Kinetic Emission of Electrons from Monocrystalline Targets*

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This paper develops a single-collision theory of the emission of electrons from a metal surface subjected to high-energy ion bombardment, which gives reasonable agreement with the data of Carlston, Magnuson, Mahadevan, and Harrison, in the 1 to 10-keV energy range. The model is based upon a Thomas-Fermi-Firsov energy-transfer calculation which has been modified to include an explicit dependence upon lattice orientation. Orientation effects appear naturally, and orientation-dependent cross sections are not required, but the distribution of possible impact parameters for a particular crystal orientation is of central importance. The theory has been used to determine semiempirical interaction potentials between the moving particle and a lattice atom. These potentials are more similar to Abrahamson's atom-atom potentials than to the Gibson potentials used in radiation-damage studies.

A RECENT theoretical study of the kinetic secondary-emission process (KSE) in the 1 to 10-keV bombardment energy range by Parilis and Kishinevskii[1] (PK) exhibits rather close agreement with experimental data obtained from polycrystalline targets. This theory is not satisfactory when compared to monocrystalline-target data. We shall discuss an alternative model which is conceptually somewhat simpler, but which gives better agreement with the modern data.

The KSE process, the emission of electrons when a surface is bombarded by high-energy ions, operates by mechanisms which are completely different from those which occur in potential secondary-electron emission (PSE), the process discussed by Hagstrum.[2] For all of our ion-lattice pairs, except Ar^+-Mo, there is evidence that the KSE process does not operate below 1 keV. The lower limit is approximately 2 keV for Ar^+-Ag. Above this threshold the data can be represented as the sum of a PSE term and the KSE contribution studied in this investigation.

Much good evidence has developed in the last 25 years to indicate that electrons are liberated by the mutual interaction between high-energy incident particles and the atoms of the lattice.[1,3–6] Our model supports a description based upon a collision between atoms, rather than an interaction between the incoming ion and the conduction electrons or with the lattice as a whole.

I. THE BASIC INTERACTION

Consider a collision between an ion or atom with energy in the low-keV range and a target atom which we shall shortly assume to be embedded in a crystal lattice. In our theory, the final number of electrons emitted from the target is sufficiently sensitive to the atomic ionization energy that we can be quite certain that the "ion" arrives at the surface in a neutral atomic state. This neutralization, from the electronic bands of the solid, is a familar process in the lower energy region where PSE is the dominant process. In our energy range the ion velocities are still sufficiently low that there is time for neutralization to occur. For convenience we shall continue to refer to the incoming particle as the "ion" and the target as the "atom."

As a result of the collision, part of the ion's kinetic energy is transferred to the atom's nucleus, which recoils. In addition, part of the ion's kinetic energy is transferred to electronic motion, because the mutual interaction between the two electronic systems forces the electrons of both ion and atom into excited states. As the colliding systems separate, some of the perturbed excited states correspond to continuum energy levels of the individual atoms, and electrons are liberated. To avoid the problems of determining the energy partition between ion and atom our results are reported on the assumption that all of the emitted electrons come from the ion. This is an oversimplification which may have to be removed when other ion-atom pairs are considered. The conduction-band electrons of the target atom are no longer associated with individual lattice atoms, and do not enter this process.

The resulting high-ionic states are unstable in the presence of the lattice's conduction-band electrons and will decay rapidly by electron capture, almost certainly by an Auger process as described by Harrower.[7] The

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[1] E. S. Parilis and L. M. Kishinevskii, Fiz. Tverd. Tela. **3**, 1219 (1960) [English transl.: Soviet Phys.—Solid State **3**, 885 (1961)]; hereafter designated by PK.

[2] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

[3] N. D. Morgolis, Zh. Eksperim. i Teor. Fiz. **9**, 1484 (1939).

[4] W. Ploch, Z. Physik **130**, 174 (1951).

[5] O. Roos, Z. Physik **147**, 210 (1957).

[6] N. N. Petrov, Fiz. Tverd. Tela **2**, 1300 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1182 (1960)].

[7] G. A. Harrower, Phys. Rev. **102**, 340 (1956).

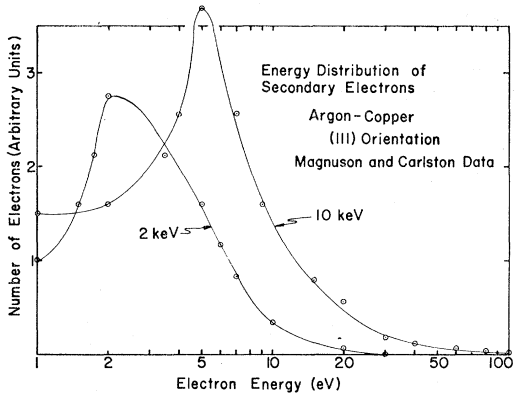

FIG. 1. Two experimental electron distributions for the electrons produced when argon bombards copper. The functions are not normalized. Note that energies greater than 20 eV are present in the 2-keV curve. The upper limit of the 10-keV bombardment curve is ~140 eV.

Auger process requires a time of the order of 10^{-14} sec, while the collision mean-free time is of the order of 5×10^{-14} sec for this energy range. If the ion returned completely to the neutral state before the next collision, the effective result would be a doubling of the number of electrons occupying high-energy states as a result of the collision process. Indirect evidence suggests that complete neutralization does not occur before the next collision. We shall consider this point in greater detail later. Some fraction of these high-energy electrons have sufficient energy to return to the target surface and appear as KSE electrons. Wolff[8] has made a detailed study of the cascade process for such electrons. In this connection, the energy distribution of KSE electrons is important. Figure 1 shows such a distribution for two bombardment energies. These curves were obtained by graphical differentiation of stopping potential curves between the electron collector and target. One-volt intervals were used for the parent curves in the sensitive region. We see that the most probable KSE electron energy is between 2 and 5 eV, but that the maximum may exceed 140 eV for a 10-keV bombardment energy. The PK theory produces only low-energy-KSE electrons; so these data are a major point in support of our model, which predicts that high energies are possible.

II. THE THEORETICAL MODEL

The PK theory assumes that electrons are liberated along the ion's path in the solid, and that these electrons have an exponentially decreasing probability of returning to the surface. This model requires assumptions about the energy dependence of the ion-atom cross section and the distribution of possible ion paths or vector ranges. The returning electrons also must suffer collision, which tend to reduce their energies. The energy available is not sufficient to support this degradation process and still produce KSE electron energies exeeeding 100 eV.[8]

On the basis of the additional information now available we are led to propose a single-collision model of the KSE process. Suppose we write

$$\gamma_{\mathrm{KSE}}{}^{(hkl)}(E_0)=K\int_0^{s_{\mathrm{MAX}}{}^{(hkl)}} n_e(s,E_{\mathrm{TFF}})P^{(hkl)}(s)ds; \quad (1)$$

where γ_{KSE} is the number of electrons emitted per incident ion when the ions are normally incident upon the (hkl) surface, s is the impact parameter, E_{TFF} is the inelastic energy, $n_e{}^{(hkl)}(s,E_{\mathrm{TFF}})$ is the number of electrons which this energy will produce, and $P^{(hkl)}(s)$ is the probability that the impact parameter s will occur in the (hkl) surface. The upper limit of this integral in each case is determined by the orientation and type of lattice under consideration. These upper limits are listed in Table I.

TABLE I. This table lists the geometrical parameters required for various integrations. All quantities are expressed in terms of r_0, half the lattice nearest-neighbor separation.

Orientation	$r_A(r_0)$	$s_{\mathrm{MAX}}(r_0)$
	Face-centered cubic	
(111)	0.904	0.668
(100)	0.707	1.000
(110)	1.000	1.061
	Body-centered cubic	
(111)	1.000	1.123
(100)	0.577	1.155
(110)	0.816	1.000

Equation 1 contains three adjustable parameters, the coefficient K and two constants which determine the electron density $\varphi(\rho)$ and the interaction potential $V(r)$. The two constants must be the same for all possible orientations (hkl) of the target crystal. Three physical processes are buried in the constant K: (1) A geometrical electron-velocity orientation probability which determines whether a liberated electron will ultimately be emitted from the surface. Close to the surface we can reasonably set the average value of this probability to $\frac{1}{2}$. (2) A factor between 1 and 2 which accounts for the additional high-energy electrons created by the Auger process. If this factor were exactly two, it would cancel the preceding geometrical factor, but we shall see that the potential-function evidence suggests that it is actually closer to unity. (3) A probability that a high-energy electron which could escape actually does so before it is scattered into the conduction band. Any electron-avalanche effects would appear in this factor. Of the three factors, (1) and (2) are clearly independent of orientation, and we would expect that (3) depends more strongly upon electron-electron effects than upon the existence of atoms in the "Fermi sea." We have assumed that K is a constant factor, independent

[8] P. A. Wolff, Phys. Rev. **95**, 56 (1954).

of E_0 and orientation, and the results bear out our assumption.

The inelastic energy E_{TFF} transferred from the ion's motion to the electron system is clearly of central importance. Experimental data are not available for the systems we wish to examine; so we must resort to an approximate theoretical calculation. Unfortunately, this calculation of the inelastic energy is the weakest link in both the PK theory and the present model.

III. THE THOMAS-FERMI-FIRSOV ENERGY

Firsov[9] has made an approximate calculation of the energy transferred from nuclear motion to the electrons. The mutual interaction of electrons is described by a Thomas-Fermi (TF) electron distribution, while the collision dynamics are determined by an interatomic potential function, $V(r)$. In Firsov's original analysis this potential was derived from the TF screening function, and he assumed that the trajectory of the moving atom was a straight line. PK[1] retained the TF interaction potential, but generalized the interaction to include all orbits consistent with the interaction potential. This approach approximates the actual interaction if the electron screening function and the interaction potential are self-consistent.

Abrahamson, Hatcher, and Vineyard[10] have published more accurate electron-distribution functions for individual atoms, but their tables do not lend themselves to the computation of electron densities when two dissimilar atoms interact, because corrections for state-function distortion would require a complete recalculation at all separations. This was not undertaken because the interaction potentials which Abrahamson[11] has developed for some systems are not available for our particular heteronuclear pairs.

Because we expect to compare these calculations with the PK theory, and because TF calculations are so much simpler to perform, we have retained the TF screened electron distribution. We have added two additional refinements to the energy calculation, which we shall call the Thomas-Fermi-Firsov (TFF) energy. Recent work by Vineyard and co-workers,[12] Robinson and Oen,[13] Beeler and Besco,[14] and Gay and Harrison,[15] indicate that a simple Born-Mayer (repulsive exponential) potential function of the form $V_{\mathrm{BM}}(r) = \exp(A+Br)$, where B is always negative, is adequate for most high-energy collision dynamics in a lattice. For self-consistency in our calculations, we fit the potential function to the electron density at some appropriate separation. The additional freedom introduced in this way is required for good agreement between the theory and experiment. In our notation, PK found for the Firsov analysis that the TFF energy E_{TFF} could be expressed as

$$E_{\mathrm{TFF}}'(s,E_0)=K_{\mathrm{TFF}}\int_{r_{\mathrm{MIN}}}^{\infty}\frac{[1-V(r)/E_0]dr}{[1-V(r)/E_0-s^2/r^2]^{1/2}}\times\int_{r/2}^{\infty}\frac{\varphi^2(\rho)d\rho}{\rho}, \quad (2')$$

with

$$K_{\mathrm{TFF}}=h/(\pi a_H^2)[E_0/2m_1)^{1/2}[Z_1+Z_2]^2,$$

where s is the collision impact parameter, a_H is the Bohr radius, $a_H=h^2/me^2=0.529$ Å, E_0 is the ion energy in the center-of-mass system, Z_1 and Z_2 are the ion and atom nuclear charges, respectively, m_1 is the ion mass, r_{MIN} is the distance of closest approach, and $\varphi(\rho)$ is the TF screening function. We used the Sommerfeld approximation for the TF function

$$\varphi(\rho)=\langle[1+(a_F\rho)^{0.8034}]^{-3.734}\rangle,$$

where $a_F=\langle a_{\mathrm{TF}}[(Z_1+Z_2)/144]^{1/3}\rangle/0.8853$, and a_{TF} is an adjustable constant. All distances are measured in units of a_{H}. We examined this calculation as defined by PK and found that its results did not agree with experiment unless we generalized the interaction potential $V(r)$ to the Born-Mayer form. This was our first modification. The second was required because our model includes lattice effects. Let us refer to the integral $d\rho$ as the *electron integral*, and the integral dr as the *dynamical integral*. The lattice influences these integrals because the presence of other atoms sets an effective upper limit to each of these integrals. These upper limits never approach infinity. We write Eq. (2') as

$$E_{\mathrm{TFF}}(s,E_0)=K_{\mathrm{TFF}}\int_{r_{\mathrm{MIN}}}^{r_{\mathrm{MAX}}(s)}\frac{[1-V(r)/E_0]dr}{[1-V(r)/E_0-s^2/r^2]^{1/2}}\times\int_{r/2}^{r_{\mathrm{EM}}}\frac{\varphi^2(\rho)d\rho}{\rho}. \quad (2)$$

The r_{EM} limit is not significant because the integrand $\varphi^2(\rho)/\rho$ becomes quite small for separations greater than r_0, the equilibrium lattice separation; so the electron integral is not particularly sensitive to its upper limit. In this calculation we chose an upper limit r_{EM} somewhat larger than r_0, and approximately equal to the smallest r_{MAX} value. The same r_{EM} value was used for all orientations, and the results are insensitive to small variations of this value.

The upper limit of the dynamical integral, which we have practically divorced from the quantum-mechanical approximations, is much more sensitive. This limit r_{MAX} is completely determined by the lattice orientation, that

[9] O. B. Firsov, Zh. Eksperim. i Teor. Fiz. **36**, 1517 (1959) [English transl.: Soviet Physics—JETP **9**, 1076 (1959)].
[10] A. A. Abrahamson, R. D. Hatcher, and G. H. Vineyard, Phys. Rev. **121**, 159 (1961).
[11] A. A. Abrahamson, Phys. Rev. **123**, 538 (1961); **130**, 693 (1963); **133**, A990 (1964).
[12] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).
[13] M. T. Robinson and O. Oen, Phys. Rev. **132**, 2385 (1963), and earlier papers referenced there.
[14] J. Beeler and D. Besco, Phys. Rev. **134**, A530 (1964), and earlier papers referenced there.
[15] W. L. Gay and D. E. Harrison, Phys. Rev. **135**, A1780 (1964).

is, the collision under consideration must be terminated, because another is beginning. When we consider only the dynamical problem of collisions in lattices, the binary-collision approximation is known to introduce errors at large impact parameters.[15] In the course of the present investigation we examined both a straight binary-collision approximation, and a mixed approximation, where the dynamics were still controlled by the strongest binary collision, but a contribution from the weaker secondary collisions was included in the total electron production. The mixed approximation was completely useless, while the binary-collision model gives quite good agreement with the data. This is further evidence in support of the usual conclusion that KSE is a single-collision process between atoms or ions. In the binary-collision model we distinguish two cases: one in which only the "surface atom" of the lattice was considered in each orientation, and the other where all atoms in the first repeat distance of penetration were allowed to contribute, see Fig. 2. The theory derived from the first case was not satisfactory, while the second gave reasonable agreement with the data.

The integral limits are illustrated for the particular case of the (100) orientation of the face-centered cubic crystal in Fig. 3. The distance r_A is *not* the interplanar separation for all orientations of both fcc and bcc lattices. In the more open cases, it may be twice the interplanar separation. The value of r_A and the maximum impact parameter s_{MAX} are listed for each orientation in Table I. Note that r_{MAX} is a function of s as well as the orientation.

We can summarize these results as follows: The binary-collision approximation produces satisfactory results if we allow the lattice orientation to determine the upper limit of integration. This limit is determined as the vector combination of a multiple of the lattice-plane separation appropriate for the particular orientation and s, the impact parameter. The final results are extremely sensitive to the choice of parameters which set the dynamical integral limits. The parameters of the calculation which depend upon the lattice; the $s_{MAX}(hkl)$, the $r_A(hkl)$, and r_{EM}; are all expressed in terms of r_0, which is half the nearest-neighbor distance in the lattice; so this part of the calculation is adjusted for a different target material when the single parameter r_0 is modified. The r_0 values and other numbers are listed in Table II.

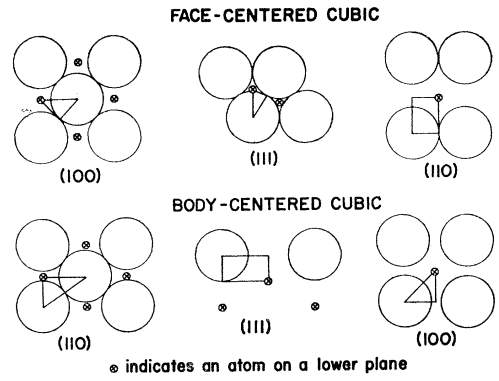

FIG. 2. The representative areas for the lattices and orientations required in these calculations.

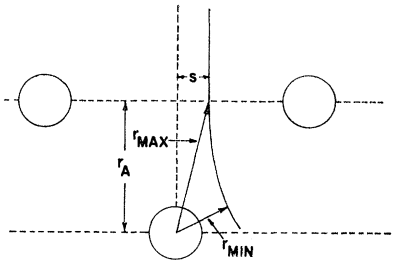

FIG. 3. The geometrical parameters are required in a single integration.

TABLE II. This table lists various lattice parameters characteristic of the individual target materials, and the *calculated* parameters of a Born-Mayer potential function for *argon and the indicated material*. The potential function may be written as either $V(r)=\exp(A+Br)$, or as $V(r)=E_A\exp(Br)$.

Target	$LU(a_H)$	$r_0(a_H)$	A	B(Å^{-1})	E_A(keV)	γ_{PSE}
			Face-centered cubic			
Copper	3.417	2.415	11.435	−4.202	92.7	0.085
Nickel	3.326	2.344	11.319	−3.878	81.7	0.090
Silver	3.856	2.722	10.858	−2.329	52.0	0.100
			Body-centered cubic			
Molybdenum	2.967	2.570	12.393	−3.713	241.0	0.040

This extreme sensitivity to the dynamical integral limits was totally unexpected. Because the Firsov calculation is based upon very approximate wave functions, we began with reasonable average impact parameters as upper limits. We then tried various limits somewhat greater than r_0. The results were uniformly unsatisfactory. We obtained reasonable agreement between theory and experiment only when we used limits appropriate for a particular orientation. Apparently the physical system will tolerate some approximations in the electron density, which is averaged during each trajectory, but insists that the dynamical limits, which are unique for each trajectory, be accurately, specified. Russek[16] has recently considered the TFF-energy problem in some detail. In particular, he has analyzed Morgan and Everhart's data,[17] which were obtained from gas-phase scattering experiments. He suspects, from a semiclassical argument, that angular-momentum effects, which Firsov completely neglects, must be

[16] A. Russek, Phys. Rev. **132**, 246 (1963), and earlier papers referenced there.

[17] G. H. Morgan and E. Everhart, Phys. Rev. **128**, 1667 (1962).

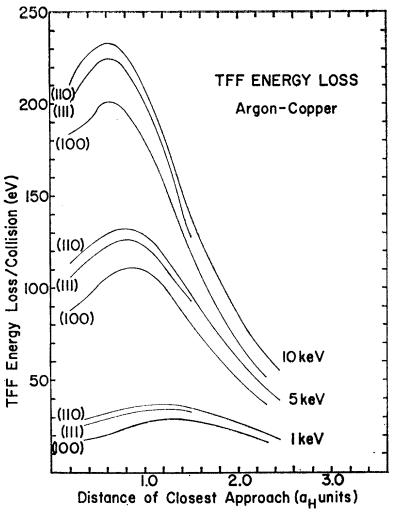

FIG. 4. The calculated TFF energy loss is shown for various energies in the argon-copper system, as a function of the distance of closest approach. The energy-dependent values of r_{MIN} are obtained with zero impact parameter. The upper limits are established by the appropriate value of s_{MAX}.

influencing the experimental results. His analysis concluded that the angular momentum inherent in the relative motion with impact parameter s should be the ultimate determinant of the energy transferred. The quantization of this angular momentum set limits upon the allowable excited states of the ion-atom compound system, which must ultimately determine the number of electrons liberated. Schwartz and Borowitz[18] have made a beginning in the direction of this calculation with a Thomas-Fermi model which includes angular momentum. However, a complete calculation of a two-atom system in this model would be a research program in itself.

If Russek's intuitively appealing analysis is correct for binary systems, and the modified TFF calculation appears to work quite well in the crystalline environment, we are led to suggest that the calculations are in some way fundamentally different in the two situations. This would not be the first time that the lattice has introduced unexpected changes in an apparently straightforward calculation. Perhaps the modified TFF calculation is actually much more realistic than we would have any reason to expect. We can only report that our calculations, which are sensitive to the limits, appear to give reasonable agreement with experiments. A less sophisticated model, which used average limits, failed. Our results are shown in Fig. 4.

IV. IMPACT-PARAMETER PROBABILITY DENSITIES

The lattice also influences the calculation in another way. We have seen that the impact parameter s together with the characteristic number r_A determines the required integral limits. The lattice also influences the distribution of all possible values of s. When no lattice is present, the probability that s lies in ds at s (that is, that s occurs between s and $s+ds$) is $P(s)=2\pi sds/\sigma$. As there are no bounds upon s, the total cross section σ can become ∞ unless s is artifically limited.

This cutoff procedure is not required in the lattice, because the other atoms establish a maximum value for s in each orientation. *The lattice also determines the probability density function $P^{(hkl)}(s)$ for each orientation.* Various definitions of this function are possible. If we refer to Fig. 2 it appears that we can consider either collisions only with the first layer atoms, or collisions with all atoms lying within one lattice-repeat distance of the surface. Further we may consider contributions from all atoms (which project into the representative area) simultaneously, or only contributions from the atom with the smallest impact parameter. We actually examined three cases:

(1) The distribution of values of s measured to the nearest surface atom;
(2) the distribution of all values of s measured to all atoms which project into the representative area; and
(3) the distribution of smallest impact parameters when all atoms are considered.

Physically, case (1) considers only nearest surface collisions, case (2) considers all collisions, and case (3) considers the hardest collisions which occur in the volume. Cases (1) and (3) presuppose a binary collision philosophy while case (2) is essentially n-body.[15] *Only case (3) gave reasonable agreement with the experimental data.*

The appropriate probability-density functions are illustrated in Figs. 5(a) and 5(b). The distribution of possible impact parameters, for approximately 50 000 points in each representative area, is calculated by an ancillary program, which computes the distance from a point in the representative area to each atom, chooses the smallest, and then tallies that distance in a table which becomes part of the main program. The number of electrons produced by the TFF energy, computed for a particular impact parameter, is weighted by the probability that impact parameter will occur in the particular orientation. Note that both the TFF energy and the probability function depend upon the lattice orientation.

V. ELECTRONS LIBERATED PER COLLISION

The PK theory uses a simple ionization cross section $\sigma(E_0)$ defined as

$$\sigma(E_0)=2\pi\int_0^{s_1}\frac{E_{TFF}(s,E_0)}{J}sds,$$

where s_1 is the largest impact parameter which will produce ionization, and J is the "average ionization potential for the outer shells of the atom." In this model the ionization process is independent of the electronic

[18] J. L. Schwartz and S. Borowitz, Phys. Rev. 133, A122 (1964).

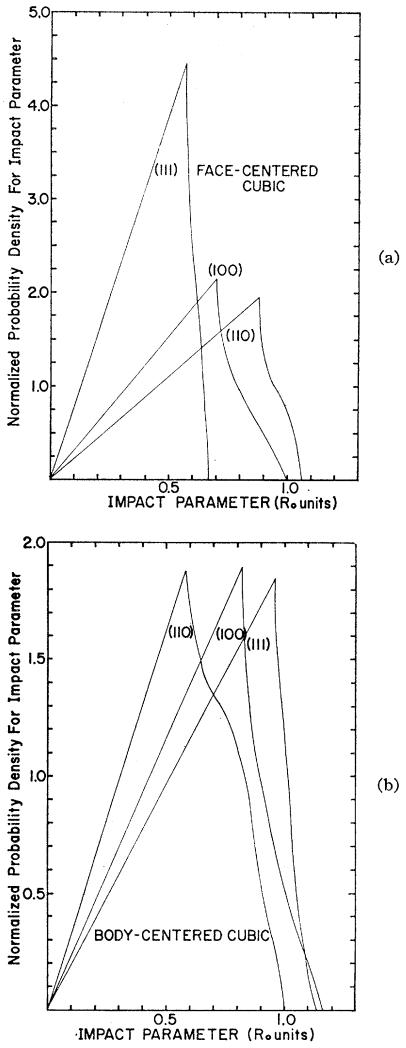

FIG. 5. The distribution of impact parameters for the various orientations of the face-centered-cubic lattice in (a) and for the orientations of the body-centered cubic lattice in (b). Note the change in vertical scale.

structure of the atom which is ionized and the degree of ionization is proportional to E_{TFF}.

We have chosen to use a more sophisticated model developed by Russek and his collaborators,[16] combined with the TFF-energy calculation, to obtain a function $n_e^{(hkl)}(s,E_{\mathrm{TFF}})$, the number of electrons liberated in a single collision. This function depends upon the impact parameter only through E_{TFF}, but we shall retain this dependence for weighting purposes; so it is specifically indicated in the functional dependence. It depends upon the crystallographic orientation because E_{TFF} depends upon this orientation. In the latest form of his theory, Russek[16] has developed three models which could possibly be used to determine $n_e^{(hkl)}(s,E_{\mathrm{TFF}})$. We have examined the "uniform"-ionization-energy and the "staggered"-ionization-energy models in detail, but have not attempted to use the staggered model with "self-consistent" ionization energies. The uniform-ionization-energy model assumes that the ionization energy per electron is independent of the number of electrons escaping. The staggered-ionization-energy model assumes that the ionization energy depends upon the number of electrons escaping. Let $p_n^{(M)}$ be the probability that n electrons will be liberated from a shell which contains M electrons. Russek shows that[16]

$$p_n^{(M)}\sim\binom{M}{n}\sum_{i=0}^{k}(-1)^i \times\binom{M-n}{i}\left[1-\frac{nE_n^{\mathrm{ION}}+iE_{n+1}^{\mathrm{ION}}}{E_{\mathrm{TFF}}}\right]^{M-1}, \quad (3)$$

where

$$k\leq(E_{\mathrm{TFF}}/E_{n+1}^{\mathrm{ION}}-nE_n^{\mathrm{ION}}/E_{n+1}^{\mathrm{ION}})\leq k+1.$$

Here M is the number of electrons available in the outermost shell of the atom, E_n^{ION} is the energy required to remove the nth of these electrons, and E_{TFF} is the energy available to effect this removal. When $E_{n-1}^{\mathrm{ION}}=E_n^{\mathrm{ION}}$ we have the uniform-ionization-energy model. Russek's values for the $p_n^{(M)}$ must be normalized; so that

$$\sum_{n=0}^{N}p_n^{(M)}=1.$$

For a given value of E_{TFF} we obtain a function $n_e(E_{\mathrm{TFF}})$, the number of electrons liberated when an energy E_{TFF} is available, from the $p_n^{(M)}(E_{\mathrm{TFF}})$ by the relation

$$n_e(E_{\mathrm{TFF}})=\sum_{n=0}^{M}np_n^{(M)}(E_{\mathrm{TFF}}).$$

In practice we compute $n_e(E_{\mathrm{TFF}})$ for a uniformly spaced set of E values and interpolate for the desired value at E_{TFF}. This procedure was practical because, for nearly filled electronic shells, $n_e(E_{\mathrm{TFF}})$ is a slowly varying function of E_{TFF}.

We were unable to obtain reasonable agreement between theory and experiment with the uniform-ionization model. In all cases the theoretical curves rose much too rapidly as the bombardment energy E_0 increased. Once a staggered-model approach was accepted we determined that the final results were surprisingly insensitive to small variations of the E_n^{ION}. In this work we have used spectroscopic values for E_n^{ION}, rather than the more convincing "self-consistent" model, as proposed by Russek, because the "self-consistent" model would necessitate a recomputation of $n_e(E_{\mathrm{TFF}})$ for each value of E_{TFF}.

As noted earlier, our calculations are based upon the assumption that all KSE electrons come from the argon. We were able to test this assumption by various choices for the E_n^{ION} in Eq. 3. We used the set of fractions $f_n\equiv E_n^{\mathrm{ION}}/E_1^{\mathrm{ION}}$ appropriate for the various ionization potentials of argon with different values of E_1^{ION} and examined the dependence of $n_e(E_{\mathrm{TFF}})$ upon

E_1^{ION} for the Ar^+-Cu system. The value of E_1^{ION} appropriate for neutral copper gave very poor results, while $E_1^{ION}=15.8$ eV (argon) gave excellent agreement with the data when we assumed an eight-electron-shell probability function. The first ionized copper was tried with both eight- and ten-electron shells. Neither was satisfactory. Large values of $E_1^{ION}\approx 25$ eV were also unsatisfactory. We checked $E_1^{ION}=17.0$ eV, and found it produced results almost as good as the value 15.8 eV. Apparently there is a range of acceptable values around 15.8 eV, which appears to be the "best" value.

This electron source assumption was made before Everhart's latest report on his experimental program.[19] He now has evidence that the excited"atoms"separate completely, and then emit electrons. We shall have to face the problem of the energy sharing mechanism, but the simple approximation appears to work in the present limited number of cases; so we continue to use it in this paper.

Electrons lost by the "ion" in its first collision will reduce its interaction potential and facilitate its subsequent motion in the lattice. The interaction potentials obtained from the present calculations are much too hard to use in radiation-damage calculations, but are at least consistent in order of magnitude with those obtained by Abrahamson for *neutral atoms*. Thus we have evidence that the first collision is between neutral atoms, while subsequent collisions occur before the ion can completely reneutralize. This suggests that most of the KSE electrons must come from the first collision, and supports a single-collision model. Auger electrons may contribute to the KSE process, but we shall see that their presence is not actually necessary.

We shall now proceed to fit the three orientations of each ion-metal system with three constants: a single scaling parameter for all three curves, and two interaction-potential parameters. The entire calculation, except the final scaling, was programmed for the CDC 1604 computer. Integrals were evaluated in 300 steps within the indicated maximum values.

VI. THE FITTING PROCESS

The argon-copper system was examined first and in greatest detail. All of the trials and tests described in the previous sections were performed on this system. So far as we have been able to determine, the set of assumptions we have outlined is the only combination of the various approximations and choices which will lead to acceptable agreement with experiment. We were very gratified that, once it was determined, the unique set of conditions carried over so successfully to the other ion-atom pairs.

As mentioned earlier, we examined the E_{TFF} dynamical integral for various types of potential functions. The TFF potential function used by PK was found to be too hard for smaller values of E_0; that is, the hard-core radius for a given energy was too large to give agreement with the data in this energy range. We attempted to soften the potential by decreasing a_{TF}, but the dynamical integral then became unrealistic, and we could not obtain good agreement with the data.

We then considered various Born-Mayer potentials. The A and B constants of these functions were obtained either by fitting the exponential function to the TF function for a range of separations, or by matching the exponential smoothly to the TF function at some separation. In all cases we found that the matching technique gave better agreement with the data than the fitting method. We must emphasize that the electron-density integral was calculated from the TF screening function, and not from the exponential used for the potential function. We were unable to obtain good agreement with the data when the electron density was screened with an exponential function. With the exponential function, the electron density goes to zero too rapidly for large values of r, and there is insufficient energy for small values of the bombarding energy. The TF function is known to be too hard for large separations in the diatomic-molecule case, but apparently in some sense it more accurately describes the electron density at large separations in a lattice than the more realistic Thomas-Fermi-Dirac approximation. All of the calculations reported are based on a TF screening function in the electron density, and a Born-Mayer potential which matches this TF expression for some small value of the separation.

The two constants a_{TF} and r_{FIT} (the matching point) completely determine A and B, the constants of the Born-Mayer potential, and conversely. The method is particularly sensitive to variations in B and in a_{TF}. A 1% variation in either was easily detectable. As the sensitivity appears as small variations of shape, which is best represented in the (111) orientation data for fcc, we generally accepted the best fit to the (111) data which had the proper magnitudes for the other two curves at the 10-keV point. If this condition was not sufficiently restrictive we attempted to fit the other curves as closely as possible. The (110) orientation was used in the same way for the bcc data.

The experimental data contain contributions from both γ_{PSE} and γ_{KSE}, which cannot be separated at the present time. Petrov[6] feels that γ_{PSE} should be essentially constant for Ar^+ on W and Ta to 6 keV. Medved, Mahadevan, and Layton[20] present evidence that the potential ejection contribution for Ar^+ on Mo is still increasing slowly at 2.5 keV. The PSE coefficient must ultimately decrease to zero as the energy of the incident particle increases, but we have no direct criteria to establish an upper energy threshold where it can be neglected. To provide uniform treatment of all systems

[19] E. Everhart, Bull. Am. Phys. Soc. **10**, 96 (1965). See also, E. Everhart and Q. C. Kessel, Phys. Rev. Letters **14**, 247 (1965); and Q. C. Kessel, A. Russek, and E. Everhart, Phys. Rev. Letters **14**, 484 (1965).

[20] D. B. Medved, P. Mahadevan, and J. K. Layton, Phys. Rev. **129**, 2086 (1963).

we have taken a value of γ_{PSE} as the experimental value of γ at which the KSE process begins to contribute, and have assumed that this value of γ_{PSE} then remains constant for all higher energies. All fitting was done with the assumption that γ_{PSE} has the same constant value for all three orientations, but in one figure we have shown how slight variations in γ_{PSE} will greatly improve the quality of the fit. For this reason, shape is a much more important fitting criteria than good agreement as the 10-keV points. In all systems we have assumed that the KSE mechanism begins to contribute at the energy where the experimental curves for various orientations begin to separate. We have no evidence that the PSE process should be orientation-dependent, but a slight orientation dependence appears to improve the fitting process.

VII. DISCUSSION OF THE INDIVIDUAL SYSTEMS

A. Argon-Copper

This system, which was the first studied both experimentally and theoretically, has already been reported in the literature.[21] It was chosen for the first theoretical studies because the data are internally more consistent. The results of the fitting are shown in Fig. 6. The semiempirical potential functions are shown in Fig. 7 with the Gibson-II[12] and two of Abrahamson's functions included for comparison.[11] We note that the Gibson II, which is a semiempirical copper-copper potential used in radiation-damage theory, is actually softer than our argon-copper potential. This is the basis of our earlier speculation that the ionic state at the time of the first collision is significantly different from all other subsequent collisions. The much softer potential between ionized argon and copper would make additional electron liberation much less probable, which tends to support the single-collision model. The PSE contribution was taken as 0.085 electrons/ion at 1 keV in Fig. 6. The KSE theory produces the separations between different orientations at 1 keV.

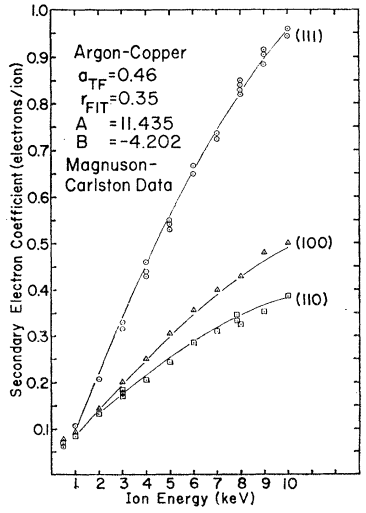

FIG. 6. The fit obtained to the argon-copper system. The indicated points are the experimental data.

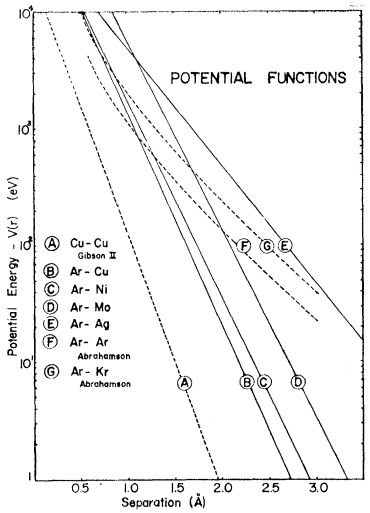

FIG. 7. Comparison of the semiempirical potential functions with other potential functions which are in general use. Apparently the new functions are much harder than ion-atom potentials, compare the Gibson II; so they are probably atom-atom potentials.

B. Argon-Silver

This system[22] is particularly interesting because apparently the PSE process dominates the KSE process to approximately $2\frac{1}{2}$ keV, see Fig. 8. The KSE contributions at 2 keV are almost equal for the different orientations and are small compared to the corresponding argon-copper values at this energy. The potential function for this system is very much harder than the argon-copper potential, see Fig. 7. It is probably consistent with the heavier target atom, but the TF approximation is not so good because the combined-atom electron density is less satisfactory when the atomic numbers differ considerably.

C. Argon-Nickel

The data for this pair[22] are less consistent internally than any of the other face-centered cubic systems. The resulting fits are correspondingly poorer, see Fig. 9. In Fig. 9 we have indicated the sensitivity of these results to small variations in the γ_{PSE} contribution. This system is particularly sensitive to small variations in a_{TF}, which scales the electron-density screening function. A 2% variation of this constant makes a noticable change in the shape of the (111) orientation curve.

D. Argon-Molybdenum

These were the only body-centered cubic system data[22] available when the theoretical analysis was being developed. This case requires a different set of integral limits, see Table I, and different impact parameter distribution functions, see Fig. 5(b). The calculated shape does not agree so well with the data as in the fcc cases, see Fig. 10, but the ordering of the curve magnitudes is

[21] G. D. Magnuson and C. E. Carlston, Phys. Rev. 129, 2409 (1963).

[22] C. E. Carlston, G. D. Magnuson, P. Mahadevan, and D. E. Harrison; preceding paper, Phys. Rev. 139, A729 (1965).

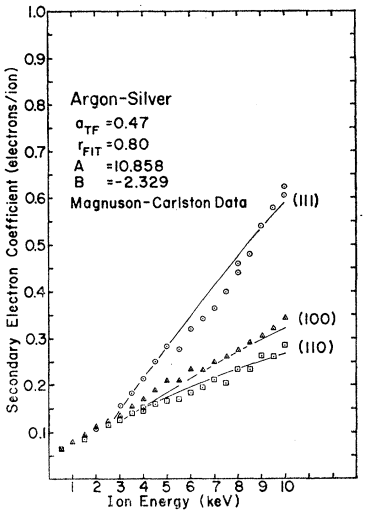

FIG. 8. Quality of fit between theory and experiment for the argon-silver system. The discrepancy near 5 keV may be caused by a variation of γ_{PSE}.

correctly predicted, as is the crossing of the (111) and (100) curves. The shape failure may be a breakdown of the Born-Mayer type interaction-potential assumption, or the TF electron density function may be inadaquate when the lattice is not close packed. We can anticipate that a spherically symmetric approximation will be less satisfactory here when the electron-density function is more distorted than in the fcc case. Practically speaking, the values of r_{FIT} required to obtain reasonable agreement in magnitudes are very small, and the lattitude for possible fits is correspondingly restricted.

VIII. SUMMARY AND CONCLUSIONS

The theory developed in this paper appears to adequately describe the main features of the KSE process. The single-collision model seems to be internally consistent, and is well supported by our present knowledge of atomic processes in solids. The agreement between theory and experiment should improve when some of the more radical simplifications are removed.

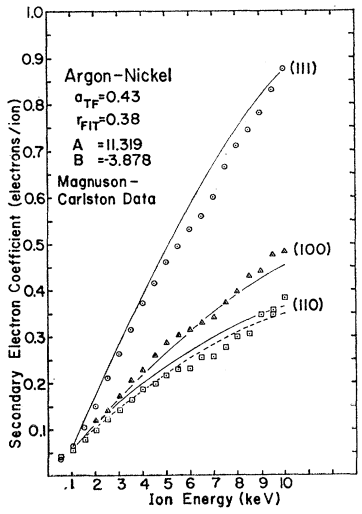

FIG. 9. The fit to the argon-nickel data. The large sensitivity to the value of γ_{PSE} is indicated by the broken line. We do not know the γ_{PSE} values with any certainty, and it is very possible that they are orientation-sensitive. This is the effect when we assume that they are orientation sensitive, but not energy sensitive above the KSE threshold.

The potential functions derived from the theory are not consistent with the potential functions in common use in radiation-damage studies at the present time, which are uniformly softer than the corresponding potential functions derived from diatomic molecular theoretical studies. This seems to indicate that in the radiation-damage studies we are dealing with moving atoms which are in relatively high ionization states, while in the KSE process the moving atom is at least approximately neutral.

The weakest portion of this theory is the TFF-energy analysis. Its surprising validity and sensitivity indicate that this area of the theory of atomic processes in solids needs further exploration. The rather broad range of applicability suggests that the validity is real, and not an accident of an individual calculation. Further refinement of the electron densities and interaction potentials are not justified until we develop more insight into the inelastic energy transfer method. Fortunately, the basic properties of the model do not depend upon this calculation.

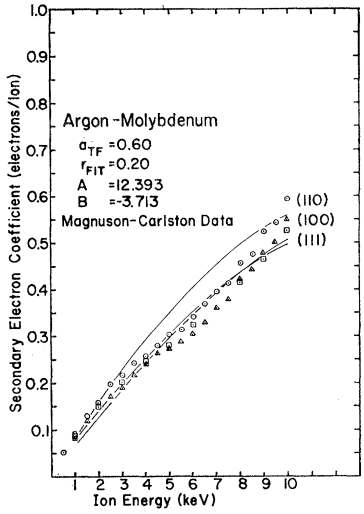

FIG. 10 The only body-centered case. The fit is much less satisfactory, but the correct ordering of the curves is apparent, and the crossing of the experimental curve is correctly predicted.

Comparison with experimental data will remain unsatisfactory until the PSE process is better understood at higher energies. In this energy range it is relatively less important, but contributes too much to ignore completely.

The theory presented here will be applied to the remaining experimental ion-atom combinations in the near future.

ACKNOWLEDGMENTS

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