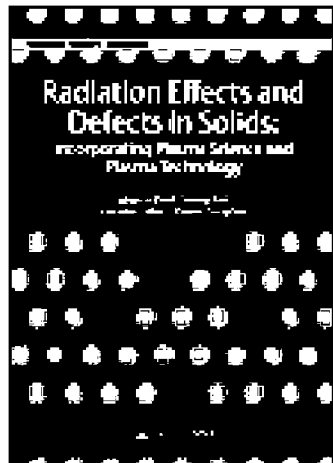




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INVITED REVIEW ARTICLE

Principles and Applications of Ion-Induced Auger Electron Emission from Solids

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We review critically the field of Auger electron emission from slow ion impact on surfaces (Auger neutralization and deexcitation), and Auger emission from the decay of inner-shell holes created by impact with energetic ions. We show how the inspection of the basic formalism of transition rates for Auger neutralization, reveals the basic physical mechanisms involved, and provides the foundation for the method of Ion Neutralization Spectroscopy (INS) created by Hagstrum and co-workers. We describe the necessary experimental techniques, and show some of the most prominent applications of INS.

We then present background information from electron-excited Auger Electron Spectroscopy (AES), we review the basic physics of inner-shell excitation by energetic light-ions (Born approximation and leading corrections to it), the case of inner-shell electron promotion in heavy ion collisions, and specific solid state effects. Finally, we discuss experimental aspects and specific examples of ion-induced Auger spectra from low Z targets, and point to possible applications.



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I INTRODUCTION

When atomic particles bombard solid surfaces, both scattered projectiles and emitted, secondary target particles carry information about the surface and near surface properties of the solid; the study of their angular and energy distributions may therefore lead to the determination of basic properties of the target like the spatial distribution of its constituent atoms and the electronic structure. The first type of property can be obtained readily, although with some limitations, through the knowledge of the flux of backscattered projectiles. Electronic properties can, on the other hand, be studied through the decay of the electronic excitation produced by the projectile, in the form of electron ejection (EE) outside the target.

The study of energy and angular distributions of electrons ejected from solids by photons and electrons has produced many useful spectroscopies for characterization of electronic, chemical, and geometrical properties of surfaces. The more powerful of these are photoelectron spectroscopy (PES),¹⁻³ low energy electron diffraction (LEED),⁴⁻⁶ Auger electron spectroscopy (AES),⁷⁻¹⁰ and electron energy loss spectroscopy (ELS).¹¹ In this review, we will be concerned with two, ion initiated, electron spectroscopies: ion-neutralization spectroscopy (INS) and ion-induced Auger electron spectroscopy (IAES).

It seems convenient to introduce at this stage some basic aspects of the behaviour of excited electrons in solids. Due to their small mass, electrons have very small momenta, at least in the energy range of a few eV or few tens of eV with which most of the work we will describe is concerned. Therefore, the de Broglie wavelength $\lambda = h/p = 2\pi/k$, associated with a quantal description, will be large, of the order of interatomic distances, making it inappropriate to think in terms of ordinary time-space concepts like classical trajectories. The long wavelengths cause strong diffraction from ordered arrays of scattering centers, the central theme in LEED from crystalline solids. It also causes electrons to spill over or tunnel through the surface potential barrier. Figure 1 shows the potential and charge density in the surface region of a Na (100) surface¹² to illustrate this point.

The transport of excited electrons in solids is governed by scattering with the ion cores, which can be elastic or quasi-elastic (with very small energy losses in phonon excitations), or with other

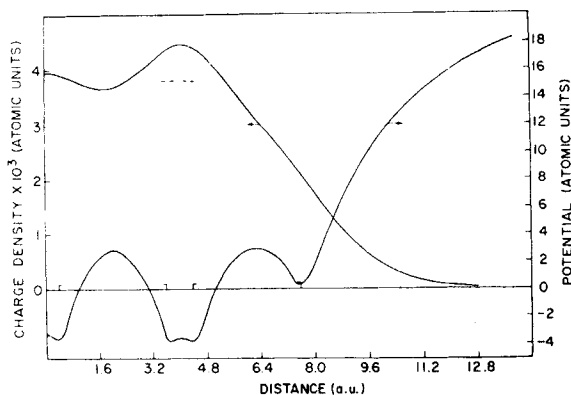


FIGURE 1 Charge density and self-consistent potential (scale 10^{-2} a.u.) averaged over the x - y plane as a function of z , for the Na (100) surface. The small brackets in the abscissa indicate the positions of the ion cores in the last two layers. (From Appelbaum and Hamann, Ref. 12).

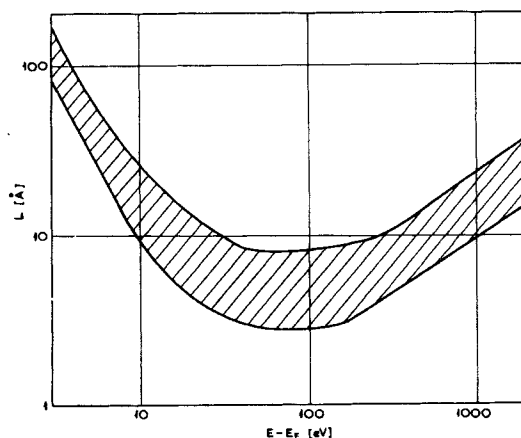


FIGURE 2 Attenuation lengths of electrons in metals as a function of energy above the Fermi level, lie in the band indicated in this figure.

electrons in which on the average an appreciable energy loss occurs to excitation of electron-hole pairs or quantized collective oscillations (plasmons). These inelastic electron-electron collisions determine electron slowing-down and consequently escape depths. Figure 2 shows the range of variation of mean escape depths L in metals.^{13,14} It is the small values of L below a few keV that gives electron spectroscopies their surface sensitivity. To make the sampling depth even smaller than shown in Figure 2 in order to just look at the surface

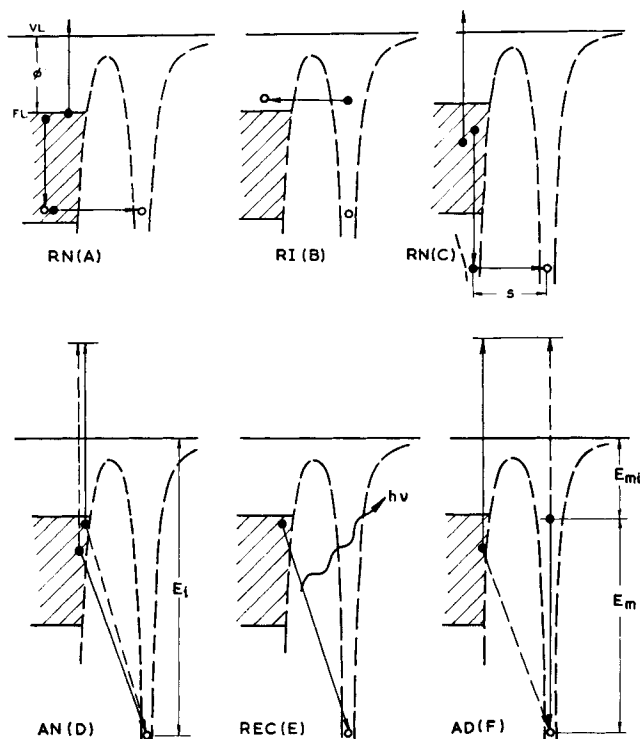


FIGURE 3 Electron energy diagrams for: (A) Resonance neutralization (RN); (B) Resonance ionization (RI); (C) RN from core level; (D) Auger neutralization (AN); (E) Radiative electron capture (REC); (F) Auger Deexcitation (AD). VL-vacuum level, FL-Fermi level, ϕ -work function. Electronic transitions are indicated by arrows, initially filled (empty) electron states in atoms or solid by filled (open) circles. Light arrows indicate secondary transitions following RN, and dashed lines in AN and AD, exchange transitions.

region, one needs a method that selectively excites electrons at or outside the surface. This can be accomplished by using very low energy ions in the technique of INS with which we will deal next.

II ION NEUTRALIZATION SPECTROSCOPY

2.1. Potential Electron Emission (PEE)

We will consider the electronic transition processes that can occur between a solid surface and a slowly moving excited or ionized atom impinging onto it.¹⁵ The main processes that have been identified are illustrated in the electron energy diagram of Figure 3, where we show electron energies at a particular distance between the ions (or atoms) and the surface. Figure 3A indicates resonance neutralization (RN) to an excited level of the neutralized atom which lies below the Fermi level, and where

an electron tunnels from the filled level in the solid into the excited level at the same energy. RN can also occur to the ground state if this lies opposite the filled band in the solid. If the energy of the remaining hole with respect to the vacuum level (VL) is larger than twice the work function ϕ , Auger processes within the band can lead to electron emission (EE). An atom close to the surface can undergo resonance ionization (RI) if the atomic level lies opposite the unfilled levels in the solid, Figure 3B. A third resonance process is shown in Figure 3C where the electron comes from a core level of a surface atom. The resulting hole in the core level can then decay by an Auger process involving two valence band electrons, and cause EE.

A second category of processes involve two-electron Auger transitions in the first step. In Auger neutralization (AN), an electron from the filled band of the solid tunnels to the atomic ground state; the energy released during the process is taken by another valence electron. This electron

may be ejected into vacuum if properly directed and if the ground-state recombination energy of the ion at a distance s from the surface, $E_i(s)$, is larger than 2ϕ (Figure 3D). The competing process of radiative electron capture (REC) (Figure 3E) is so slow that AN will completely dominate the picture. Light emission from REC has been sought for but not convincingly demonstrated.¹⁶ Metastable atoms incident on a surface can cause EE by Auger deexcitation (AD) (Figure 3F) if the excitation energy $E_m(s)$ exceeds the work function of the solid. This process, although two-electron in character like AN, involves only one electron of the solid.

One- and two-electron processes are interrelated as shown in Hagstrum's triangle diagram of Figure 4. During approach of the ion to the surface, and keeping in mind that atomic energy levels shift due to the interaction with the surface, resonance neutralization may occur if energetically allowed, followed by resonance ionization and

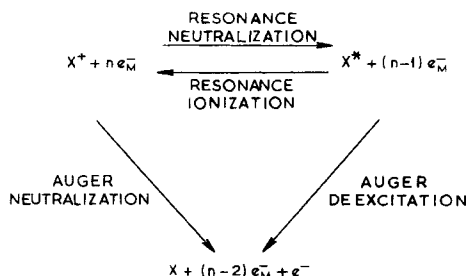


FIGURE 4 Hagstrum's triangle diagram indicating the interrelation of one and two electron processes.

Auger neutralization, or by Auger deexcitation. Different ways in which the system reaches the final state will affect the energy distribution and yield of emitted electrons as has been abundantly discussed by Hagstrum.¹⁷ All the processes shown in Figure 3 involve the potential energy of the ion-surface system and not the kinetic energy of the ion; those which lead to EE have customarily been catalogued in the literature as causing potential electron emission (PEE). We will at this point consider the two more general mechanisms of PEE, AN and AD since through the understanding of them it has been possible to develop the technique of INS.

2.1a Auger neutralization Figure 5 shows, as an example, the potential energy diagram for the interaction of a slow He^+ ion with tungsten.¹⁸ The

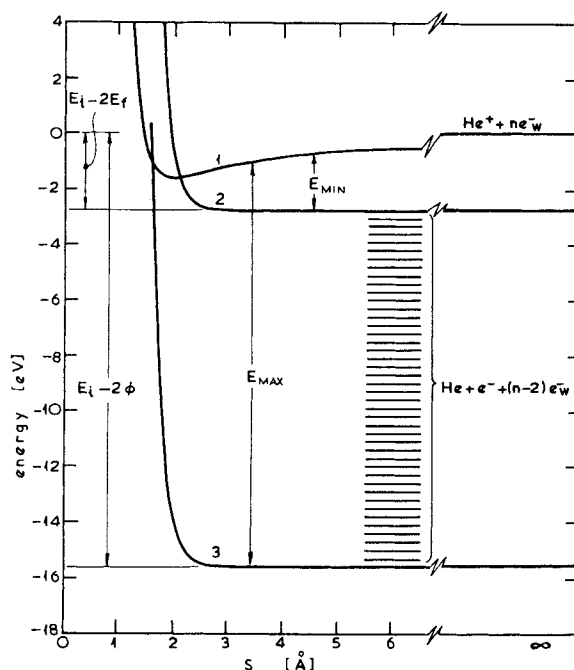


FIGURE 5 Potential energy diagram for Auger neutralization in the interaction of a slow He^+ ion with a tungsten surface.

initial state, $\text{He}^+ + ne^-_w$ evolves in energy at large distance governed by the image force interaction, $-3.6 \text{ eV/s}(\text{\AA})$. Close to the surface, a repulsive screened-Coulomb interaction takes place which depends on the impact parameter to a surface atom and on s . The final states $\text{He} + e(n-2)e^-_w$ form a band of width $2E_F$, where E_F is the Fermi energy. Since the collision is adiabatic, we can expect that transitions are vertical in the diagram of Figure 5 (i.e. the electronic transitions obey the Franck-Condon principle). Therefore, the energy difference between curve 1 and a curve lying between curves 2 and 3 must equal the kinetic energy of the excited electron E . The maximum electron energy (distance between curves 1 and 3) can be taken to define an effective ionization energy $E_i(s) = E_{\text{max}}(s) + 2\phi$.

2.1b Auger deexcitation This process can result, under ion impact, if the ion undergoes RN to an excited state of excitation energy $E_{mi}(s) > \phi$ on approach to the surface. A competing process will be RI+AN which is possible at distances s small enough so that the ionization energy $E_{mi}(s) < \phi$. This can be illustrated by using Hagstrum's triangle (Figure 4); the two sequences mentioned are $\text{RN} \rightarrow \text{AD}$ and $\text{RN} \rightarrow \text{RI} \rightarrow \text{AN}$. A potential

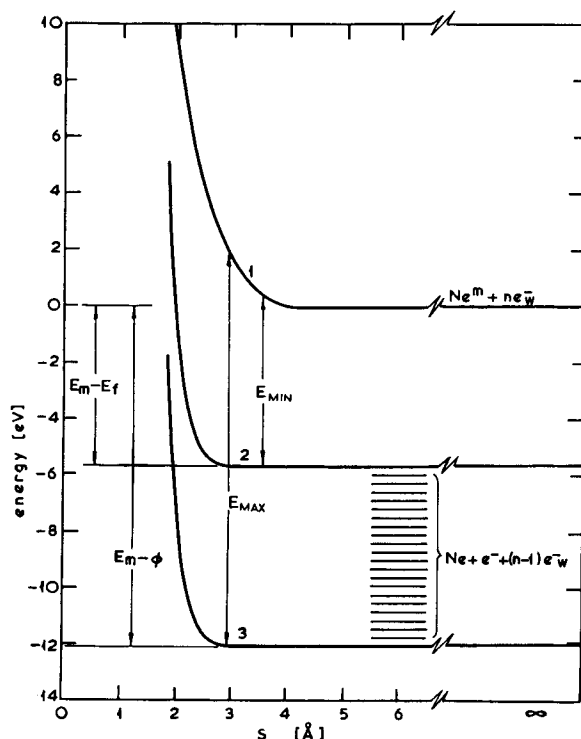


FIGURE 6 Potential energy diagram for the Auger deexcitation in the interaction of a slow metastable Ne atom with a tungsten surface.

energy diagram for AD of a Ne metastable atom on tungsten¹⁸ is shown in Figure 6. Differently from the case of AN (Figure 5), the long range interaction (in this case van der Waals attraction) is negligibly small; the repulsive interaction for Ne^m rises at considerably larger distances than for Ne due to the larger size of the metastable atom. As a consequence of this, the separation of the curves for the initial state (curve 1) and for a final state (a curve between curves 2 and 3), and therefore also E_{max} , initially increases as s decreases, in contradistinction to AN. The difference in maximum kinetic energy of emitted electrons in AN and in $\text{RN} \rightarrow \text{AD}$ have allowed Hagstrum to show the occurrence of AD.¹⁸ A demonstration of the dominating role of $\text{RN} \rightarrow \text{AD}$ in the case of low work function surfaces has recently been carried out also by Hagstrum.¹⁹

2.1c. Survey of experimental evidence Figure 7 shows EE yields γ for noble gas ions on molybdenum as a function of projectile energy.²⁰ It can

be seen that the yields are fairly constant at low energies and increase, specially for He^+ , at high energies. This increase is due to the mechanism of kinetic EE (KEE) where the energy required to liberate electrons into vacuum is provided by the kinetic energy of the projectile. It can also be observed in Figure 7 that, except for the anomalous behaviour of Ne^+ (which is due to the occurrence of the competing channel $\text{RN} \rightarrow \text{AD}$), the yields increase with increasing ground-state neutralization energy of the ions. Values of PEE yields γ_p , as a function of velocity of the ion v , can be deduced from measurements of γ for ions of different charge and of the same species, on the assumption that KEE is independent on the charge of the projectile in this velocity range.^{21,22} In this way it was deduced that γ_p varies slowly with velocity for $v < 5 \times 10^7$ cm/s.

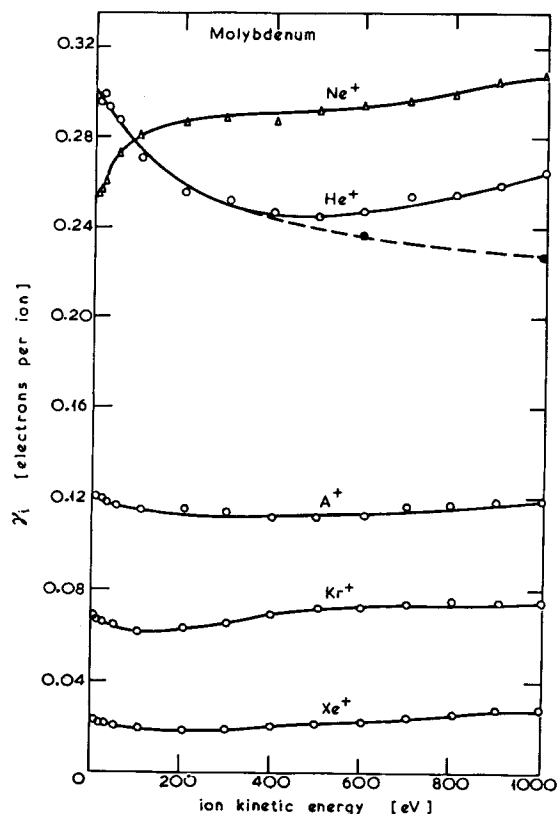


FIGURE 7 Electron yields for noble gas ions interacting with a clean molybdenum surface at normal incidence (from Hagstrum, Ref. 18).

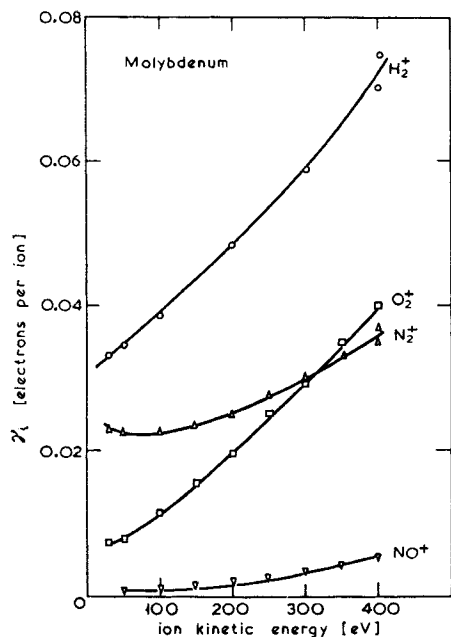


FIGURE 8 Electron yields for molecular ions interacting with a clean molybdenum surface at normal incidence (from Vance, Refs. 23 and 24).

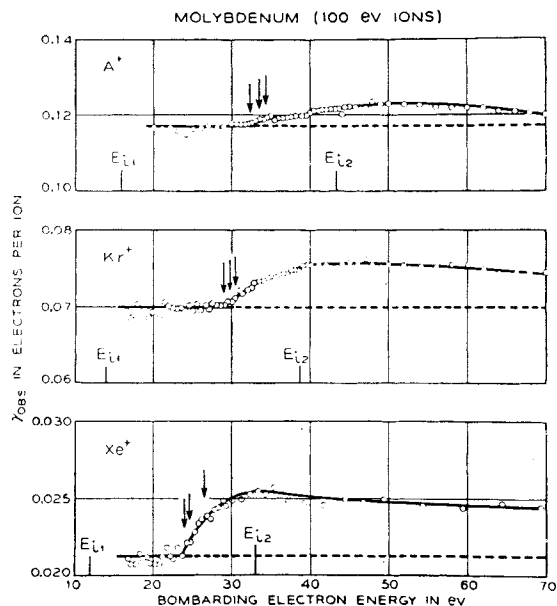


FIGURE 9 Electron yields for 100 eV Ar^+ , Kr^+ , and Xe^+ interacting with a clean molybdenum surface at normal incidence, as function of bombarding electron energy in the ion source. E_{11} and E_{12} indicate first and second ionization potentials while the arrows indicate thresholds for formation of metastable ions (from Hagstrum, Ref. 27).

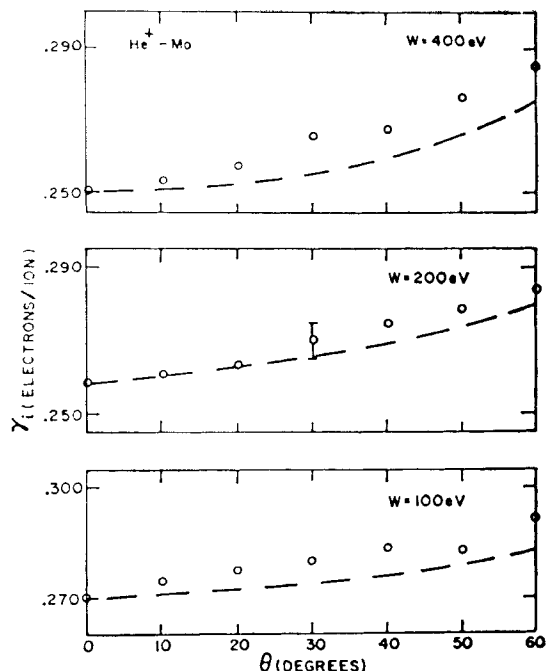


FIGURE 10 Electron yields for He^+ ions of energy W incident on a clean molybdenum surface as a function of angle of incidence. Circles are experimental points, dashed lines are theoretical expressions (see text) (from Vance, Ref. 23).

Figure 8 shows yields for low-energy molecular ions obtained by Vance on clean Mo.^{23,24} These yields are smaller than γ for atomic ions of similar ground state neutralization energy and have stronger energy dependences. This behaviour, which has not been discussed in detail, is possibly related to the different level densities in molecules as compared to atoms.^{25,26}

Figure 9 shows the variation of PEE yields with the energy of bombarding electrons in the ion source.²⁷ As electron energy increases above the ionization threshold, the formation of long-lived excited ions becomes possible, which produce larger PEE yields due to their larger recombination energy. Similar observations have been made by Vance²⁴ for non-rare-gas ions.

The effect of angle of incidence θ on PEE yields has been studied by Vance.²³ Representative results are shown in Figure 10. The data can be understood on the basis that only the component of the velocity of the ion perpendicular to the surface is important, as suggested by Hagstrum¹⁸; thus $\gamma_p(K, \theta) = \gamma_p(K \cos^2 \theta, 0)$, where K is the energy of the incident ion. Deviations from this

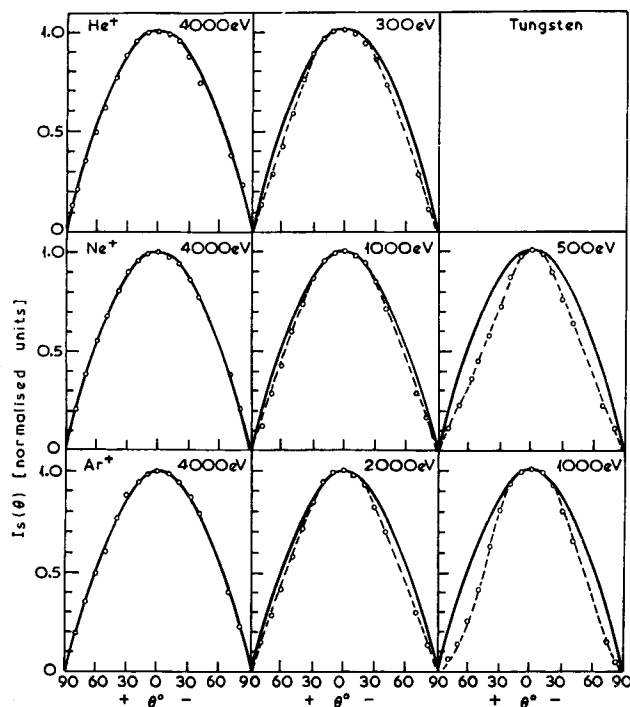


FIGURE 11 Ion energy dependence of the angular distribution of ejected electrons for He^+ , Ne^+ , and Ar^+ ions interacting with clean tungsten at normal incidence. Ordinate is electron current normalized to one at 0° . Solid line is the cosine function (from Klein, Ref. 28).

behaviour are found at energies where KEE makes a discernible contribution to the yields.

Klein²⁸ has studied the angular distribution of ejected electrons for 300 eV–4 keV noble-gas ions on tungsten. For low velocity ions, which give predominantly PEE, the angular distributions were found to be more peaked in the normal direction than the cosine distribution typical of KEE, as shown in Figure 11.

The effect of gas coverage on PEE was studied systematically by Parker²⁹ and by Hagstrum,³⁰ the general finding being that EE yields decrease with increase of adsorption and increase fast with ion energy for contaminated surfaces.

Figures 12a and 12b show energy distribution curves (EDCs) of electrons emitted from Mo under impact of several rare-gas ions at 10 eV and 40 eV respectively.²⁰ The vertical lines along the energy axis indicate the values $E_i(Y^+) - 2\phi$ for each ion. In Figure 12a the EDC for Ne^+ is as anticipated, as is the yield shown in Figure 7. The Ne^+ EDC in Figure 12b has an anomalously high maximum kinetic energy and the yield for this ion energy (Figure 7) is also anomalously high. Hagstrum¹⁸

has shown this to be due to the increasing contribution with ion energy of $\text{RN} + \text{AD}$ which produces, on the average, faster electrons most of which can leave the solid.

EDCs for 5 eV He^+ ions on different surfaces are shown in Figure 13, where it can be observed that the EDCs depend very strongly on the type of surface being bombarded. This is a clue to the possibility of using EDCs of PEE as spectroscopic tools. The need to work with very low energy ions is illustrated in Figure 14 which shows how the EDCs broaden as a result of projectile velocity.

2.1d. Transition probabilities in AN We have just shown how EDC's vary for different surfaces. We will now consider some theoretical points needed to understand the information carried in these EDCs. The transition rate for the Auger effect was first derived by Wentzel³¹ using first-order perturbation theory and is given by:

$$b_{if} = (2\pi/\hbar) \left| \left\langle \phi_f \left| \sum_{i \neq j} (e^2/r_{ij}) \right| \phi_i \right\rangle \right|^2 N(E_f) \quad (1)$$

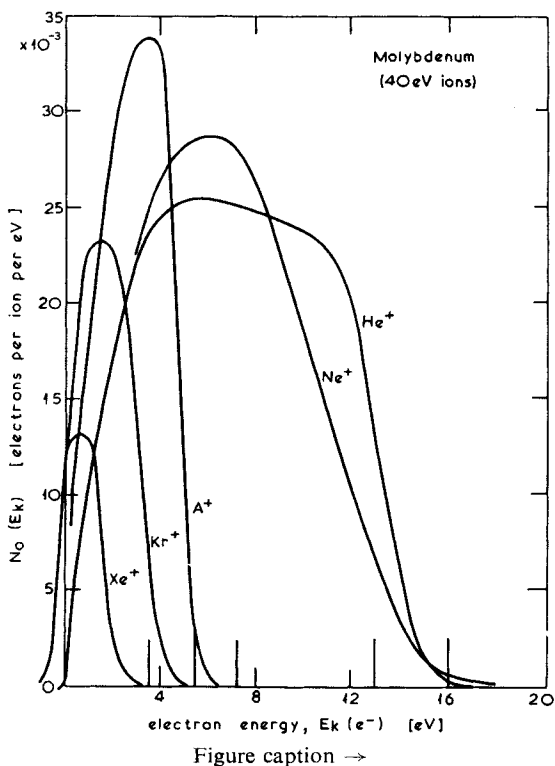
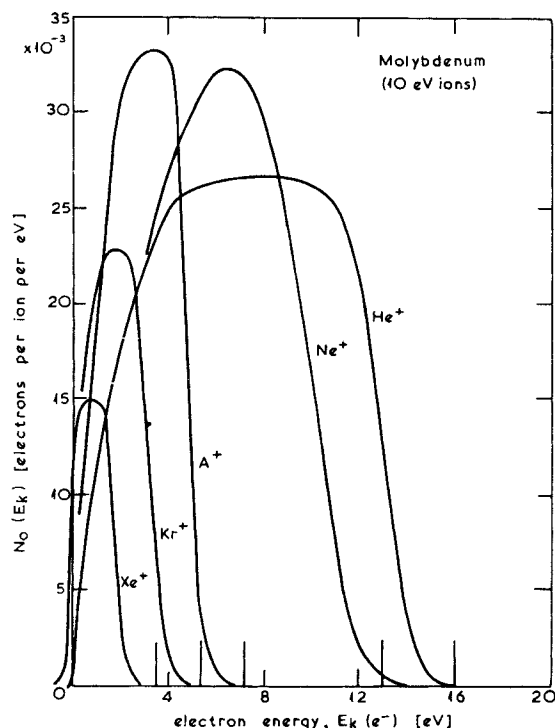


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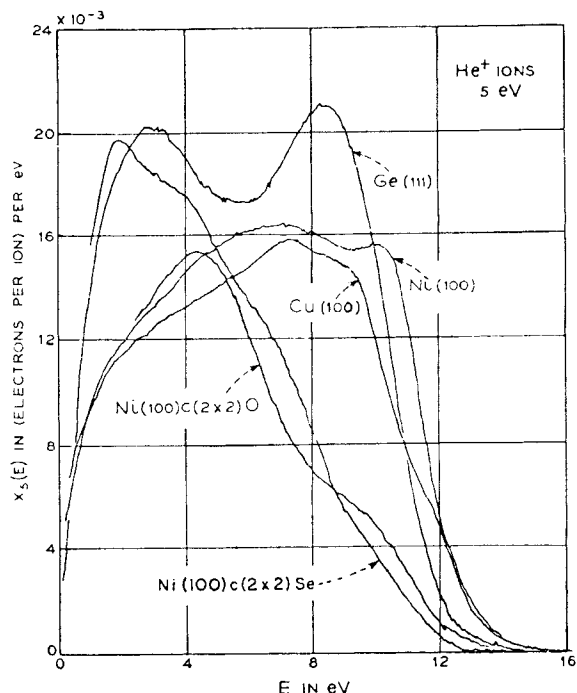


FIGURE 13 Electron energy distribution curves for 5 eV He^+ ions bombarding different surfaces at normal incidence (from Hagstrum, Ref. 17).

where ϕ_f and ϕ_i are the wavefunctions of the final and initial states, and $N(E_f)$ the density of final states. The transition is induced by the Coulomb interaction between electrons. If we make the approximation that just two electrons participate in the transition (the others being spectators), and if we write the wavefunctions as products of one-electron orbitals, we may write the matrix element in the form³²:

$$M_{if} = \iint \chi_f^*(\vec{r}_1) \psi_f^*(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \times \chi_i(\vec{r}_1) \psi_i(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2)$$

where we have neglected exchange. The relevant wave functions are illustrated in Figure 15. In a

FIGURE 12 Electron energy distribution curves for noble gas ions bombarding a clean molybdenum surface at normal incidence. (a) 10 eV ions, (b) 40 eV ions. (From Hagstrum, Ref. 20). The vertical lines above the energy axes, represent the maximum adiabatic transition energy for each ion, $E_i - 2\phi$.

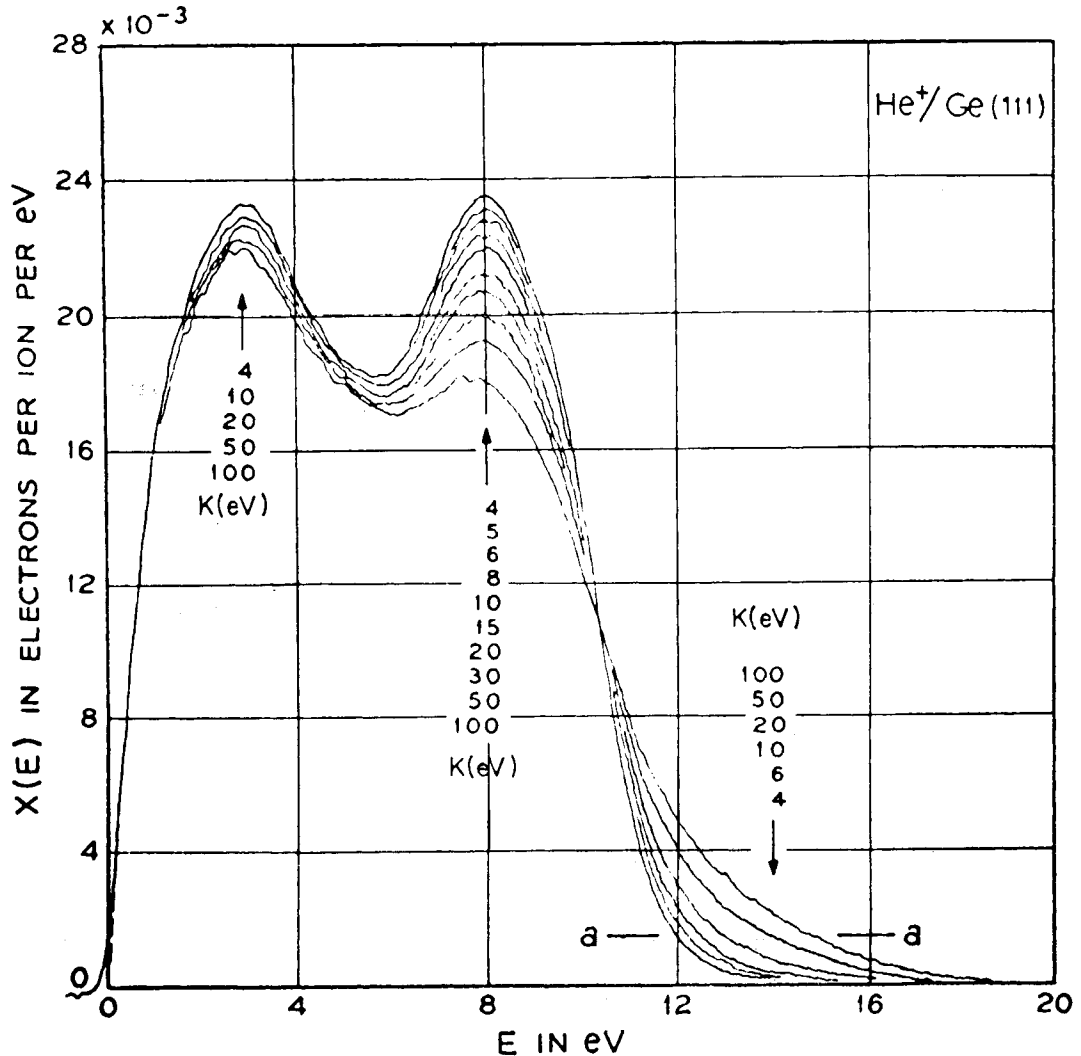


FIGURE 14 Electron energy distribution curves for He^+ interacting with a $\text{Ge}(111)$ surface at normal incidence. The parameter is the kinetic energy of the ions (from Hagstrum *et al.*, Ref. 42).

two-electron problem the initial and final wavefunctions must be antisymmetrical in their coordinates. This is allowed for by replacing

$$\chi_i(\vec{r}_1)\psi_i(\vec{r}_2) \text{ by } [\chi_i(\vec{r}_1)\psi_i(\vec{r}_2) - \chi_i(\vec{r}_2)\psi_i(\vec{r}_1)]/2^{1/2}$$

and by recognizing that transitions 1 and 2 in Figure 15, which lead to an ejected electron with the same energy, are undistinguishable experimentally. For the purpose of the following discussion it will be sufficient to use the unsymmetrized

form (1); the exchange contribution has been treated by Hagstrum³³ in some detail.

It is now convenient to write the matrix element in another form which brings light on the dependence on energy, angle and spatial coordinate. Grouping together functions in the coordinate of a single electron, on each side of the Coulomb perturbation term, one obtains¹⁸

$$M_{if} = \iint \chi_f^*(\vec{r}_1)\chi_i(\vec{r}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \times \psi_f^*(\vec{r}_2)\psi_i(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (3)$$

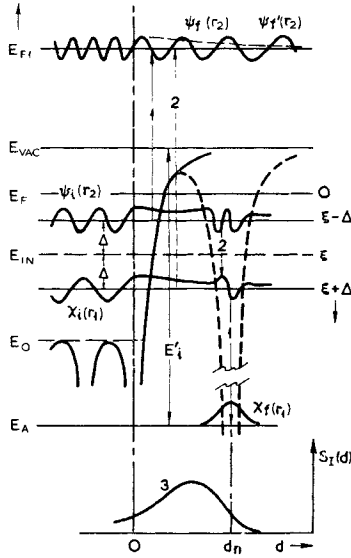


FIGURE 15 Electron energy diagram illustrating transitions for the Auger neutralization process of INS, and the relevant wave functions. ζ is the band energy measured downwards from the Fermi level. The surface sensitivity function $S_I(d)$ at the bottom of the figure indicates approximately the region near the surface from which electrons are ejected.

We may now view the matrix element as a Coulomb interaction integral between two charge clouds $F(\vec{r}_1) = \chi_f^*(\vec{r}_1)\chi_i(\vec{r}_1)$ and $G(\vec{r}_2) = \psi_i^*(\vec{r}_2)\psi_f(\vec{r}_2)$. $F(r_1)$ will be a function localized near the ion position because of the localized character of the atomic wavefunction $\chi_f^*(\vec{r}_1)$; furthermore, the Coulomb interaction will be screened inside the solid by valence electrons. We may then conclude that AN samples essentially the electronic density outside the surface; this has been discussed in detail by several workers.^{18,33-38} The matrix element will be larger the larger the “tail” of $\chi_i(\vec{r}_1)$ outside the surface, and therefore the larger the overlap with $\chi_f^*(\vec{r}_1)$. This has the following consequences:

- 1) M_{if} decreases as the symmetry character of χ_i and ψ_i goes from s to p to d at the same energy.
- 2) M_{if} increases as electron energy in the band, E , increases (as ζ decreases, Figure 15).
- 3) M_{if} is larger for initial states whose wavevector $\mathbf{k}$ is normal to the surface.
- 4) Since the Coulomb interaction favours small momentum transfers, then from (3), M_{if} will be

larger for final states ψ_f with $\mathbf{k}$ normal to the surface.

The total transition rate $R_t(s)$ as a function of ion-surface distance s is obtained by integrating Eq. (3) over all initial and final states. One thus obtains, neglecting exchange, and initial- and final-state interaction effects:

$$R_t(s) = \iiint (2\pi/\hbar) M_{if}^2 N_c(E_k) N_v(E_i) N_v(E_f) \times dE_i dE_f dE_k \quad (4)$$

where $N_v(E)$ is the density of states in the valence band.

Let us now define $P_t(s, v_0)ds$ as the probability that the ion of initial velocity v_0 will be neutralized in ds at s , and $P_0(s, v_0)$ as the probability that it reaches s without undergoing AN. Then:

$$P_t(s, v_0)ds = \frac{1}{v_0} R_t(s) P_0(s, v_0)ds \quad (5)$$

and

$$P_0(s, v_0) = \exp\left(-\int_s^\infty \frac{R_t(s)ds}{v_0}\right) \quad (6)$$

To obtain the energy distribution of emitted electrons $N_0(E_k)$, Hagstrum^{18,33} makes at this point several simplifying assumptions:

i) That the angular dependence of $R_t(s)$ can be factored out and incorporated in an average electron escape probability function $P_e(E_k)$ such that

$$N_0(E_k) = P_e(E_k) N_i(E_k) \quad (7)$$

where $N_i(E_k)$ and $N_0(E_k)$ are the energy distributions inside and outside the solid.

ii) That due to the peaked nature of the function $P_t(s)$ around a most probable value at s_m , the dependence of R_t on s can be taken care of by using $R_t(s_m)$, convoluted with an energy broadening function arising through the dependence of E_i' with s .

iii) That the density of final states $N(E_f)$ can be taken as constant.

iv) That the transition matrix element (now including exchange) can be factored into terms for the up

(*f*) and down (*i*) electrons, which, combined with the densities of states $N_v(E_f)$ and $N_v(E_i)$, yield the functions $W(E_f)$ and $V(E_i)$. At this point it can be easily seen that with these assumptions the energy distribution of internally excited electrons $N_i(E_k)$ is proportional to the convolution.

$$F(\zeta) = V * W = \begin{cases} F_1(\zeta) = \int_{-\zeta}^{\zeta} V(\zeta + \Delta) W(\zeta - \Delta) d\Delta & 0 \leq \zeta \leq \zeta_f/2 \\ F_2(\zeta) = \int_{\zeta - \zeta_F}^{\zeta_F - \zeta} V(\zeta + \Delta) W(\zeta - \Delta) d\Delta & \zeta_f/2 \leq \zeta \leq \zeta_f \end{cases} \quad (8)$$

in terms of the band energy ζ , with the relationship

$$\zeta = \frac{1}{2} (E_1' - 2\phi - E_k) \quad (9)$$

where the energy of the final level, E_k , is measured from the vacuum level.

v) That Eqs. (8) and (8') can be written as the self convolution

$$F(\xi) = U * U = \begin{cases} F_1(\xi) = \int_{-\xi}^{\xi} U(\xi + \Delta) U(\xi - \Delta) d\Delta & 0 \leq \xi \leq \xi_f/2 \\ F_2(\xi) = \int_{\xi - \xi_F}^{\xi_F - \xi} U(\xi + \Delta) U(\xi - \Delta) d\Delta & \xi_f/2 \leq \xi \leq \xi_f \end{cases} \quad (10)$$

of just one function, $U(\xi)$, which can be interpreted to represent a mean initial state transition density.

2.2. The Method of Ion Neutralization Spectroscopy

The deconvolution of Eq. (10) will give us the function $U(\xi)$, some sort of average of the density of states at and outside the surface, as modified by the presence of the ion, and weighted with an energy broadening function and an energy dependent transition matrix element. As we will see later, this function $U(\xi)$ is very useful due to the smooth variation of the matrix element across the band for states of a given symmetry. Thus, structure in the transition density function $U(\xi)$ (like position of peaks and valleys), should in most cases correlate well with similar structure in the density of initial

states $N_v(\xi)$. The method to obtain $U(\xi)$ consists of^{17,39-41}:

- Measuring the energy distribution curves $N_o^K(E_k)$ for low energy ($K < 20$ eV) ions.
- Deconvoluting the energy broadening caused by the motion of the projectile⁴² (Figure 16), to obtain³⁸ a "debroadened" distribution $N_o^0(E_k)$.
- Dividing $N_o^0(E_k)$ by the probability $P_e(E_k)$ that the excited electrons escape through the surface barrier, to obtain the distribution $N_i^0(E) \propto F(E_k)$, and, from Eq. (9) the form of the distribution $F(\xi)$. The escape function $p_e(E_k)$ is not known *a priori*, but it is possible to derive a reasonable parametrized form of it, and adjust the parameters to get agreement between the final $F(\xi)$ obtained using He⁺ and Ne⁺ ions (which involve different $N_o^0(E_k)$).
- Deconvoluting $F(\xi)$ to obtain $U(\xi)$. This is an ill-posed mathematical problem; its difficulties and the general validity of Eq. (10) have been discussed in detail by Hagstrum and Becker.^{43,44}

2.3. Experimental Conditions Needed in INS

This technique poses some difficult problems to the experimenter. This is probably what has prevented the wide use of this very powerful and unique method for the characterization of surface electronic properties. The first requirement is the use of very low energy (< 20 eV) ion beams in order to reduce to a minimum the kinetic broadening and the admixture of the RN + PI process in the EDCs. The ion beam should also be pure as regards to ion species, charge, and excitation state, since a spread in recombination energies E_i' will affect the EDCs. This beam purity is accomplished by using a mass selector and by controlling the energy of the electrons in the ion source.

An ion beam system designed by Hagstrum specifically for INS¹⁷ is shown in Figure 16. Many workers have succeeded in producing mass-analyzed low-energy ion beams; a few examples are given in Refs. 26, 45-51. This suggests that this part of the technique can be solved without undue difficulties.

Means must then be provided to energy analyze the emitted electrons. This has traditionally been done with a magnetically-shielded spherical or hemispherical collector, using the retarding potential method and analog or digital differentiation. An advantage could be gained by using an energy-dispersive electrostatic analyzer which has an intrinsically higher signal to noise ratio and allows

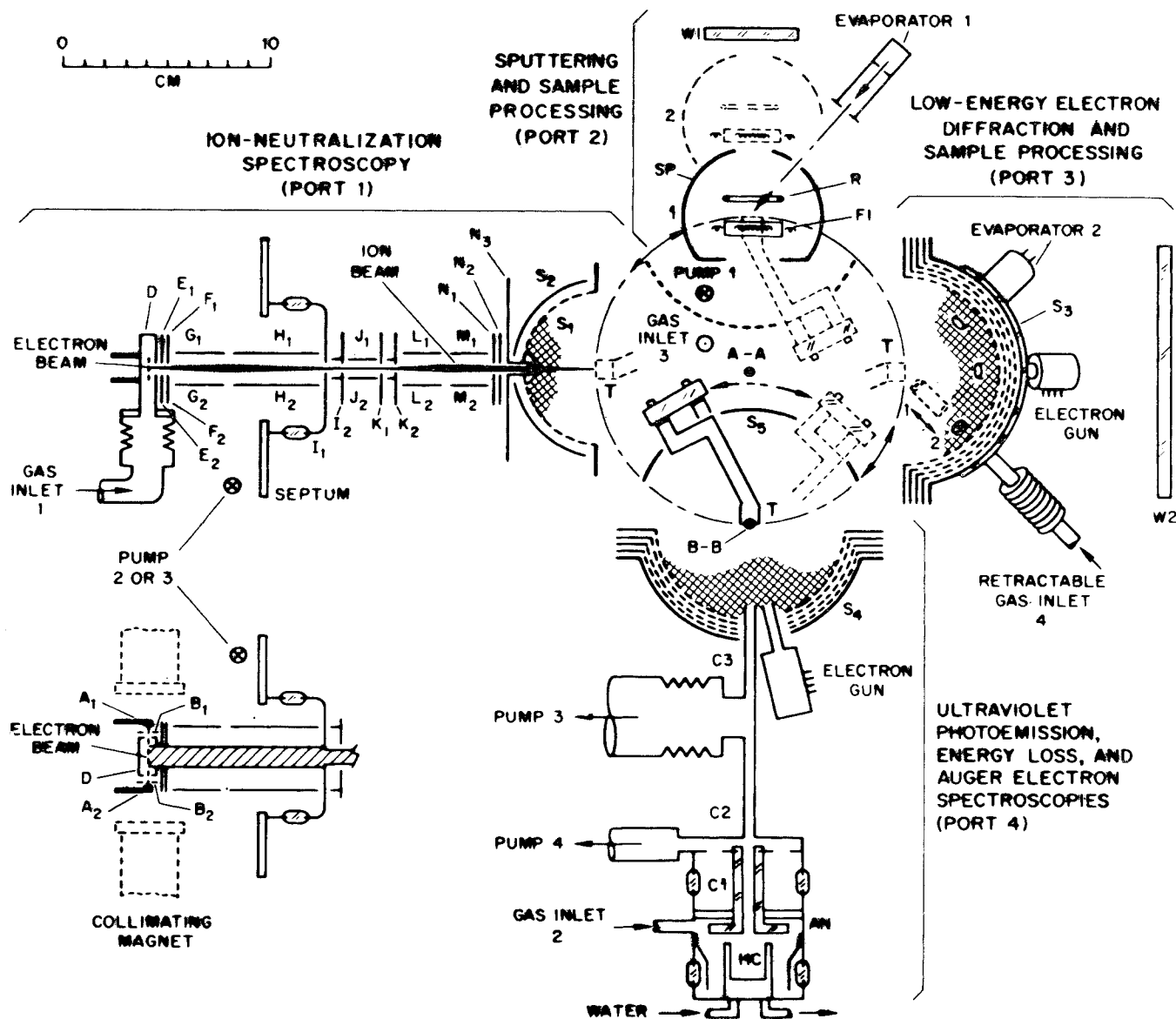


FIGURE 16 Schematic diagram of an experimental apparatus used by Hagstrum and co-workers to study INS in conjunction with other experimental techniques. For details, see Ref. 17.

the use of an electron multiplier. Since the angular distribution of emitted electrons is peaked normal to the surface (Figure 11), the best method could probably involve a spherical-sector analyzer aimed at 90° to the surface, and an ion beam incident on the surface at glancing angles. This latter feature relaxes somewhat the need of using very low energy ion beams since, in INS, what is important is to minimize the "transverse" energy $K_t = K \cos^2 \theta$, as follows from the discussion in 2.1c. On the other hand, the use of an inclined beam requires careful control of the beam angular spread since it is important to keep the "transverse" energy spread low.

The vacuum requirements for INS are similar to those of any other surface sensitive probe; one needs an ultrahigh vacuum environment. If, for instance, no more than 1% coverage from active residual gases can be tolerated during the measurement time t , then the partial pressure P_M of active gas of molecular mass M must be (at 20°C):

$$P_m < \frac{1.3 \times 10^{-10} M^{1/2}}{St \text{ (min)}} \text{ torr} \quad (11)$$

where S , the sticking coefficient of the gas on the surface, depends strongly on the molecule-substrate combination. Measurement times in INS will depend on the system and the signal to noise ratio required, but will be typically of the order of a few minutes. Therefore, and to be on the safe side, partial pressure of the active gases need to be in the 10^{-11} Torr range. This can be readily achieved using careful ultrahigh vacuum techniques.⁵²

2.4. Some Applications of INS

Figure 17 shows, as an example, the application of INS to single crystal Ni; the results for the $U(\zeta)$ function are contrasted with data obtained using UPS (ultraviolet photoelectron spectroscopy).⁴⁵ Two aspects can be visualized immediately from this comparison: (1) the larger tail of inelastic scattered electrons in UPS than in INS due to the fact that UPS also samples the bulk of the metal, and (2) the proportionally lower peak for the $3d$ electrons in INS due to the localized nature of these orbitals, which makes their tunnelling probability smaller than that of s and p electrons, as mentioned under 2.1d. This type of data has been used to demonstrate that the r.m.s. width of the surface d -band density is smaller than the corresponding values in the bulk,^{53,54} which is due to the reduced coordination number of atoms on the surface.

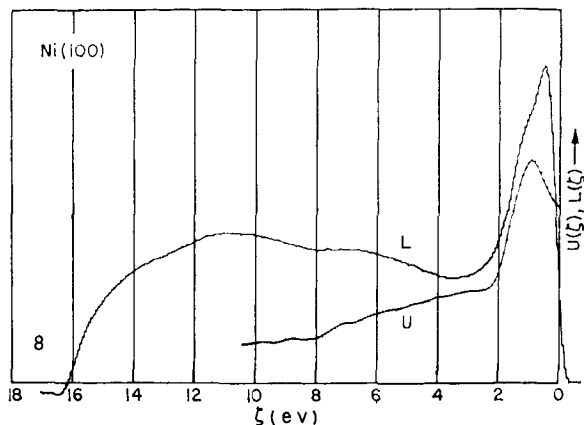


FIGURE 17 Comparison between the transition density function $U(\zeta)$ of INS with the $L(\zeta)$ function obtained using ultraviolet photoelectron spectroscopy, for a clean Ni (100) surface (from Hagstrum, Ref. 45).

Figure 18 shows transition density functions⁵⁵ for chalcogen structures on Ni(111). It can be seen that the orbital resonances depend on the type of adsorbed gas and very significantly on the local bonding of the adsorbate.

Surface band structures for different faces of a Ge single crystal⁵⁶ are presented in Figure 19, they bear only a slight resemblance to the bulk density of states, and further demonstrate the surface sensitivity of INS.

Figure 20 shows INS results³⁸ for clean and Hg-covered Si(111) 7×7 surfaces. By using He^+ at two different energies, 10 and 20 eV, it is possible to determine how the electron density decays outside the solid, since ions of different energies sample the solid, on the average, at different distances from the surface. Thus Figure 20 shows that the Hg d -component of the local density of states decays faster than the Si- p component. Hagstrum and Sakurai³⁸ were able to estimate that the 20 eV ions are neutralized on the average just $\sim 0.1 \text{ \AA}$ closer to the surface than 10 eV He^+ ions. This capability to detect wave-function variation outside surfaces is unique to INS among the electron spectroscopies for characterization of surface electronic structure.

2.5. Conclusion Regarding INS

We will conclude this section by recapitulating some points on INS. The best advantage of this technique, compared with other probes of surface electronic structure, is its extreme surface sensitivity. Coupling INS with UPS and XPS can then

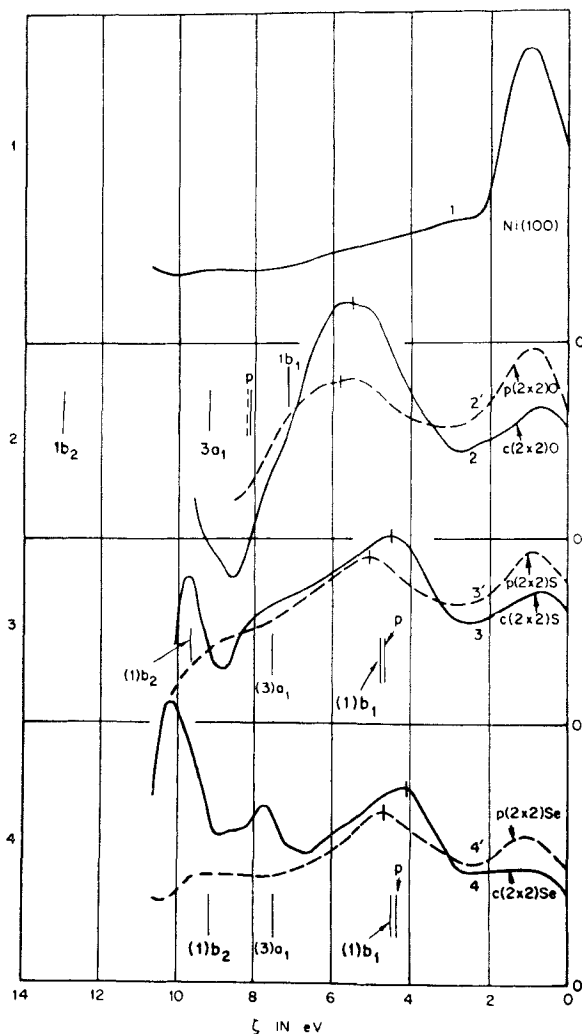


FIGURE 18 INS transition density function for Ni(100) surfaces, clean and with different adsorbed chalcogen structures. For details, see Ref. 55.

enable us, in principle, to determine how electronic orbitals change from the surface to the bulk. INS suffers the disadvantage, however, of requiring somewhat complicated experimental techniques and elaborate data reduction procedures, although a great deal of development can be expected in these areas; it is not too far fetched to imagine that in the near future INS will be incorporated on a routine basis in surface analytical instruments. Finally, the study of these electron processes at surfaces will undoubtedly help us to understand, and to use more efficiently, the techniques of low energy ion

scattering spectroscopy and secondary ion mass spectroscopy.

3. ION INDUCED AUGER ELECTRON SPECTROSCOPY (IAES)

3.1. Background from Electron-Induced AES (EAES)

The technique of electron bombardment-induced AES is a well established tool for composition analysis of solids.⁷⁻¹⁰ Here an electron beam of energy usually in the range 1–3 keV is used to excite inner-shell (core) electrons of the solid. The vacancies (or core holes) thus produced deexcite mainly by two-electron Auger processes in which one electron from a higher electron-energy state fills the hole and transfers the energy to a second electron, the Auger electron, which may be emitted and observed outside the solid. As we shall see, these Auger electrons possess a characteristic energy which is primarily a function of energy level separation, and which serves to identify the excited atom. This Auger effect is similar to AN discussed when dealing with INS, albeit there are some important differences: (1) In AES the transitions usually involve hole and electrons from the same atom, i.e., they are usually *intraatomic*, whereas in AN the transitions are *interatomic*, since the hole is carried by the incident ion and the electrons are provided by the solid; (2) In AES, the excited electron originates, on the average, from a few layers deep in the solid (Figure 2), whereas in INS electrons are emitted from the surface region. Thus, INS is a *surface* analytical tool while EAES is *not*, despite wrongly founded claims to the contrary, as pointed out by Park *et al.*⁵⁷

Auger transitions are usually identified by three letters, i.e. *WXY*, which indicate the shell of origin of the hole, *W*, and of the participating electrons, *XY*, although a complete description requires the specification of the spin, orbital and total angular momenta of the final state.³² Most of the applications in EAES are concerned with element identification from the measurement of *WXY* transition energies. A reasonable estimate of the energy of the Auger electron w.r.t. the Fermi level of the sample is⁵⁸:

$$W_{WXY}(Z) = E_W(Z) - \frac{1}{2}[E_X(Z) + E_X(Z+1)] - \frac{1}{2}[E_Y(Z) + E_Y(Z+1)] \quad (12)$$

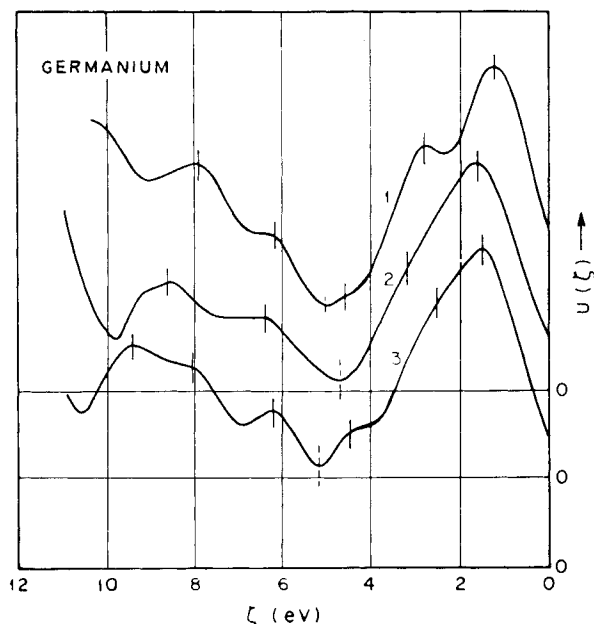


FIGURE 19 INS transition density function for three faces of Germanium. Curve 1: Ge(111); curve 2: Ge(110); curve 3: Ge(100) (from Hagstrum and Becker, Ref. 56).

where $E_i(Z)$ is the electron energy in the i th orbital of the atom, (w.r.t. the Fermi level) and $E_i(Z+1)$ is the corresponding quantity for the next heavier element. This formula takes into account exchange, and the increased binding of the outer electrons caused by the weaker screening of the nuclear charge, caused by the core hole. In practice, identification of atoms in EAES is usually based on matching spectra against “standard” graphs⁵⁹ taken from samples of known composition. The widths of Auger peaks are dictated by the convolution of the widths of all levels involved. Level widths Γ are related to level lifetime by the relation $\Gamma = \hbar/\tau$, if one neglects electronic and thermal broadening, and many-body effects.⁶⁰ Transitions involving the valence band are much wider due to the distribution of levels across the band. If we denote by ζ_0 the width of this band as measured, for instance, by X-ray emission spectroscopy (thus including the effect of the core hole and Auger broadening within the band⁶¹), then transitions involving two core levels C_1 and C_2 and the valence band $V(C_1C_2V)$ will give Auger electrons in a peak of width ζ_0 , while transitions CVV will have a width of $2\zeta_0$. Thus Auger peaks from solids, especially those involving valence band electrons, will be wider than Auger peaks from free atoms.

It is possible to proceed one step further from simple element identification by observing details of the Auger spectra. Thus, energy shifts (“chemical shifts”), which accompany changes in the valence state when chemical compounds are formed, due to variations of the “outer screening”, can serve to perform a chemical analysis, in a similar, though more complicated way than for X-ray PES, since not one, but three levels are involved. A change in the valence-band density of states is also reflected in the shape of the Auger spectra for C_1C_2V and CVV transitions, and so these spectra can serve as fingerprints for the identification of chemical compounds. Examples of studies of chemical effects in AES can be found in Refs. 63–74.

Similarly to the case of INS, a CVV Auger spectrum represents a self-convolution of a transition density $U'(\zeta)$ but, in the case of EAES, superimposed on a large background of inelastically scattered electrons.^{75–82} To obtain the transition density one must first find a way to remove this

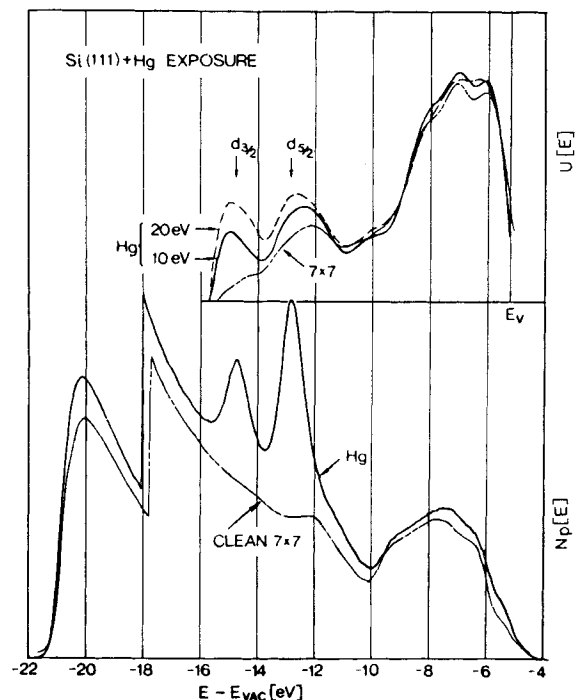


FIGURE 20 Top: INS transition functions $U(E)$ for 10- and 20-eV He^+ ions incident on a Hg-covered Si(111) surface and for 10 eV He^+ ions incident on a clean Si(111) 7×7 surface. Bottom: ultraviolet photoelectron spectra $N_p(E)$ for clean and Hg-covered Si(111) 7×7 surfaces (from Hagstrum and Sakurai, Ref. 38).

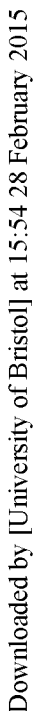
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however, it is convenient to include couplings which are large in some regions of internuclear separation, like crossings of MOs of the same symmetry; this is done using so-called “diabatic” MOs which are superpositions of adiabatic MOs but which include the important coupling terms, i.e., the levels are allowed to cross.^{103–105}

Diabatic MO energy diagrams obtained from Hartree-Fock calculations^{106,107} for Ne-Ne and Ne-O collisions are shown in Figure 21. In the absence of *ab-initio* calculations, one uses correlation diagrams which indicate how energy levels in the separated atom (SA) limit, correlate with levels in the united atom (UA) limit at zero internuclear separation. The rules for drawing diabatic correlation diagrams are^{108,109}: (a) levels of the SA and UA are correlated if they have the same number of nodes $n-l-1$ in their wave function, i.e., this number is conserved (here n is the principal quantum number and l the orbital angular momentum); (b) the projection of the orbital angular momentum on the internuclear axis, Λ , is a good quantum number and it is conserved; therefore atomic levels with orbital angular momentum l give rise to MOs with $\Lambda = 0, 1, \dots, l(\sigma, \pi, \text{etc.})$; (c) correlations are then drawn between states of the same symmetry, starting from the K-shell (1 $s\sigma$ MO) and proceeding to the valence shell, always making the correlation to the more tightly-bound atomic level available.

A consequence of the MO picture is the occurrence of electron promotion, which is the increase in principal quantum number of certain MOs in going from the SA to the UA limit. One may interpret this as a consequence of the Pauli principle since there is not space available in the nl level of the UA to accommodate two full nl levels in each atom in the SA limit. This, however, does not explain why particular levels are more promoted than others, like the $2p$ level in collisions in which the atomic number of the colliding partners are not very different (Figure 21). One may roughly visualize two competing effects occurring on approach during the collision. On the one hand, the potential energy of the electrons increase going to the UA limit due to the increase in nuclear charge. On the other hand, the electron clouds of the two atoms interact as the internuclear distance decreases, and this decreases the binding energy of the electrons; the electronic repulsion will be larger the larger the number of electrons in the subshell. This explains why d electrons can be promoted more than p electrons, and these more than s electrons.

It also explains why the electron energy starts to decrease rapidly at internuclear distances of the order of the sum of the radii of maximum charge density of the interacting subshells.

Electron promotion is the basis of a model suggested by Fano and Lichten^{110,111} to explain inner-shell excitation, at projectile velocities much smaller than velocities of inner-shell electrons in the colliding atoms. Couplings involving time variation of the internuclear distance, called radial couplings, may cause transitions at the crossings of states of the same symmetry, if the final state is not completely occupied ($3d\sigma-3s\sigma$ in Figure 21). Also, the fast rotation of the internuclear axis near the closest approach, can produce transitions by what is called rotational coupling, which connects states of $\Delta\Lambda = 1$ (like the $2p\sigma-2p\pi$ transition possible in Figure 21, if at least one vacancy exists in the $2p\pi$ orbital on approach). There are many possible cases in which other transitions may occur. Thus, the breakdown of the independent-particle description for outer-shell electrons, due to configuration interaction, allows two-electron transitions; at high velocities, holes may be formed in the outer-shells which open the possibility of transitions between previously fully occupied levels; holes may be transferred between different MOs if they are close, even in the absence of a crossing, by what has been termed vacancy sharing; etc. The degree to which these other processes will occur depends sensitively on the type of collision partners, and their velocity of relative motion. For further details, the reader is referred to review articles which describe *in extenso* inner-shell ionization induced by heavy particles.^{97,98,105,109,112–115}

When target atoms are in the solid state, some specific effects occur.¹¹⁶ Heavy projectiles travelling at low velocities inside a solid will, in many cases, have their outer electron levels submerged in the valence band of the solid, and therefore broadened. Outer-shell excitations will be quenched very fast, at least in metals, in times of the order of 10^{-16} sec. by the rapid screening response of valence-band electrons. Auger spectra from atoms decaying in the solid, and which move with velocities small compared with the Fermi velocity, should then be essentially the same as those from atoms stationary in the solid. If, however, the excited atom is sputtered and decays outside the solid and outside the influence of its surface, it will emit Auger electrons characteristic of free atoms. Another solid-state effect is related to the possibility of double-collisions. If the lifetime of an

inner-shell hole is of the order or longer than the time between collisions, a previously excited atom may transfer its vacancy to a stationary atom. It may also create new excitations which are not possible in collisions between two free atoms, and which are allowed by the existence of this vacancy. Finally, and since inner-shell excitations are favoured in collisions between like atoms, one should expect, at least for solids composed of light atoms, a substantial amount of excitation from collisions involving recoiling target atoms.^{117,118}

3.3. *Experimental Techniques in IAES*

In IAES, it is necessary that the ion beam be mass analyzed and monoenergetic, especially when working at low energies (below 10 keV) where cross sections for inner-shell ionization rise very fast with ion energy and are usually very specific to the type of projectile. Failure to do so results in irreproducible data, and this has plagued many works including very recent ones.

The type of vacuum requirements will depend on the application. Thus, if one is just interested in looking at carbon buildup during a Rutherford backscattering experiment, IAES will serve itself to monitor the quality of the vacuum. For other applications, one must remember the smallness of mean electron escape depths (Figure 2). Therefore, if one is interested in near-surface composition, an ultra-high vacuum environment will be required.

The core of the equipment is the electron spectrometer. Several different types of these have been studied; their relative merits have been discussed, together with the need for shielding against electromagnetic fields.^{119–127} Three basic types are the most commonly used, all of which are available commercially. The hemispherical retarding potential analyser (RPA), similar to that used by Hagsstrum for INS, has the main virtue that it can also be used for LEED studies, but has only moderate energy resolution ($\sim 1\%$) and intrinsically low signal to noise ratio.¹²⁸ The other two basic types are of the deflection type, the cylindrical mirror (CMA) and the 180° spherical sector (HSA) analyser. Of these, the CMA has the largest étendue (product of accepted area and solid angle) but has many drawbacks compared to the HSA, like allowing little access to the region around the sample, little flexibility as regards to changing slits and thus altering resolution, not permitting angular studies to be performed, and being very sensitive to the location of the source.¹²⁹ It is however, easier

to construct than the HSA. Either the étendue or the resolution of these spectrometers can be improved by retarding the electrons before analysis (Refs. 119, 130); retarding with focusing is, however, much easier with HSAs and these instruments should be preferred for high-resolution work. The HSA can also be fitted relatively easily with a multidetector system with the attendant huge increase in data acquisition capabilities.^{121,131}

Due to the fact that Auger spectra are superimposed on a large but smooth background of electrons, it is convenient in most cases to measure the first derivative of the energy distribution $N(E)$. This is normally accomplished by modulating the energy analyser with a small sinusoidal voltage and using phase sensitive detection techniques.¹²⁸

For deflection type analysers in the normal operating mode, the signal $S(E)$ is given by

$$S(E) \propto EN(E) \quad (13)$$

the first harmonic of the signal is, for small modulations,

$$H(E) \propto N(E) + EN'(E) \quad (14)$$

which gives nearly the desired result since $N(E)$ can normally be taken as constant, except at very low E .

When the signal is very low, the need appears to use modulation voltages too large for Eq. (14) to apply, in which case distortions appear in the spectra.^{132–135} A customary measure of signal strength is the peak-to-peak height (pph) in the differential signal. Care must however be taken in cases in which the shape of the $N(E)$ Auger peak changes (for instance as a result of a change in the chemical state), since in this case the pph in $N'(E)$ will change, even if the area under the peak in $N(E)$ does not. Furthermore, when the modulation voltage is not small enough, it will influence the pph of different Auger peaks differently, if their intrinsic widths are not the same.

3.4. *Examples*

3.4.1. High energy ions A few investigations have dealt with the use of IAES by high-energy light ions. Kaminsky¹³⁶ detected a low energy structure in Cu under impact of 400 keV H^+ and He^+ ions and 500 keV D^+ ions, but did not attempt an interpretation. Wurtz *et al.*¹³⁷ could only detect a sulphur contaminant (LVV peak) on stainless steel using $0.5 \mu A$ D^+ ions at 100 keV and a RPA.

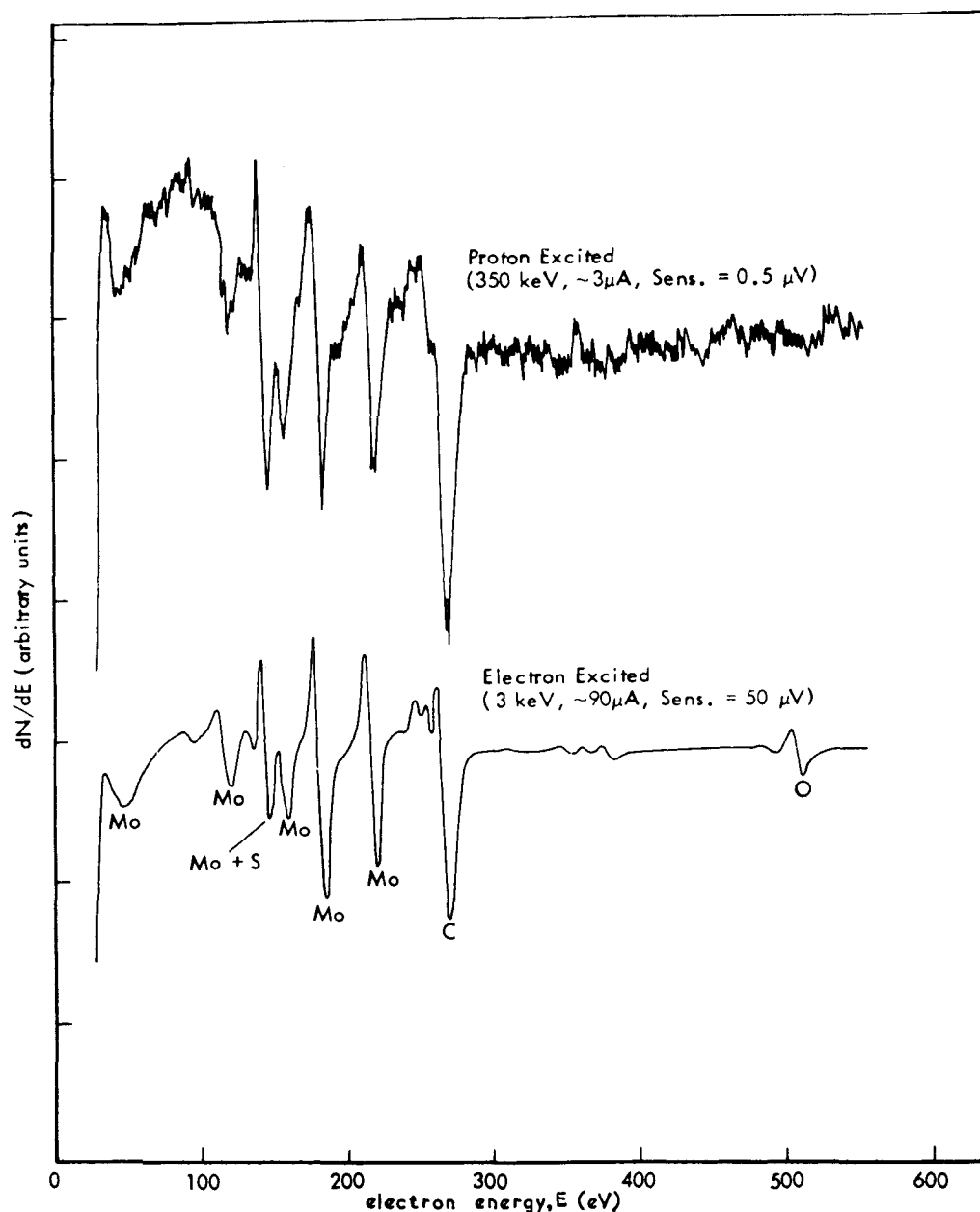


FIGURE 22 Proton and electron-excited Auger spectra of a molybdenum surface. The larger noise in the proton-excited spectrum is mainly due to instability in the beam current (from Musket and Bauer, Ref. 138).

Musket and Bauer^{138,139} analysed Mo and stainless steel samples using $3\mu\text{A}$, 350 keV H^+ and a CMA; they were able to detect low energy Mo, S, Fe and C Auger peaks, but not oxygen. A comparison of EAES and IAES spectra obtained by them on a Mo sample is shown in Figure 22. These

workers also discuss the advantage of IAES with fast protons over EAES. In the former case, the depth distribution of inner-shell ionizations is practically the same as the depth distribution of the target atoms, over the mean electron escape depths, since in this region the fast ions suffer little energy

loss and angular deflection. On the contrary, primary electrons in EAES suffer substantial energy and angular spread and can also produce efficiently secondary ionizations when they are backscattered. Musket and Bauer also propose that, since these secondary effects are minimum with fast protons, knowledge of inner-shell ionization cross sections and careful measurements of the absolute intensities of Auger signals could be used to obtain accurate electron attenuation lengths in solids. This idea was followed by Needham *et al.*^{140,141} who measured absolute *KVV*-Be and *LVV*-Al electron yields for 60–220 keV H^+ and derived the corresponding attenuation lengths using calculated cross sections. Better values would be obtained, however, using higher energy (MeV) protons for which more reliable cross section estimates can be obtained. In this connection, it is interesting to point out that Benazeth *et al.*^{142–145} did precisely the opposite, i.e., from published values of attenuation lengths they derived cross section for inner-shell excitation, to test existing theories. Further applications in this area must, however, await developments of more elaborate methods of subtracting the background under the Auger peaks.

Groeneveld *et al.*¹⁴⁶ proposed the use of high energy heavy ions for material analysis, indicating the advantages of high cross sections compared to those for electron impact, and selective excitation of specific impurity elements by judicious use of projectile type and bombarding energy, but did not give examples of actual analyses.

IAES will probably find applications when used in conjunction with techniques such as Rutherford backscattering (RBS), ion-induced X-ray emission, and nuclear analysis using Van de Graaff accelerators. At these energies, say 2 MeV, and for H^+ impact, IAES should detect any element heavier than He, if present in concentrations exceeding 0.1%. Furthermore, it should give particularly good sensitivity for the light elements which are difficult to detect by RBS or X-ray techniques and, above all, provide information on the near-surface composition of the samples. Although in most cases it will be more convenient to install a simple electron gun in the sample chamber and perform conventional EAES analysis, IAES with fast protons may prove to be easier to quantify since, as mentioned, secondary effects are very small.

The majority of the investigations on IAES have been performed with ions of energies below 100 keV. One of the primary motivations of early research was just to look at the Auger process which, accord-

ing to a theory by Parilis and Kishinevskii^{147,148} should be the main mechanism for electron emission under low energy ion impact. By now, different works have shown this mechanism to be of only secondary importance in most cases.^{149–154} Auger emission from the projectile atoms have been observed by several groups,^{144,155–167} they result mainly from backscattered projectiles decaying in vacuum, as judged by the similarity with Auger spectra from ions traversing foils^{168–170} (excitation of trapped projectile atoms is, however, also present in some cases). It was found that the widths of the peaks, attributed mainly to Doppler broadening, increase with projectile energy^{144,159,161,167} and that Auger signals from projectile atoms increase abruptly with energy from a fairly well defined threshold. (Some experiments^{156,158,160} have probably given a distorted energy dependence due to the unavoidable presence of multiply-charged atoms in the beam.)

More related to our purpose have been observations of Auger electrons from target atoms. Since the first experiments by Hennequin *et al.*,¹⁷¹ several questions have been raised: (1) Do Auger electrons come from collisions between projectiles and target atoms (P-T) or between fast recoiling and stationary target atoms (T-T)?; (2) are the narrow, “quasi-atomic” peaks (Figure 23)¹⁷² associated with atoms moving in the bulk, or in free space (sputtered)?; (3) what is the origin of the satellite peaks appearing at energies lower than the main peak?

The first question cannot be answered in a general way since it depends on the projectile–target combination. For heavy projectiles, one can expect T-T collisions to predominate at low energies. In this respect, it was shown that Al- and Si-L yields (Refs. 173, 174) for different projectiles, can be scaled if one uses the maximum energy transfer in P-T collisions as an energy scaling unit,¹⁷⁴ which corresponds to assuming T-T collisions to predominate.¹⁷⁵ In the case of low-energy light-ion impact, Auger electrons result, on the contrary, predominantly from P-T collisions.¹⁷³ Joyes¹⁷⁶ proposed that if T-T collisions dominate, the yields should be proportional to the concentration square of the element studied; this has been confirmed¹⁷⁷ experimentally. It has also been found that Ar excited Al-L and Mg-L signals are drastically reduced on adsorption of oxygen.^{172,177} This again points in the direction that T-T collisions dominate for heavy projectiles; an alternative explanation could invoke a large increase in the

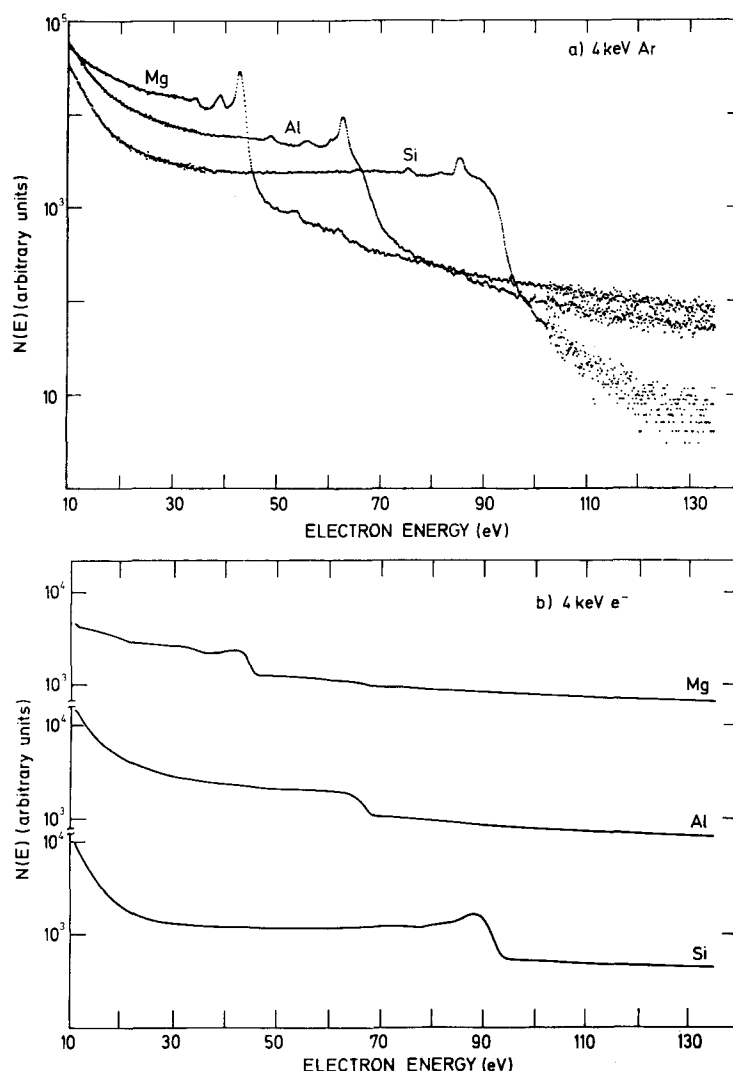


FIGURE 23 Auger spectra of Mg, Al, and Si induced by (a) 4 keV ion and (b) 4 keV electron bombardment, at 45° incidence. Data for different targets were taken under the same experimental conditions, and corrected for the energy dependence of the transmission of the analyzer (from Baragiola, Ref. 172).

fluorescence yield of the 2*p*-shell due to the transfer of valence charge, from the metal atom to the oxygen, upon chemisorption.

Auger spectra of light metals under ion bombardment show narrow peaks superimposed on a broad structure. The latter can be attributed to Auger decays inside the solid, from its similarity with the electron-excited case. The origin of the narrow peaks has been the subject of considerable controversy. The general belief has been that these peaks are due to sputtered excited atoms decaying outside the solid. On the contrary, the Toulouse

group^{145,178,179} has advocated that they result from fast recoils moving inside the solid which, because of their motion, have their valence electrons “decoupled” from the valence-band of the solid, and are, therefore, “quasi-atomic”. This model is, however, contrary to theoretical expectation. Since at these energies, recoiling atoms move with velocities much lower than the Fermi velocity, they should behave practically as stationary atoms. The conclusion that the narrow Auger peaks originate from sputtered atoms, comes from measurements of the Doppler broadening of the

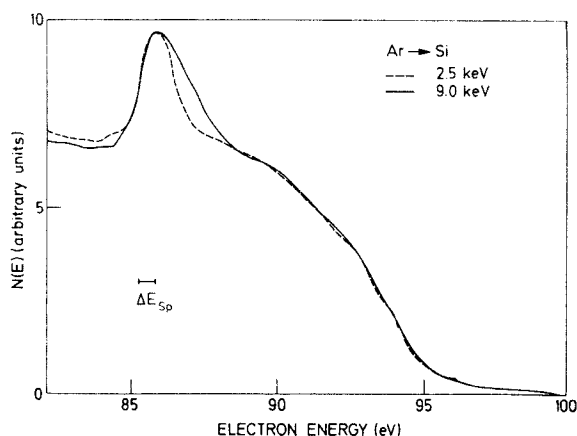


FIGURE 24 Auger spectra of Si excited by 2.5 keV and 9 keV Ar^+ ions incident at 45° (from Baragiola, Ref. 172). The curves are normalized at high electron energy.

peaks. Figure 24 shows, from an experiment in which the direction of observation is essentially normal to the target surface,¹⁷² that the broadening increases with ion energy towards higher electron energies, indicating that the emitting atoms are moving with velocity components in the direction of observation, but not in the opposite direction.

The smaller satellite peaks at low electron energies were first attributed to surface plasmon losses,^{180–184} but this hypothesis was later disregarded in favour of “quasi-atomic” losses (Refs. 167–169, 178, 185–187). A more plausible explanation, consistent with the observation that narrow peaks are associated with sputtered atoms, comes from consideration of different ways in which the outer electrons can participate in the event (Refs. 165, 172, 174, 188). Thus, in the case of Mg, Al and Si, one can identify LM_1^2 , LM_1M_2 and LM_2^2 transitions, depending upon the availability of different states in the outer shell. Calculations of Auger energies^{172,188} are in good agreement with the experiment, but a definitive assignment of all levels to particular charge states of the emitting particles is not yet possible.

The possibilities of analysis by IAES with low energy ions have not yet been explored. Elements which have been detected using projectiles in the energy range up to several tens of keV are Li, Be, C, Ne, Na, Mg, Al, Si, P, S, Ar, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Ga.^{142–145,150,155–174,177–185,187–220} The core levels which can be excited in target–target collisions, can be estimated readily from the correlation diagrams, they are K for Li to C, L for

Na to Ar, M from K to Ru, and N from Rb to Ra, where only levels bound less than 300 eV were considered. The sensitivity will in general increase with increasing ion energy, decrease with decreasing radius of the orbit (increasing binding energy) of the shell, increase with the number of electrons that are promoted, and increase the closer the masses of projectile and target atom, at the same impact energy. For projectile–target collisions one can, by looking at the correlation diagrams, decide on the projectile that will cause the larger yield.²¹⁰ A similar methodology has been proposed by Cairns *et al.*^{221–223} for heavy-ion induced X-ray analysis.

At this stage, we can say that, although studies of Auger emission by low energy ions can yield fundamental information on basic collisional problems which may be of importance to other techniques, like SIMS, its use as a general analytical tool is not to be expected in the near future.

4. SUMMARY

Of the different applications of ion-induced electron emission for material analysis that have been discussed, the technique of Ion Neutralization Spectroscopy devised by Hagstrum and co-workers is the one that has met with more success; further developments here are likely to occur as the underlying theory is better understood. Auger emission from inner-shell excitations caused by ion beams should prove useful when used in conjunction with other techniques, like Rutherford backscattering or SIMS but in most cases at present, electron initiated Auger spectroscopy can give the same answers but with more simplicity in apparatus.

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