Journal of Surface Analysis Vol.15, No. 2 (2008) pp. 177−185
L. Kövér Effective Attenuation Lengths for High (up to 15 keV) Energy Photo- and Auger Electrons in Several Elementary Solids

Paper

Effective Attenuation Lengths for High (up to 15 keV) Energy Photo- and Auger Electrons in Several Elementary Solids

L. Kövér*
Institute of Nuclear Research of the Hungarian Academy of Sciences (MTA ATOMKI)
18/c Bem tér, H-4026 Debrecen, Hungary
**lkover@atomki.hu*

(Received: April 11, 2008; Accepted: May 30, 2008)

A comparison of data obtained by using different formulae for predicting ratios of effective attenuation lengths to inelastic mean free paths for energetic (with energies up to 15 keV) electrons, and experiments is given for the case of several elemental solids such as Si, Ni, Cu, Ge, Ag, W and Au. The results demonstrate the estimated accuracy of these simple approximations as well as the decreasing effect of elastic electron scattering with increasing electron energy.

1. Introduction

Hard X-ray induced photo-and Auger spectroscopy (HAXPES) gains an increasing role in non-destructive chemical analysis of surface and interface layers of solids, especially in the case of interfaces buried deeply (in several or several ten nm depth from the surface). For quantitative analytical applications of HAXPES, reliable information on the parameters characterizing the transport of energetic electrons in solids, is necessary. However, available data for inelastic scattering of electrons with energies larger than 2 keV, are rather scarce. In practical quantitative applications of HAXPES, an important electron transport parameter is the effective attenuation length (EAL) [1], that, opposing to the inelastic mean free path (IMFP), accounts not only for the effects of inelastic electron scattering in solids, in addition, it includes the effects of elastic electron scattering as well. The general definition of EAL is [1,2]: *"The EAL is a parameter which, when introduced in place of the IMFP into an expression derived from the common AES or XPS formalism (in which elastic-electron scattering is neglected) for a given quantitative application, will correct this expression for elastic-scattering effects."* This definition leads to different expressions describing EAL for different quantitative applications [2]. Analysis of thin overlayers (e.g. the measurement of the thickness of overlayer films deposited on a substrate) using AES and XPS is such a typical application, where in many cases the signal intensities from a substrate vary nearly exponentially as a function of layer thickness. The deviations from the exponential dependence are attributable to the effects of elastic electron scattering. For a detected photo-or Auger electron emitted from a surface layer, the probability that the electron, leaving the surface in a specified state and direction, originated from a specified depth (measured along the surface normal from the surface inward the material) is described by the emission depth distribution function (DDF) [3]. When the DDF can be approximated by an exponential function over a specified range of depths, then the DDF - plotted on a logarithmic scale as a function of the depth (on a linear scale) - can be fitted to a straight line. The negative reciprocal slope of the logarithm of the DDF at a specified depth is, by definition, the average emission function decay length (EFDL) [3]. Therefore the EAL corresponds to the EFDL when the DDF is sufficiently close to exponential for a given application [4]. It should be noted, that besides the overlayer thickness, in general the EAL depends on the scattering geometry, especially on the electron emission angle, and in the case of photoelectrons, on the instrumental configuration and asymmetry parameters of the respective angular distributions. In practical applications of AES and XPS the concept of the "practical" EAL is proposed to be used [1] even in the

case of appreciable deviation of the DDF from an exponential function of the overlayer thickness. For the purpose of measurements of thicknesses of overlayer films, the practical EAL (denoted by L) is given by the following formula [1,5] :

$$L = \frac{1}{\cos\alpha}\frac{t}{\ln I_S^0 - \ln I_S} = \\ = \frac{1}{\cos\alpha}\frac{t}{\ln\int_0^\infty \Phi(z,\alpha)dz - \ln\int_t^\infty \Phi(z,\alpha)dz} \quad (1)$$

where α is the angle of electron emission with respect to the surface normal, t is the thickness of the overlayer film, z the depth measured from the surface inward the material, I_S^0 the detected peak intensity of the pure substrate, I_S the substrate peak intensity detected in the presence of the overlayer and $\Phi(z,\alpha)$ is the DDF. In many cases, L is only a relatively weak function of α, up to an emission angle of 60º [2] and it depends only slightly on the overlayer thickness in a large thickness range [5] (for emission angles larger than 60º, L usually depends strongly on the emission angle and on the maximum overlayer thickness [2]). On the basis of Eq. (1), L can be derived from measured peak intensities in the case of XPS or AES analysis of overlayer – substrate systems with known (e.g. from independent experiments) overlayer thicknesses or from calculations of the DDF using analytical expressions [6] or the Monte Carlo simulation method [5]. For practical use, two simple empirical formulae have been proposed [1,7] for estimating R, the ratio L/λ, where λ denotes the IMFP. The formula proposed by Seah and Gilmore [7], derived from EAL values obtained from Monte Carlo simulations [8] in the case of photoelectrons excited from 27 elemental solids (α = 45º) is :

$$R_{SG} = 0.979\left[1 - \omega\left(0.955 - 0.0777\ln Z\right)\right] \quad (2)$$

where $\omega = \lambda/(\lambda + \lambda_t)$ is the single-scattering albedo and Z the atomic number. λ_t denotes the transport mean free path of the electrons in the material, defined as $\lambda_t = 1/n\sigma_t$, where n is the atomic density in atoms per unit volume and σ_t is the transport cross section. σ_t can be calculated from the following equation :

$$\sigma_t = 2\pi\int_0^\pi (1-\cos\theta)\frac{d\sigma}{d\Omega}\sin\theta d\theta \quad (3)$$

where $d\sigma/d\Omega$ is the differential cross section for elastic electron scattering and θ the polar angle. The other similar empirical formula proposed (for α<60º) by Powell and Jablonski [1] based on their calculations using the kinetic Boltzmann equation within transport approximation is:

$$R_{PJ} = 1 - A\omega \quad (4)$$

The parameter A depends slightly on α and (in the case of XPS) on the angle between the direction of the exciting X-ray beam and the emitted photoelectrons, a recommended value for A is 0.7 [1]. It should be noted that these simple formulae were derived originally for electron energies below 2000 eV and the validity of their extrapolation for higher energies has not been proven yet. There is a NIST database of EAL values calculated using analytical expressions derived from solution of the kinetic Boltzmann equation within the transport approximation, however, it provides EALs for electron energies only up to 2000 eV [9].

In this report a comparison of data obtained by using formulae (2) and (4) for deriving R values for electrons in the energy range 0.5 – 15 keV, and those available from experiments, are presented in the case of elemental solids Si, Ni, Cu, Ge, Ag, W and Au. In the case of Ge the data are compared with EAL/IMFP values obtained from Monte Carlo simulations [10] and in the electron energy range below 2 keV, (for selected energies and solids) with EAL/IMFP (TPP-2M) values from the NIST database [9].

2. Results and discussion

Values for λ_t were calculated for electron energies 0.5 keV, 1.5 keV, 3 keV, 6 keV, 10 keV and 15 keV in the case of the elemental solids Si, Ni, Cu, Ge, Ag, W and Au, using the transport cross section values taken from the NIST Electron Elastic-Scattering Cross-Section Database [11]. The single-scattering albedo, ω was derived as a function of the electron energy by using these transport mean fee path data and the IMFPs obtained from the TPP-2M formula [12]. Very recently, the TPP-2M equation was estimated to have an average uncertainty of only 11% for electron energies up to 30 keV in the case of most of the elemental solids [13, 14]. For comparison with the calculated EAL values, the experimental EAL

data published recently by Sacchi et al. [15] (Cu, Ge, α = 0º) and Zemek et al. [16] (Ni, α = 0º) were used. The IMFPs used (practically the same values as obtainable using eq (7) and the constants in Table 10 of Ref. [17]) for estimating the experimental R values were taken from the respective publications [15, 16]. The calculated results are presented in Figs. 1-10.

In Fig. 1. the calculated values of the single-scattering albedo, ω are shown for the elemental solids Si, Ni, Cu, Ge, Ag, W and Au, as a function of the electron kinetic energy in the range of 0.5 keV-15 keV. Although the energy dependence of ω is similar for the different solids, indicating a very significant decrease at high energies (the change is near exponential), in the case of Si and Ge especially low ω values can be observed. A comparison of the respective R_{SG} values calculated using Eq. (2) for the seven elemental solids, as a function of the electron kinetic energy, is presented in Fig. 2., while Fig. 3. shows the corresponding R_{PJ} curves calculated from Eq. (4).

In the case of both kind of empirical estimations, at high electron energies the curves show saturation (near exponential change) and the EAL values approach the respective IMFP values, indicating the decreasing role of elastic electron scattering with increasing electron energy at high energies.

In Figs 4-10 the energy dependence of the calculated R_{SG} and the R_{PJ} values are compared for each particular elemental solids: Si (Fig. 4.); Ni (Fig. 5.); Cu (Fig. 6); Ge (Fig. 7.); Ag (Fig. 8.); W (Fig. 9.) and Au (Fig. 10.). In the case of Ni, Cu and Ge, the calculated R values are compared with the available experimental values [15, 16] as well. In addition, in the case of Ge, EAL/IMFP values calculated using the DDF from Monte Carlo simulations [10] and in the case of Si, Ni, Cu, Ge and Ag, EAL/IMFP (TPP-2M) values derived from the NIST database [9] are indicated as well in the respective Figures. It can be seen from the Figures that $R_{PJ} > R_{SG}$ in all cases, with a slight increase of the differences at very high energies. These differences are, however, very small: less, than ~ 2-3 %, except for W and Au where they are about 1%. There is a rather good agreement between the calculated and experimental values in the case of Ni and Cu (Figs 5, 6), while for Ge (Fig. 7.) the deviation between the calculations and experiment is about 13 %. In this case the results of the Monte Carlo simulation [10] confirm the tendency of the energy dependence and the MC data fall between the calculated and the experimental data (Fig. 7.) indicating that the simple formulae provide here a somewhat less accurate estimation. For Si, Ni, Cu, Ge and Ag, the R values derived by the simple formulae agree well with the respective data from the NIST database [9] (Figs 4-8).

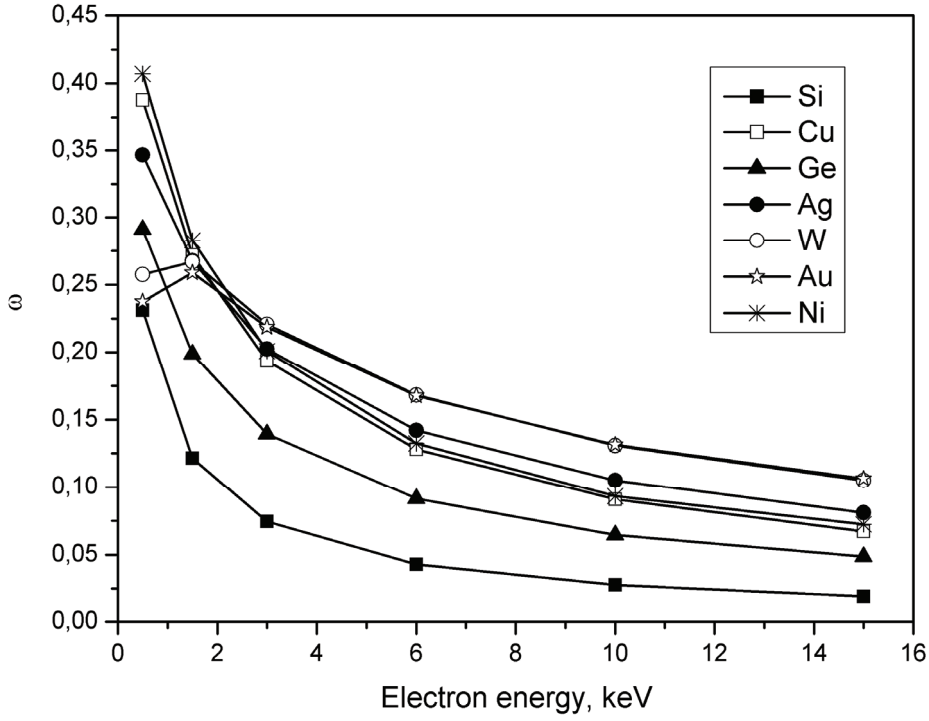

Fig. 1. Dependence of the single scattering albedo, ω, on the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solids Si, Ni, Cu, Ge, Ag, W and Au. Note that ω is calculated for selected energies, the solid lines between the calculated values in the curves are only for guiding the eyes.

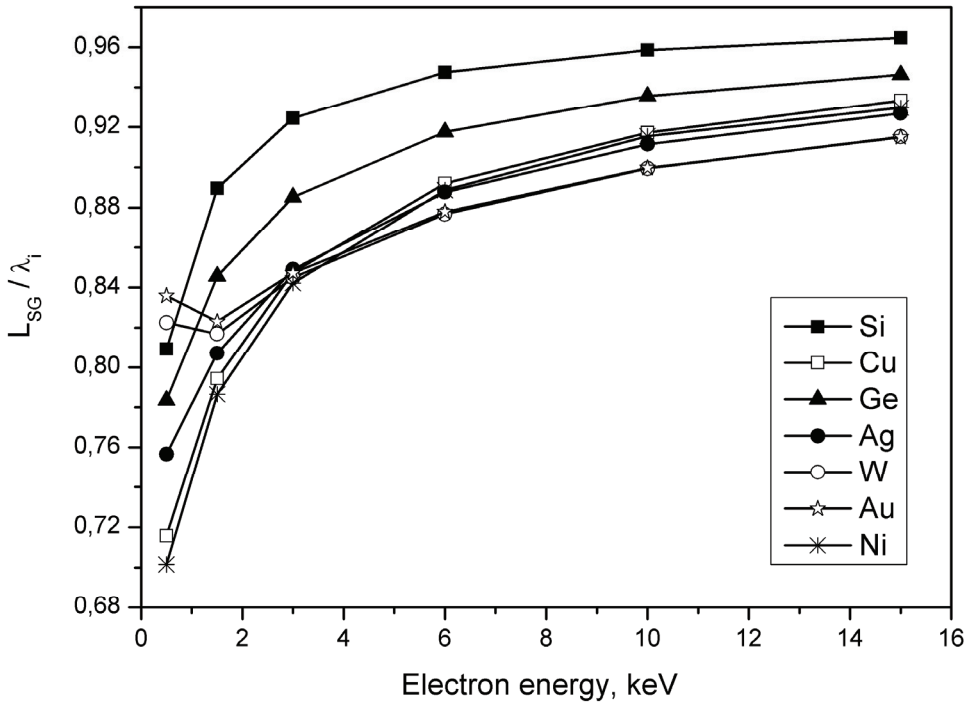

Fig. 2. Calculated values (using eq. (2)) of the ratio R_{SG}, as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solids Si, Ni, Cu, Ge, Ag, W and Au. Note that R_{SG} is calculated for selected energies, the solid lines between the calculated values in the curves are only for guiding the eyes.

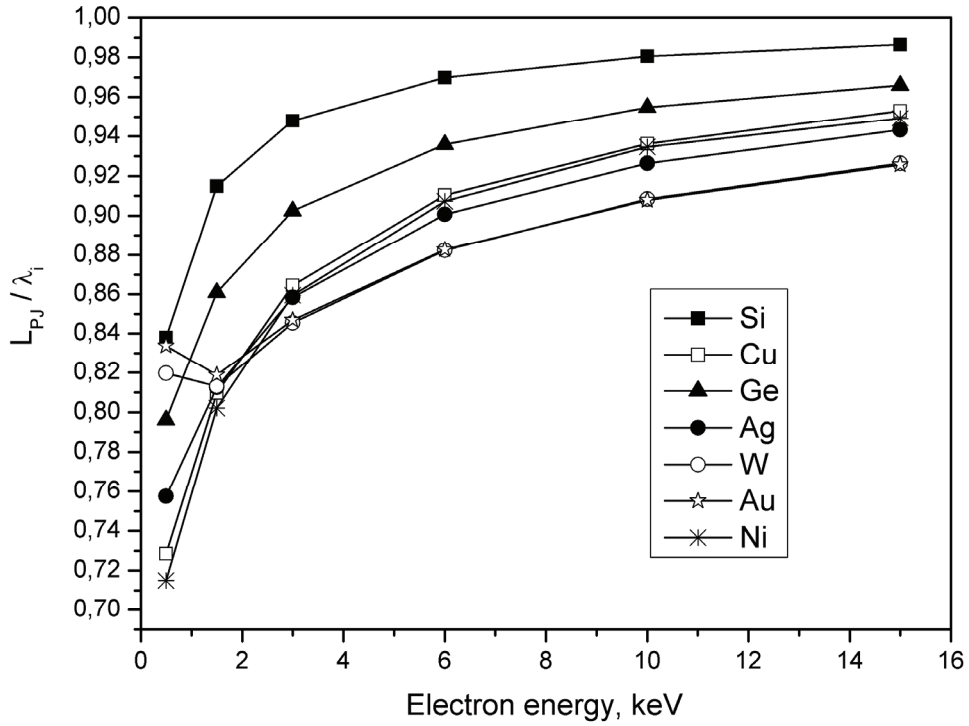

Fig. 3. Calculated values (using eq. (4)) of the ratio R_{PJ}, as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solids Si, Ni, Cu, Ge, Ag, W and Au. Note that R_{PJ} is calculated for selected energies, the solid lines between the calculated values in the curves are only for guiding the eyes.

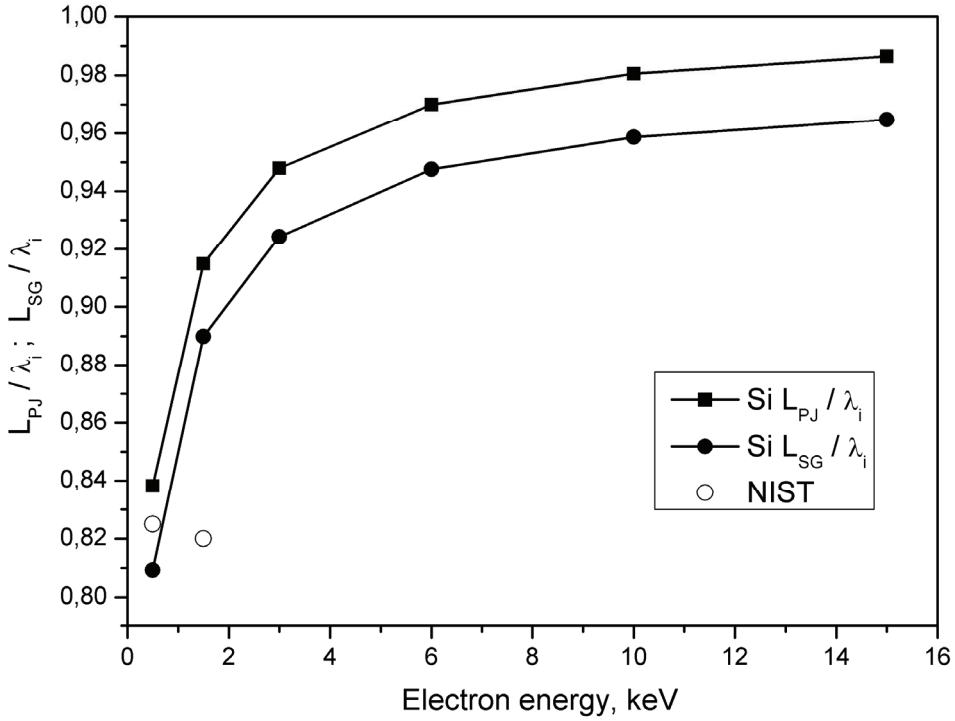

Fig. 4. Comparison of the calculated R_{SG} and R_{PJ} ratios, as well as an R value derived from data of the NIST EAL database [9] as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid Si. The solid lines are only for guiding the eyes.

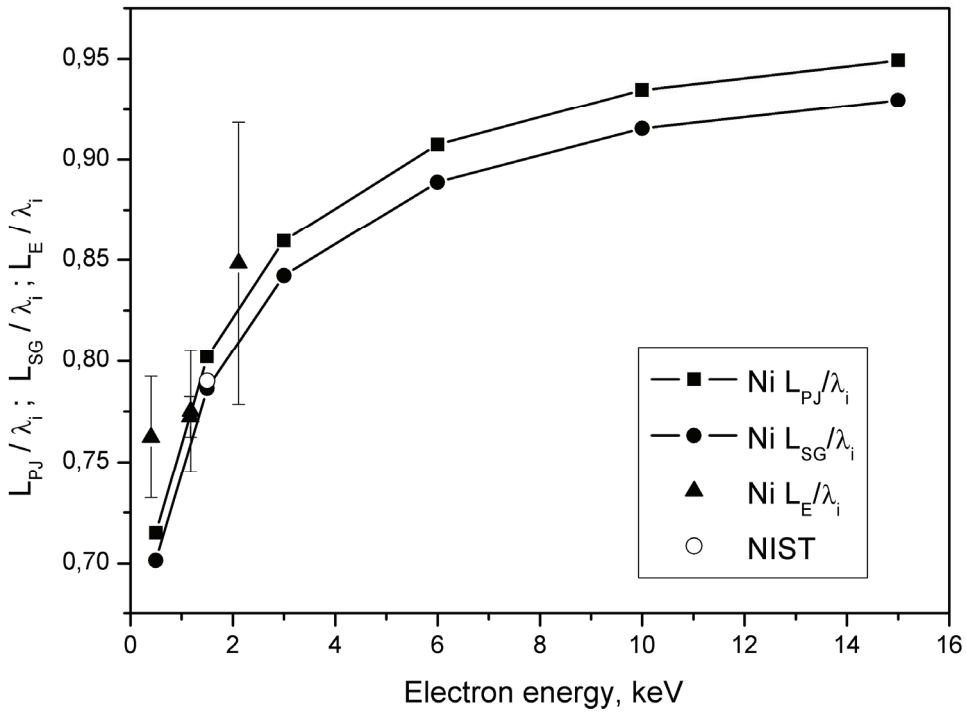

Fig. 5. Comparison of the calculated R_{SG} and R_{PJ} ratios, the available experimental R_E values [16] and an R value derived from data of the NIST EAL database [9] as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid Ni. The solid lines are only for guiding the eyes.

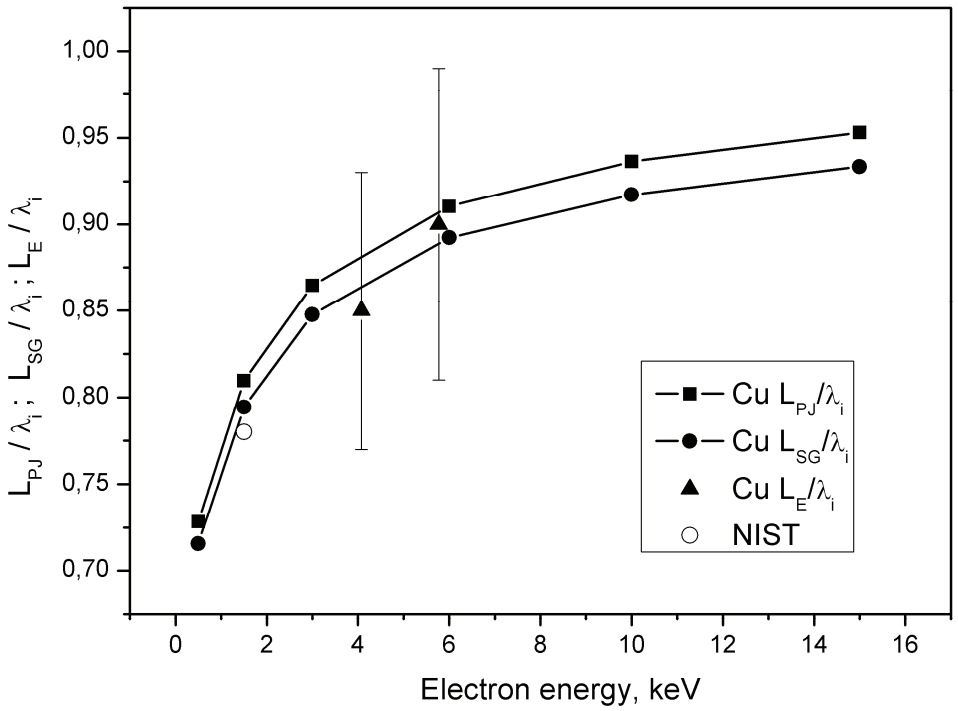

Fig. 6. Comparison of the calculated R_{SG} and R_{PJ} ratios, the available experimental R_E values [15] and an R value derived from data of the NIST EAL database [9] as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid Cu. The solid lines are only for guiding the eyes.

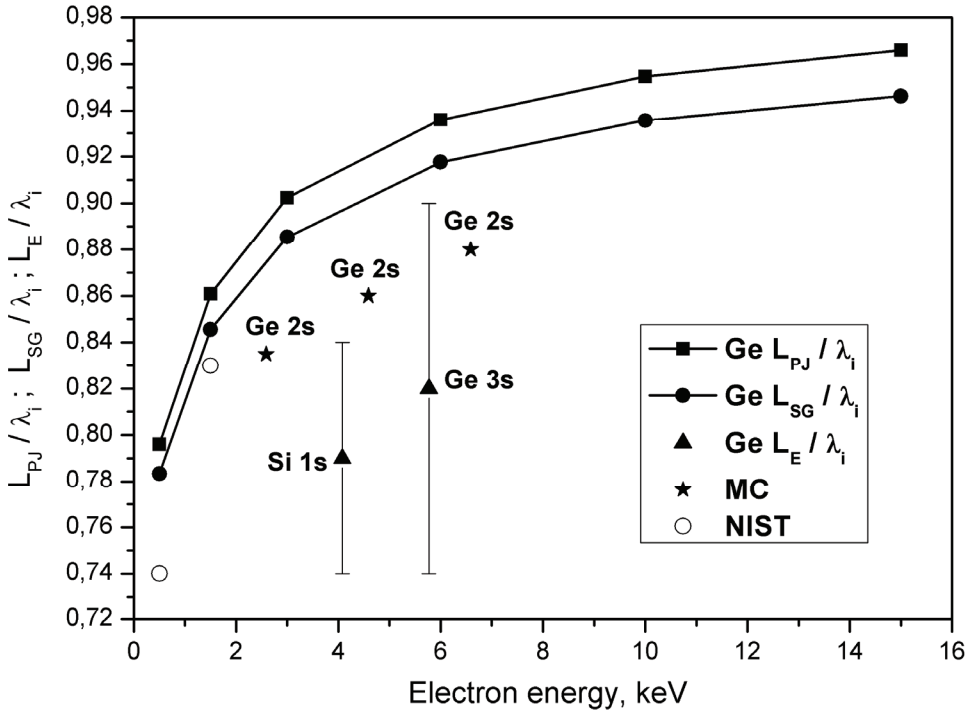

Fig. 7. Comparison of the calculated R_{SG} and R_{PJ} ratios, the available experimental R_E values [15] and the R values derived from data of the NIST EAL database [9] as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid Ge. The solid lines are only for guiding the eyes.

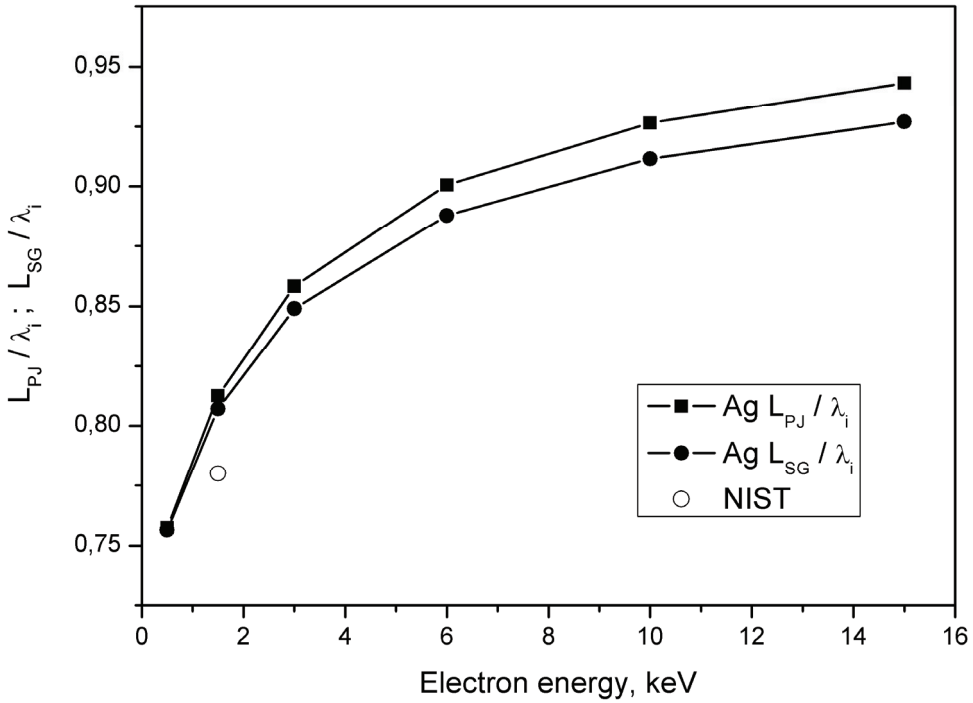

Fig. 8. Comparison of the calculated R_{SG} and R_{PJ} ratios and an R value derived from data of the NIST EAL database [9] as a function of the electron kinetic energy in the range of 0.5-15 keV, for the elemental solid Ag. The solid lines are only for guiding the eyes.

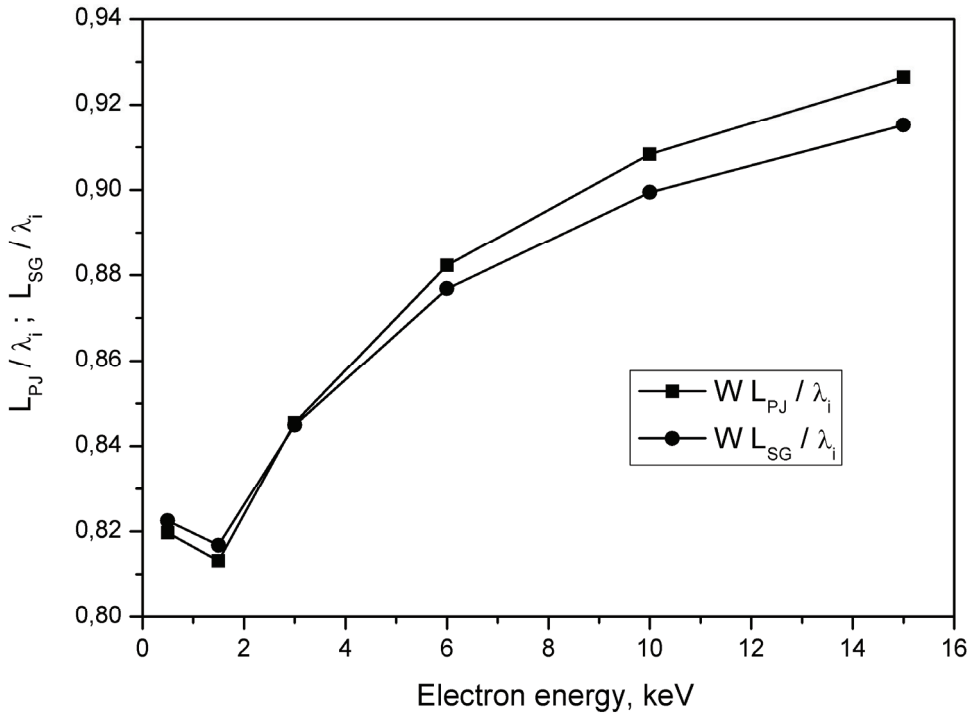

Fig. 9. Comparison of the calculated R_{SG} and R_{PJ} ratios, as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid W. The solid lines are only for guiding the eyes.

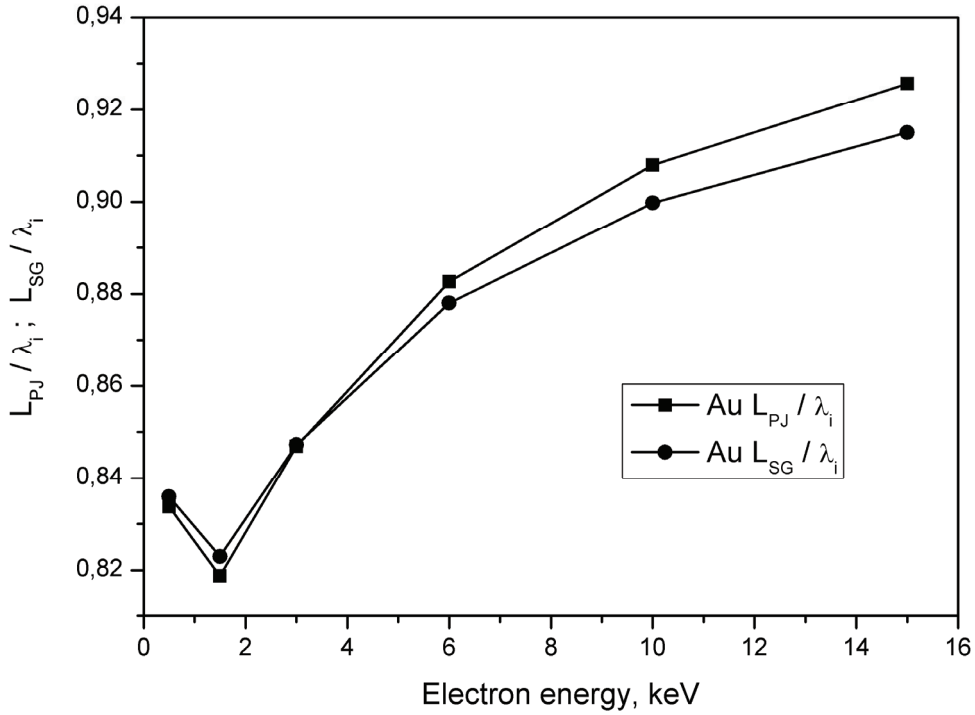

Fig. 10. Comparison of the calculated R_{SG} and R_{PJ} ratios, as a function of the electron kinetic energy, in the range of 0.5-15 keV, for the elemental solid Au. The solid lines are only for guiding the eyes.

3. Summary

A comparison of data obtained by using two different empirical formulae for predicting ratios of effective attenuation lengths to inelastic mean free paths for energetic (with energies up to 15 keV) electrons, as well as available experimental data and in addition results of Monte Carlo simulation (Ge) and ratios obtained from the NIST EAL database, is presented for the elemental solids Si, Ni, Cu, Ge, Ag, W and Au. The differences between the two formulae are in general smaller, than 2-3 % and about 1 % for W and Au, while the agreement with the available recent experimental data is very good in the case of Ni and Cu and is reasonable for Ge. In the case of Ge, the data from Monte Carlo simulation confirm the tendency of the energy dependence predicted by the formulae and provide a better agreement with the experimental data. A good agreement is observable between the formulae and the data calculated using the NIST EAL database in the case of selected elemental solids and electron energies in the range below 2000 eV. The results demonstrate the strongly decreasing effect of elastic electron scattering with increasing electron energy and provide an estimate of the accuracy expectable in the case of these simple approximations.

4. Acknowledgements

The support of the grants MTA-JSPS No. 97. and OTKA 67873 is gratefully acknowledged.

5. References

[1] C. J. Powell and A. Jablonski, *Surf. Interface Anal.* **33**, 211 (2002); A. Jablonski and C. J. Powell, *Surf. Sci. Rep.* **47**, 33 (2002).

[2] A. Jablonski and C. J. Powell, *J. Alloys and Compounds* **362**, 26 (2004).

[3] ISO 18115:2001 *Surface Chemical Analysis – Vocabulary*, ISO (Geneva, 2001).

[4] ASTM Standard E 673-98, *Annual Book of ASTM Standards* vol. 3.06, American Society for Testing and Materials, West Conshohocken, PA, 2001, p. 735.

[5] S. Tanuma, in: D. Briggs, J. T. Grant (Eds): *Surface Analysis by Auger and Photoelectron Spectroscopy*, IM Publications and Surface Spectra Ltd, Chichester, Manchester, 2003. p. 259.

[6] I. S. Tilinin, A. Jablonski, J. Zemek, and S. Hucek, *J. Electron Spectrosc. Relat. Phenom.* **87**, 127 (1997).

[7] M. P. Seah and I. S. Gilmore, *Surf. Interface Anal.* **31**, 835 (2001).

[8] P. J. Cumpson and M. P. Seah, *Surf. Interface Anal.* **23**, 430 (1997).

[9] C. J. Powell and A. Jablonski, *NIST Electron Effective-Attenuation-Length Database*. Version 1.0. Standard Reference Data Program Database 64, National Institute of Standards and Technology, Gaithersburg, 2001 (http://www.nist.gov/srd/nist64.htm)

[10] M. Novák, *PhD Theses*, University of Debrecen, Debrecen, 2008.

[11] A. Jablonski, F. Salvat, and C. J. Powell, *NIST Electron Elastic-Scattering Cross-Section Database*. Version 3.1. Standard Reference Data Program Database 64, National Institute of Standards and Technology, Gaithersburg, 2003 (http://www.nist.gov/srd/nist64.htm)

[12] S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.*, **21**, 165 (1993).

[13] S. Tanuma, C. J. Powell, and D. R. Penn, *Abstracts of the 4*th *International Symposium on Practical Surface Analysis* (PSA-07, Kanazawa, November 25-28. 2007), p. O-32.

[14] S. Tanuma, *private communication*.

[15] M. Sacchi, F. Offi, P. Torelli, A. Fondacaro, C. Spezzani, M. Cautero, G. Cautero, S. Houtari, M. Grioni, R. Delaunay, M. Fabrizioli, Gy. Vankó, G. Monaco, G. Paolicelli, G. Stefani, and G. Panaccione, *Phys. Rev. B* **71**, 155117 (2005).

[16] J. Zemek, P. Jiricek, J. Houdkova, K. Olejnik, and A. Jablonski, *Surf. Interface Anal.* **39**, 916 (2007).

[17] C. J. Powell, and A. Jablonski, *J. Physical and Chemical Reference Data* **28**, 19 (1999).