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DETERMINATION OF INELASTIC MEAN FREE PATH OF ELECTRONS IN NOBLE METALS

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The experimental values of Inelastic Mean Free Path (λ_{IMFP}) of electrons in noble metals (Ag, Au, Cu) are determined in the electron energy range 150–2000 eV. The method used consists of the measurements and theoretical calculations of the coefficient of elastic backscattering of electrons from a solid surface η_e. The obtained values of λ_{IMFP} are compared with the data available in the literature.

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1. Introduction

The value of the probability that the photoelectron or Auger electron created in the sample leaves the sample without energy loss is an important factor in the mathematical formalism of quantitative XPS or AES. Such an electron transport is characterized by several different terms in the literature i.e. inelastic mean free path (IMFP), escape depth (ED), attenuation length (AL) and also an information depth (ID). It should be pointed here that each of these terms has a separate meaning (see Ref. [1–4]). Also their values can be different. For example Powell [5] and Jabłoński et al. [3, 6–9] have shown that the difference between IMFP and AL can be equal to 30% or even more. This considerable difference originates among others from different methods of the AL and IMFP determination. Namely, the AL values have been determined from the overlayer experiments and with an assumption that the elastic scattering of the electrons can be neglected. Based on the results of such experiments performed for many overlayer–substrate systems and different electron energies Seah and Dench [10] proposed the formulae for AL value calculations for elements and compounds. IMFP values (as being inversely

related to the total inelastic scattering cross-section) were mainly obtained basing on the calculation of the total probability of inelastic scattering of electrons in solids (see Ref. [11–15]). In 1985 Jabłoński [16] proposed an experimental method by which IMFP value for given electron energy and an element can be determined from the measurements and theoretical calculations of the coefficient of elastic electron backscattering from the solid. This method was used previously [17, 18] for the determination of electron IMFP values for Ag and Cu and a few values of electron energies. In this paper we present the results of IMFP measurements for noble metals (Ag, Au, Cu) in the electron energy range 150–2000 eV (including characteristic Auger energies).

2. Description of the method

In the method proposed by Jabłoński [16] IMFP values (λ_{IMFP}) are obtained from the comparison of the elastic electron backscattering coefficient η_e measured for a given electron energy and a given sample with the value of this coefficient calculated theoretically for an assumed value of λ_{IMFP}. The measured η_e value is defined as follows:

$$\eta_e = \frac{I_{el}}{I_p} \tag{1}$$

where I_{el} — the current of electrons elastically backscattered from the sample, I_p — primary electron beam current. The theoretical η_e value is obtained for a given sample, electron energy and an assumed λ_{IMFP} value by computer simulation of electron trajectories in the sample. The computer randomizes the electron paths in a solid between successive elastic collisions as well as polar and azimuthal angles of each elastic scattering. Such operations are repeated until an electron leaves the sample or its total path will be larger than an assumed multiplicity of λ_{IMFP}. In a first case the contribution of a single electron to the total current of electrons backscattered elastically is

$$\mathrm{d}I_{el} = \exp\left(\frac{-\sum_i z_i}{\lambda_{\mathrm{IMFP}}}\right) \tag{2}$$

where $\sum_i z_i$ — total path of an electron in the sample, λ_{IMFP} — assumed value of λ_{IMFP}, if $\sum_i z_i > k^* \lambda_{\mathrm{IMFP}} \Rightarrow \mathrm{d}I_{el} \approx 0$ for $k \geq 11$.

If one performs such simulations for the same electron energy and several assumed λ_{IMFP} values one can obtain the theoretical dependence of η_e on λ_{IMFP}. From such dependence the experimental λ_{IMFP} value can be found as related to the η_e measured experimentally. The procedure of η_e measurements was presented previously [17]. Some changes were made, however, in the theoretical calculations of η_e. So, the used method of calculations is shortly described below.

2.1. Calculations of η_e

The problem of elastic scattering of electrons can be solved within the non-relativistic partial wave expansion method [19]. Considering the process of elastic scattering one can precise that:

— the incident electron is represented by a plane wave of unit amplitude traveling in the z direction:

$$\Psi_i = \exp(ikz);$$

— the scattered wave Ψ_s travels out radially from the scattering atom with an amplitude which is a function of the scattering angle θ as well as the distance r;

— the sum of these two waves

$$\Psi(r, \theta) = \Psi_i + \Psi_s$$

is a solution of the Schrödinger equation:

$$\nabla^2\Psi + (k^2 - 2m\ V(r)/\hbar^2)\Psi = 0$$

in which $k = 2\pi/\lambda$, λ is the associated de Broglie wavelength and the spherical potential $V(r)$ can be expressed as the Thomas–Fermi–Dirac one [20, 21].

The following formulae are obtained:

$$\Psi_i(r, \theta) = C_i \sum_{n=0}^{\infty} P_n(\cos\theta) g_n(r)/r,$$

$$\Psi_s(r, \theta) = C_s \sum_{n=0} P_n(\cos\theta) G_n(r)/r$$

where the g_n's and G_n's are solutions of the differential equations:

$$dg_n^2/dr^2 + (k^2 - n(n+1)/r^2)g_n = 0, \tag{3}$$

$$dG_n^2/dr^2 + (k^2 - 2mV(r)/\hbar^2 - n(n+1)/r^2)G_n = 0. \tag{4}$$

The number of electrons scattered elastically per unit solid angle is given by the differential scattering cross-section:

$$d\sigma/d\Omega = |f(\theta)|^2 = A^2 + B^2$$

where

$$A = (2k^{-1}) \sum_{n=0}^{\infty} (2n+1)(\cos 2\delta_n - 1) P_n(\cos\theta),$$

$$B = (2k^{-1}) \sum_{n=0}^{\infty} (2n+1) \sin 2\delta_n \cdot P_n(\cos\theta);$$

$P_n(\cos\theta)$ are the Legendre coefficients and δ_n the phase shifts between the asymptotic sinusoidal expressions of $g_n(r)$ and $G_n(r)$.

The value of δ_n can be obtained when $V(r)$ is becoming insignificant [22]. The curves $g_n(r)$ and $G_n(r)$ are not yet sinusoidal but as they are solutions of the same differential equation the phase remains constant. The time of computer calculation is then well limited.

In our process of calculation only numerical methods are used. Equations (3) and (4) are solved simultaneously, the procedure is based on:

— an expanded solution into a series for the known initial conditions;

— the high accuracy method devised by W.E. Milne [23] with predicting and checking the solutions of the differential equations.

Using a step of iteration equal to 5×10^{-3} Å, all our results have been obtained with a DPX 2000 Bull computer with the 68020 Motorola microprocessor.

3. Experimental

Values of η_e were measured for three noble metals (Ag, Au, Cu) in the electron energy range 150–2000 eV. As an electron energy analyzer we used 4-grid RFA with an acceptance angle 4–44° and electron energy resolution equal to 0.6%. The clean, polycrystalline Ag, Au, Cu samples (purity 99.99%) were prepared in the form of foils 7×14 mm, 0.4 mm thick. Their surfaces were cleaned with potassium ion bombardment (E_{K+} = 400 eV) and heated to ≈ 920 K. The surface purity was controlled with AES. The pressure during the measurements did not exceed 4×10^{-10} torr.

4. Results, discussion and conclusions

The results of η_e measurements for Ag, Au, and Cu are presented in Fig. 1 (solid lines), together with η_e values obtained by Schmid et al. [23] (dashed lines) who also used the RFA analyzer. As it is visible the shapes of $\eta_e = f(E)$ dependencies are quite similar, but the η_e values are different. This difference originates

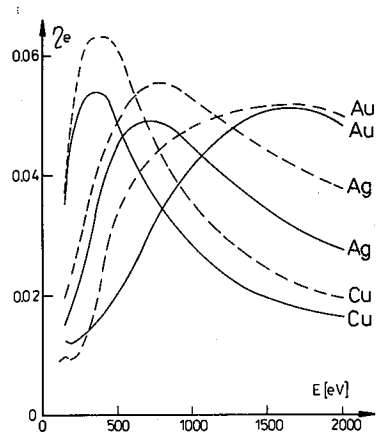

Fig. 1. The comparison of the measured η_e values with those obtained by Schmid et al. [24] (solid lines — our results, dashed lines — the results from Ref. [24]).

probably from different RFA acceptance angles (4–44° in our measurements, 6–52° in Ref. [23]). The calculated values of the amplitudes $f(\theta)$ are in good agreement with those published previously. For example in the case of electrons scattered by Ag atoms one can see:

— in Fig. 2 a comparison with the calculations of M. Fink and J. Ingram [25] obtained using the relativistic Hartree–Fock–Slater potential;

— in Fig. 3 our results are compared with those by Jabłoński [26] who used the same form of the potential $V(r)$ but with another mode of the mathematical process to get the phase δ_n.

The theoretical values of η_e were obtained for electron energies from the range 150–2000 eV and for 6 assumed values of IMFP for each value of electron

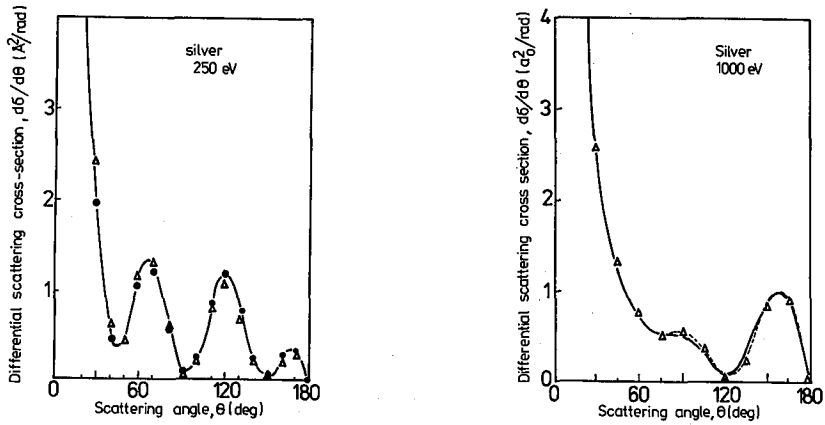

Fig. 2. The dependence of the differential cross-section for elastic scattering $2\pi f^2(\theta) \times sin\theta \, d\theta$ for electron energy equal to 250 eV (• — Ref. [25], Δ — our results).
Fig. 3. The dependence of the differential cross-section for elastic scattering $2\pi f^2(\theta) \times sin\theta \, d\theta$ for electron energy equal to 1000 eV (solid and dashed lines — the nonrelativistic and the relativistic PWEM taken from Ref. [26]; Δ — our results).

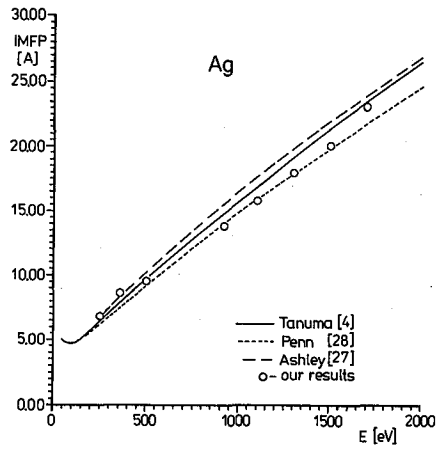

Fig. 4. Values of λ_{IMFP} as a function of electron energy determined for Ag.

energy using one million electrons impinging the surface. The determined λ_{IMFP} values compared with those recommended by Ashley and Tung [27], Penn [28] and calculated recently by Tanuma et al. [4] are presented in Figs. 4–6 as a function of electron energies. An excellent agreement of our λ_{IMFP} with those calculated theoretically is observed for silver sample. For gold and copper they differ from the theoretical values by about 10–20% or even more especially in the low energy region. However, one can notice a good agreement with Ashley and Tung [27] results for the gold sample in the high energy region. Our approach to λ_{IMFP}

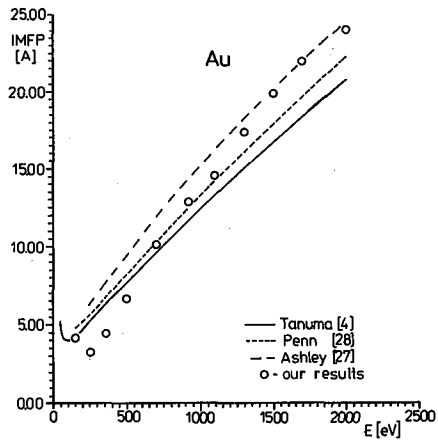

Fig. 5. Values of λ_{IMFP} as a function of electron energy determined for Au.

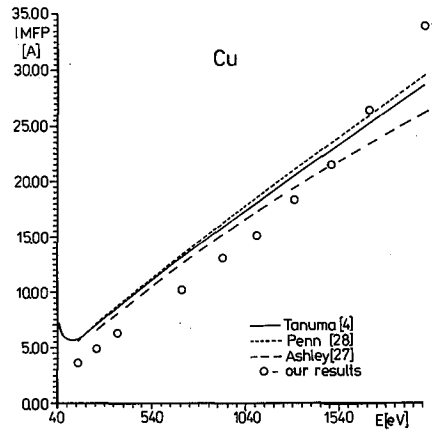

Fig. 6. Values of λ_{IMFP} as a function of electron energy determined for Cu.

determination is completely different from those used in theoretical calculations [4, 27, 28]. So, nothing can be said about the possible reasons of the observed discrepancies in the results obtained for copper and gold. Additionally it is difficult to estimate the accuracy of our method. η_e was measured with RMS $< 5\%$, the precision of computer Monte-Carlo simulations was not worse than 1%, but the results depend also on the accuracy of $f(\theta)$ theoretical calculations.

Acknowledgements

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