PHYSICAL REVIEW B VOLUME 15, NUMBER 2 15 JANUARY 1977

Charge states of fast protons in solids

M. C. Cross
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 23 September 1976)

It is shown that charge states of high-energy protons in solids may be simply understood in terms of capture into, and subsequent loss from, bound states on the proton within the solid. Both the equilibrium charge states emerging from the solid, and the approach to equilibrium within the solid, may be calculated. At high enough proton velocities gas cross sections may be used to predict the results in solids. This is directly confirmed by experimental results, taken from the literature, on solid carbon and gaseous carbon compounds.

I. INTRODUCTION

Since the pioneering work by Phillips,[1] there have been many experiments to measure the charge state of protons emerging with energies around 25–200 keV from solid targets.[2] This energy range is difficult to treat theoretically even in gases: neither high-energy (Born) nor low-energy approximation schemes give good results.[3] In solids there is in addition the difficult question of the influence of the collective screening by the valence electrons in this energy range. No theory has yet accounted for the complicated dependence of the emergent neutral fraction on material and surface condition observed in experiment.

Recently, experiments have been performed using higher-energy incident protons[4,5] (0.3–16 MeV) and neutral hydrogen atoms[6] (1–2 MeV). In this paper it is shown that these results may be understood very simply in terms of capture into, and subsequent loss from, bound states on the proton in the solid. This is in contrast to other recent theoretical studies[7-10] which have supposed that no bound state exists on the proton within the solid either because of collective screening or because "collision broadening makes a bound state unstable."[11] These theories suggest protons in solids must be treated in an essentially different way from protons in gases or heavy ions in solids,[12] with capture being at the solid's surface. However, screening is not important at high velocities, and collision broadening of the state on the proton, although often comparable to the binding energy of the state, is shown not to significantly affect the calculation of capture and loss at high-proton energies. In fact, for high enough proton velocities the charge states are simply given by scaling gas-target results to solid densities: the cross sections are unchanged.

It is an interesting possibility that the intermediate-energy results may also be understood in terms of capture and loss, but with cross sections recalculated for the new valence-electron distribution in the solid.

II. OUTLINE OF THEORY

Collective screening of the potential of fast protons in solids is not important for bound states around the proton. As is clear from the calculations of Neufeld and Ritchie,[13] the screening charge lags behind the ion a distance v/ω_p, where v is the ion velocity and ω_p the characteristic frequency of the modes important in the long-wavelength dielectric function. ω_p is the plasmon frequency if this is a well-defined collective mode, and is of similar size in solids with no well-defined plasmon mode. For v greater than a few Bohr velocities v_0 ($v_0 = 2.2 \times 10^8$ cm/sec, also a typical metal Fermi velocity) this distance becomes many Bohr radii, and screening does not affect binding in the Coulomb potential close to the proton. Physically, the solid cannot respond rapidly enough to screen a fast proton.

The instability of the bound state (i.e., finite lifetime) due to the eventual loss of the electron by a scattering off a target atom is obvious. This is equally true for the outer electrons around a heavy ion in a solid, which are conventionally treated according to capture and loss formalism.[12] It is true that for protons of energies 100 keV to a few MeV, the lifetime of the bound state is so short as to make the uncertainty in the energy comparable to the binding energy. However this will be shown to be unimportant.

I put forward the following simple theory for the charge states of fast protons in solids:

(i). The charge state is produced by capture into and loss from bound states (discrete hydrogen-atom eigenfunctions) on the moving proton, with cross sections for the processes σ_c and σ_1 per target atom.

(ii). For high enough proton velocities these cross sections are given to good approximation by gas phase experiments where possible or single-atom calculations.

The equation for the neutral fraction Φ_0, and positive fraction $\Phi_+ = 1 - \Phi_0$ at a position x along the beam in a solid with target atom density n is then

$$\frac{d\Phi_0}{dx} = (\Phi_+\sigma_c - \Phi_0\sigma_1)n, \qquad (1)$$

and the equilibrium neutral fraction

$$\Phi_0^{eq} = (1 + \sigma_1/\sigma_c)^{-1}\,. \qquad (2)$$

Negative ions may be neglected at high velocities. Successive excitation processes leading to increased loss cross sections are also neglected (a justification of this follows from the discussion of the loss cross section in Sec. III). Equations (1) and (2) are analogous to the treatment of heavy ions in solids[12]; here, though the complications of inner shell vacancies, the many possible excited states of the outer shells, and the possibility of autoionization processes of the ion once it leaves the solid, that complicate the treatment of heavy ions, are absent.

The success of the theory is shown by Fig. 1. This compares measured neutral fractions emerging from solid carbon at exit energy E with the result predicted by Eq. (2) using single carbon-atom cross sections measured in gas-phase experiments.[14] These cross sections are given by subtracting from the measured gaseous oxide and hydrocarbon cross sections the appropriate number of hydrogen or oxygen cross sections. The somewhat large error bars in Fig. 1 are estimated from the error bars on the individual cross sections. It should be noted that a large part of the scatter there comes from the oxide measurements, where the oxygen cross section dominates and the total provides a poor measure of the carbon cross section. The hydrocarbon data[14] gives much less scatter.

The success of a treatment of capture into and loss from bound states, even though the uncertainty in the energy of the bound state is comparable to the binding energy, can be simply understood in terms of the characteristic times involved. There is a characteristic time for the capture process $\tau_c \sim r_c/v$. Fast protons capture electrons from target-atom core states and r_c is roughly the radius of these states. In addition there is a time to the next loss event, the lifetime of the captured electron state $\tau_1 \sim (n\sigma_1 v)^{-1}$. The distance traveled in this time is $\lambda = v\tau_1 = (n\sigma_1)^{-1}$. A third timescale is given by the binding energy E_0 of the hydrogen-atom state: $\hbar/E_0$. As stated before, for a wide range of proton velocities above v_0 it turns out that $\sigma_1 v$ is approximately constant, to give with a typical solid-target-atom density n, a lifetime τ_1 of the same order of magnitude as $\hbar/E_0$. However, in considering the capture process these are not the important times to compare. Instead the relevant comparison is $\tau_c \ll \tau_1$. The capture process to a state on the moving proton, on a time scale τ_c, will be unaffected by the eventual loss of the electron from this state at the much later time τ_1. The capture from a target atom may therefore be calculated in the same way as from an atom of a gaseous target; the actual cross section may be different. Similar arguments apply to the loss process. Thus provided the lifetime τ_1 is long compared to the process times τ_c, the picture of capture into and loss from bound states remains good.

The cross sections would in general be changed in a solid due to the changed valence-electron distribution. In fact, for high velocities the cross sections do not depend much on the valence-electron states, and the gas-atom cross sections may be used to good approximation.

These arguments contain the essential physics behind the success of the theory as shown in Fig. 1.

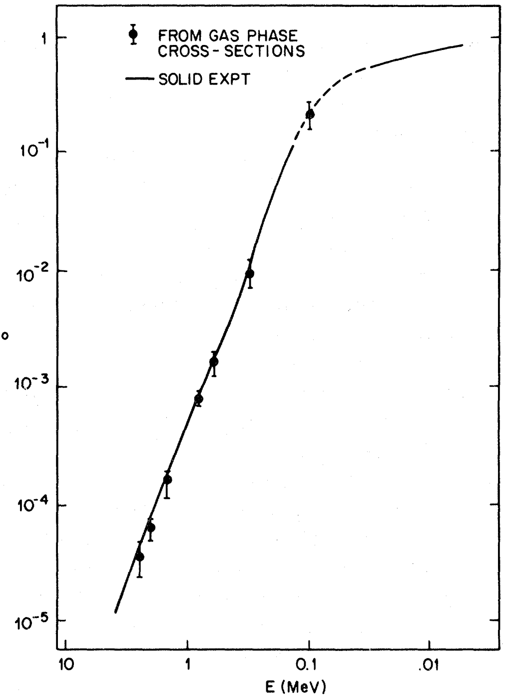

FIG. 1. Equilibrium neutral fraction Φ_0 emerging from solid carbon as a function of exit energy E. Continuous line: high-energy protons (Ref. 4), and low-energy deuterons (Ref. 15) with energy scaled to the proton energy for the same ion velocity. Broken line: protons on "dirty gold" (Ref. 16). The latter are used to interpolate between high and low energies, since at the lower-energies "dirty gold" and carbon are found to give identical results (Ref. 15). Points are calculated from gas cross sections (see text).

In Sec. III the same physics is expressed more precisely in terms of the quantum-mechanical theories of capture and loss.

III. DERIVATION

The result in quantum-mechanical terms is that capture and loss for fast protons depend on the *wave function* of the electron state on the proton, but not on the *binding energy* and *a fortiori* not on the uncertainty $\hbar/\tau_1$ in this energy.

This conclusion for the loss process is very straightforward. For proton velocities v greater than a few v_0 the loss cross section may be calculated[17] as the total scattering cross section of a target atom for scattering of an electron with a velocity distribution about the large velocity $\vec{v}$ given by the momentum distribution of the initial wave function. Essentially all scattering events result in loss of the electron. The uncertainty in the binding energy is not important. This conclusion, although derived from the impulse theory of electron loss,[17] should be independent of the exact validity of the model.

The capture process is quasiresonant and must be treated more carefully. On a Born-type approximation the cross section for capture from a state i on atom A to a state f on the moving proton B is given by

$$\sigma_{if} = (2\pi\hbar^2 v)^{-2} \int d^2p_\perp |\langle f|v|i\rangle|^2, \tag{3}$$

where the matrix element is

$$\langle f|v|i\rangle = \int\int \exp\left\{\frac{-i}{\hbar}\left[\left(\frac{E_i - E_f}{v} + \frac{mv}{2}\right) z_b + \vec{p}_\perp \cdot \vec{\rho}_b\right]\right\} \psi_f^*(\vec{r}_b) V(\vec{r}_a, \vec{r}_b)\, \psi_i(\vec{r}_a) \exp\left\{\frac{i}{\hbar}\left[\left(\frac{E_i - E_f}{v} - \frac{mv}{2}\right) z_a + \vec{p}_\perp \cdot \vec{\rho}_a\right]\right\} d\vec{r}_a d\vec{r}_b \tag{4}$$

m is the electron mass. $\vec{r}_a$ is the electron position measured from nucleus A, with components z_a parallel and ρ_a perpendicular to the velocity $\vec{v}$. Similarly $\vec{r}_b$ is the position from B. E_i and E_f are the binding energies of initial- and final-electron eigenfunctions $\psi_i(\vec{r}_a)$ and $\psi_f(\vec{r}_b)$. $V(\vec{r}_a, \vec{r}_b)$ is the interaction potential: the form chosen determines the approximation used. These equations may be derived[18] from either a wave or impact parameter approach: the integral over perpendicular momentum transfer $\vec{p}_\perp$ in Eq. (3) corresponds to an integral over impact parameters in that approach.

The total cross section for capture to the state f is the sum $\sum_i \sigma_{if}$ over occupied states i. In general i will include core states with $E_i \gg E_f$. It may be seen, independently of the form of V, that the integral over z_a gives a broad resonance condition. The maximum contribution would be expected from states i giving the stationary phase condition $E_i - E_f \sim \frac{1}{2}mv^2$. However the width of the resonance is given by the scale over which the momentum components of ψ_i decreases, and is between

$$E_i - E_f \sim \tfrac{1}{2}mv^2 \pm \hbar v/R_i, \tag{5}$$

where R_i is some characteristic radius of the orbit i. For hydrogen-like orbits $E_i \sim \frac{1}{2}mv^2 \sim \hbar v/R_i$, and the resonance is very broad. An uncertainty $\Delta E_f \ll \hbar v/R_i$ broadens the resonance by an amount small compared with the width $\hbar v/R_i$, and will change the cross section very little. The integral over z_b is not resonant for $v > v_0$, and if $\Delta E_f \ll \frac{1}{2}mv^2$, E_i (both of order $\hbar v/R_i$) the cross section will again be unchanged by the uncertainty ΔE_f. This is the central result to be proved.

It is also clear from Eq. (4) that the energy E_f is itself irrelevant for $v \gg v_0$. The cross section depends on the *wave function* ψ_f but not on the *energy* of the final state. This is particularly obvious if the Brinkman-Kramers[19] approximation for the interaction is used: $V = -e^2/r_b$. This does not give good answers for the overall value of the cross section, but is often used to calculate relative values between different cross sections. The cross section for capture from a full hydrogenlike shell with nuclear charge Z and quantum number n^* to any state in the shell n on a proton is given in closed form

$$\sigma(Z, n^*; 1, n) = \frac{2^{18}}{5}\pi a_0^2 \frac{1}{n^3}\frac{Z^5}{n^{*3}}\left(\frac{v}{v_0}\right)^8 \times \left(\frac{(\frac{1}{2}mv_0^2)^2}{(E_i - E_f - \frac{1}{2}mv^2)^2 + (\hbar v/R_i)^2}\right)^5, \tag{6}$$

with $R_i = n^* a_0/Z$, just the Bohr radius of the initial shell divided by the quantum number n^*. The quasiresonant nature and the unimportance of E_f (and therefore ΔE_f) much less than $\hbar v/R_i$ or $\frac{1}{2}mv^2$ is clearly displayed. The dependence on the final state is the well-known n^{-3} prefactor, which comes simply from the dependence of the high-momentum components of the wave function on the shell quantum number n.[20]

Capture probabilities for each impact parameter have been added. The loss probability has then been calculated. Capture and loss have been treated as independent events and phase interference effects have been neglected. In a gaseous target this is easily justified since the propagation of the states

$$|f(t)\rangle = e^{-iE_f t/\hbar}|f(0)\rangle \qquad (7)$$

over a range of long propagation times τ_1 is sufficient to randomize the phases between different final states f. In a solid when $E_f\tau_1/\hbar \sim 1$ this simple justification can no longer be made. Instead the following argument may be made: Capture to fast protons is mainly to the ground $1s$ state (according to the n^{-3} dependence), and to excited states is again mainly to s states.[21] There is little *directional* information from the capture process to influence the loss process. Phase interference effects between the s states will be small because of the different amplitudes. The averaging over phases due to the time propagation that does occur, and ranges of impact parameters and path directions, will probably wash out the remaining effects.

The energy range for which the description in terms of independent capture and loss events is expected to be valid is conveniently seen from the loss length $\lambda = (n\sigma_1)^{-1} = v\tau_1$. Values from carbon using the measured loss cross section and the atomic density n equal to 17.6×10^{22} cm^{-3} are given in Table I. λ continues to increase at higher energies. At high energies where λ is many interatomic spacings and capture and loss, involving core states, are characterized by a distance some core radius R_c, then the description is good. The lower-energy limit is more difficult to define. Typical loss cross sections for protons pass through a broad maximum at 100–50 keV proton energies, and decrease again at lower energies.[3] The minimum λ in Table I is therefore the smallest that will occur. The picture may possibly retain some validity right down to energies where screening finally dominates.

Finally in this section the use of gas (single-atom) cross sections must be justified.

The gas capture cross section may be used if the electron is captured from an inner shell. These are unaffected by binding in the solid. The minimum velocity at which this may be assumed can be seen from shell by shell calculations of various atoms.[22] The value for lithium $v > 2v_0$ for which inner (K) shell capture dominates may be taken as an optimistic lower limit.

TABLE I. Loss length $\lambda = (n\sigma_1)^{-1}$ in carbon as a function of proton energy.

Energy (MeV)	λ (Å)
2	19
1	10
0.1	3

The loss cross section is not expected to be sensitive to the valence electron distribution for proton velocities greater than a few v_0. This follows, for example, from the impact model described above, and the insensitivity of the total electron scattering cross section at high velocities to the valence electron distribution.[23]

IV. EXPERIMENTAL CONSEQUENCES

The implications of the theory go beyond simply the equilibrium neutral fraction.

A. Exit-angle dependence

Since the neutral fraction emerging is produced by equilibrium between capture and loss in the bulk solid, no dependence on the exit angle from *clean* surfaces at constant *exit* energy would be expected. To explain the observed angle dependence for gold[4] it is necessary to assume the presence of a thin layer of light atoms on the surface. 10^{16} atoms/cm^2 of carbon (a thickness of 3 Å) is sufficient to give the observed reduction in neutral fraction with increasing exit angle. The state of the surface in the experiment is not described.

B. Approach to equilibrium

This is described by Eq. (1), which may be solved to give

$$\Delta\Phi = \Delta\Phi^0 \exp[-(\sigma_c + \sigma_1)nx]. \qquad (8)$$

$\Delta\Phi$ is the deviation from equilibrium of either positive or neutral fraction at x, and $\Delta\Phi^0$ is the initial value at $x = 0$. Above 100 keV, where $\sigma_1 \gg \sigma_c$, the length over which equilibrium is approached, is simply $\lambda = (n\sigma_1)^{-1}$ already shown for carbon targets in Table I. Experiments with incident protons[4] at 7 MeV give some evidence for the long equilibrium lengths expected at high energies. Recent experiments[6] with incident neutrals at 1–2 MeV on the approach to equilibrium in thin carbon foils confirm the application of Eq. (8) and provide values for σ_1 and σ_c in reasonable agreement with the values from the gas-phase experiments.[14] Lower-energy experiments[24] suggest an equilibrium length at 500 keV/nucleon of less than 5–10 Å in carbon, consistent with the predictions of Table I. The extreme sensitivity to surface cleanliness at energies less than 200 keV suggested by Table I is well known.[16]

C. Excited-state fractions

The prediction of excited-state fractions is more difficult than predicting the neutral fraction. For high enough proton velocities the simple theory described involves a capture process exactly the same as in a gaseous target, and a loss cross section independent of the excited state. The excited state fraction is then given by the relative capture cross section from a single gas atom to the excited state. The Brinkman-Kramers approximation predicts a n^{-3} dependence on principal quantum number. More detailed calculations have been done by Hiskes[25] and Omvidar[26]: the n^{-3} is found to be good at least for large n. However it is not clear that the neglect of collision excitation processes, probably good when considering the neutral fraction, remains good when considering explicitly the excited state fraction. At lower velocities both capture and loss depend on the excitation and no simple result can be stated. As yet no experimental results for fast protons are available.

V. OTHER THEORIES

In this section, some other recent theories of fast proton charge pickup are discussed in terms of the ideas introduced in this paper.

The high-velocity results of Trubnikov and Yavlinskii[8] and Kitagawa and Ohtsuki[10] may be understood as calculations of the capture probability from the tail of the conduction electron distribution at the surface. They therefore neglect the process important at high velocities, namely capture from the target atom *cores* over the *larger distance* λ. It should also be noted that their high-velocity asymptotic dependences for the capture probability, falling off less rapidly than for capture from single atoms, are spurious. It is clear from Eq. (4) and from the simple Born approximation[22] that the asymptotic form depends crucially on the high momentum components of the wave functions of the initial and final electron states. These in turn are a function of the discontinuities in the wave functions. TY and KO use an unrealistic wave function for the conduction electrons, with discontinuous second derivatives, thus building in unphysical high-momentum components. A more realistic wave function is essential to calculate electron capture from the conduction tail, which may be important in the glancing angle reflection experiments.[32]

Yavlinskii *et al.*[7] treat a triple recombination process. Such a process would be expected to be less important than the quasiresonant capture process at high velocities. Their asymptotic dependence v^{-2} is hard to understand.

A proper comparison with the theory of Brandt and Sizmann[9] must await a detailed publication of that theory. From brief descriptions,[4,9,11,27] it appears the emphasis is on the absence of bound states in the solid, and instead[11] a build up of a "correlation in speed and direction" between the proton and electron. If correlation persists to the surface capture may then occur. This correlation has been suggested[11] to be reminiscent of the "charge exchange to a continuum state."[28] In contrast in the theory presented here, charge exchange to a continuum state is a separate process [ψ_f in Eq. (4) becomes an unbound continuum hydrogen wave function, not a discrete bound wave function] that gives rise exactly as in gas collisions[29] to the observed cusp of unbound electrons at the proton exit velocity.[30] Nevertheless the formula for the neutral fraction Eq. (2) is quoted.[5]

VI. SUMMARY

It has been shown that the charge state of fast protons in solids may be simply understood in terms of capture into and subsequent loss from bound states on the proton. By a bound state is meant a discrete hydrogen atom eigenfunction. The uncertainty in the energy of these states due to the short lifetime is not important, since neither capture nor loss process depends on the energy of the state. The emergent equilibrium fraction is produced in the bulk of the solid. The surface plays no special role merely acting as the absence of further scattering centres: on average, an electron captured to a bound state within the distance λ from the surface will be detected in that state and no further interaction with the surface is needed to produce the bound state.

For proton velocities greater than a few v_0 gas atom cross sections may be used. The solid results are then given by gas calculations scaled to higher densities. This result is an obvious conclusion of a discussion of capture and loss to bound states applicable to targets of all densities. As yet few cross sections for atoms commonly used in solid targets are available from theory or experiment. Theory[3] has mainly concentrated on inert gas atoms: clearly the same methods could be used for carbon, gold, etc. The data quoted for carbon cross sections[14] seems the most extensive available from experiment. A general expression for σ_c and σ_1 of Brandt and Sizmann, apparently based on a Thomas-Fermi atom and Born approximation, has been quoted[5]: this does not give very good agreement with measured gas values,[31] but the ratio roughly predicts the trend with target atomic number observed in solid experiments.[5]

The formalism of capture and loss may also account for the intermediate energy results. It has been suggested before[33] that argon cross sections predict fairly well solid neutral fractions. To account for the dependence on material, cross sections for the relevant atomic species with the valence electron distribution as in the solid must be known. A calculation of these cross sections in the intermediate energy range is not easy, but may be necessary to understand the data. An alternative possibility[9] is that collective screening dominates, and a careful calculation of electron pickup in the tail at the surface is needed.

ACKNOWLEDGMENTS

The author gratefully acknowledges suggestions and encouragement from L. C. Feldman, N. H. Tolk, and W. F. Brinkman.

---

[1] J. A. Phillips, Phys. Rev. 97, (1955) 404.

[2] A review is given by T. M. Buck, in *Inelastic Ion-surface Collisions* (Academic, New York, to be published).

[3] See, for example, H. S. W. Massey, E. H. S. Burhop, and H. B. Gilbody, *Electronic and Ionic Impact Phenomena* (Oxford U.P., Cambridge, England, 1974).

[4] A. Chateau-Thierry and A. Gladieux, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. D. Moak (Plenum, New York, 1973).

[5] A. Chateau-Thierry, A. Gladieux, and B. Delaunay, Nucl. Instrum. Meth. 132, 553 (1976).

[6] J.-C. Poizat and J. Remillieux (unpublished).

[7] Yu. N. Yavlinskii, B. A. Trubnikov, and U. F. Elesin, Bull. USSR Acad. Sci. Phys. 30, 1996 (1966).

[8] B. A. Trubnikov and Yu. N. Yavlinskii, Zh. Eksp. Teor. Fiz. 25, 1089 (1967).

[9] W. Brandt and R. Sizmann, Phys. Lett. A 37, 115 (1971).

[10] M. Kitagawa and Y. H. Ohtsuki, Phys. Rev. B 13, 4682 (1976).

[11] W. Brandt, in Ref. 4, p. 261.

[12] H. D. Betz, Rev. Mod. Phys. 44, 465 (1972).

[13] J. Neufeld and R. H. Ritchie, Phys. Rev. 98, 1632 (1955).

[14] L. H. Toburen, M. Y. Nakai, and R. A. Langley, Phys. Rev. 171, 114 (1968).

[15] K. H. Berkner, I. Bornstein, R. V. Pyle, and J. W. Stearns, Phys. Rev. A 6, 278 (1972).

[16] T. M. Buck, L. C. Feldman, and G. H. Wheatley, in Ref. 4, p. 331.

[17] In Ref. 3, Vol. 4, p. 2503.

[18] In Ref. 3, Vol. 4, Chap. 23.

[19] M. C. Brinkman and H. A. Kramers, Proc. Acad. Sci. Amst. 33, 973 (1930).

[20] R. H. May, Phys. Rev. 136, A669 (1964).

[21] In Ref. 3, Vol. 4, p. 2467.

[22] V. S. Nikoleav, Zh. Eksp. Teor. Fiz. 51, 1263 (1966) [Sov. Phys.-JETP 24, 847 (1967)].

[23] In Ref. 3, Vol. 2, p. 666.

[24] A. Lurio and J. F. Ziegler (unpublished).

[25] J. R. Hiskes, Phys. Rev. 180, 146 (1969).

[26] K. Omvidar, Phys. Rev. A 12, 911 (1975).

[27] M. J. Gaillard, J.-C. Poizat, J. Remillieux, A. Chateau-Thierry, A. Gladieux, and W. Brandt, Nucl. Instrum. Meth. 132, 547 (1976).

[28] J. Macek, Phys. Rev. A 1, 235 (1970).

[29] G. B. Crooks and M. E. Rudd, Phys. Rev. Lett. 25, 1599 (1970).

[30] K. Dettman, K. G. Harrison, and M. W. Lucas, J. Phys. B 7, 269 (1974).

[31] S. K. Allison, Rev. Mod. Phys. 30, 1137 (1958).

[32] C. Rau and R. Sizmann, Ref. 4, p. 295.

[33] T. M. Buck, G. H. Wheatley, and L. C. Feldman, Surf. Sci. 35, 345 (1973).