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REFLECTION SPECTRUM OF SOLID KRYPTON AND XENON IN THE VACUUM ULTRAVIOLET[†]

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The reflectance of solid Kr and Xe has been measured at 25° K and 40° K, respectively, for an angle of incidence of 15° for photon energies between 8 and 28 eV using the synchrotron radiation of DESY. Below 14 eV, a region also covered by previous absorption measurements additional spectral features have been observed. The reflectance at higher energies reveals prominent peaks for both rare gas solids. The reflectance spectra are compared with previous absorption and electron energy loss experiments.

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Introduction

For several years attention has been focused on the optical properties of the rare gas solids. Solid Krypton and Xenon have been investigated by means of absorption measurements (1, 2). Electron energy loss experiments corroborated the results in the case of Xe. (3). All these experiments showed a rich structure above the onset of absorption (10 eV for Kr and 8 eV for Xe). The resonances were attributed to excitonic and interband transitions from the valence band formed by 4p and 5p electrons respectively (4-7).

Baldini's extensive absorption studies (2) were performed at photon energies up to 14 eV with a line source which imposed a restriction on the resolution, especially at higher energies. Keil's electron energy loss experiments on Xe (3) covered the region up to 44 eV; a relatively poor resolution, however, was obtained as compared to the optical investigations. The improvement which could be achieved on the spectrum of solid Argon (8) with a simple reflection technique using synchrotron radiation stimulated the reinvestigation of the fundamental electronic excitations of Kr and Xe with this technique and the extension of the energy range up to 28 eV.

Experimental Layout and Results

The synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY (9) was monochromatized by a normal incidence monochromator in a modified Wadsworth mounting (10). The Kr and Xe were evaporated as thin films of unknown thickness onto a KCl single crystal and onto a glass plate cooled down in a He-cryostat. No significant influence of the different substrates on the reflectance could be observed. The light reflected from the solid rare gas surface was detected with an open photomultiplier Bendix 306. Cryostat and multiplier were mounted into a modified commercial ultra high vacuum system (11). Outside the cooled cryostat the chamber pressure was 5×10^{-8} Torr. The Kr and Xe being used for evaporation were of commercial origin with a purity of 99.997 % (L'Air Liquide).

The reflection spectra obtained between 8 and 28 eV are shown in Figs. 1, 2, 3 and 4. The results given by Baldini (2) and Keil (3) are shown for comparative purposes. The peak positions are compiled in Table I. While the spectral distribution of the light emerging from the exit slit of the monochromator was taken into account no absolute calibration was made during the measurements. Therefore the reflectance is given in arbitrary units. A rough estimation based on the KCl reflectance at room temperature (12) gave about 30 % at 10.14 eV for Kr and 15 % at 8.38 eV for Xe. These values, however, may be incorrect by a factor of 2. The peak heights varied slightly according to evaporation conditions (temperature of the substrate and speed of evaporation). In the figures we have reproduced those spectra obtained during continuous evaporation or immediately after evaporation. The relative heights were in general reproduceable within 10 % over the whole spectrum. Differences in the reflectance of the order of 2 %, however, could be clearly detected for photon energies a tenth of an eV apart. The absolute energy positions of the peaks are accurate within ± 5 Å, i.e. about 0.05 eV at 10 eV; the relative distances from peak to peak are more accurate, namely ± 1 Å, i.e. 0.01 eV at 10 eV. The spectral resolution of the monochromator was about 2 Å over the whole energy range.

Discussion

a) Krypton

For Kr an overall agreement with the absorption measured by Baldini can be stated for the low energy part of the spectrum (Fig. 2). However, there are several more details revealed in the reflectance spectrum among which the peak A, the two shoulders E and F and the peak M are the most prominent. Figure 1 shows the whole measured spectrum with prominent new peaks (P, Q, T) in the higher energy part.

In discussing the results at the onset of the spectrum the interpretation of Baldini's absorption measurement can be followed. We assign the sharp peaks between 10 and 13 eV to a spin-orbit split exciton series from the valence band to the bottom of the conduction band at the Γ point of the Brillouin zone. The assignment for the two Rydberg series, according to the equation $E = E_o - G \cdot n^{-2}$, is indicated in Fig. 2 and given in Table I. Here E is the energy of the peak, E_o the series limit (shown as arrows in Fig. 2), G the binding energy and n the quantum number (13). For the evaluation of E_o and G we use the $n=2$ and $n=3$ members of the series which gives values for $E_o(3/2) = 11.7$ eV, $G(3/2) = 1.6$ eV, and $E_o(1/2) = 12.4$ eV, $G(1/2) = 1.7$ eV, respectively. The inclusion of the well resolved $n=3$ members of the series in the calculation explains the slightly different values for E_o and G as compared to those of other authors (2, 6).

Peak A does not fit into this exciton series. Whereas it is apparently absent in Baldini's spectra it has been observed by Schnepp and Dressler (1) who have assigned the peak to a forbidden transition ($\Delta J=2$). This transition occurs in the gas at 9.9 eV (4). The sequence of the peaks A, B, C, D seems to be repeated in E, F, G, and H when the peak heights and energetic differences with regard to the main peaks C ($\Gamma 3/2$) and G ($\Gamma 1/2$) are compared. As yet we have no sound explanation for this resemblance.

The decrease of the reflectance at about 18 eV may be associated with the plasma energy of the 4p-valence electrons. At the present state of theoretical knowledge one can not expect to unambiguously interprete the features of the high energy part of the spectrum.

b) Xenon

Figure 3 shows the reflectance spectrum for Xe, Fig. 4 the low energy part of it in an extended scale. Again, at first sight, this spectrum agrees with Baldini's absorption spectrum below 12 eV, but there are some new features, the most striking one being the appearance of two peaks A and D on the low energy side of the sharp peaks C and E. Furthermore, there is a broad shoulder H in front of the peak J instead of two resolved small peaks in the absorption spectrum. On the other hand, there are two peaks around 9 eV, whereas only one in the absorption data. Up to approximately 15 eV, where the reflectance becomes markedly smaller, we find many characteristic peaks. Baldini (2) realized that the Xe spectrum strongly depends on annealing and temperature, so that some differences between Baldini's and our results are not surprising. We have only measured the spectrum of Xe evaporated at 40° K.

The reflectance features for Xe are interpreted in a way similar to those found for Kr. Our tentative assignment is inserted into Fig. 4 and listed in Table I. We once more find a spin orbit split exciton series. The n=1 members C and J are spin orbit split by 1.14 eV; the same value is found for the 6s-6s' splitting of the atomic levels. Values deduced from the n=2 and n=3 members of this exciton series for the energy gap and the binding energy are $E_0(3/2) = 9.1$ eV, $G(3/2) = 0.4$ eV and $E_0(1/2) = 10.0$ eV and $G(1/2) = 0.7$ eV, respectively. These values differ slightly from results based on the absorption data because of the above described differences in the spectra.

The two peaks A and D do not fit into this interpretation. They seem to be correlated to the sharp exciton peaks C and E from which their energy separation is 0.23 eV in both cases. If one assigns the peak A, already reported by Schnepp and Dressler (1) and also noticed by Keil (3) in the electron energy loss spectrum, to a level corresponding to the forbidden J=2 level of the atomic $5p^5 6s$ configuration one is led to interprete D as its n=2 member in an exciton-like series.

The maximum O has also been found in the absorption spectrum of solid Xe. It has been explained as the excitation of a metastable L(3/2) exciton (6). Since it was also found in liquid Xe (14) it appears that it should have a closer resemblance to an atomic level. According to its energy position it could correspond to the 5d atomic transition at 10.40 eV, as has been pointed out by Reilly (7).

The decrease of the reflectance at 15 eV is associated with the excitation of plasma oscillations involving 5p electrons. Keil (3) has more directly observed this as a maximum of the imaginary part of the reciprocal dielectric constant $|\mathrm{Im}\varepsilon^{-1}|$ at 15.2 eV.

As in the case of Kr it is difficult to correlate the features in the high energy part of the spectrum unequivocally to critical points of band calculations for Xe (6, 7). A band structure calculation of ε_2 for Kr and Xe and a Kramers-Kronig analysis of our reflectance data are required for a more complete interpretation.

Table I. Energy position (in eV) of the most prominent structures of the 15° reflectance spectra from the onset of excitonic absorption up to 28 eV for solid Kr and Xe.

	Kr		Xe	
A	9.82		8.15	
B	10.01		8.29	
C	10.14	$\Gamma(3/2)n=1$	8.38	$\Gamma(3/2)n=1$
D	10.23		8.75	
E	10.52		8.98	$\Gamma(3/2)n=2$
F	10.71		9.05	$\Gamma(3/2)n=3$
G	10.88	$\Gamma(1/2)n=1$	9.15	
H	10.95		9.25	
I	11.13		9.38	
J	11.26	$\Gamma(3/2)n=2$	9.52	$\Gamma(1/2)n=1$
K	11.48	$\Gamma(3/2)n=3$	9.62	
L	11.98	$\Gamma(1/2)n=2$	9.77	$\Gamma(1/2)n=2$
M	12.22	$\Gamma(1/2)n=3$	9.87	$\Gamma(1/2)n=3$
N	12.5		10.16	
O	13.35		10.28	
P	14.1		11.25	
Q	14.4		11.65	
R	15.6		11.8	
S	16.25		12.1	
T	16.95		12.6	
U	18.4		13.1	
V	18.9		13.3	
W	24.9		13.8	
X			14.5	
Y			15.1	
Z			15.2	
A'			19.3	
B'			20.6	

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Figure captions

Fig. 1 Reflectance of solid Kr at 25° K for an angle of incidence of 15° between 10 and 28 eV.

Fig. 2 Reflectance of solid Kr at 25° K for an angle of incidence of 15° between 9 and 14 eV (solid line). The dashed line gives Baldini's absorption curve (2) for an annealed film at 20° K, right ordinate. The assignment of the spin orbit split exciton series is given. Arrows indicate the series limits.

Fig. 3 Reflectance of solid Xe at 40° K for an angle of incidence of 15° between 8 and 25 eV (solid line). The dashed line represents $|\mathrm{Im}\,\varepsilon^{-1}|$ as deduced from Keil's electron energy loss experiments (3).

Fig. 4 Reflectance of solid Xe at 40° K for an angle of incidence of 15° between 8 and 12 eV (solid line). The dashed line gives Baldini's absorption curve (2) for an annealed film at 20° K, right ordinate. The assignment of the spin orbit split exciton series is given. Arrows indicate the series limits.

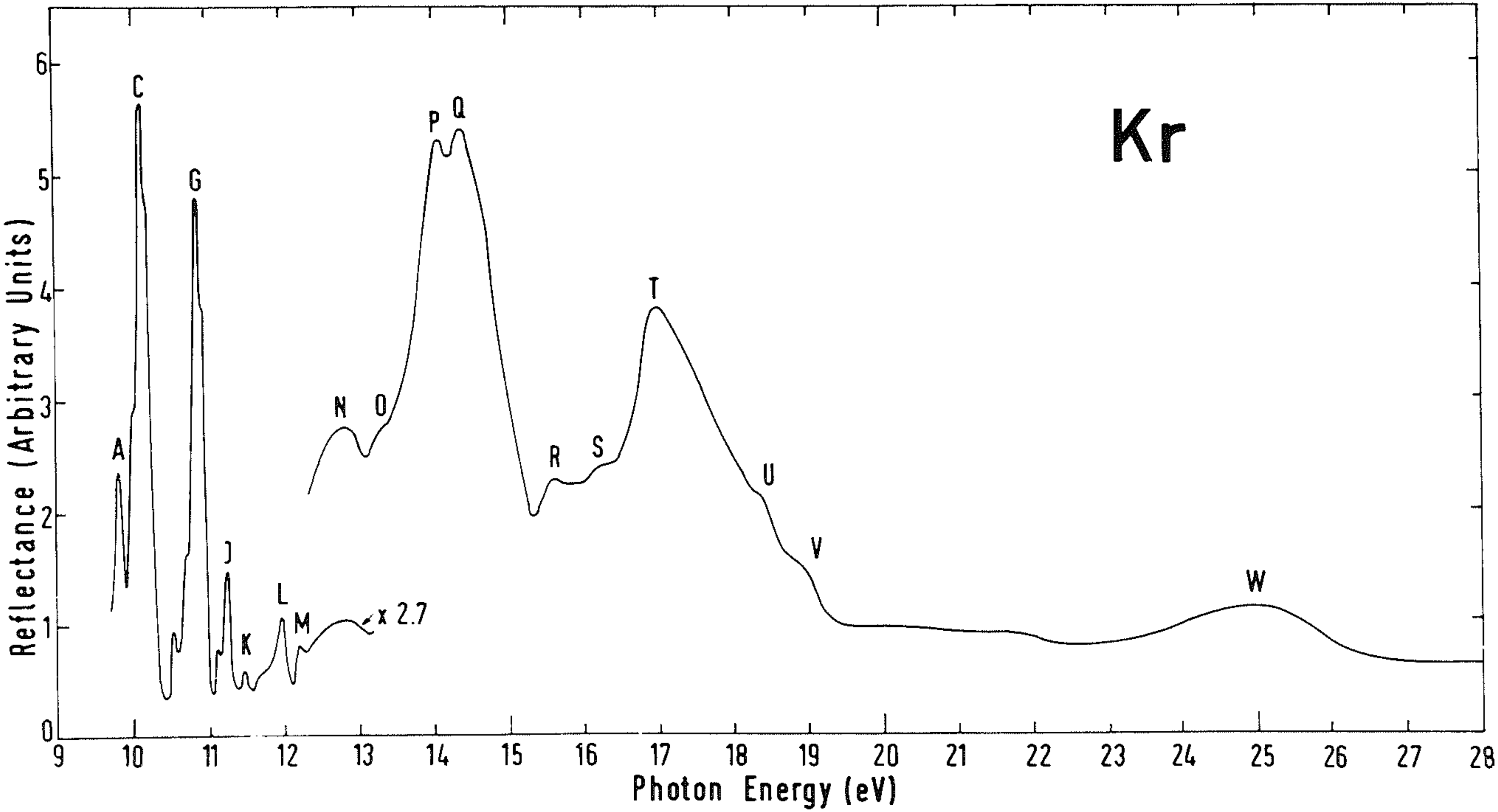
Kr
Reflectance (Arbitrary Units)
Photon Energy (eV)
0
1
2
3
4
5
6
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
A
C
G
J
K
L
M
x 2.7
N
O
P
Q
R
S
T
U
V
W

Fig.1

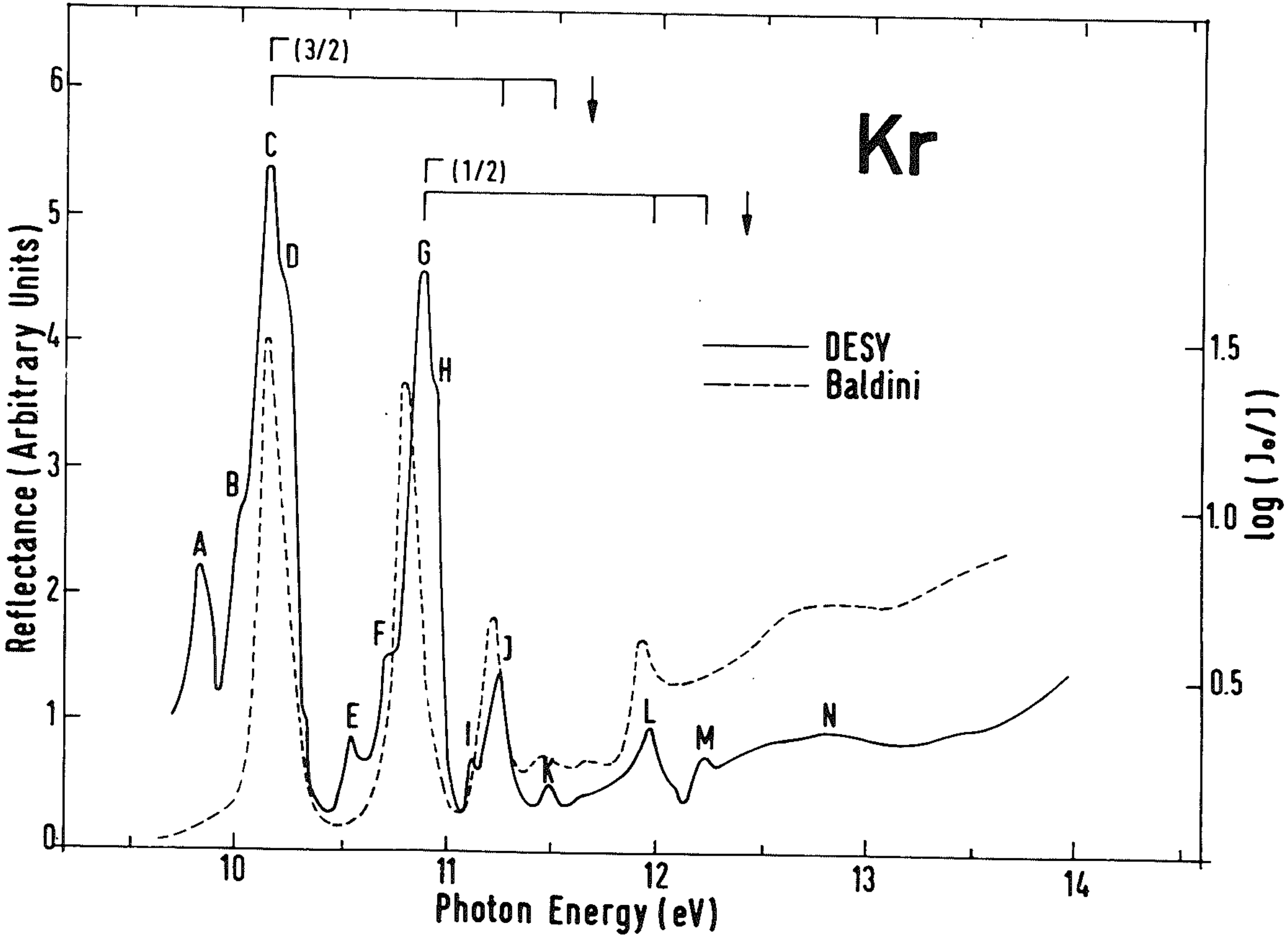
Kr
Γ(3/2)
Γ(1/2)
A
B
C
D
E
F
G
H
I
J
K
L
M
N
DESY
Baldini
Reflectance (Arbitrary Units)
0
1
2
3
4
5
6
log (J₀/J)
0.5
1.0
1.5
10
11
12
13
14
Photon Energy (eV)

Fig.2

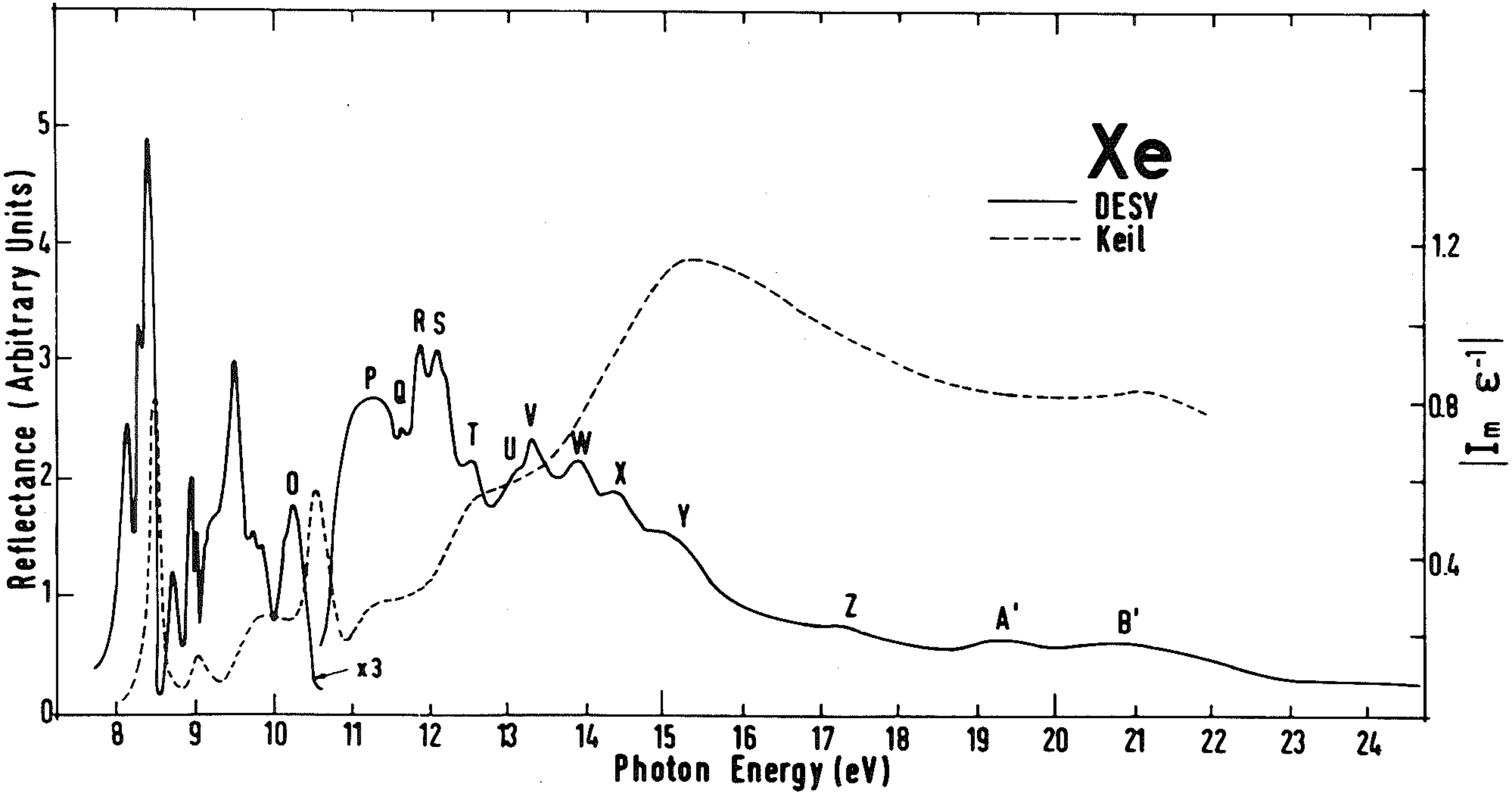
Xe
DESY
Keil
Reflectance (Arbitrary Units)
0
1
2
3
4
5
|Im ε⁻¹|
0.4
0.8
1.2
Photon Energy (eV)
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
O
P
Q
R
S
T
U
V
W
X
Y
Z
A'
B'
x3

Fig. 3

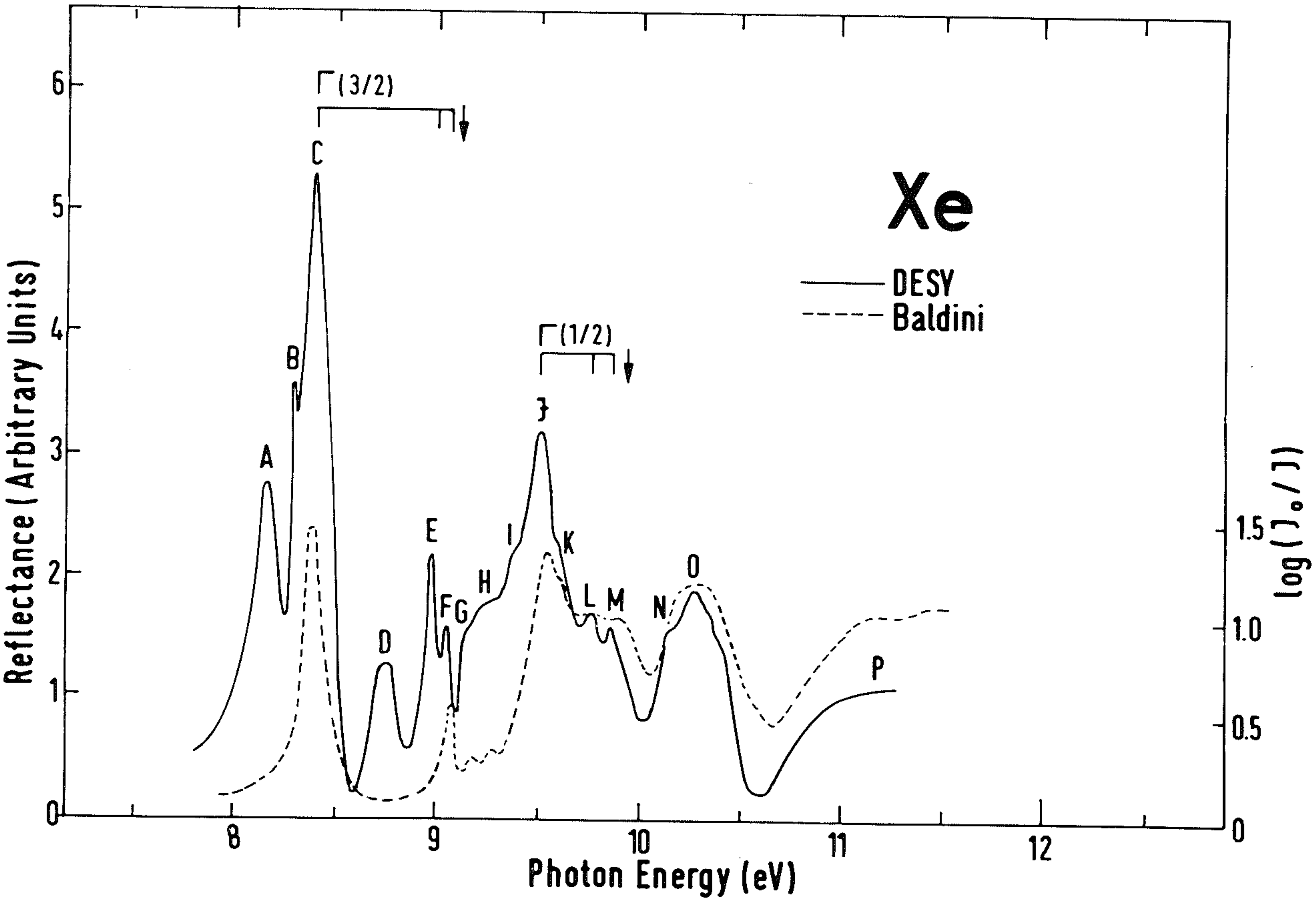
Xe
DESY
Baldini
Γ(3/2)
Γ(1/2)
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Reflectance (Arbitrary Units)
0
1
2
3
4
5
6
log(J₀/J)
0
0.5
1.0
1.5
8
9
10
11
12
Photon Energy (eV)

Fig.4