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Close Similarity Between Photoelectric Yield and Photoabsorption Spectra in the Soft X-Ray Range

by

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Because of the similarity between photoelectric yield and photoabsorption spectra in the soft x-ray region, first found by Lukirskii and co-workers, "yield spectroscopy" can be used as a successful method for investigating fine structure in the electronic excitation spectra of solids by means of the synchrotron radiation continuum. We reinvestigated the absorption structure of the 4d excitation in Ce and Pr by means of photoelectric yield measurements and found a better resolved and augmented fine structure in the energy range around 100 eV. Using a Si single crystal we were able to reproduce the structure at the $L_{2,3}$ *edge which had been previously found in absorption measurements.*

Using the continuous spectrum from a soft x-ray tube Lukirskii and coworkers[1,2] established a close similarity between photoelectric yield and absorption spectra for core excitations in several materials, mainly alkali halides. There are, however, only a few yield measurements available which allow a comparison in the low energy region. Good agreement is found for the $L_{2,3}$ spectrum[3] of Na in NaCl around 30 eV. At even lower energies the 3p excitations of K in the potassium halides[4,5] around 20 eV can be identified in both absorption (respectively ε_2) and yield spectra; the actual shape, however, of the structures is quite distorted in the yield spectra. The valence band spectra at the onset of transitions appear to be different in yield and absorption[4,5]. Few yield investigations have been performed on clean metal and semiconductor surfaces. An unpublished yield measurement[6] on an oxide-free Al surface agrees well with the known $L_{2,3}$ absorption spectrum. This indicates that the similarity between the two types of spectra is not restricted to insulators.

Synchrotron radiation[7] with its intense continuous spectrum covering the whole ultraviolet and soft x-ray region is especially suited for "yield spectroscopy". In order to further explore the possibilities of this method we have performed measurements with a variety of insulators, semiconductors, and metals. For LiF e.g. we were able to confirm the published results[2] and found excellent agreement in all the details of the structure with more recent absorption measurements[8,9] in the 60 - 150 eV range. We were able to reproduce the absorption spectrum[10] of CsI between 50 and 170 eV (with the Cs and I $N_{4,5}$ structures) and saw the increase in the absorption coefficient[11] of CdSe (below 110 eV) and of PbS (below 80 eV). We similarly found the rapid increase in the absorption[12] of Ag below 120 eV together with some fine structure around 70 eV. Measurements on Ce, Pr, and a single crystal of Si will be discussed at the end of this paper. The present investigations were of an exploratory nature and will be followed by detailed measurements under UHV conditions at a later stage. All these results prove that in the extreme UV region yield spectroscopy is a powerful tool for the investigation of absorption structure having all the advantages of using bulk samples e.g. single crystals.

Although we are aware of the fact that the general theory of photoemission is complicated and that especially the processes involved during the migration of electrons to the surface are not very well understood, the following simplified considerations appear to give a reasonable explanation of the yield spectra. After the primary absorption of a photon three processes mainly contribute to the photoelectric yield:

1. Direct excitation into the conduction band,
2. Auger emission of electrons,
3. Decay of excitons into one-electron excitations.

The fast electrons originating from these processes undergo inelastic electron-electron scattering with the probability of multiplication, the multiplication factor $\eta(\varepsilon)$ being a monotonously increasing function of the electron energy ε. The main contribution to the yield should come from electrons with energies a few electron volts above the vacuum level because in the spectral region which interests us the mean free path for inelastic scattering increases with decreasing energy, whereas the escape probability through the surface barrier increases from the vacuum level to higher energies. This should result in an effective escape depth D determined by the mean free path of these electrons. D is in the order of 30 Å for metals (see e.g. Ref. 13) and several times larger for insulators in the region where electron-electron scattering is impossible. D is small compared to the penetration depth of light in our region of interest; as a result, the total yield Y defined as the number of emitted electrons divided by the number of incident photons (reflectivity is negligibly small) is given by

$$(1) \qquad Y \propto \mu(E)\cdot D(p_1\eta(\varepsilon_1)+p_2\eta(\varepsilon_2)+p_3\eta(\varepsilon_3)),$$

$\mu(E)$ being the absorption coefficient of the photons, p_1, p_2, p_3 being the relative contributions of the processes 1. to 3. and E being the photon energy. Apart from the ε dependent bracket Y is proportional to $\mu(E)$. Since the electron energies ε_i are determined by the photonenergy E the bracket term will become a monotonously increasing function of E. We presume that the function will be structureless due to the averaging over a series of statistical scattering processes which are involved in the determination of $\eta(\varepsilon)$. Without going into the details of Eq. 1 for insulators, semiconductors and metals we would like to mention two points:

a) As has been noted before by Lukirskii et al.[2] the Auger part of Eq. 1 (apart from the region where it competes with excitonic decay) should be a true replica of $\mu(E)$.

b) Core excitons which predominantly decay into one-electron excitations are by no means supressed in the yield spectra.

Our experiments were performed by making use of synchrotron radiation emitted by the 7.5 GeV electron accelerator DESY. The continuum was monochromatized by a special monochromator[14] giving a light beam virtually free from higher order radiation at a fixed exit slit in the energy region 35 eV to 300 eV. The resolution E/ΔE ranged from 400 to 650. Behind the exit slit the light was reflected at a grazing angle of 4^0 by a gold coated mirror which, at the same time, was the cathode of an open multiplier (Bendix). The signal from this multiplier served as the reference for the yield measurements.

The spectrum, as measured by this detector, is smooth with the exception of small fine structure at the Au $N_{6,7}$ edges around 85 eV originating from the gold coating of all the optical components and a pronounced structure at the carbon K edge at 280 eV originating from hydrocarbon contamination on the optical surfaces. The reflected light beam hits the samples at normal incidence. The emitted electrons are accelerated onto the cathode of an open multiplier (Johnston). The signal of this multiplier is electronically divided by the reference signal. The spectra obtained in this way can differ from the actual yield by a factor varying smoothly with photonenergy. We call the spectra thus measured "yield spectra".

Figures 1 and 2 show the yield and the absorption spectra[15,16,17] of Ce and Pr in the region of 4d transitions. Since the samples were not prepared in situ they will be covered by some layer of oxide. For Pr it has been shown before that the absorption spectra of oxide and metal agree with each other while for Ce there is some difference. By comparing the absorption we come to the conclusion that our Ce spectrum is mainly the metal spectrum together with a small contribution from the oxide. For both Ce and Pr the yield and absorption spectra show very good general agreement. (The broad bumps at 140 eV respectively 150 eV also show up in the absorption spectra of Ref. 16.) In the yield spectra the underlying continuum of transitions from higher shells is more pronounced, compared to the fine structure, than in the absorption spectra. Similar behaviour was observed with most of the other materials mentioned above and should be explainable from a detailed consideration of Auger and other excitations for the transitions from different shells for each individual material according to Eq. 1.

More details of the fine structure are observed in the yield spectra when compared to the absorption spectra primarily due to a better signal to noise ratio. This advantage is inherent in yield spectroscopy. A theoretical explanation of the structures in the rare earth metals was achieved by Dehmer et al.[18] and Sugar[19] on the basis of atomic calculations. Due to exchange interaction the $4d^9 4f^{N+1}$ final state configuration splits into a series of wide spread sublevels. The numerical calculation performed for Ce and Pr show good agreement, also for the additional lines not found in the absorption spectra, both in position and strength of the lines (see Fig. 2).

In addition we performed measurements on a Si single crystal cleaved in air immediately before mounting. The result is shown in Fig. 3 and is compared to the absorption measurements performed by Brown and Rustgi[20] on a polycrystalline sample. Small differences could be mainly attributed to a lower resolution in our case. The main features, however, are present in both spectra. The rise of the yield at the high energy end of the spectrum is due to the first peak in the spectrum[21] of SiO_2 at 106 eV since our sample was not completely free from oxide. (This was even more pronounced when using a polished single crystal.) When measurements under UHV conditions become possible the investigation of single crystals by yield spectroscopy will certainly be of primary interest.

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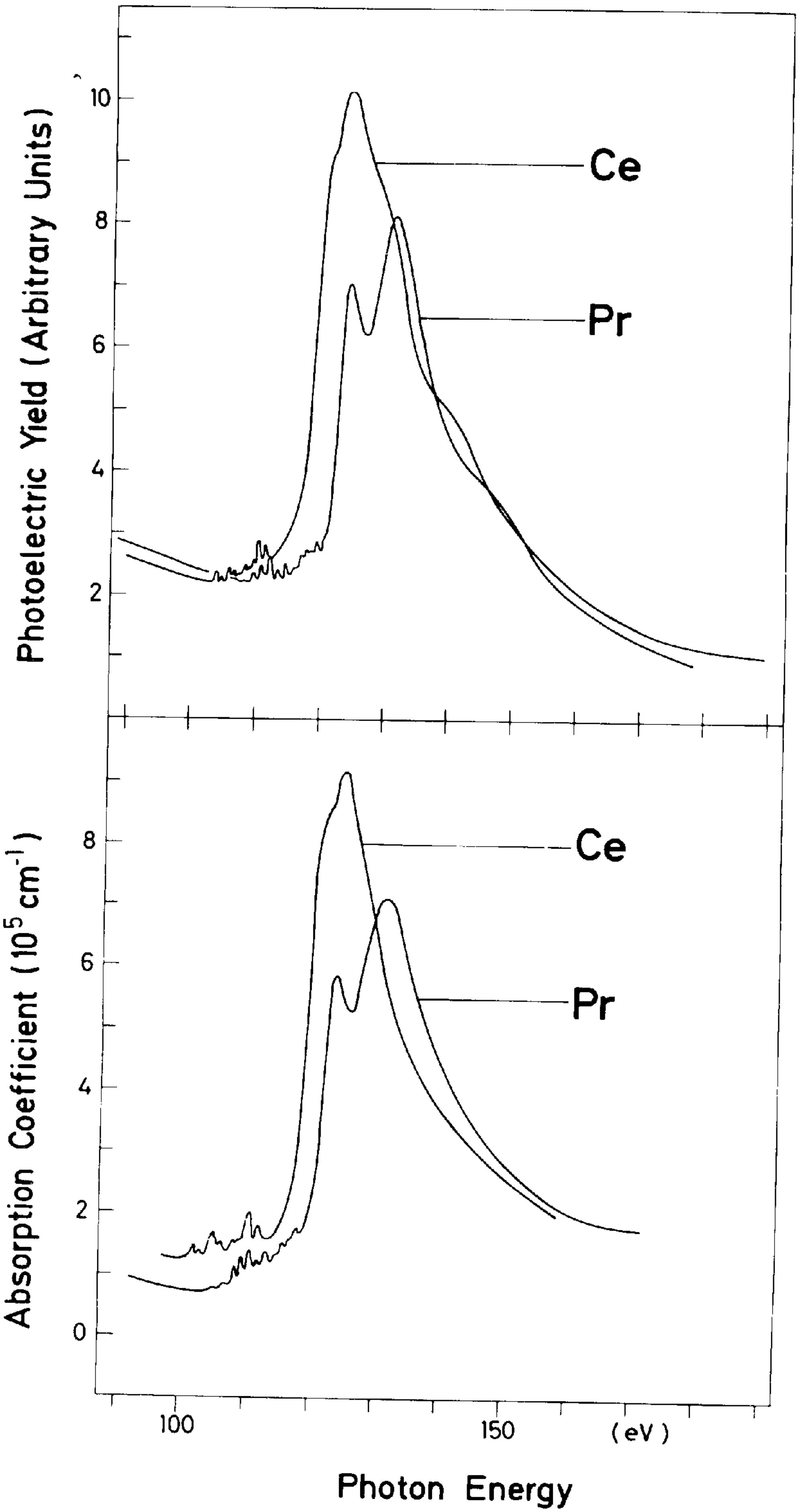
Figure captions

Fig. 1 Comparison of photoelectric yield and absorption spectra of Ce and Pr.

Fig. 2 Energy region of fine structure, yield (solid curve) and absorption (dashed curve). The vertical lines are the result of an atomic calculation[19], the length of the lines represents the oscillator strength.

Fig. 3 Comparison of the photoelectric yield measured on a cleaved Si single crystal surface and of the absorption coefficient of a polycrystalline Si film after Brown and Rustgi[20].



Photoelectric Yield (Arbitrary Units)
10
8
6
4
2
Ce
Pr
Absorption Coefficient (10^5 cm^{-1})
8
6
4
2
0
Ce
Pr
100
150
(eV)
Photon Energy

Fig. 1

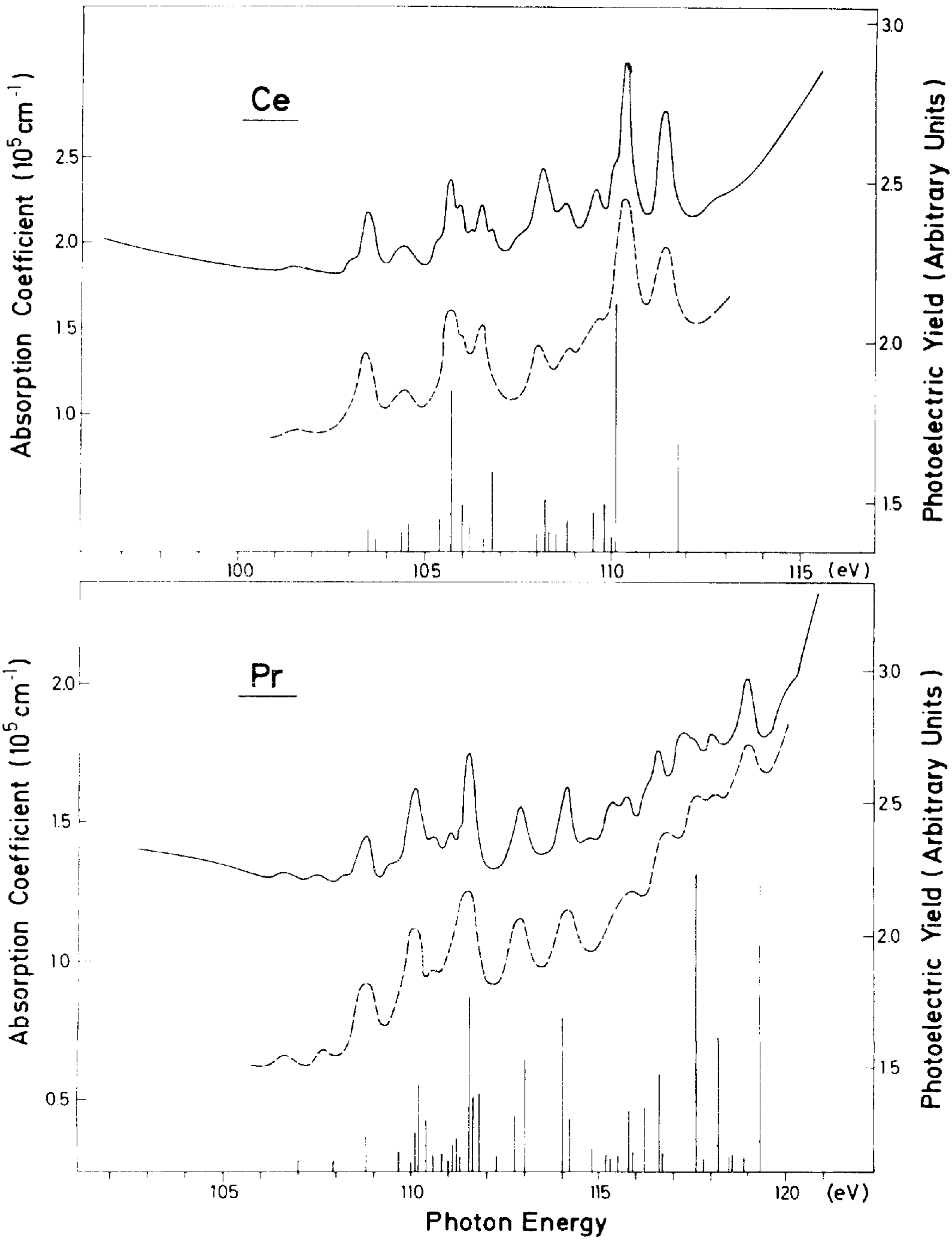
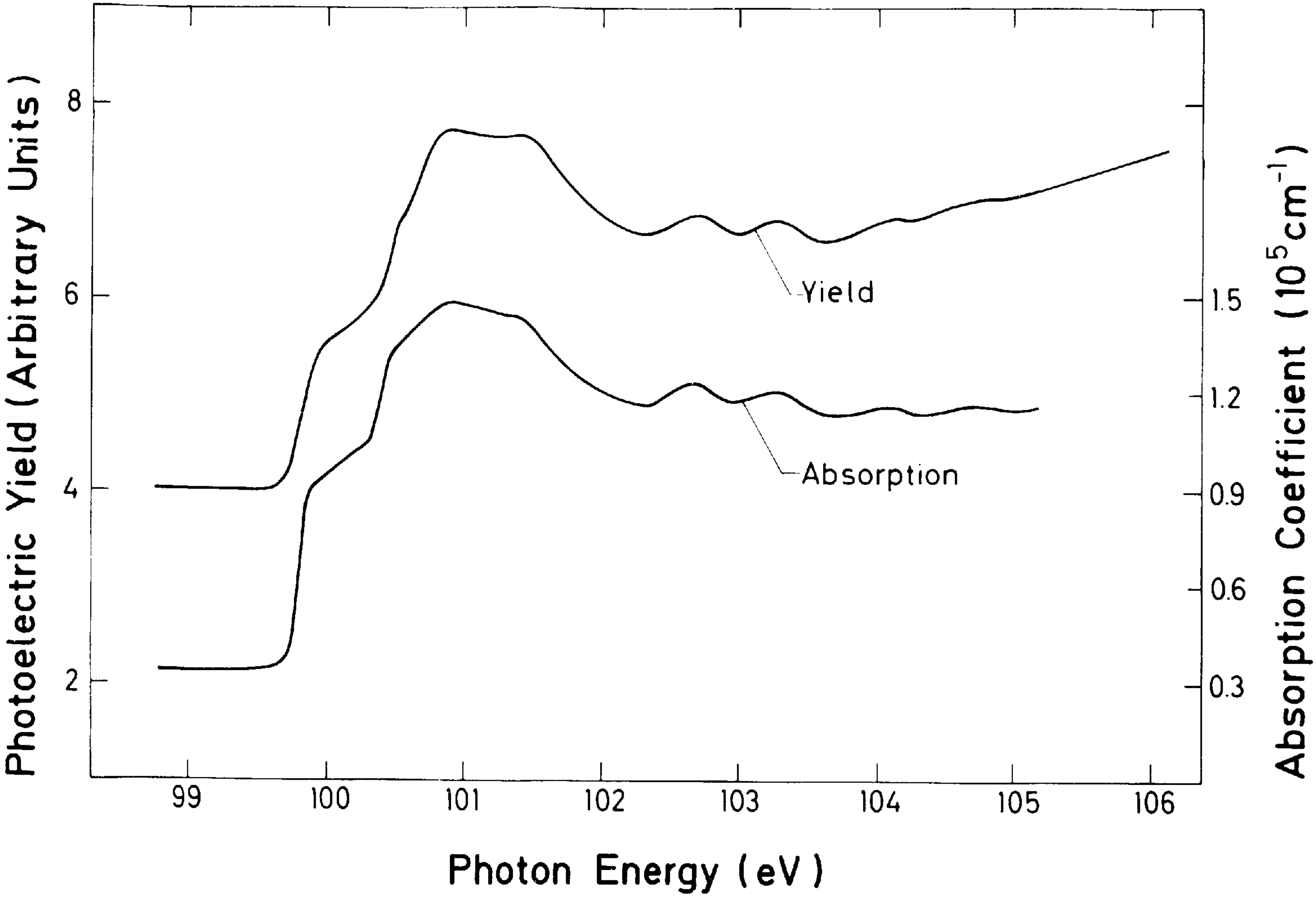

Ce
Absorption Coefficient (10^5cm^{-1})
2.5
2.0
1.5
1.0
Photoelectric Yield (Arbitrary Units)
3.0
2.5
2.0
1.5
100
105
110
115
(eV)
Pr
Absorption Coefficient (10^5cm^{-1})
2.0
1.5
1.0
0.5
Photoelectric Yield (Arbitrary Units)
3.0
2.5
2.0
1.5
105
110
115
120
(eV)
Photon Energy

Fig. 2

Fig. [illegible]


Photoelectric Yield (Arbitrary Units)
2
4
6
8
Absorption Coefficient $(10^5 cm^{-1})$
0.3
0.6
0.9
1.2
1.5
Yield
Absorption
99
100
101
102
103
104
105
106
Photon Energy (eV)