Theory of electron characteristic-energy-loss spectroscopy

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The energy distribution of intermediate-energy electrons (0.1–100 keV) reflected from a solid surface is analyzed. Account is taken of both elastic scattering and energy losses by various mechanisms: interaction with optical phonons, ionization of core and valence electrons in electron-electron collisions, the screened interaction with conduction electrons, and the loss due to the excitation of plasmons. The angular and energy characteristics of the scattering cross sections are taken into account in solving the kinetic equation for the electron flux density in a medium. The calculated results agree well with the available experimental data on the inelastic reflection of intermediate-energy electrons from amorphous and polycrystalline solids.

1. INTRODUCTION

The scattering of electrons by a solid surface is known to be accompanied by inelastic processes, which reduce (by virtue of the small electron mass) to quasielastic electron-phonon scattering and essentially inelastic electron-electron (e–e) scattering. When a monoenergetic electron beam strikes a surface, the electrons which are scattered into the rear hemisphere are distributed in energy over the entire range from zero to the energy of the primary electrons, E_p. The energy and angular spectra of the electrons which are reflected and of those which have passed through the sample contain information on the properties of the solid and can be interpreted in terms of elementary electronic and vibrational excitations in the interior and at the surface.

The inelastic-reflection problem is analogous to the problem of finding the albedo in the radiation transport problem (for brevity, we will call this problem a "generalized albedo problem"). It does not have any small parameters in the sense that an ordinary perturbation theory would, so we need to seek an exact solution for a specific model of the interaction of the electrons with the material. The only way to find an exact solution is to take a simplified approach. In addition, the reflection coefficient is a dimensionless quantity, so it is not clear at the outset which of the many dimensionless combinations of the parameters of the problem will determine the magnitude of this coefficient. In the present paper we propose an effective new method for calculating the characteristic energy loss of electrons upon reflection. The basic idea here is to find an analytic solution of the generalized albedo problem, incorporating several mechanisms for the energy relaxation of the electrons, and then sum the series for the reflected flux coming away from the surface. We determine the fine structure of the energy spectrum of reflected electrons in the interval of energy transfers not exceeding 50–70 eV. Following Landau,[1] we introduce a small parameter—the ratio of the energy lost on reflection to the energy of the primary electron—in the problem of the characteristic energy loss at intermediate beam energies. By taking this approach, we can find an analytic solution. As we will see below, this solution is an expansion of the exact solution in the small parameter.

The characteristic energy loss is usually interpreted in terms of a loss function, which is defined as $\mathrm{Im}(-1/\varkappa)$ for the volume loss and as $\mathrm{Im}(-1/(\varkappa+1))$ for the surface loss in a dielectric formalism.[2] Here $\varkappa$ is the longitudinal dielectric constant of the medium. That approach, however, ignores the dynamic nature of the characteristic energy loss, which stems from the scattering involving various mechanisms, including mechanisms which are unrelated to the excitation of the electronic subsystem of the solid. To describe the inelastic reflection of electrons as the result of a multiple scattering, the most natural approach is to use a kinetic equation. The problem of solving a kinetic equation of this sort has arisen, in particular, in connection with the description of radiation transport processes,[3,4] electron mobility,[5] photoelectron spectroscopy,[6–8] and Auger spectroscopy.[8–10] Those papers used approximate models, valid for the particular conditions considered, in order to circumvent the difficulties in solving the kinetic equation. A rigorous solution for the energy distribution of the electrons which have passed through a thin slab of material was first derived by Landau[1] for the case of a highly anisotropic small-angle ionizational scattering, under the assumption that the scattering cross sections do not depend on the electron energy. That result gives a good description of the scattering of high-energy electrons. When the solution of Ref. 1 is expanded in a series, the coefficients correspond to a Poisson distribution,[11] which is frequently used to describe the probability distribution of multiple plasmon losses.[2]

Tofterup[12] has attempted to combine Landau's formula for the ionization loss with linearly anisotropic elastic scattering, determined from an independent equation. Tilinin[13] derived an expression for the inelastic reflection coefficient for fast electrons, with $1\ \mathrm{keV} \ll E_p \ll 1\ \mathrm{GeV}$, incident normally on a solid surface. As in Ref. 1, the inelastic ionizational scattering was assumed to be highly anisotropic, and the change in the direction of the electrons was assumed to result from a large number of events of elastic scattering through large and small angles, since the total inelastic range in the medium was assumed in Ref. 13 to be significantly greater than the mean free path with respect to elastic collisions. At the intermediate energies with which we are concerned in the present paper, we need to allow for the possibility of scattering through large angles in both elastic and inelastic collisions. The Schwarzschild-Schuster approximation has been used to solve this problem in several papers.[10,14,15] In that approximation, each electron is put in one of two groups: one moving toward the surface and one moving into

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the medium. Comparison with the numerical results shows that the accuracy of that approximation is not high.

Our approach to the solution of the kinetic equation, in which the angular dependence of the elastic and inelastic cross sections is taken into account, is based on a generalization of the method of Refs. 3 and 4 for solving the albedo problem to the case of inelastic scattering. A generalization of this sort has been proposed in several papers (e.g., Refs. 13 and 16) for calculating the energy-loss spectra of electrons being reflected under conditions such that a leading role is played by the inelasticity which stems from ionizing collisions, and the spectra have no fine structure. In the present paper, in calculations on the fine structure of the characteristic-energy-loss spectra of intermediate-energy electrons which are being reflected from a surface, we consider several scattering mechanisms simultaneously: incoherent quasielastic scattering by impurities and lattice defects and also by acoustic phonons (for brevity, e–imp scattering), the interaction with optical phonons (e–ph), the ionization of core electrons and valence electrons (e–e_j), the screening of the interaction with conduction electrons, and the loss due to the excitation of plasmons. We study the approximation of isotropic scattering in detail. We show that this approximation of the actual scattering cross sections gives a good description of the characteristic-energy-loss spectra which are seen experimentally in cases in which one measures the differential (in energy) inelastic reflection coefficient, integrated over the angular distribution. The solution method proposed here has a clear physical interpretation and can be used to bring out the basic features of the inelastic reflection. In Sec. 2 we examine the parametrization of the basic ranges and the corresponding scattering form factors, which determine the form of the kinetic equation describing the relaxation of an electron flux in a medium and also the boundary condition for the reflection problem. In Sec. 3 we describe in detail the method for solving the kinetic equation through an expansion of the energy distribution of the outgoing electrons in form factors of the scattering components which are isotropic and anisotropic in terms of angular distribution. In Sec. 4 we compare the calculated results with experimental data from characteristic-energy-loss spectroscopy for metals in various groups in the periodic table.

2. KINETIC EQUATION FOR THE ELECTRON FLUX DENSITY

Let us consider the reflection of a monoenergetic electron beam which is incident on the plane surface of a bulk sample. For simplicity we assume that the medium is amorphous or polycrystalline, that no interference effects arise for the backscattered electrons, and that the potential drop at the solid-vacuum interface is small in comparison with E_p, so that we can ignore refraction and reflection of the electron waves at the interface. Since the wavelength and mean free path of an electron in the intermediate-energy range are respectively smaller than and greater than the interatomic distance, we will use a classical kinetic equation for the flux density to describe the reflection of the electrons.

The motion of an electron in a medium is accompanied by a relaxation of its energy and momentum. This is a random process. The change in the flux density over a unit length is determined by the reciprocal of the mean free path with respect to the given type of scattering; the interaction itself is characterized by a normalized distribution of the energy and momentum of the scattered electron. Let us take a look at the basic mechanisms for the scattering of electrons, which determine the reflection of the electrons (E is the energy of the electron, m and e are its mass and charge, and we are using a system of units with $\hbar = 1$).

1) According to the Pines formula,[17] the loss due to the excitation of plasma waves (e–pl) is characterized by the reciprocal length

$$l_{pl}^{-1} = \frac{e^2 m \omega_{pl}}{2E} \ln\left(\frac{E}{\omega_{pl}}\right), \tag{1}$$

where ω_{pl} is the energy of the plasmon. A scattering by collective excitations of the electron subsystem is known[18] to be accompanied by a small change in the quasimomentum of the electron with a large energy transfer. This conclusion has been verified experimentally.[19,20] In scattering by plasma waves, the quasimomentum of the electron thus remains essentially constant in terms of direction. The form factor of the plasma-loss line, F_{pl}, is approximately Gaussian[21] with a mean value ω_{pl} and a variance σ_{pl}.[2]

2) In the Born approximation the mean free path for the excitation of electrons of the conduction band of the metal (e–e_c) is[1,22]

$$l_c^{-1} = \pi e^4 n_c / \varepsilon_0 E, \tag{2}$$

where n_c is the density of conduction electrons, ε_0 is the screening constant, which is given by the expression $\varepsilon_0^2 = 16\pi^{-2} E_F$ Ry, assuming nearly free electrons, E_F is the Fermi energy, and Ry is the Rydberg. Nearly free electrons see a screened Coulomb potential; the cross section has a sharp maximum at small scattering angles. The probability density for the transfer of an energy ε in the case of the screened scattering, $F_c(\varepsilon) = \theta(\varepsilon)\varepsilon_0(\varepsilon + \varepsilon_0)^{-2}$, is normalized; $\theta(\varepsilon)$ is the unit step function.

3) During the ionization of core electrons and valence electrons (e–e_j), the mean free path is calculated in the Born approximation from an expression similar to (2) (Ref. 22), specifically,

$$l_j^{-1} = \pi e^4 n_j (E - I_j)/I_j E^2. \tag{3}$$

Here j is the index of the core level or of the valence band, for which i_j is the average ionization potential, and n_j is the density of electrons. The ionizational scattering of fast electrons ($E > 1$ MeV) in a solid approximates Coulomb scattering by an individual center; it may be modified only by screening in a many-electron system. At intermediate energies ($E = 0.1$–10 keV), however, this assertion breaks down: The electron is scattered by an effective short-range potential, since the excitation occurs not in free space but in the screened field of many atomic cores. A phenomenological analysis of the short-range non-Coulomb nature of the e–e scattering has been carried out by Kanaya and Kawakatsu[23] on the basis of some less than rigorous arguments. They showed that the decay index s of the corresponding interaction potential $V(r) = \alpha r^{-s}$ increases as the energy of the incident electron decreases. Some typical values of s are[23] $s \approx 1$ at $E > 1$ MeV (Coulomb scattering), with a monotonic increase to $s \approx 2$ as E decreases to 0.8 keV. In the e–e interaction we have singled out the part which corresponds to long-wave scattering—the interaction with collective excitations of the many-electron system (the excitation of plasmons)—so that the short-wave part of the interaction corresponds to

single-particle excitations. The ionization of d bands, in contrast with the screened scattering by electrons of the conduction band, is accompanied by isotropization of the electron quasimomentum distribution. This isotropization becomes more pronounced as the single-particle nature of the interaction becomes manifested more strongly, i.e., as the ionization potential increases.

The form factor of the ionizational-scattering line is described in the atomic limit by

$$w_j(\varepsilon)=I_j^{1/s}/(s\varepsilon^{1+1/s}), \quad \varepsilon>I_j. \tag{4}$$

The use of the atomic limit for discussing the core levels is justified since the width of core-electron level B_j is small in comparison with I_j. In an examination of the excitation of valence electrons we should allow for the circumstance that the normalized state density of these electrons, $\nu_j(E)$, is not of an atomic nature. In this case, an additional convolution arises in (4):

$$w_j(\varepsilon)=(s\varepsilon^{1+1/s})^{-1}\int \nu_j(E)\theta(\varepsilon-E)E^{1/s}\,dE. \tag{5}$$

4) The reciprocal mean free path with respect to incoherent quasielastic scattering by impurities and defects is found as the product of the density of scatterers and the total scattering cross section:

$$l_{imp}^{-1}=4\pi\mathcal{N}_{\text{eff}}|f|^2, \tag{6}$$

where $\mathcal{N}_{\text{eff}}$ is the effective density of scatterers, and f is the scattering amplitude. At intermediate energies the electrons are scattered primarily in the forward direction, so that the mean square scattering angle is small: $\langle\theta^2\rangle\ll 1$. Quasielastic scattering is not accompanied by a change in the energy of the electron. For our purposes below it is convenient to introduce a transport length,[16] the distance over which the momentum of the electron isotropizes in the course of e–imp collisions.

5) The mean free path with respect to e–ph scattering (the polarization mechanism for scattering by optical phonons) is given by[24]

$$l_{ph}^{-1}=\frac{2\alpha\omega_{ph}}{v}\frac{\omega_{ph}}{E}\ln\left[\left(\frac{E}{\omega_{ph}}\right)^{1/2}+\left(\frac{E}{\omega_{ph}}-1\right)^{1/2}\right], \tag{7}$$

where α is the Frölich coupling constant, v is the electron velocity, and ω_{ph} is the energy of the dispersion-free optical phonons. Scattering accompanied by the emission or absorption of a phonon causes a pronounced isotropization of the electron quasimomentum distribution, since the maximum values of the electron and phonon quasimomenta are approximately the same. The e–ph scattering is scattering off a crystal lattice site, accompanied (because of the large mass of the atom) by a significant change in the electron quasimomentum at a small energy transfer. The form factor of the phonon line is approximated by a normal distribution $F_{\text{ph}}(\varepsilon)$ with a mean value ω_{ph} and a variance σ_{ph}^2.

At intermediate electron energies the inelastic scattering thus consists of an isotropic component and a highly anisotropic component in terms of the quasimomentum of the electron. Accordingly, if we put aside for a moment the fine structure of the angular dependence of the scattering cross sections, which is not always known, we can assume that in all cases except that of quasielastic scattering this dependence will be either isotropic or anisotropic in a δ-function sense. We take quasielastic scattering into account in the transport approximation.[16] The physical meaning of the mathematical procedure described below is quite simple. The coefficient of the inelastic reflection of electrons from the surface of a solid, integrated over angle, is determined primarily by the ratio of the probabilities for the scattering of the electrons into the forward and rear hemispheres. This ratio is unchanged when the anisotropic scattering cross section is replaced by an isotropic cross section, and the mean free path for the quasielastic interaction is simultaneously replaced by the transport range (i.e., when the interaction probabilities are renormalized). We will not be keeping track of either the number of interactions of electrons in the medium or the angular distribution of the outgoing electrons. We accordingly restrict the present study to the inelastic electron reflection coefficient as a function of energy, integrated over the angular distribution.

By virtue of the symmetry of the problem, the electron flux density in the medium, $N(\Delta, \Omega, z)$ only depends on the coordinate z, which runs normal to the surface, and the cosine μ of the angle between the quasimomentum vector ($\mathbf{\Omega}=\mathbf{k}/k$) of the electron, with $\mathbf{k}$, and the inward normal to the surface. We replace the instantaneous electron energy E by the energy loss $\Delta=E_p-E$ for convenience. In accordance with the arguments above regarding the scattering cross sections, we write the kinetic equation as follows in the isotropic approximation:

$$\mu\frac{\partial N(\Delta,\Omega,z)}{\partial z}=-\frac{N(\Delta,\Omega,z)}{l_t}+\int d\varepsilon\,[W(\Delta,\varepsilon)N(\Delta-\varepsilon,\Omega,z) +W_0(\Delta,\varepsilon)N_0(\Delta-\varepsilon,z)], \tag{8}$$

where l is the total reciprocal mean free path, equal to the sum of the mean free paths with respect to all types of interactions considered:

$$W(\Delta,\varepsilon)=l_e^{-1}F_e(\varepsilon)+l_{pl}^{-1}F_{pl}(\varepsilon-\omega_{pl}), \tag{9}$$

$$W_0(\Delta,\varepsilon)=l_{tr}^{-1}\delta(\varepsilon)+l_{ph}^{-1}[(N_{ph}+1)F_{ph}(\varepsilon-\omega_{ph}) +N_{ph}F_{ph}(\varepsilon+\omega_{ph})]+\sum_{j=1}^{M}l_j^{-1}w_j(\varepsilon) \tag{10}$$

are the rates of the collisions which are respectively anisotropic and isotropic in terms of angular distribution, per unit distance traversed by the electron; N_0 is the spherically symmetric part of the flux density; N_{ph} are the occupation numbers of the equilibrium phonons; and M is the total number of valence subbands which are taken into account. The right side of (8) is the ordinary collision integral, in which we have singled out the processes which are accompanied by a relaxation of the electron momentum. Problem (8)–(10) is a one-electron problem, since experiments on characteristic-energy-loss spectroscopy use low-intensity beams of primary electrons, and the scattering by the secondary electrons which are produced in the course of the ionizational and plasmon loss processes can be ignored. In the case in which a plane-parallel beam of monoenergetic electrons with an energy E_p is incident on the surface at an angle μ_p from the inward normal, the boundary condition for Eq. (8) is

$$N(\Delta,\Omega,z=0)=N_p\left[\theta(\mu)\delta^2(\Omega-\Omega_p)\delta(\Delta) +\theta(-\mu)\frac{\mu_p}{|\mu|}R(\Delta,\Omega)\right]. \tag{11}$$

Here $R(\Delta, \Omega)$ is the electron reflection coefficient, differential in terms of the energy transfer and the angular distribution. An explicit expression for this coefficient must be found in the course of solving the kinetic equation. Incorporating the loss due to the excitation of surface plasmons requires consideration of the coordinate dependence of the corresponding scattering probability. A way to avoid this difficulty while remaining within the scope of the problem (8)–(11) is pointed out in Sec. 3.

3. ENERGY SPECTRUM OF INELASTICALLY REFLECTED ELECTRONS

To derive the differential inelastic reflection coefficient we need to solve the kinetic equation (8) with the boundary condition (11). The mean free paths serving as the coefficients in (8) are functions of the energy; i.e., the kinetic equation is nonlinear. To linearize it, we expand the reciprocal mean free path in powers of the Landau parameter,[1] i.e., the ratio of the energy lost upon reflection, Δ, to the energy of the primary electron:

$$l^{-1}(E)=l^{-1}(E_p)+\sum_{n=1}^{\infty} a_n(\Delta/E_p)^n. \tag{12}$$

We retain the first term of this expansion. In the equation found by this procedure, the incoming term is in the form of a convolution integral, so that it is convenient to use integral Laplace transforms $\mathscr{L}$ for a solution. For the Laplace transform of the flux density, $\mathfrak{N}(p, \Omega, \xi)=\mathscr{L}\{N(\Delta, \Omega, z)\}$, we have the equation

$$\mu\frac{\partial\mathfrak{N}(p,\Omega,\xi)}{\partial\xi}=-\mathfrak{N}(p,\Omega,\xi)+\frac{c(p)}{2}\mathfrak{N}_0(p,\xi), \tag{13}$$

where the single-reflection albedo and the reduced penetration depth,

$$c(p)=l_tW_0(p)/[1-l_tW(p)],\quad \xi=z/l_t[1-l_tW(p)], \tag{14}$$

are expressed in terms of the Laplace transforms of the collision rates which are respectively anisotropic and isotropic in terms of angular distribution, (9) and (10). The boundary condition here is

$$\mathfrak{N}(p,\Omega,\xi=0)=N_p\left[\theta(\mu)\delta^2(\Omega-\Omega_p)+\theta(-\mu)\frac{\mu_p}{|\mu|}R(p,\Omega)\right]. \tag{15}$$

The solution of generalized albedo problem (13)–(15), where the function $c(p)$ plays the role of the single-scattering albedo, has been studied quite thoroughly (see, for example, Refs. 3, 4, 13, and 16). The solution can be written

$$R(p,\Omega)=\frac{c(p)}{4\pi}\frac{|\mu|}{|\mu|+\mu_p}H(|\mu|,c(p))H(\mu_p,c(p)). \tag{16}$$

Here $H(\mu, c)$ is Chandrasekhar's H-function.[3] Taking inverse Laplace transforms, we find the differential inelastic reflection coefficient

$$R(\Delta, \Omega)=\mathscr{L}^{-1}\{R(p, \Omega)\}, \tag{17}$$

which becomes, after integration over angles, the energy distribution of the reflected electrons:

$$R(\Delta)=\int d^2\Omega\, R(\Delta,\Omega)=\mathscr{L}^{-1}\{1-[1-c(p)]^{1/2}H(\mu_p,c(p))\}. \tag{18}$$

The kinetic equation (13) is a transport equation with a complex, isotropic scattering index. An equation of this sort also describes[13,16] the backscattering of high-energy electrons at angles of incidence close to normal. However, there are some important differences in the determination of the boundary condition (15) and the explicit form of the single-reflection albedo (14) [cf. Eqs. (2.49) and (2.50), respectively, in Ref. 16], since they determine the differences in the analytic structure of the solution in these two cases. Specifically, the solution derived in Refs. 13 and 16 is a generalization of Landau's formula[1] for the ionization loss on reflection, while in the case in which we are interested in the present paper an important role is also played by processes which are unrelated to ionization. For this reason, the method used in Refs. 13 and 16, can not be used here, and the solution in our case is the result of a nonadditive superposition of contributions from various mechanisms for the scattering of intermediate-energy electrons in the medium.

To find the explicit functional dependence $R(\Delta)$, we write the single-reflection albedo in the form $c=c_0+\bar{c}(p)$, where $c_0=l_t/l_{tr}$, and we expand (18) in a series in $\bar{c}(p)$ around the point $c=c_0$:

$$R(\Delta)=\mathscr{L}^{-1}\left\{1-(1-c_0)^{1/2}H(\mu_p,c_0)+(1-c_0)^{1/2}\sum_{k=1}^{\infty}Q_k\bar{c}^k(p)\right\}, \tag{19}$$

$$Q_k=-\frac{H^{(k)}(\mu_p,c_0)}{k!}+\sum_{m=1}^{k}\frac{(2m-3)!!}{(2-2c_0)^m m!}\frac{H^{(k-m)}(\mu_p,c_0)}{(k-m)!}. \tag{20}$$

Here $H^{(k)}(\mu, c)$ is the kth derivative of Chandrasekhar's H-function with respect to the variable c. To find it, we differentiated the integral equation[3] for the H-function k times and then solved the resulting recurrence chain of k nonlinear integral equations by iteration:

$$\frac{1}{H(\mu,c)}=1-\frac{c(p)\mu}{2}\int_0^1\frac{M(\mu',c)}{\mu+\mu'}d\mu',$$

$$H^{(1)}(\mu,c)=\frac{1}{c}[H^2(\mu,c)-H(\mu,c)]+\frac{c\mu}{2}\int_0^1\frac{H^2(\mu,c)H^{(1)}(\mu',c)}{\mu+\mu'}d\mu', \tag{21}$$

and so forth. The kth derivative is expressed in terms of all derivatives of order less than k. In terms of physical meaning (19) is an expansion in the number of inelastic interactions accompanied by isotropization of the electron momentum distribution. The convergence of this expansion is ensured by the choice of integration contour in the Mellin inversion formula. It is sufficient that the contour lie entirely in the half-plane $\mathrm{Re}\, p>0$.

The magnitude of the elastic reflection coefficient which will be measured depends on the experimental energy resolution. If the region of phonon loss [see (9) and (10)] can be identified precisely, the elastic contribution will be of the form $r\delta(\Delta)$, according to (19), where the following approximate expression holds for the elastic reflection coefficient r at $E_p \gtrsim 100$ eV ($c_0 \ll 1$):

$$r=1-(1-c_0)^{1/h}H(\mu_p, c_0)\approx\frac{1}{2}c_0[1-\mu_p\ln(1+\mu_p^{-1})]. \tag{22}$$

This expression correctly predicts the overall change in the elastic reflection coefficient of the electrons when μ_p changes. The mean square single-scattering angle is a power-law function of the electron energy: $\langle\theta^2\rangle\sim E^{-a}$, where $a=1.75$–2.25 ($a=2$ for diffraction scattering). The dependence of the overall mean free path is determined by inelastic scattering mechanisms, and we have $l_t\propto E^{-1}$. Hence

$$r\approx m' E_p^{-(0.75-1.25)}, \quad E_p\gg I, \omega_{pl}, \tag{23}$$

where E_p is expressed in electron volts, and $m'=3$–8. Expression (23) agrees well with the empirical dependence $r(E_p)$ (Ref. 25).

In the region of the characteristic energy loss which we discuss below, and which involves interband excitations and the excitation of plasmons, the quantity r is renormalized as a result of scattering by phonons, and it becomes a quasielastic reflection coefficient r_q:

$$r_q=1-(1-c_0^*)^{1/2}H(\mu_p, c_0^*)=r+\sum_{k=1}^{\infty}(1-c_0)^{1/2}Q_k c_0^k,$$

$$c_0^*=c_0+(2N_{ph}+1)l_t/l_{ph}. \tag{24}$$

The phonon broadening of the electron peak is usually smaller than the instrumental function of the electron gun and thus insignificant. For our purposes below it is convenient to carry out an expansion around the point $c=0$. In this case the coefficients in (20) become universal, depending only on the experimental geometry. The explicit form of (19) is found by successively applying the convolution theorem:

$$R(\Lambda)=r_q\delta(\Lambda)+\sum_{k=1}^{\infty}Q_k R_k(\Lambda), \tag{25}$$

$$R_k(\Lambda)=\sum_{\{k\}=0}^{k}\sum_{\{j\}=0}^{\infty}B(\{k\},\{j\})\prod_{(\cdot)}{}^{*}C_{j_{(\cdot)}}(F_{(\cdot)}|\Lambda)\times\prod_{i=1}^{M}{}^{*}C_{k_i}(w_i|\Lambda), \tag{26}$$

where $\{k\}$ means that the summation in (26) is over all M core bands and valence bands which interact k_i times with band i ($i=1, 2, \ldots, M$). Here we have $\Sigma_{i=0}^{M}k_i=k$, where k_0 is the multiplicity of the quasielastic scattering; $\{j\}$ corresponds to a summation over the multiplicities of the anisotropic scattering events of various types $j_{(\cdot)}$ (the subscript here, which runs over the values c, s, B, corresponds to scattering by electrons of the conduction band, by surface plasmons, and by bulk plasmons, respectively); the * denotes the convolution

$$\prod_{i=1}^{2}{}^{*}C_i(w_i|\Lambda)=\int C_1(w_1|\varepsilon)C_2(w_2|\Lambda-\varepsilon)\,d\varepsilon; \tag{27}$$

the functions $C_i(w|\Lambda)$ are multiple autoconvolutions,

$$C_1(w|\Lambda)=w(\Lambda), \quad C_k(w|\Lambda)=C_{k-1}(w|\Lambda)*w(\Lambda); \tag{28}$$

the coefficients B are given explicitly by

$$B(\{k\},\{j\})=\frac{(n+k)!}{\prod_{i=0}^{M}k_i!\prod_{(\cdot)}j_{(\cdot)}!}\prod_{i=0}^{M}\left(\frac{l_t}{l_i}\right)^{k_i}\prod_{(\cdot)}\left(\frac{l_t}{l_{(\cdot)}}\right)^{j_{(\cdot)}},$$

$$n=\sum_{(\cdot)}j_{(\cdot)}, \tag{29}$$

and $R_k(\Lambda)$ is the electron energy distribution after a sequence of k arbitrary scattering events isotropizing the electron quasimomentum and an arbitrary number of anisotropic scattering events. Consequently, according to (25)–(29), the solution procedure proposed here, incorporating any scattering mechanism, is constructed on the basis of universal units and rules for dealing with them: The form factors of loss lines enter as autoconvolutions (27), and the scattering cross sections fix the coefficients in (29). If the scattering is accompanied by conversion to a more nearly isotropic distribution of the electron quasimomentum, then the corresponding scattering cross section enters the group of ionization scattering events. If not, it enters the group of plasmon events [see (9), (10), and (14)]. Analysis of (25)–(29) in the particular case in which only ionizing collisions are taken into account shows that $R(\Lambda)$ falls off as Λ^{-2} in the asymptotic region where losses considerably exceed the ionization potential. This result agrees completely with Landau's result; the overall electron mean free path in the medium with respect to emission upon reflection is analogous to the film-thickness parameter in the theory of Ref. 1.

If we are to effectively allow for the coordinate dependence of the cross section for the scattering of an electron accompanied by the emission of a surface plasmon in the procedure proposed here, (25)–(29), we need to note that surface plasmons, in contrast with bulk plasmons, are excited in a surface region with a thickness on the order of a few interatomic distances [$\lambda_0=a_0(\mathrm{Ry}\,E_p)^{1/2}/\omega$, where a_0 is the first Bohr radius[26]], so multiple surface loops are generally suppressed. This suppression occurs unless we choose the experimental geometry in a special way (e.g., a grazing-incidence scattering of electrons[11,26]) in order to increase the total time spent by the electrons near the surface. The necessary changes involve the factors which appear in (29). In the first place, it is necessary to replace $(n+k)!$ by $(n+k-j_s)!$ and to simultaneously eliminate the factor j_s from the denominator of (29), since the ratio of the factorial factors is a generalized binomial coefficient and is related to a combinatorial effect: The total number $(n+k)$ of interactions can arise from a variety of permutations, and the factorial factors determine the number of such permutations which lead to a given electron energy distribution. Second, the replacement of the factor $(l_t/l_s)^{j_s}$ by $P_{j_s}(\lambda/l_s)\times\exp(-j_s l_s/l_{\mathrm{iso}})$ incorporates the change in the relation among the relative components of the scattering accompanied by the emission of a surface plasmon and those which isotropize the electron quasimomentum in the surface region. Here $P_k(x)$ is a Poisson distribution for the probability for the excitation of k surface plasmons; $\lambda=\lambda_0/\mu_p$ is the optical thickness of the corresponding surface layer, where the oblique incidence of the primary beam is taken into ac-

count; the factor $\exp(-L/l_{iso})$ describes the attenuation of the electron flux density as a result of all isotropizing interactions is (l_{iso} is the corresponding electron mean free path); and $L = j_s l_s$ is the distance traversed by an electron in the pertinent region.

4. COMPARISON WITH EXPERIMENTAL DATA; DISCUSSION OF RESULTS

In the preceding section we derived and studied in detail an analytic expression for the coefficient of inelastic electron reflection as a function of energy, integrated over the angular distribution. In the present section we compare the results of our calculations with experimental data from the literature (Figs. 1–5). Because of the arbitrary normalization of the data in the literature, we have scaled the calculated results to bring a single point of the calculated characteristic-energy-loss spectrum into coincidence with a single point of the experimental spectrum. Specifically, we chose the absolute maximum. In all cases, the measurements have used polycrystalline samples, so that diffraction effects were ignored in the calculations. The insets in Figs. 1–5 show the necessary data on the state densities $\nu_j(E)$ [see (5)] of the valence bands and on the ionization potentials. The core levels were assumed to be of an atomic nature, while the conduction band was assumed to be parabolic with an effective mass equal to the mass of a free electron. The parameters of the plasmon-loss form factors—the energies and widths of the lines of surface (ω_s) and bulk (ω_B) plasmons—are given in Ref. 2. The values of the phenomenological parameter s, which characterizes the potential of the e–e interaction, are $s \approx 2$ at $E_p < 800$ eV and $s \approx 3/2$ at 800 eV, $E_p < 2$ keV, according to Ref. 23.

It follows from Sec. 3 that in order to calculate the characteristic-energy-loss spectrum (25)–(29) we need to calculate the coefficients Q_k in (20) by solving a chain of coupled nonlinear integral equations (21) for the H-function and its derivatives. In practice, we calculated the derivatives up to ninth order inclusively, so no more than nine isotropizing scattering events could be taken into account in the reflected flux. The calculations show that the component attributable to scattering with a multiplicity greater than four is no higher than 5%. The accuracy of the calculations based on (21) was checked by finding how well the normalization conditions on the Chandrasekhar H-function[3] and its derivatives were satisfied.

a) Aluminum is frequently used as a test object in solid state theory, since it is a metal with nearly free electrons. The band structure of polycrystalline aluminum has been studied thoroughly.[27] Figure 1a shows energy spectra calculated in accordance with Sec. 3 of the present paper, along with experimental spectra.[28] At small values of Δ the behavior $R(\Delta)$ is determined by the screened e–e scattering. Between the third (partially filled) Brillouin zone and the vacant fourth zone there is a gap about 1.0 eV wide.[27] This gap is substantially smaller than the Fermi energy, so the excitation threshold does not give rise to an additional maximum in the spectrum, although the consideration of these features of the energy structure is important for determining the overall behavior $R(\Delta)$. In the experiments this gap has been noticeable only in the differential spectra.[29]

A common feature of the theoretical characteristic-energy-loss spectra which have been found (Figs. 1–5) is that they exhibit a fine structure which is more clearly expressed than that in the experimental spectra. One reason for the difference is the particular choice of boundary conditions on the transport equation. We derived a Green's function for the kinetic equation, while a solution for arbitrary boundary conditions would be a convolution of this Green's function with a source function. The half-width ΔE of the energy distribution of the primary electrons is usually 0.1–0.5% of E_p, and a convolution with a function with a fairly broad maximum will smooth out the small-scale structural features in the spectrum. Figure 1b demonstrates the behavior of the energy spectrum as ΔE changes. If the instrumental half-width is large, maxima separated by even several electron volts cannot be resolved.

The major maxima $R(\Delta)$ in aluminum are associated with plasmon losses. Comparing the energy spectra found at various energies E_p, Chiarello *et al.*[28] drew several conclusions about the behavior: 1) As E_p is varied, the relative

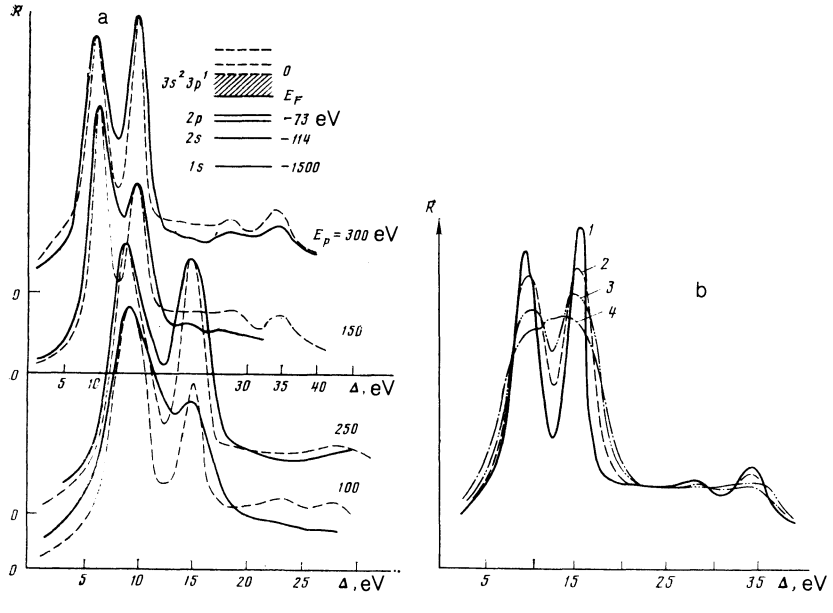

FIG. 1. Characteristic-energy-loss spectrum in the case of reflection from polycrystalline aluminum. a: Solid line—Experimental data of Ref. 28; dashed line—calculated from (25)–(29). The inset is the model of the band structure[27] which was used in the calculations. For clarity, the origins of the scales for the various E_p have been shifted. b: Effect of the half-widths of the distribution function of the primary electrons on the characteristic-energy-loss spectrum. Results calculated for $E_p = 300$ eV: 1) $\Delta E = 0$; 2) 0.5 eV; 3) 1.0 eV; 4) 2.0 eV. (In the insets in Figs. 1 and 3, E_F has been erroneously printed instead of $-E_F$.)

intensities of the bulk and surface plasmon losses change considerably. 2) The energies of the bulk and surface plasmon losses do not depend on E_p. 3) The plasmon maxima become significantly broader as E_p is reduced. Using the results of the present calculations, we can interpret those aspects of the characteristic-energy-loss spectra in the following way. First, a change in the relative intensity of the maxima corresponding to single-plasmon losses stems from the difference in the scales of the changes in the mean free paths with respect to the excitation of surface and bulk plasmon and also an increase in the electron emission depth with increasing E_p. Second, the anisotropy of the e–pl scattering means that the reflection of an electron which has emitted a plasmon can occur only after an additional scattering event, accompanied by isotropization of the electron quasimomentum—i.e., after a quasielastic or ionizational e–e scattering event. As a result of the combination of a loss due to the excitation of plasmons with scattering by electrons of the conduction band, the major maxima become asymmetric: $R(\Delta)$ at $\Delta > \omega_B$ falls off more slowly than at $\Delta < \omega_s$. The plasmon maxima themselves are broader than the intrinsic plasmon-loss width. The magnitude of this broadening is the weighted sum of two terms: a first term associated with the superposition of the lines of the screened e–e_c and e–pl scattering events and second term associated with the interference of these mechanisms. The weights are the probabilities of the corresponding processes. In the case $\sigma_{\text{pl}} \ll \omega_{\text{pl}}, \varepsilon_0$ we have

$$\sigma = \sigma_{pl} + (8\pi)^{1/2} \frac{\sigma_{pl}^2}{\varepsilon_0} \left[\frac{l_{pl}}{l_c} \frac{\varepsilon_0^2}{(\varepsilon_0 + \omega_{pl})^2} + \frac{l_t}{l_c} \right]. \qquad (30)$$

The broadening is accompanied by a shift of the maximum. Using the approximation $\sigma_{\text{pl}} \ll \varepsilon_0$ and the method of steepest descent, we find from (26)

$$\omega = \omega_{pl} + (8\pi)^{1/2} \frac{\varepsilon_0 \sigma_{pl}^2}{(\varepsilon_0 + \omega_{pl})^2} \frac{l_{pl}}{l_c} - \pi^{1/2} \frac{\sigma_{pl}^3}{2\varepsilon_0^2} \frac{l_t}{l_c}. \qquad (31)$$

Here, in contrast with (30), the terms associated with the superposition and the interference of the e–e_c and e–pl scattering events have different signs and are small quantities of second order in the parameter $\sigma_{\text{pl}}/\varepsilon_0$. As a result, the shift is small: at $\sigma_{\text{pl}}/\varepsilon_0 = 0.05$ we have the estimate $|\omega - \omega_{\text{pl}}| < 0.05\,\omega_{\text{pl}}$. According to (30), the dependence of σ on E_p stems from the energy dependence of the mean free path. Under the conditions $E_p \gg \omega_{\text{pl}}, \varepsilon_0$, this dependence is only slightly nonlinear; the ratios l_t/l_c and l_{pl}/l_c and also σ become independent of E_p, as is observed experimentally. The situation changes at $E_p \sim \omega_{\text{pl}}$. From (5)–(7) we find that the ratio l_c/l_{pl} is on the order of $\ln(E_p/\omega_{\text{pl}})$ and decreases with decreasing E_p. The broadening of the plasmon-loss lines is thus due to the participation of nonplasmon loss mechanisms in the formation of the plasmon maxima.

b) We carried out calculations on the inelastic reflection of electrons for metals with d-electrons for the particular cases of Cu (Fig. 2) and α-Fe (Fig. 3). Experiments carried out to measure the de Haas-van Alphen effect have shown that the Fermi surface of these metals is approximately a free-electron sphere, but there is a system of d bands below it. In the case of copper, a d band lies 1.5 eV below E_F, while in the case of α-Fe it lies 0.5 eV below E_F. The d states introduce additional features in the inelastic reflection of electrons. The ionization potential for an interband transition from the d band to unfilled states in the connection band has a width on the order of the band itself, so that the maxima caused in the characteristic-energy-loss spectra by the internal structure of the condition band are very rounded. We know that d-band states are highly localized. Since the excitation of electrons is determined by the overlap of wave functions, in expression (3) for the mean free path we need to consider a geometric correction factor $\gamma \approx (a_d/a_0)^3$, where a_d is the localization radius of the d electrons, $a_0 \approx 3a_d$ and $\gamma \approx 0.04$. At these parameter values we find a satisfactory agreement of the experimental and theoretical results.

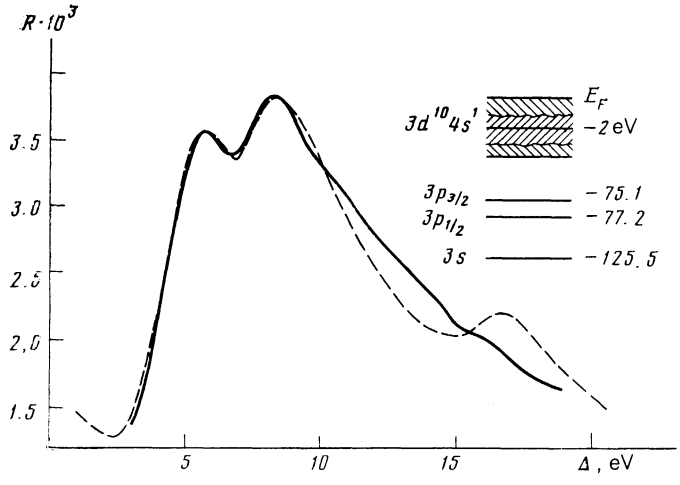

FIG. 2. Characteristic-energy-loss spectrum in the case of reflection from the surface of polycrystalline copper ($E_p = 75$ eV). Solid line—Experimental data of Ref. 30; dashed line—calculated from (25)–(29). The inset shows the band structure of Cu according to Ref. 31.

To show how the electron characteristic-energy-loss spectrum is built up from the form factors for single scattering events— while not being a simple superposition of these form factors—we show in Fig. 4 some model energy spectra found for cases in which one of the scattering mechanisms (e–e or e–pl) is "turned off": The corresponding scattering

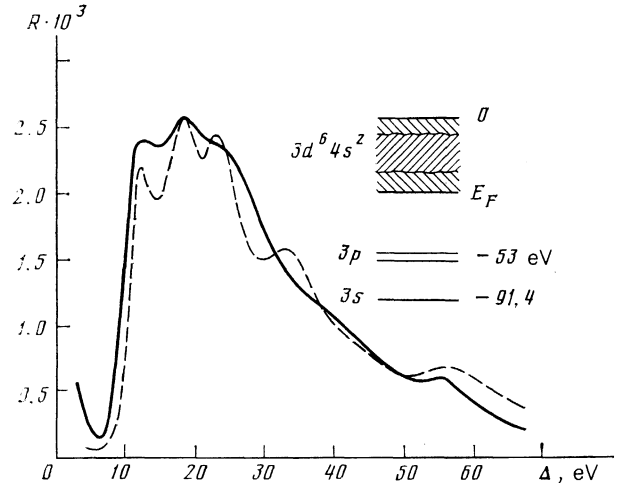

FIG. 3. Characteristic-energy-loss spectrum in the case of reflection from the surface of α-Fe ($E_p = 200$ eV). Solid line—experimental data of Ref. 32; dashed line—calculated from (25)–(29). The inset shows the band structure according to Ref. 33.

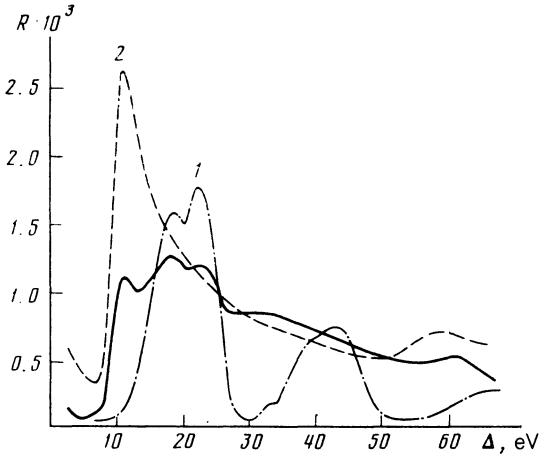

FIG. 4. Analysis of the components of the overall characteristic-energy-loss spectrum of α-Fe ($E_p = 200$ eV) attributable to various inelastic-scattering mechanisms. 1, 2—the e–e and e–pl scattering mechanisms are turned off.

mechanism is eliminated by taking the limit of an infinite characteristic energy transfer in the interaction.

In the case of Cu (Fig. 2), the characteristic-energy-loss spectrum has two major maxima. The first, at $\Delta \approx 8$ eV, results from the excitation of bulk plasmons. The second, at $\Delta \approx 5$ eV, forms as the result of a superposition of a surface-plasmon loss and the excitation of d electrons (the center of gravity of the d band lies at a depth of 4.5 eV below the Fermi surface). The rounded maximum at $\Delta \approx 18$ eV is attributed to a double-scattering plasmon loss. By making a comparison with the model calculations we can determine the origin of these maxima. As a result of the composite e–e and e–pl scattering, the maximum of the double-scattering plasmon loss, Δ^*, shifts toward larger values of Δ ($\Delta^* > 2\omega_B$).

In the characteristic-energy-loss spectrum for α-Fe (Fig. 3) we see three maxima $\Delta \sim \omega_{\text{pl}}$, two of which are associated with losses due to the excitation of surface and bulk plasma waves, while the third, and lowest-energy, maximum is due to the ionization of d states. The random coincidence of ω_s and the center of gravity of the d band which occurs in Cu does not occur in this case, and all three of the maxima are well resolved. The peak at $\Delta \approx 55$ eV represents the loss due to the ionization of the $3p$ core state. The overall behavior of the inelastic electron reflection spectra is also determined by the scattering by electrons of the conduction band, and all the comments which we made regarding aluminum continue to hold here.

c) The picture of electron states for rare earth elements is rather complicated. Although the conduction band is usually close to a band of nearly free electrons, the presence of d and f shells causes the number of possible interband transitions to be large, and the characteristic-energy-loss spectra of the rare earth elements have a complex structure. Figure 5 shows experimental[34] characteristic-energy-loss spectra for erbium, along with spectra calculated from (25)–(29). The major maximum at $\Delta \approx 13.5$ eV is due to a loss when a bulk plasmon is excited. The maximum of the double-scattering bulk-plasmon loss is also well defined. The structure at $\Delta < 10$ eV forms as a result of transitions from an s–p–d hybrid band to vacant states in the f band (the maximum at $\Delta \approx 5$ eV). The rounded maximum at $\Delta \approx 12$ eV is due to the same transitions, but in this case double transitions. The last maximum is poorly expressed because of both the line broadening caused by the increase in the multiplicity of the scattering and the superposition of a bulk plasmon on the steep slope of the maximum. The poorly expressed maximum at $\Delta \approx 18$ eV is the result of a composite scattering process: an interband transition from the s–p–d band and a loss due to the excitation of a bulk plasmon. The transitions from the $3d$ band form a peak at $\Delta \approx 40$ eV. The characteristic-energy-loss spectrum is also determined by processes of higher multiplicity: Their probabilities are considerably smaller than the probabilities for a single-event loss, and the linewidths are greater, so that such transitions can be seen only in the differential spectra.

5. CONCLUSION

We have examined the characteristic energy loss of intermediate-energy electrons reflected from solid surfaces. We have developed a new method for solving the kinetic equation which, along with the boundary conditions, describes the inelastic reflection. Using it, we have carried out the first theoretical study of the fine structure which appears

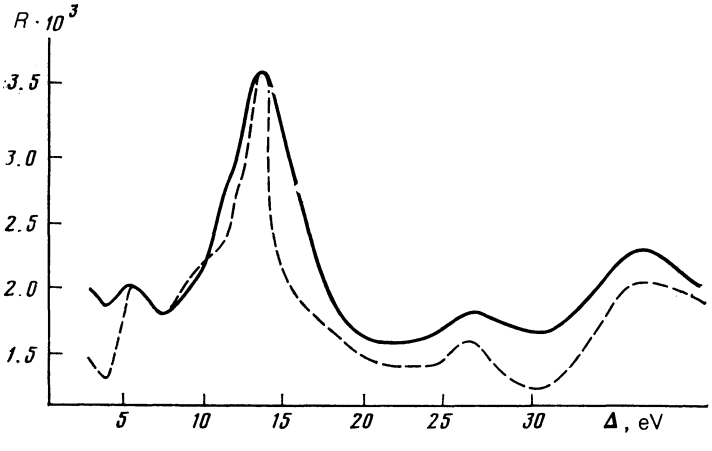

FIG. 5. Characteristic-energy-loss spectrum for the case of reflection from the surface of Er ($E_p = 1$ keV). Solid line—experimental data of Ref. 34; dashed line—theoretical predictions of the present paper.

in the characteristic-energy-loss spectra because of the various mechanisms by which the electrons interact with a solid. We have derived an explicit expression for the flux density of the backscattered electrons in interactions with amorphous and polycrystalline targets. For the first time, we have taken into consideration not only the energy relaxation but also the momentum relaxation of the electron flux density. As a result, we have been able to distinguish the relative contributions of the various energy-loss mechanisms to the overall characteristic-energy-loss spectrum in the case of reflection. Since the solution which has been found is analytic, it becomes possible to explain several experimental aspects of inelastic reflection in a solid: (1) It has been found possible to unambiguously relate features of the fine structure in the characteristic-energy-loss spectra with characteristics of the elementary excitations of the solid. (2) It has been shown that the experimentally observed departure from equal spacing of the maxima representing multiple plasmon losses is a consequence of the angular dependence of the inelastic scattering cross sections. (3) Because of the dynamic nature of the reflection and the nontrivial mutual effects of the various energy-loss mechanisms, the overall characteristic-energy-loss spectrum is not a simple superposition of the contributions of these mechanisms. We have predicted some new effects, in particular, a dependence of the observed energy and width of a plasmon maximum on the experimental geometry.

It can be concluded from these results that the approach proposed here for describing the interaction of intermediate-energy electrons with solid surfaces can serve as the foundation for a characteristic-energy-loss spectroscopy.

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