

Slow Particle-Induced Electron Emission from Solid Surfaces*

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With 39 Figures

1. Introduction

In the following review we will deal with electron emission from solid surfaces resulting from impact of relatively slow particles (in the given context we denote by *particle* any neutral or charged atom, molecule or cluster, whereas electrons as projectiles remain definitely excluded unless explicitly stated). By *slow* we refer qualitatively to the impact energy range below one keV/amu (impact velocity below $0.2 \text{ amu} \approx 4 \times 10^5 \text{ m/s}$). Phenomena related to particle-induced electron emission ("PIE" – the rather common use of "secondary electron emission" for such processes should be avoided) from solid surfaces can be roughly ascribed to two different mechanisms:

Kinetic Emission ("KE") is caused by transfer of kinetic projectile energy onto the electrons and atomic cores in the solid or in some adsorbates at the solid surface, which may result in a variety of physical processes eventually leading to the ejection of electrons from the solid surface. In KE processes the kinetic energy and mass of the projectile are of foremost importance, whereas a number of other projectile properties as its chemical configuration (atomic or molecular or clustered), charge state (neutral or positively singly or multiply charged or negatively charged) and electronic, vibrational or rotational state (in respective ground state or excited states) are usually not of concern. However, this assumption is only justified at relatively high impact velocity. In the context of the present review we will sometimes check the extent of its applicability. Since KE from its very principle should disappear toward low impact velocity, a corresponding threshold impact velocity should exist, but its precise location is generally not well defined.

The physical processes and experimental experiences related to KE are discussed at length in a review by Hasselkamp (1991) in this volume.

Potential Emission ("PE") is the principal mechanism for electron emission if the kinetic energy of the projectile remains of less influence than its "internal" properties which have just been mentioned. For slow projectiles the charge state plays a rather significant role on the electron emission, and the projectile species is also of concern because of the potential energy related to ion production from the corresponding neutral atomic or molecular ground state species. This potential energy is carried by the ion toward the solid surface

*List of Abbreviations see end of this chapter.

and deposited during recombination of projectiles into their neutral ground state. Recombination involves various rapid electronic transitions which may lead to the electron emission.

It is important to note that the PE processes do not require any kinetic projectile energy and therefore no impact velocity threshold is given. However, toward higher impact velocity the PE processes will become superimposed by KE effects which then eventually may dominate (see above).

In the present review we are primarily interested in such low projectile velocities where the PE contributions remain dominant. We will be using the acronym "*sPIE*" for *slow particle-induced electron emission* as a qualitative distinction against KE-dominated processes, which are the subject of other contributions to the present volume.

For most practical applications of PIE the involved impact velocities are not sufficiently low to exclude KE influences completely or even approximately. Therefore it will be necessary to regard the influence of KE in all studies on PE where the projectile velocity reaches up to or surpasses the corresponding KE threshold region.

In the earlier literature on PIE, informations on potential emission are rather scarce and – almost as a rule – not very reliable. Only a few groups have produced still nowadays valid experimental data, mainly because of the very important influence of target surface conditions on the PE process and the comparably small PE contributions in the presence of usually more important KE-related background effects.

In first place we refer to the important studies of H.D. Hagstrum at Bell Laboratories/USA, which started in the early fifties and can be regarded as the foundation of modern PE work both from an experimental (Hagstrum 1953, 1954a, Hagstrum et al. 1965, Chaban et al. 1990) and theoretical (Hagstrum 1954b, 1977) point of view. Seminal contributions to the field of PE have also been provided by experimental work of U.A. Arifov and coworkers in Tashkent/USSR (Arifov et al. 1969, 1971) with the support of a strong theoretical group. Publications from both groups serve as valuable sources for earlier studies in the field. General reviews on both experimental and theoretical contributions from other groups active in the fifties and early sixties have been given by Kaminsky (1965) and Carter and Colligon (1968). Some informations on PE can also be found in treatises on gaseous electronics and related fields, cf. e.g. McDaniel (1964), but to our knowledge there exists no recent extensive survey dealing specifically with PE. However, the processes fundamental to potential emission are commonly included in the numerous surveys on PIE.

Investigations of potential emission have long been plagued by their extreme surface-sensitivity and the related experimental demands on ultrahigh vacuum conditions and target preparation. In fact, Hagstrum has utilized the very surface sensitivity of PE for a particular surface spectroscopy (so-called ion neutralisation spectroscopy – "INS", Hagstrum 1956a, 1978), which

later became somewhat superseded by the closely related metastable atom de-excitation spectroscopy ("MDS", cf. e.g. Ertl 1986).

Although UHV experimental technology has rapidly become widely available, there have not been many important studies on PE in the seventies and early eighties, apart from further contributions by the groups already mentioned.

Still more recently, an important boost to the field has been provided by the growing availability of slow multicharged ions ("MCI") as projectiles. Their use tremendously enlarged the parameter space for PE studies and the importance of PE also at higher impact energy, exposed genuinely new effects and thus led to important further insights in PE-related phenomena just in the last few years. This has also attracted interest from the theoretical side, mainly because of a close relation of PE with the processes of ion-induced desorption, secondary ion emission and low energy ion reflection from surfaces, all of which are of considerable importance for surface investigations. With highly charged projectiles one can also study the phenomenon of "Coulomb explosion" (Bitensky et al. 1979, Bitensky and Parilis 1989) as well as the conversion of approaching highly charged ions into "hollow atoms" which then give rise to characteristic soft X-ray emission (Briand et al. 1990). Both processes should most clearly develop at the lowest achievable MCI impact velocities.

It is therefore quite fitting to speak of a recent renaissance for the field of potential emission as a good justification for the present review which has been organized in the following way.

Chapter 2 will deal with experimental methods for investigation of sPIE and in particular PE. In Chap. 3 a short glimpse on the theoretical background for PE will be followed by discussions of recent experimental data and their interpretation, with particular emphasis on the use of slow multicharged projectile ions and data obtained by the present authors and their affiliates.

Finally, Chap. 4 has been dedicated to the threshold impact velocity region for KE in the presence of PE, where a recently achieved clearer distinction between the two mechanisms will be presented.

Based on this experience we will finally redefine the mechanisms of PE and KE in a physically more stringent way than so far common.

2. Experimental Techniques for Investigation of sPIE

As already mentioned in the introduction, studies on sPIE have been conducted for many decades, but most of the available results should be regarded with reservations because of insufficiently well defined experimental conditions. State-of-the-art investigations in this field must take into account

the precise state of the projectile as well as the target surface. As a general rule, projectile particle beams have to be carefully defined according to their geometry and kinetic (impact) energy, and the internal particle energy (possible presence of excited states, etc.) must be known as well (cf. Sect. 2.1).

The target surface has to be prepared by means of now rather common standard techniques, which means that application of UHV technology (base pressure in the target chamber not higher than typically 10^{-10} mbar) is indispensable (Sect. 2.2). In the course of such experiments the reactants (in first place the emitted electrons) should be detected according to their geometry, species and energy (Sect. 2.3). In the present context we deal mainly with neutral and ionized atoms/molecules as projectiles, while electrons are the principal secondary particles. In addition, consideration of processes closely related to PE are of interest (e.g. slow ion scattering, secondary ion emission, ion-induced desorption and photon emission) together with the appropriate experimental techniques.

From the detected reaction products the main features of PE processes can be derived. In first instance the electron emission yield (Sect. 2.4), the energy distribution of ejected electrons (Sect. 2.5) and the electron emission statistics (Sect. 2.6) will constitute a basis for further physical considerations on the processes of interest.

2.1 Preparation of Slow Particle Beams

As the most common projectiles for sPIE investigations we consider singly or multiply charged ions with their impact energy ranging from a few eV up to a few keV. Such ion beams can be produced by a variety of ion sources (Brown 1987), which should be carefully selected in view of the particular needs (ion species, charge states, desired particle fluxes). It is important to recognize that as a general rule the ion source constitutes a most important component of the experimental setup and can greatly influence both the efficiency and reliability of the whole experiment.

An enhanced ion kinetic energy spread caused by the particular ion source may require the incorporation of ion energy/velocity selectors into the beam optics, together with means for mass selection, ion transport and acceleration/deceleration in front of the target surface. Furthermore, the elevated gas pressure resulting from ion source operation might call for a differential pumping stage between the ion source and the target chamber.

Fast (keV range) neutral projectiles can be produced by charge exchange of primary ions in suitable target gases or via ion scattering with neutralization at well defined single crystal surfaces.

Preparation of neutral projectiles with impact energies below typically 100 eV requires special techniques to achieve well defined projectile geometry and kinetic energy (Scoles 1988).

Of particular interest is the characterisation of projectile particles according to their internal energy. The admixture of long-lived excited (metastable)

states is often of great influence and should be quantitatively taken into account. A number of techniques have been developed for determination of metastable ion/neutral beam fractions in ion-atom collision experiments (see e.g. Gilbody 1978, Hofer et al. 1983, Schweinzer and Winter 1989) which are directly applicable for the present purposes.

In a number of experiments, fast (multi-keV up to MeV) projectiles have been applied under grazing incidence angles θ in order to obtain small "vertical" impact energies $E_i = E \sin^2 \theta$. However, such a situation is fundamentally different from the case where decelerated ions impinge in normal direction onto the surface, for the following two reasons.

- 1) The moving particle "sees" the momentum space of surface valence electrons as modified by a Galilei-transformation (van Wunnik et al. 1983), which causes an effective broadening of the Fermi edge when seen by the moving projectile, similar to but much more pronounced than thermal broadening. The energetic relations between valence electrons of the surface and the electronic states of an approaching particle are decisive for the electronic transitions to be described in Sect. 3.1. Consequently, electrons with energies above the Fermi edge in the projectile rest frame become available for electron transitions from the surface to the projectile (RN) as well as now empty states below the Fermi edge can serve for transitions from the particle to the surface (RI). This Galilei transformation also causes an increase in energy of electrons emitted from the valence band with increasing parallel ion velocity (i.e. a similar effect as a decreasing work function, Misković and Janev 1989) and also permits processes to take place which would be energetically forbidden for ions with low impact energy.
- 2) Precautions are necessary to avoid violent atomic collisions with single surface atoms which would dominate any effects due to the potential energy of the projectile. First of all, targets with a perfect flat surface (i.e. flat on an atomic scale, which means relatively large, well oriented and prepared single crystals with extremely few terraces) have to be used. Secondly, as has been pointed out recently by Winter and Zimny (1988), for grazing incidence and a planar scattering potential the scattering parameter has to be chosen such that the distance of closest approach remains larger than the so called "Firsov screening length"

$$a_F = 0.885a_0 (Z_1^{1/2} + Z_2^{1/2})^{-2/3} \quad (2.1)$$

with a_0 the Bohr radius and Z_1, Z_2 the projectile and target atomic numbers, respectively. The critical angle θ_c for this condition to prevail can be calculated from the characteristic planar channeling angle (Gemmell 1974).

$$\theta_c = \sqrt{\frac{2\pi Z_1 Z_2 e^2 a_F n_s}{E_0}} \quad (2.2)$$

with n_s the planar density of atoms at the surface and E_0 the primary ion energy.

Important contributions from violent collisions causing kinetic emission processes have to be expected in all experimental situations where these rather stringent limitations for grazing incidence experiments are not met.

2.2 Target Preparation

Electron emission from low energy ion impact results almost exclusively from interactions of the projectile with the very first surface layer. Therefore, the electronic density of states of the surface together with the electronic state of the ion determines the emission yield, energy distribution, angular dependence, etc. Only carefully prepared surfaces will assure reproducible data for PE investigations.

In appropriate experiments the usual requirements in surface physics have to be carefully fulfilled, and suitable in situ-surface analytical techniques must be incorporated. This is the reason why data on electron emission which have been performed in vacua above typically 10^{-9} mbar are only of limited significance. It is important to know the chemical composition of the surface with respect to adsorbates, since adsorbed sub-monolayers can alter the work function, the density of states of the valence band and thus the electron emission, as well.

In particular, for single crystal surfaces the crystallographic orientation is of interest, especially if angle-dependent investigations are performed and low impact energy is simulated by grazing incidence of fast particles.

There are two different possibilities to assure reproducible data.

- 1) Use targets for which many data on preparation techniques are available and which are known to pose no great "difficulties" for preparation.
- 2) Still more appropriately, in situ surface-sensitive analytical methods like AES (Auger-Electron Spectroscopy), PES (Photoelectron Spectroscopy) as well as ISS (Ion Surface Scattering) should be used.

A clean surface may be defined as to be annealed and at an ambient temperature with an overall surface contamination of less than a few percent of a monolayer (10^{13} atoms /cm²). At any case, appropriate vacuum conditions are necessary to keep a such prepared surface clean as long as the measurements takes place.

The preparation of surfaces is extremely material-dependent, but in general the possibilities for noble gas ion sputtering (see the recent review by Taglauer 1990), heating of the surface and flooding with reactive gases are necessary for target preparation. In most cases heating in good vacuum causes impurities of the bulk material to segregate (enrichment) at the surface which must than be sputtered away or removed by heating under elevated oxygen or hydrogen gas pressure. By repetitive application of these methods (some-

times necessary during several days) a clean and reproducible surface can be prepared.

A useful summary of important techniques for the preparation of clean surfaces after a sample has been brought into an ultra-high vacuum environment (i.e. after mechanical and/or electro-chemical polishing and of residue removal) can be found in Musket et al. (1982) and Grunze et al. (1988).

For a number of elements the only way to achieve a clean surface for the present purposes is either in-situ deposition of thin films via sputtering or evaporation, or in-situ fracturing or cleaving of appropriate samples.

2.3 Detection of Reaction Products

Investigation of particle-induced electron emission in first instance involves quantitative detection of the electrons emitted from the target surface.

In the most simple situation this can be achieved by measuring the current of these electrons, given sufficiently high projectile particle fluxes and emission yields (electron currents at least in the pA range). However, in the majority of experimental situations the projectile fluxes are too low for such an approach and thus the resulting small electron fluxes can only be detected by means of counting techniques (application of open multi-stage electron multipliers, channel electron multipliers, channel plates, etc.). This is especially relevant for the angular dependence or the energy distribution of emitted electrons. Appropriate measures have to be taken to assure constant electron detection efficiency irrespective of the electron impact energy and incidence angle at the active detector region, and also to avoid disturbing effects from heavy particle impact (reflected neutral and/or ionized projectiles, secondary ions) as well as energetic photons "seen" by the active detector region. Special problems can also arise in view to the compatibility of the electron detector with the necessary UHV preparation procedures (baking of UHV apparatus, target cleaning etc., cf. Sect. 2.2).

2.4 Measurement of Electron Emission Yields

Electron emission yields (i.e. the mean number of electrons emitted per impinging projectile particle, usually denoted by γ (see also Sect. 2.6) are determined by measuring the fluxes of both the projectile particles and the emitted electrons (cf. Sect. 2.3). With charged projectiles this can be simplified by measuring target currents with and without permitting the electrons to leave the target, which can be controlled by an appropriate target bias with respect to its environment. Precautions have to be taken against possible disturbances from charged particle reflection, secondary ion emission and spurious electron production due to impact of reflected or scattered projectiles or electrons, all possibly causing additional electron emission from the target region. In general, for such measurements projectile fluxes corresponding to not less than one nA are necessary. For smaller fluxes the electron

yield can only be measured by counting both the projectiles and the emitted electrons and then calibrating such obtained relative figures to already known absolute yield data. In such experimental situations the usually rather limited acceptance angle of the electron detector calls for a series of measurements at different electron ejection angles, from which the correct values for the global electron yield have to be derived.

This is especially important because the often made assumption of simple dependences for the electron emission yield on the ejection angle can introduce large experimental errors.

The use of neutral projectiles poses special problems, because determination of their flux requires relatively complicated experimental techniques. Whereas with sufficiently high projectile fluxes microcalorimetric techniques can be applied, recently the use of liquid He-cooled semiconductor bolometers for detection of rather small neutral particle fluxes has become common (cf. Scoles 1988). The latter technique can also be utilized for the present purposes. However, incorporation of suitable devices into the common experimental setups for PIE investigations requires considerable constructional efforts, in particular for the liquid He cryostat needed for cooling of the bolometer unit.

2.5 Measurement of Ejected Electron Energy Distributions

Setups for the joint measurement of electron emission yields (cf. Sect. 2.4) and the energy distribution of emitted electrons in connection with slow particle impact on solid surfaces are usually derived from Hagstrum's instruments (Hagstrum 1954a, Chaban et al. 1990). They may include up to three highly transparent grids inside a hemispherical collector (cf. Hofer et al. 1983), in a similar way as for conventional low energy electron diffraction (LEED) systems. Measurements with this type of equipment will accept electrons with practically zero ejection energy and their emission within almost half of the solid angle, but are only applicable with total electron currents not smaller than typically ten to hundred pA. Moreover, they feature only rather poor electron energy resolution (≥ 1 eV FWHM, cf. Hasselkamp 1991).

As such comparably high electron currents are not commonly available, various standard types of electron energy analysers equipped with electron counting detectors are being applied (see e.g. de Zwart et al. 1989, Zeijlmans van Emmichoven et al. 1988), which permit considerably higher energy resolution (≤ 0.1 eV FWHM), but may seriously discriminate the low energy part of the electron energy distribution $K(E_e)$. They also cover rather small solid angles of ejection, which makes a series of measurements at different ejection angles necessary.

2.6 Measurement of Electron Emission Statistics

In sPIE processes involving neutral and singly charged particles the observed yields are typically smaller than unity. If KE is the exclusive (i.e. for neutral projectiles) or dominating process, the electron emission will exhibit a statistical behaviour, i.e. for impact of a single projectile particle ejection of either zero or one, two, etc. electrons from the target surface can result. Consequently, the electron emission yield γ is actually the weighted mean of the so-called electron emission statistics (ES), which itself is represented by the series of probabilities W_n for the emission of a given number n of electrons:

$$\gamma = \sum_{n=1}^{\infty} nW_n \quad \text{with} \quad \sum_{n=0}^{\infty} W_n = 1 \quad . \quad (2.3)$$

The ES for PIE have been of longstanding interest in the context of single particle counting with ion-electron converters and secondary electron emission multipliers, because the corresponding counting losses are determined by the probability W_0 for emission of no electron. Studies of ES have therefore been carried out by various groups for a large number of projectile-target combinations (e.g. Bernhard et al. 1965, Delaney and Walton 1966, Staudenmaier et al. 1976).

In these studies the primary emphasis was to clarify precise shapes of the emission probability distributions, since fitting of an appropriate standard distribution (e.g. a Poissonian) to the experimentally determined relative values for W_n with $n \geq 1$ could lead via extrapolation to the not directly observable value for W_0 and thus to the absolute electron emission yields.

Recently, such ES measurements have been extended to much lower ion impact energies than so far attainable (Lakits et al. 1989a, 1990a, Aumayr et al. 1991). As a consequence, comparison of sPIE data resulting from bombardment of a given target surface with isoenergetic neutral, singly and multiply charged projectile species has become possible. This opened up the way for a clearer distinction between contributions from respectively PE and KE to apparent total electron emission data (for further details cf. Sect. 3.4 and Chap. 4).

3. Review on Potential Electron Emission Processes

In the present chapter we will deal exclusively with electron emission caused by the *potential energy* of a projectile particle that approaches toward (or recedes from) a solid surface.

As already stated at several occasions, only particles moving with relatively low kinetic energy with respect to the surface will cause exclusively potential emission, as a result of their internal energy (i.e. because of their

being ionized and/or highly excited), whereas at higher impact energies the total (or apparent) electron emission can also be caused by kinetic processes. Contributions from PE and KE are generally not separable in an unambiguous manner. However, from a measurement of electron statistics for PIE processes such a distinction among PE and KE effects has become possible, as will be further discussed in Chap. 4.

In the context of Chap. 3, possible KE contributions will not be further dealt with except as a background for the PE processes of interest.

3.1 Models for Potential Electron Emission

Potential emission (PE) is caused by neutralization and deexcitation processes taking place in front of the surface, where essentially no kinetic energy of the projectile is needed to induce these processes. In the following we will deal with phenomena of electron emission due to deexcitation and neutralization of excited atoms as well as singly and multiply charged ions (MCI) at solid surfaces.

The standard model for electron emission resulting from the interaction of slow ionized or excited particles with surfaces is due to Hagstrum (1954b), who developed a semiempirical theory on the basis of his own experimental results and earlier considerations, e.g. from Shekter (1937).

In this model he regarded charge exchange processes between the electronic states of the surface and the incident particle. These electronic transitions were described within an adiabatic picture which requires no exchange of energy between electronic and nuclear motion. The involved energy levels are slightly shifted upwards, thus leading to a lower binding energy than for the situation of a free particle far from the surface, which primarily results from the interaction of the active electron with the negative image charge of the positively charged projectile core.

Hagstrum obtained transition rates for electronic transfer from the surface valence band to a particle in front of this surface, which depended roughly exponentially from the surface-particle distance d . The transition rates are related to the overlap of the atomic wave functions of surface atoms and the projectile, which both in first approximation decay exponentially with d . All quantum-mechanical calculations of transition rates which have been carried out later on (e.g. Hentschke et al. 1986) showed the validity of this assumption. Consequently, the highest transition probability is to be expected between surface states with the lowest binding energy (i.e. those situated near the Fermi edge) and highly excited projectile states.

Hagstrum also regarded the transition probability as independent from the ion impact energy. He showed that the distance where these transitions take place most probably (i.e. for the maximum of the transition probability) is about 3 Å for He⁺ with 10 eV kinetic energy, and moves closer to the surface with increasing particle velocity.

In a rough approximation, the distance d_q where multiply charged ions start to interact with a surface has been shown by Delaunay et al. (1987a) to be proportional to the charge state q .

In a more detailed approach, Apell (1987) assumed that these transitions start at a distance d_q where the ionic Coulomb potential becomes equal to the binding energy of electrons at the Fermi edge, and for a q -times ionized atom he derived a distance of

$$d_q [\text{\AA}] \approx 3q . \quad (3.1)$$

With a similar "over barrier model" and additional inclusion of the electron and ion image potentials Snowdon (1988) obtained

$$d_q [\text{\AA}] \approx q + 3.7 , \quad (3.2)$$

which for highly charged ions becomes much smaller than the value given by (3.1).

A charged particle in front of a metallic surface causes the metal electrons to form image charges. The image plane does not coincide with the surface of the top layer of atoms, because the metal electrons will penetrate by about 1 \AA into vacuum .

In a general view, the ion-surface system is subject to two influences (see Varga 1987 and Andr  1989).

- 1) The ion "feels" an attractive potential and thus will be accelerated toward the surface, gaining kinetic energy by the classical image force until it has become fully neutralized. A simple calculation (Varga 1987) of this energy gain ΔE_{kin} normal to the surface with the earlier derived distance of interaction (3.1) yields

$$2.5 q \leq \Delta E_{\text{kin}} [\text{eV}] \leq 4q . \quad (3.3)$$

- 2) The potential energy of the ion-surface system changes with the mutual distance d , where for $d \leq 2 \text{\AA}$ the classical image potential concept remains applicable. At smaller distances the potential energy is usually assumed to remain constant, simply to avoid divergence problems. The valence electron to be captured by the incoming ion "sees" besides the field of the ion core also the field of its own image charge and the image charge of the ion core, which for positive ions yields an eigenstate which is shifted upwards, i.e. to lower binding energies. For sufficiently large distances ($d \geq 2 \text{\AA}$) from the surface the resulting binding energy shift $\Delta W = W_i - W'_i$ can be described by

$$\begin{aligned} \Delta W &\approx (2q - 1)/4d \\ \Delta W [\text{eV}] &\approx 3.6 (2q - 1)/d[\text{\AA}] \end{aligned} \quad (3.4)$$

with W_i and W'_i the potential energies for infinite separation and a distance d , respectively.

The linear relationship between the initial charge state and the corresponding distance of first interaction (with $d[\text{\AA}] \approx 3q$ from (3.1), (3.4) yields $\Delta W [\text{eV}] \approx 2.4 - 1/q$) leads to the estimate, that for each neutralization step (i.e. decrease of q by one) the binding energy is shifted in first approximation by $\Delta W \geq 1.2$ eV for low charge states, which increases to $\Delta W \leq 2.4$ eV with a higher initial charge state. This shift reduces the potential energy available for electron emission. Since the energetic relations between electrons of the surface and the approaching particle are decisive for the processes to be described below, effects connected with the projectile velocity have to be considered, especially if low “vertical” velocities are simulated by grazing incident projectiles (cf. Sect. 2.1)

The Galilei-transformed broadening of the Fermi edge in the frame of the moving projectile (van Wunnik 1983) in the model presented in Fig. 3.1 makes electrons in states above the Fermi edge available for RN processes as well as opens up states below the Fermi edge for RI transitions. The same Galilei transformation also causes an increase of the kinetic energy of electrons emitted from the valence band with increasing parallel ion velocity in the same way as a decreased work function (Misković and Janev 1989).

It should be pointed out that this energy shift depends on the total ion velocity and not just on the surface-normal velocity component, the latter however being responsible for the amount of image charge-induced energy shift of the binding energy in the moment of the electron transition.

In Fig. 3.1 electron binding energy schemes for three different classes of transitions are shown. We distinguish one-electron transitions as resonance ionization (RI), resonance neutralization (RN) and quasiresonance neutralization (QRN), from two-electron transitions as Auger neutralization (AN), Auger deexcitation (AD) and autoionization (AI). Finally, also radiative deexcitation (RD) might be possible. W'_i and W'_{ex} are the ionization and excitation energy of the particle near the surface, respectively. The time scale for transitions of interest covers the range of $10^{-13} - 10^{-16}$ s if not otherwise specified.

In the following these processes will be discussed in somewhat more detail.

One-electron Transition Processes

Resonance transitions. Resonance transitions into excited projectile states (cf. Fig. 3.1a) generally dominate the particle-solid interaction because of the much larger spatial extension of the involved wave functions in comparison to the corresponding ground states. As a consequence, such resonance transitions can take place already at a rather large distance from the surface.

Resonance processes are non electron-emitting precursors for the subsequently possible electron-emitting two-electron transitions.

Resonance Neutralization (RN). RN involves electron transfer from the surface valence band into the incident ion and can take place if unoccupied electronic states of the atom become energetically degenerate with those of

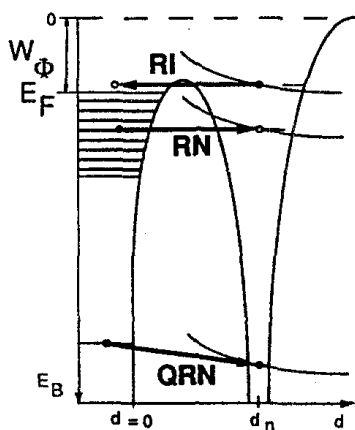


Fig. 3.1a. Resonance transitions

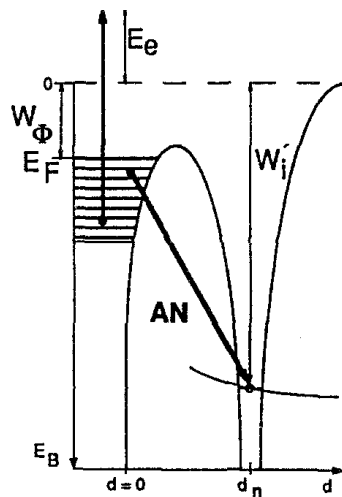


Fig. 3.1b. Auger neutralization

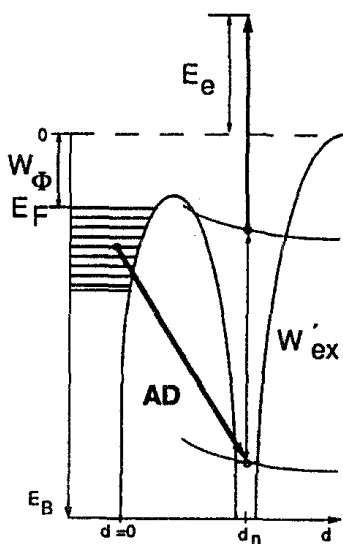


Fig. 3.1c. Auger deexcitation

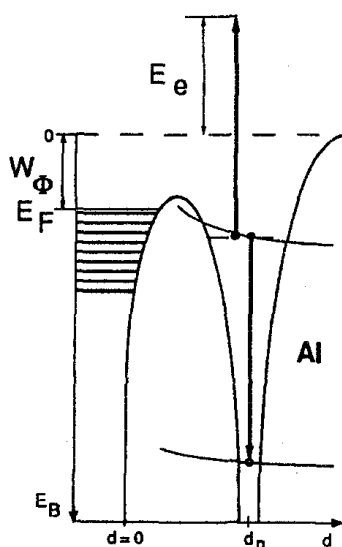


Fig. 3.1d. Autoionization

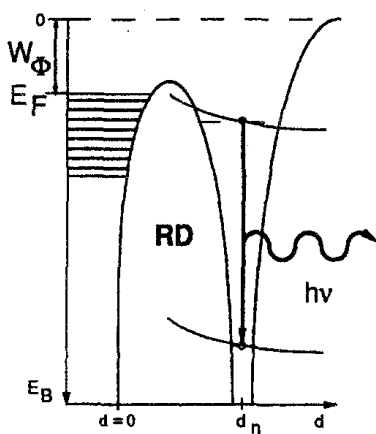


Fig. 3.1e. Radiative deexcitation

Fig. 3.1 a-e Electron energy diagrams showing transition- and deexcitation processes for an atom in front of a surface, E_B ... binding energy, d ... particle-surface distance. The shaded region is the filled portion of the conduction band of the solid surface, W_Φ ... work function, E_F ... Fermi energy. Full dots indicate occupied states, open circles indicate free states. The shift of the electron energy levels with distance is indicated qualitatively and the respective binding energies are denoted with W'_i or W'_{ex} . E_e kinetic energy of possibly emitted electrons

electrons in the valence band. In a potential curve diagram such RN transitions correspond to crossings between the initial (ion plus solid) and final state (excited neutralized particle plus solid).

Resonance Ionization (RI). Resonance ionization (RI) is inverse to RN and can take place if the binding energy of an occupied excited state in the particle is smaller than the surface work function W_ϕ , i.e. if empty levels in the conduction band become energetically resonant with occupied atomic levels.

Quasi-resonance Neutralization (QRN). QRN is a near-resonant transition from more tightly bound localized target states (core states) to projectile states. Such processes can only occur in close collisions since an interpenetration of the involved inner electronic orbitals has to be assured. QRN was found responsible for oscillatory ion survival probabilities in ion-surface-scattering (ISS) experiments (Erickson and Smith 1975).

Two-electron processes

Auger neutralization (AN). This process (cf. Fig. 3.1b), by decreasing the charge state of the ion, can eject an electron from the surface valence band if the involved neutralization energy is at least twice the work function W_ϕ . Two electrons of the surface valence band will be involved, one neutralizing the ion and the other one, gaining energy via electron-electron interaction, to be ejected with a maximum kinetic energy E_e

$$E_e \leq W'_i - 2W_\phi \quad (3.5)$$

W'_i is the effective recombination energy of the neutralized particle ("neutralization energy"), which decreases with the AN process taking place closer to the surface because of an increasing level shift with decreasing distance. The energy distribution of electrons emitted due to AN corresponds to a self-convolution of the electronic surface density of states (S-DOS) and depends on the Auger transition matrix elements and the available potential energy W'_i . An increasing impact energy shifts the peak of the ejected electron distribution to lower kinetic energy, while its maximum energy will be increased because of the collisional broadening of the distribution.

Auger deexcitation (AD). An excited particle (cf. Fig. 3.1c) in the absence of available empty resonant levels in the valence band (i.e. if the binding energy ($W'_i - W'_{ex}$) of the excited electron in the particle is larger than the surface work function W_ϕ) may interact with an electron of the valence band. The such excited electron can be ejected from the particle while a surface electron is transferred into a lower particle state. The maximum energy of a such emitted electron is given by

$$E_e \leq W'_{ex} - W_\phi \quad (3.6)$$

with W'_{ex} (excitation energy) being independent of the particle-surface distance and therefore also of the particle velocity, since the initial and final charge states are identical and thus subject to similar level shifts. The energy distribution of electrons emitted due to such an AD process directly reflects the electronic surface density of states (S-DOS) multiplied by an energy-dependent escape probability. In first order no shift of the related electron energy distribution is to be expected for changing the particle impact energy.

Autoionization (AI). This process can be ascribed to an intra-atomic Auger deexcitation of a doubly/multiply excited atom or ion, with one or more electrons being emitted and one transferred to a lower state of the particle (cf. Fig. 3.1d). AI is of particular interest for MCI neutralization, during which multiple excited states with high quantum numbers might be produced via multiple RN. AI is similar to the AD process, with all involved electrons belonging however to the projectile atom. Therefore, a comparably narrow energy distribution of emitted electrons can be expected. The energy E_e of emitted electrons as in the other cases results from the potential energy difference of the particle before and after the transition. Since AI always increases the charge state at least by one, the energy E_e will be increased by a value of ΔE_e , if particles decay near a surface as compared to AI in free space, because the level shift ΔW for the final state (charge state $q + 1$) is larger than for the initial state (charge state q). ΔE_e increases with the transition occurring closer to the surface, because the difference in the level shifts increases with decreasing distance (Hagstrum and Becker 1973). From (3.4) we can estimate the value of ΔE_e by

$$\Delta E_e [\text{eV}] \approx 1.8/d [\text{\AA}] . \quad (3.7)$$

Radiative Deexcitation (RD). For singly charged ions approaching a surface, getting rid of the deexcitation energy by photons (cf. Fig. 3.1e) is highly improbable as compared to the above described radiationless electron transitions, because the involved radiative lifetimes of typically 10^{-8} s is about 10^6 times longer than the transition times for radiationless deexcitation. However, for highly charged ions radiative deexcitation can become competitive because of their rapidly increasing radiative transition rates (for hydrogen-like ions the radiative transition rate is proportional to the fourth power of the charge state, Bethe and Salpeter 1957). Donets (1983) and Donets et al. (1985) have observed X-rays for impact of slow ($E_i \approx 0.4 \text{ keV/amu}$) Ar^{17+} and Kr^{35+} ions (both ions being hydrogen-like) on Be and Cu targets, respectively. Observed emission of photons clearly corresponded to $1s - 2p$ and $1s - 3p$ transitions, and even some contributions from $1s - np$ (with $n \geq 4$) transitions in multiply excited Ar and Kr atoms have been observed. The photon energy corresponding to the $1s - 2p$ transition was shifted toward higher energy with respect to the well known K_α line from a free atom, but still at somewhat lower energy as compared with the estimated $1s - 2p$ transition in He-like Ar or Kr ions. This result clearly shows that in the most probable

case a $2p$ electron jumps to the $1s$ state when the MCI is almost completely neutralized.

Recently, X-ray emission due to impact of Ar^{17+} with 340 keV on Ag has been studied (Briand et al. 1990). In this paper the conclusion had been obtained that by the multiple electron capture processes into high projectile levels so called “hollow” particles are being formed. These particles contain inner shell vacancies, which become later filled via emission of X-rays.

Calculation of PE Transition Rates. Only a few papers have been published with quantitative considerations of the yield and also the energy distribution for PE emission (Hagstrum 1954b, Hofer 1983, Hofer and Varga 1984, Wouters et al. 1989, Zeijlmans van Emmichoven et al. 1990). All these calculations have been performed by modeling the emitted energy distributions with the help of semiclassical approximations. From a known S-DOS (Hofer 1983, Hofer and Varga 1984, Wouters et al. 1989 and Zeijlmans van Emmichoven et al. 1990) or assuming a constant S-DOS (Hagstrum 1954b) the electron energy distribution can be simulated in a first approximation if all possible transition processes like AN, AD or AI are regarded.

Much more efforts have been devoted to calculate transition rates for the above mentioned neutralization- and deexcitation processes. The driving force behind this work has been the quantification problem in surface analytical techniques like ISS (ion surface scattering spectroscopy) and SIMS (secondary ion mass spectroscopy). Therefore and because of practical reasons (see below) mainly transition rates for resonant charge transfer (RI and RN) have been investigated (see a recent review by Amos et al. 1989).

In all quantum mechanical calculations of particle surface interaction it is assumed that the motion of the atomic nucleus can be treated classically, thus involving a classical trajectory $R(t)$. The total Hamiltonian for the system can then be reduced to one for the electronic motion only, associated with a one-electronic Hamiltonian $\mathcal{H}(R) = \mathcal{H}(t)$ which depends parametrically on the nuclear position and via the latter on time.

Therefore, the problem becomes one of solving a time-dependent Schrödinger equation

$$\mathcal{H}(t)|\phi(t)\rangle = i\partial|\phi(t)\rangle/\partial t \quad (3.8)$$

for the electronic wave functions $|\phi(t)\rangle$ representing the particle and the valence band of the surface, respectively.

It is hardly possible to obtain an exact form for this Hamiltonian. Progress has been made by Blandin et al. (1976) and Bloss and Hone (1978) by adopting the time-dependent Anderson-Newns (TDAN) Hamiltonian which is a generalization of the time-independent one originally introduced by Anderson (1961) and Newns (1969). It was found that the Anderson-Newns Hamiltonian contains most of the physically important aspects of the problem. Even though this model leads to formally simple equations, it appears to be impossible to obtain analytical solutions. In order to extract physically meaningful

results it is necessary to resort to numerical methods or to apply approximations. One of them is to describe resonant charge transfer (Amos et al. 1989) within the frame work of one-electron theory, i.e. by approximating the Hamiltonian by the sum of one-electron operators. This theory has been quite successful in explaining much of the experimental data.

Since Auger transitions play an important role in many particle-surface scattering systems, a more rigorous theoretical treatment is required as has been shown e.g. by Hentschke et al (1986) and Snowdon et al. (1986), who calculated transition rates for AN of low energetic protons scattered on Au and Al. They found that the transition rate over a wide range of ion-surface separations d can be well represented by the simple exponential form Ae^{-ad} , where A and a are constants. This dependence has already been adopted by Hagstrum (1954b).

The conclusion that the theory of surface-charge transfer should be formulated by using many-electron wavefunctions was already drawn by Tully (1977) who laid the foundation for this theory. Only a few many-electron calculations have been made so far, as for example by Kasai and Okiji (1987), Brako and Newns (1985a,b), and Sulston et al. (1988). The results differ qualitatively from those of the one-electron treatments. At the moment most of the calculations are restricted to surfaces which are represented by a non-interacting Fermi gas with a realistic work function and particles with a single, non-degenerated valence level with a realistic binding energy.

A major theoretical effort should now be devoted not only to obtain more quantitative results but also to develop a framework which can encompass all types of charge-transfer processes, including not only the resonance-, but also Auger- and quasi-resonant transitions. The application to more realistic systems should than be a next step.

Recently, Bardsley and Penetrante (1991) have developed an interesting classical approach to treat PE for impact of highly charged ions on metal surfaces. They regarded the PE process as a tunneling of electrons from the metal valence band via the distance-dependent potential barrier into vacuum, under the combined influences of the (point like) projectile charge and its image charge. Electron motion is assumed as classical and a Monte Carlo method is applied to calculate yields and energies of the electrons extracted into vacuum. The calculations are stopped at a projectile distance of several Ångströms in front of the surface, where quantum effects on the final electron energies can no more be neglected. These calculations provide interesting new aspects for the evolution of PE during the approach of highly charged slow ions toward a metal surface.

3.2 Experimental Results on PE – Total Electron Yields

The yield (or more precisely total yield) γ of electrons emitted from a target surface as a result of PE is defined as their total number per impinging projectile particle

$$\gamma = N_e/N_p = qI_e/I_q \quad (3.9)$$

where N_e and N_p are the fluxes (particles per second) of electrons emitted from and projectiles arriving at the target surface, and I_e and I_q are the corresponding electric currents of electrons and initially q -times charged projectile ions, respectively.

At least for single crystal surfaces strong deviations from an often assumed smooth take-off angle dependence of the angular-differential potential emission yield might occur. However, in the context of this review we will not discuss this feature in more detail, since systematical measurements for both single-crystalline and polycrystalline surfaces are lacking.

An impressive amount of PE total yield measurements can be found in the older literature (cf. references in Kaminsky 1965, Carter and Colligon 1968). Unfortunately, the greater part of these data cannot be regarded as definite because of reasons already explained in Chap. 1.

The most extensive and reliable work is due to H.D. Hagstrum (see a number of corresponding references in Kaminsky 1965, Carter and Colligon 1968), who has thoroughly investigated the PE process in dependence on charge state and species of projectiles as well as the material and surface conditions of targets materials. Most of Hagstrum's investigations have been made with singly charged noble gas ions in their ground state, but long-lived highly excited ("metastable") atoms, singly charged molecular and metastable highly excited atomic ions as well as multicharged ions have also been applied for a number of investigations. Furthermore, measurements have been carried out for different polycrystalline target materials in both atomically clean state and with varied coverage of some adsorbates as H_2 , N_2 , CO_2 etc. The typical projectile impact energy range was chosen from a few eV up to 1 keV.

A large amount of yield measurements, primarily with singly charged ions as projectiles, has been performed by Arifov et al. (1969), including investigations with single crystal targets for metals as well as insulators.

In the following, by way of examples from our own investigations, we will shortly review the typical dependence of the total PE yield on the potential energy and impact (i.e. kinetic) energy of projectile ions, and on the target surface conditions. We will not discuss the influence of the projectile impact angle, for which the reader is referred to Sect. 3.1.

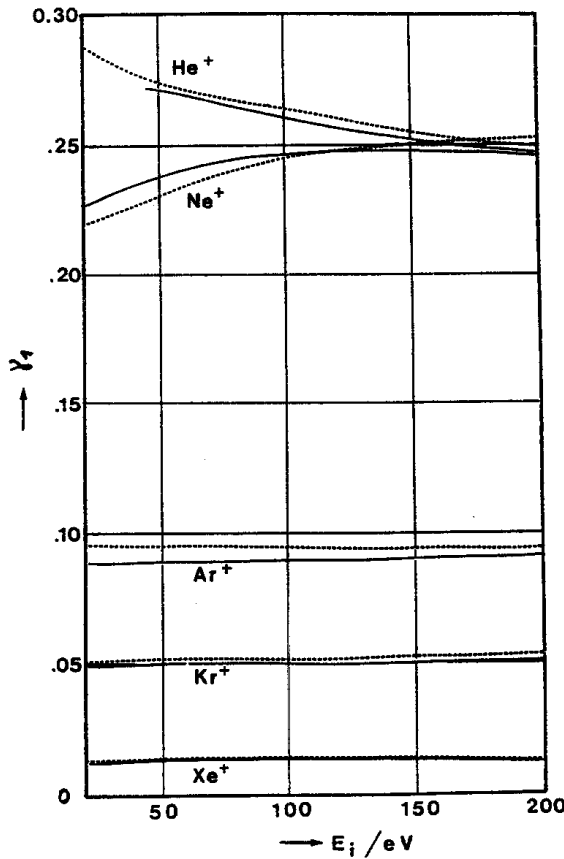


Fig. 3.2. PE yield γ for impact of singly charged noble gas ions on clean polycrystalline tungsten at kinetic energies between 20 and 200 eV (full line, Varga 1978). Dotted line represents results taken from Hagstrum (1956b) for comparison

3.2.1 Singly Charged Projectiles

Figure 3.2 (adapted from Varga 1978) shows results obtained for perpendicular impact of singly charged ground state noble gas ions on clean polycrystalline tungsten in comparison with equivalent results from Hagstrum (1956b). The latter data originated from earlier ones (Hagstrum 1954a) after their correction for the influence of metastable admixtures in the projectile fluxes (see also below). Note the very good agreement despite a time span of more than twenty years between both sets of investigations, the very pronounced dependence on the projectile species (i.e. the involved potential energies) and the relatively weak influence of the projectile impact energy in the range covered, except for the Ne^+ projectiles, where a marked decrease of γ can be observed in the lowest impact energy range. This has been explained by Hagstrum (1954b) to result from the contribution of RN-AD to the neutralization of Ne^+ on clean W, whereas for all other ion species only AN processes can take place.

From the bulk of available data, which have been obtained with a variety of projectile ions impinging on both clean and gas-covered target materials, a qualitative dependence of γ on the projectile potential energy W_i and the target surface work function W_ϕ can be formulated

$$\gamma = \alpha(\beta W_i - 2W_\phi) \quad . \quad (3.10)$$

Note, that this relation does not contain the projectile impact energy, cf. above. The shape of (3.10) has been theoretically derived by Kishinevskii (1973), who obtained $\alpha = 0.2/\varepsilon_F$ with ε_F the target surface Fermi energy, and $\beta = 0.8$. Using a least square fit to available experimental data, Baragiola (1979) obtained $\alpha = 0.032$ and $\beta = 0.78$ for a number of target species (all energies given in eV).

According to this relation, γ will apparently increase with the projectile potential energy and with a decreasing surface work function. This is also clearly demonstrated by γ data obtained with respectively clean and electronegative gas-covered target surfaces, cf. Hagstrum (1956d) and Fig. 3.3 from Hofer (1983). Increase of the oxygen coverage corresponds to an increasing work function. In the same figure also the influence of W_i is nicely demonstrated by comparing data for respectively ground state and metastable projectiles, as has first been demonstrated by Hagstrum (1956b, 1960) and later confirmed by Varga and Winter (1978), cf. Fig. 3.4.

Available results with molecular ions follow same tendencies as observed with atomic ions.

Apart from the influence of the surface work function, no clear relation between the S-DOS (surface density-of-states) of a target and the corresponding PE yield has been demonstrated, whereas the ejected electron energy distribution can be strongly influenced. The latter fact has also been utilized for the development of a particular surface spectroscopy ("INS", cf. Sect. 3.3).

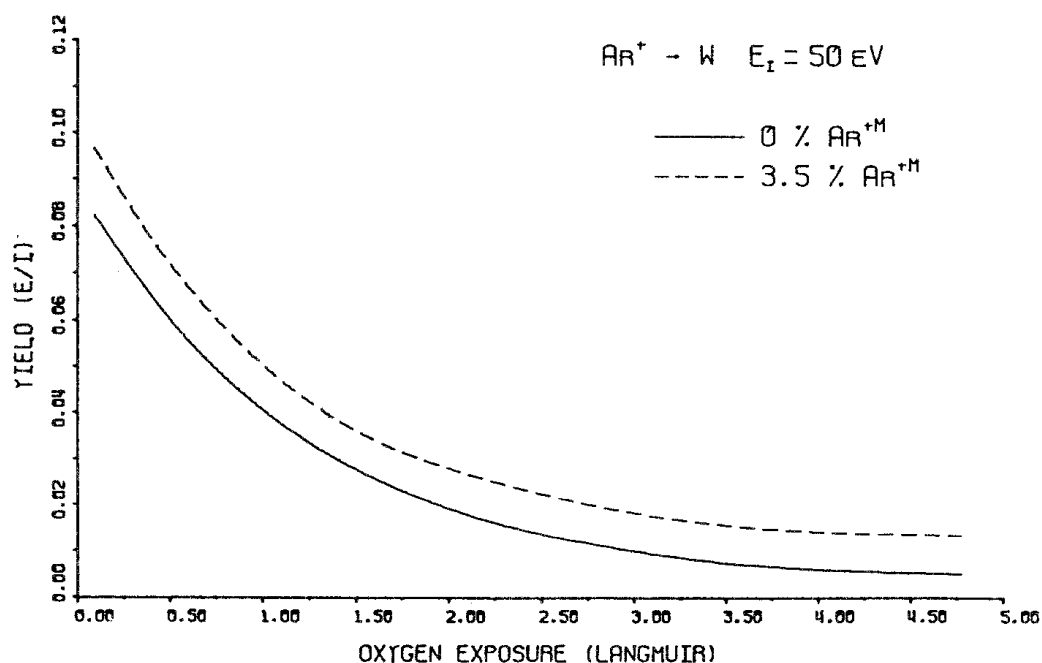


Fig. 3.3. PE yield γ induced by impact of 50 eV singly charged Ar^+ ions on tungsten without (full line) and with 3.5% admixture of highly excited metastables (dashed line), for varying oxygen coverage (Hofer 1983)

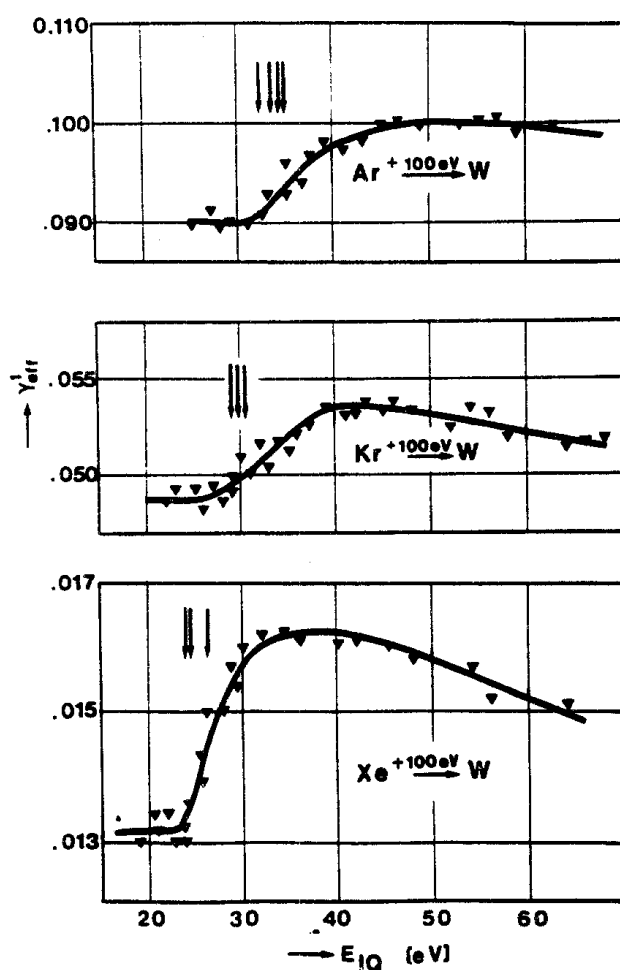


Fig. 3.4. Effective PE yield γ from clean tungsten for impact of 100 eV singly charged noble gas ion beams with metastable ion admixture dependent on E_{IQ} , the electron impact energy in the ion source. Appearance potentials for metastable states have been indicated by arrows (Varga and Winter 1978)

3.2.2 Excited Neutral Projectiles (Metastable Atoms)

Several groups have investigated the long-known fact that highly excited slow atoms can give rise to PE (cf. references in Kaminsky 1965). This emission is usually caused by AD occurring in front of the surface, from where electrons will be ejected if the available excitation energy exceeds the surface work function. For many metastable atoms their excited states energetically coincide with states populated via RN from the surface into a singly charged ground state ion of the same species. In such cases the metastable atom yields should be about the same as for the corresponding ground state ions. For a further discussion of this situation cf. Sect. 3.3.1. AD of metastable atoms can be applied for a rather sensitive surface spectroscopy (MDS, see Boiziau 1981, Ertl 1986).

3.2.3 Doubly Charged Projectiles

The work of Hagstrum also includes extensive investigations on PE due to impact of doubly charged noble gas ions, e.g. on clean Mo (Hagstrum 1956e)