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DEPENDENCE OF INELASTIC ELECTRON MEAN FREE PATHS ON ELECTRON ENERGY AND MATERIAL

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The inelastic mean free paths (IMFPs) of low-energy electrons in solids are important for defining the surface sensitivities of electron spectroscopies for surface characterization. We have developed a new general formula for predicting IMFPs over the electron energy range 200-2000 eV. The new formula is based on separate IMFP calculations for 27 elements and 4 compounds. The IMFPs for each material were fitted to the Bethe equation for inelastic electron scattering, and the two Bethe parameters were related to simple material parameters (density, atomic or molecular weight, number of valence electrons, and band-gap energy for nonconductors). The resulting general formula permits convenient determination of the IMFP dependence on electron energy for a given material and the material dependence for a given energy.

The IMFP is inversely related to the total cross section for inelastic electron scattering and the atomic density; it is frequently obtained from theory and certain types of experiments. A related quantity, the electron attenuation length (AL), is obtained from overlayer-film experiments and with use of a model in which the effects of elastic electron scattering are ignored.[1] The same simple model is also currently used in quantitative surface analyses by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS); it is important then to know the dependence of the AL on electron energy and material. Depending on the analytical approach employed, the AL dependence on energy is required when AES or XPS intensities of different elements in the same specimen material are compared. Alternatively, the AL dependence on material is required when it is desired to "correct" elemental sensitivity factors for the particular matrix or compound being analyzed. It has been estimated that the IMFP may exceed the AL by about 15%; the difference is greatest for high atomic numbers and low electron energies.[2]

Several formulas have been proposed for IMFPs and ALs.[1] Although these formulas are convenient and useful guides, they have shortcomings. Seah and Dench[4] proposed an AL formula based on AL measurements that could have systematic errors as high as 50-100%.[1] Szajman et al.[5] have proposed an IMFP formula based on a single-mode (bulk plasmon excitation) model that is a good approximation for free-electron-like solids but less so for other materials. Both formulas show a material-independent energy dependence (that is different in each formula) although subsequent work has demonstrated that the energy dependence is, in general, related to the material.

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IMFP Calculations

Penn[3] has developed a new algorithm for calculating IMFPs of low-energy electrons in solids. IMFPs are calculated from experimental optical data (to describe the dependence of the inelastic scattering probability on energy loss) 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 about the specific modes and relative probabilities of inelastic scattering). Theory is needed for describing the dependence of scattering probability on momentum transfer since experimental information is inadequate.

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); details of the calculations will be presented elsewhere.[6] These materials were selected because optical data over the typical photon energy range 1-2000 eV were available even though interpolations based on atomic photoabsorption calculations were needed for over half of the materials.

The IMFP calculations were made for electron energies between 100 and 2000 eV; the solid lines in Figs. 1-2 show our results for aluminum and gold. It had been found earlier that the Bethe equation for inelastic-electron-scattering cross sections in matter provided a good empirical fit to measured AL and calculated IMFP values over an extended energy range.[7] We have similarly found that the Bethe equation provided a fit within 3% of the IMFPs calculated for our 31 materials over the 300-2000eV energy range; at 200 eV, the deviation in the fit could be up to 8%. The solid lines in Figs. 1 and 2 show the results of these fits for aluminum and gold.

It is convenient to write the Bethe equation in the form

$$\lambda_i = E/[E_p^2 \beta \ln(\gamma E)] \quad \text{Å} \qquad (1)$$

where λ_i is the IMFP, E the electron energy (in eV),

$$E_p = 28.8(\rho N_V/A)^{1/2} \quad \text{eV} \qquad (2)$$

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. (1) have been determined from the fits of the calculated IMFP values for each material to the Bethe equation. We have found that these parameters could be related empirically to simple material constants. Least scatter was found with the following equations:

$$\beta = -2.52 \times 10^{-2} + [1.05/(E_p^2 + E_g^2)^{1/2}] + 8.10 \times 10^{-4} \rho \quad (3)$$

and

$$\gamma = 0.151\rho^{-0.49} \quad (4)$$

where E_g is the band-gap energy for nonconductors.

Discussion

The curves labeled TPP in Figs. 1 and 2 show plots of Eqs. (1)-(4) for Al and Au and agree reasonably well with the corresponding solid lines, results of the individual IMFP calculations. The average rms difference between the individual IMFP calculated values and the results of Eqs. (1)-(4) for the 31 materials 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 considered excessive on account of uncertainties of the optical data, the empirical basis of Eqs. (3) and (4), and the small number of nonconductors in the analysis.

Figures 1 and 2 also show results of the IMFP formula due to Szajamn et al.[5] (curves denoted SLJL) and the AL formula of Seah and Dench[4] (curves labeled SD). These figures also contain AL values reported for Al[8] and Au.[9-12]

It is difficult from comparisons of the type shown in Figs. 1-2 to determine whether particular results are "correct" on account of uncertainties in the AL measurements and approximations in the calculations.[1] Nevertheless, there is good agreement in the AL data for aluminum in Fig. 1 and the several curves except for the Seah and Dench result at energies above 500 eV. However, Fig. 2 for gold has a much larger spread in the IMFP calculations and the AL measurements.

It is difficult to estimate the uncertainties of our IMFP values, but they are believed to be in the vicinity of 10-20%.[6] These uncertainties are likely to be systematic; that is, the calculated IMFP values are systematically high or low compared to the "true" values. However, our algorithm is very useful for determining with good accuracy the material dependences of IMFP values at particular electron energies and the energy dependence of IMFP data for particular materials. Equations (3)-(4) were developed for a limited number of materials, but it is reasonable to believe that they should be applicable to other materials although it is possible that they may be revised as further IMFP calculations are made.

Since the differences between IMFP and AL values for a particular material could be about 15%,[2] a figure at least comparable with likely errors in AL measurements or IMFP calculations, Eqs. (1)-(4) could also be a useful guide to AL values. We emphasize that Eqs. (1)-(4) were developed only for the 200-2000eV energy range; further work is required to extend the formula to both higher and lower energies.

Conclusions

We have developed a general IMFP formula based on separate IMFP calculations for 27 elements and 4 compounds. The new formula provides a convenient means for determining the IMFP dependence on electron energy for a particular material and the IMFP dependence on matrix or material for a given energy. The new formula should also be a useful but more approximate guide for estimating attenuation lengths.

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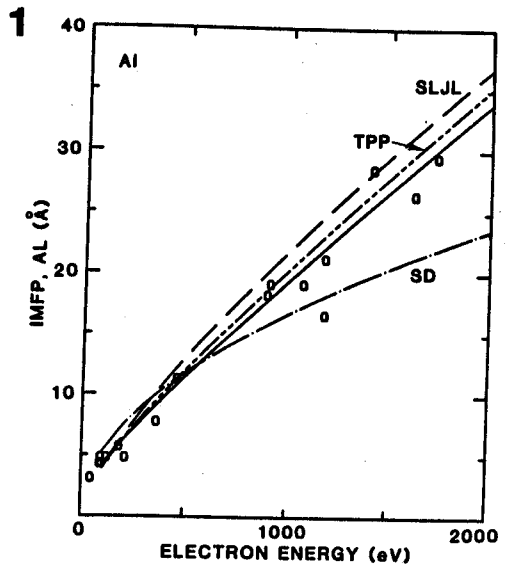

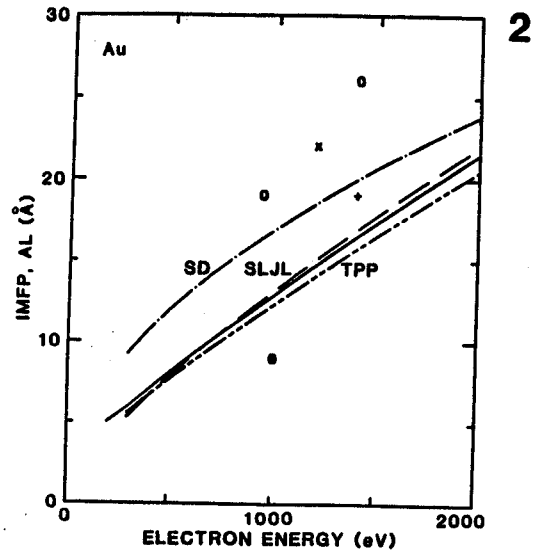

FIG. 1.--Comparison of IMFP and AL results for aluminum. Solid line shows IMFP values calculated with Penn algorithm[3] and experimental optical data;[6] curve TPP is result of general formula [Eqs. (1)-(4)] using parameter values for Al; curve SLJL is IMFP formula of Szajamn et al.;[5] and curve SD is AL formula of Seah and Dench.[4] Open circles are the AL values of Tracy.[8]

FIG. 2.--Comparison of IMFP and AL results for gold, see caption to Fig. 1. Points show experimental AL values: ○ Klasson et al.;[9] ● Brunner and Zogg;[10] + Henke;[14] and × Baer et al.[12]