Photoelectron determination of mean free paths of 200–1500-eV electrons in potassium iodide

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The total inelastic mean free path in polycrystalline KI for electrons of energy 200–1500 eV has been measured to an accuracy of approximately ±12% by a photoelectron overlayer technique. Values range from 28 Å at 192 eV to 70 Å at 1404 eV. A theoretical model, based on a semiempirical tight-binding approximation, modified to take account of the attractive and repulsive effects of the K^+ and I^- ions on the incident electrons, has been used to calculate such mean free paths in KI. The agreement of these calculations with the experimental results is good.

I. INTRODUCTION

A wide variety of electron spectroscopic techniques are now in use for the study of electronic structures of solids. If techniques such as photoelectron and Auger spectroscopy are to become truly quantitative, then an accurate knowledge of the energy-dependent attenuation length or total inelastic mean free path in solids $\lambda(E)$ of electrons of energy in the range 100–2000 eV is of primary importance. Recent studies have shown that the energy dependence of the total inelastic scattering cross section for electrons in metals and their oxides is similar, but the results obtained by a variety of methods reveal that the mean free path given by different authors for a particular material are often inconsistent. Compilations of this work include those of Bauer,[1] Tracy,[2] Powell,[3] Brundle,[4] and Lindau and Spicer.[5]

Following the determination of accurate attenuation lengths in Al_2O_3,[6] Battye *et al.* measured the variation of $\lambda(E)$ in the energy range 50–1500 eV for the strongly ionic solids NaCl and NaF.[7] A photoelectron overlayer technique, described in detail in Refs. 6 and 7, was used. Battye *et al.* have reviewed a number of possible theoretical models for the treatment of inelastic scattering of electrons in solids at these energies,[6] and have successfully applied a tight-binding model to the calculation of $\lambda(E)$ in NaCl and NaF.[7] This model was also used to predict the likely variation of attenuation length with energy for other alkali halides. An alternative approach to the problem of calculating $\lambda(E)$ in all types of solids has been presented by Powell.[3]

More recently, Penn has calculated inelastic mean free paths for electrons of energy greater than 200 eV in free-electron-like materials,[8] in all elemental solids (except the rare earths and actinides), and in a few compounds such as Al_2O_3 and SiO_2.[9] This theoretical work, like that of Powell,[3] makes use of the relationship between the differential inelastic scattering cross section and the complex dielectric function. A survey of available cross-section data for ionization of inner-shell electrons by incident electrons has also been presented by Powell.[10] Owing to the paucity of data, however, the bulk of this discussion was limited to K-shell and L-shell ionization of light atoms.

In this paper we report measurements of $\lambda(E)$ for KI in the energy range 200–1500 eV. The results are compared with the predictions of Battye *et al.*[7] and with the theory of Penn.[8,9] The tight-binding model is further improved by taking account of the attractive and repulsive effects on the incident electrons of the positive and negative ions in the solid, and agreement with the experimental results is found to be enhanced. Values given by the application of Penn's theory compare less satisfactorily.

II. EXPERIMENTAL METHOD AND RESULTS

An x-ray photoelectron spectroscopic overlayer technique was used in conjunction with a cylindrically symmetric spectrometer as previously described in Refs. 6 and 7. Thick gold and silver substrates were prepared by evaporation, and the intensity of selected substrate photoelectron lines was measured following successive depositions *in situ* of thin overlayer films of KI.

The intensity of several overlayer photoelectron and Auger lines, as a function of film thickness, was also monitored. For each substrate line, the relative intensity for a given overlayer thickness was then determined by dividing the measured intensity by the intensity of that line at zero overlayer thickness. For each overlayer line, the relative intensity was determined with respect to an (infinitely) thick overlayer. Throughout the experiment, the x-ray flux from either an aluminum or carbon anode was kept constant by an electron-emission controller, which ensured a constant
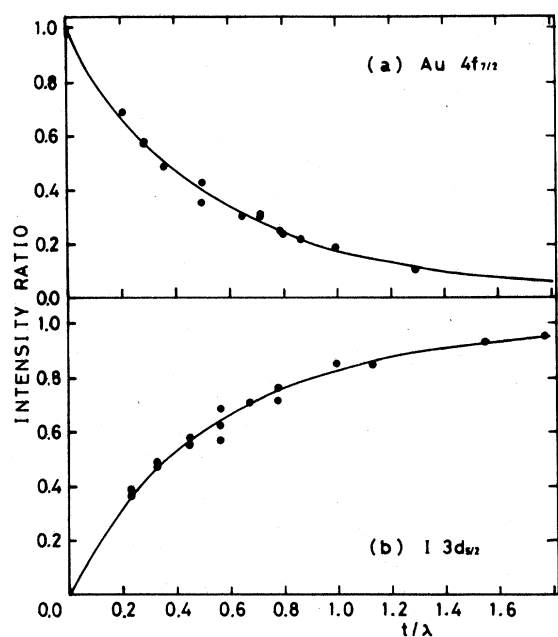
FIG. 1. (a) Attenuation of the Au $4f_{7/2}$ photoelectron line by KI films of thickness t. (b) Growth of intensity of the I $3d_{5/2}$ line as a function of film thickness. These data have been fitted as described in the text to obtain the continuous lines shown and $\lambda(E)$ values (in thin films) of 87 and 55 Å, respectively.

current flow between the filament and anode of the x-ray source. Film thickness and deposition rate were monitored and controlled by a quartz-crystal control system previously calibrated using a multiple-beam interferometer. Typical results are shown in Fig. 1.

The geometry of the spectrometer, and to a minor extent the asymmetry of photoemission, implies that the observed relative intensity of substrate (or overlayer) photoelectron lines will not

decay (or grow) precisely exponentially with overlayer thickness. These factors have been discussed in detail in Refs. 6 and 7. In Ref. 6 in particular it is shown analytically (and illustrated graphically) that the effect of variations in the photoemission angular asymmetry parameter β is very small, but that the correction which allows for the geometry of the spectrometer is significant. The expressions for the variation in intensity with overlayer thickness, appropriate to our spectrometer, have been given in Refs. 6 and 7. A computer program was used to fit the relative intensity versus overlayer thickness data at each electron energy to these expressions using the iterative Newton-Raphson method, $\lambda(E)$ being the only adjustable parameter. Appropriate asymmetry parameter values, for example $\beta = 2$ for electrons from s levels, were used—see Fig. 1.

Electron attenuation lengths for KI were determined at 13 energies between 192 and 1404 eV using the above procedures, and the results are given in Table I. Also shown are details of the photoelectron or Auger lines used and of the exciting radiations employed. As determined gravimetrically, the density of evaporated KI films was 81% of the bulk value of 3.13×10^3 kg m^{-3}, and the attenuation length results given in column 4 of Table I have therefore been converted to values appropriate to bulk samples. These values are shown in column 5 and in Fig. 2. The uncertainties quoted in Table I are root-mean-square errors derived from the least-squares data fitting procedure discussed above, and therefore include errors associated with random experimental uncertainties as well as statistical considerations.

Deviations of experimental results from the quasiexponential expressions are a sensitive test of film uniformity. Some degree of nucleation in the thin layers of KI necessary for the determin-

TABLE I. Attenuation lengths of electrons of various energies in KI. Details are given in the text.

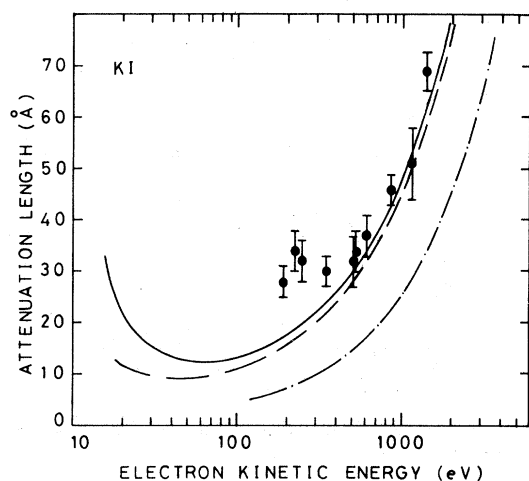| Line	Photon	Electron energy E_0 (eV)	λ (Å) thin films	λ (Å) bulk KI
Au $4f_{7/2}$	Al$K\alpha$	1404	87±6	70±6
Au $4f_{5/2}$	Al$K\alpha$	1400	85±8	68±7
Au $4d_{5/2}$	Al$K\alpha$	1153	65±7	52±6
I $3d_{5/2}$	Al$K\alpha$	867	55±6	45±5
I $3d_{3/2}$	Al$K\alpha$	856	58±7	47±4
I $3p_{3/2}$	Al$K\alpha$	612	46±4	37±4
I $M_4N_{4,5}N_{4,5}$	Al$K\alpha$	515	42±4	34±4
I $M_5N_{4,5}N_{4,5}$	Al$K\alpha$	505	40±6	32±5
Ag $M_4N_{4,5}N_{4,5}$	Al$K\alpha$	355	38±3	31±3
Ag $M_5N_{4,5}N_{4,5}$	Al$K\alpha$	350	37±5	30±4
K $3p$	C$K\alpha$	259	40±4	32±4
I $4d$	C$K\alpha$	227	42±4	34±4
Au $4f$	C$K\alpha$	192	35±3	28±3

FIG. 2. Measured energy dependence of the electron attenuation length in KI. In three cases, the energy separation between adjacent data points is insufficient to display them individually and an average value, with reduced error bars, is shown (see Table I). Theoretical predictions of the original (---), modified (——) tight-binding models and Penn (—·—) are also shown.

ation of $\lambda(E)$ at the lower energies ($\lesssim 300$ eV) was suspected during the present experiment, but a careful study of the data involving use of the islanding model introduced in Ref. 7 indicated that all the films in question were in fact uniform.

III. THEORETICAL CONSIDERATIONS

Following the measurement of attenuation lengths in Al_2O_3, Battye et al.[6] reviewed several possible theoretical models to explain the results: (a) a tight-binding model, in which collective processes (e.g., plasmon generation) are assumed to be weak and the valence electrons of the sample are considered to be tightly bound; (b) a Mott scattering model, in which the valence-band electrons are considered to be entirely free; and (c) a screened-Coulomb-potential model employing a potential of the form $V(r) = (e^2/4\pi\epsilon_0 r)e^{-r/r_0}$ where r_0 is a screening radius.

A. Tight-binding model

In subsequent studies of NaCl and NaF, Battye et al.[7] presented evidence that collective processes in the alkali halides are indeed weak, and noted that the outermost valence bands are relatively tightly bound. All levels were therefore treated as if they were tightly bound core levels, and the semiempirical expression given by Lotz[11] for the total inelastic-electron-scattering cross section for free atoms was used, namely,

$$\sigma = \sum_i a_i q_i \{1 - b_i \exp[-c_i(E_0/E_i - 1)]\}$$
$$\times \ln(E_0/E_i)/E_0 E_i . \tag{1}$$

In Eq. (1), E_0 is the energy of the electrons scattering from an atom having a set of energy levels E_i, each occupied by q_i electrons. The constants a_i, b_i, and c_i have been determined empirically by Lotz.[12] This formula was applied to the alkali halide solids by calculating the cross section for both the alkali-metal and halide ions (σ^+ and σ^-, respectively), using the best experimental binding energy values E_i for these solids. The total inelastic scattering cross section (σ) was then found from

$$\sigma = \sigma^+ + \sigma^- . \tag{2}$$

The additive nature of the individual cross sections should be noted. The attenuation length was determined using the expression $\lambda(E) = 1/N\sigma$, where N is the number density of ion pairs. The success of this approach in fitting the experimental data was sufficient to allow Battye et al. to predict attenuation lengths for the other alkali halides.

B. Modified tight-binding model

Although binding-energy values appropriate to the constituent ions were used in the above calculations, no account was taken of the effect of the ionic charge centers on the paths of the incident electrons before they scatter inelastically from the ions. The probability of finding an electron near the center of a positive or negative free ion, relative to the probability of finding it in the (uniform) incident beam, is given by,[13]

$$P^{\pm} = 2\pi |\alpha| / |1 - \exp(\mp 2\pi |\alpha|)| . \tag{3}$$

A simple Coulomb field of the form $V(r) = \pm pe^2/4\pi\epsilon_0 r$ is used in deriving this expression, p being the partial charge on the ion,[14] and

$$\alpha = \pm pe^2 m_e^{1/2} / [4\pi\epsilon_0 \hbar(2eE_0)^{1/2}]$$
$$= \pm 3.69 p/E_0^{1/2} .$$

E_0 is the incident electron energy in electron volts.

For any solid alkali halide, which clearly contains equal numbers of positive and negative ions, the probability of finding an electron near the center of an ion, relative to the probability of finding it in the vicinity of an ion pair, may be written

$$\mathcal{P}^{\pm} = 2P^{\pm}/(P^+ + P^-) . \tag{4}$$

The factor 2 arises because each electron has a probability of scattering from a positive and a negative ion, such that

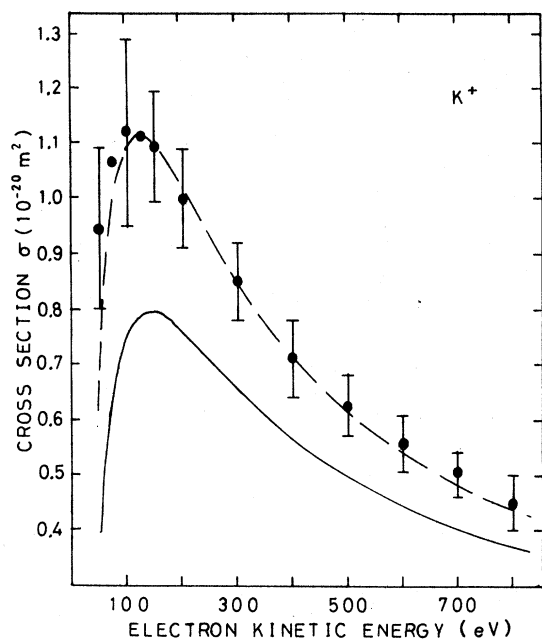$$\sigma = \mathcal{P}^+ \sigma^+ + \mathcal{P}^- \sigma^- , \tag{5}$$

FIG. 3. Absolute electron impact cross section for single ionization of K^+ ions as quoted by Massey and Burhop compared with the theoretical predictions of Lotz (——) and of the present work (--).

where

$$\mathcal{P}^+ + \mathcal{P}^- = 2 .$$

In order to demonstrate the significance of this effect, we consider the case of free K^+ ions. The absolute cross section for single ionization of K^+ ions by electron impact has been measured by Lineberger et al.[15] over the electron energy range from threshold to 1000 eV, using a crossed-beam technique. Their results, as reported by Massey and Burhop,[16] are shown in Fig. 3. The Lotz formalism has been used to calculate this cross section, using electron binding-energy values for K^+ ions taken from Refs. 11, 17, and 18, and the results are shown as the continuous line in Fig. 3. If attractive effect of the ionic charges on the electron paths is now included, we may correct the calculated values by multiplying them by the factor $2P^+/(1+P^+)$, since in this case we are comparing the probability of finding an electron near a K^+ ion with the probability of finding it near an uncharged scattering center. The result of this correction is shown as the dashed curve in Fig. 3 where it may be seen that agreement with the experimental values is now excellent. McDowell and Williamson,[19] following a procedure introduced by Geltman,[20] used Eq. (3) to multiply theoretical cross-section values for the ionization of H^- ions to account for the repulsive effect of the ionic charge on the incident electrons. We have at-
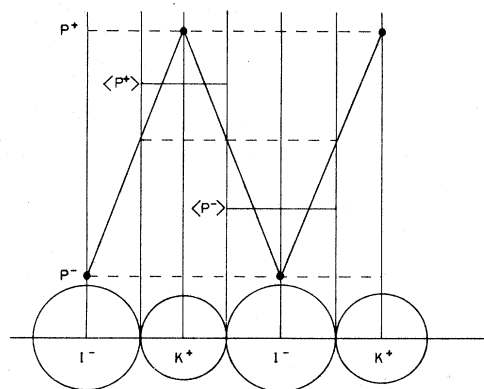

FIG. 4. Assumed spatial variation in P as discussed in the text.

tempted to show here that Eq. (3) alone is not adequate to account correctly for this effect.

Equation (3) for $P^\pm$ applies to isolated ions only. In an ionic solid, the Coulomb field surrounding each ion pair will be complex, and hence the above formalism cannot be strictly applied to such cases. We have therefore assumed that the probabilities defined in Eq. (3) are correct at the center of each positive and negative ion, and that there is a linear variation in P between the ions. Under this assumption we may define an average value $\langle P^\pm \rangle$ across each ion as shown in Fig. 4. Equation (4) then becomes

$$\mathcal{P}^\pm = \frac{2\langle P^\pm \rangle}{\langle P^+ \rangle + \langle P^- \rangle} \tag{6}$$

$$\mathcal{P}^\pm = \frac{2[2r^\mp P^\pm + r^\pm(P^+ + P^-)]}{P^+(3r^- + r^+) + P^-(3r^+ + r^-)} , \tag{7}$$

where $\mathcal{P}^\pm$ are defined in Eq. (3) and $r^\pm$ are the appropriate ionic radii, obtained from Ref. 21.

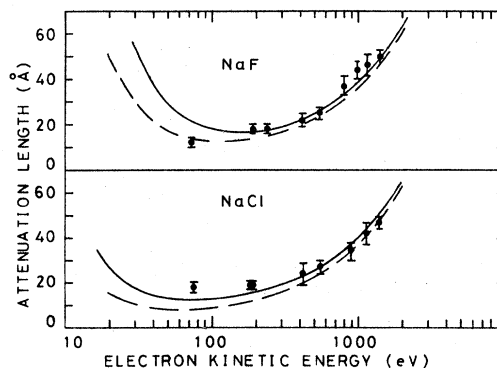The modified values of $P^\pm$ given by Eq. (7) were then used in Eq. (5) to calculate improved values

FIG. 5. Measured energy dependence of the electron attenuation length in NaCl and NaF from Ref. 7. Theoretical predictions of the original (--) and modified (——) tight-binding models are also shown.

of the total inelastic scattering cross section and hence of the attenuation length. Figure 2 shows the experimental and calculated values of attenuation length from KI. The dashed curve is that derived by Battye et al.,[7] while the continuous curve shows the improvement in the agreement between experiment and theory obtained when the modified tight-binding theory described above is used. Figure 5 shows similar improvements for the cases of NaCl and NaF reported earlier.[7]

C. Penn's theory

As stated above, Penn has recently calculated values of the electron mean free path for inelastic scattering as a function of energy for a wide range of solids. In particular, he has given formulas for the calculation of mean free paths in compounds. The total mean free path λ is subdivided into two contributions, due to electron collisions with valence and core electrons,

$$\lambda^{-1} = \lambda_v^{-1} + \lambda_c^{-1}.$$

The precise meaning of "valence" and "core" is not defined by Penn, although a sample calculation for Al_2O_3 is given and provides some insight into this question.

The dielectric theory of Quinn[22] has been used by Penn[8] and exchange and correlation effects introduced, leading to the following expressions for λ_v and λ_c:

$$\lambda_v = E_0 / [a_v(\ln E_0 + b_v)],$$

$$\lambda_c = E_0 / [a_c(\ln E_0 + b_c)],$$

where a_v and b_v are parameters depending on the average distance between valence electrons in a

given sample, and a_c and b_c are parameters derived originally by Powell.[3]

In applying this formalism to the case of KI, we have taken the valence electrons to be $I^-(5s^2 5p^6)$ and the highest core levels for each constituent to be $K^+(3p^6)$ and $I^-(4d^{10})$, respectively. Then $\lambda = E_0 / [7.83(\ln E_0 - 1.68)]$, which is plotted in Fig. 2 as the dash-dot curve. It may be seen that these results are less satisfactory than the modified tight-binding model values. Penn's theory was initially developed for the case of free-electron-like materials where an accuracy to 5% was claimed. Although the theory is subsequently extended to non-free-electron materials, however, it was estimated by Penn that such mean free values may be in error by as much as 40%.

IV. CONCLUSIONS

The total inelastic mean free path in polycrystalline KI for electrons of energy 200–1500 eV has been measured to an accuracy of approximately ±12% by a photoelectron overlayer technique. Values range from 28 Å at 192 eV to 70 Å at 1404 eV. A theoretical model, based on a semiempirical tight-binding approximation, modified to take account of the attractive and repulsive effects of the K^+ and I^- ions on the incident electrons, has been used to calculate such mean free paths in KI. The agreement of these calculations with the experimental results is good.

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