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Soft X-Ray Absorption Spectroscopy of Metals and Alloys

by

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Soft X-Ray Absorption Spectroscopy of Metals and Alloys

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Absorption spectra of transition and light metals in the soft x-ray range were obtained during the past years using the 7.5 GeV electron synchrotron DESY as a light source. The spectra of the transition metals Ti to Ni showed structures which are inconsistent with a simple band model. Recent atomic theories appear to give a much better understanding of these results. The implication from these theories that alloys of transition metals should show mainly a superposition of the individual spectra is supported by our experiments on Cu/Ni and other alloys. - The absorption coefficient of the light metals at the edge is enhanced ("edge singularity") or diminished depending on the symmetry of the excited electrons initial state. This edge feature is followed by both faint structures and prominent broad maxima. First experiments on the influence of alloying on the spectrum of Al near the $L_{2,3}$ edge are described. These investigations led to the development of a differential two beam spectrometer.

1. INTRODUCTION

Electron synchrotrons have found extensive use as light sources for the soft x-ray and the vacuum ultraviolet range during the past few years. With their help a large amount of absorption data on different materials has been accumulated. This paper is concerned with two groups of metals which have been investigated at the DESY synchrotron during the past years. These are the transition metals Ti to Ni near the $M_{2,3}$ edge and the light metals Li, Be, Na, Mg, Al in the region of the K resp. $L_{2,3}$ absorption. These investigations

have recently led us into the investigation of alloys which is still in progress and of which first results will be shown.

2. EXPERIMENTAL

A. Synchrotron Radiation

Synchrotron radiation (see e.g. Haensel and Kunz (1967), Godwin (1969), Gähwiller et al. (1970)) is emitted tangentially to the orbit of the electrons in a narrow-cone. It is highly polarized and its spectral intensity can be calculated in absolute terms from the known number of circulating electrons. The spectrum is smooth and extends at a 7.5 GeV accelerator like DESY down to $\sim$405 Å. Figure 1 gives the useful flux of photons at the synchrotron laboratory of DESY at 40m from the source into a 2 cm wide collimator. The vertical extension of the beam depends on the wavelength but is typically $\pm$2 cm.

Figure 2 shows the light beam arrangement at DESY. The experiments need to be directly connected to the synchrotron by a high vacuum system. The incoming beam is divided by grazing incidence mirrors into three separate beams and on each of them several monochromators and spectrographs are arranged. Because of radiation safety requirements all instruments have to be operated by remote control. In addition precautions are necessary to protect the accelerator from vacuum hazards. All this renders the arrangement to be by fare more complex and complicated than an ordinary x-ray tube.

Nevertheless advantages are such that presently more than a dozend synchrotron radiation (SR) laboratories are in operation or planned all over the world. Table I gives a survey on these installations. For those who do not want to penetrate too much into the details of synchrotron radiation theory but rather

wish to get a rough estimate of the intensity and the spectral distribution of radiation for a specific accelerator two equations might be useful:

$$(1) \qquad \lambda_c(\text{Å}) = 5.59\ R(m)\cdot\left(E(GeV)\right)^{-3}$$

$$(2) \qquad I\left(\frac{\text{photons}}{\text{sec}\cdot\text{eV}\cdot\text{mA}\cdot\text{mrad}}\right) = 4.5\cdot 10^{12}\cdot j(mA)\cdot\left(R(m)\right)^{1/3}\cdot\left(E_{phot}(eV)\right)^{-2/3}$$

Equation (1) gives the parameter λ_c commonly referred to as cut-off wavelength. Radiation has been used down th $\lambda \cong \lambda_c/10$ but intensity is very much down at this wavelength as can be seen from Fig. 1.

Equation (2) gives the number of photons emitted into a 1 mrad wide horizontal angular sector and a 1 eV energy intervall for the asymptotic region $\lambda >> \lambda_c$ (the dashed part in Fig. 1). Note that Eq. (2) is independent of the electron energy E. Since the dependence on the radius R is so weak a good rule of thumb is to compare intensities from different synchrotrons and storage rings by just comparing the currents j. For accelerators the nominal current has to be multiplied by an appropriate duty cycle.

For spectral decomposition of the synchrotron light we used a grazing incidence Rowland monochromator and a fixed exit slit, plane grating monochromator which was especially developed for this purpose. The second instrument (Kunz et al. (1968), Dietrich and Kunz (1971)) is capable of suppressing higher order radiation.

B. Film Preparation

Metal films were prepared by evaporating onto organic substrate films or onto Al films. The highly oxidizable metals were prepared in situ. The alloy films were evaporated simultaneously from two sources under the control of an

oscillating quartz monitor onto collodium substrates. In several cases these films were embedded between two 50 - 100 Å thick carbon films and the collodium was dissolved afterwards.

3. TRANSITION METALS

A. Pure Metal Spectra

The spectra of the transition metals Ti to Ni were investigated in the region of the 3p electron transitions (Sonntag (1969), Sonntag et al. (1969)) and are reproduced in Fig. 3. All spectra are characterized by a big prominent structure. Indeed a prominent peak is expected from a one electron model because of the unfilled 4d states in these metals into which the 3p electrons should be preferably excited. The observed structure, however, is by far too broad (eg. 25 eV in Cr) to be identified with the density of unfilled d states which should extend over an energy range of less than 4 eV. A similar situation occurs for several transition metals from the third series (Haensel et al. (1969a)) and for the empty f states of the rare earth metals (Haensel et al. (1970b)), when exciting d electrons. In contrast the $L_{2,3}$ absorption spectra of the transition metals Ti to Ni show a width of only a few electron volts. (Bonnelle (1968)).

The fact that the magnitude of the structure is considerably reduced in the spectrum of Cu where the d shell is filled shows that this structure definitely has its origin in the empty d states. Already ESCA measurements by Fadley and Shirley (1970) have demonstrated a possible mechanism for the spreading of oscillator strength over a wider energy range. Exchange interaction between the unfilled d shell and the 3p hole could split the excited state into several lines. Dehmer et al. (1970) have put this onto a sound theoretical base. Their model calculation shows that exchange splitting could amount to as much as 20 eV. In order to account for the fact that almost nothing of this line structure is left in the spectra one needs

to assume that autoionization interaction with the background continuum broadens and smeares the structure (Fano and Cooper (1969)). Features at the onset of the Mn and Co spectra and the Pt spectrum (Haensel et al. (1969a)) remind of the typical depression known from some of the autoionization line shapes (Fano and Cooper (1968)). The smaller width of the $L_{2,3}$ absorption spectra (Bonnelle (1968)) seems to be understandable because of a much weaker exchange interaction between states in shells with different main quantum number than of those with the same main quantum number.

B. Alloys

If thus the shape of the spectra is mainly determined by an intra-atomic phenomenon the question arises, how much of the spectrum is determined by band effects at all. We have therefore investigated the spectra of alloys of different transition metals with each other. We have compared the transmission spectrum of an alloy film directly with that of a sandwich film containing both constituents on top of each other.

Figure 4 shows our result (Gudat and Kunz (1971)) for Cu/Ni 1:1. Within the experimental accuracy no difference can be detected. This indicates that in the alloy the spectra of both atoms are superimposed proportionally. Both types of atoms behave independently. Similar results were obtained for alloys of Cr/Mn and Fe/Mn. The samples were prepared by simultaneous evaporation from two sources without any subsequent annealing of the films. Although the metallographic structure of the films is not very well defined in such a case this seems to be irrelevant for the conclusions we have arrived at.

A similar insensitivity of the emission spectra of the transition metal alloys on composition has been reported by Curry et al. (1968). All this shows that atomic theories give a good first order approach to the interpretation of these spectra.

4. LIGHT METALS

A. Pure Metal Spectra

Figure 5 shows the $L_{2,3}$ absorption spectrum for Al (Haensel et al. (1970a)) as being a characteristic example of the similar ones of Na and Mg. At the edges (which are split into L_2 and L_3) a sharp peak is observed similar to more prominent ones in Na and Mg. The edge is followed by small structures which could have to do something with density of states effects although they have not yet been identified to our knowledge. The structure culminates in a broad prominent maximum at about 100 eV which is followed by several other broad maxima. This structure for Al was reported already by Fomichev (1967) and has not yet found any convincing explanation. The maxima are absent in one electron atomic calculations (see Fig. 5) and recent measurements on Na vapour (Haensel et al. (1971)) do not show them either.

The structure at the edges is shown in more detail in Fig. 6 (Haensel et al. (1969b), Kunz et al. (1970), Gähwiller and Brown (1970), Ejiri et al. (1970)). The L spectra show a steep increase with a peak at the edge while the K edges rise rather smoothly. This bears great similarity to the edge structure of the equivalent emission spectra. This behaviour has been attributed (Mahan (1967), Nozières and Dominicis (1969), Friedel (1969), Hopfield (1969) and others) to the influence of the unshielded part of the hole potential not only on the ejected electron but on all the metal electrons. The explanation of this phenomenon goes beyond the one-electron approximation. If the core level is a p-state the result is a singularity of μ at the edge. The shape of the cross section in the region immediately following the edge is:

$$\mu \propto \frac{1}{\Delta E^{\alpha}} \qquad (3)$$

ΔE is the distance from the edge and α is a positive exponent equal to ~ 0.5 (Ausman and Glick (1969)). (Actually a prominent peak rather than a singularity is expected due to Auger and temperature broadening.) On the other hand no singularity should occur at the onset of an s-electron transition. For these transitions α is expected to be negative but of small absolute magnitude. The theoretical results are complementary in emission and absorption.

It should be mentioned however that the peaks in emission are much weaker than in absorption and the absolute magnitude of the spike has still to be calculated theoretically.

B. Alloys

It seems to be promising to use such sharp edge materials as Na, Mg and Al both as a solvent and as a solute for low concentration alloys. We and also a Japanese group (Yamaguchi et al. (1971)) have started alloy measurements using aluminum as the host. The measurements of Yamaguchi et al. show clearly the disappearance of the edge-peak and a softening of the edge structure when alloying Ni and Mn into Al.

We have investigated Al/Au and Al/Ti alloys (Gudat et al. (1971)) which were prepared by simultaneous evaporation of the two constituents. Figure 7 shows our result. The alloy spectrum is compared to a sandwich film of equivalent composition. The resolution in the present experiments was not sufficient to observe the edge peak. Clearly a broadening and a shift of the edge can be seen even with this low resolution. The shoulder at ~ 85 eV seen also in Fig. 5 has disappeared. An additional absorption at ~ 2.4 eV from the edge shows up (~ 2 eV with Ti). Since the metallographic state of the samples which were not annealed

is not well enough defined we do not want to go into any physical interpretation of these results at the present stage.

The main interest in these measurements was to test a differential two beam densitometer for the soft x-ray range (Fig. 8). A beam splitter is mounted behind the exit slit of our monochromator. The beam splitter consists of a rotating mirror which is rotating in synchronism with the pulsed emission from the synchrotron. The transmissivities ($T_{1,2}$) of two films are compared with each other. By a lock-in technique the quantity $(T_2-T_1)/(T_2+T_1)$ is measured directly. Figure 7 also shows this spectrum in reasonable agreement with the directly obtained spectra. We hope to improve the method so that we shall be able to measure this quantity with an accuracy of 10^{-3}. This should enable us to measure low concentration alloys where theoretical interpretation has developed farthest.

5. CONCLUSION

The foregoing examples of absorption measurements have shown that the absorption spectra of these metals cannot be considered simply as a reflection of the density of unoccupied states. The hole created during the absorption process causes a non-negligible disturbance to the final states (through exchange interaction in the case of the transition metals, through the unshielded part of its potential in the light metals causing the edge-peak). The wide spread attitude to regard such spectra as slightly distorted density of states curves appears to be open to critism (see especially Harrison (1968)). Nevertheless interesting phenomena occur which deserve attention at their own right.

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Table I: Accelerators and storage rings used as light sources

Projects	E(GeV)	R(m)	I(mA)	λ_c (Å)	Remarks
NBS (Washington)	.18	.83	1	800	
INS-SOR (Tokyo)	1.3	4.0	30	10	
Frascati	1.1	3.6		15	
DESY (Hamburg)	7.5	31.7	10-30	.3	
Wisconsin Storage Ring	.24	.54	10	220	exclusively used as a light source
Glasgow	.33	1.25	0.1	195	
Bonn	2.3	7.65	30	3.5	
Moscow	0.66	~3		60	
DNPL (Daresbury)	4.0	23.8	40	1.8	SR-Lab near completion
INS-SOR (Tokyo) Storage Ring	0.3	1	100	200	planned for exclusive use as light source starting ~ 1973/74
ACO (Orsay) Storage Ring	.6	1.1	500	30	SR-Lab planned for ~ 1973
SLAC (Stanford) Storage Ring	2.5 (3.5)	12.7	250	4.5	SR-Lab planned for ~ 1973
DESY (Hamburg) Storage Ring	1.75 3.5	12.12	6000 200	12.7 1.58	SR-Lab planned for 1973/74

Figure Captions

Fig. 1 Spectral distribution of photons emitted into a vertical 2 cm wide slit at 40 m distance from the electron beam as a function of photon energy. The dashed line gives the asymptotic behaviour for $\lambda \ll \lambda_c$.

Fig. 2 Arrangment of the DESY synchrotron radiation laboratory. The beam is split into several sub-beams by grazing incidence mirrors. Presently about ten monochromators and spectrographs are operated at the facility. EO = electron orbit, CH = chopper, M 1-3 = mirror, B 1-2 = beam shutter, X-DIFF = X-ray diffractometer, UHV S = UHV sample chamber, S = sample, FM = focussing mirror, R 1-3 = Rowland spectrograph, PG = DESY spectrograph, X-MONO = X-ray monochromator, S M-VAP = metal vapous, W 1-4 = Wadsworth monochromator.

Fig. 3 Absorption coefficient for the elements Ti to Cu in the $M_{2,3}$ region. (Reproduced with permission from Kunz (1971)).

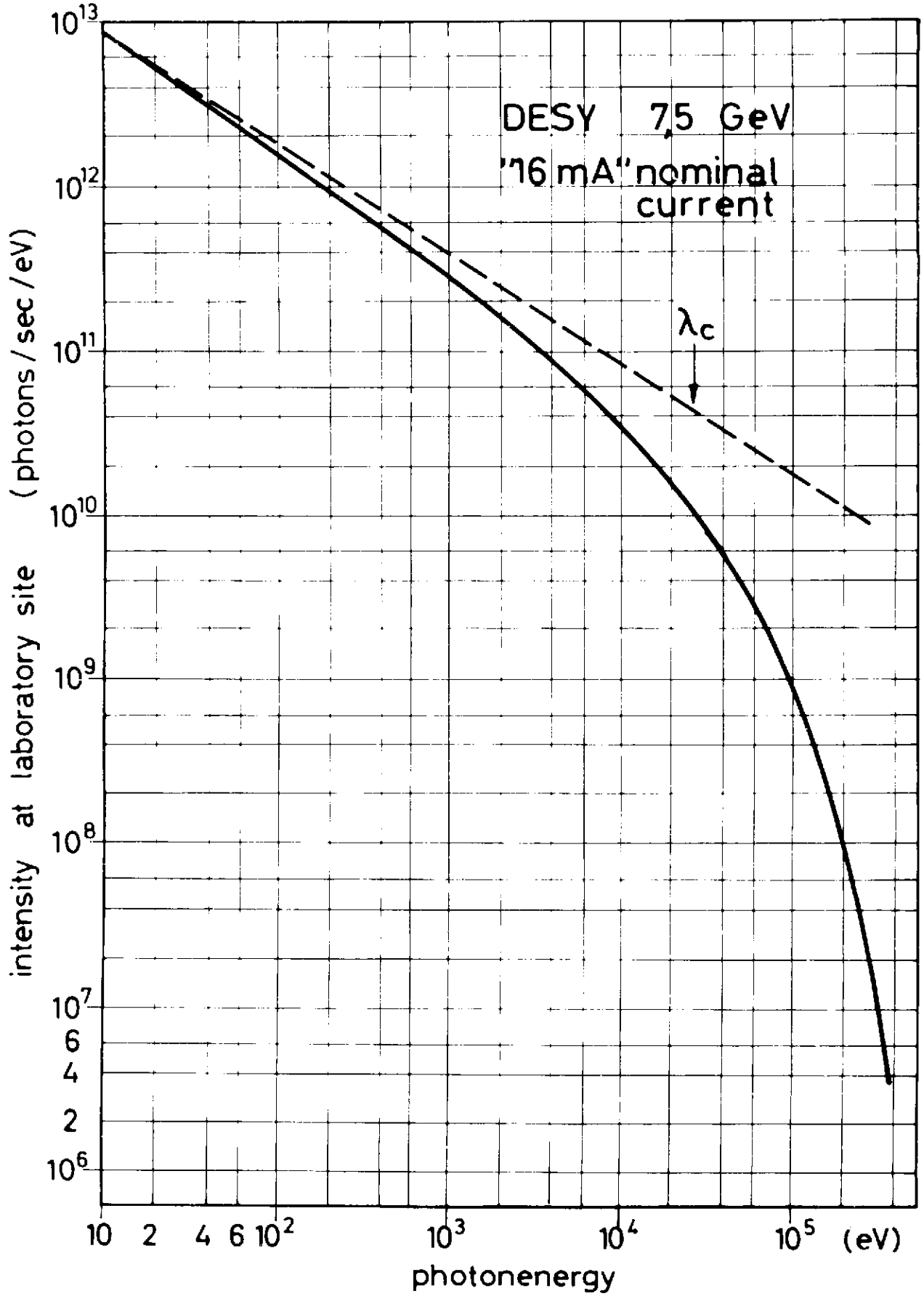
Fig. 4 Original spectra of a Cu/Ni alloy and a Cu+Ni sandwich film. In order to obtain a real transmission spectrum the curves would have to be divided by the spectrum shown as a dashed line. The insert shows the measuring technique. M1 is a combined multiplier and reflector.

Fig. 5 Absorption coefficient μ of Al in the $L_{2,3}$ region. The dashed curve gives atomic calculations (Cooper (1967) private commun.) (After Haensel et al. (1970)).

Fig. 6 Shape of the $L_{2,3}$ edges of Na, Mg, Al and the K edges of Li and Be. (Reproduced with permission from Kunz (1971)).

Fig. 7 Spectra of an Al/Au alloy and an Al+Au sandwich film. The insert shows an original spectrum measuring the difference in the transmissivities of the two samples divided by the average. This was done using the beam splitting technique shown in Fig. 8.

Fig. 8 Beam splitter for the soft x-ray range behind the exit slit of the DESY monochromator (Dietrich and Kunz 1971, Kunz et al. 1968). Alternative light pulses transmit the upper and lower foils. Lock-in amplifiers serve to extract $(T_2-T_1)/(T_2+T_1)$ where $T_{1,2}$ are the transmissivities.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λ_c
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photonenergy
(eV)
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10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
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6
10^{2}
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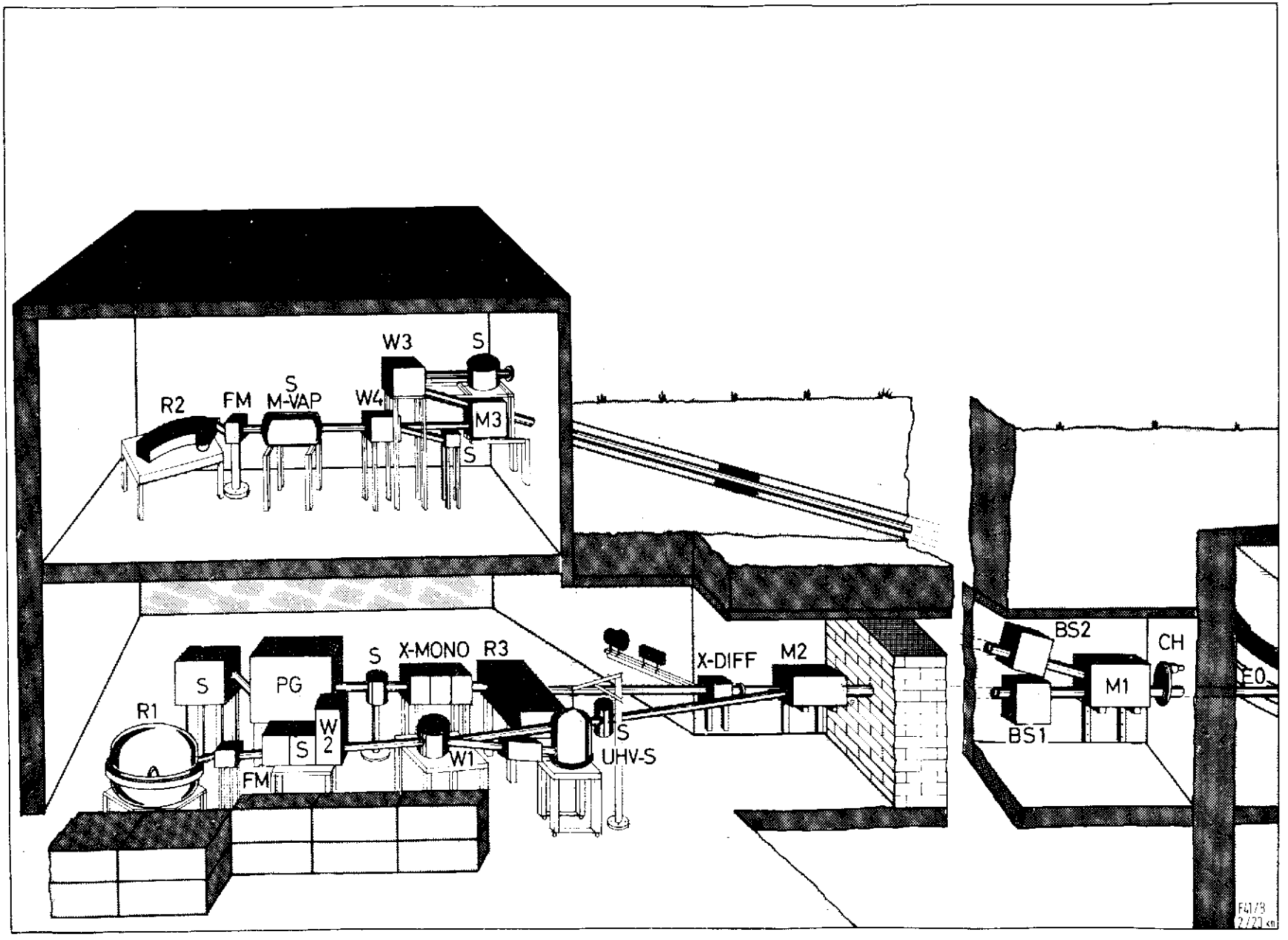
10^{4}
10^{5}

Fig. 1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FM
S
M-VAP
W4
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R3
X-DIFF
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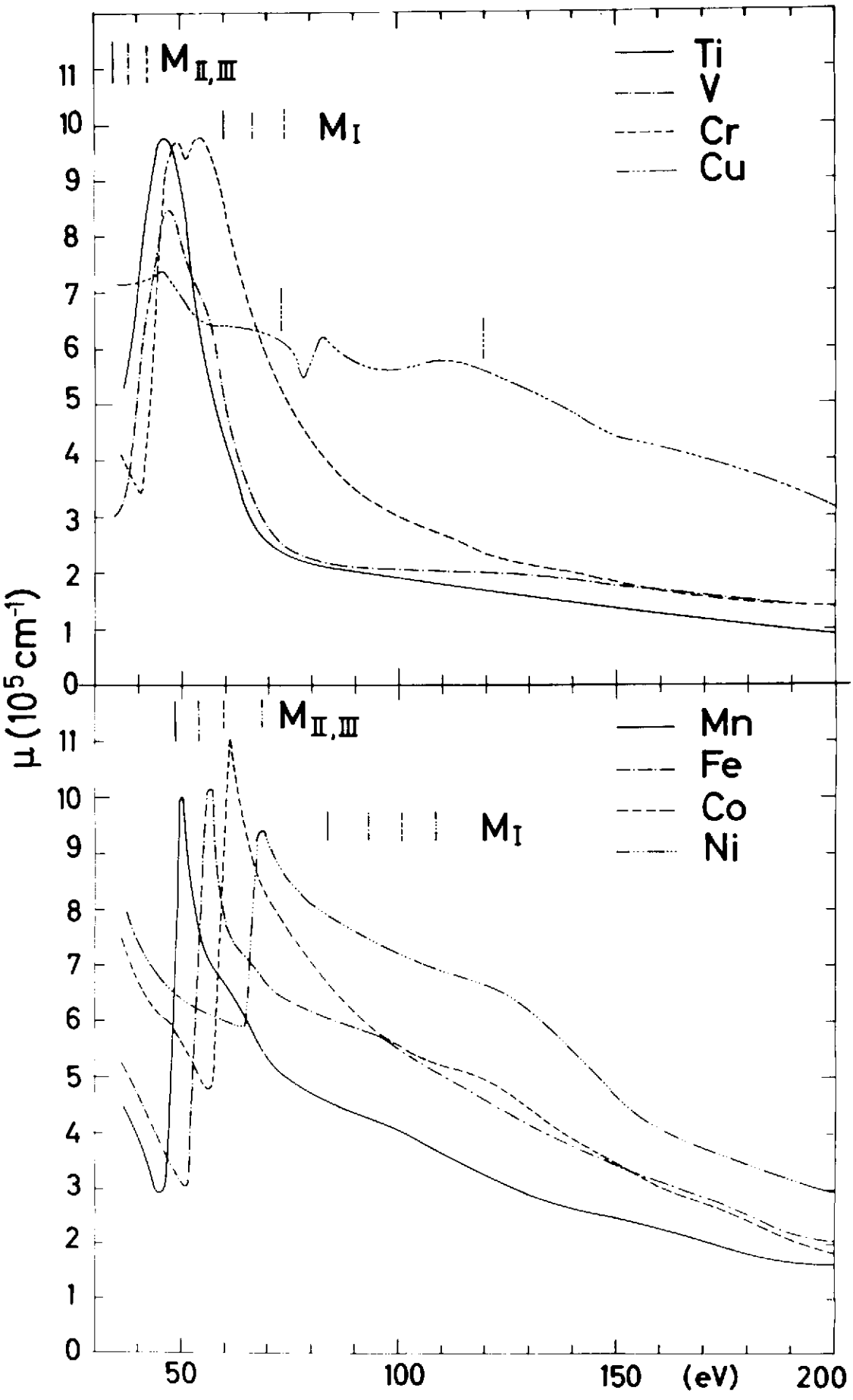
W1
BS1
FM

Fig. 2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Ti
V
Cr
Cu
Mn
Fe
Co
Ni
$\mu(10^5 cm^{-1})$
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3
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7
8
9
10
11
50
100
150
(eV)
200

Fig. 3

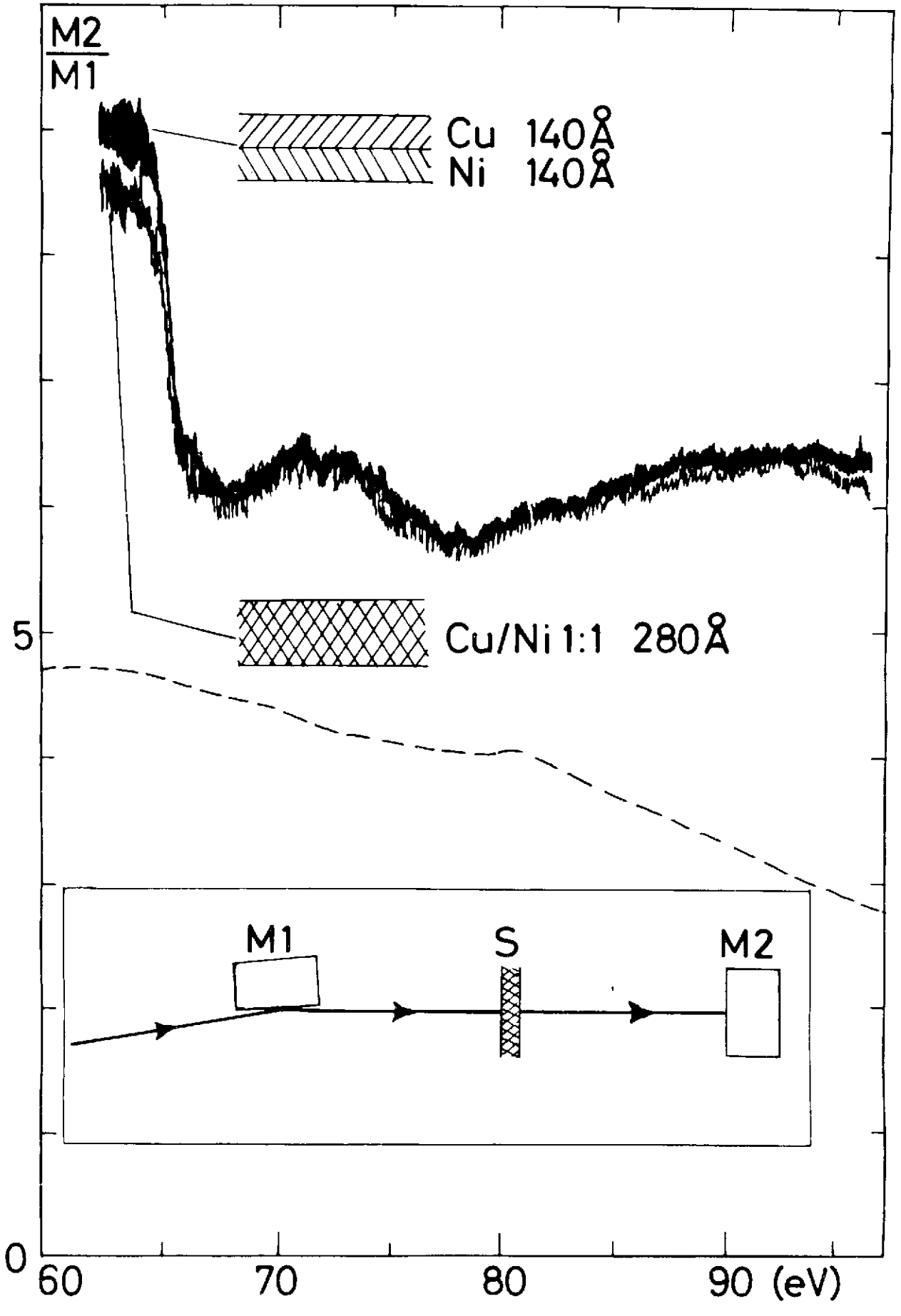
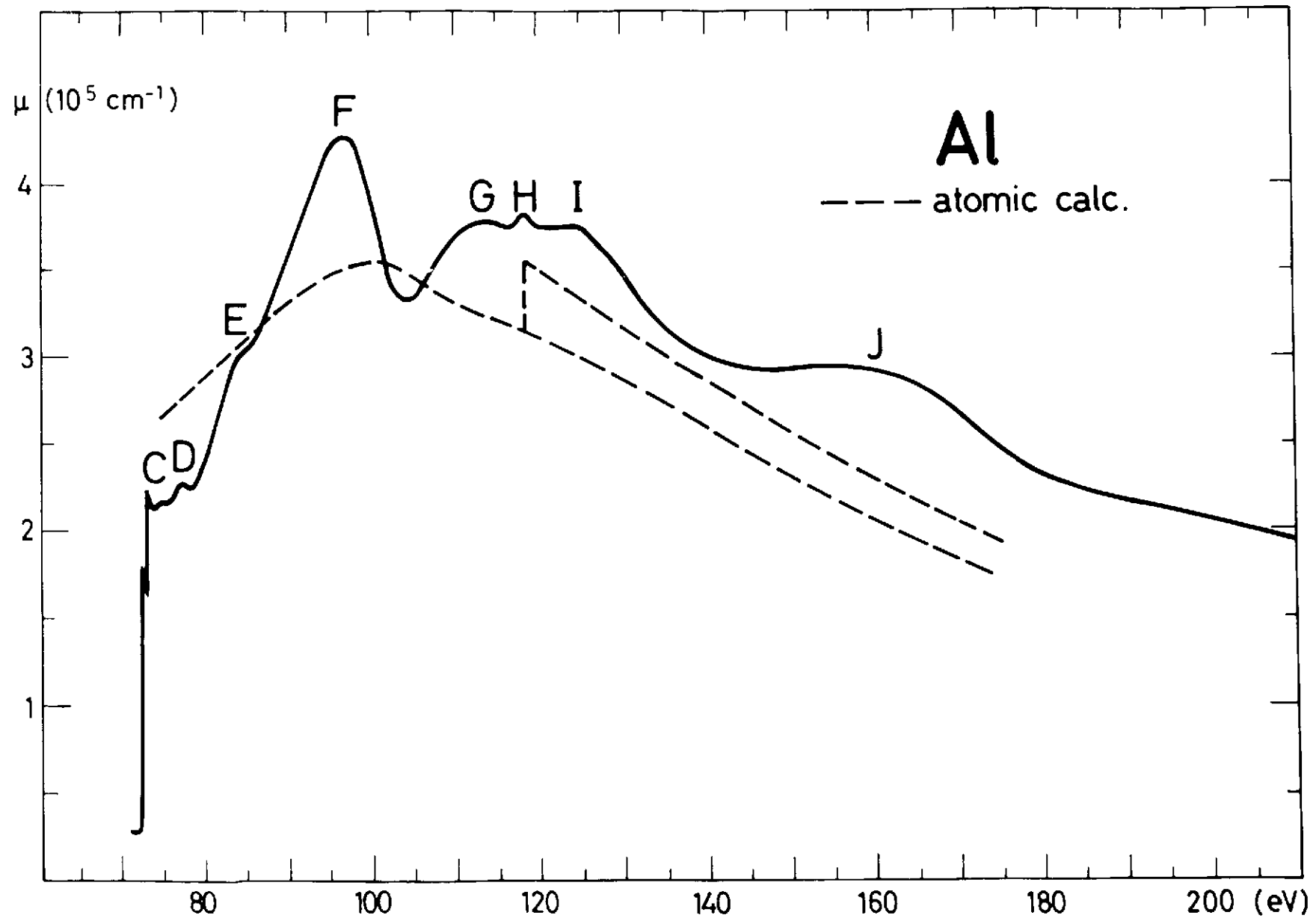


Fig. 4


μ (10⁵ cm⁻¹)
Al
atomic calc.
C
D
E
F
G
H
I
J
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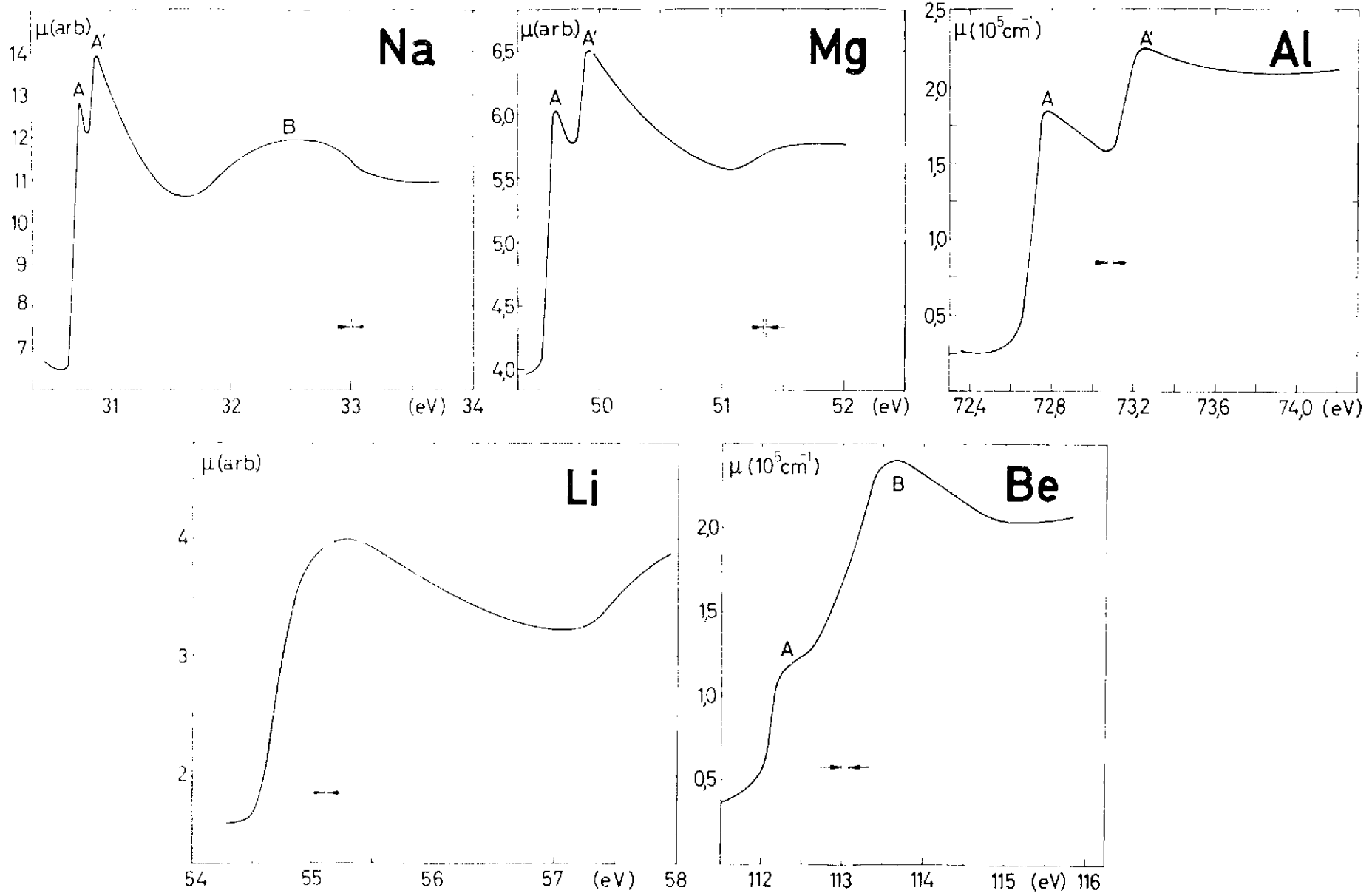
2
3
4
80
100
120
140
160
180
200 (eV)

Fig. 5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A'
B
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A
A'
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6,0
5,5
5,0
4,5
4,0
34
50
51
52
(eV)
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μ(10⁵cm⁻¹)
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A'
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1,0
0,5
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72,8
73,2
73,6
74,0 (eV)
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3
2
54
55
56
57
(eV)
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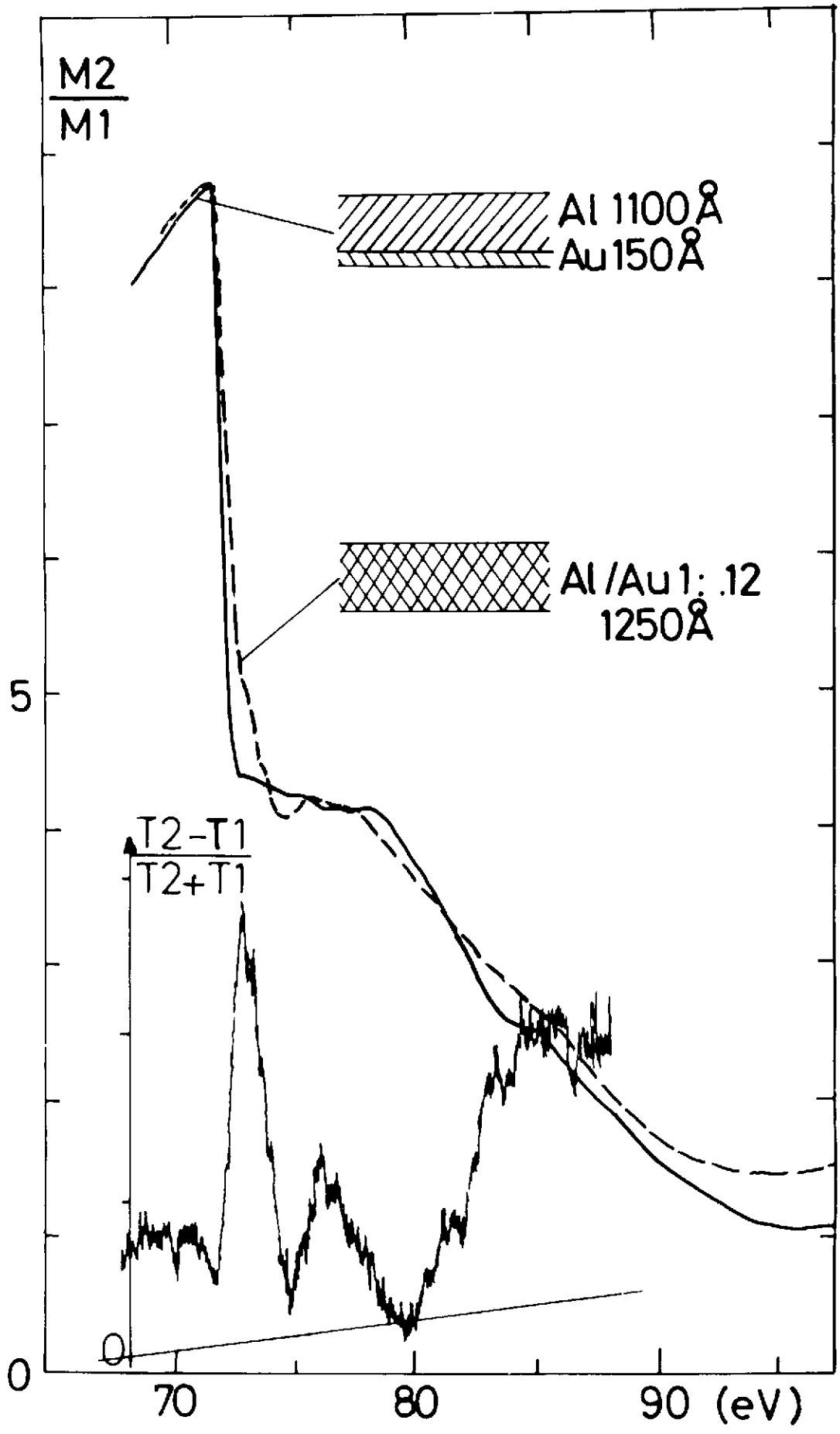
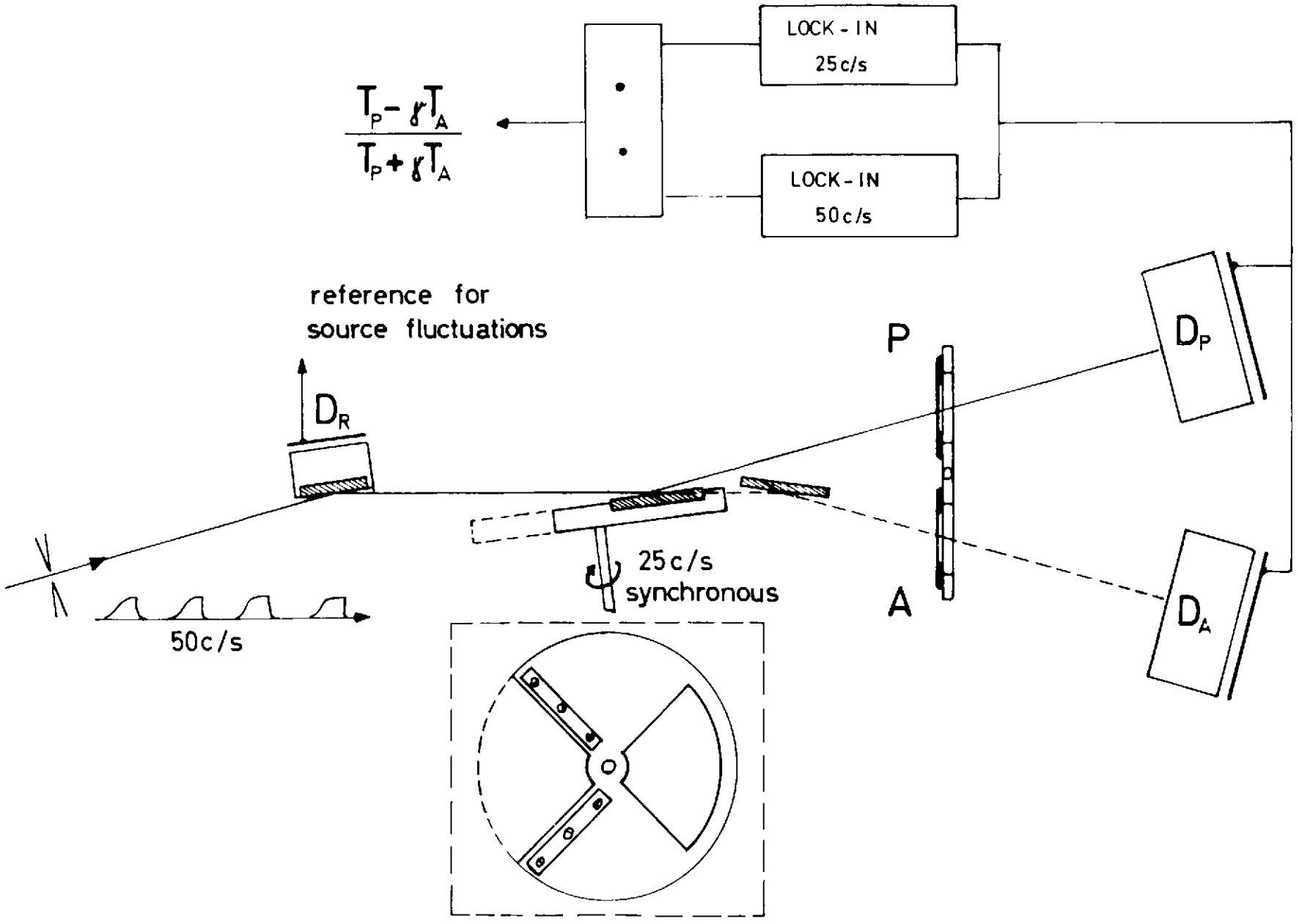


Fig. 7


LOCK - IN
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reference for
source fluctuations
D_R
P
D_P
D_A
A
25 c/s
synchronous
50 c/s

Fig. 8