

DESY 70/41
August 1970

DL
10. SEP. 1970

OPTICAL ABSORPTION OF CERIUM, CERIUM OXIDE, PRASEODYMIUM,
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ULTRAVIOLET

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Optical Absorption of Cerium, Cerium Oxide, Praseodymium,
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The optical absorption of the rare earths Ce, Pr, Nd and Sm has been measured in the energy region 100 eV to 180 eV. The absorption spectra of the oxides of Ce, Pr and Nd have been determined in the same energy region. Synchrotron radiation of the 7.5 GeV electron synchrotron DESY was used as a light source. Transitions from the 4d level of the rare earths contribute the main part of the absorption in this energy region. At the onset of these transitions we found a number of sharp absorption maxima. This fine structure is followed by a broad absorption maximum, about 15 eV above the onset of 4d transitions, which is due to d+f continuum transitions. The absorption spectra of Ce and Ce-oxide show a marked difference whereas the absorption spectra of Pr and Nd are very similar to those of their oxides.

Die optische Absorption der seltenen Erden Ce, Pr, Nd und Sm und der Oxide von Ce, Pr und Nd wurde im Energiebereich von 100 eV bis 180 eV gemessen. Als Lichtquelle diente die Synchrotronstrahlung des 7,5 GeV Elektronen-Synchrotrons DESY. Im untersuchten Energiebereich liefern Übergänge aus den 4d Niveaus der seltenen Erden den Hauptbeitrag zur Absorption. Einer Reihe von scharfen Absorptionsmaxima, am Einsatz

dieser Übergänge, folgt ungefähr 15 eV oberhalb des Einsatzes ein breites Absorptionsmaximum, das auf Übergängen aus den 4d Niveaus in unbesetzte f-symmetrische Kontinuumzustände beruht. Die Absorptionsspektren von Ce und Ce-Oxyd zeigen deutliche Unterschiede, während die Absorptionsspektren von Pr und Nd den Absorptionsspektren ihrer Oxyde sehr ähnlich sind.

Systematic absorption measurements in the vacuum ultra-violet have been done on the transition metals¹⁻³ and the lanthanides^{4,5} in order to study the variation of the absorption spectra along the periodic table. Transitions from deep lying core levels to continuum states give the main contribution to the optical absorption in this energy region. In the absorption spectra these transitions show up as broad absorption bands rising near threshold energy and extending to much higher energies. These absorption maxima are especially prominent for d+f transitions. This has not only been found for the transition metals¹⁻³ and the lanthanides^{4,5} but also for the d transitions of gaseous and solidified Kr and Xe^{6,7} and for the d transitions of the Rb- and Cs-halides⁸. Fano and Cooper⁹ have shown that many of the gross features of the absorption spectra of gases and solids in the vacuum ultraviolet can be explained by an one-electron model for free atoms. It is clear that this model will not hold for transitions from inner shells in solids near the threshold.

Whereas no sharp structure has been found near the threshold of inner shell transitions for most of the transition metals Fomichev et al.^{4,5} have detected many sharp absorption lines in the lanthanides near the onset of the 4d transitions. They suggested that these fine structures may be due to transitions of 4d electrons into unoccupied states of the partially filled 4f shell.

The measurements of Fomichev et al.^{4,5} have been performed at a pressure of $5 \cdot 10^{-5}$ Torr, which is relatively high for those lanthanides which oxidize very easily. In order to make sure that the sharp absorption peaks are not due to oxides we repeated the measurements on the highly oxidizable lanthanides Ce, Pr, Nd and Sm in a better vacuum. Additionally, we measured the absorption of the oxides of Ce, Pr and Nd in the same energy region. The absolute value of the absorption coefficient has been determined for the metals.

The experimental layout for these measurements is similar to that described in Ref. 7. The 7.5 GeV electron synchrotron DESY was used as a light source. We used a Rowland type spectrometer working at grazing incidence. The resolution was 0.06 eV to 0.15 eV for the measurements of the fine structure and 0.5 eV for the measurements of the broad d+f maximum.

The samples were mounted between the light source and the spectrometer. We used thin films evaporated in situ from tungsten boats onto zapon or carbon foils. The pressure in the system was lower than 10^{-6} Torr. We did not succeed in preparing the oxides in the same way since the carbon or zapon substrates did not stand the high temperatures necessary for evaporation. Consequently the oxides were evaporated onto carbon foils mounted on glass slides. Subsequently the foils were floated off on water. During evaporation of the oxides the electric resistance of the evaporated film was measured in order to make sure that the oxides had not been reduced to the metallic state. The electric resistance of a 2000 Å thick oxide layer of Ce, Pr and Nd was $> 10^{10}$ Ω. Sm-oxide, however, was reduced during evaporation and therefore the absorption could not be determined. The film thickness was determined from the frequency shift of an oscillating quartz calibrated by Tolansky interferometry. The thickness of the foils ranged from 150 Å to 2500 Å.

The absolute values of the absorption coefficient of Ce, Pr, Nd and Sm in the photon energy range 90 eV to 190 eV are shown in Fig. 1. For Ce-oxide, included in this figure, the absolute value of the absorption coefficient was not determined experimentally but obtained by adjusting the absorption coefficient in such a manner that the absorption of Ce-oxide integrated over the measured energy region was equal to the corresponding value for Ce. The energy positions of the broad maxima are compiled in Table I. For Ce-oxide the absorption peak is shifted to higher energies as compared to the metal, but the gross shape of the absorption curve is the same.

Figure 2 shows the range of the fine structure near the onset of the $N_{IV,V}(4d)$ absorption. The general shape of the fine structure is in good agreement with the results of Fomichev et al.⁴. In addition to the peaks shown in Ref. 4 we have found some more smaller peaks resulting from our increased resolution. The energy positions of the absorption peaks in this region are given in Table I. The shape of the absorption spectra of Ce-oxide and Ce are quite different though the energy position of the maxima are almost the same for both materials.

The spectra of Pr and its oxide as well as the spectra of Nd and its oxide are identical within the accuracy of our measurements over the whole investigated energy region and, therefore, are not shown in both figures. The energy positions of the 4d electrons, as given by Bearden et al.¹⁰, are indicated in both figures by vertical bars. The absolute accuracy of the μ values is estimated to be ± 10 per cent, the relative accuracy in adjacent regions is about 10^{-4} cm^{-1} . The accuracy of the values given in Table 1 is about 0.1 eV. They differ from Fomichev's⁴ and Zimkina's⁵ values by up to 0.8 eV.

The broad absorption maxima (Fig. 1) we found about 15 eV above the onset can be explained by transitions of the 4d electrons to f-symmetric continuum states. These transitions are suppressed at the onset by a centrifugal barrier. With increasing atomic number the distance of the maximum from the onset of the transitions is decreasing. This shift of the maximum towards the threshold and the general shape of this maximum can roughly be understood in terms of the model for free atoms given by Fano and Cooper⁹. No explanation in terms of this model can be given for the shoulder we found for Ce and Ce-oxide and for the splitting of the maximum into two maxima for Pr, Nd and Sm.

A discussion of these broad maxima in terms of known band calculations on La, Pr, Nd and Gd^{11,12} is impossible since these calculations are restricted to a region of 2 eV above the Fermi Level. Most of these calculations do not include the highly localized 4f states. Only for Gd has a narrow band of 4f states been obtained. Because of these limitations it is very difficult to compare the experimental results in the region of the fine structure, extending over 15 eV, with the results of band calculations. A further complication results from the facts that the position of the Fermi level is very uncertain and that we did not succeed in identifying the corresponding spin-orbit mates, though the spin-orbit splitting of the 4d levels is 3.5 eV and 5 eV as calculated by Herman and Skillman¹³.

The identity of the absorption spectra of Pr and Nd with the spectra of their oxides supports the suggestion made by Fomichev et al.⁴, that the fine structure is due to transitions of 4d electrons to unoccupied 4f levels. These 4f levels may be very localized for Pr and Nd and are, therefore, not affected by oxidation. Herman and Skillman¹³ showed that for free Pr, Nd and Sm atoms the 4f wavefunction is localized within the closed Xe-shell. That is not the case for Ce, and this may be the reason for the different spectra we obtained for Ce and for its oxide.

A calculation of the number N_{eff} of effective electrons contributing to the absorption between 90 eV and the onset of the 4p transitions (~ 240 eV) has been made. An extrapolation of our results has been made between 180 eV and 240 eV according to Zimkina's⁵ results. The number N_{eff} is 8.8 for Ce, 8.5 for Pr, 9.1 for Nd and 9.6 for Sm, which is very close to the expected value of 10 electrons.

We would like to thank the Deutsche Forschungsgemeinschaft for financial support.

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Table I Energy (in eV) of the peaks observed in the absorption spectra of the lanthanides and their oxides as shown in Fig. 1 and Fig. 2 (labelled)

	Ce	Ce-oxide	Pr	Nd	Sm
A	101.25		106.70	112.18	126.65
B	103.48	103.45	107.70	113.45	128.06
C	104.56	104.47	108.83	114.51	128.33
D	105.77	105.81	110.12	114.88	129.32
E	106.06		110.54	115.95	130.96
F	106.58	106.52	111.53	116.38	131.47
G	108.06	107.64	112.81	116.62	132.82
H	108.93	108.21	114.16	117.25	
J	109.70	109.37	115.93	117.93	
K	110.36	110.35	116.74	118.34	
L	111.52	111.50	117.49	120.00	
M			118.02	121.83	
N			118.90		
	124.3	125.0	129.9	124.4	137.2
		130.8	131.4	126.5	140.0
				127.9	149.0
				134.1	
				137.2	

Figure Captions

Fig. 1 Absorption spectra of Ce, Ce-oxide, Pr, Nd, Sm from 90 eV to 180 eV.

1

Fig. 2 Fine structure of Ce, Ce-oxide, Pr, Nd and Sm at the onset of the 4d absorption.

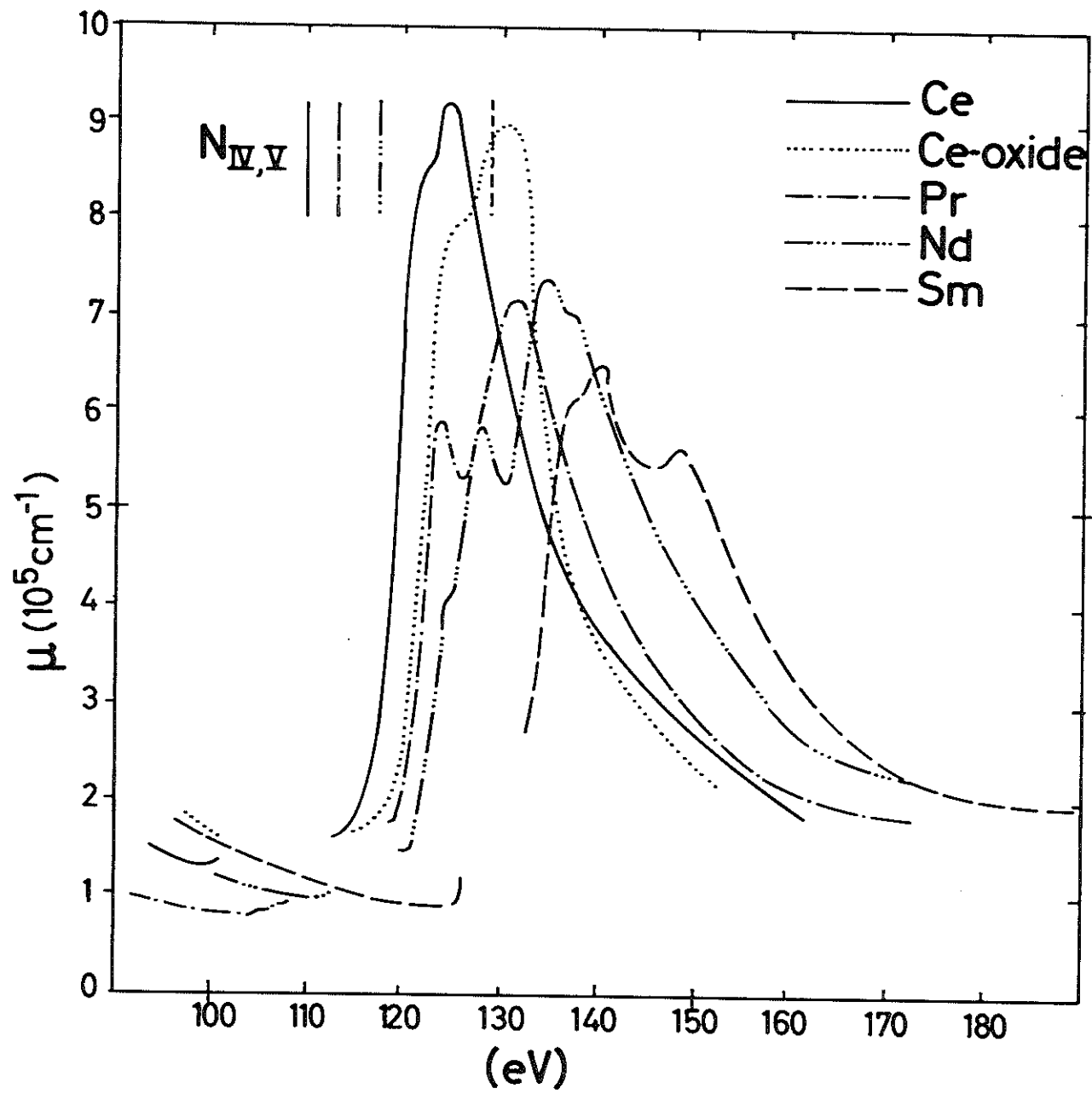


Fig. 1

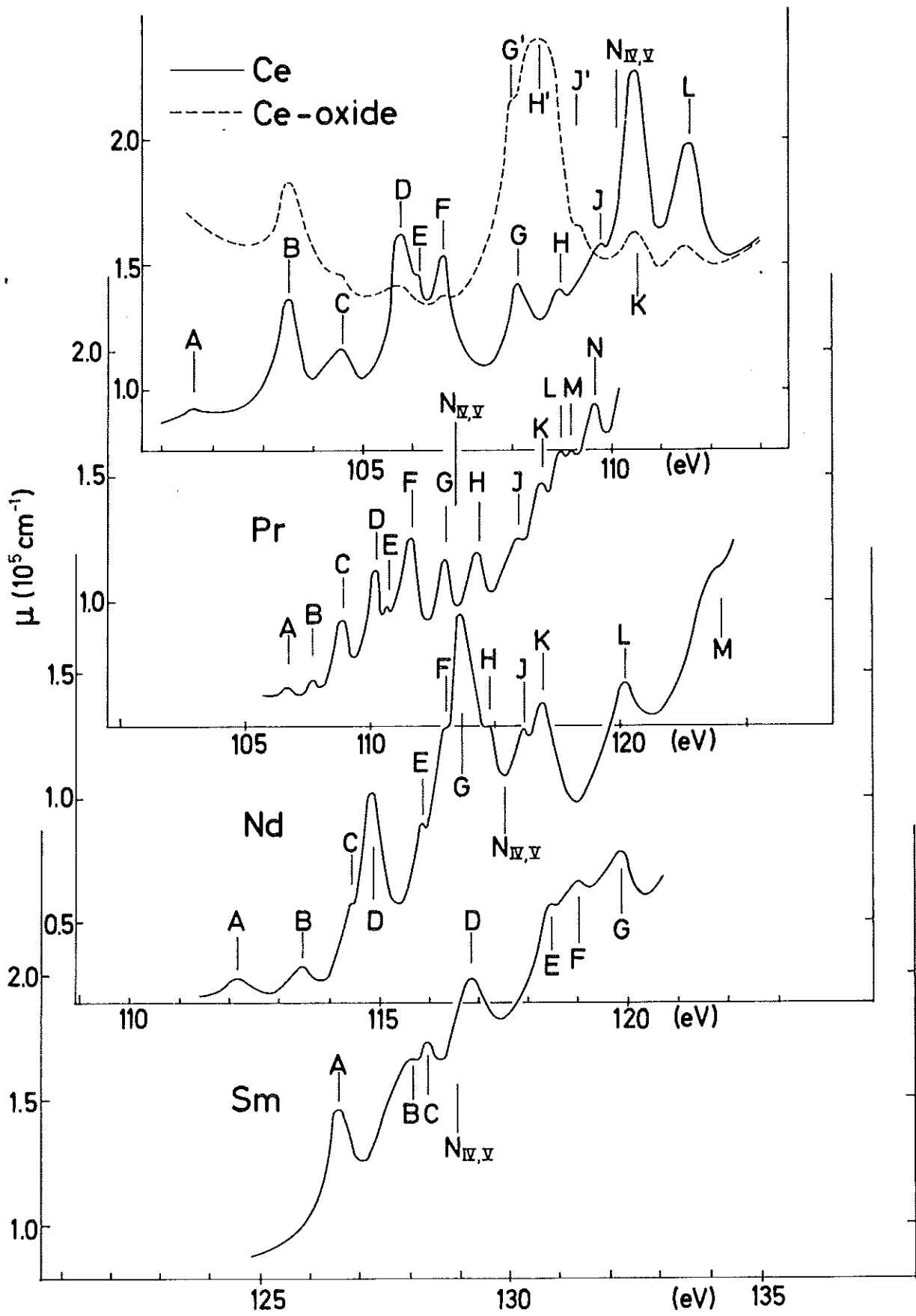


Fig.2