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Journal of Electron Spectroscopy and Related Phenomena, 62 (1993) 95–109
0368-2048/93/$06.00 © 1993 – Elsevier Science Publishers B.V., Amsterdam

Use of sum rules on the energy-loss function for the evaluation of experimental optical data[1]

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(First received 27 October 1992; in final form 11 November 1992)

Abstract

We present an evaluation of optical data for Al, Si, Ti, Mo, W, and Ir based on two sum rules for the energy-loss function, the familiar f-sum rule and another sum rule based on a limiting form of the Kramers–Kronig integral. These sum rules were used to evaluate sets of energy-loss function data constructed first from tabulated optical data which have been supplemented by interpolations in the 40–100 eV range for Ti, Mo, W, and Ir. A second set of energy-loss function data was constructed for each material by substituting energy-loss function values calculated from the optical data of Windt et al. (Appl. Opt., 27 (1988) 246, 279) in the 10–525 eV range. The deviations in the results of the sum-rule tests with the second set of optical data were about twice those found for the first set. We conclude that the first set of optical data is preferred over the second set.

Introduction

We have recently reported results of calculations of electron inelastic mean free paths (IMFPs) for a group of 27 elements and for a group of 15 inorganic compounds over the electron energy range 50–2000 eV [1–4]. These calculations are based on an algorithm developed by Penn [5] and make use of experimental optical data for photon energies typically between 1 and 10^4 eV.

For over half of the materials we examined, there were gaps in the tabulated optical data [6–10], often between 40 and 100 eV. In such cases, we made interpolations based on atomic photoabsorption calculations [11]. An assessment of the accuracy of this procedure and of the overall accuracy of

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[1] Dedicated to the memory of John C. Fuggle, who was a friend and colleague of one of the authors (C.J.P.) over many years.

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the optical data was made with the use of two sum rules [1–4] (to be described below).

An extensive series of new optical measurements for 21 materials over the photon energy range 10–525 eV has been published by Windt et al. [12,13]. These authors measured reflectance at six angles of incidence between 0 and 89° for 36 photon energies and determined optical constants taking into account beam polarization, film thickness, and surface roughness.

We report here an evaluation of the optical data for six of the materials examined by Windt et al., based on sum rules for the energy-loss function. We describe these sum rules in the following section and then present results of our sum rule tests for Al, Si, Ti, Mo, W, and Ir. These materials were selected for analysis here because we were interested in making use of the experimental Windt et al. data for our IMFP calculations (in place of the interpolated data based on photoabsorption calculations). In addition, a preliminary comparison had shown noticeable differences in plots of the energy-loss functions for the six materials obtained from the tabulated optical data [6–10] we had used previously and from the newer optical data [12,13]. The materials selected for analysis here were also of interest because some of them (Si, Mo, W, Ir) are under current consideration for the fabrication of multilayer films to be used for X-ray mirrors.

Sum rules

The optical properties of a solid are described by the complex dielectric constant $\varepsilon(\omega) = (n + ik)^2$, where n is the refractive index, k is the extinction coefficient, and ω is the light frequency. Smith [14] has reviewed a number of powerful sum rules for $\varepsilon(\omega)$ and other optical functions that can be used to assess the reliability and internal consistency of sets of measured data. These sum rules have been used, for example, by Shiles et al. [15] to identify an excess of oscillator strength for the optical absorption of aluminum in the vicinity of the L edge [6] and to propose revisions to the data based on the sum rules.

The cross section for inelastic electron scattering is proportional to the energy-loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ [16,17]. Our calculations of IMFPs were based on values of the energy loss function obtained from optical measurements of $\varepsilon(\omega)$ for each material [1–4].

We evaluated the energy-loss function data for each material using two sum rules, the oscillator strength or f-sum rule and a limiting form of the Kramers–Kronig (KK) integral [14,18–20]. The f-sum is the effective number of electrons per atom or molecule Z_{eff} contributing to the inelastic scattering, and is given by

$$Z_{\mathrm{eff}} = (2/\pi\Omega_p^2) \int_0^{\omega_{\max}} \omega \mathrm{Im}[-1/\varepsilon(\omega)] \mathrm{d}\omega \qquad (1)$$

where $\Omega_p = (4\pi n_a e^2/m)^{1/2}$, $n_a = N_a \rho/M$ is the density of atoms or molecules, N_a is Avogadro's number, ρ is the bulk density, and M is the atomic or molecular weight. When the upper limit in eqn. (1) $\omega_{max} = \infty$, Z_{eff} should be equal to Z, the total number of electrons per atom or molecule.

The KK relations can be utilized to calculate $\mathrm{Re}[1/\varepsilon(\omega)]$ from $\mathrm{Im}[1/\varepsilon(\omega)]$ if values of the latter quantity are available over a sufficiently wide frequency range. It is convenient to define a quantity P_{eff} from a simplified form of the KK relations when $\mathrm{Re}[1/\varepsilon(\omega)]$ is calculated in the limit $\omega \to 0$. P_{eff} is then given by

$$P_{eff} = (2/\pi)\int_0^{\omega_{max}} \omega^{-1}\,\mathrm{Im}[-1/\varepsilon(\omega)]\mathrm{d}\omega + \mathrm{Re}[1/\varepsilon(0)] \tag{2}$$

For conductors, $\mathrm{Re}[1/\varepsilon(0)]$ is zero and, in the limit $\omega_{max} \to \infty$, P_{eff} should be unity; eqn. (2) is then the perfect-screening sum rule [19,20]. For nonconductors, the refractive index n is much greater than the extinction coefficient k at low frequencies and eqn. (2) becomes

$$P_{eff} = (2/\pi)\int_0^{\omega_{max}} \omega^{-1}\,\mathrm{Im}[-1/\varepsilon(\omega)]\mathrm{d}\omega + n^{-2}(0) \tag{3}$$

where $n(0)$ is the limiting value of n as $\omega \to 0$. As before, in the limit $\omega_{max} \to \infty$, P_{eff} should be unity. Equations (2) and (3) will be termed the KK-sum rule.

The f-sum rule for the energy-loss function (eqn. (1)) has been used frequently in the analysis of optical data (see, for example, ref. 15). Equations (2) and (3), however, appear to have been used infrequently. It is clear from inspection of eqns. (1)–(3) that the main contributions to the integral of eqn. (1) occur for large frequencies, whereas the main contributions to the integrals of eqns. (2) and (3) occur for small frequencies. The use of both sum rules is therefore advantageous for assessing the overall reliability and consistency of a set of energy-loss function data, particularly because the IMFP is proportional to an integral of the energy-loss function over frequency and the main contributions to this integral occur for intermediate frequencies. The specific frequency regions important for each sum-rule integral will be apparent in the results presented below for each material.

Results

Figures 1–6 show plots of the energy-loss functions for Al, Si, Ti, Mo, W, and Ir as a function of photon energy $\hbar\omega$. In each figure, the full lines (——) indicate values of the function

$$\mathrm{Im}[-1/\varepsilon(\omega)] = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$$

where

$$\varepsilon_1 = n^2 - k^2$$

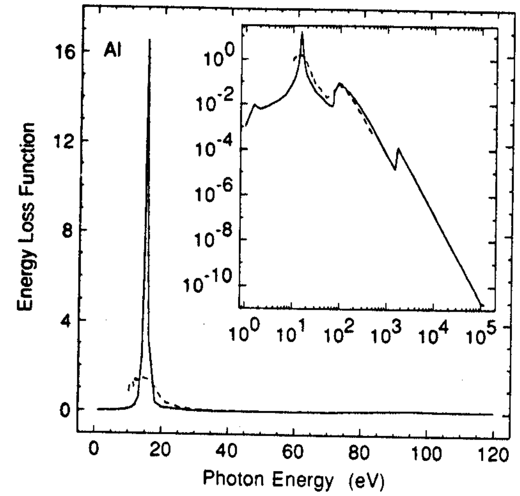

Fig. 1. The energy-loss function as a function of photon energy for aluminum as determined from tabulated optical data [6–10] (——); the energy-loss function obtained from the optical data of Windt et al. [12,13] (- - -); the main part shows the energy-loss function in the 0–125 eV range; the inset shows the energy-loss function over a larger range of energy loss on logarithmic scales.

and

$$\varepsilon_2 = 2nk$$

as determined from the tabulated optical data [6–10]. The long-dashed lines (— — —) indicate the interpolations we have made based on photoabsorp-

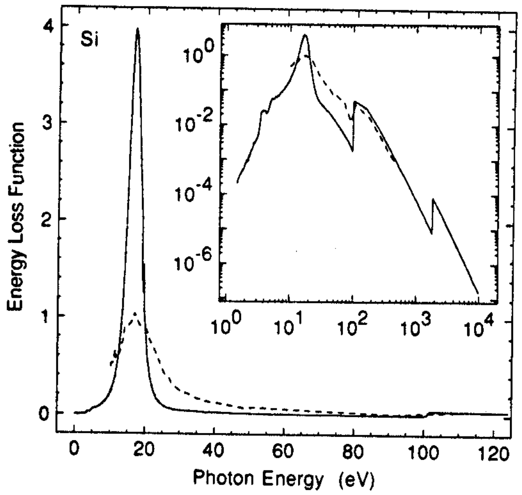

Fig. 2. Energy-loss function data for silicon; see caption to Fig. 1.

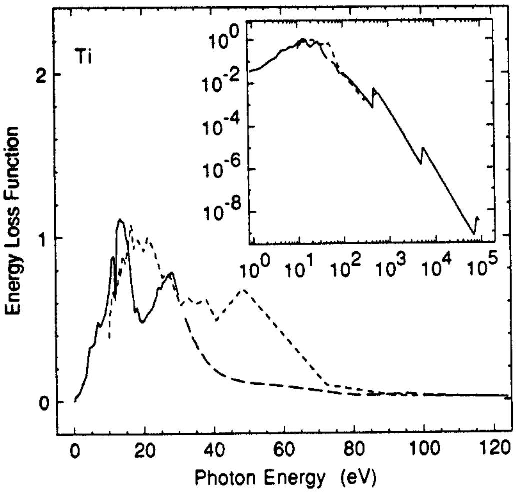

Fig. 3. Energy-loss function data for titanium; see caption to Fig. 1; interpolated values based on photoabsorption calculations [11] (— — —).

tion calculations [11] for Ti, Mo, W, and Ir. The short-dashed lines (- - -) show plots of the energy loss function in the 10–525 eV range from the optical data of Windt et al. [12,13].

For aluminum and silicon, the largest peak in the energy-loss function is due to volume plasmon excitation. This peak in Figs. 1 and 2 is much stronger and narrower for the energy-loss function results from the tabulated data than from the data of Windt et al. For the four transition metals (Ti,

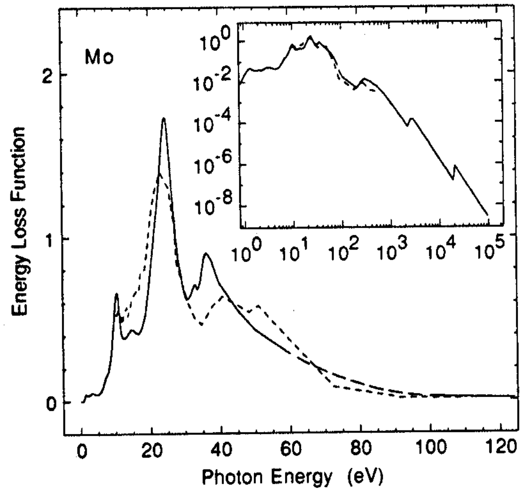

Fig. 4. Energy-loss function data for molybdenum; see captions to Figs. 1 and 3.

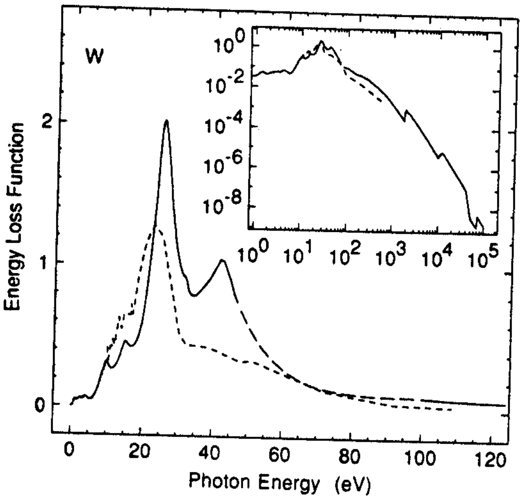

Fig. 5. Energy-loss function data for tungsten; see captions to Figs. 1 and 3.

Mo, W, and Ir), there are varying differences visible in Figs. 3–6 between the energy-loss functions determined from the tabulated data and the data of Windt et al. We have made similar comparisons (not presented here) for six other materials. For C, Zr, and Nb, there were significant differences in the energy-loss functions determined from the tabulated optical data and the Windt et al. data, whereas for Ru, Rh, and SiC the differences were small.

Figures 7–12 show the results of our applications of the sum-rule tests

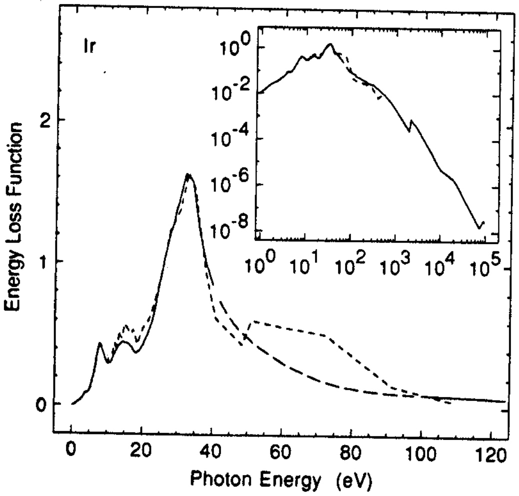

Fig. 6. Energy-loss function data for iridium; see captions to Figs. 1 and 3.

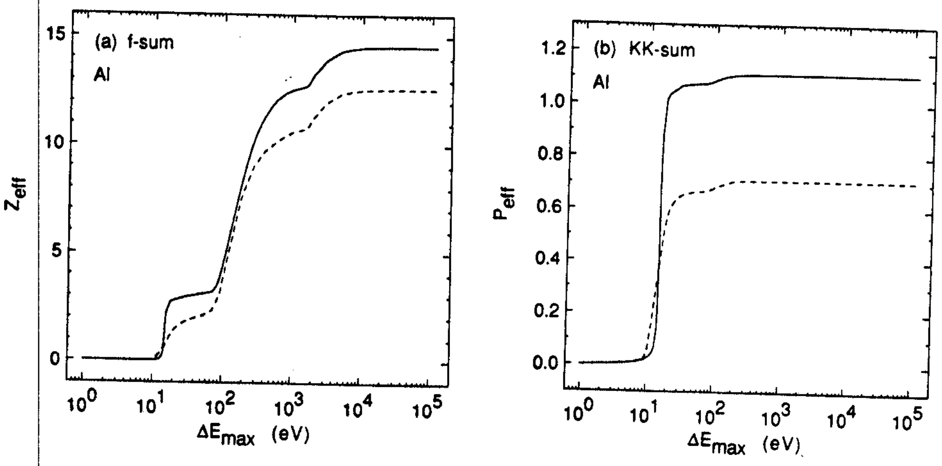

Fig. 7. Plots of (a) Z_{eff} determined from eqn. (1) and (b) P_{eff} determined from eqn. (2) for aluminum as a function of the upper limit in the integration $\Delta E_{max} = \hbar\omega_{max}$; (——), evaluation of Z_{eff} and P_{eff} from the tabulated optical data and with our interpolations as a function of the upper limit of the integration; (– – –), similar plots of Z_{eff} and P_{eff} with the substituted values of the energy-loss function determined from the data of Windt et al. [12,13] over the 10–525 eV range.

(eqns. (1)–(3)) to the energy-loss function data presented in Figs. 1–6; eqn. (2) was used for the metals and eqn. (3) for Si. The full lines in Figs. 7–12 indicate evaluations of Z_{eff} and P_{eff} from the tabulated optical data and with our interpolations as a function of the upper limit in the integrations, $\Delta E_{max} = \hbar\omega_{max}$. The short-dashed lines in Figs. 7–12 are similar plots of Z_{eff} and P_{eff} where we have substituted the values of the energy-loss function

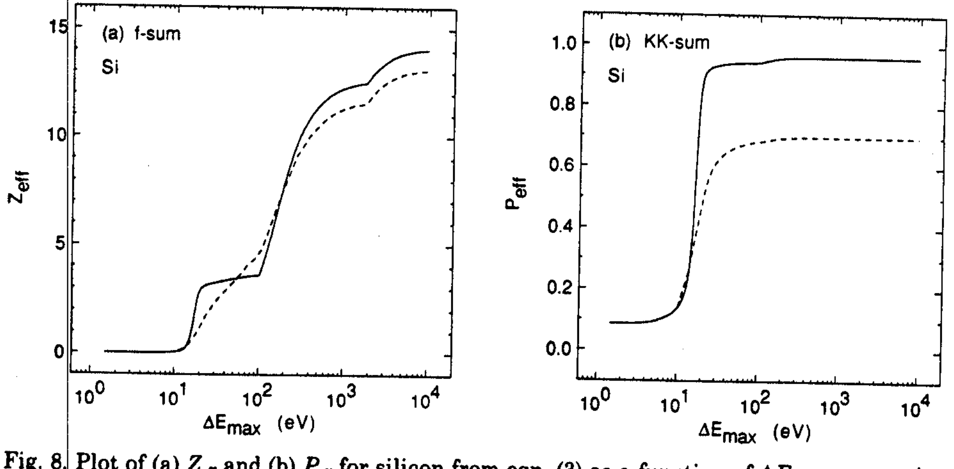

Fig. 8. Plot of (a) Z_{eff} and (b) P_{eff} for silicon from eqn. (3) as a function of ΔE_{max}; see caption to Fig. 7.

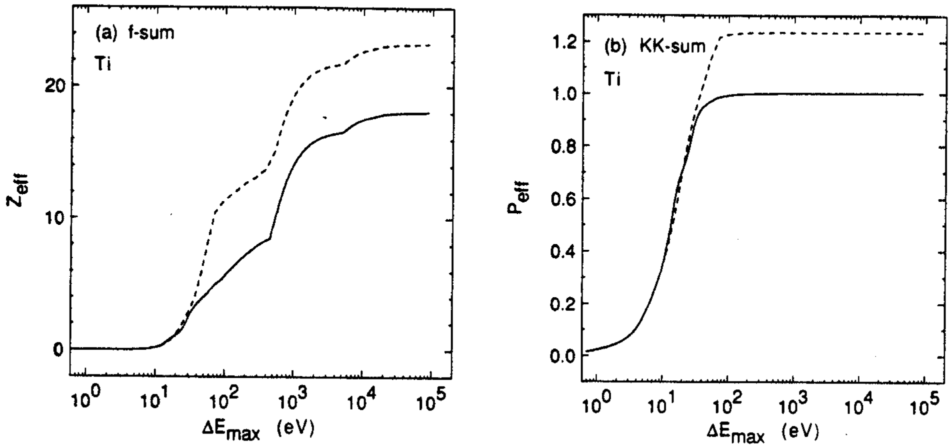

Fig. 9. Plot of (a) Z_{eff} and (b) P_{eff} for titanium as a function of ΔE_{max}; see caption to Fig. 7.

determined from the data of Windt et al. over the 10–525 eV range for values obtained from the earlier tabulated data. We realize that these substitutions can lead to some noticeable and unphysical discontinuities in the energy-loss functions at about 10 and 525 eV (e.g. for aluminum in Fig. 1), but such discontinuities are of little importance in our use of the sum rules to assess internal consistency and reliability of sets of data.

The maximum values of ΔE_{max} in Figs. 7–12 are about 10^4 eV for Si and about 10^5 eV for the other five elements. The f-sum integration is thus over a sufficiently large range to include contributions from all shells, although

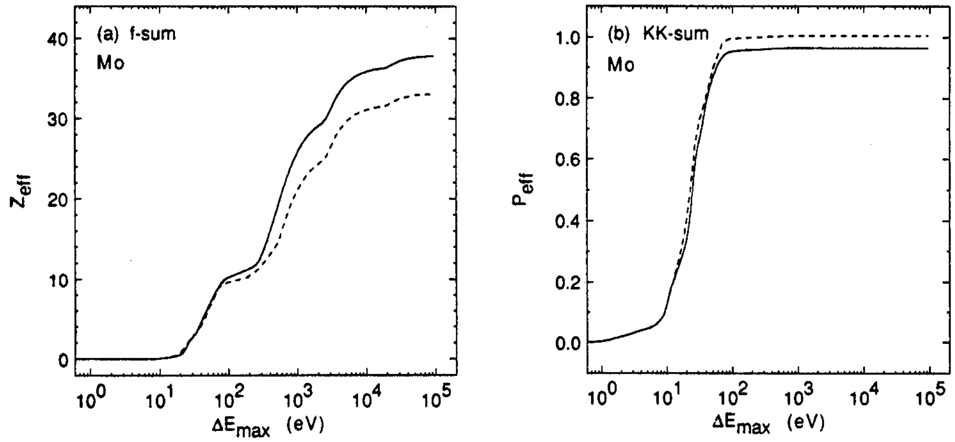

Fig. 10. Plot of (a) Z_{eff} and (b) P_{eff} for molybdenum as a function of ΔE_{max}; see caption to Fig. 7.

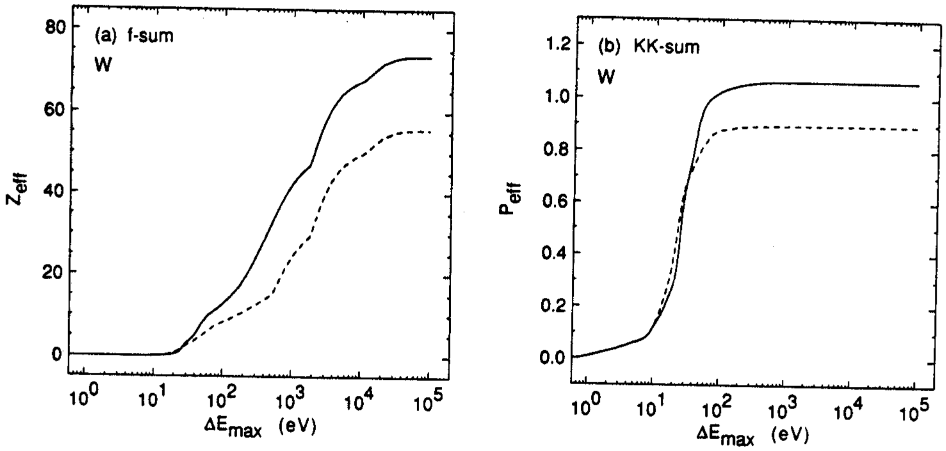

Fig. 11. Plot of (a) Z_{eff} and (b) P_{eff} for tungsten as a function of ΔE_{max}; see caption to Fig. 7.

there may be a slight underestimate in the values of Z_{eff} here for W and Ir, which have K-shell binding energies of 69.5 and 76.1 keV, respectively [21].

The numerical results of the two sum-rule integrations are shown in Tables 1 and 2 for each element and for each set of optical data. Table 1 gives the percentage difference in the maximum value for Z_{eff} (for the largest value of ΔE_{max} in the integrals of eqn. (1)) compared to Z. The percentage difference between the maximum value of P_{eff} (for the largest value of ΔE_{max} in eqns. (2) and (3)) compared to unity is listed in Table 2. Table 3 contains the r.m.s. values of the percentage errors in Tables 1 and 2 for each element based on the tabulated optical data [6–10] and the optical data of Windt et al. [12,13].

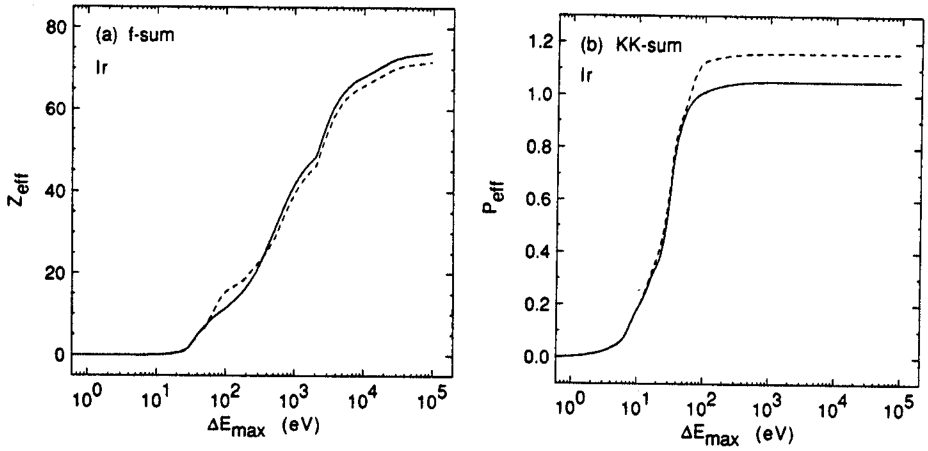

Fig. 12. Plot of (a) Z_{eff} for (b) P_{eff} for iridium as a function of ΔE_{max}; see caption to Fig. 7.

Table 1
Percentage difference in the maximum value of Z_{eff} from eqn. (1) compared to the atomic number Z for Al, Si, Ti, Mo, W, and Ir, based on the tabulated optical data [6–10] and the optical data of Windt et al. [12,13]

Element	Percentage difference	
	Tabulated optical data	Optical data of Windt et al.
Al	12.1	−2.9
Si	0.5	−6.3
Ti	−17.7	5.9
Mo	−10.0	−21.2
W	−0.5	−24.5
Ir	−3.8	−6.7

Discussion

Windt et al. [12,13] point out that their thin film samples were prepared by electron beam evaporation onto polished silicon wafers at room temperature in a vacuum with a pressure of about 7×10^{-4} Pa (5×10^{-6} Torr). The samples had nominal thicknesses of 1000 Å and were exposed to air before the reflectance measurements were made; these measurements were typically completed in 2–3 days. Auger depth-profile measuements were made to characterize film composition although it is not specified whether these measurements were made before or after the measurements of reflectance and surface roughness. It should also be noted that the published depth profiles show relative Auger intensities rather than relative elemental concentrations. Windt et al. report that their Al and Si samples were "highly oxidized" [13] although the oxygen Auger signal for the Al film was localized to the outermost film surface. For Ti, Mo, and W, the depth profiles indicated that oxygen was present at substantial levels throughout

Table 2
Percentage difference in the maximum value of P_{eff} from eqns. (2) and (3) compared to the expected value of unity for Al, Si, Ti, Mo, W, and Ir, based on the tabulated optical data [6–10] and the optical data of Windt et al. [12,13]

Element	Percentage difference	
	Tabulated optical data	Optical data of Windt et al.
Al	11.1	−29.2
Si	−3.9	−30.1
Ti	0.3	23.5
Mo	−3.5	0.4
W	6.3	−10.5
Ir	5.2	15.8

Table 3
R.m.s. values of the percentage errors for the f-sum and the KK-sum shown in Tables 1 and 2 for Al, Si, Ti, Mo, W, and Ir, based on the tabulated optical data [6–10] and the optical data of Windt et al. [12,13]

Element	R.m.s. percentage error	
	Tabulated optical data	Optical data of Windt et al.
Al	11.6	20.7
Si	2.8	21.7
Ti	12.5	17.1
Mo	7.5	15.0
W	4.5	18.8
Ir	4.6	12.1

the film and that carbon was present on the outermost surfaces of the Ti, Mo, W, and Ir films [12].

We now give brief comments on the energy-loss data for each element in Figs. 1–6 and the corresponding sum-rule results presented in Figs. 7–12 and Tables 1 and 2.

Aluminum

The energy-loss function for Al from the data of Windt et al. [13] in Fig. 1 shows a weaker and broader peak in the vicinity of $\hbar\omega = 15\,\mathrm{eV}$ than the corresponding peak based on the data of Hagemann et al. [6]. There is no evidence in the plot based on the Windt et al. data in Fig. 1 of a maximum in the vicinity of $\hbar\omega = 24\,\mathrm{eV}$, the expected position of the maximum in the energy-loss function for Al_2O_3 [6].

The maximum value of Z_{eff} based on the tabulated optical data for Al [6] is 12.1% larger than the expected value of 13. This discrepancy has been analyzed by Shiles et al. [15], who have proposed a modified set of optical data that better conforms to expectations based on the f-sum rule and other considerations. Although the maximum value of Z_{eff} obtained using the Windt et al. data is only 2.9% less than the expected value, the maximum value of P_{eff} is 29.2% lower than unity.

Silicon

As for Al, the peak in the energy-loss function for Si in Fig. 2 based on the Windt et al. data [13] is weaker and broader in the vicinity of $\hbar\omega = 17\,\mathrm{eV}$ than the peak based on tabulated optical data [8,11]. There is again no maximum in the vicinity of $\hbar\omega = 23\,\mathrm{eV}$, the expected position for the maximum in the loss function for SiO_2 [8].

The f-sum rule is reasonably satisfied (Table 1) for both sets of data shown in Fig. 2. The maximum value of P_{eff} for Si in Table 2, however, is appreciably less than the expected value of unity for the data of Windt et al.

Titanium

The plots of the energy-loss functions for Ti in Fig. 3 based on the tabulated data [7,9–11] and the data of Windt et al. [12] are considerably different for photon energies between 15 and 70 eV. Some structure associated with excitations from the Ti3s and Ti3p levels is expected in this energy range [21,22] but with not as large an intensity as suggested by the Windt et al. data.

The maximum value of Z_{eff} for Ti (Fig. 3(a) and Table 1) is 17.7% less than the expected value, perhaps because of inadequate consideration of 3s and 3p excitations. The maximum value of P_{eff} determined from the Windt et al. data is 23.5% larger than the expected value.

Molybdenum

The plots of the energy-loss functions from the tabulated data [8,10,11] and the data of Windt et al. [12] for Mo in Fig. 4 differ somewhat in the relative intensities and positions of the principal features for photon energies between 20 and 70 eV. The maximum value of Z_{eff} (Table 1) from the Windt et al. [12] data is 21.2% less than the expected value; the corresponding value from the tabulated data [7,8] is 10.0% less than the expected value. The maximum values of P_{eff} (Table 2) are close to unity for each set of data.

Tungsten

The plots of the energy-loss function for W in Fig. 5 from the tabulated data [8,10,11] and the data of Windt et al. [12] show appreciable differences in structure and relative intensities for photon energies between 10 and 500 eV. The f-sum and KK-sum rules are satisfied reasonably well (Tables 1 and 2) with the tabulated optical data [7,8], but there are larger differences between Z_{eff} and P_{eff} and the corresponding expected values when the Windt et al. data are utilized in the integrations.

Iridium

The plot of the energy-loss function for Ir in Fig. 6 from the optical data of Windt et al. [12] shows structure for photon energies between 50 and 90 eV that is not present in our interpolation based on the tabulated data [8,10,11]. Some structure in this range is expected due to the excitation of electrons from the Ir4f and W5p levels [21].

The maximum values of Z_{eff} from the two sets of optical data for Ir in Table 1 do not differ appreciably. The maximum value of P_{eff} from the Windt et al. data in Table 2, however is 15.8% greater than unity, whereas the value from the tabulated optical data is much closer to the expected value.

To conclude this section, Table 3 shows that the r.m.s. values of the sum-rule errors based on the tabulated optical data for the six elements are less than those using the Windt et al. data. This comparison suggests that the tabulated optical data are to be preferred (e.g. for IMFP calculations) over the Windt et al. data. It is very likely that the poorer results associated with the Windt et al. data are due to lack of sufficient elemental purity in their films. Their optical data may be correct for their preparation and measurement conditions but, as noted by Windt et al. [12,13], would not be considered as representative of films prepared and maintained under the vacuum conditions needed to ensure film purity.

The use of the f-sum rule and the KK-sum rule for the energy-loss function (eqns. (1)–(3)) has therefore been useful in assessing the internal consistency and validity of two sets of optical data for six elements. Although there may be inaccuracies associated with the tabulated optical data and with our interpolations for some elements in the 40–100 eV photon energy range, the average of the r.m.s. errors based on the tabulated data in Table 3 is 7.3%, whereas that for the Windt et al. data is 17.6%.

It is clear from the plots in Figs. 7–12 that the f-sum rule involves excitations of all atomic electrons; for the six elements considered here, excitations with energies up to about 10^5 eV must be considered. However, the KK-sum saturates when the limit ΔE_{max} is about 100 eV. The f-sum rule and KK-sum rule are thus useful for evaluating possible errors in the contributions of high-energy excitations and low-energy excitations, respectively, to the energy-loss function. Additional optical sum rules [14] can be employed to evaluate other optical functions and to identify data subsets that may be in error.

Summary

We have evaluated two sets of values of the energy-loss function for Al, Si, Ti, Mo, W, and Ir based on two sum rules, the f-sum rule and the KK-sum rule. The sets of energy-loss function data were first calculated from tabulated optical data [6–10] and interpolations in the 40–100 eV energy range based on atomic photoabsorption calculations for Ti, Mo, W, and Ir. We constructed second sets of energy-loss function data for each element by replacing data in the 10–525 eV range in the first set with values calculated from the optical constants reported by Windt et al. [12,13].

We have performed the sum-rule integrations for each set of energy-loss function data and find that these are satisfied better with the first set of energy-loss function data than with the second set (constructed with the Windt et al. data). The optical measurements of Windt et al. were made with thin-film samples that had been prepared in a conventional high-vacuum chamber, exposed to air, and transferred to a reflectometer chamber for measurements taking 2–3 days. It is therefore likely that the deviations found in the evaluations of the sum rules from the expected values with the Windt et al. data are associated with oxidation or surface impurities.

The f-sum rule and the KK-sum rule are useful for assessing the reliability and internal consistency of energy-loss function data calculated from optical measurements (e.g. for the calculation of electron inelastic mean free paths [1–4]). These sum rules, together with sum rules for other optical quantities [14], are valuable for identifying data subsets that may be in error.

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