Collision Theories of Cathode Sputtering of Metals at Low Ion Energies

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The periodicity of the threshold energies, as seen in a plot vs atomic number, is more pronounced for threshold energies determined from the part of the yield curve at the lowest ion energies, which obeys a quadratic law, than for "cut-in" energies determined with a linear law from the adjacent somewhat higher ion energy range. The relationship of the "empirical sputtering relation" of Wehner [Phys. Abstr. **62**, 719 (1959)] with the threshold formula, formerly derived by the author, is clarified. It is shown that in the case that the rebounding particle is believed to be a displaced target atom, the assumption of a very large "effective" mass of the struck atom must also be made to explain the rebound at angles as observed in ejection patterns of single-crystal planes. Arguments are presented that the author's model is consistent with the observed higher yields of metals with completely filled *d* shells, such as Cu, Ag, and Au. The energy losses connected with the impulses used up in Debye waves, as assumed in the author's theory, are shown to be in good agreement with Silsbee's calculations of the energy losses in similar collisions.

INTRODUCTION

IT is not surprising that several theories[1–7] on cathode-sputtering at low ion energies were developed after a broader experimental base had been established by different experiments on threshold energies[8] and on the deposit-spot patterns of single crystals.[9]

The problems given by the experiments were (1) to derive from basic concepts a formula for the threshold energies at normal ion incidence, and a law for the sputtering rate, (2) to explain the phenomena observed at oblique ion incidence, (3) to give a satisfying theoretical explanation for the surprising geometry of the deposit spot pattern from sputtering of single-crystal planes near threshold energies at normal ion incidence, and (4) to explain the change of these patterns with increased sputtering energies.

After a few years of further experimentation by Strachan and Harris,[10] Wehner,[11,12] Wolski,[13] Honig,[14] and the author, it is of highest interest, and the purpose of this paper, to compare published theories and the empirical formulas (i.e., those developed without a definite theoretical-mathematical basis), with regard to their compliance with the four main objectives pointed out above and to correct misconceptions or misinterpretations of the published theories.

1. THRESHOLD ENERGIES FROM THE PARABOLIC PART OF THE YIELD CURVE VS ION ENERGY AS COMPARED WITH "CUT-IN" ENERGIES FROM THE ADJACENT LINEAR PART

It was early recognized that a threshold for the ion energy exists, below which sputtering does not occur; that this energy is different for different target materials; and that sputtering at an oblique incidence angle of the ion requires less energy than sputtering at normal ion incidence.

The importance of determining the real threshold can be illustrated with the deposit spot patterns of silver at ion energies near threshold. If, for example, a {110} single-crystal plane of Ag is sputtered with normal ion incidence at 40 ev which is close to the real threshold, only four elongated spots along the diagonals of a rectangle appear. A center spot shows up if the energy is only increased to about 50 ev, and the pattern is completely changed when the same plane is sputtered with 100-ev ion energy.[15] The simplest patterns near threshold can easily be connected with the crystal structure of the bombarded surface and presented the basis for disclosing the mechanism of sputtering in the collision theory of the author.[2,3] To check the derived formulas for the threshold energy and the sputtering rate, the values of the real threshold energies of different metals with different kinds of ions are of primary importance.

The threshold energies were first determined as the lowest ion energies at which deposits on a substrate due to sputtered atoms could be detected, thus by "detection of deposits."[8] A refinement of the threshold measurements, besides new information, was expected from plotting the yields obtained with different ion energies. The yield curve for sputtering of Pt with Xe^+ ions (Wehner and Medicus[16]) was considered as a prototype for determining the threshold energies from yield curves. The plot of the yields S vs ion energies V_i

[1] E. B. Henschke, Wright Air Development Center Technical Note 55-474, June, 1955 (unpublished).
[2] E. B. Henschke, Phys. Rev. **106**, 737 (1957).
[3] E. B. Henschke, J. Appl. Phys. **28**, 411 (1957).
[4] D. E. Harrison, Jr., Phys. Rev. **102**, 1473 (1956).
[5] E. Langberg, thesis, Princeton, 1956 (unpublished).
[6] R. H. Silsbee, J. Appl. Phys. **28**, 1246 (1957).
[7] E. Langberg, Phys. Rev. **111**, 91 (1958).
[8] G. K. Wehner, Phys. Rev. **93**, 633 (1954).
[9] G. K. Wehner, J. Appl. Phys. **26**, 1056 (1955).
[10] I. F. Strachan and N. L. Harris, Proc. Roy. Soc. (London) **B69**, 1148 (1956).
[11] G. K. Wehner, Phys. Rev. **108**, 35 (1957).
[12] G. K. Wehner, Phys. Rev. **112**, 1120 (1958).
[13] S. P. Wolski, Phys. Rev. **108**, 1131 (1957).
[14] R. E. Honig, J. Appl. Phys. **29**, 549 (1958).
[15] See reference 3, p. 416.
[16] G. K. Wehner and G. Medicus, J. Appl. Phys. **25**, 693 (1954).

showed, for higher energies, a straight line which in extension to cut the abscissa gave the energy value V_0, called "cut-in" energy, which obeyed the linear law $S \propto (V_i - V_0)$, while the lower part of the curve was parabolic. When a plot of $S^{\frac{1}{2}}$ versus V_i is made for this part, a second straight line is obtained which in extension to the abscissa gives a second "cut-in" energy V_0'. Therefore, the quadratic law $S \propto (V_i - V_0')^2$ holds for the lower part of the yield curve. The "cut-in" energy from the plot of S vs V_i was $V_0 = 85$ ev, while the "cut-in" energy for the lower parabolic part was $V_0' = 40$ ev, which is very close to the lowest ion energies of 30 and 35 ev at which a yield could be measured. Thus, V_0' is very much closer to the real threshold energy than the V_0 value.[17]

When evaluating the measured sputtering yields for a series of metals, Wehner[12] assumed for the metals investigated a linear character of the yield curves by drawing a best-fitting straight line connecting the yield values in a plot of the yield S vs ion energy V_i and cutting the abscissa to determine the "cut-in" energies V_0 from this plot. No attempt was made to determine the "cut-in" energies from a plot of $S^{\frac{1}{2}}$ vs V_i nor to determine the real threshold energies, except for W (reference 11) where the threshold has been determined; however, it has never been used.

From the Pt-Xe^+ example, described above, it must be assumed that the V_0 "cut-in" energies are considerably higher than the lowest energies at which sputtering yields have been measured and that they are also much higher than the threshold energies $E_{\min}$, formerly measured by detection of deposits.[18] A comparison of the V_0 energies[19] with the $E_{\min}$ values[20] shows indeed this fact. Examples are:

Element :	Si	Fe	Ge	Mo	W	Pt
V_0 (ev) :	110	125	100	145	120	85
$E_{\min}$ (ev):	60	60	40	80	80	40

With regard to these large differences one cannot agree that it is correct to identify "cut-in" energies with "threshold energies," as was done by Wehner with the words: "At very low ion energy, i.e., near the 'cut-in' energy, formerly called 'threshold energy,' . . . ."[21]

On the other hand, it is still more surprising that some of the investigated metals have a V_0 energy considerably lower than $E_{\min}$, such as follows:

Element :	Ti	Zr	Hf	Th
V_0 (ev) :	50	85	90	85
$E_{\min}$ (ev):	110	120	150	120

As seen from the curves for Ti,[22] for Zr,[23] for Hf,[24] and for Th,[25] it is remarkable that no yield has been determined at energies below 100, 100, 125, and 100 ev, respectively, for these values. The V_0 are without any doubt considerably influenced by the tendency to consider the measurement points as lying, in each case, on a straight line, in order to define the "cut-in" energies V_0'.

As seen from the Pt-Xe^+ example, explained in detail above, straight lines derived from a plot of $S^{\frac{1}{2}}$ vs V_i for the very low ion energies would have given "cut-in" energies V_0' much closer to the real threshold or to the lowest values of ion energies at which a yield has been observed. However, this has not been tried nor were attempts made to determine the real thresholds otherwise.

Since no physical law is known which allows one to calculate the real threshold from the "cut-in" energies V_0 and since no physical meaning can be connected with the latter values, it follows that the "cut-in" energies V_0 can hardly be considered as characteristic for the sputtering phenomena at low ion energies.

On the other hand, the real threshold energy has the physical meaning that at energies lower than this value no sputtering occurs. The $E_{\min}$ energies obtained by "detection of deposits" are therefore much closer to the real threshold than the V_0 "cut-in" energies.

A method to determine the threshold energies from the sputtering rate curve with sufficient accuracy has been proposed[26] and successfully applied by the author in measuring the threshold for 15 metals sputtered with A^+ ions, to be reported in the near future. This method utilized only the lowest parabolic part of the yield curve. The threshold energy values determined by this method are very close to and only a little bit lower than the lowest ion energy at which a yield can be measured in a reasonable time.

2. THE PERIODICITY OF THE THRESHOLD ENERGIES

An attempt to replace the "cut-in" energies V_0 has been made by Wehner[11] with the introduction of the $V_{0.25}$ values, which are the ion energies at which the yields have the values of 0.25 atom per incident ion.

In the same paper, a plot of the $V_{0.25}$ values for 25 metals vs atomic number was published, and is reproduced here as Fig. 2. This plot shows, due to the marker lines for the noble gases, some similarity with the characteristic features of a plot of the threshold energies $E_{\min}$, obtained by "detection of deposits," which was first published by the author[27] and is reproduced here as Fig. 1. This plot had been made to show the

[17] G. K. Wehner, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, New York, 1955), p. 268.
[18] The values $E_{\min}$ were first labeled V_0^* by Wehner (see reference 8).
[19] See reference 12, Fig. 6.
[20] See reference 8, Table I, lower values.
[21] See reference 12, p. 1122.
[22] See reference 12, Fig. 1.
[23] See reference 11, Fig. 13.
[24] See reference 11, Fig. 15.
[25] See reference 25, Fig. 18.
[26] See reference 2, p. 752.
[27] See reference 2, Fig. 20.

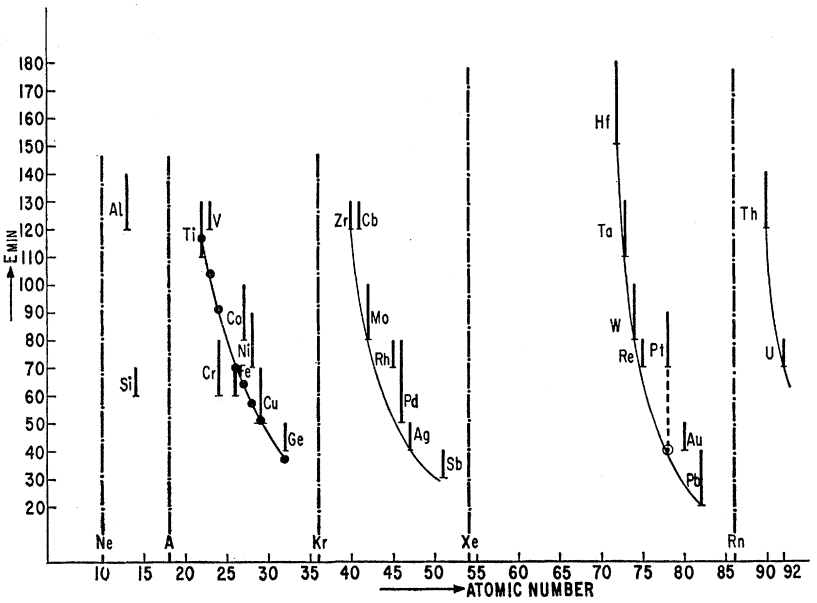

FIG. 1. Plot of threshold energies vs atomic number, measured by detection of deposits, published by Henschke (reference 2), showing the periodicity of the threshold energies and the influence of the filling of the d shells. The calculated values of the curve in the fourth period are proportional to the squares of the collision radii, which are determined by the number of the electrons in the d shell.

periodicity of the threshold energies by drawing the dividing lines for the noble gases.

The periodicity of the $E_{\min}$ threshold energies has been theoretically derived by the author[2] from a sputtering rate formula. This theoretically derived formula revealed that the threshold energy must be proportional to the square of the radius c_M of the collision sphere of the target atom. This means that the threshold

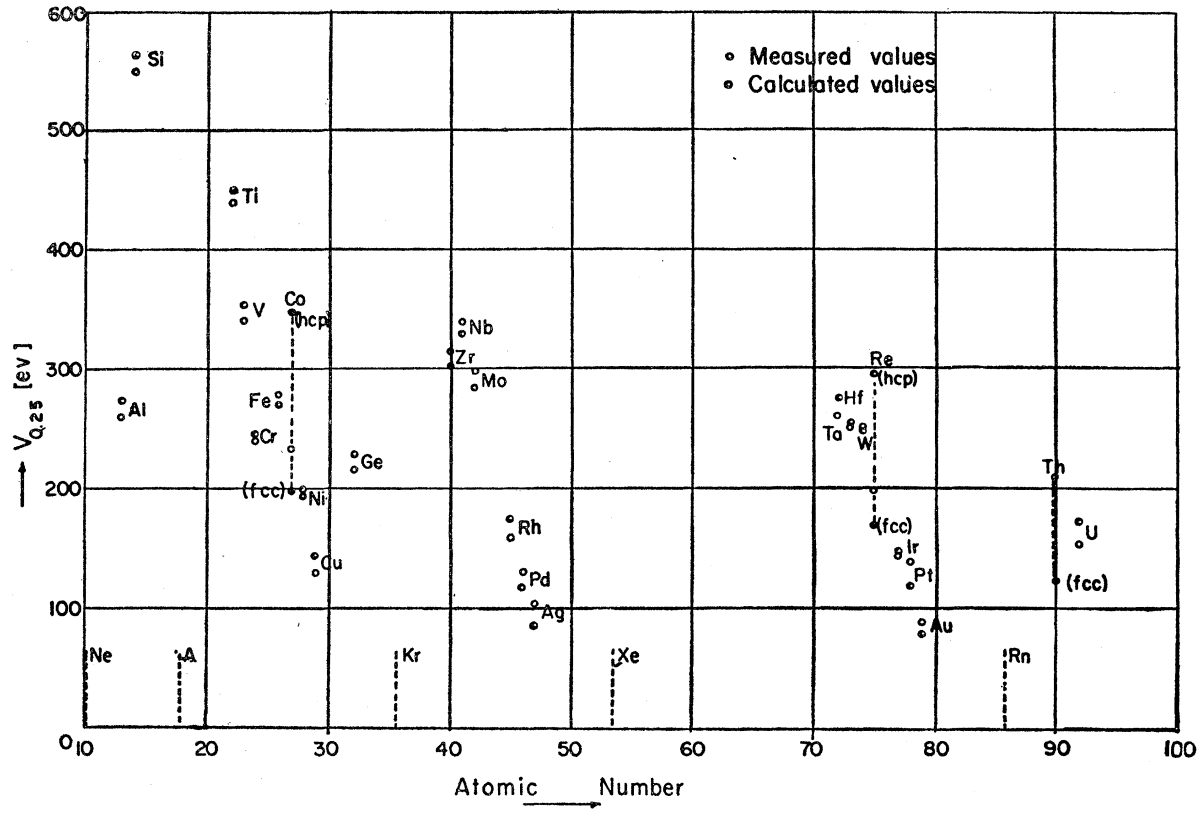

FIG. 2. Plot of the energy values $V_{0.25}$ vs atomic number, published by Wehner (reference 11), showing observed and calculated values within the periods of the periodic system according to the formula $V_{0.25}=KK'H/\mu$ with the momentum transfer factor $\mu=m/(m+M)$, the constants K and K', and the heat of sublimation H.

energy can be considered as proportional to the cross section of the target atom. A calculation of the collision radii of the metals of the fourth period of the periodic system, for which the threshold energies have been determined by detection of deposits, was made using a formula[28] in which d, the number of electrons in the subshell M 3d, was the determining quantity. This number shows clearly the influence of the "filling of the d shell" on the threshold energy in this period. Similar curves in the fifth and sixth period, drawn in Fig. 1 without calculation, indicate the same influence of the filling of the N 4d and O 5d shells on the threshold energies.

From a comparison of Fig. 1 with Fig. 2, in which the $V_{0.25}$ values are plotted vs atomic number, and also in comparison with Fig. 3, in which the "cut-in" energies V_0 vs atomic number are presented,[29] it can be seen that neither the $V_{0.25}$ energy values nor the "cut-in" energies V_0, since these values are not well determined, as explained above, disclose the periodicity of the threshold energies and the influence of the filling of the d shells as well as the data in Fig. 1, where the real threshold energies or values very close to them have been plotted.

It is not necessary to discuss a sputtering law[30] connecting the $V_{0.25}$ energy values with the heat of sublimation and a momentum transfer factor $\mu=M/(m+M)$, since this law was apparently replaced in a following paper by Wehner (reference 12) by a new empirical relation in which the momentum transfer factor no longer plays a role.

3. THE RELATIONSHIP OF THE "EMPIRICAL SPUTTERING RELATION" OF WEHNER WITH THE AUTHOR'S THRESHOLD FORMULA

When summarizing the experimental results reported for 24 metals, Wehner,[31] using now the energy transfer factor $\eta=4mM/(m+M)^2$, established a new empirical law with the sentence: "The conclusion to be drawn is that the 'cut-in' energies of different metals are in a first approximation proportional to H/η, with the dimensionless proportionality factor between 8 and 20 which can be compared favorably with Langberg's calculated value of 14." Since he had identified the term "cut-in" energy with the value formerly called "threshold energy," this is a new empirical threshold relation, which he compares with the law derived by Langberg[5] and also with the theory of the author in the abstract of that paper[12] with the quotation: "Results for Hg^+-ion bombardment support theories developed by Langberg and Silsbee but disagree with a theory published by Henschke. Conditions may be different, however, for the case of bombardment with light ions such as hydrogen or helium." While Wehner's objections

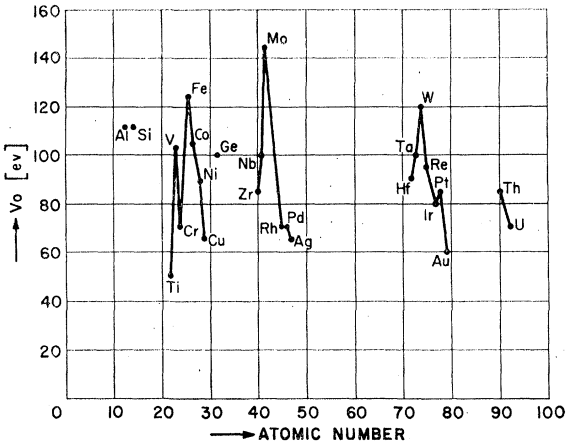

FIG. 3. Plot of the "cut-in" energies V_0 vs atomic number, published by Wehner (reference 12), showing less pronounced periodicity and dependency from the filling of the d shells than the plot in Fig. 1 of the threshold energies, formerly determined by detection of deposits.

against the author's theory made in the article concern only the rebound mechanism, also assumed for ions heavier than the target atom, the impression is given from the first sentence of this quotation that the results for Hg^+-ion sputtering, the basis of the new empirical formula, are not covered by or are not even in agreement with the theory of the author.[2,3]

The second sentence considers the author's theory as possibly correct for very light ions but not for the heavier A^+ ions nor for Hg^+ ions. This point will be discussed later in Secs. 4 and 5.

It can easily be seen that the statement in the first sentence quoted above is not correct. The results of Hg^+-ion bombardment are well in agreement with the author's theory,[2] as can be shown immediately from the fact that the new empirical formula, established by Wehner,[12] is identical in each term, and even in the indicated numerical limits for the proportionality constant, with the simplified threshold formula, formerly derived by the author[2] for normal ion incidence.

The author's formula for the threshold energy, $E_{\min}$,[32] is

$$E_{\min}=g(m,M)\times\Delta H_{298}\times f(\alpha_{hkl},\delta)\times\Delta H_{hkl}/\Delta H_{298}, \quad (1)$$

where

$$g(m,M)=(m+M)^2/mM, \quad (2)$$

and

$$f(\alpha_{hkl},\delta)=\frac{1}{(1+\delta)^2\cos^2\alpha_{hkl}[1-(1-\delta^2)\cos^2 i]}. \quad (3)$$

For the calculations of threshold energies the values f', defined by

$$f'=f(\alpha_{hkl},\delta)\times\Delta H_{hkl}/\Delta H_{298} \quad (4)$$

[28] See reference 2, Eq. (8.2).
[29] See reference 12, Fig. 6.
[30] See reference 11, p. 45.
[31] See reference 12, p. 1123.
[32] See reference 2, Eq. (5.12).

TABLE I. Proportionality constants $C=4f'$, supposed to have values between 8 and 20 in the newly established empirical "cut-in" energy law of Wehner,[a] $V_0=(H/\eta)C$, as calculated from the factor f' in Henschke's threshold formula, $E_{\min}=g\Delta H_{298}f'$, showing the identity of these laws.

System	Element	$g=4/\eta$	$H=\Delta H_{298}$	V_0[c]	f'[b]	$E_{\min}$[b] (ev)	$C=4f'$
bcc	V	6.18	5.2	105	3.75	120	15.00
	Cu	6.11	3.68	65	2.68	60	10.72
	Fe	5.84	4.2	125	2.45	60	9.80
	Cb	4.70	7.6	105	3.39	120	13.56
	Mo	4.56	6.75	145	2.16	80	10.4
	Ta	4.01	8.7	100	3.44	120	13.76
	W	4.01	8.75	120	2.28	80	9.12
fcc	Al	9.54	3.29	110	3.8	120	15.2
	Ni	5.68	4.41	90	2.8	70	11.2
	Cu	5.48	3.56	65	2.56	50	10.24
	Rh	4.40	6.0	70	2.65	70	10.60
	Pd	4.29	4.05	70	2.87	50	11.48
	Ag	4.27	3.04	65	3.1	40	12.4
	Pt	4.00	5.86	85	3.0	70	12.0
	Au	4.00	3.94	60	2.55	40	10.20
	Pb	4.00	2.02		2.48	20	9.92
	Th	4.02	6.5	85	4.6	120	18.4

[a] See reference 12.
[b] See reference 2, p. 746, lower values.
[c] From Fig. 6, of reference 12.

have been plotted for the bcc crystals[33] and also for fcc crystals.[33] The formula (1) can then be written in a simpler way as

$$E_{\min}=g\times\Delta H_{298}\times f'. \tag{5}$$

On the other hand, in the proposed empirical formula for the "cut-in" energy V_0, which is termed as "formerly called threshold energy," this energy is given by the formula

$$V_0=(H/\eta)C, \tag{6}$$

where H is the heat of sublimation, identical with ΔH_{298} in (1), η is given by

$$\eta=4mM/(m+M)^2, \tag{7}$$

so that $g=4/\eta$, and finally C is a dimensionless proportionality factor supposed to be between 8 and 20.[34] Both formulas (5) and (6) are identical, if

$$C=4f'. \tag{8}$$

Therefore, if the values of f', formerly calculated for bcc and fcc metals,[35] multiplied by 4, are in the range between 8 and 20, then it has been proved that the experimental data on threshold energies of these metals are in agreement with the empirical formula of Wehner. This is indeed the case, in spite of the discrepancies between $E_{\min}$ and V_0 as seen from the data of the Table I.

While the proportionality constant C in formula (6) is unrelated to other important parameters involved in the collisions, the term f' in the author's threshold formula (1) is connected with the incidence angle i of the ion, with the angle α_{hkl}, which is the angle between the surface normal and the centerline between the lower surface atom and the upper surface atom involved in the rebound collision, with the dissipation coefficient δ, and also with the ratio of the heat of sublimation ΔH_{hkl} of the specific single crystal plane (hkl) to the one ΔH_{298} for a polycrystalline surface.

The value of this more comprehensive formula (5) will be shown with regard to measurements of yields and threshold energies for 15 metals with A^+ ions to be reported in the near future.

[33] See reference 2, Fig. 8.
[34] See reference 12, pp. 1123 and 1124.
[35] See reference 2, Table I.

4. THE REVERSAL OF MOMENTUM IN SPUTTERING THEORIES BASED ON TWO-BODY COLLISIONS

Theories of cathode sputtering based on consecutive two-body collisions have been developed by the author[1–3] and by Langberg.[5]

Langberg[5] made no attempt in his theory to explain the deposit spot patterns of single-crystal planes. The two-body collisions in his theory are only concerned with upper surface atoms. These kinds of collisions can be treated as two-body collisions between free particles, as done by Langberg. The same was done in the author's theory[2] with the collisions which lead directly to the ejection of upper surface atoms, such as the single collisions in sputtering at oblique ion incidence, or the second and third collisions in case of double or triple collision sputtering, respectively (see Fig. 1, reference 2).

Collisions of the ion, or of a knocked-on upper surface atom, with a lower surface atom which must be assumed to explain certain features of the deposit spot patterns are not considered at all in Langberg's theory.

In the author's theory the derivation of the threshold and sputtering yield formulas as well as the explanation of the details of the deposit spot patterns have been performed with the same fundamental concept, namely, that collisions of the ion with target atoms in the direction to the inside of the target cannot be treated as collisions between free particles. The bulk of the target is behind the struck atom and produces a very large "effective" mass compared to the mass of the ion or to the mass of the target atom. Therefore, a rebound of the striking particle occurs in such a collision, no matter whether its mass is lighter, heavier, or equal to the mass of the target atom.

It will be shown that in collision mechanisms, in which the striking particle is not the ion, but a knocked-on upper surface atom, the same assumption of a very large effective mass of the struck target atom due to its connection with the bulk must also be made to account for the rebound. Without assuming a rebound in such inwardly directed collisions, the deposit spot patterns cannot be explained.

To make this most important point absolutely clear, a discussion of some possible kinds of collision mechanisms, as drawn in Fig. 4(a) to Fig. 4(f), may be very helpful.

While Fig. 4(a) represents the simplest case of oblique ion incidence, which has been used in the theory

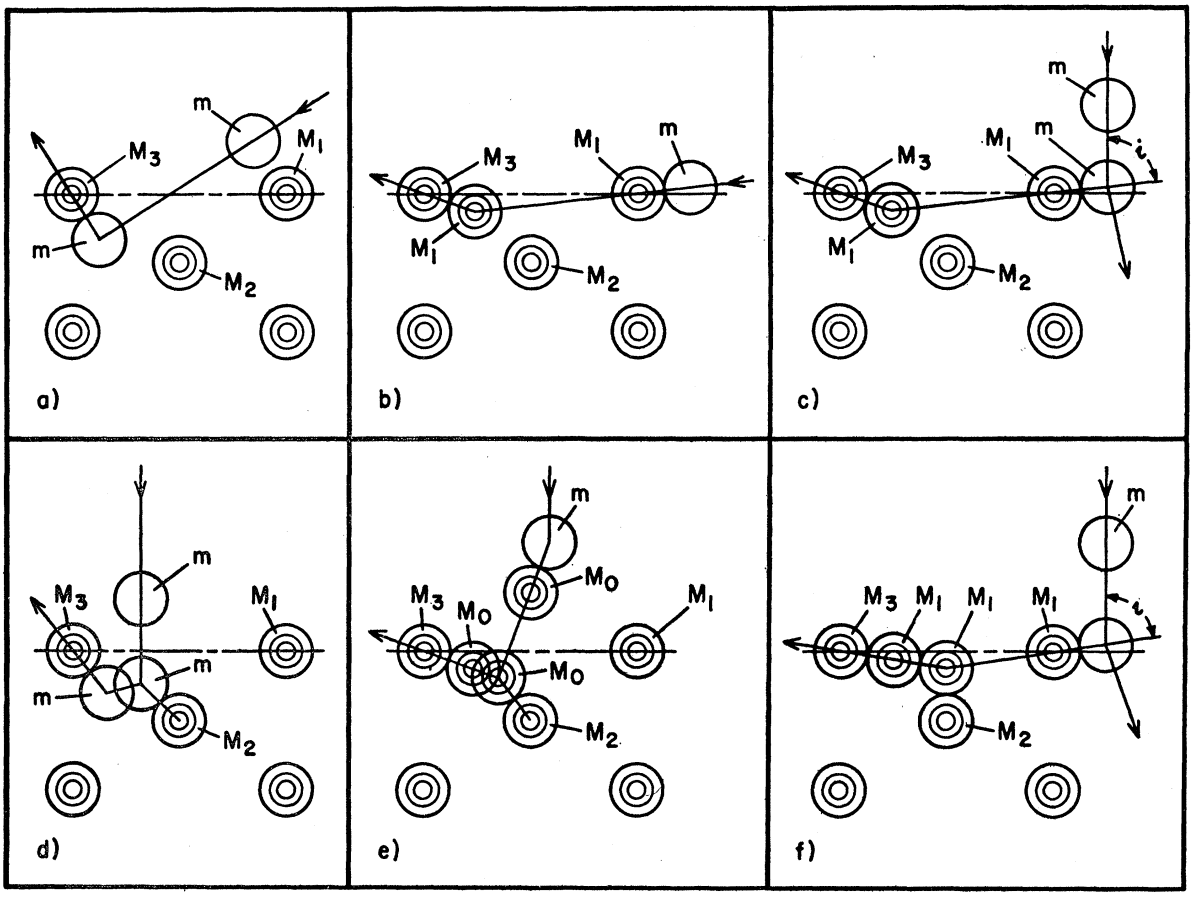

FIG. 4. Different kinds of sputtering mechanisms. (a) Simplest one-collision sputtering at oblique incidence of the ion m, requiring the least amount of ion energy to eject the upper target atom M_3. (b) Sputtering collision at oblique ion incidence, similar to (a); however, a knocked-on upper surface atom is assumed to eject the surface atom M_3. (c) Two consecutive two-body collisions at normal ion incidence are assumed to be necessary to eject the surface atom M_3. This mechanism has been used by Langberg[7] for the derivation of a threshold formula. (d) The perpendicularly incident ion m collides with the lower surface atom M_2 to rebound and to eject the atom M_3 in a second collision, requiring the least amount of ion energy. (e) Three two-body collisions at normal ion incidence, the first one between the ion m and the upper surface atom M_0, the second one between the atom M_0 and the lower atom M_2, in which M_0 rebounds to eject the atom M_3. (f) Three two-body collisions at normally incident ions collisions, similar to (e), however, requiring more ion energy than in (e) and much more than in (d), because of the large incidence angle i of the ion on the atom M_1, which rebounds on M_2 to eject the atom M_3.

of the author[2] as the one requiring the least amount of ion energy for sputtering, Fig. 4(b) shows a variation of it, in which the ion m strikes first an upper surface atom M_1 and moves it in this collision to hit the atom M_3 of the surface on its lower hemisphere in order to eject it. It is immediately obvious from Fig. 4(b) that more energy is required to remove the atom M_3 from the surface than in Fig. 4(a), because the atom M_1 has to be displaced from its lattice position first, which requires additional energy.

Still more energy than in Fig. 4(b) is needed for the case in Fig. 4(c) in which the atom M_1 is removed from its lattice position not in a head-on collision but in an oblique collision with the ion m, originally directed normally to the surface. In this case only a part of the ion energy, determined by the cosine of the incidence angle i, is effective. This mechanism has been utilized by Langberg[7] in his sputtering theory, to derive a threshold energy law.

In the sputtering mechanism of Fig. 4(b) to Fig. 4(c) two consecutive two-body collisions are necessary for the reversal of momentum. Lower surface atoms are not concerned at all in these collisions. The simplest collision requiring the least amount of energy, is the one in Fig. 4(a) which, therefore, has been used in the theory of the author[2] for the derivation of the threshold energy law for oblique ion incidence.

However, with the mechanisms of Fig. 4(a) to Fig. 4(c) it is not possible to explain the various ejection angles, as observed in the deposit spot patterns of single-crystal planes, occurring at normal ion incidence.

To explain these kinds of patterns a double-collision mechanism, as drawn in Fig. 4(d), has been assumed by the author.[36] In this case the ion m hits the lower surface atom M_2 directly with the incidence angle i and rebounds in such a direction that the upper surface

[36] See reference 2, Fig. 1(b).

atom M_3 is hit on its inside hemisphere to be ejected in this second collision.

Many variations of collisions at normal ion incidence equivalent in effect to the one in Fig. 4(a) can be conceived, and have been considered by the author. The examples of Fig. 4(d) to Fig. 4(f) have in common that either the ion or an upper surface atom, moved in the course of the collision, collides with the lower surface atom M_2, and that the reversal of momentum occurs in this collision by the rebound of the striking particle on the lower surface atom M_2. It can be seen immediately that the mechanisms of Fig. 4(d) in which the ion m hits directly the lower surface atom M_2, required the least amount of energy to sputter the upper surface atom M_3.

In Fig. 4(e) an upper surface atom M_0 is hit by the ion m in almost a head-on collision and moved against the target atom M_2. In this collision M_0 rebounds to hit the upper surface atom M_3 and to sputter it.

In Fig. 4(f) the ion m hits the upper surface atom M_1 in an oblique collision with the incidence angle i. In the recoil of this atom the lower surface atom M_2 is hit and in the rebound of M_1 from M_2 the upper atom M_3 is ejected in the third collision. Because of the large incidence angle i, still more energy is necessary for sputtering than with a mechanism according to Fig. 4(e), which, as pointed out, requires more energy than the simple 2-collision ejection mechanism of Fig. 4(d).

Therefore, if all three mechanisms of Fig. 4(d) to 4(f) are equally possible then the mechanism of Fig. 4(d) would predominate near threshold because it requires the least amount of energy. For this reason the theory of the author has been based on this model.

To decide the question whether all three mechanisms are possible or not, if perfectly elastic collisions between free particles are assumed, as done by Silsbee[6] and Wehner,[12] it is sufficient to consider only head-on collisions. In oblique collisions the tangential component of the velocity remains unchanged, while the normal component of the initial velocity, v_{0n}, that means the component acting in the direction of the centerline of the two particles at the moment of contact, must be reversed in direction during the rebound. This reversed velocity component together with the unchanged tangential component produce the velocity v_1 after the collision in the right direction to eject the upper surface atom M_3 in the following collision. For the assumed conditions the normal component v_{1n} of the velocity of the striking particle of mass M at rest is given by the equation

$$v_{1n}=\frac{m-M}{m+M}v_{0n}, \tag{9}$$

where v_{0n} is the normal component of the striking particle before the collision.

If this equation is applied to the mechanism of Fig. 4(d), i.e., if the collisions are assumed to be between free particles and perfectly elastic, then the striking particle must have a lighter mass m compared with the mass M of the struck particle M_2, to allow the rebound of the particle, because only then a negative sign of v_{1n} in Eq. (9) is obtained. Apparently from this picture Wehner[12] concluded that the mechanism of the author's theory may be possible for lighter ions, such as Ne^+ or He^+, but not for heavier ions like Ar^+ and Hg^+ ions. Silsbee[6] considers from the same reasons a "forward scattering" of the heavy Hg^+ ions, thus a positive velocity.

In the cases of Fig. 4(e) and Fig. 4(f) the particles colliding with the lower surface atoms M_2 are not the ions with the mass m, but the upper surface atoms M_0 and M_1, respectively, with the mass M, which have been removed from their positions in the lattice by the impacts of the ions m. Since in these cases the letter m in the equation (9) must be replaced by M, it is seen immediately that the velocities of the striking atoms M_0 and M_1, respectively, after the collisions with M_2 become *zero*. Therefore, if the colliding particles are considered to be freely movable, a rebound of the striking atoms with the mass M, as drawn in Fig. 4(e) and Fig. 4(f), would not be possible either.

The mechanisms drawn in Fig. 4(e) and Fig. 4(f) are in accordance with the picture, described by Wehner with the words: "Energy and momentum are transferred from the neutralized ion to a first target atom in a collision which more or less resembles a hard-sphere collision. This target atom then transfers energy to other close neighbors and, finally, a small amount of the original energy with a momentum now directed to the outside, may separate a surface atom in the neighborhood of the place of impact."[21] Therefore, the criticisms of Silsbee[6] and Wehner[12] that the rebound of the heavy Hg^+ ion is not possible would also apply to the collision mechanisms as described in this quotation and represented in Fig. 4(e) and Fig. 4(f). When the colliding particles have equal mass M, none of the mechanisms of Fig. 4(d) to Fig. 4(f) would be possible, if the colliding particles are considered as freely movable.

However, it will be shown in the next paragraph that these sputtering mechanisms are well possible, because the struck particles are part of the bulk and produce a rebound of the striking particle in each case due to their very large "effective" mass.

5. THE REBOUND IN COLLISIONS DIRECTED TO THE INSIDE OF THE TARGET

In the sputtering mechanisms, as sketched in Fig. 4(a) to Fig. 4(c), only collisions between upper surface atoms are involved. In none of these collisions do the struck upper surface atoms acquire a momentum directed to the inside of the bulk. Therefore, considerations of a rebound of the striking particles are not necessary; these collisions can be treated as between

free particles as done in the author's theory of sputtering at oblique ion incidence, and also by Langberg.[7]

The sputtering conditions, however, are completely different for perpendicular ion incidence with mechanisms such as in Fig. 4(d) to Fig. 4(f). The lower surface atoms M_2, struck either by the ion m or by a knocked-on target atom M_1 with a momentum directed to the inside of the bulk, are not free to move in this direction as the upper surface atoms can do in the case of obliquely incident ions. The whole bulk stands behind the atoms M_2 in the direction of the impulse.

To make this important fact plausible it does not make much difference which kind of model is used for the target metal crystal. If we take a hard-sphere model with close-packed planes and with cohesive forces between the spheres, then, e.g., in an fcc {110} surface, the lower surface atom hit by the ion in normal inside direction can be considered as being supported by five close-packed rows acting like supporting columns or even better as resting on top of five intersecting close-packed planes extending to the inside of the bulk which act like interconnected solid walls. The number of the atoms in these rows or planes may be very large. If they are all in close contact with each other and cohesive forces are assumed between them, they can only move together. This would certainly mean to move an effective mass M_{eff} very large compared to the ion mass m, or to the mass M of the target atom, if this is the incident particle.

Therefore, the mass M of the struck particle in Eq. (9) must be replaced by the very large effective mass M_{eff}. This means that the mass of the impinging particle m has to be assumed always to be much smaller than the "effective" mass M_{eff} of the struck atom, so that no matter how large or small the mass m is, the condition

$$m \ll M_{\text{eff}} \tag{10}$$

is always fulfilled. This is identical with the condition of a rebound of the striking particle, because in this case the velocity v_1 of this particle after the collision, according to Eq. (9), becomes

$$v_{1n} = -v_{0n}. \tag{11}$$

From this picture a rebound of the striking particle takes place in an inwardly directed collision with a lower surface atom, no matter whether the mass of the impinging particle is lighter, e.g., a He^+ ion, or heavier, e.g., and Ar^+ or a Hg^+ ion, or if its mass is equal to the mass of the target, as assumed in Fig. 4(e) and Fig. 4(f). The lower surface atom with the bulk behind it reacts as a solid wall. Collisions of a mass m with a solid wall are treated in classical mechanics with ordinary collision equations between two masses m and M by assuming the mass M to be very large compared to m.

Of course, the hard-sphere model with close-packed rows and close-packed planes, as used here for the demonstration of the condition (10) for collisions with inside directed impulses, cannot be assumed to represent the real structure in a metallic crystal. The author has considered the collision spheres in his theory[2] to be determined by the largest closed electronic shells, thus much smaller in radii than the radii determined by the lattice constant and a close-packed row in the unit cell. In this picture the close-packed rows and planes are no longer really closely packed by the spheres, since now smaller spheres are positioned at the lattice points as positive ions and are surrounded by an electron cloud in which electrons are shared by several atoms. This gives the picture of the atoms being connected by strong springs with all the neighbors in the close-packed rows and with weaker springs in the other rows with next nearest neighbors. However, with this more realistic picture of the bonds in metal crystals the same conclusion about the rebound of the impinging particle will be obtained.

The impulse applied to a target atom and directed to the inside has to stretch the springs representing the bonds with the upper surface atoms, and the springs going to the neighbors in the same plane too. However, it has to compress the springs leading from the atom hit by the ion, down into the lattice in several different directions. The second atom in each row is again spring-connected with the same number of other close-packed rows going down and this is true for each atom of the close-packed rows. The bonds with the upper atoms and with the atoms in the plane try to pull back the struck atom by tension, while the other bonds resist the movement by compression. All the springs described act together to apply a strong retractive force on the mass m of the impinging particle when it is moving in inside direction.

The movement of the particle m at low ion energy is stopped almost immediately and then reversed in direction by the action of these restoring forces. The mass m regains its kinetic energy and the springs return into their equilibrium state. This is the action to which the impinging particle m is submitted and which is identical with a rebound, in which the velocity v_1 after the collision is again determined by the Eq. (11).

6. THE MOST PROBABLE SPUTTERING MECHANISMS

When summarizing the last two sections one arrives at the following statements: If the collisions involved in the mechanisms of Fig. 4(d) to Fig. 4(f) are considered to occur as between freely movable particles, then these mechanisms would only be possible for ions very much lighter than the target atom. The mechanisms Fig. 4(d) to Fig. 4(f), however, have to be considered as possible also for heavier ions, because the lower surface atoms represent in collisions directed to the inside of the bulk such a large "effective" mass so that the impinging particles rebound from the lower

surface atom in each case whether the mass of the impinging particle is lighter, heavier or equal to the mass of the target atom.

Although the three mechanisms Fig. 4(d) to Fig. 4(f) are possible, they are not equivalent with regard to the lowest ion energy required to eject the surface atom M_3 nor with regard to the ejection angles. Theoretical and experimental work on cathode sputtering at low ion energies has been concerned with the derivation of threshold formulas and the experimental determination of the lowest ion energies at which sputtering occurs. It can be seen immediately that the mechanism Fig. 4(b) requires more energy to eject the upper surface atom M_3 than the one in Fig. 4(a), because the ion m has to move first the atom M_1 from its place and to transfer its energy to this atom. Even more energy than in Fig. 4(b) requires the mechanism in Fig. 4(c), in which perpendicular incidence of the ion m is assumed, so that only a part of the ion energy determined by the cosine of the incidence angle i is effective in the ejection of the atom M_3.

Similarly, the mechanism requiring by far the highest ion energy is the one in Fig. 4(f), again because of the incidence angle i. Less energy is needed for the case of Fig. 4(e), and the least energy is required for the mechanism of Fig. 4(d), the one used for this reason together with the single collision sputtering of Fig. 4(a), in the collision theory of the author.[2,3] Since it has been shown that the choice of the target atom M_1 as striking particle in Fig. 4(e) and Fig. 4(f), instead of the ion m in Fig. 4(d), offers no advantage in explaining the rebound and no reason can be seen that the ion impact and rebound cannot occur, it must be concluded that the mechanism, as described by Fig. 4(d), is much more likely to occur at low ion energy than a mechanism according to Fig. 4(e) or even Fig. 4(f).

The drawings of the lattice in Fig. 4 correspond to a (111) plane perpendicular to a (110) single-crystal plane. From the deposit spot patterns of this plane at lowest ion energy it can be concluded that the wide range of ejection angles can be explained easily with the mechanism Fig. 4(d) than with one according to Fig. 4(e) or Fig. 4(f). These kinds of mechanisms, of which many more can be conceived, e.g., such as corresponding to the triple collision sputtering collisions in the author's theory, are only variations of the fundamental collisions, as shown in Fig. 1 in the author's theory (reference 2), which require much more ion energy, and which therefore are not suitable to present the prototype of sputtering collisions at low ion energy.

7. THE HIGH SPUTTERING YIELDS OF METALS WITH COMPLETELY FILLED *d* SHELLS SUCH AS Cu, Ag, AND Au

Wehner gives no justification for his statement[31] that in the author's theory "one should expect that Cu, Ag, and Au would exhibit low sputtering yields" while the opposite is true. However, even if the accommodation coefficient of the Hg^+ ion be unity, as claimed by Wehner with reference to an unpublished report, it cannot be seen how the above conclusion can be deduced. The remark at the end of the same paragraph that "the process described in the author's theory is possible only when light ions bombard heavy target materials" indicates that the deductions are based on the fact that the Hg^+ ion is heavier than the atoms of Cu, Ag, or Au, so that the impulse is inwardly directed after the collsion, as seen from Eq. (9), and this may be the reason for the complete accommodation of the Hg^+ ions. This deduction, however, is not conclusive, in the first place, since it may be well conceivable that the neutralized Hg^+ ion may be trapped for some reasons, not known yet, after the collisions which caused the ejection of the upper surface atoms.

The main objection against Wehner's conclusion, however, is that the fundamental assumption in the author's theory about the "effective" mass of the struck atom [see Eq. (10) above] is not considered at all.

From the author's theory it follows, on the contrary, that the yields for Cu, Ag, and Au should be expected to be higher for the following reasons. If the *d* shells are filled and only one valence electron is shared by lattice neighbors in the electron cloud between the atoms, then the largest closed electronic shells can be assumed to have almost the largest possible extention. The ratios of the nearest neighbor distance to the diameter of the largest closed electronic shell for Cu, Ag, and Au have the values 1.328, 1.1425, and 1.050, respectively, while the same ratio, e.g., for Al is 1.983. Therefore, the probability that an upper surface atom is hit in the rebound in an appropriate manner to be ejected from the surface is much higher for a metal atom with filled *d* shells, such as Ag, Cu, and Au, than for a metal such as Al, where the largest closed electonic shells are much smaller in size. Lower threshold energies and higher sputtering yields should, therefore, be expected for Cu, Ag, and Au from the author's theory.

8. THE DISSIPATION COEFFICIENT δ AND THE ENERGY LOSS IN DEBYE WAVES DURING SPUTTERING

Silsbee[6] critized the factor $(1-\delta)$ which the author[2] introduced as a lattice interaction coefficient, to account for the energy to phonon excitation (Debye waves) during the collisions. Silsbee said: "The magnitude of $(1-\delta)\sim 0.5$, which he (the author) obtains by fitting observed threshold energies, seems excessive on the basis of the arguments given above and by Langberg, which suggest very small values of $(1-\delta)$." Later Silsbee, in the same paper, plots the fractional energy loss $\Delta E/E$ vs pulse energy E for a focused energy pulse in copper and finds these values to be between 0.2 at 1 ev and about 0.02 at 100 ev. "This small interaction with neighboring chains (20% loss per collision at 1 ev)

is in accord with the arguments given in the first section justifying the treatment of the problem as a sequence of two-body collisions. The energy loss calculation represents a detailed estimate of the validity of that assumption and raises some question about Henschke's[2] value of 0.5 for his "lattice interaction coefficient."

Silsbee apparently overlooked the fact that the author[2] introduced the factor $(1-\delta)$ not as proportional to the energy loss but as proportional to the impulse[37] R_d used up in Debye waves by setting [see Eq. (3.6) or reference 2]

$$R_d=R_0(1-\delta), \quad 0\leq\delta\leq 1. \tag{12}$$

No effort had been made in that paper[2] to evaluate the energy loss connected with the impulse R_d. However, this may be done here and it will be seen that the energy loss associated with the impulse R_d fits very well the data given by Silsbee.[6]

The impulse R_d is obviously acting on the mass M of the target-atom, since phonon excitation occurs within the target when displacement of atoms M of the target are involved. Therefore, from the general relationship between the momentum p and the energy E for a mass point M given by $E=p^2/2M$, it can be concluded that the energy involved in the impulse R_d is given by

$$\Delta E=R_d^2/2M, \tag{13}$$

and with the relation (12)

$$\Delta E=R_0^2(1-\delta)^2/2M. \tag{14}$$

On the other hand, R_0 is given by[38]

$$R_0=\frac{mM}{m+M}(v_0-V_0), \tag{15}$$

with m the mass of the ion, v_0 the velocity of the impinging ion before the collision, V_0 the initial velocity of the target atom; here $V_0=0$, since M is assumed to be at rest before the collision. Therefore the energy loss is given from (14) and (15) by

$$\Delta E=\frac{m^2M^2(1-\delta)^2}{(m+M)^2 2M}v_0^2 \tag{16}$$

from which by introducing $E_0=\frac{1}{2}mv_0^2$, the ion energy before the collision, the equation for the fractional energy loss $\Delta E/E_0$ with the use of Eq. (2) results in

$$\frac{\Delta E}{E_0}=\frac{mM}{(m+M)^2}(1-\delta)^2=\frac{(1-\delta)^2}{g(m,M)}, \tag{17}$$

[37] See reference 2, p. 738.
[38] See reference 2, Eq. (3.4).

TABLE II. Energy loss by Debye waves per collision $\Delta E/E_0=(1-\delta)^2/g(m,M)$ for threshold energies (Hg^+ ions) at normal ion incidence.

System	Element	$g(m,M)$[a]	E_{min}[b] (ev)	δ[a]	$\Delta E/E_0$
bcc	V	6.18	120	0.52	0.038
	Cr	6.11	60	0.57	0.030
	Fe	5.84	60	0.63	0.024
	Cb	4.70	120	0.55	0.042
	Mo	4.56	80	0.59	0.038
	Ta	4.08	120	0.54	0.052
	W	4.01	80	0.625	0.035
fcc	Al	9.54	120	0.45	0.032
	Ni	5.68	70	0.52	0.041
	Cu	5.46	50	0.53	0.040
	Rh	4.40	70	0.54	0.049
	Pd	4.29	50	0.51	0.056
	Ag	4.27	40	0.49	0.061
	Pt	4.0	70	0.50	0.063
	Au	4.0	40	0.53	0.055
	Pb	4.0	20	0.54	0.053
	Th	4.02	120	0.42	0.057

[a] See reference 2, Table I.
[b] Wehner (reference 8), lower values V_0*(Hg).

which is very much different from $(1-\delta)$, as has been assumed and discussed by Silsbee. The values calculated for the threshold energies of seven bcc and ten fcc metals using Hg^+ ions with the formula (18) are listed in Table II.

Silsbee[6] calculated values for several processes which in actual solids contribute to a loss of energy as the pulse propagates along a close-packed chain. He gives estimates of the loss due to the effects of (1) thermal lattice vibrations, (2) alloying or isotopic mixture, and (3) interaction with neighboring chains.

There are two effects due to the thermal vibrations, estimated with 0.0001 and 0.025, using parameters appropriate to copper at room temperature. The second effect is estimated with $\Delta E/E_0\sim 10^{-4}$. The last effect can be taken from Silsbee's curve Fig. 3 which gives for 50 ev, the threshold energy of Cu-Hg^+, determined formerly by Wehner[9] (by detection of deposits), the value of $\Delta E/E_0\sim 0.019$. All these losses together give as the total loss $\Delta E/E_0\sim 0.045$ for the threshold energy of Cu. On the other hand, the loss calculated from formula (18) above with $\delta=0.53$ and the threshold energy of $E_0=50$ ev of Cu-Hg^+ [35] gives according to Table II a loss of $\Delta E/E_0=0.040$.

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