decide whether or not they are observing the  $\beta$  phase in their experiments.

## CONCLUSIONS

The transition in solid mercury has not previously been observed at low pressures because of the rapid decrease in the transition rate as the transition pressures decrease. The overpressure needed to initiate the transition increases until at 93°K it is of the order of the transition pressure itself, and the transition can only be made to proceed irreversibly. The transition cannot be made to take place at constant pressure below 93°K because of the increased hindering effect of the potential barrier which more than offsets the increased thermal driving force furnished by undercooling. The transition can be observed in an isothermal experiment upon the increase of pressure because the large difference in molar volume between the two phases allows a great deal of effective undercooling to aid the thermal driving force. The mechanism for the phase change which was observed at 4°K must be quite different, and may be due to the shearing deformation experienced by the sample.

Certain discrepancies were observed in the density of solid mercury at zero pressure, and these led to inconsistencies in the calculated thermodynamic properties of the two phases. These discrepancies should be investigated in some detail. The structure of the new phase, as well as its other physical properties, would be of interest, also, although the temperature region in which it is stable (below 93°K), and the conditions needed to produce it make these experiments quite difficult.†

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† Note added in proof.-Dr. C. S. Barrett has informed the author (private communication) that a re-examination of the x-ray data has removed to a great extent the discrepancies in the mercury data at 78°K.

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# Analysis of Low-Energy Sputtering<sup>\*</sup>

EDWIN LANGBERGT RCA Laboratories, Princeton, New Jersey (Received November 5, 1957)

It is postulated that for low-energy sputtering the interatomic energy and distance relation can be represented by a Morse curve, and that the energy transfer in the lattice proceeds essentially by two-particle (i.e., binary) collisions.

Based on these assumptions, a two-collision sputtering mechanism near the threshold is described. Under optimum energy transfer conditions, the analysis of this process gives the ion energy for a sputtering threshold of a surface particle tied by N bonds.

It is shown further that under a prolonged ion bombardment a surface contains particles with a number of bonds N, ranging from a maximum determined by a complete surface to a minimum determined by inaccessible bonds to underlying surface layers.

#### 1. INTRODUCTION

URRENT experimental work in low-energy sput- $\checkmark$  tering<sup>1</sup> provides strong evidence that a classical collision mechanism may explain satisfactorily the observed phenomena. Two such collision theories

Based on this information, the form of the sputtering yieldenergy function is derived, consisting of a parabolic and a linear part. Predicted and experimental Pt-Hg<sup>+</sup> curves are compared, and the agreement is excellent.

Two thresholds are defined: the lower threshold is the actual intercept of the yield curve, whereas the upper threshold corresponds to the intercept of the linear part of the yield curve. The two thresholds are computed for 20 metals bombarded by the Hg<sup>+</sup> ion. The agreement with experimental values and the empirical threshold formula of Wehner is satisfactory.

recently have been proposed: one by Henschke,<sup>2</sup> and the other by the author.<sup>3,4</sup> Both theories rely basically on the description of low-energy sputtering as a series of two-particle collisions.

There are, however, important differences: Henschke<sup>2</sup> assumes that the ejecting collision is always between the deflected ion and an atom; the analysis presented here postulates a final collision between two lattice atoms. The former work<sup>2</sup> uses a rigid collision radius

<sup>\*</sup> Based on a dissertation presented to the Department of Electrical Engineering at Princeton University in partial fulfillment of the requirement for the Ph.D. degree.

<sup>†</sup> Now at Avco Manufacturing Corporation, Research and Advanced Development Division, Lawrence, Massachusetts.

An excellent review and a list of references of the theoretical and experimental work to 1955 are given by G. K. Wehner, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 239.

<sup>&</sup>lt;sup>2</sup> E. B. Henschke, Phys. Rev. 106, 737 (1957).

<sup>&</sup>lt;sup>3</sup> Edwin Langberg, Ph.D. thesis, Princeton University, April 25, 1956 (unpublished).
<sup>4</sup> Edwin Langberg, Bull. Am. Phys. Soc. Ser. II, 2, 83 (1957).

and the theory of collisions with restitution; here, a Morse curve collision interaction is presumed, and from it, both energy transfer and loss to the lattice are found.

In both cases, there appears to be a satisfactory agreement with the limited experimental data available; however, this analysis arrives at the experimental threshold values without the use of adjustable constants.

# 2. BASIC ASSUMPTIONS

This paper describes a particle collision model for sputtering applicable when the energy of the bombarding ion is at most a few times higher than the threshold energy. Based on this model, the sputtering yield and the sputtering threshold are evaluated.

A basic element in the investigation of transport of energy resulting from the ion impact is the coupling between lattice particles of the bombarded solid. Since the bulk of experimental work on sputtering involves metal targets, the characteristic of the metallic lattice bond is of special interest.

The simplest model of a bond is the rigid sphere. It has the disadvantages of somewhat arbitrary choice of the sphere radius and lack of provision for changes of radius with energy. The linear "spring" model is applicable only at considerably lower energies than those encountered in even low-energy sputtering

Next to the rigid sphere and linear "spring" models, one of the simplest bond models is the Morse curve. Its use for the metallic bond has been suggested by Slater.<sup>5</sup>

When the equilibrium energy U(d) = 0, the curve is defined as:

$$U(r) = \varphi \{ \exp[a(d-r)] - 1 \}^2, \qquad (1)$$

where U(r) is the potential energy as a function of distance r,  $\varphi$  is the energy required to break the bond, d is the equilibrium spacing, and a is a lattice parameter related to compressibility. Fortunately, the analysis presented here does not depend critically on the bond energy functions, and hence, it is believed that the description of the metallic bond energy by the Morse potential is sufficiently accurate.

Motion in a medium of many particles is generally a collective phenomenon, involving continuous and simultaneous interaction of many particles. In some special cases, motion in a many-particle system can be approximated by a series of consecutive two-particle (i.e., binary) collisions. Then in each collision, the energy and momentum of the colliding particles are conserved. Their trajectories can be computed from the initial conditions independently of the motion of the rest of the system. The condition of applicability of the consecutive binary-collision approximation is that the collision be completed before the two colliding particles interact with other particles. To test the applicability of this approximation to the motion of the lattice atoms in the case of low-energy sputtering, an equation of motion for a one-dimensional lattice coupled by Morse curve bonds was set up.<sup>3</sup> This problem reduces to a system of nonlinear differential equations which was solved for the initial conditions, corresponding to a typical situation in low-energy sputtering. From the outcome, the binary-collision approximation between free particles is considered reasonable, provided that the correction is included for the binding energy which has to be dissipated to "free" the particles.

#### 3. MODEL OF SPUTTERING AT NORMAL ION INCIDENCE

A single collision by an ion<sup>6</sup> incident normal to the surface cannot account for sputtering because the recoiling atom cannot clear the surface. Hence, at least two collisions are required to case sputtering: one collision is between the neutralized ion and the first surface particle; and the second collision is between the struck first surface particle and its surface neighbor, or between the recoiling ion and another surface particle.<sup>2</sup> Clearly, processes which involve more than two collisions cannot be excluded; e.g., a three-collision process is described by Henschke.<sup>2</sup> The processes with higher collision number involve longer paths and higher dissipation, and hence, require higher energies. For this reason, in the study of thresholds at normal ion impact, the analysis is limited to a two-collision process.

The model evaluated here, and shown in Fig. 1, consists of the ion of mass M colliding with a surface particle  $m_1$ , followed by a collision of particle  $m_1$  with another surface particle  $m_2$ . The two collisions between the three particles are considered at first as consecutive binary collisions between free particles.

The evaluation of the energy transfer in the first collision is straightforward since it is assumed that the recoil angle of the originally stationary particle is known. The collision geometry, as shown in Fig. 1, and the energy and momentum conservation laws determine the maximum potential energy stored in the second collision:

$$U(R) = \frac{m_2}{m_1 + m_2} \eta_1 E \cos^2 \alpha \left( 1 - \frac{d^2 \cos^2 \alpha}{R^2} \right), \qquad (2)$$

where E is the initial ion kinetic energy,  $\eta_1 = 4Mm_1/(m_1+M)^2$ , and R is the distance of closest approach between lattice particles  $m_1$  and  $m_2$ .

To optimize the energy transfer conditions with respect to the recoil angle, set

$$\partial U(R)/\partial \cos^2 \alpha = 0,$$
 (3)

which gives the required angle  $\alpha_1$ 

$$\cos^2\alpha_1 = R^2/2d^2.$$
 (4)

<sup>&</sup>lt;sup>5</sup> J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), Chap. 27.

<sup>&</sup>lt;sup>6</sup> The ion very likely becomes neutralized before reaching the surface. The term ion, as used here, implies the impinging particle.



FIG. 1. Collision model for sputtering at normal ion incidence; (a) shows a (110) cut in full (001) surface in an fcc metal. The details of the sputtering collision are shown in (b).

Hence, under optimum conditions of recoil,

$$\bar{U} \equiv U(R) \big|_{\alpha = \alpha_1} = \frac{m_2 \eta_1 E R^2}{4(m_1 + m_2) d^2}.$$
 (5)

It should be pointed out that in the differentiation used above, R is considered independent of  $\alpha$ . This is not rigorously true; however, most interatomic potential models show on compression a rapid increase of potential energy with distance R. For a given metal and energies corresponding to a sputtering threshold, the approximation  $\partial R/\partial \alpha \simeq 0$  is justified. It can be shown<sup>3</sup> that the kinetic energy  $K_2$  acquired by the second surface particle under optimum conditions is related to the peak potential energy by

$$K_2 = 2\bar{U}(R)m_1/\gamma(m_1 + m_2). \tag{6}$$

The value of  $\gamma$  depends on the function U(r). It is shown<sup>3</sup> that, under typical low-energy sputtering conditions,  $\gamma$  is approximately constant:  $\gamma = 0.63$ .

So far the computation has been carried out on the assumption of two collisions between three *free* particles; it remains now to include the effects of binding.

To sputter the second surface particle, tied by N bonds of energy  $\varphi$ , requires an escape energy somewhat higher than the binding energy  $N\varphi$ . This increase, by a factor which we call  $\sigma$ , is due to some transfer of kinetic energy to the neighboring atoms during the second collision. The evaluation of  $\sigma$  by the perturbation method<sup>3</sup> gives, for the conditions of interest,  $\sigma \simeq 1.1$ .

Another correction which has to be included is the result of the binding of the first particle. To "free" the first particle, its binding energy, on the average equal to the sublimation energy H, has to be supplied by the ion. Based on conservation laws and known recoil angle  $\alpha$ , the additional ion energy required to "free" the first particle is

$$E' = H/\eta_1 \cos^2 \alpha. \tag{7}$$

Upon using the condition of optimum recoil in Eq. (4),

$$E' = 2Hd^2/\eta_1 R^2.$$
 (8)

This process implies only motion of the first particle  $m_1$  within the lattice; direction of momentum imparted to  $m_1$  is such that it cannot sputter.

Hence, the ion energy at the threshold of sputtering consists of a component E' required to "free" the first particle, added to the component necessary to sputter the second particle E''. The latter is obtained by setting the right-hand side of Eq. (6) equal to  $\sigma N \varphi$ , using Eq. (5), and noting that  $H = n\varphi/2$ :

$$E'' = 16HNd^2\gamma\sigma/n\eta_1\eta_2R^2, \qquad (9)$$

where  $\eta_2 = 4m_1m_2/(m_1+m_2)^2$ , and *n* is the number of nearest neighbors.

The ratio R/d can be determined now from the known peak potential energy  $[K_2=N\varphi\sigma$  in Eq. (6)] and the Morse potential function, Eq. (1):

$$\frac{R}{d} = 1 - \frac{1}{ad} \ln \left\{ 1 + \left[ \frac{N \sigma \gamma (m_1 + m_2)}{2m_1} \right]^{\frac{1}{2}} \right\}.$$
 (10)

Equations (8) and (9) together with (10) specify the threshold energy  $E_N$  for a lattice atom tied by N bonds. For a lattice consisting only of one element, we have  $m_1=m_2, \eta_2=1$ ; using the numerical values for  $\gamma$  and  $\sigma$ , we obtain

$$E_N = \frac{10H}{\eta_1} \left( 1.1 \frac{N}{n} + 0.2 \right) \left[ 1 - \frac{1}{ad} \ln(1 + 0.83N^{\frac{1}{2}}) \right]^{-2}.$$
 (11)

The lattice parameters for various elements are given in Table I.

The derivation of the sputtering threshold in Eq. (11) is based on the optimum energy transfer conditions. From the known transfer of kinetic energy, the angles  $\alpha$  and  $\beta$  can be evaluated. It can be shown<sup>3</sup> that, under these circumstances, the recoil direction is above the plane of the surface (Fig. 1,  $\delta > 0$ ), and so, the particle can escape without further collisions.

It should be emphasized that the angle  $\delta$  refers to the hypothetical situation after the particle reaches its full kinetic energy, but before the kinetic energy is dissipated in breaking of the bonds. Hence, the final escape direction depends not only on the angle  $\delta$  but also the number and position of the neighboring particles.

Metal	$H^{\mathrm{a}}$	$m^{\mathrm{b}}$	d°	k°	ad	ad	$(ad)^{-2}$				
Face-centered cubic, $n = 12$											
Al	3.252	26.96	2.858	22.14	1.129	3.227	0.09603				
Ni	4.413	58.69	2.487	48.9	1.440	3.582	0.07794				
Cu	3.557	63.54	2.551	36.9	1.394	3.556	0.07908				
$\mathbf{Rh}$	5.986	102.91	2.684	77.43	1.556	4.177	0.05732				
$\mathbf{Pd}$	4.034	106.7	2.745	54.1	1.585	4.350	0.05285				
Ag	3.036	107.9	2.883	30.4	1.369	3.948	0.06416				
Pt	5.856	195.2	2.769	80.0	1.600	4.429	0.05098				
Au	3.925	197.2	2.878	51.9	1.574	4.529	0.04875				
$\mathbf{Pb}$	2.016	207.2	3.492	15.31	1.193	4.164	0.05767				
II and a later product of 12											
		Hexago	onal clos	е-раскес	n, n = 12						
Ti	4.919	47.90	2.934	38.3	1.208	3.543	0.07966				
Co	4.554	58.94	2.503	48.4	1.411	3.531	0.08021				
Zr	5.422	91.22	3.195	30.3	1.023	3.269	0.09358				
$\mathbf{H}\mathbf{f}$	7.374	178.6	3.170	36.6	0.964	3.056	0.10708				
Body centered cubic $n = 8$											
37	5 205	5005	2 627	72 2	1 2 2 6	2 102	0 00212				
Č.,	3.203	50.95	2.027	13.3	1.520	J.40J	0.08243				
Cr E	3.007	52.01	2.493	72.26	1.007	2 645	0.03792				
Ch	7 617	02.05	2.470	85.0	1 1 1 2 0	3 3 6 8	0.07372				
Mo	6 765	92.91	2.833	128	1 537	1 1 2 1	0.05721				
To	8 675	180.0	2.720	101	1 206	3 441	0.03721				
W	8 745	183.0	2.004	146	1 444	3 048	0.06416				
**	0.745	100.9	2.700	140	1.111	5.740	0.00110				
Diamond, $n=4$											
Si	3.910	28.06	2.346	142	1.507	3.535	0.0804				
Ge	3.398	72.60	2.445	117.7	1.470	3.594	0.0776				

TABLE I. Atomic constants for metals.

 <sup>a</sup> H = heat of sublimation at 298°K, in ev. Computed from L. L. Quill, The Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics (McGraw-Hill Book Company, Inc., New York, 1950), first edition, p. 13.
 <sup>b</sup> Atomic weights, Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1950–1), thirty-second edition, p. 301.
 <sup>c</sup> J. Wasser and L. Pauling, J. Chem. Phys. 18, 747 (1950); d = closest neighbor spacing in A, and k = atomic spring constant in kilodynes/cm.
 <sup>d</sup> Morse potential constant in A<sup>-1</sup>, computed by Langberg.<sup>3</sup>

#### 4. NUMBER OF BONDS OF A SURFACE PARTICLE

Information about the number of particle bonds N is required to use the threshold equations derived in Sec. 3. The evaluation of number of bonds N is relatively simple when an ideal low-index crystal plane is considered, but under actual environmental conditions, it is considerably more involved:

Firstly, most sputtering experiments are done with polycrystalline materials, and thus, the orientation of the crystallites varies over the surface.

Secondly, even in a case of a single-crystal surface after prolonged ion bombardment, many surface particles are removed or knocked into interstitial positions.

Thus, the probability of finding surface atoms with adjacent surface vacancies or with distorted bonds is high. It will be noted that the probability of breaking particle bonds in the primary collision is much higher, and the energy threshold lower, than that corresponding to sputtering in the secondary collision. Hence, bombardment with ions of energy even less than the sputtering threshold energy may lead to formation of surface imperfections.

It appears from these considerations that the distribution of the number of surface bonds N is not specified uniquely by the target material, but depends to a large extent on the treatment of the surface. Specifically, the same distribution is not expected at the beginning of the sputtering process and after sputtering has continued for some time. The breaking up of the surface must be especially thorough when the surface is "cleaned off" by high-energy ion bombardment before the measurement.

The discussion here will be limited to the case of a clean surface after sputtering has been continued for a sufficiently long time, so that the distribution of N reaches an equilibrium value. In the discussion of such a surface stabilized by prolonged ion bombardment, it is convenient to distinguish between bonds to other surface particles (accessible bonds  $N_0$ ) and bonds to particles in the underlying first or second surface layer (inaccessible bonds  $N_1$ ,  $N_2$ ).

When as a result of sputtering of a region, a fresh surface is exposed, the number of bonds in that region is equal to the full number of bonds  $N_{a}$ ,

$$N_a = N_0 + N_1 + N_2. \tag{12}$$

When the region is bombarded further, the accessible surface particles are removed one by one until finally, the last particle of this particular surface layer is sputtered by a collision with its remaining surface neighbor. The number of bonds holding the latter particle is equal to the number of inaccessible bonds plus one bond belonging to its colliding surface neighbor:

$$N_b = N_1 + N_2 + 1. \tag{13}$$

Hence, under prolonged ion bombardment, the largest number of bonds holding a surface particle corresponds to the full surface  $(N_a)$ , and the smallest number is  $N_b$ .

The number of bonds to different surface layers is given in Table II. In experiments performed with polycrystalline samples, where no information is available on the orientation of the crystallites, the numbers  $N_a$  and  $N_b$  will be chosen from the surface orientation in Table II which gives the largest and

TABLE II. Number of bonds to different surface layers.

	Fcc			Hcp	Bcc		Diamond				
	(100)	(110)	(111)	(112)	0001	(100)	(110)	(111)	(100)	(110)	(111)
$N_0$	4	2	6	2	6	0	4	0	0	2	0 0
$N_1$	4	4	3	3	3	4	2	3	2	1	3 1
$N_{2}$		1		2				1			

smallest number, respectively. The results are given in Table III.

# 5. SPUTTERING YIELD CURVE AT LOW ION ENERGIES

To compare theoretical predictions with experimental results, an expression for the sputtering yield as a function of ion energy is derived. Sputtering yield S is defined as the average number of sputtered particles per incident ion. More specifically, sputtering yield from particles tied by N bonds is defined as  $S_N$ .

It is shown<sup>3</sup> that based on probability considerations,  $S_N$  is a linear function of the excess of ion energy over the threshold energy  $E_N$ .

$$S_N = P_N(E - E_N) \quad \text{for} \quad E > E_N, \qquad (14.1)$$

$$S_N = 0 \qquad \text{for} \quad E < E_N, \qquad (14.2)$$

where under the given conditions  $P_N$  is a constant.

It was pointed out in Sec. 4 that a surface stabilized by prolonged ion bombardment contains particles with a number of bonds ranging from  $N=N_b$  to  $N=N_a$ .

The yield from such a composite surface is a sum over N of individual  $S_N$ 's from  $N = N_b$  to  $N = N_a$ :

$$S = \sum_{N=N_{a}}^{N=N_{b}} P_{N}(E - E_{N}).$$
(15)

The highest and the lowest threshold energies corresponding to  $N_a$  and  $N_b$  are defined as  $E_a$  and  $E_b$ . Within the general accuracy of this analysis, it makes little difference if the summation over the discrete variable in Eq. (15) is replaced by integration over a continuous variable  $E_N$ .

$$S = \int_{E_b}^{E_a} P(E_N) (E^{\bullet} - E_N) dE_N.$$
(16)

It is assumed that, because of randomness of the surface, the probability  $P(E_N)$  of finding a particle with a sputtering threshold  $E_N$  is constant in the range

$$E_b \leq E_N \leq E_a:$$

$$P(E_N) = b \quad \text{for} \quad E_b \leq E_N \leq E_a, \quad (17.1)$$

$$P(E_N) = 0 \quad \text{elsewhere.} \quad (17.2)$$

Combining Eqs. (16) and (17) gives the required sputtering yield function:

$$S=0 for E < E_b, (18.1) S=\frac{1}{2}b(E-E_b)^2 for E_b \le E \le E_a, (18.2) S=b(E_a-E_b)[E-\frac{1}{2}(E_a+E_b)] for E > E_a. (18.3)$$

The result obtained in Eqs. (18) is compared with experimental values of sputtering yield from Pt in Hg discharge obtained by Wehner.<sup>1</sup>

It will be noted that Pt has a fcc lattice, so that n=12,  $N_a=9$ , and  $N_b=4$ . Using the values of H and (ad) from Table I gives:  $E_b=E_4=54.7$  ev,  $E_a=E_9=116$  ev. The yield under these conditions is plotted in Fig. 2.



FIG. 2. Sputtering yield curve for Pt-Hg+.

The experimental points are plotted on the same graph; the constant b in Eqs. (18) has been chosen for best fit.

It will be noted that both the curvature and the threshold of the sputtering yield curve are independent of the choice of b. Hence, the satisfactory agreement between the experimental and the theoretical points in Fig. 2 is significant even though Eqs. (18) contain an adjustable parameter b.

#### 6. COMPARISON OF PREDICTED AND MEASURED SPUTTERING THRESHOLDS

Figure 2 shows a certain ambiguity in the definition of the experimental sputtering threshold. There are two possibilities for correcting this ambiguious situation: one possibility is to define the threshold  $E_T$  as the intercept of the extrapolated linear part of the sputtering curve. From Eq. (18.3),

$$E_T = \frac{1}{2} (E_a + E_b). \tag{19}$$

The other possibility is to define the threshold at the actual start of the yield curve, in which case the threshold energy is equal to  $E_b$ .

Wehner<sup>7</sup> has performed sputtering threshold measurements for many metals in a Hg arc discharge. In

TABLE III. Number of lattice bonds.

Lattice	n	$N_a$	Nb	
fcc	12	9	4	
hcp	12	9	4	
bcc	8	6	3	
diamond	4	3	2	

<sup>7</sup> G. K. Wehner, Phys. Rev. 93, 633 (1954).

Metal  $1/\eta_{1}$  $H/\eta_1$  $E_a$  $E_b$  $E_T$ Experimental<sup>a</sup> fcc Al 2.393 7.782 213 90.8 152115-135 Ni 1.428 6.302 152 67.6 110 65-85 45-65 Cu 1.368 4.866 118 52.5 85.5 Rh Pd 1.116 6.680 139 64.5 102 65–75 1.103 4.449 89.8 42.065.9 45-75 Âg Pt 1.099 3.337 73.2 33.4 53.3 35-45 1.0005.856 116 54.7 85.6 65-85 Au Pb 3.925 1.00076.6 36.2 56.535 - 4515-35 1.000 2.01642.219.5 30.9 hcp Ti 1.607 7.904 193 85.5 139 105-125 70.3 72.8 115 121 75–95 115–125 Co 1.424 6.485159 Zr Hf 1.163 6.306 169 1.003 7.396 217 90.7 153 145 - 175bccv 1.548 8.057 178 89.0 134 115-125 Ċr 1.529 5.607 107 55.7 81.4 55 - 75Fe 1.468 66.2 98.6 55-65 6.156 131 Cb 1.156 8.805 201 99.8 150 115-125 Mo 1.142 7.725 147 76.5 112 75-95 1.003 8.700 194 97.1 Та 146 115-135 W 1.002 8.763 174 89.5 132 75-95

TABLE IV. Sputtering thresholds for Hg ion.

<sup>a</sup> See Wehner.<sup>7</sup>

private communication,<sup>8</sup> he explained that the values quoted in his paper lie somewhere between  $E_b$  and  $E_T$  as defined above.<sup>9</sup> Using Eq. (11) and the values of  $E_a$  and  $E_b$  defined in Sec. 5, the thresholds for 20 metals have been computed and compared with Wehner's experimental results. The results are presented in Table IV.

It can be seen that the agreement is satisfactory: out of 20 metals examined, only 1 metal (Fe) falls fully outside the predicted threshold range. Considering the experimental accuracy and the accuracy of the analysis used, the agreement for the 19 metals is as close as can be expected.<sup>10</sup>

TABLE V. Values of  $A_i$  and  $B_i$ .

Lattice	Aa	Аь	$A_T$	Ba	$B_b$	$B_T$
fcc and hcp	11.58	6.92	9.25	162	48.0	105
bcc	11.6	7.3	9.45	128	46	87

<sup>8</sup> G. K. Wehner (private communication).

<sup>9</sup> Wehner's result includes a correction equal to the difference between the ionization energy and the work function. Since the need for the correction is doubtful,<sup>1,3</sup> it will be subtracted again from his threshold values. The correction amounts to about 5 volts, so that experimental threshold ion energy will be obtained from results quoted<sup>7</sup> by subtracting 5 ev. In case of Pt, the quoted values for threshold are from 70 to 90 ev, the corrected values are 65-85 ev, and the computed values 55-86 ev.

<sup>10</sup> It will be noted that even though the experimental results for Si and Ge are available, no attempt has been made to compute the threshold for these semiconductors. A fundamental assumption in this analysis is that the interatomic forces are central; i.e., that the force is a function of interatomic distance only. It is well known that the Ge and Si bonds are strongly directive, so the central force approximation is much worse than in metals. It remains now to compare the empirical sputtering threshold law due to Wehner<sup>7</sup> with the threshold law predicted in this analysis.

It can be shown<sup>3</sup> that, if the velocity of sound used by Wehner<sup>7</sup> is replaced by the lattice parameter (ad), Wehner's empirical formula becomes

$$E = CH/\eta_1 a^2 d^2, \tag{20}$$

where C=187 for fcc and hcp lattices, and C=167 for bcc lattice.

For comparison, it is convenient to plot the three thresholds defined before as a function of the lattice parameter  $(ad)^{-2}$ . In the range of interest, the thresholds are given very closely by an approximate equation

$$E_i = \frac{H}{\eta_1} \left[ A_i + \frac{B_i}{(ad)^2} \right], \tag{21}$$

where the subscript i denotes the required threshold, and the constants  $A_i$  and  $B_i$  are listed in Table V.

Equations (20) and (21) are plotted in Figs. 3 and 4. Figures 3 and 4 show very good agreement between the threshold values computed in this analysis and both the Wehner empirical formula and his experimental results. The main difference between the empirical formula and the derived law is that the first specifies some kind of an average between the two thresholds, whereas the second actually specifies  $E_b$  and  $E_T$ . Considering this conceptual difference, the two formulations agree as closely as can be expected. As for agreement with the experimental values, it will be noted that out of the twenty metals examined, seventeen metals fall mainly within the computed interval, two (Hf and W) fall partially within this interval, and only one (Fe) lies outside.

#### 7. DISCUSSION

The reliable experimental data on low-energy sputtering are at present very limited. The agreement between theoretical and experimental results alone can be considered hardly sufficient evidence for validity of the model proposed here.



FIG. 3. Normalized threshold energy for Hg ion, fcc and hcp structure.



Therefore, it may be appropriate to discuss in some detail the basic assumption of the model: the key question is the "effective mass" of a lattice atom in collision with an ion. If the effect of lattice binding is small, the collision will be expected to be essentially as between free particles and the "effective mass" of the lattice particle will be equal to its actual mass. On the other hand, if the binding with the neighbors is tight, an ion colliding with a lattice will behave as though colliding with a particle of large "effective mass."<sup>2</sup> These two are the asymptotic solutions to the motion of a periodic coupled structure represented by the lattice.

The actual solution of the general three-dimensional nonlinear lattice is quite involved. However, a problem of one-dimensional lattice of particles coupled by Morse curve-type "springs" is manageable. It has been solved<sup>3</sup> for typical low-energy sputtering conditions: a copper ion approaching with kinetic energy of about 30 ev and colliding with copper lattice.

The results are shown in Fig. 5; there is no evidence of large "effective mass" as assumed by Henschke.<sup>2</sup> On the contrary, a free-particle-collision model appears a



FIG. 5. Motion in a one-dimensional lattice coupled by Morsecurve-type forces; distance is normalized with respect to the Morse-curve constant  $q_i = ax_i$  and the normalized time is  $r = ta(\varphi/m)^{\frac{1}{2}}$ .

more suitable approximation. Accordingly, it seems reasonable to presume that the same approximation will be valid in a three-dimensional lattice for conditions typical of low-energy sputtering.

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