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The investigation of transitions from inner shells to the conduction band of the sodium halides complements information on the electronic band structure gained from optical measurements in the region of fundamental absorption.<sup>1,2,3</sup> We studied photoabsorption due to transitions from the  $L_{2,3}$ -shell of  $\text{Na}^+$  in the four sodium halides ( $\text{NaF}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$  and  $\text{NaI}$ ) with onset at photon energies of about 32 eV ( $\sim 370 \text{ \AA}$  wavelength). Similar measurements have been performed by O'Bryan.<sup>4</sup> We obtained improved results by using

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the synchrotron radiation of the 6-GeV electron synchrotron DESY as a radiation source with a continuous spectral distribution.<sup>5</sup> The samples were prepared in situ as thin films by vacuum evaporation from molybdenum boats onto aluminum foils of about 1000 Å thickness. The aluminum foils served as carriers and as prefilters for the suppression of reflection of the grating into higher orders for measurements in the 36 to 73 eV photon energy range (Al L<sub>2,3</sub>-edge at 73 eV). Mg-filters were added for measurements in the 32 to 50 eV range (Mg L<sub>2,3</sub>-edge at 50 eV). The samples were mounted between the radiation source and a grazing incidence spectrometer with a resolution, which ranged from 0.03 eV at 30 eV photon energy to 0.06 eV at 60 eV. Details of the experimental arrangement have been described elsewhere.<sup>6</sup> All measurements have been performed at room temperature.

Figure 1 shows the energy dependence of the absorption coefficient derived from our measurements. As the sample thickness not has been determined, the absorption coefficient is given in arbitrary units. The peaks are labeled with capital letters beginning at the onset of absorption structure. There is some uncertainty in the determination of the height of peak A in the fluoride.

Table I gives the values for the energy of the different peaks. The energy calibration of the spectrometer has been performed with Xenon and Krypton absorption lines<sup>7</sup> in the

first, second and third orders. The calibration is especially good for the most prominent peak B, since it is lying between members of a line series of Xenon in the second order.

In all halides we find a residual continuous absorption at energies lower than the onset of the discrete structures. This may be due to high lying valence band transitions which are 20 to 25 eV from the threshold energy. The first peak at the onset of the discrete structure is the double peak AB resulting from spin-orbit splitting in the  $L_{2,3}$  shell of  $Na^+$ . The width of the two peaks increases from the iodide to the fluoride, so that the spin-orbit splitting can be easily seen in the iodide, but can hardly be seen in the fluoride. The energy separation of the peaks A and B increases from the fluoride to the iodide. For energies just above the first peak AB other relative sharp maxima occur. Then a relatively broad minimum followed by a general increase of the absorption is observed in all four halides leading to the peak F in NaF, G in NaCl, E in NaBr, and F in NaI. This structure shifts systematically to lower energies in passing from the fluoride to the iodide. At energies above this step some further structure has been found up to 71 eV.

Some of the peaks have been also found by O'Bryan.<sup>4</sup> The energy values are in good agreement with his, especially the first prominent peak B (A has not been resolved by O'Bryan) in the chloride, bromide, and iodide. Creuzburg<sup>8</sup> found some of the structure in electron energy loss experiments on the sodium halides. His peak energies are in excellent agreement with our results, especially for the peak B, where there is agreement within 0.1 eV. Other electron energy loss data were given by Best.<sup>9</sup>

The small width of the first double peak AB makes it reasonable to assume that it is caused (similar to the case of the structure in the fundamental absorption region<sup>1</sup>) by exciton excitation. To what extent the peaks at higher energy are caused by excitons or are due to singularities in the band structure will be the subject of further studies. A detailed discussion of our results and a comparison with theoretical considerations is in preparation.

We received by private communication knowledge of measurements on NaCl made by Sagawa.<sup>10</sup> Our results are in excellent agreement with his.

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Table I. Position of the peaks in the absorption spectra  
(part 1) of the sodium halides. The position is given in eV

Maximum		Present study	O'Bryan <sup>a</sup>	Electron energy loss <sup>b</sup>
NaF	A	32.92±0.05		
	B	33.13±0.02	33.7	33.20
	C	35.5 ±0.1		
	D	39.15±0.05		39.6
	E	41.6 ±0.1		42.0
	F	46.31±0.05		46.3
	G	49.70±0.05		49.8
	H	52.66±0.05		
	I	56.3 ±0.5		
	J	64.1 ±0.5		
	K	69.5 ±0.5		
NaCl	A	33.16±0.05		
	B	33.43±0.02	33.3	33.45
	C	34.5 ±0.1	34.5	34.5
	D	36.52±0.05	36.8	36.6
	E	37.9 ±0.1		
	F	40.6 ±0.1		
	G	43.07±0.05	45	
	H	44.3 ±0.1		
	I	50.0 ±0.1		
	J	63.0 ±0.1		
	K	68.11±0.05		
	L	70.96±0.05		
NaBr	A	32.96±0.02		
	B	33.21±0.02	33.2	33.25
	C	33.96±0.05	34.2	
	D	36.38±0.05	36.5	
	E	42.21±0.05	44	
	F	48.0 ±0.1		
	G	58.1 ±1.0		
	H	67.81±0.05		
	I	70.47±0.05		

Table I. Position of the peaks in the absorption spectra  
(part 2) of the sodium halides. The position is given in eV

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Maximum		Present study	O'Bryan <sup>a</sup>	Electron energy loss <sup>b</sup>
NaJ	A	32.79±0.02		
	B	33.11±0.02	33.1	33.15
	C	34.16±0.05		
	D	35.55±0.05	35.8	
	E	37.0 ±0.1		
	F	40.56±0.1	42	
	G	43.2 ±0.1		
	H	46.2 ±0.1		
	I	55.51±0.05		
	J	59.17±0.05		
	K	61.0 ±0.1		
	L	62.9 ±0.1		
	M	67.66±0.1		

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<sup>a</sup> Ref. 4

<sup>b</sup> Ref. 8.



Figure caption

Fig. 1 Spectral dependence of the photoabsorption  
of the sodium halides near the sodium  
 $L_{2,3}$  edge

