DEUTSCHES ELEKTRONEN - SYNCHROTRON DESY

Absorption Measurements of Copper, Silver, Tin,

Gold and Bismuth in the Far Ultraviolet

by

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ABSORPTION MEASUREMENTS OF COPPER, SILVER, TIN, GOLD AND BISMUTH IN THE FAR ULTRAVIOLET[+]

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A b s t r a c t

Absorption measurements on Copper, Silver, Tin, Gold and Bismuth in the spectral range 50 to 340 Å were performed using the synchrotron radiation of the 6 GeV electron synchrotron DESY. The results are compared with previous measurements and theoretical predictions. A calculation of the partial oscillator sums from the available data gives rough agreement with the theoretically expected values.

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I. Introduction

High energy circular accelerators for electrons are excellent
radiation sources for the extreme ultraviolet and soft x-ray region,
where conventional sources are weak. Synchrotron radiation is
suitable for gas absorption experiments, for the measurement of
optical constants of solids, and since the intensity can be
calculated absolutely also for the absolute evaluation of photo-
and fluorescence-yield and secondary calibration of radiation
sources and detectors. For general information see[1,2].

Synchrotron radiation at Deutsches Elektronen-Synchrotron DESY
has already been utilized for a check of the theory of synchrotron
radiation in the x-ray region[3], for experiments on plasma resonance
absorption in aluminium[4,5] and for studies on the applicability of the
source as a radiometric standard[6]. In this paper we discuss measure-
ments of the absorption coefficient of Cu, Ag, Sn, Au and Bi in the
spectral range 50 to 340 Å. Preliminary results of these measurements
have been reported already[7]. An analysis of the results by
calculating partial oscillator sums gives valuable information
about the contribution of the various subshells to the absorption.

The predominant feature of our measurements is that we have found
a rather smooth behaviour of the absorption coefficient over the
spectral region studied rather than the usual structure with sharp
absorption edges in the x-ray region and in the longer wavelength
part of the spectrum. Similarily Codling et al.[8] with Sn and
Sagawa et al.[9] with Al have shown that the main absorption is
shifted from the position of the edges to higher energies and
smeared out. In addition, gas absorption measurements of Ederer on
Xe showed this effect earlier[10]. The results of our measurements
which covered a large wavelength region and were performed on five
different substances indicate that the smearing out of the absorption
coefficient and the absence of prominent edges is not unusual but
rather a quite typical behaviour in the extreme UV-region. This is
in agreement with theoretical calculations by Cooper[11], by Farnoux
and Héno[12] and by Manson and Cooper[13].

In the following sections we will describe our experimental
arrangement (section II), our data handling procedure (section III)
and our results (section IV).

II. Experimental Layout

The synchrotron radiation emitted by the electrons is polarized
and concentrated into a very narrow cone around the instantaneous
flight direction. Only light emitted from a very short part of the
electron orbit around the tangential point passes through the entrance
slit of a spectrograph 40 m away. We have essentially parallel light
coming from a very small source, illuminating a 20 mm long slit
mounted normally to the synchrotron plane.

The continuous spectrum of the synchrotron radiation spans wavelengths
from the radio region to the x-ray region (at DESY down to 0.1 $\overset{o}{A}$ for
6 GeV electrons). In our region of interest the intensity of the
synchrotron radiation is nearly independent of the electron energy
for energies higher than 2 GeV.

Our experimental arrangement is shown in Fig. 1. The grazing-
incidence vacuum spectrograph used an original Siegbahn concave
grating (G) with 576 lines/mm, radius of curvature 1 m and an entrance
angle of 84°. As the intensity of the x-ray portion of synchrotron
radiation is very high at DESY we had an intense background when the
entrance slit was illuminated directly by the synchrotron beam.
Therefore, we deflected the light by 10° with a mirror (M). Light
with wavelength $\lambda > 50 \overset{o}{A}$ is specularly reflected into the entrance
slit whereas light of shorter wavelengths is diffusely scattered.

Originally we used at the position M a plane mirror, opening the
entrance slit to a width of 1 mm, thus illuminating the grating with
essentially parallel light. The spectrograph was not used in a
Rowland mounting but the focal curve for parallel light was
approximated in our wavelengths region by the circle on which the
exit slit moved. We achieved a resolution of about 2 $\overset{o}{A}$. In this
arrangement we eliminated the x-ray background and in addition

gained intensity by a factor of about 4 compared with an equivalent
Rowland-mounting in which the entrance slit is illuminated directly.

In an improved arrangement we returned to a Rowland-mounting using
a concave mirror M. The mirror had a radius of curvature of 12 m
forming an image of the radiation source just at the entrance slit
50 cm from the mirror. We calculate a width of 60 μm for the image
of the about 5 mm wide source (radial beam width in the synchrotron).
The width of the image is additionally increased by about 50 μm
due to spherical aberration. The gain in intensity compared with
a direct illumination of the entrance slit is about 40 multiplied
by the reflectivity of the mirror.

The detector mounted behind the exit slit was an open electron
multiplier (B) (Bendix M 306) which is very convenient for measuring
intensities varying by several orders of magnitude. For scanning
measurements with photomultipliers unlike the case of photographic
plates the instabilities of the current in the synchrotron have a
large effect on the measurement. By dividing the output signal of
the Bendix multiplier by a signal proportional to the current in
the synchrotron[14] this disadvantage was overcome.

III. Performance of the Measurements

The use of a continuous radiation source for quantitative measure-
ments in a wide spectral range introduces difficulties as a result
of the different orders reflected by the grating. In our measurements
we also encountered a background of straylight. For our entrance
angle the grating did not reflect light of wavelengths below 50 Å.
Therefore, between 50 Å and 100 Å the spectrum was free from
higher orders. For wavelengths larger than 100 Å the effect of the
higher orders could not be neglected. The separation of the different
components of the radiation was effected by using prefilters of Be ,
Al and Mg and by reducing the data from a series of about 15 samples

of different thicknesses ranging from 50 Å to 6500 Å. The samples
were prepared by evaporating spectroscopically pure metals from
W- and Ta-boats onto Zapon foils of equal thickness (about 500 Å)
supported by a fine copper mesh. The pressure during evaporation
was about $2 \cdot 10^{-6}$ Torr. The evaporation rate was 10 Å/sec.

The film thickness was monitored by a quartz oscillator during
evaporation. The thickness of all films thicker than 1000 Å was
additionally measured by a weighing method and a Tolansky interfero-
meter. The latter two methods agreed and also were consistent with
measurements made with the quartz oscillator. The oscillator was
repeatedly calibrated with an about 6000 Å thick film. The error
in thickness ranged from about 3% for the thickest foils to about
20% for very thin foils.

Besides the metal foils a Zapon reference foil and a spectrum
without any foil were measured. These measurements served also to
control the stability of the system and the radiation damage to
the Zapon film.

For about 30 discrete wavelengths within the range 50 Å to 340 Å the
ratio T of the transmission with foil divided by the transmission
of the Zapon foil was evaluated. The separation between two neigh-
bouring wavelengths chosen for evaluation depended on the structure
in the spectrum.

By plotting the logarithm of T against the thickness d of the
foil in the region 50 Å to 100 Å one obtains a straight line the
gradient of which is the absorption coefficient μ. Above 100 Å
ln T as a function of d is no longer a straight line (see Fig.2).
By taking into account that we have two components (first and second
order) we succeeded in approximating the curve by the following
equation up to about 180 Å:

$$T = K_1 \cdot e^{-\mu_1 d} + K_2 \cdot e^{-\mu_2 d}$$

K_1 is the fraction of the intensity due to first order, K_2 the fraction due to second order. μ_1 is the absorption coefficient of the metal for the first order, μ_2 is the absorption coefficient for the second order.

In our case the following relations hold:

$$K_1 > K_2$$

$$\mu_1 > \mu_2$$

for $d \to 0$

$$\ln T = -(\mu_1 K_1 + \mu_2 K_2) d$$

for $d \to \infty$

$$\ln T = \ln K_2 - \mu_2 d$$

This gives two intersecting straight lines as shown in Fig.2. Evaluating the gradients of the two straight lines and K_2 from this diagramm one can calculate the absorption coefficient μ_1 using the given formulas.

For wavelengths longer than 180 Å this method could not be used because in this region the stray light background could not be neglected. By using a 2000 Å thick foil of Al the second order and the stray light were suppressed almost completely in the wavelengths region from 170 Å to 340 Å. Thus we could evaluate the absorption coefficient μ by the gradient of one straight line (Fig. 2).

A check of the μ values was obtained by using Be, Al and Mg prefilters and evaluating the hight of the edges as a function of the thickness of the foil. By this method which is independent of the composition of the light one gets the absorption coefficients for the measured metals at 110Å,170Å and 248Å.

As we always evaluated the μ values from a series of foils of different thicknesses our μ values are not effected by reflection and surface layers.

IV. Results

The measured absorption coefficients μ are shown in Figs. 3a to 7a. The error in photon energy is about ±0.5 eV at 35 eV and ±8 eV at 200 eV. The error in the values of μ amounts to about ±15% and is caused mainly by errors in correcting for higher order contributions, inaccuracies in film thickness measurement and changes in the zapon films due to irradiation effects. For tin the error may be ±25%.

For Cu (Fig.3a) we find good agreement with measurements of Neupert[15] in the overlapping region while the measurements of Tomboulian et al.[16] are about 30% lower than our values.

For Ag (Fig.4a) our measurements agree well with values of Lukirskii et al.[17] above 120 eV. The values of Robin[18] are 30% lower.

Our measurements on Sn (Fig.5a) agree well in the overlapping region with values by Codling et al.[8] taken from their transmission curves.

For our measurements on Au (Fig.6a) we find good agreement with values by Lukirskii et al.[17] and Jaeglé et al.[19]. The values of Canfield et al.[20] below 50 eV (not shown) are about 40% higher than ours.

For Bi (Fig.7a) our results agree well with those of Jaeglé et al.[21]. The values of Hunter et al.[22] taken from their transmission curves are about 30% lower than ours: but they are also in disagreement by about the same amount with the values of Sasaki and Ejiri[23]. Some of the low energy results shown in Fig.3a to 7a will be discussed later.

K_1 is the fraction of the intensity due to first order, K_2 the
fraction due to second order. μ_1 is the absorption coefficient
of the metal for the first order, μ_2 is the absorption coefficient
for the second order.

In our case the following relations hold:

$$K_1 > K_2$$

$$\mu_1 > \mu_2$$

for $d \to 0$

$$\ln T = -(\mu_1 K_1 + \mu_2 K_2) d$$

for $d \to \infty$

$$\ln T = \ln K_2 - \mu_2 d$$

This gives two intersecting straight lines as shown in Fig.2.
Evaluating the gradients of the two straight lines and K_2 from
this diagramm one can calculate the absorption coefficient μ_1
using the given formulas.

For wavelengths longer than 180 $\overset{o}{A}$ this method could not be used
because in this region the stray light background could not be
neglected. By using a 2000 $\overset{o}{A}$ thick foil of Al the second order
and the stray light were suppressed almost completely in the
wavelengths region from 170 $\overset{o}{A}$ to 340 $\overset{o}{A}$. Thus we could evaluate the
absorption coefficient μ by the gradient of one straight line
(Fig. 2).

A check of the μ values was obtained by using Be, Al and Mg
prefilters and evaluating the hight of the edges as a function
of the thickness of the foil. By this method which is independent
of the composition of the light one gets the absorption coefficients
for the measured metals at 110$\overset{o}{A}$,170$\overset{o}{A}$ and 248$\overset{o}{A}$.

The effective number N_{eff} of absorbing electrons between energies E_1 and E_2 is:

$$N_{eff} = \frac{m\,c}{\pi e^2 L h} \frac{A}{\rho} \int_{E_1}^{E_2} \mu\, n\, d E \qquad (1)$$

with Avogadros number L, atomic weight A, density ρ and n real part of the index of refraction.

In the case of integrating over the contribution of a single subshell we expect to get N_{eff} equal to the number of electrons per atom in the subshell. This is only true if other core states can be neglected (see for example[11]). We will interpret our results under this assumption but care should be taken not to emphasize minor deviations. For $E_1 = 0$ and $E_2 = \infty$ N_{eff} is rigorously equal to the total number of electrons/atom.

For evaluating Eq. (1) we put $n = 1$, which we believe gives not more than 10% overestimation in our region. For Cu we made a rough estimation of n by means of a Kramers-Kronig relation. We show an original and a corrected curve in Fig.3b.

The smooth behaviour of the curves for N_{eff} in Figs.3b to 7b reflects the absence of prominent edges in the absorption spectra. We encountered some difficulties in establishing a satisfactory connection between our measurements and those of other authors performed at lower energies. For some substances , Sn for example, there is a gap in the reported measurements, while for others there is a big discrepancy between different authors. Thus the selected value N_{eff} at our lowest energy may be somewhat arbitrary.

Cu

We started at 26 eV (Fig.3b) taking N_{eff} = 3 according to Beaglehole[27] continuing with Neuperts[15] and our data. At the onset of the $M_{II,III}$ edge which shows as a small jump (Fig.3a) N_{eff} is ∿6 meaning that the oscillator strength for the 11 (4s and 3d) electrons is far from being exhausted[11]. At the high energy limit of our measurements N_{eff} reaches only 14 which shows that the M shell oscillator strengths are distributed over a wide energy range. This behaviour had been calculated for the 3d electrons by Beaglehole[27]. A similar spread of the 3p contribution was calculated by Manson and Cooper[13].

Ag

Fig.4b shows the N_{eff}-curves of Ehrenreich and Philipp[28] (up to 25 eV) and the data of Robin[18] (up to 50 eV) fitting our curves at N_{eff} = 11 at 50 eV. The 11 (5s and 4d) electrons are exhausted at a somewhat too low energy, but the saturation at $N_{eff} \approx 20$ which we find at our highest energies seems to be quite reasonable if we assume the 8 electrons of $N_{II,III}$ and N_I are exhausted there.

Au

We connect our N_{eff}-curve (Fig.6b) to the data of Manson and Cooper[13] which are based on the measurements of Canfield et al.[20]. N_{eff} = 11 (6s and 5d electrons) is reached at 55 eV. We can neglect the $N_{VI,VII}$ contribution in our region since according to calculations of Manson and Cooper[13] and Farnoux and Héno[12] the contribution of these electrons lies at much higher energies which is also confirmed experimentally by Jaeglé et al.[19]. The data seem to be quite reasonable as N_{eff} = 19 (including O_{II}, O_{III} and O_I contributions) is reached at about 180 eV in a kind of saturation.

Sn

Since our measurements (Fig.5b) agree well with those of Codling
et al.[8] we included their results in the sum calculation. (Below
the sharp $N_{IV,V}$ edge valence-electron contribution may be roughly
exhausted giving a value of 4). The saturation at about 18 electrons
at the upper limit of our measurements compared to the total of also
18 electrons for the whole N shell and the value of about 11 at the
onset of the $N_{II,III}$ edge are quite reasonable.

Bi

Because of large discrepancies between the measurements of different
authors we have not calculated N_{eff} values for energies below
36 eV. Thus we have chosen rather arbitrarily $N_{eff} = 0$ at 40 eV.
But $N_{eff} = 5$ (the number of valence electrons) should not be very
inaccurate a value at 24 eV where Hunter et al.[22] found the very
sharp onset of O_{IV} transitions. The overall contribution between
24 eV and the saturation at about 200 eV gives about 20 electrons
which is in quite good agreement with the expected value of 19 for
O_V to O_I electrons. ($N_{IV,V}$ absorption should be again shifted to
higher energies as in Au[21,12].) In trusting the position of O_{III}
edge there is a notably high value of about 16 electrons for O_{IV},
O_V contribution compared to an expected value of 10.

Cu is characterized by a rather low absorption coefficient and a
smearing out of the oscillator strength over a region much larger
than that covered by our measurements. Au, Ag, Sn and Bi behave quite
differently from Cu but similar to each other. The saturation
behaviour at the right values of N_{eff} demonstrates quite reasonably
that O-shell (or N-shell) contributions are exhausted at 100 to 150 eV.
However the onset of p electron transitions ($N_{II,III}$ and $O_{II,III}$)

is not at all indicated by a change of slope in the N_{eff} curves. This result is quite unexpected. The N_{eff} we obtain at these edges if we use the atomic values for the position of these edges as given by Cauchois[24] is always too high, especially for Bi, but even for Au, Ag and Sn where it seems quite improbable that an abrupt exhaustion of d electron transitions and an abrupt onset of p electron transitions coincide to give a smooth μ and N_{eff} curve.

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Figure Captions

Fig. 1 Experimental arrangement at the accelerator.

EO = electron orbit, V = valve, BS = beam shutter,

VT = vacuum tube connection between accelerator

and experiment, SH = sample holder, M = mirror,

ES = entrance slit, G = grating, RA = rotating arm,

B = exit slit and open multiplier, Sh = shielding.

Fig. 2 Transmission T of Ag as a function of film thickness

d with and without a 2000 Å thick Al prefilter.

Wavelength 177 Å. K_2 gives the fraction of second

order radiation.

Fig. 3 Copper

a) absorption coefficient μ,

b) effective electron number N_{eff} as a function of

photon energy. The theoretical values by Beaglehole

include only 3d electrons.

Fig. 4 Silver

a) absorption coefficient μ,

b) effective electron number N_{eff} as a function of

photon energy.

Fig. 5 Tin

a) absorption coefficient μ,

b) effective electron number N_{eff} as a function of

photon energy. The zero point of N_{eff} is chosen

arbitrarily.

Fig. 6 Gold

a) absorption coefficient μ,

b) effective electron number N_{eff} as a function of

photon energy.

Fig. 7 Bismuth

a) absorption coefficient μ,

b) effective electron number N_{eff} as a function of

photon energy. The zero point of N_{eff} is chosen

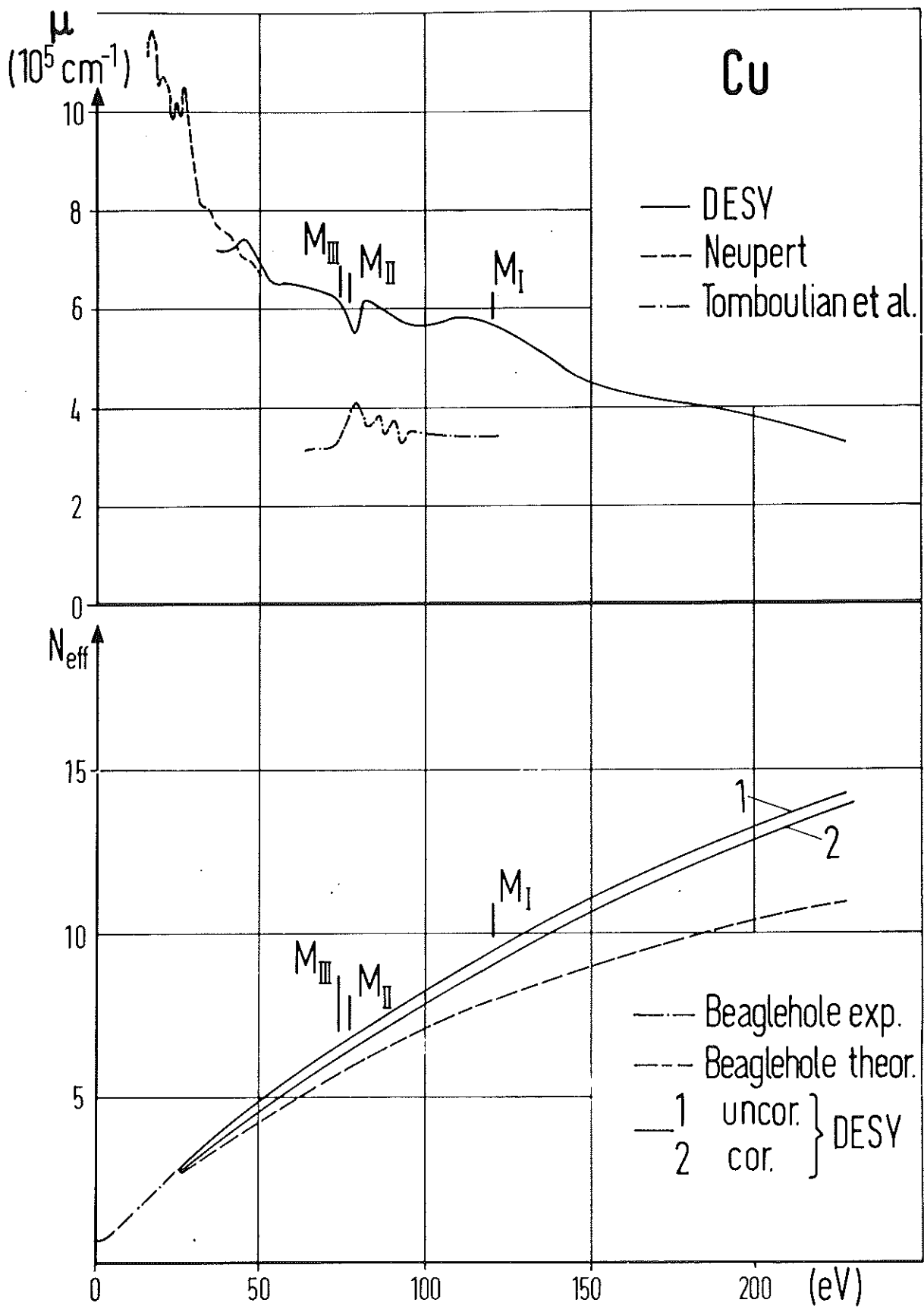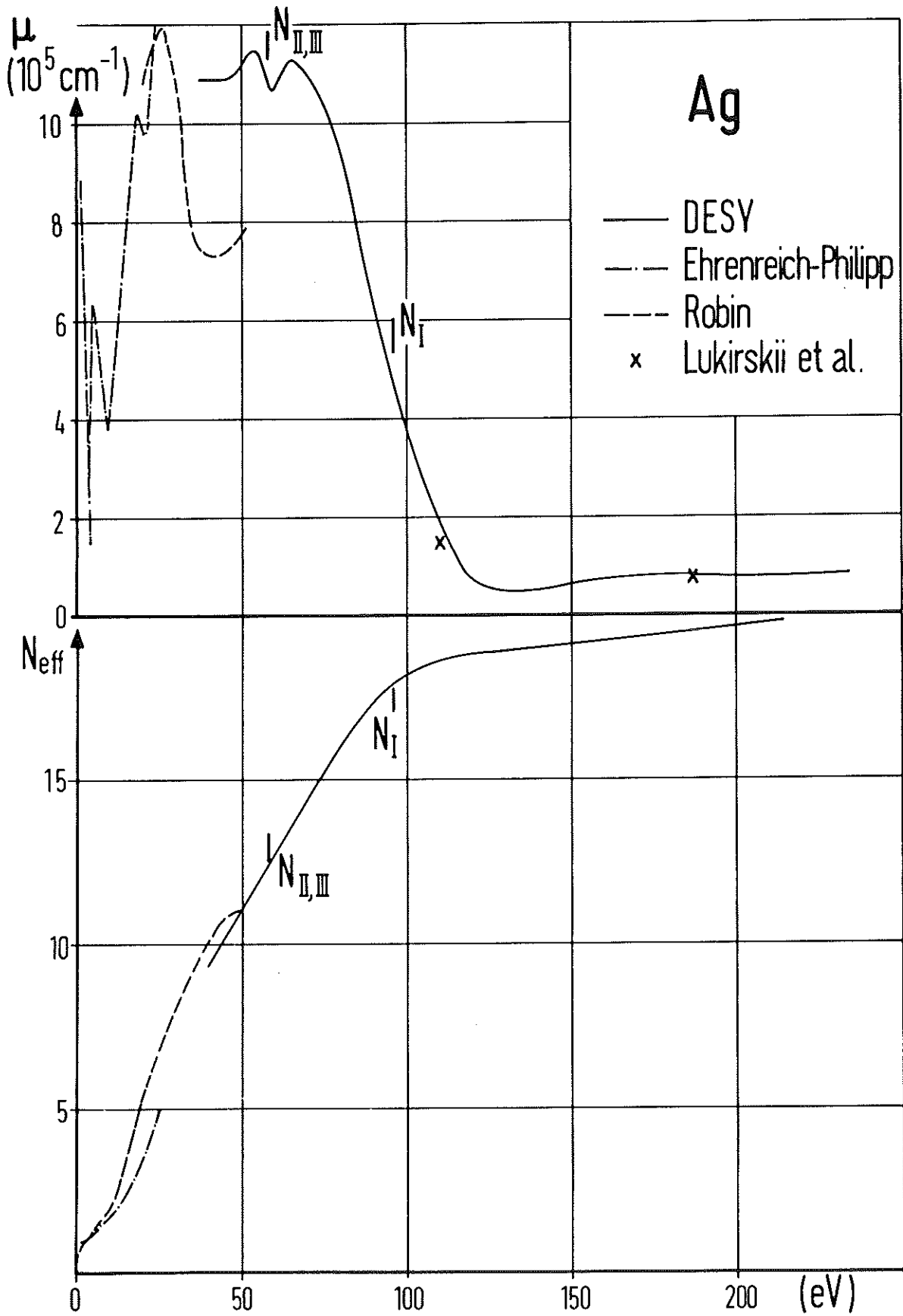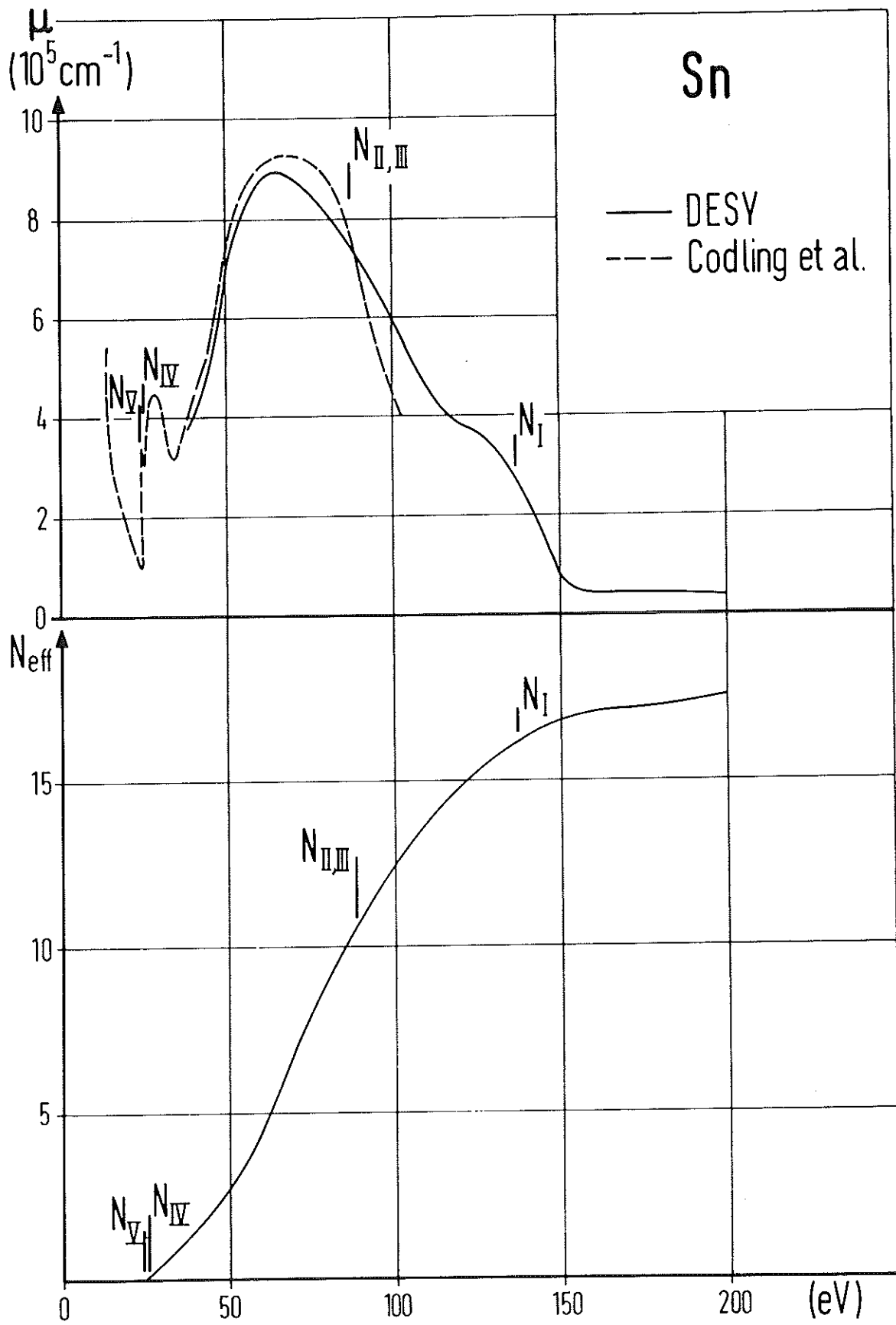arbitrarily.

Figure 1

EO
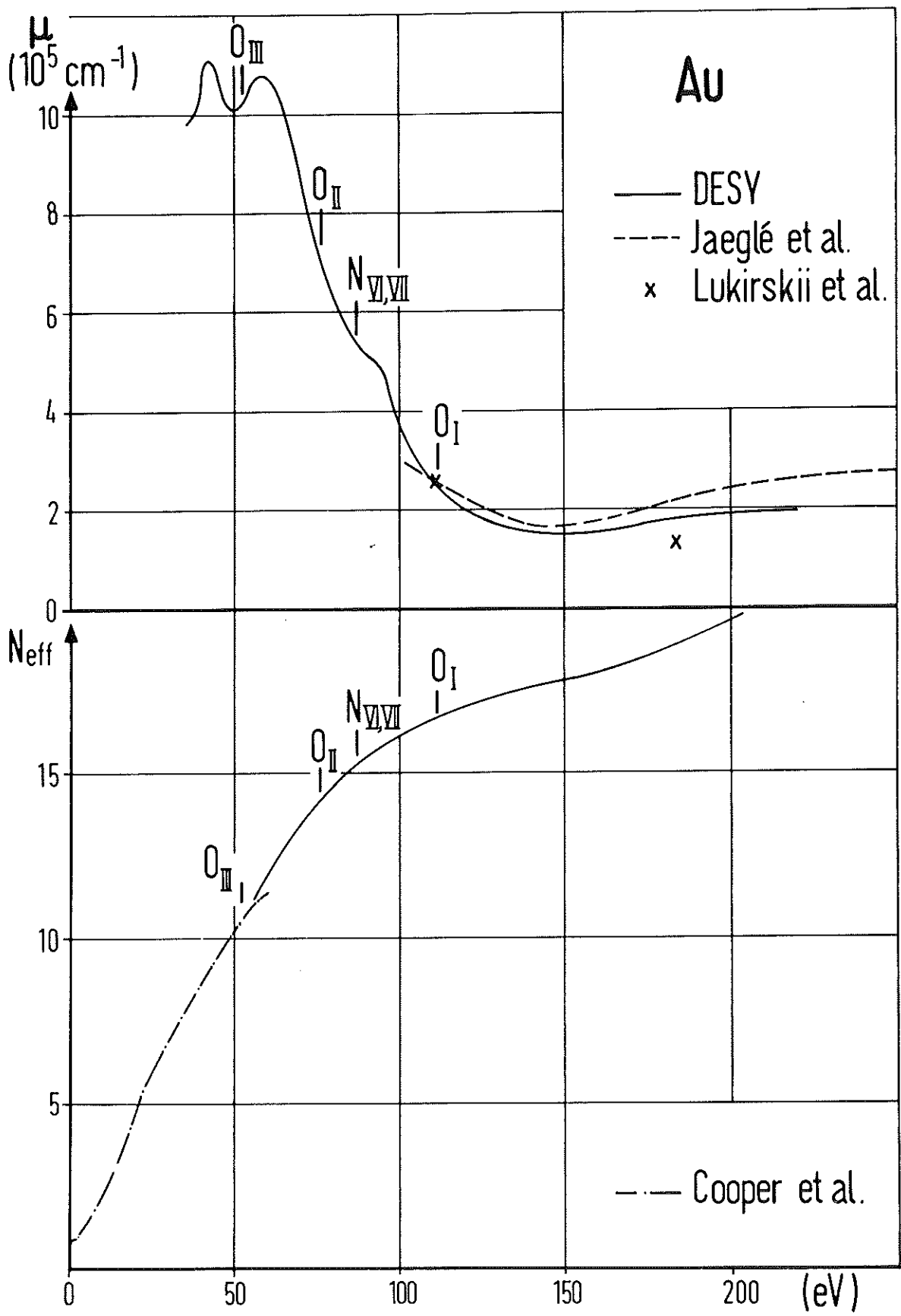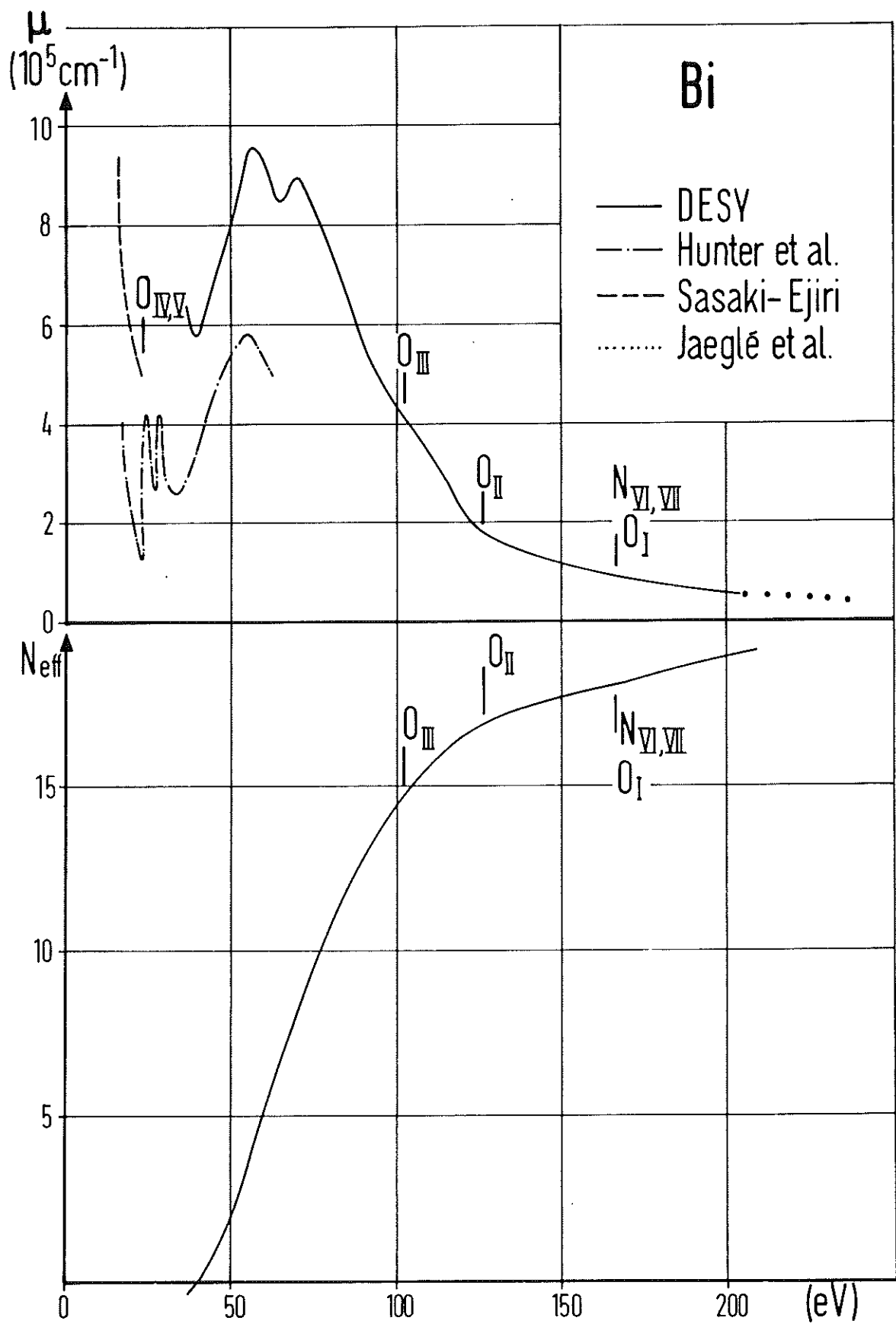
VT

ES M

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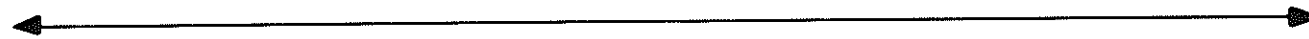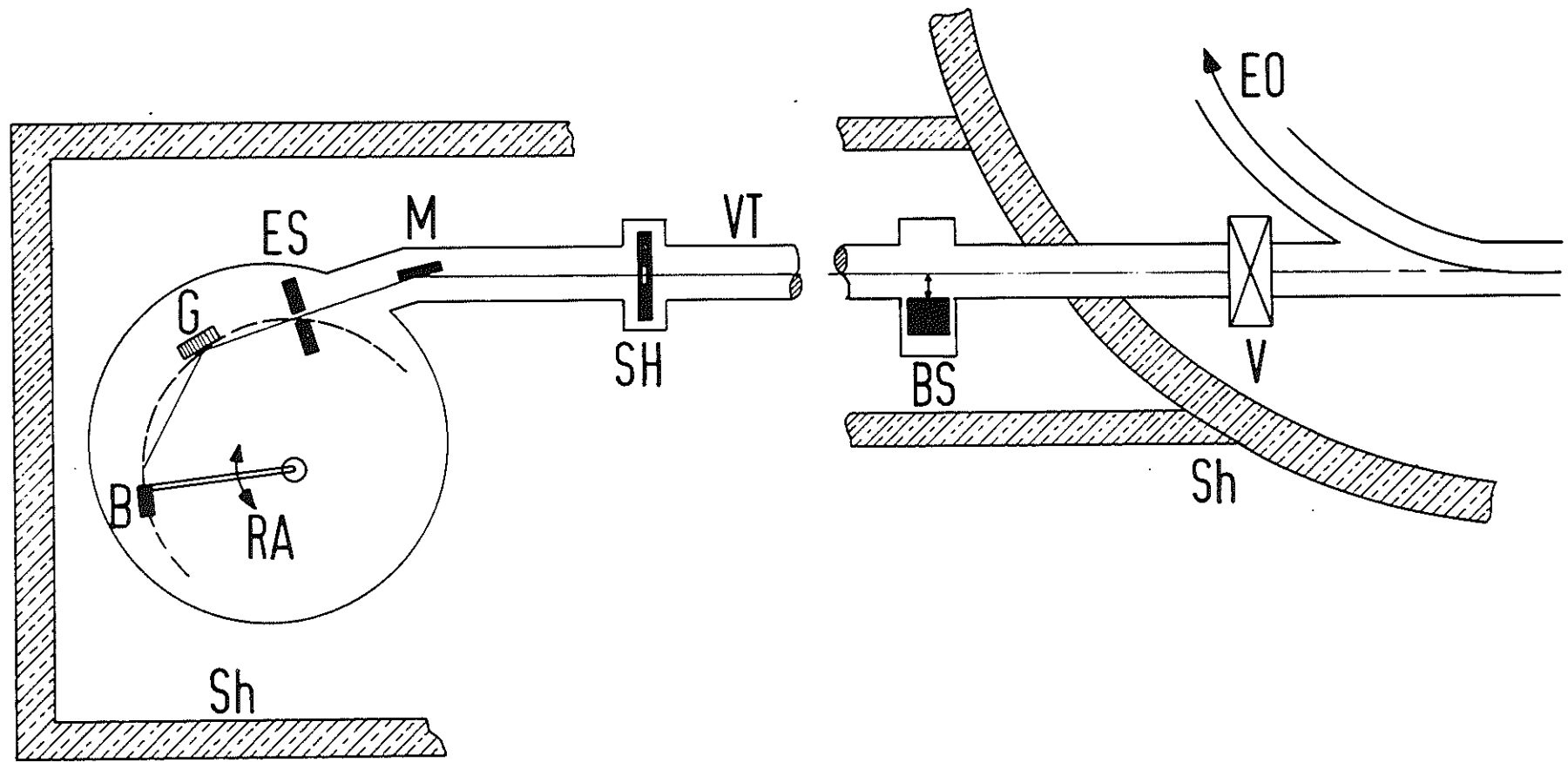
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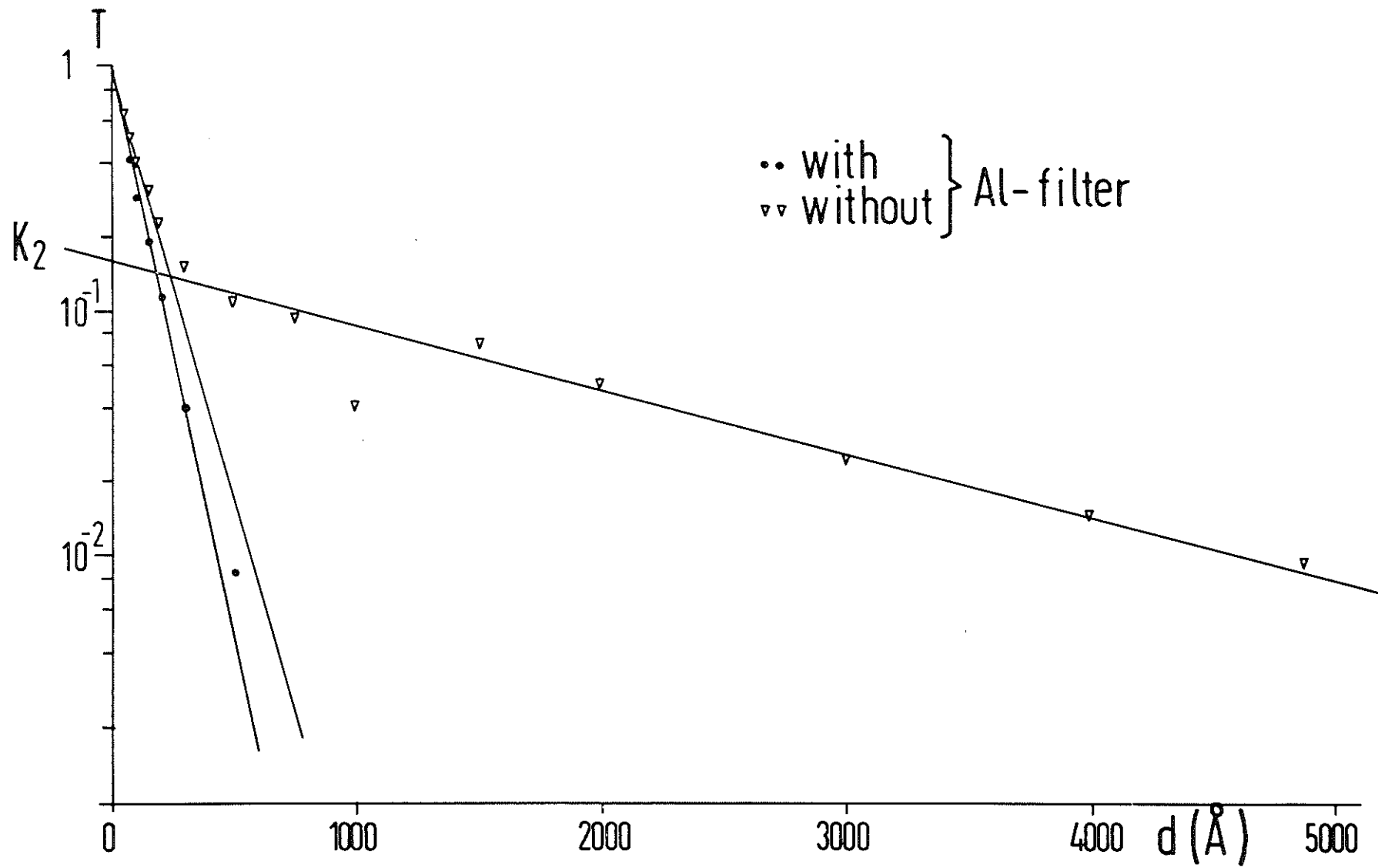
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7