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ANGULAR DEPENDENT PHOTOELECTRIC YIELD AND OPTICAL CONSTANTS OF Al BETWEEN 40 TO 600 eV

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Abstract

Total photoelectric yield measurements were performed on ~ 800 *Å thick Al films evaporated in ultrahigh vacuum on glass substrates. Fitting of the photoelectric yield as a function of angle of incidence using Pepper's equations yielded optical constants in excellent agreement with those obtained from reflectance measurements on the same films. This establishes a convenient method for determining optical constants and yields in addition values for film thickness and electron escape depths.*

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Accurate determination of optical constants in the XUV (vacuum ultra violet-/ soft x-ray-) region is difficult and the available data in the literature are full of unresolved contradictions. We demonstrate here that the determination of the total photoelectric yield as a function of the angle of incidence on a mirror made of a conducting material or of a thin film of such a material on a well defined substrate, is sufficiently specific to obtain accurate optical constants. Pepper [1] has given the relevant formalism to calculate the angular dependent photoelectric yield for a thin film on a substrate already in 1970. We have used these equations in a fitting procedure to obtain the real- and imaginary parts (ϵ_1, ϵ_2) of the dielectric function, film thickness, and average escape depth of the photoelectrons.

The central assumption in this formalism is that the number of escaping photoelectrons is determined by the energy absorbed in the topmost layers of the sample. The escape probability is given by a weight factor exponentially decaying with distance from the surface. As we shall discuss below this special choice of the escape function is the weakest point in Pepper's theory but fortunately the optical constants are quite insensitive to the details of this probability factor. Only the relative intensity of photoemission as a function of angle of incidence θ for a given photonenergy $\hbar\omega$ needs to be measured. This contains all the necessary information. The information is very specific (1) due to interference structures in regions where the film is transparent enough to allow for a strong reflected wave from the back side of the film to interfer, (2) due to the onset of total reflection resulting in a decrease of photoelectric yield at well defined grazing angles (this contains mainly information on ϵ_1) and (3) due to the shape of this decrease (which contains information on ϵ_2). This method was applied before by Arakawa and co-workers [2,3] with the primary goal to obtain electron escape depths of Al at $21.2\,eV$ and for C between 20 eV and 64 eV photon energy. In addition the real part of the index of refraction was obtained. By greatly improving the experimental accuracy and by covering a large spectral range we demonstrate here that this method has the potential of becoming as important as the other techniques now in use [4] to determine optical constants in the XUV range. On the same samples on which the total photoelectric yield was measured under ultra high vacuum (UHV) conditions, reflectivity versus angle of incidence was measured giving independent results for the dielectric constants with standard evaluation procedures [4]. Thus the two methods could be compared directly. In addition, values for the escape depth of photoelectrons were extracted.

Pepper [1] gave a rigorous treatment of the photooptical behavior of thin films in the local limit. He calculated expressions for the reflectance, the transmittance and the divergence of the Poynting vector in the film. These expressions are valid for arbitrary values of angles of incidence of the photons and arbitrary values of the local dielectric function of the film and of the substrate. They are given for s- and p-polarized radiation. Since our measurements are performed with s-polarized radiation no complications due to the surface photoeffect are expected. In calculating the photoelectric yield diffusion of the primary excited photoelectron to the surface, multiplication due to electron-electron scattering along its path and escape through the surface potential barrier are all condensed in the simple function $C \cdot e^{-y/L(\hbar\omega)}$. Here L($\hbar\omega$) denotes the photon energy dependent electron escape depth. The energy dependence of L($\hbar\omega$) is clearly due to several reasons. It is the mean over a wide energy distribution evolving around the original location of absorption after a series of scattering events. C is a constant. Following Pepper's notation the total relative yield for a film of thickness d may be written as

$$Y = C \cdot \int_0^d e^{-y/L(\hbar\omega)} \cdot \eta(y) dy = C \cdot F(L),$$

where $\eta(y)$ is the volume absorptance which is proportional to the negative divergence of the Poynting vector. The function F(L) is completely determined by the optical constants $\tilde{\epsilon}$, the photon energy $\hbar\omega$, the photon polarization and the angle of incidence θ. Defining the quantity $G(\theta) = Y(\theta)/Y(0)$ as the relative total photoelectric yield the unknown factor C cancels out, since it does not depend on θ. The angular dependence of G(θ) is determined by the optical properties of the material and by the value of the electron escape depth L($\hbar\omega$). The expressions for $\eta(y)$, F(L), G(θ) and the reflectance are rather complex and the reader is referred to Pepper's paper for details.

In this work the reflectivity and the relative yield as a function of angle were measured for the same sample with a UHV-reflectometer equipment [5]. The spectrally pure radiation was supplied by the "BUMBLE BEE"-monochromator, which is especially designed for good suppression of higher harmonics in the XUV [6]. This monochromator is installed at the synchrotron radiation laboratory **HASYLAB** and obtains radiation from the storage ring **DORIS**. Our reflectometer is equipped with a rotatable sample holder with an electron collector, a diode detector, an e-gun evaporator and a quartz-crystal thickness monitor to estimate the film thickness during and after evaporation. The sample and the detector are rotatable with an angular resolution of about 0.005°. Measurement is assisted by computer control. Thin films of aluminium were e-gun evaporated from high purity Al in UHV onto an optically flat glass mirror. The evaporator was placed at a distance of 17cm to the substrate ensuring a good compromise between uniform film thickness and short duration of the evaporation. Before evaporation the pressure in the reflectometer chamber was about $4 \cdot 10^{-10}$ mbar, while during evaporation the pressure rose up to 10^{-7} mbar. Immediately after evaporation the pressure decreased to 10^{-9} mbar and measurements were started.

Before evaporating onto the borosilicate glass substrate its optical constants were determined by the multiangle method [3]. The Al films were found to be stable with respect to their optical properties. Measuring the reflectivity and the total yield of the Al films 20 h after evaporation the same spectra were reproduced within the experimental error limit. Especially near the O-K-edge and the Al-$L_{2,3}$-edge, an oxide layer grown on the sample surface during measurements would have lead to a measureable change in reflectivity. For photon energies below the Al-$L_{2,3}$-edge Pepper's reflectivity expressions for a film supported by a bulk were fitted to the experimental data by the method of least squares, to derive the optical constants of thin Al films. Therefore a χ^2-function was minimized :

$$\chi^2 = \sum_{i=1}^{n} g_i \cdot [R_{exp}(\theta_i) - R_{theo}(\theta_i)]^2 \quad .$$

The weights are given by $g_i = \sigma_i^{-2}$ whereby σ_i denotes a measuring error due to statistical sources for each experimental point . **Fig.1** shows a plot of a measured reflectivity curve of an Al sample for a photon energy of $\hbar\omega = 65.3\,eV$ with a logarithmic R scale. The solid line is a result of a least-squares-fit. Each point of the dotted line in the middle of the figure shows the difference of the theoretical value minus the experimental value of the reflectivity in units of the standard deviation σ_i of the supporting point i. The strong interference pattern of the reflectivity curve, which allows to determine the value of film thickness d from the fit with high accuracy, is typical for photon energies below the Al-$L_{2,3}$-edge. The theoretical expression for the reflectivity $R_{theo}(\theta_i)$ depends on 5 adjustable parameters, the optical constants of the film $\tilde{\epsilon}_{Al}$, the optical constants of the substrate $\tilde{\epsilon}_{sub}$ and film thickness d. $\tilde{\epsilon}_{Al}$ and d were used as fitting parameters, while the optical constants of the substrate, as determined also by multiangle measurements served as fixed parameters. Above the Al-$L_{2,3}$-edge the interference structures in the reflectivity curves disappear and thus the simpler Fresnel equations for the reflectivity of a bulk material could be used.

The photoelectric yield as a function of angle of incidence, $Y(\theta)$, relative to the yield for normal incidence, $Y(0)$, was evaluated applying the same fit criteria as for the reflectivity data. For photon energies below the Al-$L_{2,3}$-edge Pepper's equations for films were applied to yield values for the optical constants $\tilde{\epsilon}_{Al}$, of the film thickness d and of the electron escape depth $L(\hbar\omega)$. As in the case of the reflectivity the optical constants of the glass substrate were kept as fixed parameters. Above the Al-$L_{2,3}$-edge again the films revealed a pure bulk behaviour and the corresponding expressions of the total yield for the bulk could be applied in the fit procedure. The application of Pepper's equations for films also gave resonable results in this case but caused unnecessary complications in the fit procedure. **Fig.2** shows the measured total yield as a function of angle corresponding to the reflectivity spectrum shown in **Fig.1**. In both cases the value of σ_i was 1% of the experimental value. **Fig.(3,4)** summarizes the fit results of the dielectric functions ϵ_1 and ϵ_2 obtained by both methods. The circles denote the values of the reflectivity method, while the crosses refer to the total yield method. The value of the film thickness determined from the reflectivity is $d = 768 \pm 10$Å while that from the total yield method yielded $d = 773 \pm 9$Å. For both methods complete s-polarization was assumed, but it was tested that the fit results do not depend on the degree of polarization as long as it lies above 85% s-polarization. In our experimental arrangement this is the case. The variation of the electron escape depth with the photon energy is shown in **Fig.5**. The agreement of the results obtained by the two different methods is noteworthy. We consider this to be a solid proof for the total yield method to be at least as reliable as the reflectivity method. It may even give better values since the problem of an independent detector is eliminated and since moreover a surface roughness may have less influence. The latter conjecture stems from the observation that the decrease of $Y(\theta)$ at the highest values of θ is decisive in determining the optical parameters. This decrease is determined by the reflectivity of the sample. In the case of a not to large surface roughness, however, the sum of specularly and of scattered light is practically equal to the specularly reflection of a perfectly smooth surface. The thus determined ϵ_2 of Al in the region before the onset of the Al-$L_{2,3}$-edge [7] is considerably smaller than any other values given in the literature. We attribute this to the fact that we were able to prepare our samples in situ under much better conditions than anyone before. Any small contamination of oxygen or other impurities will increase the absorption coefficient in a region where it is so low.

The strange resonance behaviour of $L(\hbar\omega)$ around the Al-$L_{2,3}$-edge and the increase of L for $\hbar\omega \geq 400eV$ is surprising. A real physical process which could cause such variations of L in fairly limited regions appears to be improbable since the photoelectrons which escape have practically lost the primary information about the initial photon energy due to inelastic multiple scattering processes. We therefore tried to find other reasons for these excursions of $L(\hbar\omega)$.

Our conjecture is that the exponentially decaying escape function gives too much weight to primary absorption occuring in the topmost layer. This appears to be unphysical since a primarily excited photoelectron could escape from there without multiplying in a cascade of electron-electron scattering events. This multiplication, however, which all the electrons excited with high photon energies have undergone, is considerably increasing the escape probability. We therefore modified the escape function formally as

$$C \cdot [1 + a_1(y/L)]e^{-y/L}$$

in order to eliminate by a proper choice of a_1 the too high escape probability for near surface excitations. Model calculations showed that the effect of such a modification is unimportant in most parts of the spectrum but becomes effective in regions where ϵ_2 is small which is exactly where the excursions of L occur. By proper choice of a_1 these excursions could be removed. Since, however, our choice of the modified escape function is quite arbitrary, we abstained to recalculate our fits with this new function. The addition of further fit parameters would bear the danger of overinterpreting our results.

In concluding, we have demonstrated that the measurement of the relative photoelectric yield of bulk material or of thin films on well defined substrates provides sufficient information to determine optical constants in a wide spectral range of the XUV. This could become a convenient technique with many advantages also for other materials than Al. The determination of the electron escape depths, for which such measurements were used before, is also possible but before the method can fully be exploited in this direction, an improved theoretical understanding is needed.

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(see also DESY report SR-74/7)

Figure Captions

Fig.1 Reflectivity $R(\theta)$ versus angle of incidence θ at a photon energy of $\hbar\omega = 65.3\,eV$. The dotted line in the middle of the figure shows the deviation of theory minus experiment in units of σ_i. For explanation of this quantity see text.

Fig.2 Total photoelectric yield $G(\theta)$ versus angle of incidence θ normalized to yield at normal incidence at a photon energy of $\hbar\omega = 65.3\,eV$. The yield spectrum was obtained from the same sample as the reflectivity shown in figure 1.

Fig.3 Real part of the dielectric function ϵ_1 versus photon energy $\hbar\omega$. The crosses denote the fit results of the total yield measurements, while the circles refer to the reflectivity method.

Fig.4 Imaginary part of the dielectric function ϵ_2 versus photon energy $\hbar\omega$. As in figure 3 the crosses mark the values obtained by the total yield method and the circles those of the reflectivity measurements.

Fig.5 Electron escape depth L versus photon energy $\hbar\omega$. The error bars shown in the figure were obtained by the fit procedure. For a critical discussion of these data see text.

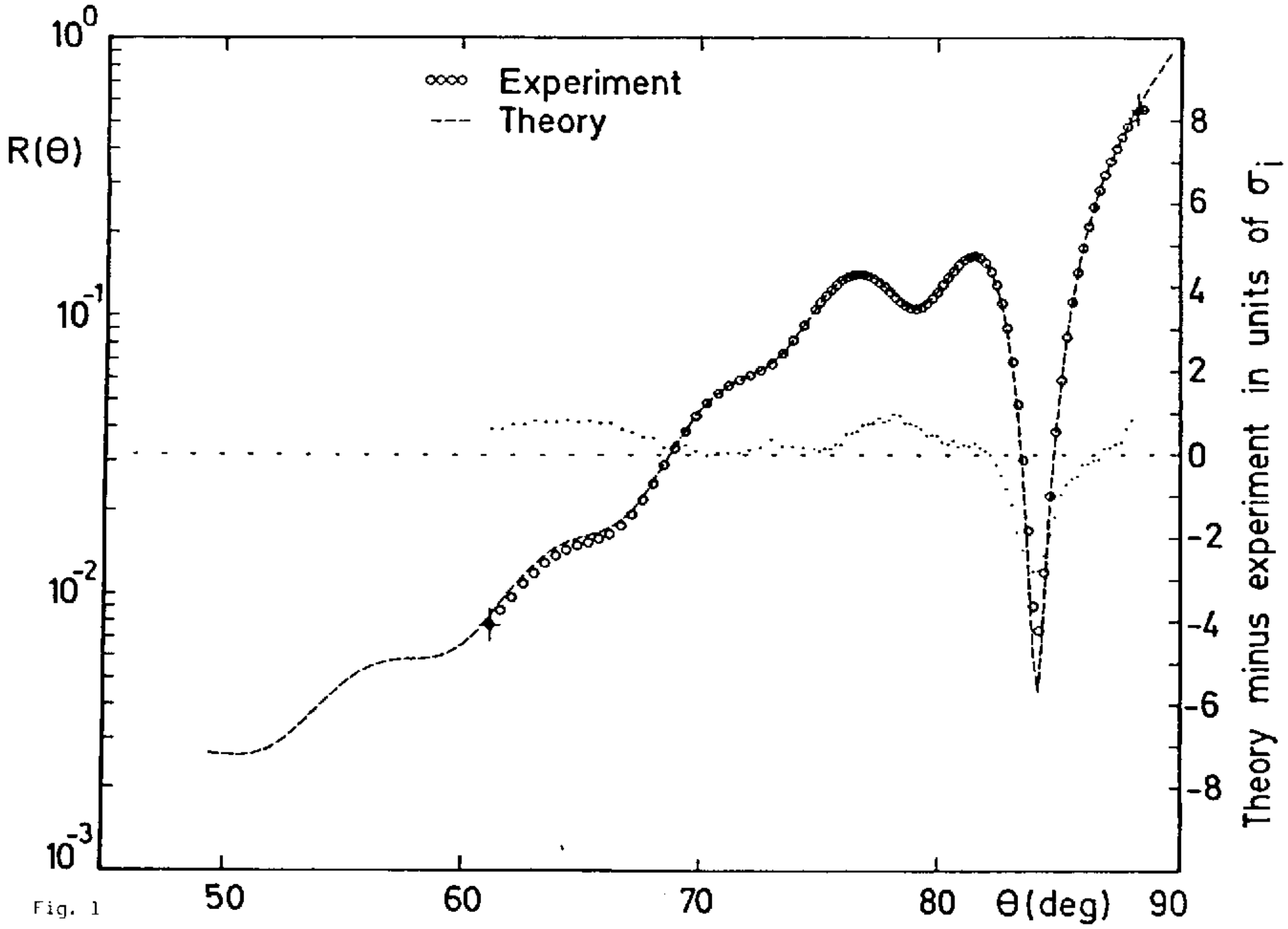

Fig. 1

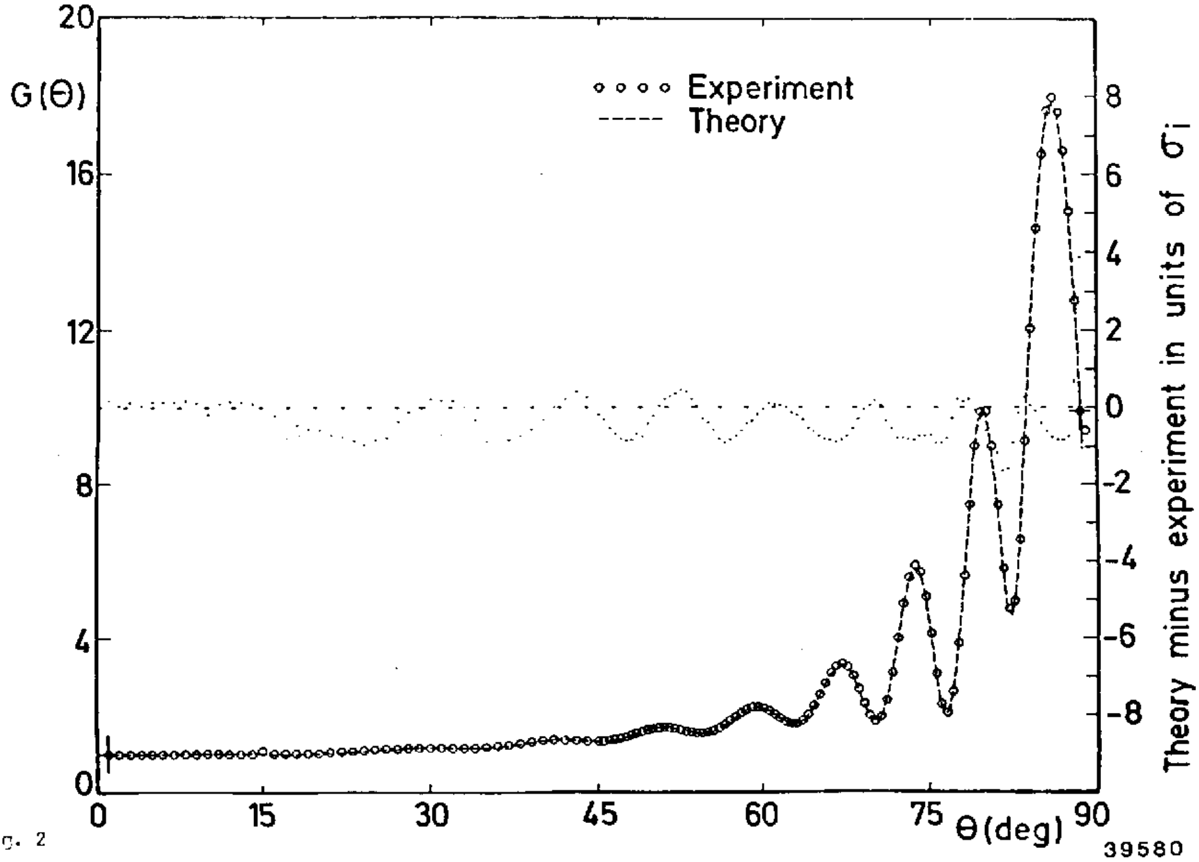

Fig. 2

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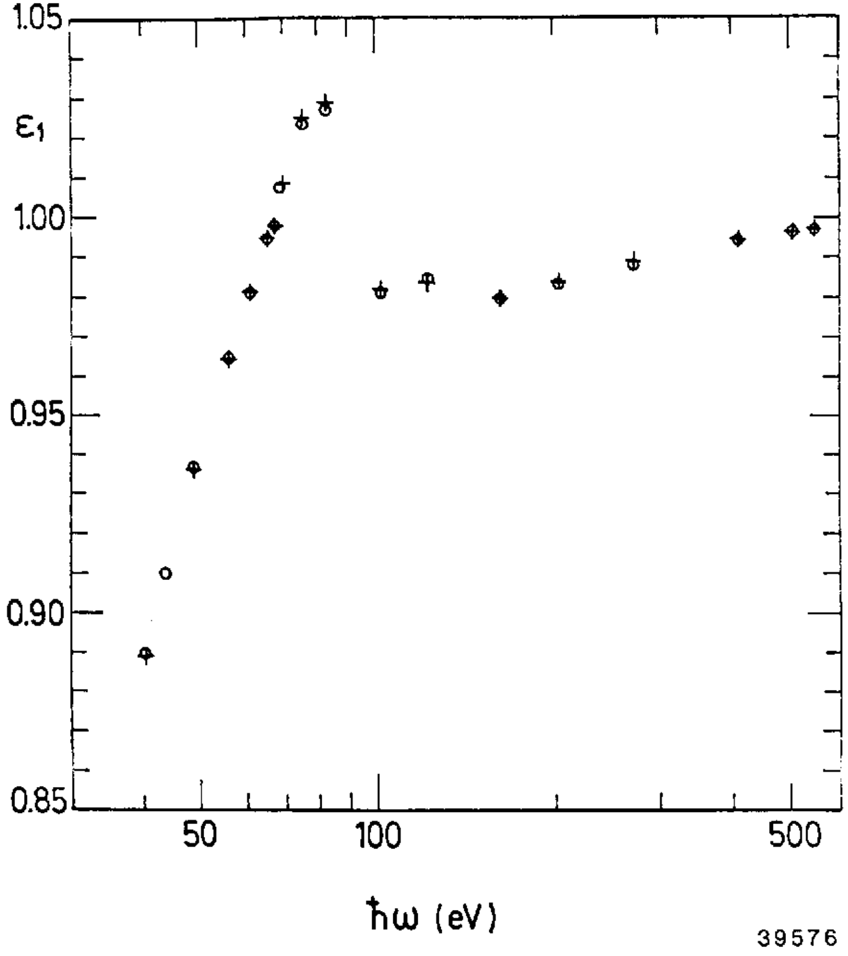
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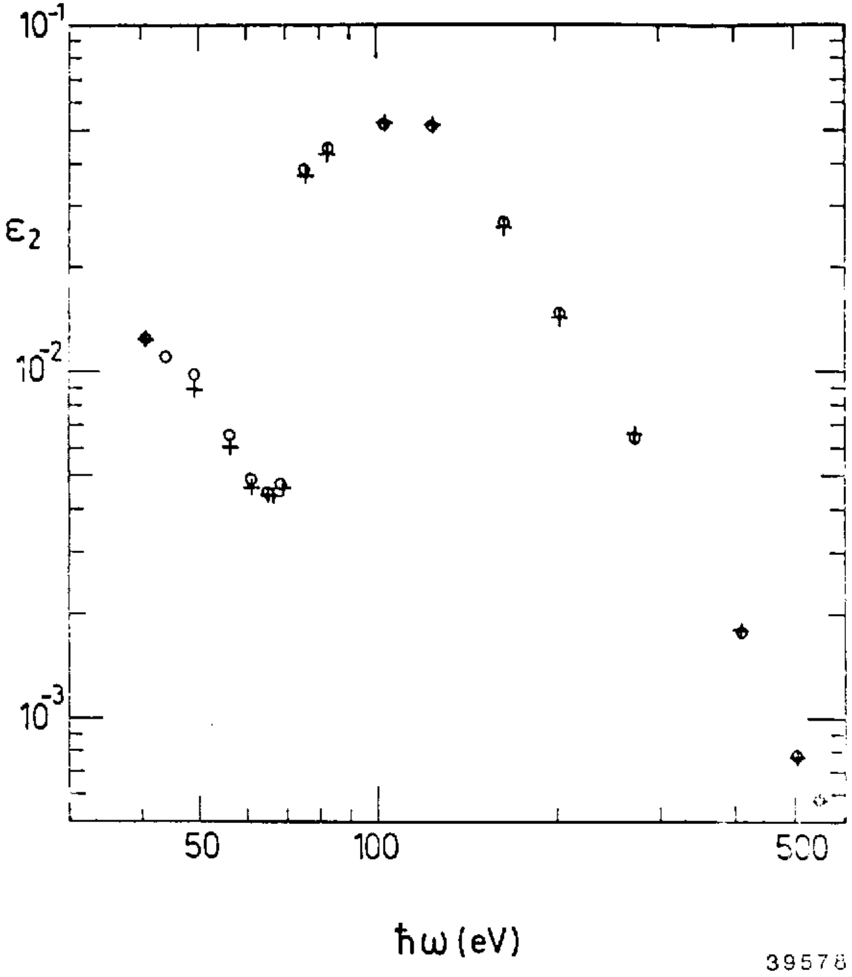
1.00
0.95
0.90
0.85
ε_1
50
100
500
$\hbar\omega$ (eV)
39576

Fig. 3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10^{-2}
10^{-3}
ε_2
50
100
500
$\hbar\omega$ (eV)
39578

Fig. 4

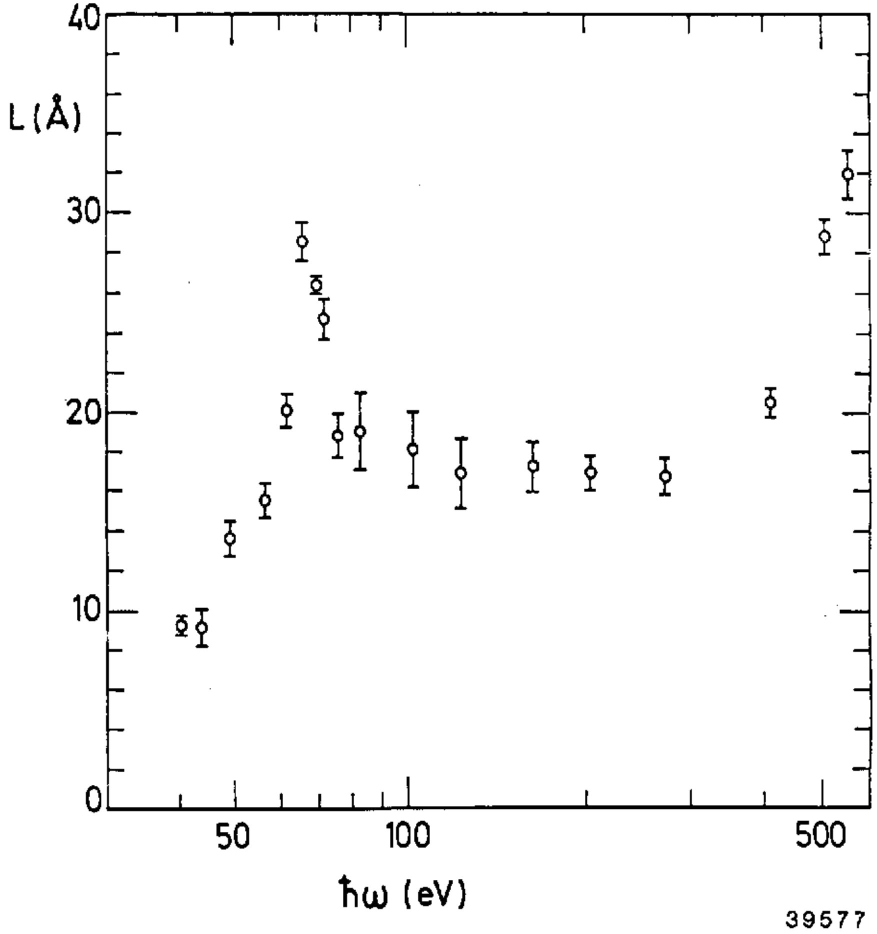

Fig. 5