PHYSICAL REVIEW B VOLUME 25, NUMBER 5 1 MARCH 1982

Electron emission from aluminum and copper under molecular-hydrogen-ion bombardment

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(Received 22 April 1981)

The secondary electron yields from polycrystalline aluminum and copper under H^+-, $H_2{}^+$-, and $H_3{}^+$-ion bombardment are compared as a function of ion velocity. The ratios obtained by dividing the yields for $H_2{}^+$ and $H_3{}^+$ ions with the yield for protons increase with ion velocity. The rate of increase is higher for aluminum targets than for copper targets. The experimental results are explained by considering the charge states of the molecular constituents during penetration of the first few atomic layers important for the electron emission process. Both effects caused by close single-particle collisions and distant plasma collisions are considered.

I. INTRODUCTION

During the last few years much effort has been made to investigate the interaction of energetic molecular ions with solids. Especially the penetration of swift molecular ions through thin foils has been studied.

From stopping theory it is well known that the charge state of penetrating ions influences the electronic stopping power. Since the electron yield, obtained at the bombardment of solids by energetic light projectiles, is essentially given by the electronic stopping power,[1,2] also the electron yield must be influenced by the charge states of the bombarding projectiles. However, in the literature only a few secondary electron measurements have been reported where the charge-state effect has been studied. Most secondary electron emission measurements have been performed with single ionized atoms and only a few results have been reported for molecular ions. This is unfortunate, since electron emission measurements using molecular ions provide a unique possibility to get information about the behavior of bombarding molecules during penetration of the outermost layers of a solid. In this work we show how the electron yield for molecular hydrogen ions can be estimated by studying the charge states of the molecules and their constituents during penetration of the thin surface layer important for the electron emission process.

II. EXPERIMENTAL

The secondary electron yield has been measured using polycrystalline aluminum and copper targets bombarded by H^+, $H_2{}^+$, and $H_3{}^+$ ions in the energy range of 10 to 350 keV for aluminum and 10 to 400 keV for copper.

The experiments have been performed in an ultrahigh vacuum system connected to the 50-kV electromagnetic isotope separator and the 400-kV ion accelerator at our laboratory. The gas pressure in the target chamber was in the range of 7×10^{-10} to 1×10^{-9} Torr during operation. In order to obtain the necessary clean surface conditions of the target, we always performed a self-sputtering process just before the measurements were made. In all the experiments the aluminum and the copper targets were kept at 250 and 400 °C, respectively.

The total experimental error in the yields has been estimated to be within $\pm5\%$, and the relative error between the yields for the different kinds of ions is within $\pm2\%$. A detailed description of the experimental system, the target treatment, the experimental conditions, and the experimental procedure is given in Refs. 3–6.

III. RESULTS

In Fig. 1 the secondary electron yield γ is plotted versus ion energy for $H_2{}^+$ and $H_3{}^+$ ions bombarding copper. For $H_2{}^+$ ions the yield increases significantly in the range of 10 to 200 keV but it is then almost constant up to the maximum energy of 400 keV. For $H_3{}^+$ ions the yield increases in the whole energy region but the rate of increase decreases with energy.

For $H_2{}^+$ and $H_3{}^+$ ions impinging on aluminum the results are shown in Fig. 2. The curves have

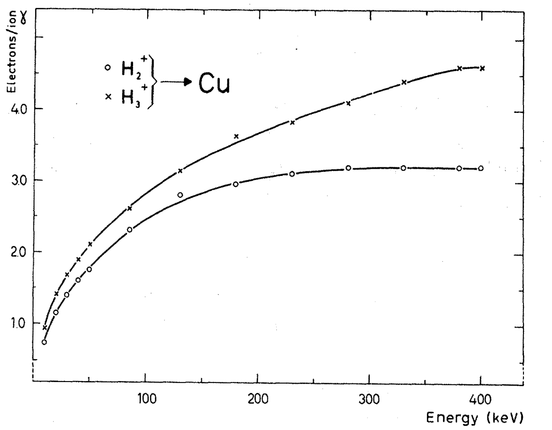

FIG. 1. Secondary electron yield from polycrystalline copper as a function of ion energy for H_2^+ and H_3^+ ions.

the same shape as for copper targets, except at the high energies where the yield induced by H_2^+ ions decreases and the yield for H_3^+ ions is almost constant.

Figure 3 shows γ versus ion energy for protons bombarding copper and aluminum.[5,6] The yields for the molecular hydrogen ions and protons with equal velocity are compared in Figs. 4 and 5. The ratios between the yields are calculated from the values given by the solid lines in Figs. 1, 2, and 3. The ratios increase with ion velocity both for aluminum and copper targets, but the rate of increase is higher for aluminum. For copper the maximum values of $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ are equal to 2.0 and ~2.8, respectively. However, for aluminum $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ are equal to ~2.3 and 3.3, respectively, at the high-ion velocities, even though the maximum velocities are lower than for copper.

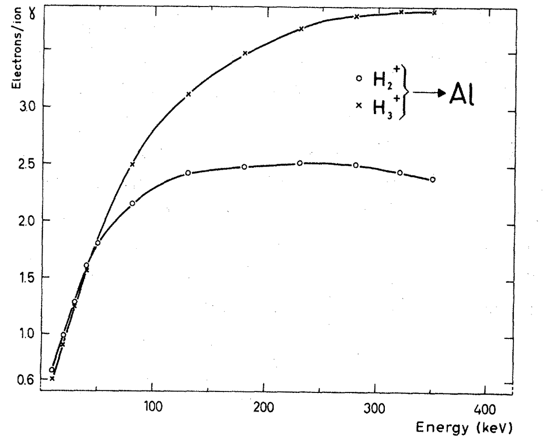

FIG. 2. Secondary electron yield from polycrystalline aluminum as a function of ion energy for H_2^+ and H_3^+ ions.

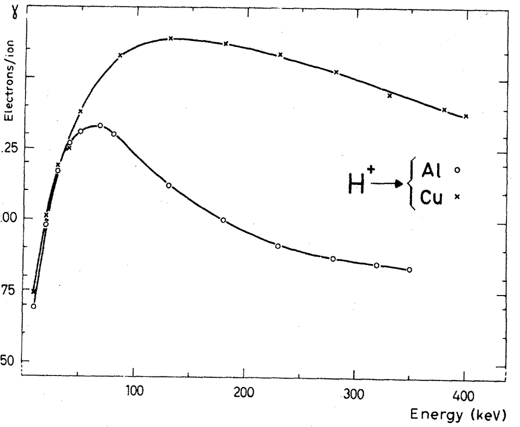

FIG. 3. Secondary electron yield vs ion energy for protons impinging on copper and aluminum.

IV. THEORY

A. General

The basic relation for γ is given by the equation[2,7]

$$\gamma = \Lambda D \ , \tag{1}$$

where Λ is a constant determined only by properties of the target material and D is the mean energy per unit depth deposited in electronic excitation at the target surface by a bombarding ion.

An explicit expression for Λ has been derived by Schou.[7] However, the expression contains some

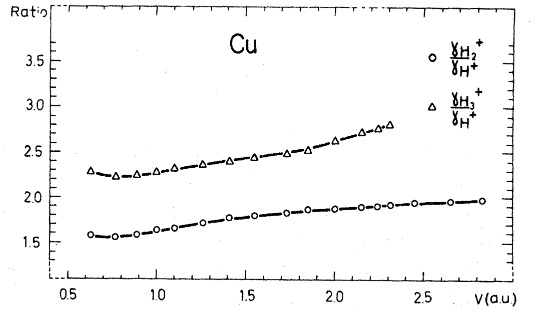

FIG. 4. Secondary electron yield for H_2^+ and H_3^+ ions bombarding copper, normalized to the yield for protons, as a function of ion velocity.

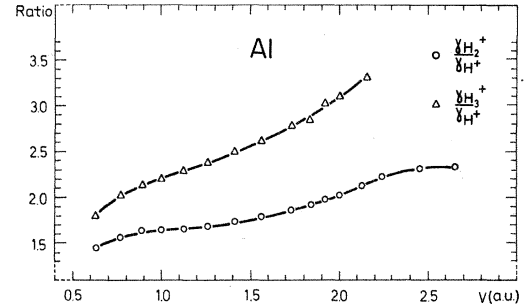

FIG. 5. Secondary electron yield for H_2^+ and H_3^+ ions bombarding aluminum, normalized to the yield for protons, as a function of ion velocity.

quantities which are not accurately known at the present, e.g., the stopping power for low-energy electrons. Therefore, Λ will here be treated only as a material constant which drops out when the ratios $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ are considered.

The deposited energy density D can be split into the contributions due to electronic and nuclear stopping of the bombarding ion according to[2]

$$D = D_{(p)} + D_{(r)} , \qquad (2)$$

where $D_{(p)}$ and $D_{(r)}$ are the mean energy per unit depth deposited in electronic excitation by the primary ion and by recoiling target atoms, respectively. $D_{(p)}$ depends on the electronic stopping of the bombarding ions, while $D_{(r)}$ is related to the nuclear stopping.

For the ion velocities of interest in this work the nuclear stopping power is orders of magnitudes smaller than the electronic stopping power. Therefore, $D_{(r)}$ is neglected in the following.

The surface value of $D_{(p)}$ can be expressed in the form[2,7]

$$D_{(p)}(x=0,E,\cos\varphi) = \beta(E,\cos\varphi) N S_e(E) , \qquad (3)$$

where x is the depth inside the target, E the initial ion energy, φ the angle of ion incidence, $NS_e(E)$ the electronic stopping power, and $\beta(E,\cos\varphi)$ a dimensionless factor which accounts for the influence of ion backscattering and energy transport by excited target electrons on $D_{(p)}(0)$.

In particular, if ion scattering and energy transport by electrons are ignored, $\beta = 1$ at perpendicular incidence. Generally, β needs to be evaluated by means of transport theory.[7]

Equation (1) for γ can now be written as

$$\gamma = \Lambda \beta(E,\cos\varphi) N S_e(E) . \qquad (4)$$

Since β turns out to be a slowly varying function of energy,[7] one finds that γ is proportional to $S_e(E)$ over quite large energy regions, as reported by several authors.[5,6,8-10]

B. Application to molecular hydrogen ions

At the projectile velocities used in this work there are unfortunately only a few measurements and calculations of the stopping power for molecular hydrogen ions.

However, one theoretical approach is to use the dielectric formalism which has been applied to stopping power calculations for atomic ions by many authors (for a review see Ref. 11). In this formalism the target medium is characterized by a dielectric function and from this function the stopping power for the bombarding projectiles can be calculated. In particular, at projectile velocities v larger than a certain threshold velocity v_{th}, which is determined by the target material,[12] e.g., $v_{th}(\text{Al}) \approx 1.24$ a.u., the collisions between the target electrons and the bombarding particles can be divided into (1) close single-particle collisions and (2) distant plasma resonance collisions. Since excited plasmons may decay into single or multielectron excitation, as has been outlined by some investigators,[13,14] both types of collisions may contribute to electron emission. At $v < v_{th}$ no generation of plasma oscillations occurs.

In close collisions the molecular constituents act as independent particles, but in distant collisions they act as a united charge as long as the internuclear distance is less than v/ω_0, where ω_0 is the resonance frequency of the target medium.[15]

Brandt and Ritchie[15] have given an expression for the relation between the dwell time in the target and the internuclear distance for a dicluster, consisting of constituents with atomic numbers and masses (Z_1,M_1) and (Z_1',M_1'), in the case of an unscreened Coulomb explosion,

$$t = t_0\{\xi^{1/2}(\xi-1)^{1/2} + \ln[\xi^{1/2} + (\xi-1)^{1/2}]\} , \qquad (5)$$

with

$$\xi = R(t)/R(0)$$

and

$$t_0 = \{R(0)^3/[(M_1^{-1} + M_1'^{-1})2Z_1Z_1'e^2]\}^{1/2} ,$$

where t is the dwell time and $R(t)$ is the internuclear distance.

Equation (5) gives that a H_2^+ ion impinging on aluminum with a velocity $v=1.5$ a.u. penetrates ~ 40 Å before the two molecular constituents behave as independent particles in distant collisions, i.e., $R(t)>v/\omega_0$, if $R(0)=1.29$ Å.[15] At higher velocities this penetration distance increases significantly.

In metal targets the majority of secondary electrons originates from a surface layer with a thickness of 10–20 Å. Thus, during penetration of this layer energetic molecular hydrogen ions act as united charges in distant collisions and, furthermore, since the energy loss is proportional to the square of the projectile charge,[12] a fully stripped hydrogen molecule with n constituents loses more energy into plasma resonance excitations than n independent protons ($n^2>n$).

The electrons of a H_n^+ molecule are equally shared by the atomic constituents, i.e.,

$$H_n{}^+=\left[\frac{1}{n}H^+ +\frac{n-1}{n}H\right]n=H^+ +(n-1)H\ ,$$

so on the average the molecule may be regarded as one proton and $n-1$ hydrogen atoms. Inside the solid, electron capture and loss processes take place. Schematically, it may look as shown in Fig. 6 during penetration of the surface region. The possibility of forming negative ions is neglected and complications due to excited states are not taken into account. If the model in Fig. 6 is used the following quantities may be introduced.

$p_{H^+(H)}(x,\vec{v})$: probability of an impinging proton (hydrogen atom) with velocity $\vec{v}$ being in the initial charge state at the depth x.

$f(x,\vec{v})$: the fraction of the energy originally deposited at the depth x, which is finally deposited at the target surface, during bombardment by a hydrogen projectile with velocity $\vec{v}$.

At perpendicular incidence and at the ion velocities used in this work, the energy loss during penetration of the surface region is small compared to E and ion scattering in the surface region is negligible. Then, according to Eq. (3),

$$D_{(p)}(0,E,\cos\varphi)=\beta(E,\cos\varphi)NS_e(E)\ ,$$

the normalization condition for f reads

$$\int_0^{\langle\infty\rangle} f(x,\vec{v})dx=\beta(\vec{v})\ , \qquad (6)$$

where β is expressed in velocity variables.

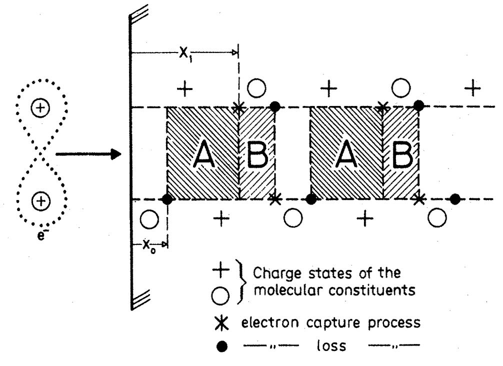

FIG. 6. Schematic diagram of a H_2^+ ion penetrating the surface region of a solid.

According to Brandt[16] and Yarlagadda *et al.*[17] the proton equilibrium charge state is close to or equal to $+1$ at the ion velocities used in the present work. Therefore, it seems appropriate to assume that a H_n^+ molecule will initially have the charge state $+1$ but after a distance x_0 (see Fig. 6) it will stay almost completely stripped, i.e.,

$$P_{H^+}(x>x_0,\vec{v})=1$$

and

$$P_H(x>x_0,\vec{v})=0\ .$$

Using this model $D_{(p)}(0,E,1)$ for a neutral hydrogen atom can be written as

$$D_{(p)}(H)=\alpha f_0 D_{(p)}(H^+)+(1-f_0)D_{(p)}(H^+)\ , \qquad (7)$$

where $0\lesssim\alpha\lesssim 1$ and

$$f_0=\frac{1}{\beta}\int_0^{x_0} f(x,\vec{v})dx\ ,$$

i.e., α is the ratio between the stopping powers for hydrogen atoms and protons, and f_0 is the fraction of β which arises in the distance x_0. Furthermore, regarding, on the average, a H_n^+ molecule as one proton and $n-1$ atoms $D_{(p)}(H_n^+)$ takes the form

$$D_{(p)}(H_n{}^+)=[1+\alpha(n-1)]f_0D_{(p)}(H^+)+(1-f_0)[(1-x_R)n+x_Rn^2]D_{(p)}(H^+)\ , \qquad (8)$$

where x_R is the fraction of $D_{(p)}(H^+)$ which originates from resonance processes. The term x_Rn^2 in (8) represents the contribution from the resonance collisions where the fully stripped molecule acts as a united charge. The factor n^2 occurs because the energy loss is proportional to the square of the projectile charge.[12]

It may be mentioned that using a model with less restrictive assumptions than used here, i.e., not assuming that a $H_n{}^+$ molecule stays completely stripped after the distance x_0, gives a relation for $D_{(p)}(H_n{}^+)$ quite similar to Eq. (8).[18] However, the comparison with experiment becomes more complicated than here since some of the input quantities are difficult to obtain.

C. Comparison between experiment and theory

For the determination of $D_{(p)}(H_n{}^+)$ by means of Eq. (8) α is needed. Unfortunately, in the literature data from which α can be extracted, i.e., stopping power data for hydrogen atoms, are scarce. However, from Eq. (8) we found that

$$D_{(p)}(H_3{}^+)=2D_{(p)}(H_2{}^+)-D_{(p)}(H^+)+\Delta\ , \quad (9)$$

where

$$\Delta=2x_R D_{(p)}(H^+)(1-f_0)\ .$$

Thus, except for the contribution from Δ, which differs from zero only at $v>v_{th}$, the electron yields for $H_3{}^+$ ions can be predicted using the yields measured for H^+ and $H_2{}^+$ ions. This provides a thorough test of the theory since three independent measurements, performed under identical conditions, are involved.

In order to estimate Δ let us first consider x_R, the fraction of energy loss caused by plasma resonance excitations. For copper electron energy loss and optical measurements show that the plasma oscillations have a broad range of frequency response.[19] The major peak is centered around

$$h\omega_0 \approx 20 \text{ eV}\ .$$

Using this value of ω_0 and a value

$$R(0)\approx 1.29\ \text{Å}$$

for $H_2{}^+$ ions given by Brandt and Ritchie,[15] one finds that v must be larger than 1.8 a.u. if the molecular constituents are to act as a united charge in distant collisions since it requires that $R<v/\omega_0$. Thus, the velocities used here are relatively low for the generation of plasma excitations by molecular ions. Furthermore, the different components of the broad-frequency response function may interfere by rapidly damping the plasma oscillations.[20] Therefore, x_R is put equal to zero as a first approximation and consequently $\Delta=0$. The following relation is then obtained from Eq. (9) for copper targets,

$$\gamma_{H_3{}^+}=2\gamma_{H_2{}^+}-\gamma_{H^+}\ . \quad (10)$$

For aluminum, which is a free-electron-like metal with a sharp peak at $h\omega_0=15.3$ eV, the response function of the plasma oscillations v must exceed ~ 1.4 a.u. if x_R is not to be equal to zero, since for $v \lesssim 1.4$ a.u., $R(0)>v/\omega_0$. A rough estimate of Δ can be obtained in the following way. For $n=2$ Eq. (8) reads

$$D_{(p)}(H_2{}^+)=D_{(p)}(H^+)[2-f_0(1-\alpha)]+\Delta\ . \quad (11)$$

Consequently,

$$\Delta \gtrsim D_{(p)}(H_2{}^+)-2D_{(p)}(H^+)$$

since

$$f_0(1-\alpha)\gtrsim 0\ .$$

As a first approximation, giving a minimum value, we have used

$$\Delta=D_{(p)}(H_2{}^+)-2D_{(p)}(H^+)\ .$$

Since Δ always must be larger than zero this estimate gives only a contribution to $D_{(p)}(H_2{}^+)$ at the high velocities where $\gamma_{H_2{}^+}/\gamma_{H^+}>2$. However, this may be reasonable since x_R increases with velocity and, therefore, Δ is expected to be of larger importance at high velocities.

The following relation is now obtained for aluminum targets:

$$\gamma_{H_3{}^+}=2\gamma_{H_2{}^+}-\gamma_{H^+}+\Delta_{est}\ , \quad (12)$$

where

$$\Delta_{est}=\begin{cases}0 & \text{for } \gamma_{H_2{}^+}/\gamma_{H^+}\lesssim 2\\ \gamma_{H_2{}^+}-2\gamma_{H^+} & \text{for } \gamma_{H_2{}^+}/\gamma_{H^+}\gtrsim 2\end{cases}\ .$$

In Fig. 7 the yields obtained by means of Eqs. (10) and (12) are compared with the measured yields normalized to the yield for protons. For both aluminum and copper targets measurements and theoretical predictions agree within less than 10%. This agreement is considered encouraging. In Table I the values of $f_0(1-\alpha)$ and $x_R(1-f_0)$ extracted from the measured γ values are listed.

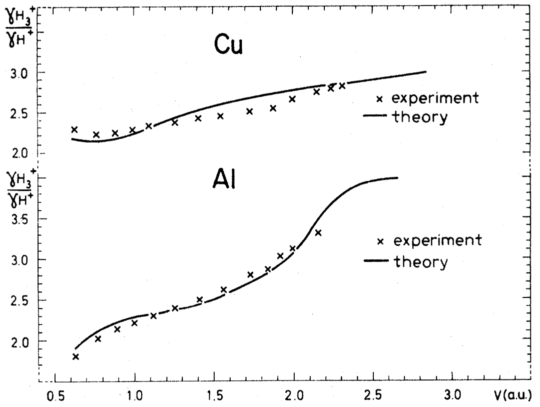

FIG. 7. Ratio between the secondary electron yields for H_3^+ ions and protons as a function of ion velocity.

At $v \lesssim v_{th}$ the values of $f_0(1-\alpha)$ are taken from the $\gamma_{H_2^+}/\gamma_{H^+}$ values, while at $v \gtrsim v_{th}$ the $\gamma_{H_3^+}/\gamma_{H^+}$ values must also be used to obtain both $f_0(1-\alpha)$ and $x_R(1-f_0)$.

V. DISCUSSION

In the present work we have treated the so-called molecular effects in the electron yields for H_2^+ and H_3^+ ions by considering the charge states of the impinging molecules and their constituents. For H_2^+ ions such effects have also been reported by Baragiola *et al.*[21]

The values of $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ smaller than 2.0 and 3.0, respectively, appear because $D_{(p)}(H)$ is smaller than $D_{(p)}(H^+)$, i.e., the electronic stopping power for neutral hydrogen atoms is lower than for protons. The increase of $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ with v is because the fraction of $D_{(p)}(H_n^+)$ deposited during penetration of x_0, i.e., the distance the molecule penetrates before it becomes fully stripped, decreases with v while the energy deposited in the region where the molecule is fully stripped becomes more important for the generation of secondary electrons. At high enough velocities $\gamma_{H_2^+}/\gamma_{H^+}$ and $\gamma_{H_3^+}/\gamma_{H^+}$ may be even larger than 2.0 and 3.0, respectively, due to the resonance collisions in which the molecule acts as a united charge. Values of $S_e(H_n^+)/S_e(H^+)$ larger than n ($n=2,3$) at high projectile velocities have been found also by other authors.[22-24]

Equation (9) implies that the electron yields measured for H^+ and H_2^+ ions can be used in the calculations of the yield for H_3^+ ions. This simplifies the comparison between experiment and theory since some of the quantities in Eq. (8) are not known very accurately, e.g., α, x_R, and f_0. The approximations made in the calculations of Δ for aluminum targets have a too-limited accuracy for the Δ values to be regarded as precise. However, from the extracted values of the parameters in Table I it can be seen that Δ plays only a minor role at the projectile velocities used here. Δ contributes less than 5% to $D_{(p)}(H_3^+)$ but is expected to be of larger importance at higher ion velocities, i.e., when equipartition in the stopping power occurs.[12]

TABLE I. Extracted values of the parameters $f_0(1-\alpha)$ and $x_R(1-f_0)$ for aluminum and copper targets.

Ion velocity (a.u.)	Aluminum		Copper	
	$f_0(1-\alpha)$	$x_R(1-f_0)$	$f_0(1-\alpha)$	$x_R(1-f_0)$
0.63	0.55		0.42	
0.75	0.45		0.44	
1.00	0.35		0.36	
1.25	0.31		0.28	
1.40	0.26		0.22	
1.60	0.23	0.02	0.18	
1.80	0.17	0.03	0.14	
2.00	0.03	0.03	~0	~0
2.15	~0	0.08	~0	~0
2.30			0.03	~0

ACKNOWLEDGMENTS

Financial assistance was received from the Swedish Natural Science Research Council, the Swedish Board for Technical Development, and the Nordic Committee for Accelerator-Based Research. The authors are very much indebted to Professor P. Sigmund, Odense University, Denmark, for many enlightening discussions. One of us (B. S.) is grateful to the board for Nordiska Forskarkurser for a scholarship making possible a stay at the Odense University, Denmark.

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