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PROPOSED FORMULA FOR ELECTRON INELASTIC MEAN FREE PATHS BASED ON CALCULATIONS FOR 31 MATERIALS

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A new general formula is proposed for determining electron inelastic mean free paths (IMFP's) for 200–2000 eV electrons in solids. The new formula is based on separate IMFP calculations for 27 elements and 4 compounds using an algorithm due to Penn. This formula is believed useful for determining the IMFP dependence on electron energy for a given material and the material-dependence for a given energy. The new formula should also be a reasonable guide to electron attenuation lengths which have been difficult to determine with the needed accuracy.

Values for inelastic mean free paths (IMFP's) and attenuation lengths (AL's) of low-energy electrons in solids are important for quantitative surface analysis by Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). In addition, IMFP's and AL's determine the surface sensitivity of a number of electron spectroscopies used for surface characterization. The terms IMFP, AL, and escape depth are frequently used interchangeably, but each has a separate meaning [1,2]. The IMFP can be obtained from theory and certain types of experiments, while the AL is obtained from overlayer-film experiments and with use of a model in which the effects of elastic electron scattering are ignored. The escape depth is the product of the AL and the cosine of the angle defined by the analyzer direction and the surface normal in an AES or XPS experiment. It has been estimated that the IMFP may exceed the AL by about 15%, the difference being greatest for high atomic numbers and low electron energies [3].

We have performed new IMFP calculations for 27 elements and 4 compounds using an algorithm due to Penn [4]. The calculated IMFP's were found to be well described by the Bethe equation for inelastic electron scattering over the energy range 200–2000 eV [5]. We then found empirically that the two parameters in the Bethe equation for each material could be simply related to several other material constants. These relationships have then led us to a

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general IMFP formula which we propose for use with other materials. Specifically, the new formula is considered useful for determining the IMFP dependence on electron energy for a particular material and the IMFP dependence on material for a given energy. Since AL measurements of the needed accuracy are difficult [2,6], the new formula is suggested as a reasonable but more approximate guide to AL's. The new formula is compared to the IMFP formula of Szajman et al. [7] and the AL formulas of Seah and Dench [8].

The IMFP is given by [4]:

$$\lambda_i = E_k/kM_I, \tag{1}$$

where E_k is the electron energy, k its momentum, and

$$M_I = \frac{e^2}{2\pi^2}\int \frac{d^3q}{q^2}\,\mathrm{Im}\left[\frac{-1}{\epsilon(q,\ E_k - E_{k-q})}\right]. \tag{2}$$

In eq. (2), $\epsilon(q, \omega)$ is the complex dielectric constant which depends on momentum transfer q and energy loss $\hbar\omega = E_k - E_{k-q}$ in an inelastic scattering event. The complex dielectric constant is not known for most materials and so we approximate it in such a way that it satisfies the following three conditions.

(a) $\epsilon(0, \omega)$ is identical to the experimentally determined optical dielectric function $\epsilon(\omega)$.

(b) The momentum-dependence of $\epsilon(q, \omega)$ is determined by the statistical approximation developed by Lindhard and coworkers [9] and by Tung et al. [10].

(c) The quantity $\mathrm{Im}[-1/\epsilon(q, \omega)]$ in eq. (2) satisfies the oscillator-strength sum rule and the perfect-screening sum rule [11].

We use the approximation [4]:

$$\mathrm{Im}\left[\frac{1}{\epsilon(q,\ \omega)}\right] = \int_0^\infty d\omega_p G(\omega_p)\,\mathrm{Im}\left[\frac{1}{\epsilon_L(q,\ \omega;\ \omega_p)}\right], \tag{3a}$$

where

$$G(\omega) = (2/\pi\omega)\,\mathrm{Im}[-1/\epsilon(\omega)], \tag{3b}$$

and $\epsilon_L(q, \omega; \omega_p)$ is the Lindhard dielectric function for an electron gas with a density of electrons corresponding to the plasmon energy $\hbar\omega_p$. IMFP's can thus be calculated using experimental optical data to describe the dependence of the inelastic scattering probability on energy loss [eq. (3b)] and the Lindhard dielectric function to describe the dependence of the scattering probability on momentum transfer. This hybrid approach takes advantage of available optical data (thus avoiding any assumption of the relative strengths of valence-electron and core-electron excitations) [12]; theory is needed for the q-dependence of the scattering probability since experimental information is inadequate.

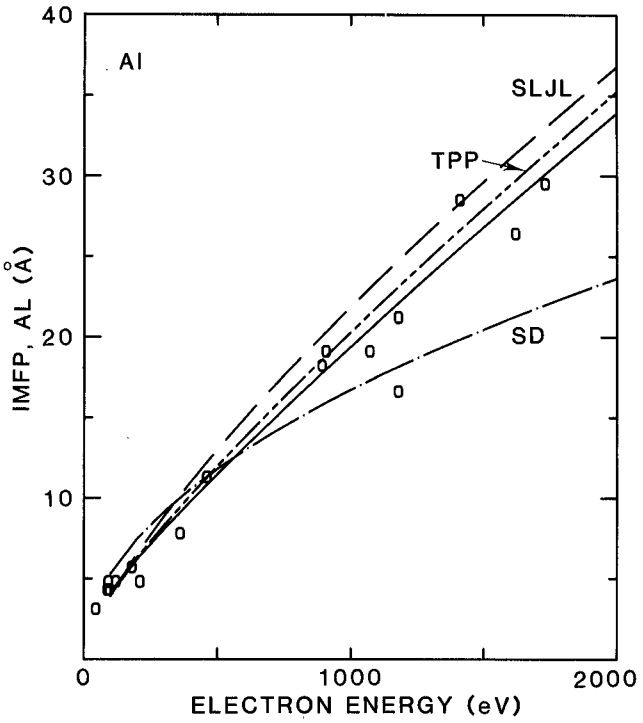

Fig. 1. Comparison of IMFP and AL results for aluminum. The solid line shows IMFP values calculated from eqs. (1)–(3); the curve denoted TPP is the result of the general formula [eqs. (4)–(7)] using parameter values for Al; the curve designated SLJL is the IMFP result of Szajman et al. [7], eq. (9); and the curve denoted SD is the AL result of Seah and Dench [8], eq. (10). The open circles are the AL values of Tracy [19].

IMFP calculations have been made for 27 elements (C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi) and 4 compounds (LiF, Al_2O_3, SiO_2, and ZnS); the details of these results will be presented elsewhere [13]. These materials were selected as optical data over the typical photon energy range 1–2000 eV were conveniently available [14–16], although interpolations based on atomic photoabsorption calculations [17] were needed to fill gaps in the data for over half of the materials.

The IMFP calculations were made for electron energies between 100 and 2000 eV. The solid lines in figs. 1–4 show the results of these calculations for four prototypical elements: aluminum, copper, silver, and gold. It has been found earlier that the Bethe equation for inelastic-electron-scattering cross sections provides a good empirical fit to measured AL [18] and calculated IMFP [12] values over an extended energy range. We have similarly found that

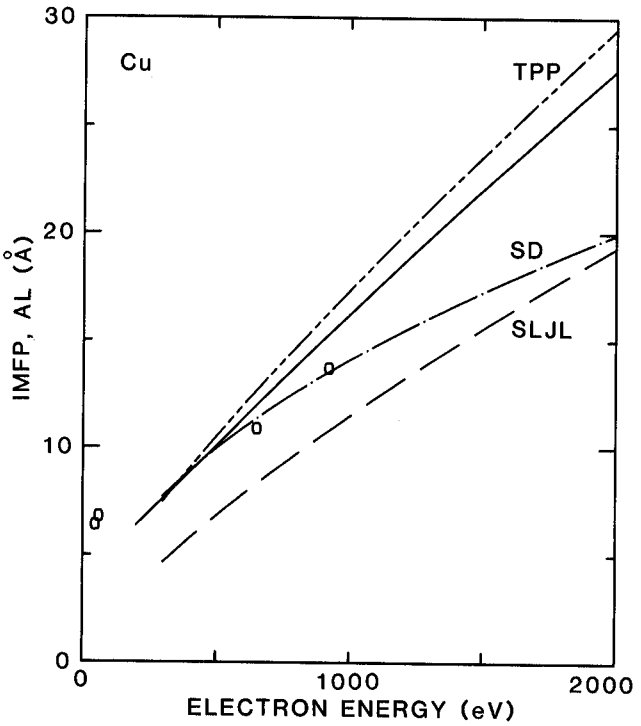

Fig. 2. Comparison of IMFP and AL results for copper; see caption to fig. 1. The open circles are the AL values of Seah [20].

the Bethe equation provided a fit within 3% of the IMFP's calculated for our 31 materials over the 300–2000 eV energy range; at 200 eV, the deviation in the fit could be up to 8%.

It is convenient to write the Bethe equation in the form:

$$\lambda_i = E/\left[E_p^2 \beta \ln(\gamma E)\right] \text{ Å}, \tag{4}$$

where E is the electron energy (in eV),

$$E_p = 28.8(\rho N_v/A)^{1/2} \text{ eV}. \tag{5}$$

N_v is the total number of valence electrons per atom or molecule, the density ρ has been expressed in g cm^{-3}, and A is the atomic or molecular weight. For a metal such as copper, N_v is computed from the number of 4s and 3d electrons, in this case 11. Values of the two parameters β and γ in eq. (4) have been determined from the fits of the calculated IMFP values for each material to the Bethe equation; these parameters obviously determine the magnitude and energy dependence of λ_i.

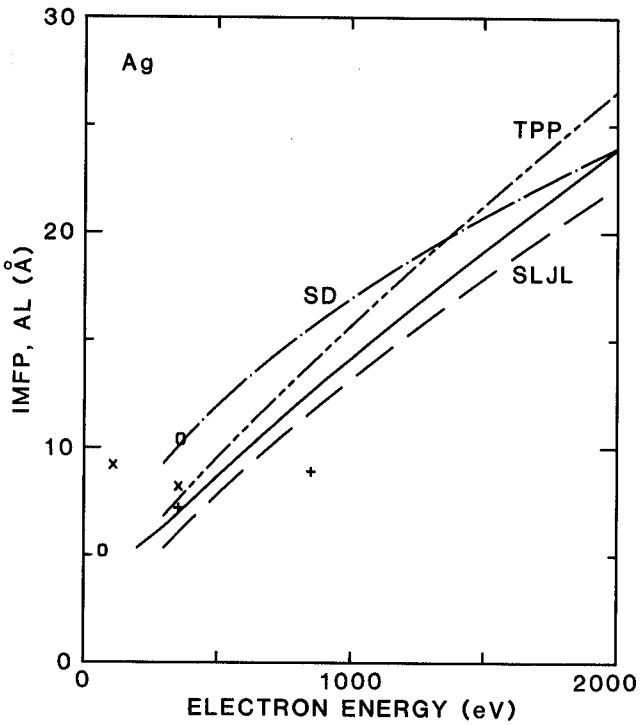

Fig. 3. Comparison of IMFP and AL results for silver; see caption to fig. 1. The points show AL values: (○) Palmberg and Rhodin [21]; (+) Jackson et al. [22]; and (×) Seah [23].

We have examined whether the parameters β and γ could be related to common material constants such as ρ, N_v, and A. We have found empirically the following relations:

$$\beta = -2.52 \times 10^{-2} + 1.05/\left(E_p^2 + E_g^2\right)^{1/2} + 8.10 \times 10^{-4}\rho, \tag{6}$$

and

$$\gamma = 0.151\rho^{-0.49}, \tag{7}$$

where E_g is the band-gap energy for non-conductors.

The curves labelled TPP in figs. 1–4 show plots of eqs. (4)–(7) for Al, Cu, Ag, and Au. These curves agree reasonably well with the corresponding solid lines, the specific IMFP results of eqs. (1)–(3). For the 31 materials considered here, the rms difference between the individual IMFP calculated values and the results from eqs. (4)–(7) was about 12%; the largest differences were for C (32%), ZnS (31%), Ir (27%), SiO_2 (26%), Re (21%), Si (19%), Pd (18%), Nb (17%), Bi (16%), Ta (16%), and Ni (16%). These differences were not consid-

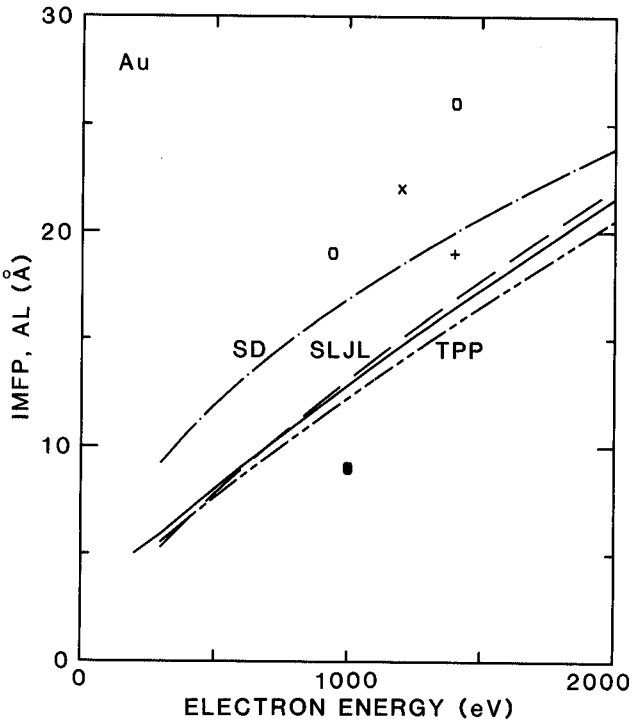

Fig. 4. Comparison of IMFP and AL results for gold; see caption to fig. 1. The points show experimental AL values: (○) Klasson et al. [24]; (●) Brunner and Zogg [25]; (+) Henke [26]; and (×) Baer et al. [27].

ered excessive on account of uncertainties of the optical data, the empirical basis of eqs. (6) and (7), and the small number of non-conductors in the data set.

Figs. 1–4 also show plots of two other formulas. Szajman et al. [7] have obtained a simple IMFP formula for $E > 300$ eV:

$$\lambda_i \approx 1.8\bar{E}E^{3/4}/E_p^2 \text{ Å}, \tag{8}$$

where $\bar{E}$ is the centroid of the energy-loss function $\mathrm{Im}[-1/\epsilon(\omega)]$. For nonconductors, $\bar{E} = E_p + E_g$. For free-electron-like solids, $\bar{E} \approx E_p$ and eq. (8) becomes

$$\lambda_i \approx 1.8E^{3/4}/E_p. \tag{9}$$

The curves denoted SLJL in figs. 1–4 are plots of eq. (8).

Seah and Dench [8] have made an analysis of AL measurements and proposed the following relations for the AL, λ_a: for elements,

$$\lambda_a = 538aE^{-2} + 0.41a^{3/2}E^{1/2} \text{ nm}, \tag{10a}$$

and for inorganic compounds,

$$\lambda_a = 2170aE^{-2} + 0.72a^{3/2}E^{1/2} \text{ nm}. \quad (10b)$$

In eq. (10), a is the average monolayer thickness (in nm) defined by

$$a^3 = 10^{27}A/\rho n N_a,$$

where n is the number of atoms in the molecule and N_a is Avogadro's number. The lines labelled SD in figs. 1–4 are plots of eq. (10).

Figs. 1–4 contain AL values for Al [19], Cu [20], Ag [21–23], and Au [24–27]. While comparisons of the formulas and AL values in figs. 1–4 are useful, it is difficult to determine whether a particular result is "correct" on account of likely systematic errors [2]. Nevertheless, there is good agreement in the Al data and the several curves for Al in fig. 1 except for the Seah and Dench formula at energies above 500 eV. There is a greater spread in the curves for Cu, Ag, and Au in figs. 2–4 and among the AL data from different laboratories.

We now comment on the accuracy and potential utility of eqs. (4)–(7) as a general means of calculating IMFP's for other materials. Eqs. (1) and (2) are based on the assumption that the Born approximation is valid and on the neglect of vertex corrections, self-consistency, exchange, and correlation [4]. For $E > 200$ eV, these effects are estimated to introduce errors of order 10% for free-electron-like solids such as Al; for other solids, the errors could be larger. A second source of uncertainty arises from the approximation of eq. (3). Reasonable IMFP values are obtained with $\text{Im}[-1/\epsilon(0, \omega)]$ values from experimental optical data since inelastic electron scattering occurs predominantly in the forward direction where the momentum transfer is relatively small. The q-dependence of $\text{Im}[-1/\epsilon(q, \omega)]$, however, does affect the magnitude of the IMFP's but it is very difficult to estimate the errors associated with our use of eq. (3). The present algorithm is expected to be more accurate at the higher energies considered here [4].

We believe that the uncertainties arising from the approximations just mentioned are likely to be systematic; that is, the calculated IMFP values will be systematically high or low compared to the "true" values. Nonetheless, the algorithm is considered very useful for determining with good accuracy the material dependence of IMFP values at particular electron energies and the energy dependences of IMFP data for particular materials. Fig. 5 is a plot of the IMFP's computed here for the 31 materials and shows clearly the range of IMFP values (here a factor of about 2.5) at any energy. A larger IMFP range would be found if materials of lower density (e.g., alkali metals) had been included. The material-dependence of the parameter γ, eqs. (4) and (7), overcomes a deficiency of the Szajman et al. formula [eq. (8)] and the Seah and Dench formula [eq. (10)] in that each shows an energy dependence that does not depend on material, a result in conflict with experiment [18,28].

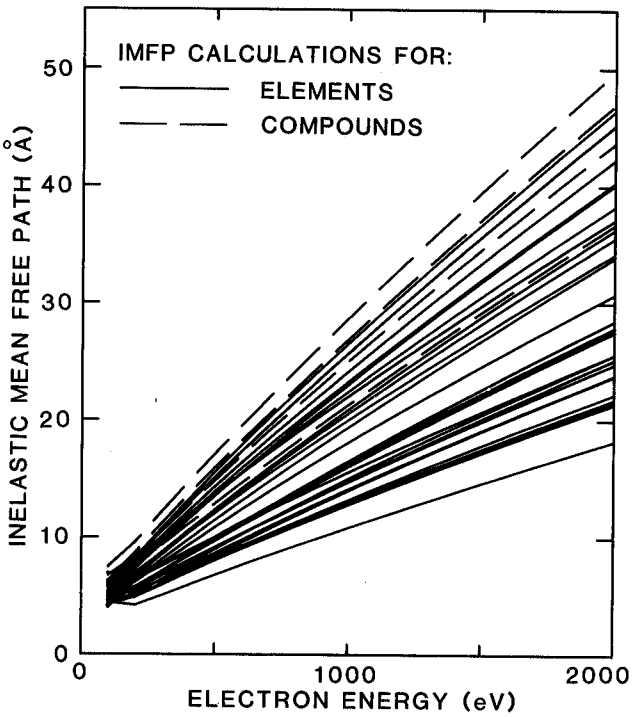

Fig. 5. Plots of IMFP's versus electron energy for elements (solid lines) and compounds (dashed lines).

Eqs. (4)–(7) have been developed based on our IMFP calculations for a limited number of materials. We believe it reasonable that these formulas should be applicable to other materials although it is possible that they may be revised as further IMFP calculations are made.

As noted earlier, the differences between AL and IMFP values for a particular material could be about 15% [3]. Such differences are less than the likely errors in AL measurements and many IMFP calculations [2]. We therefore suggest that eqs. (4)–(7) could be a useful guide to AL values although additional uncertainties due to elastic electron scattering would be expected for high atomic numbers and low electron energies. We emphasize that eqs. (4)–(7) were evaluated and found useful for the electron energy range 200–2000 eV; further work is required to extend the formula to both lower and higher energies.

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