

ON THE ENERGY DISTRIBUTION OF SPATTERED CLUSTERS

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Our previous model on dimer sputtering is extended to the formation of larger clusters. The general formalism for the calculation of the momentum distribution function of these clusters is given. A simple analytical expression is obtained for the distribution function of any cluster in the high energy limit. Comparison of this expression with experimental data on the energy and angle distribution of W_k^+ clusters at high energies shows good agreement. The experimental results on K_2 and KI sputtering with low energies are recompared with the theory. For the ionic crystal KI, evidence is obtained that sputtering of non adjacent K and I atoms from the lattice gives an important contribution to dimer formation. The role of the binding energy E_b of the particles with respect to the surface is discussed.

1 INTRODUCTION

In a previous paper¹ (referred to as I in the following), we considered a simple model for the description of dimer formation during sputtering from solid targets. Since the results of this model compare rather favourably with experiment,¹ it makes sense to extend this theory to the formation of higher clusters. In the present paper the generalized formalism is given for the calculation of the energy distribution of sputtered k -particle clusters. For the high energy limit, a simple analytical expression is obtained for the energy distributions of k -particle clusters. The high energy experimental results on W_k^+ clusters, sputtered from tungsten surfaces, are found to be well described by this expression.

During the course of these calculations it was found that the original formula of the energy distributions of dimers, as presented in I, contained an error which urges a recomparison with experimental results. In the present paper the correct dimer formula is given, which also is found to give agreement with the experiments.

2 THE MECHANISM OF CLUSTER SPATTERING

In this section the formulation of the mechanism as given in I, is generalized for k -particle cluster sputtering. The basic assumptions are then:

- 1) Particles belonging to a single collision cascade leave the surface at the same time t_0 .
- 2) The constituent particles of a cluster originate from the same collision cascade. A set of k particles

located at $x_1, x_2 \dots x_k$ on the surface will form a cluster if at the initial time t_0 the sum of the total potential energy $V(x_1 \dots x_k)$ and the relative kinetic energy $\epsilon^{(k)}$ of the k particles does not exceed the threshold for any dissociation channel of the cluster $\epsilon_{\text{diss}}^{(k)}$:

$$\epsilon^{(k)} + V(x_1 \dots x_k) \leq \epsilon_{\text{diss}}^{(k)} \quad (2.1)$$

3) The formation of clusters with more than k particles is excluded.

4) Particles belonging to a certain collision cascade are initially uncorrelated. Thus the momentum distribution function of any k -particle cluster factorizes at time t_0 into a product of one-particle functions.

In the following dS/dE denotes the probability density for a particle to be sputtered with energy E and in the solid angle Ω , dS/dV the probability density to be sputtered with velocity V and in the solid angle Ω and $\phi(P)$ the probability density to be sputtered with momentum P . Using the relations $\phi(P)dP = \phi(P, \Omega)P^2 dPd\Omega = dS/dE dEd\Omega = dS/dV dVd\Omega$ it follows that

$$\phi(P) = M^{-1}P^{-2} dS/dV = M^{-1}P^{-1} dS/dE \quad (2.2)$$

$$(E = \frac{1}{2} MV^2, P = MV)$$

where M is the mass of the sputtered cluster. In order to be able to perform numerical calculations, an additional assumption will be made:

5) The initial one particle energy and angle distribution functions mentioned under 4 are of the form

$$dS/dE = C_j E(E + E_b^{(j)})^{-(n_j+1)} f_j(\Omega) \quad (2.3)$$

where $E_b^{(j)}$ is the binding energy of an atom of species j with respect to the surface, n_j is a constant, C_j a normalization factor and $f_j(\Omega)$ the angular distribution of the sputtered atoms.^{2,3}

In many cases condition (2.1) excludes the formation of a k particle cluster if these k particles are initially not neighbours. This is due to the circumstance that usually $V(x_1 \dots x_k)$ is close to zero for such a set of particles, whereas $\epsilon^{(k)}$ is always positive and $\epsilon_{\text{diss}}^{(k)} \leq 0$. For small clusters formed from neighbouring particles it often makes sense to approximate $E_d = \epsilon_{\text{diss}}^{(k)} - V(x_1 \dots x_k)$ by the lowest dissociation energy $E_d^{(g)}$ of the cluster in the gasphase. In general however, $E_d \leq E_d^{(g)}$. Thus condition (2.1) can be rewritten as

$$\epsilon^{(k)} \leq E_d \leq E_d^{(g)} \quad (2.4)$$

In the present paper the momentum distributions $\phi^{(k)}(\mathbf{P})$ of k -particle clusters will be calculated explicitly. From this, one obtains the energy distributions dS/dE and the velocity distribution dS/dV easily with (2.2).

3 CALCULATION OF CLUSTER DISTRIBUTION FUNCTIONS

3.1 General Formalism and Dimer Formula

The calculation of the distribution function for clusters proceeds along the same line as described in I, section 3. Consider a cluster to be built up from two sub-clusters 1 and 2. Let ϵ_j be the relative kinetic energy of the particles in subcluster j at time t_0 at which the subclusters leave the surface. Then, the normalized probability density for these clusters to have relative kinetic energy ϵ_{12} and centre-of-mass momentum \mathbf{P} is given by

$$\begin{aligned} \phi_{12}(\mathbf{P}, \epsilon_{12}, \epsilon_1, \epsilon_2) = & \int d\mathbf{p}_1 \int d\mathbf{p}_2 \phi_1(\mathbf{p}_1, \epsilon_1) \phi_2(\mathbf{p}_2, \epsilon_2) \\ & \cdot \delta(\epsilon_{12} - E_{\text{rel}}) \delta(\mathbf{P} - \mathbf{P}_{\text{cm}}) \end{aligned} \quad (3.1.1)$$

where \mathbf{p}_j is the total momentum vector of sub-cluster j , and $\phi_j(\mathbf{p}_j, \epsilon_j)$ the normalized momentum and initial internal energy distribution function for sputtered subclusters of species j . The relative kinetic energy is given by

$$E_{\text{rel}} = \frac{1}{2} \mu (\mathbf{p}_1/m'_1)^2 - (\mathbf{p}_2/m'_2)^2,$$

in which m'_j is the mass of subcluster j and $\mu = m'_1 m'_2 / (m'_1 + m'_2)$ the reduced mass of the system. The transformation to centre of mass and relative variables is given by

$$\mathbf{P}_{\text{cm}} = \mathbf{p}_1 + \mathbf{p}_2, \quad \mathbf{p} = (\mathbf{p}_1/m'_1 - \mathbf{p}_2/m'_2) \quad (3.1.2)$$

The transformation in I, (3.2) second formula is not allowed since it contains a factor M^{-1} instead of M^{-3} . In these variables, $\phi_{12}(\mathbf{P}, \epsilon_{12}, \epsilon_1, \epsilon_2)$ can be written as

$$\begin{aligned} \phi_{12}(\mathbf{P}, \epsilon_{12}, \epsilon_1, \epsilon_2) = & \int d\mathbf{P}_{\text{cm}} \int d\mathbf{p} \phi_1((m'_1/M)\mathbf{P}_{\text{cm}} + \\ & \mathbf{p}, \epsilon_1) \phi_2((m'_2/M)\mathbf{P}_{\text{cm}} - \mathbf{p}, \epsilon_2). \end{aligned}$$

$$\begin{aligned} \delta(\epsilon_{12} - p^2/2\mu) \delta(\mathbf{P}_{\text{cm}} - \mathbf{P}) = & 2\mu \int d\mathbf{p} \phi_1(q_1\mathbf{P} + \mathbf{p}, \epsilon_1) \\ & \phi_2(q_2\mathbf{P} - \mathbf{p}, \epsilon_2) \cdot \delta(p^2 - 2\mu\epsilon_{12}) \end{aligned}$$

in which

$$q_j = m'_j / (m'_1 + m'_2) \equiv m'_j / M.$$

After some manipulations, described in I chapter 3, and introducing

$$\zeta = (2\mu\epsilon_{12})^{1/2}, \quad \text{and } \mathbf{p} = p\mathbf{u},$$

\mathbf{u} being the unit vector along \mathbf{p} , this reduces to

$$\begin{aligned} \phi_{12}(\mathbf{P}, \epsilon_{12}, \epsilon_1, \epsilon_2) = & \mu\zeta \int d\mathbf{u} \phi_1(q_1\mathbf{P} + \\ & \zeta\mathbf{u}, \epsilon_1) \phi_2(q_2\mathbf{P} - \zeta\mathbf{u}, \epsilon_2) \end{aligned} \quad (3.1.3)$$

For *dimer* formation, $\phi_j(\mathbf{p}_j, \epsilon_j)$ are the distribution functions of the atoms $\phi_j^{(1)}(\mathbf{p}_j)$, for which of course $\epsilon_j = 0$. The normalized dimer distribution $\phi^{(2)}(\mathbf{P})$ is then obtained from (3.1.3) by integration over ϵ_{12} from zero under condition (2.4):

$$\phi^{(2)}(\mathbf{P}) \equiv \phi_{12}(\mathbf{P}) = \int_0^\infty d\epsilon_{12} \phi_{12}(\mathbf{P}, \epsilon_{12}) h(E_d - \epsilon_{12}) \quad (3.1.4)$$

where the Heaviside step function $h(E_d - \epsilon_{12})$ fixes ϵ_{12} in the bounded interval $[0, E_d]$. Thus

$$\begin{aligned} \phi^{(2)}(\mathbf{P}) = & \int_0^{E_d} d\epsilon_{12} \phi_{12}(\mathbf{P}, \epsilon_{12}) = \\ & (2\mu E_d)^{1/2} \int_0^1 d\zeta \zeta^2 \int d\mathbf{u} \phi_1^{(1)}(q_1\mathbf{P} + \zeta\mathbf{u}) \phi_2^{(1)}(q_2\mathbf{P} - \zeta\mathbf{u}) \end{aligned} \quad (3.1.5)$$

with $m'_j \equiv m_j$, the atomic mass of particle j . According to assumption V using (2.2) one has for $f(\Omega) = \cos \theta$ (θ is the angle with the surface normal \mathbf{e})

$$\phi_j^{(1)}(\mathbf{p}_j) = N_j (\mathbf{p}_j \cdot \mathbf{e}) h((\mathbf{p}_j \cdot \mathbf{e})) \cdot (p_j^2 + L_j)^{-(n_j+1)} \quad (3.1.6)$$

and

$$N_j = 2n_j(n_j - 1)L_j^{n_j-1}/\pi, \quad L_j = 2m_j E_b^{(j)} \quad (3.1.7)$$

As in I, the dimer distribution function $\phi^{(2)}(P, \theta)$ then becomes

$$\begin{aligned} \phi^{(2)}(P, \theta) = N_1 N_2 & \int_0^{(2\mu E_d)^{1/2}} d\xi \cdot \xi^2 \int_0^{2\pi} d\psi \cdot \\ & \int_{-\min(1, q_1 P \cos \theta / \xi)}^{+\min(1, q_2 P \cos \theta / \xi)} dz \\ & \cdot (q_1 P \cos \theta + \xi z)(q_2 P \cos \theta - \xi z) \\ & \cdot [q_1^2 P^2 + \xi^2 + 2q_1 P \xi \{\sin \theta (1 - z^2)^{1/2} \sin \psi + z \cos \theta\} \\ & \quad + L_1]^{-(n_1+1)} \\ & \cdot [q_2^2 P^2 + \xi^2 - 2q_2 P \xi \{\sin \theta (1 - z^2)^{1/2} \sin \psi + z \cos \theta\} \\ & \quad + L_2]^{-(n_2+1)} \end{aligned} \quad (3.1.8)$$

which reduces for $\theta = 0$, (i.e. sputtering of dimers in the normal to the surface) to

$$\begin{aligned} \phi^{(2)}(P, 0) = 2\pi N_1 N_2 & \int_0^{(2\mu E_d)^{1/2}} d\xi \cdot \xi^2 \int_{-\min(1, q_1 P / \xi)}^{+\min(1, q_2 P / \xi)} dz \\ & \cdot (q_1 P + \xi z)(q_2 P - \xi z) [q_1^2 P^2 + \xi^2 + 2q_1 P \xi z + L_1]^{-(n_1+1)} \\ & \quad [q_2^2 P^2 + \xi^2 - 2q_2 P \xi z + L_2]^{-(n_2+1)} \end{aligned} \quad (3.1.9)$$

The energy distribution dS/dE and the velocity distribution dS/dV for dimers are found with formula (2.2). In I, this analogous transformation has erroneously not been made. As a result of both these corrections (see also formula (3.1.2)), the present result for dS/dV for dimers contains a factor $M^2 V^2$ which did not appear in the previous result in I.

The asymptotic behaviour of $\phi^{(2)}(P, \theta)$ for P tending to zero and infinity is derived in the same way as in I, chapter 3.2, and results in

$$\phi^{(2)}(P, \theta)_{P \rightarrow \infty} \sim (4\pi/3) \cdot N_1 N_2 \cdot q_1^{-(2n_1+1)} q_2^{-(2n_2+1)} \cdot (2\mu E_d)^{3/2} \cdot P^{-2(n_1+n_2+1)} \cos^2 \theta$$

$$\phi^{(2)}(P, \theta)_{P \rightarrow 0} \sim 2\pi N_1 N_2 (\frac{1}{2} q_1 q_2^2 + \frac{1}{2} q_1^2 q_2 + 1/6 q_1^3 + 1/6 q_2^3).$$

$$\int_0^{(2\mu E_d)^{1/2}} d\xi \cdot \xi [\xi^2 + L_1]^{-(n_1+1)} [\xi^2 + L_2]^{-(n_2+1)} P^3 \cos^3 \theta \quad (3.1.10)$$

so that the dimer energy distribution dS/dE behaves as follows: it starts from zero proportional to E^2 , passes through a maximum and falls off to zero at higher energy as $E^{-n_1-n_2-0.5}$.

3.2 High Energy Distribution Function for a k -Particle Cluster

The formalism developed in chapter 3.1 allows the calculation of the distribution function of any k -particle cluster. The cluster distribution function $\phi_{12}(P, \epsilon_{12}, \epsilon_1, \epsilon_2)$ is given by formula (3.1.3):

$$\begin{aligned} \phi_{12}(P, \epsilon_{12}, \epsilon_1, \epsilon_2) = \mu \xi & \int du \phi_1(q_1 P + \xi u, \epsilon_1) \\ & \cdot \phi_2(q_2 P - \xi u, \epsilon_2) \end{aligned} \quad (3.2.1)$$

Clearly, $\epsilon_{12} + \epsilon_1 + \epsilon_2$ represents the total internal kinetic energy $\epsilon^{(k)}$ of the atoms in the cluster at time t_0 . The bound cluster distribution function $\phi_{12}(P)$ is found by integration over $\epsilon_{12}, \epsilon_1$ and ϵ_2 under condition (2.4):

$$\begin{aligned} \phi_{12}(P) = \int_0^\infty \dots \int_0^\infty d\epsilon_{12} d\epsilon_1 d\epsilon_2 \\ \cdot \phi_{12}(P, \epsilon_{12}, \epsilon_1, \epsilon_2) h(E_d - \epsilon_{12} - \epsilon_1 - \epsilon_2) \end{aligned} \quad (3.2.2)$$

in which the Heaviside function $h(E_d - \epsilon_{12} - \epsilon_1 - \epsilon_2)$ takes into account that the initial internal kinetic energy never exceeds the dissociation energy E_d of the cluster at time t_0 . It can easily be proved that under assumption IV, (3.2.2) is independent of the choice of sub-clusters 1 and 2. Therefore these formula allow the calculation of any cluster distribution function, starting with the monomer distribution functions $\phi_j^{(1)}(\mathbf{p}_j)$.

For the high energy asymptote of the cluster distribution function, the term ξu in (3.2.1) can be neglected. This is due to the fact that in (3.2.2) ξ ranges through the bounded interval $[0, (2\mu E_d)^{1/2}]$ due to condition (2.4) and because ϵ_j is bounded from below ($\epsilon_j \geq 0$). Thus, for P tending to infinity

$$\begin{aligned} \phi_{12}(P, \epsilon_{12}, \epsilon_1, \epsilon_2) \sim \mu \xi \int du \phi_1(q_1 P, \epsilon_1) \phi_2(q_2 P, \epsilon_2) \\ \propto \epsilon_{12}^{1/2} \phi_1(q_1 P, \epsilon_1) \phi_2(q_2 P, \epsilon_2) \end{aligned} \quad (3.2.3)$$

Formulae (3.2.3) and (3.2.2) are convenient starting points for the study of the behaviour of the k -particle cluster distribution $\phi^{(k)}(P)$ at high energies, starting with monomer distributions $\phi^{(1)}(\mathbf{p})$. This will be done explicitly for homonuclear k -particle clusters X_k , the generalization to different situations is obvious.

For the construction of a k -particle cluster distribution function from the monomer distribution function, we define the parameter $\epsilon_{1,k-1}$, being the relative kinetic energy of particle k and the subcluster consisting

of all $k-1$ subsequent particles. Then, for dimers X_2 formula (3.2.3) becomes

$$\phi^{(2)}(\mathbf{P}, \epsilon_{1,1}) \propto \epsilon_{1,1}^{1/2} \phi^{(1)}(\mathbf{P}/2) \phi^{(1)}(\mathbf{P}/2) = \epsilon_{1,1}^{1/2} [\phi^{(1)}(\mathbf{P}/2)]^2 \quad (3.2.4)$$

For trimers, one finds

$$\phi^{(3)}(\mathbf{P}, \epsilon_{1,1}, \epsilon_{1,2}) \propto \epsilon_{1,2}^{1/2} \phi^{(1)}(\mathbf{P}/3) \phi^{(2)}(2\mathbf{P}/3) \propto \epsilon_{1,1}^{1/2} \epsilon_{1,2}^{1/2} [\phi^{(1)}(\mathbf{P}/3)]^3 \quad (3.2.5)$$

and so on. In a similar way, for a k -particle cluster

$$\phi^{(k)}(\mathbf{P}, \epsilon_{1,1} \dots \epsilon_{1,k-1}) \propto \left\{ \prod_{x=1}^{k-1} \epsilon_{1,x}^{1/2} \right\} \cdot [\phi^{(1)}(\mathbf{P}/k)]^k \quad (3.2.6)$$

Note that $\sum_{x=1}^{k-1} \epsilon_{1,x}$ is the internal kinetic energy $\epsilon^{(k)}$ of the cluster at t_0 . Integration over all $\epsilon_{1,k-1}$ yields the distribution function $\phi^{(k)}(\mathbf{P})$. Since $\phi^{(k)}(\mathbf{P}, \epsilon_{1,1} \dots \epsilon_{1,k-1})$ is factorized into a product of $\epsilon_{1,x}^{1/2}$ and $\phi^{(1)}(\mathbf{P}/k)$, one gets

$$\phi^{(k)}(\mathbf{P}) \propto \left\{ \int_0^\infty \dots \int_0^\infty d\epsilon_{1,1} \dots d\epsilon_{1,k-1} \prod_{x=1}^{k-1} \epsilon_{1,x}^{1/2} h(E_d - \sum_{x=1}^{k-1} \epsilon_{1,x}) \right\} \cdot [\phi^{(1)}(\mathbf{P}/k)]^k \propto [\phi^{(1)}(\mathbf{P}/k)]^k \quad (3.2.7)$$

From the asymptotic distribution functions of the atoms (see section 2)

$$dS/dE \propto E^{-n} f(\Omega); \phi(\mathbf{P}) \propto P^{-(2n+1)} f(\Omega) \quad (3.2.8)$$

the behaviour of the k -particle cluster distribution function at high energy is according to (3.2.7) and (2.2)

$$\phi^{(k)}(\mathbf{P}) \propto P^{-(2n+1)k} f^k(\Omega) \quad (3.2.9)$$

For a heteronuclear particle $Y_{k_1} Y_{k_2}$ one finds in the same way for the high energy asymptote

$$\phi^{(k)}(\mathbf{P}) \propto P^{-(2n_1+1)k_1 - (2n_2+1)k_2} f_1^{k_1}(\Omega) f_2^{k_2}(\Omega) \quad (3.2.10)$$

where the index of n and $f(\Omega)$ refers to the monomer distribution functions of X and Y .

4 COMPARISON WITH EXPERIMENTS

4.1 Asymptotic Behaviour

Staudenmaier⁴ reported the energy distributions dS/dE of some W_k^+ clusters, sputtered from a polycrystalline tungsten surface by bombardment with 150 keV He⁺, Ne⁺, Ar⁺, Kr⁺, Xe⁺ and Cu⁺ ions. The clusters were detected under an angle of 40° with the surface normal. The energy spectra of W^+ , W_2^+ and W_3^+ ions were measured over a wide energy range and showed an E^{-n} behaviour at higher energies.

Since the energy distribution of neutral W, sputtered from polycrystalline tungsten is not known, it is not possible to calculate the energy spectra of the cluster ions for the whole energy range. The asymptotic behaviour of the energy spectra at the high energy limit of W_k^+ ($k > 2$) and W_k however can be calculated from the reported W^+ and W_2^+ asymptotes according to formula (3.2.10). This of course implies that W_k^+ clusters are assumed to be formed from the association of one W^+ ion and $k-1$ W atoms, which are independently sputtered. From the reported values of n for

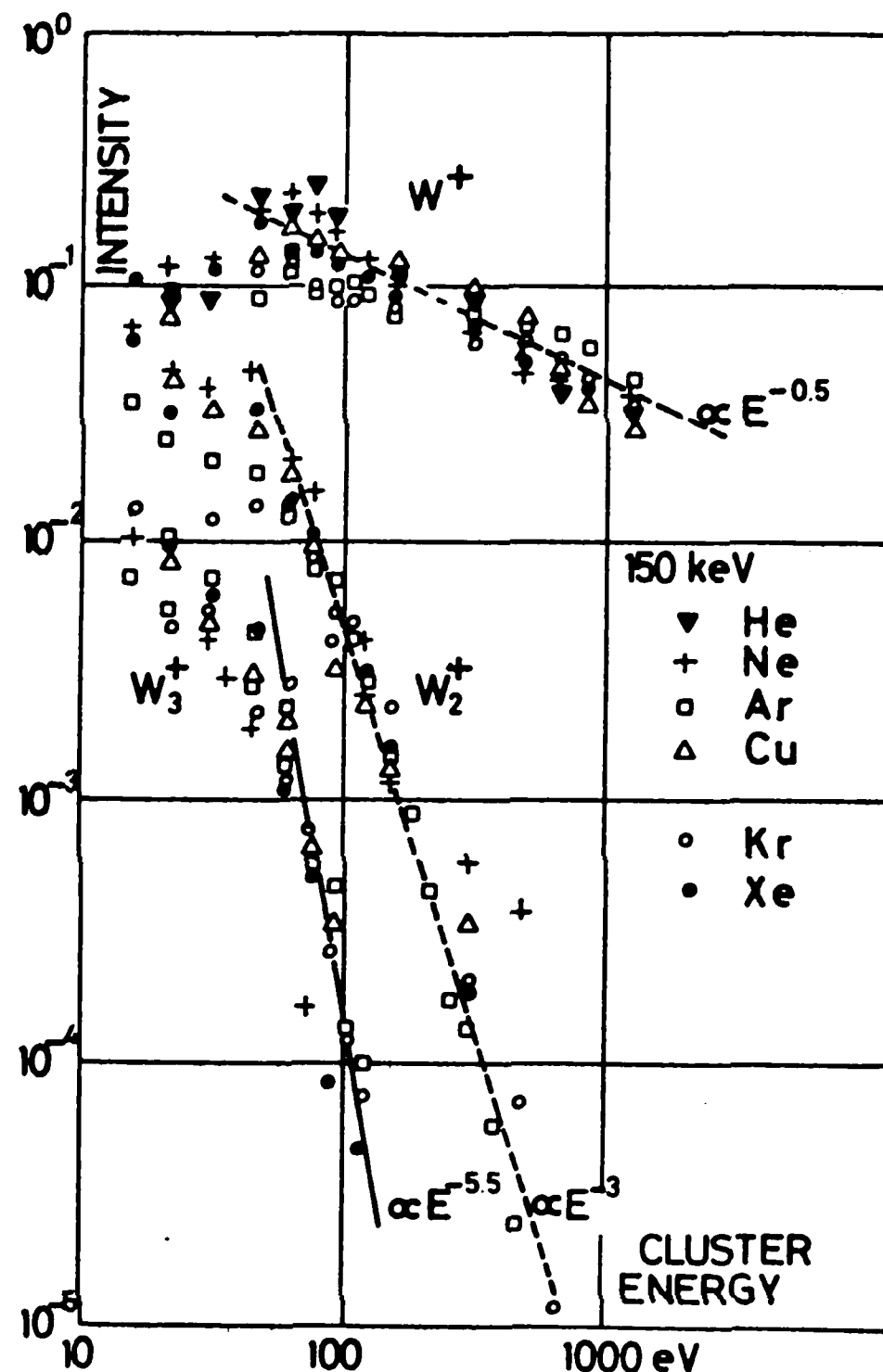


FIGURE 1 Energy distribution of W^+ , W_2^+ and W_3^+ clusters, sputtered from a polycrystalline tungsten surface, as reported by Staudenmaier.⁴ The dashed lines are the experimental E^{-n} energy distributions, the solid line represents the theoretical asymptotic behaviour for W_3^+ , as predicted from the W^+ and W_2^+ curves.

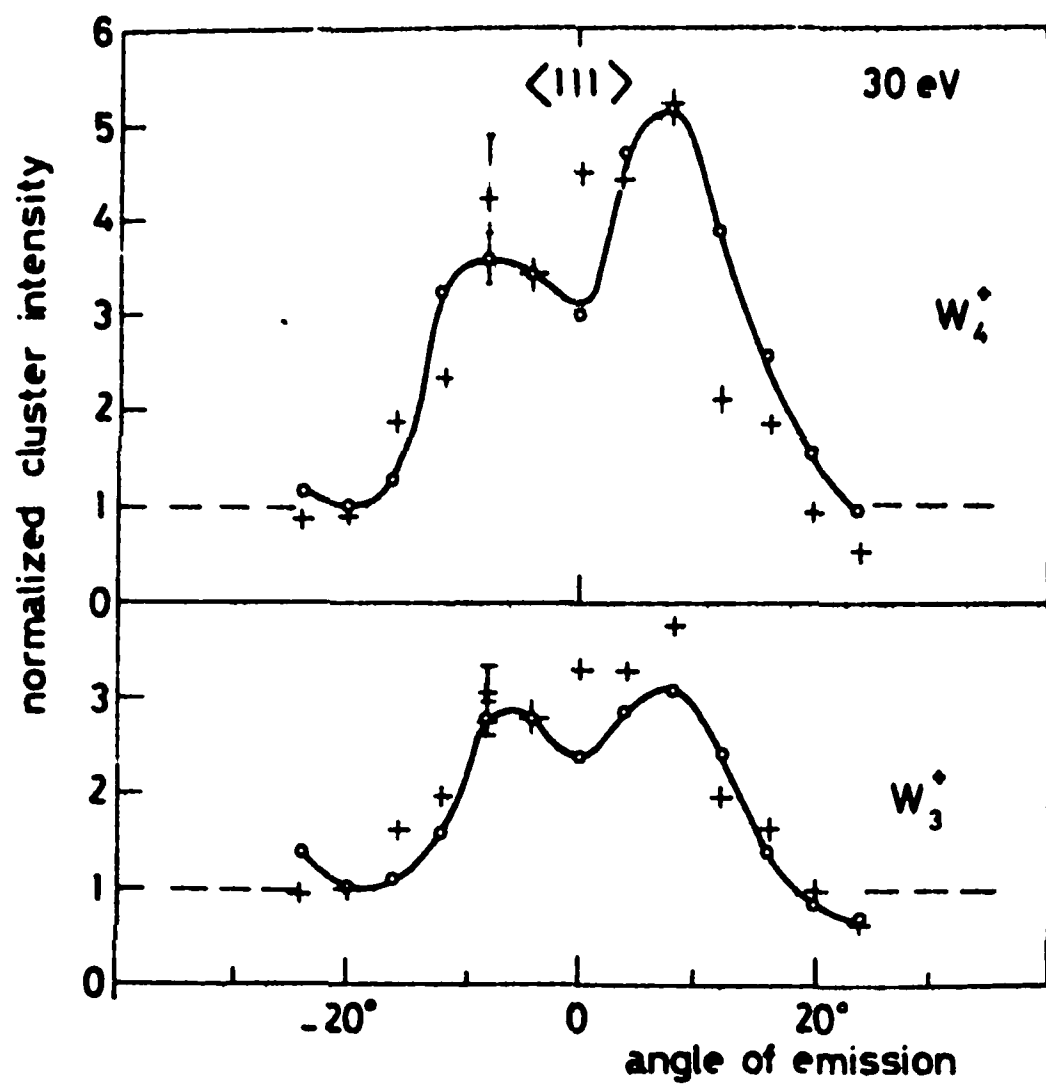


FIGURE 2 Angular distributions of W_3^+ and W_4^+ clusters at 30 eV. The points are experimental data of Staudenmaier.⁶ The crosses are the theoretical points, predicted from Staudenmaier's W^+ and W_2^+ distributions at 30 eV.⁶ The theoretical points have been normalized at -4° . The error, indicated at -8° is obtained from the experimental error in the W^+ and W_2^+ distributions.

W^+ and W_2^+ (0.5 and 3 respectively) one find the W asymptote to be E^{-2} , which is the value to be expected from the sputtering theory.^{2,5} The W_3^+ asymptote is found to be $E^{-5.5}$. Comparing this asymptotic behaviour with the experimental data of Staudenmaier, one concludes that the agreement is within the experimental error, as can be seen from Figure 1.

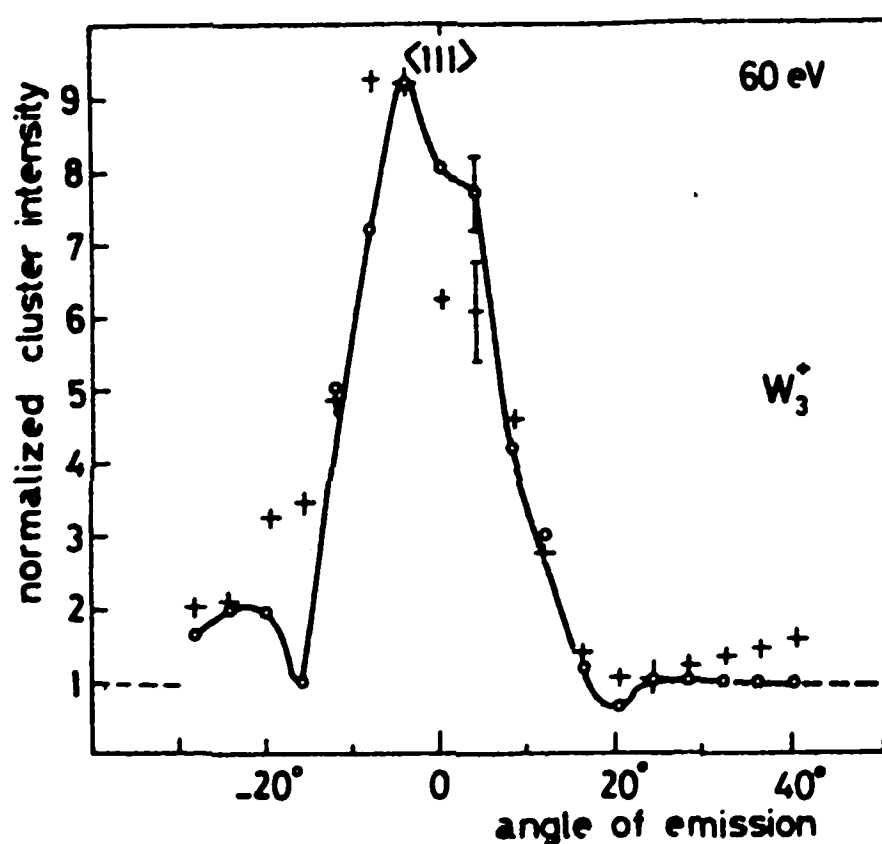


FIGURE 3 Angular distribution of W_3^+ clusters at 60 eV. The points are the experimental data of Staudenmaier.⁶ The crosses are theoretical points, predicted from Staudenmaier's W^+ and W_2^+ distributions at 60 eV.⁶ The theoretical points have been normalized at -4° . The error, indicated at 4° is obtained from the experimental error in the W^+ and W_2^+ distributions.

Further measurements of Staudenmaier⁶ enable us to test the predicted angular distributions of sputtered clusters in the high energy limit. Angular distributions of W_k^+ clusters ($k \leq 4$) were reported around the $\langle 111 \rangle$ direction of a tungsten single crystal (the surface normal being $\langle 110 \rangle$) at 30 eV, and of W_k^+ ($k \leq 3$) at 60 eV. All W_k^+ clusters show a maximum intensity around the $\langle 111 \rangle$ direction.

From formula (3.2.10) the angular distributions of W_3^+ and W_4^+ clusters at a given energy are easily calculated from the reported W^+ and W_2^+ distributions. In Figures 2 and 3 the calculated distributions of these clusters at 30 eV and 60 eV respectively are compared with the experimental distributions. They are found to be in agreement within the experimental uncertainty.

4.2 Low Energy Distributions of Dimers

Since formula (3.1.9) leads to a somewhat different result for the dimer distributions dS/dV compared to those in 1, in this section the data on K_2 and KI sputtering will be rediscussed. In Figure 4, the experimental energy distribution of K_2 is given, measured by Baede *et al.*⁷ The open and closed points are the measured points of Baede, with and without the corrections discussed in.⁷ Using the parameters of the monomer distributions of K , as reported by Politiek and Kistemaker³ ($n = 1.525$ and $E_b = 0.55$ eV), the dimer distribution could not be fitted with the theoretical distribution obtained from (3.1.9) and (2.2). Taking however $E_b = 0.3$ eV, the theoretical curve coincides with the experimental points over a wide energy range. To demonstrate the sensitivity of the theoretical curve for changes in E_b , in Figure 4 also the curves for $E_b = 0.25$ eV and $E_b = 0.35$ eV have been drawn. All curves have been normalized at 1.1 eV, as is the cause in Baede's plot.

Measurements of the energy distributions of K , I and KI sputtered in the normal direction of a polycrystalline KI target under 6 keV Ar^+ bombardment have been reported previously⁸. The parameter n was found to be 2 for I atoms and 1.5 for K atoms. The binding energy E_b of the atoms can be obtained by fitting the experimental curves with formula (2.3). This yields $E_b = 0.7$ eV and 0.4 eV for K and I atoms respectively.¹

The dissociation energy of KI molecules in the gas phase is 3.3 eV,^{9,10} The closest distance R_0 of K^+ and I^- ions in the lattice is 3.5 Å⁹ which is somewhat larger than the distance of 3.0 Å¹⁰ between K and I in the molecule. For this internuclear separation, the value E_d can be calculated to be 3.0 eV.¹⁰ This

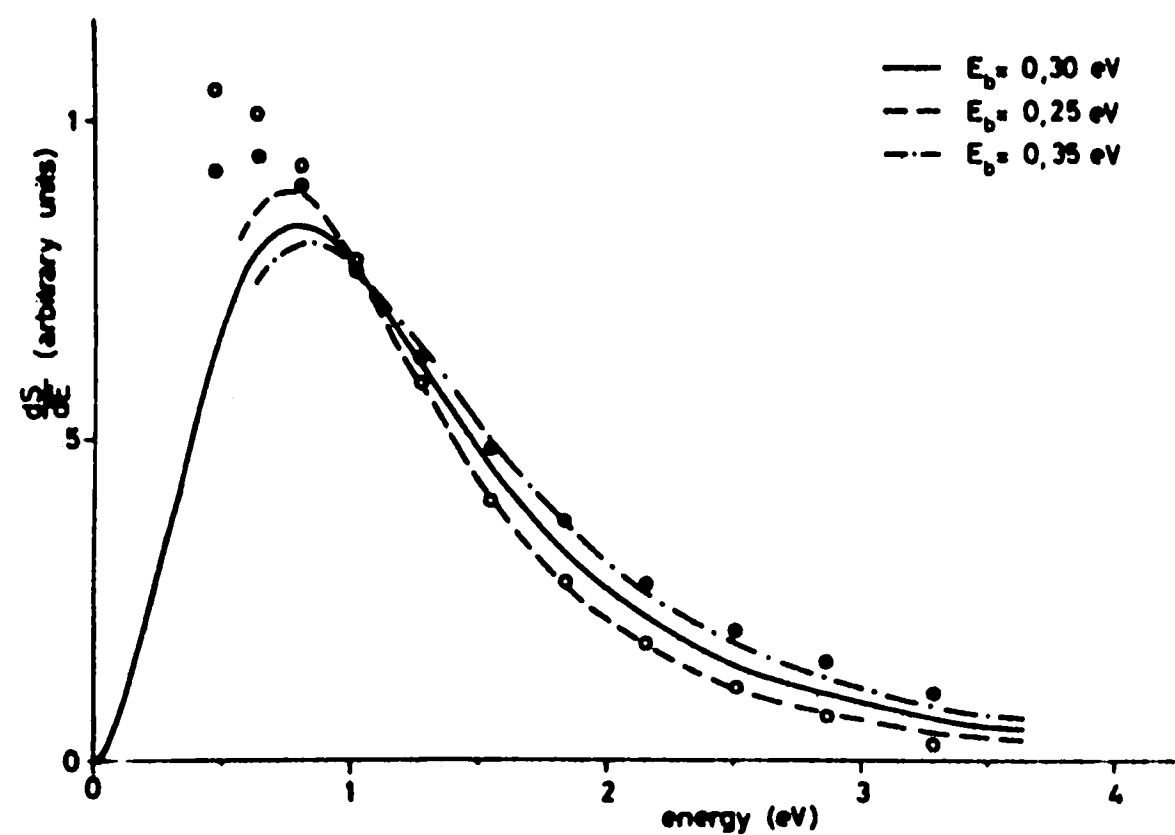


FIGURE 4 The energy distribution of K_2 dimers sputtered from a polycrystalline K target. The lines represent the theoretical curves with $E_d = 0.55$ eV, $n = 1.525$ and $E_b = 0.25$ eV, 0.30 eV and 0.35 eV. The open and closed circles are the experimental points of Baede *et al.*,⁷ respectively with and without the two corrections discussed by these authors. All curves have been normalized at 1.1 eV.

difference however does hardly influence the shape of the theoretical energy distribution.

Contrary to the covalent molecule K_2 , the potential energy of the ionic KI molecule has a very long range due to the Coulomb attraction; this range extends to the crossing point of the covalent and the ionic potential curve in this molecule at 11.3 Å.¹¹ It can therefore be expected that sputtering of non-adjacent K and I atoms from the lattice also gives a contribution to dimer formation. The KI crystal has a fcc NaCl type structure. In this lattice, there are four possible configurations of K and I atoms with a distance below 11.3 Å, at 3.5, 6.1, 7.8 and 10.5 Å. From the Coulomb potential the value of E_d for an internuclear separation of 6.1, 7.8 and 10.5 Å are calculated to be 1.1, 0.6 and 0.1 eV respectively. The probabilities for sputtering a KI pair in either of the contributing configurations are taken to be equal. Evaluation of formula (3.1.9) then shows that K and I at 10.5 Å gives hardly any contribution to dimer formation, but the other configurations cannot be neglected.

In Figure 5 the experimental energy distribution of KI is compared with the theory. The solid line represents the sum of the three contributions with $E_d = 3.0$ eV, $E_d = 1.1$ eV and $E_d = 0.6$ eV. The theoretical curve has been normalized by fitting it with the experimental point at 4.2 eV. Again, lower E_b values than expected have to be chosen to get the optimal fit to the theoretical curve with the experimental data. In Figure 5, $E_b = 0.2$ and 0.1 eV for K and I respectively. Such changes in E_b however influence only the shape of the theoretical curve below 3 eV.

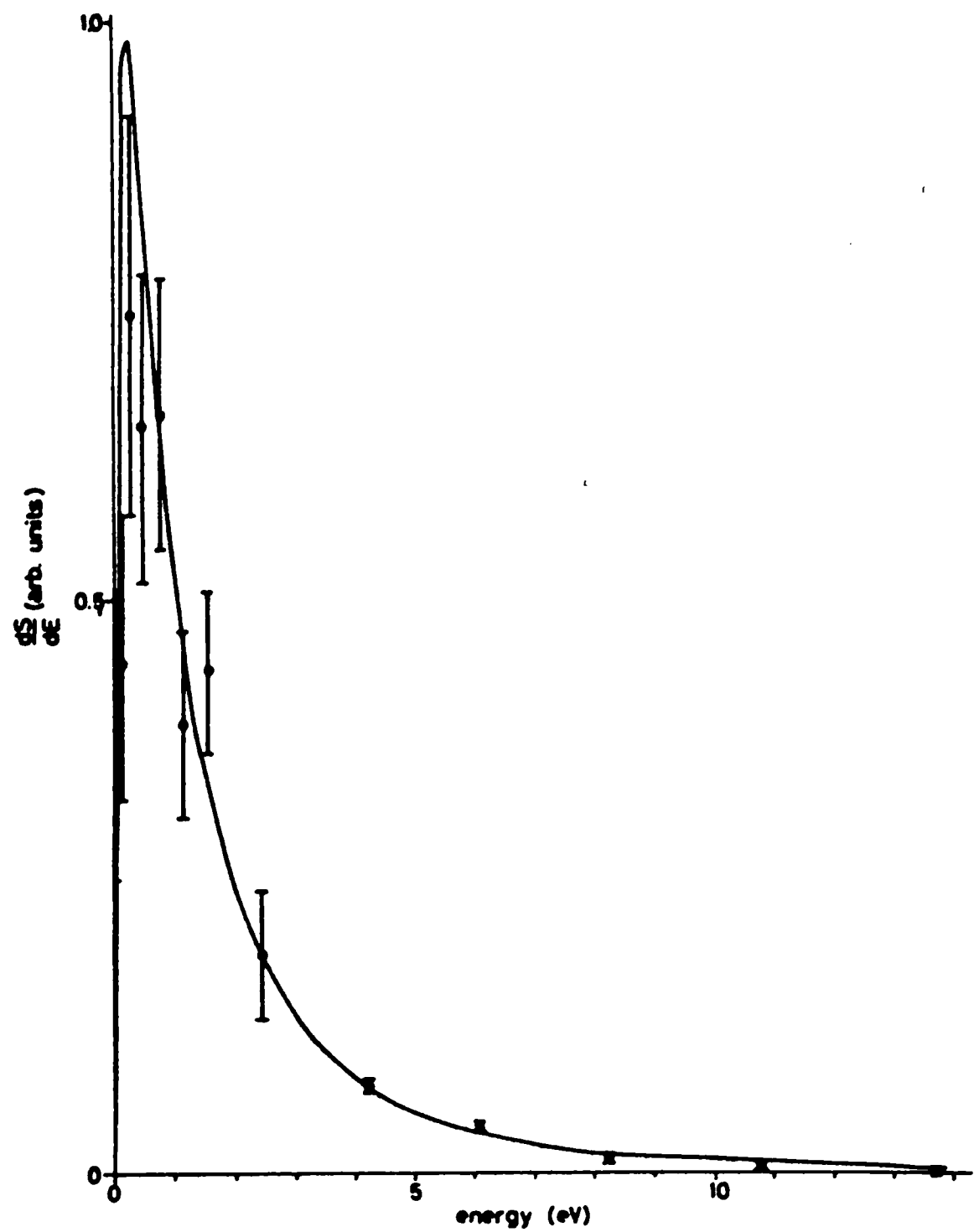


FIGURE 5 The energy distribution of KI. The solid line represents the theoretical curve (see text). The parameters of the monomer distributions are $n = 1.5$, $E_b = 0.2$ eV for K and $n = 2$, $E_b = 0.1$ for I. The points are the experimental data.⁸ The curve has been normalized at 4.2 eV.

If only the contribution with $E_d = 3.0$ eV is taken into account, the resulting curve cannot be fitted with the experimental points above 3 eV for any choice of E_b . The sum of all contributions however agrees well with the experimental data, as can be seen from Figure 5. From this it can be concluded that dimer formation from non-adjacent particles in the lattice is indeed important for ionic crystals.

Finally the dimer to monomer ratios for K_2 and KI at a given energy, calculated with (3.1.9) and (3.1.6) are found to be an order of magnitude higher than the experimental results. In view of the statistics of occurrence of the various surface configurations of the particles to be sputtered, this seems to be a reasonable result.

5 CONCLUSION

The high energy results of section 4 indicate clearly that the present theory indeed explains the energy distributions of clusters. This means that clusters are

formed by recombination of independently sputtered atoms, and that their energy distributions are determined by the E^{-n} power laws of the monomer distributions. Moreover, from the KI results it can be concluded that for ionic crystals various configurations of the atoms on the surface contribute to dimer formation. On the other hand, at the lowest energies there are deviations between theory and experiment, since the value of E_b in the dimer formula has to be chosen considerably lower than expected from the monomer distribution to get a fit with the experimental curves. This may indicate that the present theory under assumption 5 is a rather crude approximation. In fact, this assumption states that the binding energy acts only upon the individual atoms of the cluster, thus decreasing both its initial center of mass energy and the relative motion in the cluster. It is likely however, that the binding energy plays a more complicated role in cluster formation. In many cases the atoms of the cluster originally have been quite close together on the surface, so that the sputtered aggregate closely resembles a molecule. Therefore it can be expected that part of the binding energy acts on the whole cluster, and does not influence the relative motion of the atoms in the cluster. Such refinements of the theory however will never change

the asymptotic behaviour of the energy distribution at the high energy limit, since the binding energy can then always be neglected with respect to the kinetic energy of the cluster. The asymptotic behaviour remains therefore the same as in section (3.2), being only determined by the behaviour of the monomer distributions at high energy.

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