of the particle. The

analysis reported in [8] shows that when inert-gas atoms approach the surface of a metal their ionization energy decreases [$E_i'(s) < E_i(s=\infty)$]. The value of this decrease can be estimated. The $E_i'(s)$ dependence can be seen in the lower right corner of Fig. 11. It is E_i' which determines the maximum kinetic energy of the excited electrons (if it is assumed that $\sigma = 0$).

Knowing $N_V'(\epsilon)$, putting $N_c(\epsilon) = \text{const}$, and taking into account the difference between E_i' and E_i, it becomes possible to calculate the probability that the Auger process will occur when the particle is located at a distance s from the surface. We are interested, however, directly in the energy distribution of the electrons produced as a result of a large number of individual processes, which occur in general at different distances from the surface of the solid. To this end we can obtain from $R_t(s)$ a function $P_t(s, v_0)$ such that $P_t(s, v_0)ds$ is the probability that the process occurs when the particle is in the distance interval (s, s + ds) from the surface. Indeed, it is easy to find the probability P_0 that the particle moving from infinity with a velocity v_0 will reach a point located a distance s from the surface without experiencing an Auger transition:

$$P_0(s, v_0) = \exp\left(-\int_s^\infty R_t(s)\frac{ds}{v_0}\right). \quad (2)$$

Then

$$P_t(s, v_0)\,ds = R_t(s)\,P_0(s, v_0)\frac{ds}{v_0}. \quad (3)$$

If we approximate $R_t(s)$ by an exponential function

$$R_t(s) = A\exp(-as), \quad (4)$$

we get

$$P_t(s, v_0) = \frac{A}{v_0}\exp\left[-\left(\frac{A}{av_0}\right)\exp(-as) - as\right], \quad (5)$$

which goes through a maximum when

$$s = s_m = \frac{1}{a}\ln\frac{A}{av_0} \quad (6)$$

and is shown in the lower right corner of Fig. 11. It has a rather sharp peak that does not depend on v_0 (the position of the maximum value of P_t depends on the velocity of the approaching particle and shifts closer to the surface of the body with increasing velocity, in accordance with (6)). Thus, if $R_t(s)$ can be approximated by an exponential function, then $P_t(s, v_0)$ is represented by a curve similar to that shown in Fig. 11, and it can be shown that the average distance between the particles and the surface, at which the particles experience Auger transitions, differs little from s_m. Since $P_\Omega(\theta, \epsilon_f, s)$ should not change strongly under small variations of s, the author assumes that it can be replaced by $P_\Omega(\theta, \epsilon_f, s_m)$; this was already used in deriving the complete expression for $R_t(s)$.

The distribution with respect to the energies of the excited electrons inside the solid is given by

$$N_i(\varepsilon_f) = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} P_t(s, v_0)\,P_f(\varepsilon_f, s)\,P_\Omega(\theta, \varepsilon_f, s)\sin\theta\,d\theta\,d\varphi\,ds. \quad (7)$$

Here $P_f(\epsilon_f, s)\,ds$ is the probability that the electron, which acquires energy as the result of the Auger process occurring when the ion was situated at a distance s, will have an energy in the range from ϵ_f to $\epsilon_f + d\epsilon_f$. This probability can be determined in terms of the already-known functions and the so-called Auger transformation (see formula (73) of [43]). Taking into account the statements made above concerning the function $P_\Omega(\theta, \epsilon_f, s)$ and using the normalization condition

$$\int_0^{2\pi}\int_0^{\pi} P_\Omega(\theta, \varepsilon_f, s)\sin\theta\,d\theta\,d\varphi = 1, \quad (8)$$

we can rewrite this expression in the form

$$N_i(\varepsilon_f) = \int_0^\infty P_t(s, v_0)\,P_f(\varepsilon_f, s)\,ds. \quad (9)$$

This distribution over the energies of the excited electrons inside the solid is shown in Fig. 11. The only electrons that can go out to the vacuum are those which move towards the surface at an angle smaller than the total-internal-reflection angle θ_c, which is equal to

$$\theta_c = \arccos\left(\frac{\varepsilon_0}{\varepsilon_f}\right)^{1/2}. \quad (10)$$

The distribution of such electrons ver the energies inside the solid is given by the expression

$$N_0(\varepsilon_f) = N_i(\varepsilon_f)\int_0^{2\pi}\int_0^{\theta_c} P_\Omega(\theta, \varepsilon_f, s_m)\sin\theta\,d\theta\,d\varphi = N_i(\varepsilon_f)\,P_e(\varepsilon_f), \quad (11)$$

where $P_e(\epsilon_f)$ is the probability that the excited electron with energy $\epsilon_f = \epsilon_0 + E_f$ will escape to the vacuum.

Different assumptions can be made with regards to $P_e(\epsilon_f)$. The simplest is that the excited electrons have an isotropic distribution, the barrier on the surface of the solid is plane, and the electrons that started to move from the surface cannot change direction and escape to the vacuum. This assumption leads to

$$P_e(\varepsilon_f) = \begin{cases} \frac{1}{2}\left[1 - \left(\frac{\varepsilon_0}{\varepsilon_f}\right)^{1/2}\right] & \text{for } \varepsilon_f > \varepsilon_0, \\ 0 & \text{for } \varepsilon_f < \varepsilon_0. \end{cases} \quad (12)$$

However, the use of such an expression leads to too low calculated values of γ_p

$$\gamma_p = \int_{\varepsilon_0}^\infty N_0(\varepsilon_f)\,d\varepsilon_f = \int_0^\infty N_0(E_f)\,dE_f. \quad (13)$$

The author therefore uses a modified expression for $P_e(\epsilon_f)$, containing two more parameters (sixth and seventh):

$$P_e(\varepsilon_f) = \begin{cases} \frac{1}{2}\left[1 - \left(\frac{\varepsilon_0}{\varepsilon_f}\right)^{\beta}\right]^{\alpha} & \text{for } \varepsilon_f > \varepsilon_0, \\ 0 & \text{for } \varepsilon_f < \varepsilon_0. \end{cases} \quad (14)$$

(A different expression for $P_e(\epsilon_f)$, containing one unknown parameter, was used in [8].) The author used as a justification for such a choice of $P_e(\epsilon_f)$ the presumed rather sharp angular anisotropy of the distribution of the excited electrons, and the distortion of the shape of the barrier at the surface of the solid by the primary particle. The general form of the $P_e(\epsilon_f)$ plot is shown in Fig. 11, which shows also the distribution of the secondary electrons in vacuum $N_0(E_f)$, obtained from $N_i(\epsilon_f)$ with $\epsilon_f > \epsilon_0$ by decreasing it by P_e.

The described calculations are valid, in general, only if $R_t(s)$ does indeed depend exponentially on s, and each ion experiences Auger neutralization also as it approaches the surface and there are no other mechanism of ejecting the electrons to the vacuum.

Hagstrum's theory of Auger neutralization explains most of the experimental facts. Without going into details, we mention only the principal ones:

1) The coefficient γ_p depends essentially on the nature of the bombarding ions, primarily on E_i, for the larger E_i the larger the energy transferred to the electrons and the more electrons escape to the vacuum.

2) The maximum energy of the electrons excited by slow ions depends on E_i (more accurately, on E_i'); in the case when the thermal excitation of the electrons at the level above the Fermi level can be neglected, this energy is determined by the quantities $E_i' - 2\varphi$ for a metal and $E_i' - 2(\epsilon_0 - \epsilon_v)$ for a semiconductor.

3) The form of the spectrum of the secondary electrons excited by slow ions bombarding semiconductor materials is determined primarily by the density of the states in the valence band of the semiconductor. Using Hagstrum's calculations [43], we can refine certain details, and in particular estimate the widths of the individual bands makings up the valence band.

4) When the kinetic energy of the ions is increased, the energy distribution of the electrons becomes smeared; in particular, their maximum energy increases. This broadening of the spectrum, which is observed even at minimum energies of the ions used in the experiments (4 eV), is attributed [32,33] to non-adiabatic excitations of the electrons in the solid by the moving ion. Within the framework of the theory, non-adiabatic excitation of the electrons is one of the possible causes of the broadening of the distribution described by the function I in (1). At energies E_0 on the order of 400 eV for He^+, and higher for the ions of other inert gases, kinetic ejection of the electrons can take place. It depends very strongly on E_0 and is characterized by an entirely different distribution of the 1 electron energies (see Ch. III). It cannot be described within the framework of the theory described above.

5) With increasing kinetic energy of the ions, a change takes place not only in the form of the spectrum of the secondary electrons, but also in the values of γ_p (even in the absence of kinetic ejection). In the case of metals, this can be explained theoretically [8,9]. The monotonic decrease of $\gamma(E_0)$ with increasing energy of the He^+ ions and the very weak increase of $\gamma(E_0)$ with increasing E_0 for Ar^+, Kr^+, and Xe^+ are connected with the dependence of E_i' on the ion velocity, since the average particle—surface distance at which neutralization takes place decreases with increasing particle velocity. In the case of Ne^+, for which $\gamma(E_0)$ increases rapidly in the ion-energy interval 10—100 eV, it is assumed that when E_0 is increased resonant neutralization of the bombarding particles becomes possible, by virtue of this they are subjected further to Auger deactivation, a process which is more effective from the point of view of electron ejection. There are no published attempts to calculate the $\gamma(E_0)$ dependence in the case of semiconductor targets. An exception is [34], where a highly simplified calculation was made of the ejection of electrons from BaO on the basis of the theory of [8].

Unfortunately, no thorough theoretical analysis of potential ejection of electrons from dielectrics has ever been made. Small values of γ_p are predicted in [44] for dielectrics, but this does not agree with the experimental data [35-39,185,186].

Speaking of the theory of excitation of electrons in solids at the expense of the internal energy of the bombarding particles, it must be noted that this theory is very far from complete in spite of the fact that the main mechanism of the phenomenon has been known a long time. From our point of view, there are still two questions to be answered.

The first concerns the need for taking into account in the theory the fact that time T required to perform the experiments is not equal to zero, and that electrons are located at levels higher than the Fermi level. Measurements made at higher temperatures [14] have shown that under certain conditions (choice of definite types of ions and targets), appreciable temperature variations of $\gamma(T)$ are observed, possibly as a result of resonant phenomena preceding the Auger processes (we note that and indication of a $\gamma(T)$ dependence for semiconductor targets is contained also in [27]). There is no doubt that a more thorough study of the temperature dependence of $\gamma(T)$ and of the electron energy distribution will yield valuable information on the role of the resonant processes preceding the electron-excitation act.

Second, it is assumed in the existing theories that each particle is neutralized in its own ground state even while it moves towards the surface, i.e., before it begins to be abruptly decelerated by the repulsion forces when the atoms come very close together. This, on the one hand, makes normalization possible, since the total neutralization probability is equal to unity and each ion furnishes one Auger electron (the

theory does not consider resonant neutralization in the ground state). On the other hand, this affords some justification for the assumption that the potential barrier between the bombarding particle and the solid body is not fully destroyed, and $R_t(s)$ can be represented by the usual exponential (which in turn causes $P_t(s)$ to have a maximum in the region $s > 0$). If such is the case in the bombardment by slow ions, then the correctness of this assumption becomes more and more doubtful with increasing E_0 (the quantity s_m, which characterizes the position of the maximum of $P_t(s)$, decreases with increasing E_0 even in the existing variant of the theory, and it can become too small to have a physical meaning; in addition, owing to the change of the barrier, there will probably occur a "smearing" of the $P_t(s)$ peak). It must therefore be assumed that at sufficiently large ion energies E_0 the ions can enter in close interaction with the lattice particles without experiencing Auger neutralization. As indicated above, it is quite difficult to obtain experimental data on potential ejection of the electrons at large values of E_0, for it is accompanied by an intense kinetic ejection of the electron, which increases sharply with increasing E_0 [24-26] and makes it impossible to assess whether a certain lowering of γ_p is observed. The available information (see, for example,[20]) make it apparently possible to assume that there are no large changes of γ_p up to ion energies on the order of 2—3 keV.

When speaking of the nature of the electrons making up the secondary emission, we have assumed so far, following the authors of the cited papers, that these are the same excited electrons that have acquired energies and momenta sufficient for emergence to the vacuum as a result of a primary Auger process, and have lost nothing on the way to the surface. Yet this is not at all obvious. First,[16] it is necessary to take into account the energy lost by the fast Auger electrons ("electro-electron interactions"). This should cause the distribution of the electrons escaping to the vacuum to be poorer in fast particles than the distribution of the Auger electrons. On the other hand, the number of slow electrons escaping to the vacuum may increase somewhat. This is due, in particular, to the fact that such electrons can appear as the result of energy loss by those fast Auger electrons having a momentum directed in such a way that they cannot leave the metal. Attempts to estimate the contribution of these electrons ("tertiary" with respect to the bombarding ions and "secondary" with respect to the Auger electrons) were made in [45] and [46]. According to the former paper, the contribution of such electrons to the potential emission produced by He^+ ions from a metallic target reaches 50%, whereas according to the latter their number does not exceed several per cent. However, in spite of the thoroughness of the analysis made in [46], the large number of assumptions that must be made in the evaluation of the experimental data does not make it possible, from our point of view, to regard the result as perfectly reliable.

It seems that there is one more circumstance that must be carefully analysed. The point is that resonant or Auger transition of an electron from the solid to the ion level in the valence band of the semiconductor (or in the filled part of the conduction band of the metal) produces a hole (or two holes). When the hole is filled by an electron from a high energy level, the released excess energy can be transfered to one more electron. Such an Auger effect within the band, unless it has zero probability, can serve as a source of additional secondary electrons, most of which are probably relatively slow.

Considerations involving the Auger effect in the conduction band have already been advanced to explain the form of the spectra of the photoelectrons excited by light quanta in the vacuum part of the ultraviolet (see. e.g.,[47]). As to semiconductors, it has been reliably established that if the energies of the fast holes (as well as electrons) greatly exceed the width of the forbidden band, they can lead to impact ionization and produce secondary electrons and holes. Thus, the total number of electrons excited in a solid and having energies considerably higher than thermal may turn out to be larger than is customarily assumed. It is not excluded likewise that allowance for the mechanisms indicated above for the dissipation of the energy remaining in the solid after neutralization of the bombarding particle (we note that in a number of cases resonant neutralization directly to the ground case is possible!) will explain why the theoretical values of γ [8,43] are too low, and the theoretical $N_0(E_f)$ distribution (especially in the case of semiconductor targets) is poor in slow electrons, if the distribution $N_i(\epsilon_f)$ is assumed isotropic. (In spite of Hagstrum's clever qualitative justification for the use of a function $P_e(\epsilon_f)$ of a special type [43], the validity of its use cannot be regarded as completely proved.)

Thus we conclude that when solids are bombarded with relatively slow particles, when no electrons are excited directly by the kinetic energy of the particles, the electrons can be excited by the internal energy of the system (if the latter is not very small). These electrons acquire as a rule an appreciable fraction of the total particle-neutralization energy, and their number is apparently not fewer then one electron per bombarding singly-charged ion or metastable atom. The number of excited electrons increases when multiply-charged and excited ions are used. It can be assumed that electron-electron interactions and the energy relaxation in the band produced by the resonant transitions or the Auger transitions connected with the neutralization of the ion, the total number of electrons excited in the solid (particularly in the conduction band of a semiconductor) may

greatly exceed the number of "primary" Auger electrons.

III. KINETIC EJECTION OF ELECTRONS TO VACUUM

Until recently, the excitation of electrons of a solid by the kinetic energy of bombarding atomic particles (principally ions) could be assessed only from the emission of some of these electrons to vacuum (called kinetic ion-electronic emission or kinetic ejection). This phenomenon has been under study for more than fifty years. However, its investigation has been made difficult by many circumstances: The bombarded surface must be atomically pure or have a controlled adsorption coating; electron emission is accompanied by reflection of the primary particles and by ejection of negative ions, etc. Methods have now been developed to carry out measurements under clean conditions, separating the electronic component proper of the secondary current in a wide range of target temperatures [4,48-54]. Inasmuch as a detailed survey of the data for polycrystalline metals is available,[6] we confine ourselves here only to a short summary of the main results of these investigations. We consider in greater detail the results for single-crystal metals and also for dielectrics and semiconductors.

1. Ion-electron Emission of Metals. Polycrystalline Targets

1.1. Absolute values of the coefficient γ_k and its dependence on the ion energy. It has been established that extraction of electrons by slow ions bombarding pure metallic target is very small. At energies $E_0 \lesssim 1$ keV, the values of γ_k are as a rule much smaller than unity. Experiments performed in 1951 [55,56] with alkali ions (which cause no potential ejection of electrons from pure metals, $\gamma_p = 0$, $\gamma = \gamma_k$)), have shown that no kinetic emission occurs at ion energies E_0 on the order of several hundred eV, and even several keV. Very small values of γ for E_0 on the order of several hundred eV were indicated later also by other workers [57-59] (compare with the experiments of [11], where the electron emission from metals bombarded with Ne^+, Ar^+, Kr^+, and Xe^+ ions with $E_0 < 1$ keV is attributed exclusively to potential extraction of the electrons).

At ion energies on the order of several keV, an increase of the coefficient γ_k is observed with increasing ion energy, as a rule in linear fashion [4,16,49,55,60,63]. The characteristic data for certain ions are shown in Fig. 12. This has given grounds for assuming the existence of a threshold for the kinetic ejection of electrons by ions,[16,61], and for characterizing the phenomenon itself in this energy region with the aid of two parameters: the threshold energy E_0' and the slope $C = d\gamma/dE_0$ for the linear section of the $\gamma(E_0)$ curve:

$$\gamma(E_0) = \gamma_p + \gamma_f = \gamma_p + C(E_0 - E_0'). \qquad (15)$$

The constant C for pure metals does not exceed 0.2 electron/ion per keV.

With further increase of the ion energy (in an interval of several dozen keV), the growth of γ_k with increasing E_0 is gradually slowed down and usually a linear increases of the coefficient γ_k with the velocity v_0 of the bombarding particles is observed [25,51,65,66]. Extrapolation of the linear sections of $\gamma(v_0)$ to $\gamma = 0$ gives a value $v_0' = (0.6 - 2) \times 10^7$ cm/sec, sometimes called the threshold velocity.[25] Characteristic data for several types of particles bombarding molybdenum are shown in Fig. 13. Unfortunately, no systematic measurements were made with pure targets at energies of several dozen keV and higher. It is only known that for light atoms such as hydrogen and helium, for which the threshold energy is minimal and a transition to a linear $\gamma(v_0)$ relation is observed already at several keV, the

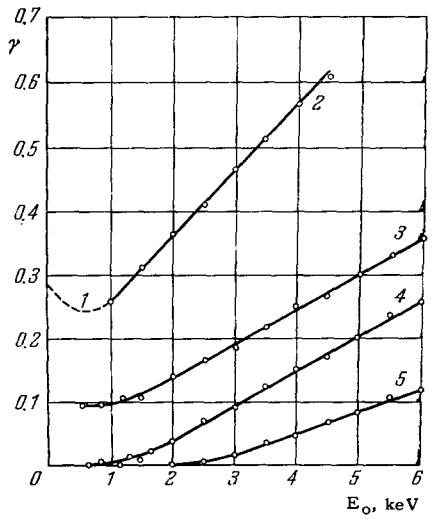

FIG. 12. Dependence of the coefficient γ of a tungsten target on the ion energy. 1 – He^+ [11], 2 – He^+ [13], 3 – Ar^+ [65], 4 – K^+ [49], 5 – Cs^+ [64].

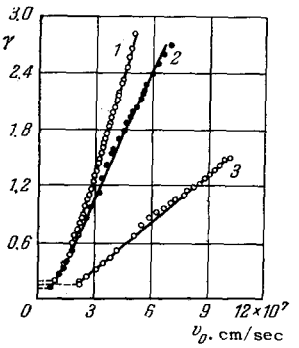

FIG. 13. Coefficient γ of a molybdenum target vs. velocity of the bombarding ions [66]. 1 – Ar^+, 2 – Ne^+, 3 – He^+.

$\gamma_k(E_0)$ plot reaches a maximum at $E_0 \sim 150$ keV, and γ_k decreases with further increase of the primary-particle energy.

The maximum values of the coefficient γ of pure metallic targets are relatively small. In the case of hydrogen they do not exceed 1—2 electron/ion.[67]. For heavier ions they reach larger values, but not more than 10—15.

1.2. Dependence of the coefficient γ on the nature of the target and on the state of its surface. Ion-electronic emission is exceedingly sensitive to the surface state of the target. Formation of the thinnest film on the surface, by sorption of residual gases or by particles of the bombarding beam, alters the emission radically.[55] As a rule, this is accompanied by an increase of the kinetic ejection of the electrons.[4,55]. Unfortunately, no systematic study was made of the dependence of the emission on the character and degree of the adsorbed coating, although it is clear that it is determined exclusively by the work function - the emission usually increases both when the target is treated with cesium and when it is oxidized, although the two processes modify the work function in different fashions. This is apparently due to the fact that production of the surface film not only changes the electron emission probability, which depends on the work function, but also the electron excitation probability. Very promising in this connection are observations of the ion-electronic emission of certain metals in the presence of hydrogen[68,69]. When the hydrogen pressure is increased near the target, the values of γ_k can either increase or decrease as functions of the temperature of the bombarded object (Fig. 14). It can be assumed that the character of the variation of γ_k with increasing gas pressure is determined by the type of gas adsorption, which can vary when the target temperature is varied.

No connection between the coefficient γ_k and various properties of the bombarded metals has been established so far. Experiments with single crystals have shown (see below) that the values of γ_k depend significantly on the orientation of the ion beam relative to the principal axes of the crystal. This gives grounds for assuming that it is hardly meaningful to attempt to relate uniquely the values of γ_k with some property of the metal if polycrystalline targets with unknown orientations or single-crystal dimensions are used. It is of interest to note, at the same time, that the melting of pure metal (Sn, Pb) is usually not accompanied by a significant change of its ion-electronic emission.[56,60].

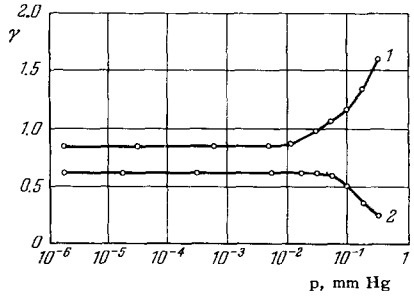

FIG. 14. Coefficient γ of copper target vs. hydrogen pressure in the measuring chamber [68,69]. The target was bombarded with H_2^+ ions having $E_0 = 8.4$ keV. 1 – T ≈ 300°K, 2 – T ≈ 1200°K.

1.3. Influence of target temperature on the values of the coefficient γ. It was shown in [55] that the coefficient itself has γ_k no temperature dependence, and the changes observed in it on occasion are connected with changes in the coating of foreign particles on the target surface. Experiments with alkali ions [4,49] and argon ions [14] have by now demonstrated the independence of γ_k of the temperature for high-melting-point metals up to 2000°K.

1.4. Dependence of the coefficient γ_k on the electric field intensity at the target surface. An increase in the electric field at the surface of the target can cause some increase in the ion-electron emission (but by not more than a factor 2—3 when the electric field intensity is increased $\mathcal{E} = (2 - 2.5) \times 10^5$ V/cm [71]). According to experiments in which a study was made of the emission of electrons knocked out of a film by α particles passing through it [72]; the logarithm of the secondary current increases in proportion to $\mathcal{E}^{1/2}$. Measurements made by N. H. Petrov and N. S. Temkina (in which a tungsten filament was bombarded by atoms and molecules of hydrogen with energies of several keV) have also shown that the increase in the emission can be attributed to an increase in the probability of escape of excited electrons as a result of a lowering of the Schottky surface barrier.

1.5. Influence of the nature of the ions on the kinetic ejection of electrons. Electron emission depends strongly on the type of the primary particle, but the character of this dependence has been far from sufficiently studied. Whereas at ion energies on the order of several dozen keV it can be assumed that the electron emission is proportional to the nuclear charge of the bombarding particle (see, e.g., the data of [25]), at lower energies the picture is much more complicated. The possibility of a potential ejection of electrons comparable with the kinetic ejection, and the presence of a threshold energy for the excitation of this ejection (different for different ions) as well as other circumstances, bring about a situation wherein, as noted in [73], simple comparison of the values of γ at a specified energy E_0 or velocity v_0 of the ions does not describe the phenomenon completely. At the same time, the investigated assortment of bombarding particles is not large enough to be able to relate uniquely the threshold energy and the slope of the $\gamma(E_0)$ line at low ion energies with certain properties of the ion.

It is definitely known that within the limits of one group of elements of the periodic table the threshold energy for the excitation of electrons in vacuo increases, and the slope of the $\gamma(E_0)$ curve decreases, with increasing nuclear charge of the bombarding particle [5,16,58,64]. Experiments with inert-gas and alkali-metal ions [4,16] have shown also that the kinetic electron emission caused by ions of neighboring elements of these two groups is almost the same (cf. e.g., the data for K^+ and Ar^+ in Fig. 12). The authors of [60] assume that this is due to the closeness of the masses of the bombarding particles. However, as noted in [65], another important factor may be that these ion pairs have not only close masses but also a similar electron-shell structure: the inert-gas ions become apparently neutralized even before a close contact with the target particles is produced, whereas the capture of an electron by an alkali ion has low probability. There are indications that the electron-shell structure affects also the magnitude of the emission at low ion energies.[65] There is no doubt that an investigation of the kinetic ejection of electrons by different ions near the threshold energy will yield valuable information on the mechanism of the phenomenon.

Unfortunately, so far no thorough study has been made of the extraction of electrons by isotope ions. Attempts of this type were made numerous times, but in none of the investigations were atomically-pure surfaces employed. The most interesting, perhaps, are measurements [187] made with several isotopes of the same element.

Several attempts were made to study the influence of the charge of a bombarding particle on the ion-electron emission. As indicated above, the potential ejection of electrons increases when the charge of the ion is increased. The data on kinetic ejection are contradictory. Bombardment of contaminated metals or targets made of the alloys used as effective secondary-electron emitters by neutral atoms knocks out more electrons than bombardment by positive ions [74,75], and negative ions produce more electrons than atoms or positive ions [59]. Cleaning the metallic targets by incandescence decreases the difference between the electron emissions produced by ions with different charges [59]. For relatively pure metals, the information available indicates that the kinetic ejection does not depend on the charge of the bombarding particle.[4,25,76]. It can be assumed that in those cases when the velocity of the incident ion is not too large, its charge state is established even before the first strong collisions with the lattice particles, and this charge should then actually influence only the potential ejection of the electrons. The appearance of a dielectric film on the metal surface can hinder the electron exchange between the incoming particle and the solid*; this may explain the aforementioned dependence of the coefficient γ_k on the particle charge.†

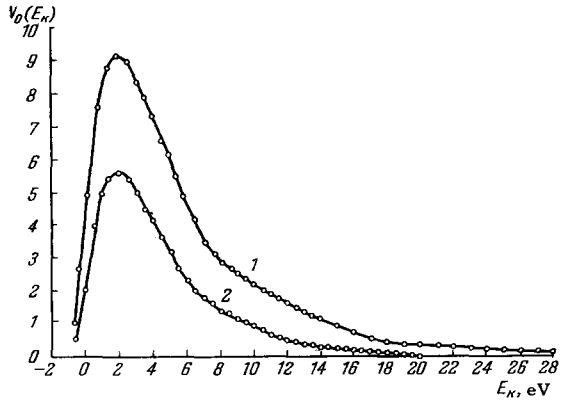

FIG. 15. Energy distribution of electrons extracted from molybdenum by ions (1) and atoms (2) of neon with E_0 = 1.5 keV.[86]

Considerable attention has also been paid to the ejection of electrons by molecular ions, primarily hydrogen ions.[25,65,77-79]. It has turned out here that for outgassed metals the coefficient γ_k is proportional, at constant v_0, to the mass of the molecule, thus confirming the "autonomous" behavior of each of its fragments. Work with complex molecular as such as C_nH_m has led the authors of [80,81] to the conclusion that at constant E_0 the number of electrons excited in vacuo increases with the number of particles contained in the molecule. The mechanism of electron extraction by such ions has not been discussed.

1.6. Dependence of the coefficient γ_k on the angle of incidence of the ions on the target. The coefficient γ_k of polycrystalline targets increases with increasing ion incidence angle θ and doubles when θ is increased from zero (normal incidence) to 60°, varying approximately like sec θ.[71] Similar data were obtained for polycrystalline copper [82]. More detailed investigations were made with single-crystal targets (see below).

It is shown tn [55] that a decrease of the energy of the bombarding K^+ and Li^+ ions leads to a weakening of the dependence of the kinetic ejection on the angle of incidence of the ions, and that when $E_0 \gtrsim 1$ keV the electron emission is practically independent of θ. For single-crystal metallic targets, no such investigations have been made as yet.

1.7. Emission-angle distribution of secondary electrons. Information on the emission-angle distribution of the secondary electrons are available only

*We recall in this connection that adsorption decreases the potential ejection of electrons from metals and semiconductors.

†A number of investigations with fast-atom beams were made recently in France [188,189].

for metallic targets that are not atomically pure[83,84]. It is described, in first approximation, by a cosine law.

1.8. Energy distribution of secondary electrons. Even in the first experiments on electron-ion emission it was shown that the energies of the electrons are usually low and that even at $E_0 \approx 10$ keV they do not exceed 20—30 eV. More recent investigations have shown that the electron energy distribution is close to Maxwellian, thus permitting some authors to introduce the concept of the "temperature" of the excited electron gas, usually amounting to thousands or tens of thousands of degrees (see, e.g.,[84]). No singularities were observed on the electron energy distribution curve.

Figure 15 shows typical energy distribution curves of electron knocked out by neutral atoms and ions of neon bombarding a molybdenum target.[86] It is seen that the bulk of the secondary electrons knocked out by atoms with $E_0 = 15$ keV have relatively low energies, not higher than 10 eV. This agrees with the data[11] on the kinetic ejection of electrons by He^+ ions with $E_0 > 0.4$ keV. There is no doubt that a more thorough and purposeful investigation of the electron energy distribution should yield important information for the understanding of the mechanism of the phenomenon.

1.9. Statistics of individual acts of ion-electron emission. A number of investigations, performed mostly by German scientists, were devoted to the "multiplicity" of the ion-electron emission, i.e., they determined the number of electrons released by an individual bombarding particles. According to the latest published data[87,88] the electron-distribution curve differs somewhat from a Poisson distribution.

2. Ion-electronic Emission of Metals. Single-crystal Targets

Recently, a number of investigations were made with single-crystal metal targets.

2.1. Ion-electronic emission from different faces of a single crystal. It has been shown[89,90] that ion-electronic emission from individual faces of metallic single crystals can differ appreciably. Figure 16 shows $\gamma(E_0)$ plots for a copper single crystal (face-centered cubic lattice) bombarded with Ar^+ ions. It is seen that emission from the (111) and (110) faces induced by normally incident ions with $E_0 > 3$ keV varies by more than a factor of 2. Qualitatively similar results were obtained also when Al, Mg, and Ni crystals were bombarded with Ne^+, Ar^+, Kr^+, and Xe^+. For single-crystal molybdenum (body-centered cubic lattice), the differences in the coefficient γ for different faces were much smaller. The results are attributed by the authors to different "transparencies" of the crystal lattice in different directions[89,91]: the less "transparent" the lattice, the more probable the collision between the ion and the particles of the body in the upper layers, and the larger the coefficient γ.

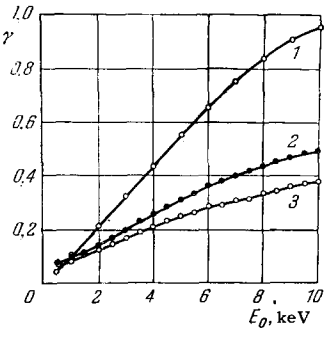

FIG. 16. Coefficient γ of single-crystal copper target vs. energy of Ar^+ ions [90]. The bombarded faces are: 1 – (111), 2 – (100), 3 – (110).

The fact that on going from face to face the values of γ can change so strongly is very important. It turns out that the ordering in the arrangement of the particles in the crystal lattice influences strongly not only the sputtering of the crystals and the reflection of the particles[92,93] but also the ion-electronic emission, and that allowance for this ordering and for its action on the character of motion of the primary particle in the solid is most essential.

Unfortunately, references[89,90] are not free of methodological shortcomings. The most important of them is that an intense ion beam was used to maintain the target in a clean state. There is no doubt that during the bombardment process the structure of the surface layer of the body could be greatly distorted, and this could not fail to affect the measurement results.

2.2. Dependence of the coefficient γ_K on the angle of incidence of the ions on the face of the single crystal. The influence of the ordered arrangement of the particles in the crystal lattice on the motion of the ions and on the energy lost by them is well illustrated also by the dependence of the ion-electronic emission on the angle of incidence of the bombarding particles on the face of the single crystal.

The nonmonotonic character of the dependence of the ion-electronic emission from metallic crystals on the angle of incidence of the ions was first indicated in[94]. A study of the angular dependence of the emission from the (100) face of a copper single crystal[82] has made it possible to relate the maxima on the $\gamma(\theta)$ curve with the directions in which the crystal lattice has the largest transparency (directions with small values of Miller indices). By way of an example, Fig. 17 shows a plot of $\gamma(\theta)$ (the (100) faces of single-crystal copper crystal was bombarded with Ar^+ ions with $E_0 = 20$ and 30 keV). Subsequently data which were qualitatively similar were obtained[95-103] also for other metallic targets bombarded with ions of different gases.

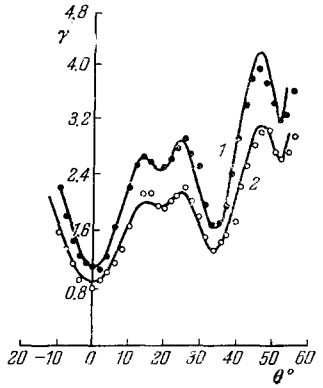

FIG. 17. Dependence of the coefficient γ of the (100) face of single-crystal copper on the angle of incidence of Ar^+ ions with E_0 = 30 keV (1) and 20 kev (2) [82].

It turned out [99,103] that the nonmonotonic nature of the angular dependence of the coefficient of ion-electronic emission is the more strongly pronounced, the heavier the bombarding ions. Figure 18 shows experimental data [103] obtained when the (111) face of a copper single crystal is bombarded with inert-gas ions with energies 276 keV. The curves of Fig. 18a were plotted with the angle of incidence of the ions θ varied and with the ion beam always in the $(1\bar{1}0)$ plane; the curves of Fig. 18b were plotted at constant angle of incidence of the ions on the target, $\theta = 35°$, by rotating the target around the [111] axis (in this case only the azimuth φ was varied).

An investigation was also made of the influence of the target temperature on the $\gamma(\theta)$ dependence [98,190]. As expected [100], owing to the increase in the thermal lattice vibrations with increasing temperature, the $\gamma(\theta)$ plot becomes smoothed out, but the nonmonotonicity is retained up to T = 900°C. (So far, no measurements were made at higher temperatures.)

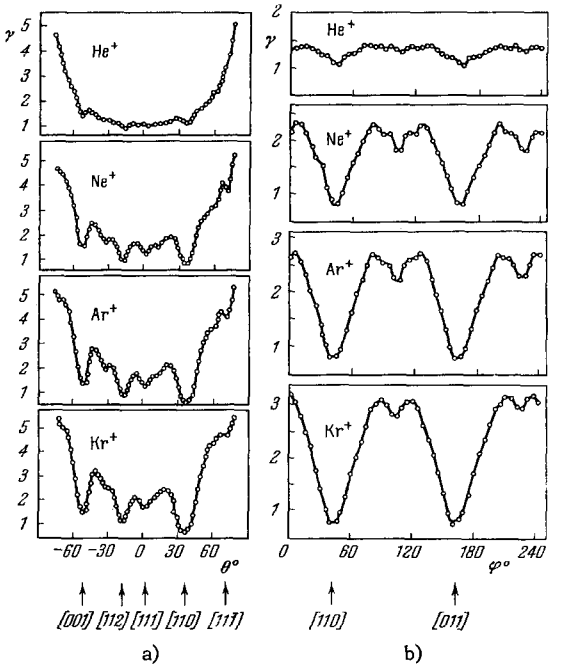

FIG. 18. Dependence of the coefficient γ of the (111) face of single-crystal copper bombarded by ions with E_0 = 26 keV, on the orientation of the direction of the primary beam relative to the crystallographic axes of the target [103]. Details are given in the text.

3. Ion-electronic Emission of Dielectrics and Semiconductors

It is obvious that to clarify the nature of the kinetic ejection of electrons it is necessary to investigate the ion-electronic emission of all three classes of solids—metal, dielectrics, and semiconductors. Experiments on the ion-electronic emission of the dielectrics were in this connection of fundamental significance, since they should have provided the answer to the question whether the "free" electron are essential for the appearance of kinetic extraction of electrons.

3.1. Possibility of kinetic excitation of bound electrons; absolute values of γ_k for dielectrics. The first experiments in this direction were made back in 1937 [104]. Bombardment of different substances by ions with energies up to 1 keV has revealed that no electron emission takes place at all when NaCl crystals are bombarded, and that the coefficients of ion-electron emission γ_k for ZnO, Cu_2O, and CuO, are always smaller than for zinc and copper, other conditions being equal. This has led the authors of [104] to the conclusion that the ion-electronic emission is due to excitation of conduction electrons. Subsequent investigations of the kinetic extraction of electrons by alkali-metal ions from films of alkali-halide compounds sputtered in vacuum [105-109] and from oxide films of tungsten and tantalum [110], however, have cast doubts on the correctness of this conclusion. According to the data of [105-110], the coefficients γ_k for dielectric films turned out to be much larger than for pure metals. It was established also [105,106,110] that the magnitude of the coefficient γ_k increases monotonically when the energy of the primary ions is increased. Unfortunately, the composition and the structure of the films investigated in [105-110] were not known sufficiently well and could vary during the course of the measurements. Therefore the quantitative results obtained, for example, for alkali-halide compound films, can hardly be regarded as characteristic for these compounds themselves.

The most important progress in the investigation of the kinetic ejection of electrons from dielectrics was made by G. M. Batanov [35,52,111-115], who developed a pulse measurement procedure [52,111,115], and also in [36-40,116-118]. The use of a pulse procedure has made it possible to eliminate charging of the target surface by the beam of positive ions, and go over to an investigation of bulky dielectrics possess-

Table I. Threshold ion energies E_0', keV

Material	Bombarding ions					
	Hydrogen ions	He^+	Ar^+	Li^+	K^+	Cs^+
Glass No. 46	<0.1	<0.1	0.16	—	0.17	—
Muscovite	—	—	—	—	0.30	—
LiF	—	—	—	—	—	0.42
NaF	—	—	—	—	0.33	0.43
NaCl	—	—	—	0.16	0.2	0.33
KCl	—	—	—	—	0.2	—
KBr	—	—	—	—	0.14	0.3

ing definite compositions and structures, particularly alkali-halide single crystals. In addition, when a procedure involving short rectangular pulses was used, it was possible to reduce to a minimum the variation of the properties of the investigated object during the course of the measurements, and also to determine the nature of the negatively-charged particles emitted by the dielectric (see, for example,[52,113]).

The researches by Batanov have established that the coefficients of ion-electronic emission γ_k for glass[111] are approximately equal to the values of γ_k for contaminated metals. At the same time it turned out that the values of γ_k for alkali-halide single crystals cleaved in air, and also for alundum, ceramics, and muscovite greatly exceed[52,112-115] the corresponding values of γ_k for contaminated metals. Thus, a value $\gamma_k = 12$ electron/ion was registered by bombarding single-crystal NaCl with lithium ions having $E_0 = 6$ keV.[113] Following Batanov's work, the existence of kinetic ejection of electrons from dielectrics, and consequently the possibility of excitation of bound electrons by ions, could no longer be doubted.

3.2. Dependence of kinetic ejection on the ion energy. It was established experimentally that kinetic ejection of electrons from dielectrics, just as in the case of metals, is practically nonexistent if the energy of the bombarding particles does not exceed a certain threshold energy E_0'; at energies $E_0 > E_0'$, γ_k begins to increase rapidly with increasing E_0. The values of E_0' obtained by Batanov[114] are listed in Table I. It is seen that for all investigated ion-dielectric combinations the values of E_0' fluctuate between 0.1 and 0.5 keV, i.e., they exceed by one order of magnitude the binding energies of the electrons in the crystals. Values of E_0' close to those listed in Table I were obtained also in[118] for single crystals of KCl, KBr, and LiF bombarded by potassium ions. It is interesting that the values of E_0' turned out to be smaller by approximately one order of magnitude for dielectrics than for high-melting-point metals. However, just as in the case of bombardment of high-melting-point metals, an increase of E_0' with increasing mass of the primary ion is observed.* The values of E_0' for semiconductors (germanium, silicon) bombarded with potassium and cesium ions are, according to[116,119], 0.5—1 keV.

Just as in the case of metals, the dependence of the coefficient γ_k of semiconductors and dielectrics on the energy of the primary particles is linear in a certain energy interval $E_0 > E_0'$, and the values of $d\gamma_k/dE_0$ for the latter can reach 2—5 electron/ion-keV (see, for example,[114]). However, the energy interval in which the $\gamma_k(E_0)$ dependence is linear turned out to be narrower for dielectrics than for high-melting-point metals and semiconductors heated in vacuum.[114,118] Typical $\gamma_k(E_0)$ obtained for single-crystal KCl[118] bombarded by potassium ions are shown in Fig. 19 (curves 1 and 2). Curve 1 was

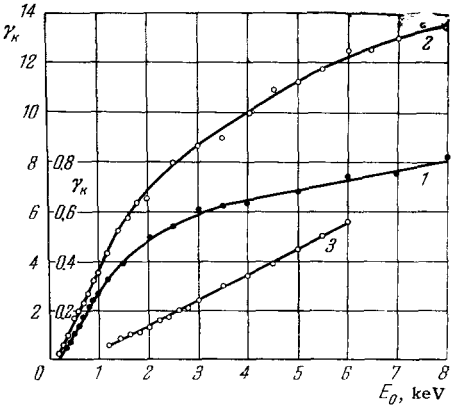

FIG. 19. Dependence of the coefficient γ of the (100) face of single-crystal KCl on the energy of K^+ ions incident on the surface in a normal direction ($\theta = 0$) and at an angle $\theta = 62°$ (curves 1 and 2, respectively, left-hand scale). Curve 3 (right-hand scale) is the same for polycrystalline niobium [118].

*Attempts were also made in [114,118] to establish the dependence of E_0 on the types of ions contained in the crystal, and on the minimum electron binding energy in the crystal $e\chi + \Delta E$ ($e\chi$ – electron affinity energy, ΔE – width of forbidden band). However, the relations observed there cannot be regarded as finally established, owing to the relatively small number of investigated objects and owing to the lack of reliable data on the values of $e\chi$ for most crystals.

plotted with normal incidence of the ions on the (100) face, and curve 2 with the ions incident on the same face of the single crystal at an angle $\theta = 62°$ (the angle θ was reckoned from the normal to the surface, and the ion beam was in the (001) plane). In the same figure, curve 3 (right-hand scale) represents the $\gamma_k(E_0)$ plot obtained by bombarding a polycrystalline niobium target with potassium ions ($\theta = 0$). It should be noted that when glass No. 46 and muscovite were bombarded with potassium ions, the deviations of the $\gamma_k(E_0)$ dependence from linearity were likewise observed already at energies $E \sim 1$—1.5 keV, and in the region of higher energies the $\gamma_k(v_0)$ dependence became linear [114]. A linear dependence of the coefficient of kinetic ejection of electrons on the velocity of the bombarding particles was observed [111] for glass No. 46 also when light ions (hydrogen, helium) were used for the bombardment. It was again established thereby that the slower growth of γ_k with increasing velocity of the incident particles is observed already at $v_0 \sim (4—6) \times 10^7$ cm/sec, i.e., much earlier than for metals, for which the linearity of the $\gamma_k(v_0)$ function is retained [25] at least up to $v_0 \sim 2 \times 10^8$ cm/sec.

3.3. Dependence of kinetic ejection on the type of bombarding particle. Figure 20 shows a plot of $\gamma(A)$ based on the data of [38,39,115] for single-crystal NaCl bombarded with different ions having an energy 0.6 keV. We see that the greatest extraction is produced by the lightest ions, namely protons. Considerable ejection of electrons is observed also in bombardment by helium ions. But in the latter case, however, a noticeable potential ejection of the electrons is likewise possible, and therefore the value of γ_k due only to the kinetic energy of the helium ion should be somewhat lower than the value of γ indicated in the figure. It is interesting that the coefficients of ion-electronic emission γ in bombardment by potassium and argon ions are approximately the same, and amount to ~0.7 electron/ion. Since the argon ions cannot produce intense potential emission, it must be concluded that the kinetic ejection of the electrons by K^+ and Ar^+ ions from NaCl is the same as in the case of metals.[4,16] The same is also observed for other crystals. Thus, when KBr crystals are bombarded with potassium and argon ions having an energy 0.6 keV, the values of γ are close to 1 electron/ion; for LiF they are much smaller, ~0.3 electron/ion [39].

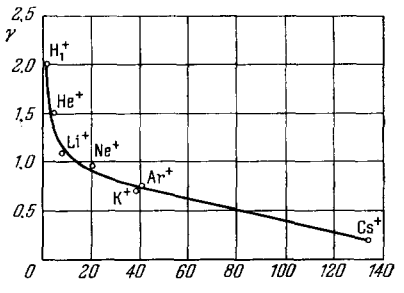

FIG. 20. Dependence of the coefficient γ of the (100) face of single-crystal NaCl on the mass of the bombarding particles [38,39,115]. H_1^+, He^+, Li^+, Ne^+, K^+, Ar^+, and Cs^+ ions with $E_0 \approx$ 0.6 keV were normally incident on the surface.

3.4. Influence of the target temperature on the values of γ_k. Conflicting information was obtained on the dependence of the coefficients of ion-electronic emission of dielectrics on the temperature. According to [113-115], a change in the temperature of alkali-halide crystals from 20°C to 400°C does not cause a change in the value of γ_k. However, in investigations performed somewhat later [39,116,191] it was noted that raising the temperature of alkali-halide single crystals bombarded by potassium and hydrogen ions is accompanied by a decrease of the ion-electronic emission, and the larger the energy of the bombarding particles, the greater the decrease.

The presence of a temperature dependence of γ_k can be due both to loss of energy by the excited electrons in electron-phonon collisions, and to a change in the state of the surface of the bombarded crystal.* The fact that no change in the positive and negative ion-ionic emission coefficients was observed in [116,191] when the temperature was raised from 20°C to 400°C, and also the fact that the decrease of γ_k becomes stronger with increasing energy of the primary ions, are evidence in favor of the first assumption. Finally, it was observed in [191] that the $\gamma_k(T)$ dependences are reversible and that a decrease of γ_k with increasing sample temperature depends on the orientation of the velocity vectors of the primary particles relative to the principal axes of the crystal. According to [191], the closer the direction of incidence of the ions to normal and the more transparent the corresponding crystallographic direction (larger depth of penetration of the ions), the stronger the decrease of γ_k with increasing temperature. These peculiarities can also be naturally attributed to variation in the energy losses upon scattering of the excited electrons by the lattice vibrations.

The presence of a temperature dependence of the coefficient γ_k, due to the electron-phonon interaction, is of fundamental significance, since it points to a volume character of the kinetic ejection of electrons.

3.5. Energy distribution of secondary electrons. Some indications in favor of the volume character of the phenomenon are afforded also by investigations of the spectrum of the secondary electrons. It was established in [52,116] that with increasing energy of

*The alkali-halide single crystals were bombarded by potassium ions [116] and by hydrogen ions [39] in the (100) direction, and therefore the "temperature" change in the "transparency" of the single crystal due to thermal atom vibrations should lead to a $\gamma_K(T)$ dependence opposite to that observed in the experiment.

the bombarding particles the maximum energies of the secondary electrons* increase, but the fraction of the fast electrons in the total number of secondary electrons decreases. Such a change in the energy distribution can be naturally attributed to the fact that when the energy of the primary particles increases the number of electrons excited at greater and greater depths under the surface increases. The secondary electrons created inside the volume move towards the surface and lose part of their kinetic energy, emerging into the vacuum relatively slowly.

An analysis of the energy distribution curves of electrons knocked out from a KCl crystal by He^+ ions (see Fig. 10) shows that in this case the electrons which are ejected as a result of neutralization of the ions are faster than the electrons excited by the kinetic energy of the ions [40].

3.6. Dependence of γ_k on the ion incidence angle.

a. Dielectrics. Just as in the bombardment of metallic single crystals, kinetic ejection of electrons turned out to depend on the angle of incidence and on the orientation of the beam of bombarding particles relative to the crystallographic axes of the target.[39,117,118] Typical dependences of the coefficient of ion-electron emission γ_k on the ion incidence angle θ, obtained [117] by bombarding single-crystal KBr by potassium ions with energies 6, 4, 2, and 1 keV, are shown in Fig. 21. The angle $\theta = 0$ corresponds to normal incidence of the ions on the (100) face of the single crystal. It is seen from the figure that the $\gamma_k(\theta)$ dependences are not monotonic: At angles of incidence close to 0, ± 26, and ± 45°, a minimum of electron emission is observed. At these angles of incidence, the direction of motion of the incident particles coincide with the crystallographic directions [100] ($\theta = 0°$), [210] ($\theta = \pm 26°$), and [110] ($\theta = \pm 45°$). The deepest minimum corresponds to the [100] direction, which is the most "transparent" in the potassium-bromide lattice. Curve 5 of the same figure shows the $\gamma_k(\theta)$ dependence for a polycrystalline KBr film [118] (K^+ ions, $E_0 = 4$ keV). Similar results were obtained also by bombarding single crystals of KCl and LiF with potassium ions [39,118].

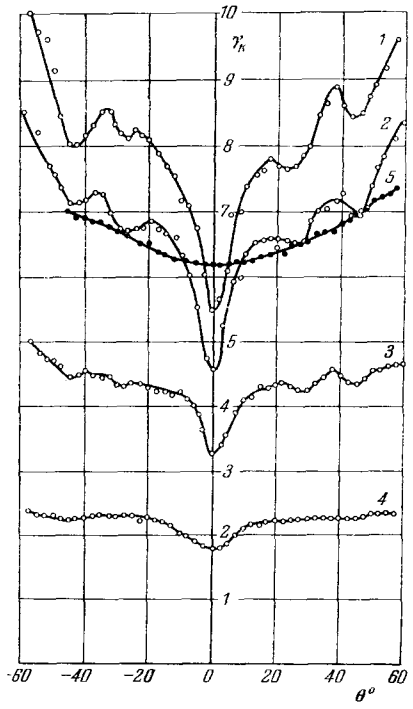

FIG. 21. Dependence of the coefficient γ_k of the (100) face of single-crystal KBr on the angle of incidence of the potassium ions. Ion energy: 1 – 6 keV, 2 – 4 keV, 3 – 2 keV, 4 – 1 keV. Curve 5 – for a sputtered KBr film and $E_0 = 4$ keV.[117,118].

It is seen from Fig. 21 that there is a general tendency for γ_k to increase when the angle of incidence of the primary ions on the surface of the single crystal is increased. This form of the $\gamma_k(\theta)$ can be easily explained [118] by assuming that the velocity distribution of the excited electrons is isotropic in space, and that the thickness of the layer from which the electrons can still escape to the vacuum is smaller than the maximum depth of their production in the crystal. Indeed, in this case an increase in the angle of incidence of the ions should be accompanied also by an increase in the number of inelastic collisions occurring in the layer responsible for the secondary emission, meaning also an increase of γ_k. With increasing bombarding-particle energy, the maximum depth of formation of secondary electrons decreases, and the growth of the coefficient γ_k with increasing θ should slow down, as was indeed observed in experiment (see Fig. 21). The same causes can also explain the somewhat different forms of the $\gamma_k(E_0)$ dependences obtained at different ion incidence angles (see Fig. 19, curves 1 and 2). The smaller the angle θ, the larger the thickness of the surface layer in which the bombarding particle is decelerated, and consequently the slower should be the increase in the number of emitted electrons with increasing energy of the primary ions.

It must be noted that the very existence of a nonmonotonic angular dependence $\gamma_k(\theta)$ is evidence in favor of the volume mechanism of excitation of the electrons [118]. Indeed, if the ion-electron emission were to be due to excitation of the electrons localized on surface levels, then the function $\gamma_k(\theta)$ could be nonmonotonic only as a result of a nonmonotonic dependence of the coefficient of the cathode sputtering and of the ion-ion emission on the orientation of the primary-particle beam relative to the crystallographic axes (excitation of electrons from the surface states by scattered ions and by lattice particles knocked out from the sites and moving from the volume of the crystal into the vacuum). However, the

*When alkali-halide single crystals are bombarded with potassium ions of energy from 0.4 to 3 keV, the maximum energies of the secondary electrons amount to 7.5 – 10 eV.[52]

coefficients of positive ion-ion emission K_+ and of negative ion-ion emission K_- of a KBr single crystal bombarded with potassium ions of 6 keV energy change [116] with increasing angle of incidence from 0 to 20°, only from 0.3 to 0.5 and from 0.075 to 0.14, and the energy of the secondary ions as a rule does not exceed 20 eV,[115] i.e., it is much lower than the threshold energy E_0' for kinetic ejection of the electrons. It is seen therefore that when the angle of incidence of the primary particles varies, the changes in the number of electrons excited from the surface states by the secondary ions should be smaller by several orders of magnitude than those observed in the experiments. The situation is similar with the excitation of electrons from the surface states by sputtered atoms (according to the data of [120], for normal incidence of argon ions with energy 6 keV on the (100) face of single-crystal KBr, the coefficient of cathode sputtering is ~0.6—0.7).

Thus, the entire aggregate of the experimental data accumulated to date on the kinetic extraction of electrons from dielectrics can be explained only if one starts from the assumption that the phenomenon has a volume character. In other words, it can be stated that the excitation of the electrons from the valence band of the dielectric makes, if not the main contribution, at least an appreciable contribution to the secondary electron emission.

It should be noted that V. M. Lovtsov and later L. P. Moroz and A. Kh. Ayukhanov [121-124] have shown that the ion-electron emission of vacuum-sputtered alkali-halide-compound films is also a volume effect. In [124] they even succeeded in estimating the effective depth of emergence of the secondary electrons excited by the ions, which was found to be 1.3—1.4 times smaller than the depth of emergence of electrons in the case of secondary electronic emission.[125]

b. Semiconductors. It was observed in [126] that ion-electronic emission from single-crystal germanium is also determined by the orientation of the beam of bombarding particles relative to the principal axes of the crystal (see Fig. 25a). It was established here that although the kinetic ejection of the electrons from the germanium by potassium ions is indeed a volume effect, the only electrons that can emerge to the vacuum are those excited in the first surface layers of the target (for single-crystal germanium coated with an amorphous oxide layer $\gamma_k \propto \sec\theta$). The decrease in the coefficient γ_k when the direction of motion of the ion beam approaches the transparent crystallographic directions [110], [111], and [112] cannot be attributed to a decrease in the total number of excited electrons, for just the opposite takes place in this case (see Sec. IV). The decrease of γ_k with approach of the ion beam to the crystallographic directions with small Miller indices [126] is apparently due to a decrease in the number of electrons excited in the surface layer from which escape to vacuum is still possible. This can be due both to a decrease in the number of electrons excited by the primary particle per unit length along the trajectory, and to a decrease in the path length traversed by the particle in the same surface layer. A second cause in the decrease of γ_k is in all probability the decrease in the number of fast excited electrons as a result of a decrease in the number of "close" collisions with the lattice atoms (we have in mind collisions with small impact parameters). Certain additional information on the excitation and kinetic ejection of electrons by ions, which can be obtained by simultaneous investigation of radiation conductivity and ion-electronic emission, will be reported in Ch. VI.

The investigations made to date of the kinetic ejection of electrons from single crystals allow us to state [117,126] that the dependence of the coefficient of ion-electronic emission γ_k on the direction of motion of the bombarding particles should be inherent in all single crystals without exception, regardless of their electric conductivity and type of chemical bond.

3.7. Main differences between ion-electron emission of metals, dielectrics, and semiconductors and their qualitative explanation. The main differences in the laws governing the kinetic ejection of electrons reduce to the fact that the values of the coefficients γ_k are much larger when dielectrics are bombarded with positive ions, and the values of the threshold energies E_0' are approximately ten times smaller than in the case of high-melting-point metals. It is obvious that these differences can be due both to differences in the conditions of electron excitation, and to different conditions of their motion in the solid and their escape to the vacuum. According to [114], the values of the threshold energies of the ions are determined only by the conditions of the excitation, inasmuch as the energy losses of the electrons along the path to the surface and the magnitude of the potential threshold on the interface between the solid and the vacuum should influence only the changes in the total number of the emitted electrons. Starting from this assumption, G. M. Batanov explained [114,115] also the existence of threshold ion energies much larger than the binding energy of the electrons in the crystals, and the tenfold difference in the threshold energies for metals and dielectrics on the basis of the theory of electronic transitions in a quasimolecule produced when a bombarding ion collides with one ion or atom of the solid.

The differences in the values of γ_k for metals, semiconductors, and dielectrics are due to a considerable degree to differences in the mechanisms of energy loss by the excited electrons and the conditions for emergence in vacuum [113,119]. Inasmuch as the concentration of the electrons in the conduction band of the dielectric and (as a rule) the semiconductor is exceedingly low, the interaction of the excited electrons with them can be neglected (the effective energy-loss mechanism present in metals is elim-

inated). Therefore the main mechanisms for energy loss in the case of dielectrics and semiconductors are electron-phonon interactions and excitation of bound (tertiary) electrons. It is obvious that the lower the height of the potential threshold $e\chi$ on the interface between the solid and the vacuum, the larger the number of electrons excited by the ions in the conduction band capable of escaping from the crystal. Moreover, the smaller $e\chi$ compared with the width ΔE of the forbidden band, the larger should be the fraction of the excited electrons having a kinetic energy sufficient to overcome the potential barrier on the boundary of the solid, but insufficient to excite tertiary electrons from the valence band (the role of the second effective mechanism of energy losses is reduced). Finally, if $e\chi \ll \Delta E$, then the energies of both the secondary electron (excited by the ion) and the tertiary electron (excited by the secondary electron) can turn out to be larger than $e\chi$ after the impact-ionization act; as a result, the number of electrons emitted to the vacuum may even increase. Thus, the better the inequality $e\chi \ll \Delta E$ is satisfied and the smaller the absolute value of $e\chi$, the larger should be the observed values of the ion-electronic emission γ_k. An analysis of the available experimental data confirms the correctness of the last conclusion. The coefficients of ion-electronic emission increase, according to the literature data, in the following sequence: germanium [119], silicon [116], glass No. 46 [111], and alkali-halide single crystals [52,116]. This is precisely the sequence that can be expected in accordance with Table II.

It is of interest [116,118] to compare the values of the coefficients γ_k for alkali-halide single crystals and such a most important characteristic of their band structure as the width of the forbidden band ΔE. It has turned out (Fig. 22) that the increase in ΔE on going from KBr to NaCl, NaF, and LiF is indeed accompanied by a decrease in the coefficient γ_k. Inasmuch as the values of γ_k are determined to a considerable degree by the electron affinity energies $e\chi$, it was proposed in [116] that the values of $e\chi$ for the indicated crystals are apparently very close. The values of γ_k for single-crystal KCl do not fit on the $\gamma_k(\Delta E)$ curve, this being due in all probability to the smallness of $e\chi$ in KCl compared with the remaining investigated single crystals. It should be noted in this connection that a similar dependence on the gap width ΔE was observed also for the coefficients of secondary electron emission σ [127], and the values of σ for KCl again turned out to be anomalously high.

Table II. Values of ΔE and $e\chi$ of certain materials

	ΔE (eV)	$e\chi$(eV)
Germanium	0,66	4
Silicon	1.1	4
Glass No. 46	~4.5	3÷4
Alkali-halide compounds	6.5÷11.5	0÷1

4. Theory of Kinetic Ejection of Electrons

There is no single universally accepted opinion concerning the mechanism of kinetic ejection of electrons. Inasmuch as a review of a rather large number of earlier investigations can be found in [6,128], we shall dwell here only on the two main hypotheses concerning the mechanism of the phenomenon, which are being discussed at the present time. One of them attributes the ion-electronic emission to excitation of bound electrons by the ion, whereas the other attributes it to the occurrence of plasma oscillations in the solid.

Following the authors of [129,130], we can attempt to consider kinetic emission of electrons as a result of impact ionization of the atoms in the surface layer of the solid. In this case, the processes occurring when the surface is bombarded with ions are represented in the following fashion: [16] When the bombarding particle approaches an atom (or ion) of the target, it slows down, so that at least part of its translational energy goes over into potential energy of electron-shell deformation. If the latter is so large that the perturbed state of one of the electrons of the system turns out to be at a level corresponding to the quasi-continuous spectrum of the unoccupied states in the solid, then this electron can go over from the region of the colliding particles. By the same token, part of the kinetic energy of the ion will be lost in the inelastic process. The fact that for this process it is

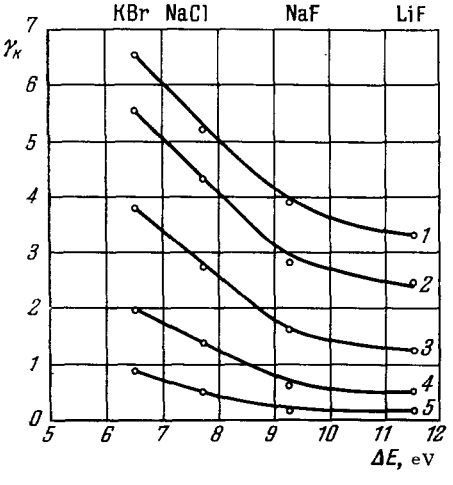

FIG. 22. Connection between the values of the coefficient γ_k and the width of the forbidden band ΔE for alkali-halide crystals [116]. The bombardment was made by potassium ions. 1 – E_0 = 6 keV, 2 – 4 keV, 3 – 2 keV, 4 – 1 keV, 5 – 0.5 keV.

necessary to have a sufficiently strong perturbation of the system explains the existence of an energy threshold of the ion-electronic emission. The "free" electrons do not take part in this process, since it is assumed that in the case of interaction with ions having an energy on the order of several keV, they cannot acquire a velocity sufficient to leave the solid.

With respect to the nature of the electrons escaping to the vacuum we can make two assumptions. These may be just the electrons from the system comprising the ion and the target "atom," which have acquired during the collision an energy sufficient to go off to the vacuum (direct excitation). But in addition, generally speaking, one can expect the appearance of secondary emission also as a result of a two-stage mechanism, in which free electrons already take part [16,131], namely, the directly excited electron is at the Fermi level (or close to it), and the level made free as a result of its departure is filled then by some electron from the conduction band, with the energy released by the Auger effect being transferred to another electron, which becomes capable as a result of leaving the solid (the process is analogous to that described earlier [132]). It is obvious that the second mechanism is far from being operative at all times, and in particular, it can hardly occur in dielectrics and semiconductors bombarded by ions which are not too fast.

The main problem, still unsolved to date, is how to calculate the energy lost by the ion in the inelastic process. Modern theories [91,131] make use of a method proposed by O. B. Firsov [133], who considered ion-atom collisions. The excitation energy of the system, δE, is related here to a unique "heating" of the electron clouds of the colliding particles, as a result of their assimilation of the translational-motion energy of the nuclei (the statistical model).

The theory of [131] considers the excitation of bound electrons of a solid to the Fermi level and above. The energy transferred to the electrons is given by the formula

$$\delta E(p, E)=\frac{\hbar v}{\pi a_H^2}(Z_1+Z_2)^2\int\limits_{r_{\min}}^{\infty}\frac{\left[1-\frac{V(r)}{E}\right]dr}{\sqrt{1-\frac{V(r)}{E}-\frac{p^2}{r^2}}}\int\limits_{r/2}^{\infty}\frac{\varphi(\rho)\,d\rho}{\rho}, \quad (16)$$

where E and v are the energy of the ion in the c.m.s. and its velocity; $a_H=\hbar^2/me^2$ is the Bohr radius; Z_1 and Z_2 are the charges of the nucleus of the ion and of the target atom, respectively; r_{min} is the closest approach of the nuclei during the collision act; p is the collision parameter; V(r) is the repulsion potential acting between the atoms at small distances; $\varphi(\rho)$ is the Tomas-Fermi function.

Assuming that more than one electron can be excited in the collision act, we can estimate the cross section σ of such a process by means of the formula

$$\sigma(v_0)=2\pi\int\frac{\delta E}{J}p\,dp, \quad (17)$$

where J is a certain average excitation potential.

Then, taking into account the depth of production of the excited electron, we can write for the kinetic-emission coefficient the following expression:

$$\gamma_f=\int\limits_0^{x_s}\sigma(v)\,wNe^{-\frac{x}{\lambda}}dx, \quad (18)$$

where N is the number of atoms in one cm^3 of metal; x_s is the depth at which the ion is still capable of ionizing; λ is the mean free path of the electrons in the solid, and w is the probability of emergence of the excited electron from the metal. A detailed calculation of w is practically impossible, primarily because we do not know the energy distribution of the excited electrons. To estimate w it becomes necessary to make a number of rather arbitrary assumptions, and to make use of information on the potential ejection of electrons by inert-gas ions [11]. Calculation by means of formula (18) gives a qualitative idea of the form of the $\gamma_k(E_0)$ dependence and a few other characteristic features of the phenomenon.

An attempt to take into account the influence of the ordering of the structure of the crystal on the ion-electronic emission was undertaken by the authors of [91]. In order to avoid difficulties connected with allowance for the depth of production of the secondary electrons, their energy, the escape probability, etc., they used a single-collision model, writing

$$\gamma_f^{(hkl)}(E_0)=k\int\limits_0^{p_{\max}^{(hkl)}}n_e(p,\delta E)\,R^{(hkl)}(p)\,dp, \quad (19)$$

where $\gamma_k^{(hkl)}$ is the coefficient of secondary emission when the (hkl) face is bombarded by a beam of ions directed normally to surface; δE is the energy consumed in the inelastic process; n_e is the number of electrons released as a result of a collision with an impact parameter p, in which an energy δE is lost; $R^{(hkl)}(p)\,dp$ is the probability that the collision on the surface (hkl) will occur with an impact parameter p, which cannot be larger than a certain quantity p_{max} determined by the geometric factors and dependent on the type of face. The coefficient k is a constant that does not depend on the structure of the bombarded surface.

The probability density of a collision with a specified impact parameter, $R^{(hkl)}(p)$, can be determined from geometrical considerations. The best agreement between theoretical calculations and experimental data is obtained when account is taken only of collisions having the smallest impact parameter, with both surface atoms and with atoms of a deeper layer. The change in the direction of the motion of the primary particle after collision is disregarded, since the single-impact model is used.

The main problem is to calculate the value of δE and the related value of n_e. The energy lost to inelastic processes is calculated by means of a formula similar to (16) but (unlike [131]) the upper limits of

the integrals are assumed to be bounded. Whereas the second integral ("electronic") depends relatively weakly on the upper limit, so that it can be regarded as being the same for different faces, the first ("dynamic") integral turns out to be very strongly dependent on the character of the face. The upper limit of this integral r_{max} is determined both by the structure of the face and by the impact parameter. The authors were unable to obtain agreement between the calculated curves and the experimental data by using the same potential as in [131]. A potential of the Born-Mayer type had to be used to reconcile the theory with the experiment.

Calculating the values of δE for the fundamental planes of face-and volume-centered cubic lattices, and using the data of [134], it is possible to estimate the value of n_e. It is assumed here that the electrons of the bombarding particle are excited (the calculation were made for argon ions). As a result, the authors succeeded in obtaining data that describe qualitatively the course of the experimental curves $\gamma_k(E_0)$ for different faces of metallic single crystals [90]. In the theory of [91], a large role is given to the charge of the particle at the instant of collision with the target "atom," since the charge affects the character of the interaction and consequently the form of the repulsion potential. It is not clear, however, to what extent this circumstance is actually important. It is in general very difficult to estimate the charge of an atomic particle moving in a solid with an energy of several keV. In addition, when the particles come close together, the interaction potential is clearly determined not by the outermost shell and by the particle charge alone. From the point of view of this theory, the extraction of electrons by Ar^+ and K^+ ions should be different, whereas, at any rate for polycrystalline targets, these ions produce identical kinetic emission [5,16]. Furthermore, in view of the changeover to the single-collision model, this theory can hardly be regarded as progressive.

Attempts to explain the nonmonotonic angular dependence of the ion-electron emission were made also earlier [82]. Calling attention to the analogy between the corresponding curves for the ion-electronic emission and cathode sputtering, the authors used the theoretical paper [135] to calculate the ion-electronic emission, and then its temperature dependence [100], which made it possible to obtain a curve that was quite close to the experimental ones.

A fairly recent paper [136] proposes a variant of the theory of [131] with allowance for the influence of the anisotropy of the crystal on the kinetic ejection of electrons by ions. The author of [136] has shown that the screening of lower (deep) atomic layers by the high-lying ones should actually lead to the experimentally observed [82] nonmonotonic $\gamma_k(\theta)$ dependences. He also estimated theoretically the "smoothing" of the $\gamma_k(\theta)$ as a result of thermal vibrations of the atoms, which take place when the temperature of the single crystal is increased.

It should be noted that not one of the theoretical papers [91,131,136] in which the hypothesis of excitation of bound electrons is developed, analyzes in detail the excitation mechanism itself. Attempts to understand the process of electron excitation in the case of close collisions of atomic particles having energies of hundreds eV up to tens of keV were made in some papers devoted to the study of atomic collisions, but the final solution of the problem is still a thing of the future.

A different point of view on the mechanism of electron excitation by ion bombardment of solids was advanced in 1962 by M. M. Bredov. He proposed that the ion-electronic emission is the result of plasma oscillations produced in the solid as a result of penetration of the ion into its surface layer. A similar point of view was advanced by the authors of [26]. That electron emission can be due to emergence of plasma waves to the surface is indicated also in [100,137]. However, there is still no mathematical treatment of the problem, and it is difficult to assess the fruitfulness of this hypothesis.

Summarizing the foregoing, we can note that when surfaces are bombarded by atomic particles with energies on the order of several keV, electrons are as a rule excited and emitted into the vacuum. The number of secondary electrons (which reaches in individual cases tens of electrons for each bombarding particle with energy $E_0 \lesssim 10$ keV) depends strongly on the properties of the bombarded substance, on the nature and energy of the ions, and also on their angle of incidence on the target. A threshold of ion-electron emission is observed, which amounts to ~1 keV and more for metals bombarded by arbitrary ions, except the lightest ones (hydrogen, helium), and much less for dielectrics of the type of alkali-halide salts. The phenomenon has a volume character, as is convincingly evidenced by the dependence of the coefficient γ_k on the angle of incidence of the ions on the single-crystal samples and by other experiments. There is no doubt that the electrons ejected to the vacuum constitute only a small fraction of all the excited electrons. There is still no theory capable of explaining the phenomenon by starting from a detailed physical model of the main mechanism of electron excitation.

IV. RADIATIVE (INDUCED) CONDUCTIVITY OF SEMICONDUCTORS BOMBARDED BY IONS

An investigation of the ion-electronic emission cannot yield sufficiently complete and exact information on the excitation of the electrons, for in this case one registers only those electrons which were capable of overcoming the potential threshold on the interface between the solid and the vacuum. On the other hand, the probability of escape of an electron to the vacuum is determined by many parameters (depth of excitation, initial direction of the velocity

vector, initial energy, scattering and energy loss along the path to the surface, magnitude of energy threshold) and therefore cannot be calculated exactly. In this connection, to study the excitation of electrons in a solid by heavy atomic particles, it was advantageous to make use of other secondary phenomena, the investigation of which would make it possible to determine the total number of electrons excited in the substance by the decelerating ions and atoms. Such phenomena include, in particular, radiative (induced) conductivity, which occurs when semiconductors are bombarded with ions and atoms, and which was first observed [138] for germanium and then investigated in [139-143,39].

1. Electric Conductivity of Solids Irradiated by Beams of Atomic Particles

In the general case the electric conductivity of a semiconductor bombarded by atomic particles can change as a result of a large number of factors. First, the fast moving particle can transfer part of its kinetic energy to a bound electron in the semiconductor and transfer the latter to the conduction band. We shall assume that two excess carriers are produced in each excitation act, an electron in the conduction band and a hole in the valence band, and assume that the concentration of the impurity centers in the semiconductor is low, and therefore the impurity centers do not part in the excitation process. Second, the excess carriers can be produced in the semiconductor as a result of the potential energy of the ion-plus-solid system [140], in analogy with the situation occurring in potential ejection of electrons. The increase in the electric conductivity of the crystal as a result of kinetic or potential excitation of the bound electrons will be called radiative (induced) conductivity.

In addition, the electric conductivity of solids bombarded by atomic particles can change as a result of thermal heating of the lattice, and also as a result of formation and accumulation of radiation defects in the crystal (for example, Frenkel defects) and penetration defects (which penetrate into the volume of the primary-beam particle).

In order to register the radiative conductivity, and not the changes in the electric conductivity due to heating or defect formation, a pulsed measurement procedure was used in [138-143,39]. The flux of primary ions was modulated by rectangular pulses with duration longer by a factor 3—4 than the lifetime of the nonequilibrium carriers, and with a low repetition frequency. An analysis of the obtained results, and particularly a comparison of the oscillograms of the radiative-conductivity current upon bombardment with ions and electrons (for details see [139,140]) has shown that the changes in the electric conductivity observed in [138-143,39] were due in all cases to excitation of electron-hole pairs.

2. Dependence of the Radiative Conductivity on the Energy of the Bombarding Particles

So far radiative conductivity has been investigated essentially only for one semiconducting material—germanium—bombarded by ions of hydrogen [141], deuterium [39], lithium [143], sodium [143], and potassium [138-140,142,39], with energies from 100 to 10 000 eV. It was observed that incidence of an ion beam on the surface of the semiconductor sample always leads to a temporary increase in its electric conductivity, and the larger the kinetic energy of the incident particles, the greater this increase. A typical dependence of the ratio of the radiative conductivity current ΔI to the strength of the primary ion current I_1 on the energy of the incident potassium ions is shown in Fig. 23. It is seen from the figure that the value of the coefficient $\kappa = \Delta I/I_1$, which is proportional to the total number of carriers excited in the semiconductor by the primary particle and the lattice atoms displaced by it, increases monotonically with increasing ion energy E_0. We note that the increase of κ with change in the energy E_0 is faster than linear.

3. Dependence of the Radiative Conductivity on the Type of Bombarding Particles. Number of Excited Electron-hole Pairs.

The use [138-143,39] of a rather large set of bombarding ions has made it possible to establish also the dependence of the efficiency of electron excitation on the bombarding-particle mass. A summary plot of the data for germanium bombarded with ions and electrons with energies $E_0 = 3$ keV is shown in Fig. 24. The excitation of the carriers in the germanium by electrons was investigated in detail, in particular by V. S. Vavilov (see, for example, [144,145]). He has established that the average energy $\bar{\epsilon}$ lost by the electron to the production of one pair of carriers is approximately 3 eV, and if the energy of the primary particles greatly exceeds the width of the forbidden band, this value does not depend on the initial energy. Assuming for electrons $\bar{\epsilon} = 3$ eV, we can, using the diagram of Fig. 24, estimate the total number of electron-hole pairs excited in germanium when any ion with initial energy 3 eV is slowed down in

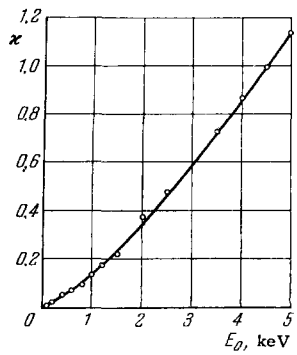

FIG. 23. Dependence of the coefficient κ on the energy of K^+ ions bombarding a germanium target [39].

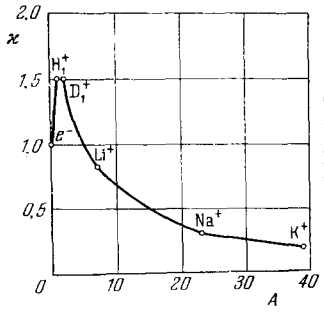

FIG. 24. Dependence of the coefficient κ of single-crystal germanium on the mass of the bombarding particles [39]. The electrons e^- and the ions H_1^+, D_1^+, Li^+, Na^+, and K^+ were incident on the surface normally.

germanium. To this end it is sufficient to multiply the corresponding value of $\kappa = \Delta I/I$, taken from the data of Fig. 24, by the number of pairs produced in the germanium by one electron, which in this case is equal to $E_0/\bar{\epsilon} = 1000$.

The decrease of κ on going from protons and deuterons to heavier particles agrees well with the existing notions concerning the interaction of particles with matter. Indeed, an increase in the mass of the bombarding particles should lead to an increase in the energy transferred to the lattice atoms (the atomic weight of germanium is A = 72.6), i.e., to a more effective deceleration. In addition, an increase of A with E_0 constant denotes a transition to slower particles, and when the velocity decreases, the cross section for inelastic collisions should naturally decrease, too.

It is seen from Fig. 24 that protons and deuterons excite in germanium more electron-hole pairs than electrons having the same initial energy. The higher values of κ for protons and deuterons, compared with electrons, can also be explained qualitatively [141].

When a fast electron is decelerated in matter, secondary, tertiary, etc. electrons and holes are produced, with kinetic energy E_e that greatly exceed the width of the forbidden band ΔE. So long as the condition $E_e \gg \Delta E$ is satisfied, it can be assumed with a high degree of accuracy that the only mechanisms of energy loss are the inelastic ionization collisions. When the energies of the electrons and holes decrease as a result of the deceleration, so that E_e is only several times larger than the width of the forbidden band ΔE, the principal role is assumed by the energy loss in electron-phonon collisions [146] (excitation of optical phonons by electrons and holes). Finally, when the energies E_e become smaller than ΔE, the probability of the inelastic process with formation of an electron-hole pair becomes in general equal to zero. Owing to these factors, the average energy $\bar{\epsilon}$, lost to the production of an electron-hole pair when semiconductors are bombarded by fast electrons, γ quanta, or x-rays turns out to be much larger than the width of the forbidden band (for germanium $\bar{\epsilon} \approx 3$ eV). It is obvious that to explain the unusually high values of κ obtained by proton and deuteron bombardment, it is natural to assume, in connection with the foregoing [141] that, unlike the electrons, γ quanta, or x-rays, the hydrogen and deuterium ions excite in germanium essentially only "slow" electrons and holes with energies $E_0 < \Delta E$.

To ensure high values of κ it is also necessary that the energy loss in elastic collisions between the bombarding particles and the lattice atoms be small. This requirement is well satisfied when germanium is bombarded by hydrogen and deuterium ions, owing to the favorable ratio of the masses of the colliding particles and to the relatively high velocities of the primary ions.

4. Concerning the Threshold of Radiative Conductivity

It was already noted above that radiative conductivity in semiconductors bombarded by ions can result either from kinetic or from potential excitation of electrons. However, the character of the $\kappa(E_0)$ dependences, and also the absolute numbers of the excited electron-hole pairs, show that in the investigations [138-143,39] kinetic excitation of the carriers always prevailed. This raises the question whether there exists a threshold for radiative conductivity analogous to the threshold for kinetic ejection of electrons to the vacuum. In one of the earlier investigations [139] of radiative conductivity of germanium, the threshold energy was estimated to be 300—400 eV for potassium ions. In later experiments [39], however, it was observed that electrons are excited in germanium even when bombarded with potassium ions having 100 eV energy.* Thus, when germanium is bombarded with potassium ions, the threshold energy for the radiative conductivity is apparently smaller than 100 eV. We recall in this connection that the threshold energy for kinetic ejection of electrons by potassium ions is ~500 eV for germanium [119]. The large value of the threshold energy in the case of ion-electronic emission can be readily understood, since an energy of 0.66 eV is required to excite an electron into the conduction band, and not less than 4.66 eV is required to excite the electron into the vacuum.

5. Influence of Crystal Structure on Radiative Conductivity

The radiative conductivity of germanium, like the kinetic ejection of electrons, turns out to depend on the orientation of the primary-particle beam relative to the crystallographic axes [142]. Figure 25a shows a plot of $\kappa = \Delta I/I$ on the angle of incidence of the potassium ions on the target. In this experiment, the

*Potential excitation of electrons from the valence band to the conduction band of germanium is impossible in this case, since the ionization potential of potassium is 4.34 eV, and the width of the forbidden band and the distance from the vacuum level to the bottom of the conduction band of germanium are respectively 0.66 and 4 eV.

beam of ions with 6-keV energy was always in the (110) plane, the angles of incidence θ were equal to $-30°$, $-10°$, and $+22°$, corresponding to the crystallographic directions [112], [111], and [110]. The increase in the coefficient κ when the velocity vector of the incident ions approached the "transparent" directions [110], [111], and [112] were due to the fact [142] that this approach decreased the probability of elastic collisions with the lattice atoms. At the same time, the probability of inelastic collisions remains essentially unchanged. As a result, the total number of excited electrons turns out to depend on the crystallographic direction in which the ion has moved; the more "transparent" the direction, the larger this number.*

Figure 25a shows also the dependence of the coefficient γ_k of kinetic ejection of electrons on the angle of incidence of the bombarding particles, obtained [126] for the same target as the $\kappa(\theta)$ curve. Comparison of the curves shows that the total number of excited electrons is maximal precisely at those angles θ, for which the number of electrons emitted to the vacuum is minimal. An explanation of the decrease of γ_k when the ion beam approaches directions having small Miller indices was already presented by us in Sec. 3 of Chap. III.

Comparison of the results of investigations of radiative conductivity produced by bombardment with potassium ions and with electrons makes it possible to determine the total number of electrons excited when one potassium ion is decelerated in matter, and then estimate, from the data of Fig. 25a, the fraction δ of the secondary electrons emerging to the vacuum. The results of such an estimate, carried out [39] for Ge, are shown in Fig. 25b. The function $\delta(\theta)$ is modulated deeper than the functions $\kappa(\theta)$ and $\gamma_k(\theta)$; the values of δ fluctuate between 0.14×10^{-3} and 0.5×10^{-3}. Thus, only one out of 2000—7000 excited electrons emerges to the vacuum. So low an emergence probability is obviously the consequence of the fact that the overwhelming number of the electrons excited in the conduction band have kinetic energies insufficient to overcome the potential threshold on the solid-vacuum interface. Comparison of the dependences of the coefficients of ion-electronic emission γ_k and radiative conductivity κ on the energy of the bombarding particles shows [139] that in the case

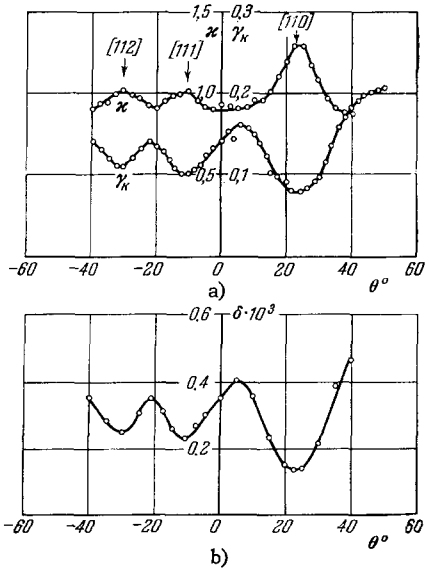

FIG. 25. Dependence of the coefficients γ_k, κ, and δ on the incidence angle θ of K^+ with $E_0 = 6$ keV on the surface of single-crystal germanium [39,126,142].

of germanium bombarded by a beam of potassium ions the fraction of excited electrons emerging to the vacuum is practically constant in the range of E_0 from 1 to 10 keV. A simultaneous study of the radiative conductivity and the kinetic extraction of the electrons [142,126] has also made it possible to establish that the radiative conductivity (excitation of electrons responsible for the change in the electric conductivity of germanium) is, as expected, more of a volume effect than a kinetic ejection (excitation of the electrons responsible for the ion-electronic emission).

6. Excitation of Electrons in Silicon and in Cadmium Sulfide

The excitation of electron-hole pairs was investigated also in silicon [147] bombarded with hydrogen ions with energies from 18 to 225 keV. Unfortunately, the total number of electrons excited by one hydrogen ion was not determined in that investigation; all that was established was that this number increases approximately linearly with increasing energy of the bombarding particles.

Radiative conductivity was recently observed in silicon and in cadmium sulfide [192] bombarded with hydrogen ions of ~1 keV energy. According to preliminary estimates the efficiencies for the excitation of bound electrons by ions and by electrons turned out to be of the same order.

7. Theoretical Notions Concerning the Excitation of Electrons by Atomic Particles

Until recently, the excitation of electrons was considered theoretically only for fast atomic particles

*It was proposed in [142] that the nonmonotonic angular dependence of the radiative conductivity can be due also to different contributions of the surface recombination of the carriers, as a result of the fact that the depths of penetration of the ions into the single crystals may differ for different crystallographic directions by several times. However, special measurements made by I. A. Abroyan, A. I. Titov, and N. T. Khvostikova, and also calculations made by L. A. Tsekhnovicher, have shown that differences in the depths of penetration of potassium ions with energies 1 – 10 keV cannot lead, in the case of germanium, to the observed $\kappa(\theta)$ dependences.

Table III

Type of ion	Energy E_i, eV	Number of pairs excited at $E_0 = E_i$	Minimum energies, lost in inelastic collisions	Minimum fraction of energy lost in inelastic collisions
Hydrogen	150	75	50 eV	0.3
Deuterium	300	150	100 eV	0.3
Lithium	1000	280	185 eV	0.18
Sodium	3500	350	230 eV	0.07
Potassium	6000	440	290 eV	0.05

with velocities $v_0 \gg v_H$ (v_H – electron velocity in hydrogen atom) (see, for example,[1]). As to low velocities, it was simply assumed in theoretical considerations of the deceleration of slow atomic particles in matter, following N. Bohr[1], that the excitation ceases completely when $v_0 \lesssim (1/20)v_H$. In 1949, F. Seitz proposed[148] a different criterion, which was subsequently widely used in theoretical and experimental studies of different radiative effects (see, for example,[2]). According to Seitz, it is assumed that at particle energies $E_0 > E_i$ practically the entire energy is consumed in inelastic collisions, i.e., in electron excitation, $E_i = (1/8)(M/m)\Delta E$, where M is the mass of the incoming particle, m the mass of the electron, and ΔE is the minimal energy necessary to excite the electron, i.e., the width of the forbidden band. It is assumed at the same time that when $E_0 < E_i$ only elastic collisions take place between the particles and the crystal-lattice atoms.

Research[138-143,39] performed on radiative conductivity of germanium has made it possible to estimate the possible errors connected with the use of Seitz's criterion. Table III taken from[39], lists the experimental data on the excitation of electron-hole pairs in germanium by different ions with initial energy equal to E_i. The same table lists also the minimum energies and the minimal energy fractions lost by the ions in inelastic collisions; the latter were calculated for $\Delta E = 0.66$ eV. It is interesting that the minimal energy fraction lost by the ions with initial energy E_i in inelastic collisions turn out to depend on the mass of the bombarding particle.

The most serious attempt to consider theoretically the interaction between slow atomic particles ($v_0 < v_H$) with matter was recently made by J. Linhard and his co-workers[149,150]. Since the mutual penetration of the electron clouds of particles colliding at not too low energies should be appreciable, many electrons of the atoms (ions) take part in the collision. This has made it possible for the authors of[149,150] to use the statistical Tomas-Fermi model of the atom.* A theoretical analysis has shown that in the interval $v_0 < v_H$ the cross section for decelerating a particle by interaction with electrons, S_e, increases linearly with increasing particle velocity:

$$S_e \approx 8\pi e^2 a_H \frac{Z_1^{7/6} Z_2}{Z} \frac{v_0}{v_H}. \qquad (20)$$

Here e is the electron charge, a_H the radius of the Bohr orbit in the hydrogen atom, and Z_1 and Z_2 are the atomic numbers of the bombarding particle and of the target atom, respectively, and

$$Z^{2/3} = Z_1^{2/3} + Z_2^{2/3}.$$

An atomic particle moving in matter loses part of its kinetic energy in elastic and inelastic (electron excitation) collisions. Following[149], we denote by η that part of the kinetic energy which is transferred to the electrons.

Assuming that the cross section S_n for the deceleration of the particle in elastic collisions does not depend on the energy E_0 in the region $E_0 < E_{1c}$, E_{2c}, and regarding "electron deceleration" as a continuous process, the authors of[149] found, in particular, that

$$\eta = \frac{2}{3}\left\{E_{1c}^{-1/2} + \frac{1}{2}E_{2c}^{-1/2}\right\} E_0^{3/2}, \qquad (21)$$

where

$$E_{1c} \approx \frac{A_1^3}{(A_1+A_2)^2} \frac{Z^{4/3}}{Z_1^{1/3}} 500 \text{ eV} \qquad (22)$$

$$E_{2c} \approx \frac{(A_1+A_2)^2}{A_1} Z_2 125 \text{ eV} \qquad (23)$$

In the derivation of (21) it was also assumed that the energy transferred in elastic collisions to the lattice atoms is small compared with the kinetic energy of the moving particle E_0.

The values of the energy $\overline{\eta}$ calculated in formula (21) for potassium, sodium, and lithium ions of energy 3 keV decelerated in germanium are respectively ~250 eV, ~500 eV, and ~2000 eV. At the same time, according to the experimental data[139,143], when these ions are decelerated in germanium from $E_0 = 3$ keV, approximately 200 (K^+), 400 (Na^+), or 800 (Li^+) electron-hole pairs are excited. Assuming[143] that an energy ~1 eV is consumed in the production of one pair, the experimental values of η are found to be 200, 400, and 800 eV. The agreement between theory and experiment turns out to be perfectly satisfactory.

*At very low energies of the colliding particles, for example when $E_0 < 100$ eV, the interpenetration of their electron shells is small, and the statistical approach to the solution of the problem becomes invalid. However, it is assumed that the excitation of the electrons by such slow particles is also negligibly small, so that it can make no appreciable contribution to the total magnitude of the inelastic energy loss.

V. GLOW EXCITED BY ION BOMBARDMENT OF SOLIDS AND IONOLUMINESCENCE

Bombardment of surfaces by ions is accompanied, besides emission of electrons and atomic particles, by the occurrence of electromagnetic radiation, which can be due to a great variety of causes. Therefore, before using the experimental data to obtain information on the excitation of electrons, it is necessary to analyze thoroughly the nature of this radiation.

1. Electromagnetic Radiation Due to Emission by Atoms Leaving the Surface as a Result of Cathode Sputtering

It has been long known that the section of a surface bombarded by alkali-element ions begins to glow, and the color of the radiation depends on the nature of the ions. Mayer's experiments [151] have shown convincingly that this radiation is due to the de-excitation of alkali atoms.

It was found at the same time that the main emitter is not the surface of the metal itself. A luminous layer, the thickness of which can reach several millimeters and depends on the primary-particle energy, is produced as a rule above the surface. This shows that the phenomenon is due not to the glow of the solid, but to emission from particles that leave the solid either as a result of cathode sputtering or simply as a result of scattering of the ions accompanied by neutralization in the excited state. Knowing the lifetimes of the atoms in the excited state and measuring the dependence of the radiation intensity in the glowing zone as a function of the distance from the surface, it is possible to obtain information on the energy of these particles. Recent investigations [152,153] make it possible to assume that the main source of the excited atoms (at least when molybdenum is bombarded with cesium ions of energy 0.5—2.5 keV) are the primary-beam particles previously absorbed in the surface layer of the metal, to which the bombarding ions transfer an energy sufficient to emerge to the vacuum (cathode sputtering). The energies of the knocked-out excited atoms and their distribution over the emission angles were determined from an analysis of the dimensions and shape of the luminous layer.

The emission of light quanta by excited atoms and ions of copper leaving the surface of a copper sample as a result of cathode sputtering by Ne^+ and Ar^+ ions with energies in an interval of several dozen keV was investigated in [154,155]. Besides the Cu I and Cu II lines, the emission spectrum revealed lines due to de-excitation of singly-charged ions of the inert gas. (It is interesting to note that no lines connected with the de-excitation of the inert-gas atoms were observed.) The dependence of the intensity of the emission due to de-excitation of the particles indicated above on the angle of incidence of the Ne^+ and Ar^+ ions on a single-crystal target was nonmonotonic and was the same for all particles (the same for all wavelengths). The form of the Cu I spectral line ($\lambda = 3247$ Å) was analyzed in [155] and more detailed information was obtained on the dependence of its intensity on the angle of incidence of the ions on the target and on the angular distribution of the radiation at this wavelength. By using different orientations of the radiation receiver (monochromator with a multiplier as a detector) relative to the target, the authors have shown that the emission of the bombarded section of the target is not directional (i.e., isotropic), and comes from a luminous layer 0.25—0.35 mm thick over the surface. The energy of the particles leaving the target could be estimated from the Doppler broadening of the spectral line and turned out to be relatively large (more than 1 keV), increasing with increasing angle of incidence of the ions on the target.

Thus, from data on such a glow it is possible to estimate the energies of the atoms leaving a target as a result of cathode sputtering, and possibly also the energies of the scattered primary particles. However, the emission of the atoms and the ions is capable of completely masking the emission produced inside its volume, if the latter emission exists. Therefore, in attempting to use data on the glow of solids to obtain information on de-excitation of electrons in the solids by ion bombardment, it is necessary to take into account, and where possible reduce to a minimum, the emission from the excited particles located above its surface.

2. Radiation Produced by Ion Bombardment of Metals

Attempts to observe the glow of metals under the influence of positive ions were made many times, but no convincing data proving the existence of this emission have been obtained as yet.

M. A. Eremeev, L. Kh. Litmanovich, and A. D. Volkova have shown that when sufficiently pure metals are bombarded with alkali-element ions of energy lower than 10 keV, the emission of photons with energies exceeding several eV (if produced at all) is small, and that for quantitative measurements it is necessary to control very carefully the experimental conditions, so as to eliminate the possibility of distorting the results by side effects (particularly x-radiation produced by deceleration of secondary electrons).

Radiation from a nickel target bombarded by hydrogen, helium, and neon ions with energies 0.3—3 keV was observed by the authors of [156,157]. According to their estimates, one photon is produced on the average for 10^5 bombarding ions (the photons were registered with a glass-window multiplier, so that hard quanta, if present, might not be recorded under the conditions of these experiments). The

largest number of photons was observed when the target was bombarded with hydrogen ions, and the smallest in the case of neon. The authors indicate that outgassing the target by heating decreased the glow intensity. A continuous radiation was observed in [158] in the wavelength interval 3300—5200 Å when nickel was bombarded with hydrogen ions of 200 keV energy. Experiments with other metals bombarded with both fast hydrogen ions and with potassium ions having an energy of several keV [159,160] revealed in individual cases (for example, for a silver target) peaks in the optical part of the spectrum, the appearance of which are attributed by the authors to excitation of plasma oscillations in the metal by ion bombardment. However, the extent to which the data obtained by the authors are free of effects due to emission from excited atoms is not clear, all the more since the character of the angular distribution of the glow observed by them for a silver target is somewhat reminescent of the distribution obtained earlier [152,153,154]. Electromagnetic radiation with wavelengths 2000—6000 Å, produced when metals are bombarded by fast gas ions, was investigated in [154,155]. As indicated, the overwhelming part of the emission was due to de-excitation of excited particles leaving the surface. No continuous spectrum was observed, which also gives grounds for assuming that the emission of the photons from the metals themselves is small. Unfortunately, the threshold sensitivity of the apparatus is not indicated in these papers, so that it is impossible to estimate the upper limit of the number of emitted quanta.

Let us consider briefly the main processes that can cause a practically inertialess emission of photons by ion bombardment.

First, we can expect radiation to appear as a result of neutralization of the bombarding particles at the surface. However, as indicated earlier (see Ch. II), the probability of radiative neutralization should be very low. This is confirmed by experiments [154] in which no emission of inert-gas atoms was observed.

Neutralization with emission can turn out to be noticeable, probably, only at very low bombarding-ion energies.

In principle, bremsstrahlung can appear as a result of the rapid deceleration of the particle. The available data in the ion-energy under consideration, reveal no such radiation. This is apparently connected to a considerable degree with peculiarities in the deceleration of atomic particles in the surface layer of the material.

Finally, emission is possible as a result of the transition of the solid from the excited state, produced as a result of absorption of the primary-particle kinetic energy, to the ground state; this transition is of greatest interest for our purposes. Such transitions can occur both by emission of characteristic radiation (interband transitions), which is observed when metals are bombarded by very fast ions (see, for example, the data for mercury ions with $E_0 \sim 2$ MeV [161]) and yields information on the "affected" electron shells, and by emission of radiation with a continuous spectrum, connected with intraband transitions. (We note that an attempt was made in [162] to calculate theoretically the excitation of the K shell by α particles.) The possibility of radiation connected with plasma oscillations of the electron gas in the metal, if such are excited in the metal by ion bombardment, was also indicated in [159,160]. The spectrum of this radiation will probably not be continuous.

Unfortunately, in spite of the fact that the problem of generation of light as the result of bombarding metals with ions is very interesting not only for the understanding of the mechanism of the interaction of atomic particles and the surface, but for many other branches of solid-state physics, the presently available experimental data are too scanty to draw any conclusions.

3. Luminescence Produced When Semiconductors and Dielectrics Are Bombarded by Ions (Ionoluminescence)

The glow of certain semiconductors and dielectrics subjected to ion bombardment turned out to be so intense, that it found extensive practical use. As a rule, however, radioluminescence is employed, i.e., glow induced by very fast particles produced principally as a result of nuclear transformations (nuclear-radiation counters, "self-luminescent" paints, etc.). The glow induced in luminors are ions with energies on the order of several dozen keV and lower (ionoluminescence) is used exclusively only to produce images in an ion projector [163] and in a few other devices.

There is no doubt that the main mechanism producing the radiation in ionoluminescence is the same as in the excitation of luminescence by other means: The glow is due to radiative transitions of the system from the excited to the ground state; for certain substances the probabilities of these transitions can be quite large compared with the probability of nonradiative transitions. However, the mechanism of excitation of the system, the mechanism for transfer of the energy of the bombarding particles to the electrons of the solid, should depend strongly on the nature and energy of the bombarding particles. In particular, very fast charged particles lose their energy essentially in inelastic collisions, transferring this energy to the electrons, which can cause additional sequential ionization in the crystal and excitation of more and more electrons. At the same time, ions and atoms with energies on the order of several keV should experience essentially elastic collisions with the atomic particles of the lattice, and can hardly

Table IV

Type of ion	E_0', keV	n	Type of ion	E_0', keV	n
H_2^+	3.5±0.5	1.11±0.06	K^+	4.0±0.5	2.35±0.13
Li_2^+	4.0±0.5	1.67±0.10	Ar^+	2.0±1.0	3.11±0.27
Na^+	3.5±0.5	3.36±0.20	Rb^+	1.8±1.0	3.89±0.60

generate fast electrons. We shall not consider radioluminescence here, and turn directly to investigations of ionoluminescence, which unfortunately are very few. This is probably due to two causes: 1) the rapid decrease in the luminescence yield of the sample during the course of bombardment—the "destruction" or "aging" of the phosphor; 2) imperfection of the surface layer of the sample and the presence of foreign films on the surface, which do not make it possible to identify the electronic properties of the semiconductor layer, in which the main deceleration of the atomic particles takes place, with its volume properties.

Destruction of phosphors was investigated practically in all the studies devoted to ionoluminescence [164, 170]. It was shown that the degree of destruction is determined uniquely by the ion flux. As a rule, when the number of particles incident on the sample is $\sim 10^{12}$ cm^{-2}, the luminescence yield at E_0 = const decreases by at least one-half. It is obvious that these changes in the luminescent properties of the substance are due to the fact that the atomic particles penetrating into its surface layer produce different structural damage in the latter. This makes it possible to investigate the character of the changes occurring in the surface layer of the material (see, for example, [171,172]) and to determine the depth of penetration of the ions [165,167] by studying the cathodoluminescence properties of the material before and after ion bombardment. Similar investigations were performed for a number of luminors (see [169]), and also for SiC single crystals bombarded with lithium ions [173]. Figure 26 shows plots of the cathodoluminescence yield as a function of the electron energy for different energies of the ions acting on the crystal. There is no doubt that the excitation of the electrons and the glow produced by their recombination occur in a surface layer having a thickness of the same order as the depth of penetration of the ions.

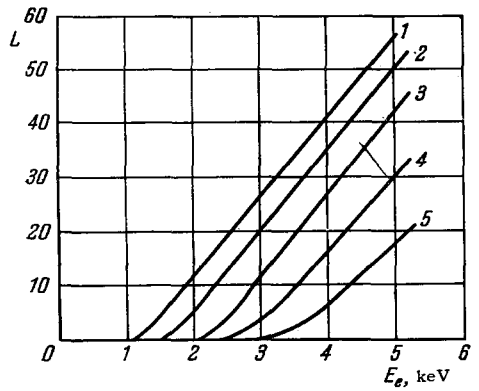

FIG. 26. Dependence of the cathodoluminescence yield L of single-crystal SiC on the energy E_e of the exciting electrons [173]. The crystal was first bombarded by lithium ions with different values of E_0: 1 – 2 keV, 2 – 3 keV, 3 – 4.8 keV, 4 – 7 keV, 5 – 11 keV.

There is very little information on ionoluminescence of crystals not yet damaged by ion bombardment. In such experiments it is customary to decrease the damage to the sample, to have the ion beam scan the surface of the target, as a result of which the irradiation dose on each section of the surface does not exceed 10^{10}–10^{11} cm^{-2}.

It is assumed that ionoluminescence increases with increasing ion energy E_0 like

$$L \sim (E_0 - E_0')^n.$$

By way of an example, Fig. 27 shows data [170] on ionoluminescence of ZnS-Ag, produced by Na^+, K^+, Rb^+, and Ar^+ with energies up to 25 keV.

Within the limits of measurement error, lnL increases linearly with $E_0 - E_0'$; the values of E_0' and n for ZnS-Ag are listed in Table IV.

In accordance with the data of [164], the value of n for H_2^+ ions is close to unity. In experiments [174] in which CsI(Tl) crystals were bombarded by protons and deuterons, it was shown that the radiation yield increases linearly as the particle energy is increased

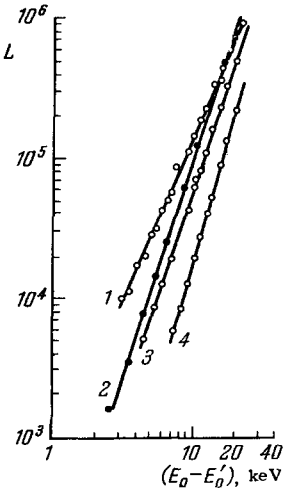

FIG. 27. Ionoluminescence yield L of ZnS:Ag phosphor vs. ion energy E_0.[170] 1 – K^+, 2 – Na^+, 3 – Ar^+, 4 – Rb^+. The values of E_0' are listed in Table IV.

Table V. Values of $B = L_{ion}/L_{electron}$ in per cent

Phosphor / Ion	ZnS : Ag	ZnS : CdS : Ag	ZnS : ZnSe : Ag	ZnS : CdS : Cu	ZnO : Zn	Zn_2SiO_4 : Mn	$CaWO_4$	$CaSO_4$: Mn
Li^+	2.2	5	3.1	3	5.8	—	6.4	6.7
Na^+	—	1	—	—	5	2.9	2.5	—
K^+	1.0	1	0.8	2.3	4.5	2.0	1.8	1.8
Rb^+	0.7	0.35	0.1	—	—	1.3	1.1	1.4
Cs^+	0.15	0.35	0.1	0.95	4.0	0.8	0.7	0.8

from 25 to 100 keV, and extrapolation yielded $E_0' = 10$ keV. The yield from the deuterons were 1.3 times larger than the yield from protons having the same energy. However, when $E_0 < 25$ keV, a certain deviation from a linear dependence was observed, in the direction of a larger luminescence yield, so that the values of E_0' obtained by extrapolation, both indicated in that reference and those listed in Table IV, are to some degree arbitrary.*

Measurements performed by other authors at lower ion energies [168,169,175] show that the energy E_0' for different phosphors does not exceed 1.5 keV, and as a rule is larger for substances in which a relatively large electron energy (large "dead potential") is necessary for the excitation of cathodoluminescence. This indicates that the excitation of the electrons is possible in principle even at lower energies of the ions, but is not accompanied by radiative recombination, since the main processes are completed in the phosphor layer closest to the surface, which is usually damaged and has a complicated composition.

In first approximation, the ionoluminescence brightness increases linearly with increasing bombarding-ion current density [168-170], although it is possible to expect in individual cases, especially at large irradiation intensities, that this will not take place.

Practically no measurements of the spectral composition of the radiation were made. According to the data of [176], the spectral composition of the glow of willemite in photo-, cathodo-, and ionoluminescence, at least in the main band, is the same and varies during the "aging" process. Accordingly, no differences were noted during the course of the $L(E_0)$ curves in the registration of the total light flux from the luminor, and the flux separated by means of interference filters [170]. So far, practically no study was made of the inertia of the ionoluminescence and of the rate of decrease of the glow after the ion bombardment is stopped.

Observations of the decrease in the emission intensity of different substances, described in [177,178], show that the decrease in the glow after the cessation of the bombardment is exponential, does not depend on the wavelength of the investigated radiation and on the energy of the bombarding ions (H_2^+, Ne^+, Ar^+, and a few others). At the same time, it turned out to depend on the nature of the ions, being smaller for light particles than for heavier ones.

A direct determination of the number of excited electrons from luminescence data is possible, but calls for knowledge of the probabilities of the radiative transitions. It is therefore simpler to attempt to obtain information on the number of excited electrons by comparing iono- and cathodoluminescence [179]. If the ions lose their energy essentially by elastic collisions with the lattice particles, then the number of electrons excited in the luminor by the ions is expected to differ greatly from the number excited by electrons of the same energy.

Experiments have shown that luminor brightness produced by ion bombardment is lower than that produced by electron bombardment Table V lists information on the ratio B of the brightnesses of iono- and cathodoluminescence under identical excitation conditions (particle energy, current density [169], for $E_0 = 6$ keV). These observations are evidence that the energy lost by the ion to electron excitation is quite large. As a rule, the difference in the transfer of energy to excitation of the electrons of the solid by primary ions and electrons does not exceed 0.01, and is close to 0.1 for light ions.* This is also indicated by estimates of the energy yield [164], which show that the energy carried away in the form of light when a phosphor is bombarded by H_2^+ ions reaches several times 10% of the energy of the bombarding ions (in the experiments of [164], $E_0 = 20$—30 keV).

Thus, in spite of the fact that ionoluminescence has not been sufficiently studied, it can be concluded even now that the number of electrons excited in

*Ionoluminescence of MgO and Zn_2SiO_4:Mn was investigated recently in [193,194]. Information on iono- and cathodoluminescence of single-crystal SiC is given in [196].

*For SiC single crystals bombarded by electrons and hydrogen ions, this ratio is even larger, reaching 0.3 – 0.5.[196]

crystals such as luminors by ions of relatively low energy is quite appreciable, and is smaller only by a factor of several times ten than the number of electrons excited under identical conditions in cathodoluminescence. There is no doubt that further study of ionoluminescence, and also a theoretical analysis of the obtained results, which has not yet been made (with the exception of a short paper [180] in which an attempt is made to explain the experimental data of [181]) will yield very important information for the understanding of the mechanism of excitation of electrons in a solid by relatively slow atomic particles.

VI. CONCLUSION

The entire assembly of the data under consideration shows convincingly that even when the energies of the bombarding atomic particles are lower than 1 keV, a considerable fraction of their kinetic energy is consumed as a rule in the excitation of the electrons of the solid. This is confirmed particularly clearly by experiments on radiative conductivity and ionoluminescence, described in Chapters IV and V. In particular, when germanium is bombarded with hydrogen ions with $E_0 = 1$ keV, approximately 600 electron-hole pairs are generated in it [141], i.e., the overwhelming part of the energy of the bombarding particles is transformed into electron-excitation energy, and does not go into formation of stable structural damage. It is characteristic, that the threshold energy for the excitation of electron-hole pairs is likewise very small: according to the available estimates [39], it is lower than 100 eV (in bombardment of germanium by potassium ions). In exactly the same way, experiments on ionoluminescence offer evidence of the large efficiency of transformation of energy of the bombarding particles into energy of electromagnetic radiation, which could hardly be possible without preliminary excitation of the electrons in the solid by some method. Although the absolute values of the coefficient of kinetic ion-electronic emission γ_k is in most cases not very large (γ_k does not exceed, as noted above, 10—20 electrons per bombarding particle), they nontheless offer also evidence that a considerable fraction of the energy of the primary particle is transferred to the electrons in the solid. Indeed, in order for the electrons to escape to the vacuum they must overcome the potential barrier at the boundary of the solid, so that the number of particles emerging to the vacuum will be definitely lower than the total number of excited electrons. This is experimentally confirmed [39]. If it is recognized that the electrons cannot emerge from a large depth because of the energy lost on the path to the surface, and that on the average half of the excited electrons move from the surface into the target, then the conclusion that the number of excited electrons is large is sufficiently plausible. It must also be noted that, as shown by experiments, the energy of the secondary electrons is in general not small, being of the order of several eV, and reaching 10—15 eV for some electrons [58,86].

The mechanisms whereby the electrons are excited in the solid when relatively slow atomic particles are decelerated are in general unknown. The general problem of the magnitude of the energy lost by the primary particles themselves has been discussed in a number of papers. The authors of these papers made use, as a rule, of experiments on the deceleration of atomic particles passing through thin films, and experiments on the study of the depth of penetration of particles into solids. Frequently, the total energy lost by the primary particle was subdivided into losses in elastic and inelastic collisions. However, apart from the fact that this terminology itself is in our opinion inappropriate when applied to interactions between atomic particles and a solid, being ambiguous, such a delineation based on such experiments is in general quite difficult, especially for the ion-energy interval under consideration.

At the present time it is hardly possible to gain from such experiments reliable information on the fraction of the energy transferred to the electrons, and all the more on the mechanism of the electron excitation; these were therefore not considered in the present review.

Attempts to represent the concrete model of excitation of electrons upon collision between the primary particles and the solid were made only in explanations of the kinetic ejection of electrons [16,128,131,136]. As already noted, there are two approaches, in one of which one considers the excitation of bound electrons in short-range pair collisions of two particles, where an energy δE is transferred to the electrons by some mechanism, and in the other the phenomenon is attributed to the occurrence of plasma oscillations, without a discussion of the mechanism whereby these oscillations are generated.

However, taking into consideration the indicated processes, which undoubtedly can be responsible for a definite number of excited electrons, it is necessary at the same time to analyze also the possibility of electron excitation not only by the primary particle itself, but by those structural changes which it is capable of producing, including by the recoil "atoms." The idea of the role of the recoil atoms in ion-electronic emission was advanced earlier, for example in [105,123] (the "relay mechanism"), but no serious analysis of this hypothesis was made. An attempt was also made to take into account electron excitation by recoil atoms in [149].

From our point of view, an account of the influence of the dynamic effects in the lattice on the excitation of the electrons in a solid is indispensible, especially to explain the appearance of rather slow electrons (for example, those responsible for radiative con-

ductivity and ionoluminescence). Recent investigations have shown that the depth of penetration of particles in a solid, cathode sputtering, ion-ionic emission, etc. are strongly influenced by the ordering of the particles in the crystal lattice (see the reviews published in UFN [92,93,182]. A number of experiments described in Chapters III and IV offer evidence that the laws governing the excitation of electrons in single crystals recall those laws which are characteristic of the phenomena listed above, particularly, the observed nonmonotonic angular distributions, etc. This raises the question of a thorough analysis of the possibilities of electron excitation in a solid, connected with the ordered motion in the solid of both recoil "atoms" and the primary particle itself.[195]

In the case of "focused" momentum transfer from atom to atom (as also in the case of disordered collisions), the degree to which individual particles of the crystal come close together can be quite appreciable, since their energies greatly exceed the average energy of the thermal vibrations. However, the ordering of the motion can greatly increase the total time that the atomic particles remain in the closest-approach state. Indeed, in the case of central elastic collisions in an isolated infinite chain of identical atoms, the time that the system stays in the state of closest approach of the neighboring particles, as well as the time of any other state, is infinitely large. But an increase in the time of strong interpenetration should undoubtedly lead to an increased role of inelastic processes, and consequently, to an increase in the number of excited electrons compared with the case of disordered collisions of the particles. It is known that even a static increase of the pressure is capable of noticeably changing the energy structure of the solid. On the other hand, when the ion moves in a crystal, there should occur for short instants of time tremendous local pressures capable seemingly to affect the energy structure of a limited region of the crystal and to ensure excitation of a part of the electrons to higher energy states.

In addition, one cannot exclude the possibility that ordered motion of the primary particles themselves in a crystal along a "channel" is capable of producing collective ordered motions of atomic particles of arrays in the "channel," and also of electrons, i.e., to the possible formation of plasmons. In this connection, we call attention to the fact that according to data on the radiative conductivity, the number of electrons excited in a crystal is maximal when the crystal is bombarded with ions in the direction of the maximum transparency. In this case, the total number of collisions with the crystal atoms and the degree of ordering of the collisions are maximal, which, from the point of view indicated above, should actually ensure a maximum number of excited electrons. At the same time, when the primary particle motion is of this character (motion along a "channel") it does not experience frontal collisions inside the solid, and the number of electrons produced by such collisions should be small. Experiments show that in such conditions one observes a minimum ion-electronic emission.

This raises therefore the question whether the electrons producing the radiative conductivity and the ionoluminescence are indeed produced by the same mechanism as the electrons which escape to the vacuum in ion-electronic emission. The latest experimental data [39] indicate that radiative conductivity appears in germanium at much lower bombarding-ion energies than the threshold energy E_0' for ion-electronic emission. This is explained by the fact that to excite a valence electron in the conduction band of germanium it is sufficient to impart to this electron energy of only 0.66 eV, whereas to excite it in vacuum approximately 4.7 eV are required. One can assume that such a large difference in the values of the energy necessary to effect each of these processes causes also a difference in the methods of electron excitation. Ordered motion of the lattice particles and of the ions along channels leads to an effective excitation of a large number of slow electrons, whose threshold excitation energy is small and depends on the properties of the crystal. Fast electrons, on the other hand, are produced by a different mechanism, which requires a sufficiently close approach of the interacting atomic particles.

One must also bear in mind that the energy imparted to the electrons of the solid is stored in the solid and should be released in due course via the Auger effect and via electronic transitions accompanied by phonon emission. Therefore, a certain contribution to the appearance of slow electrons in the conduction band can be made also by processes of dissipation of the energy stored in the solid during the time of formation of the "primary" excited electrons, processes in general analogous to those considered earlier in Ch. II.

It is still impossible to draw any final conclusions concerning the role of various ways of exciting electrons in a solid bombarded by atomic particles, since there are not enough experimental data or theoretical papers dealing with electronic processes in a dynamically perturbed crystal lattice. One might think that a detailed analysis of the electronic processes in a crystal lattice that assumes a nonstationary state as a result of penetration of a bombarding particle (with allowance for the ordered arrangement of the atoms in the crystal and the influence of this order on the motion of the particle) would not only explain the mechanism of excitation of electrons in ion bombardment, but also yield information necessary for the solution of many more general problems in solid-state physics.

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