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Measurement of Photoabsorption of the  
Lithium-Halides Near the Lithium K Edge

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Most of the work on optical absorption of alkali halides has been performed in the fundamental absorption region and gives information about transitions from p-like valence band states to s- and d-like conduction band states<sup>1</sup>. The investigation of transitions from s-symmetry core states (e.g. K shells) to p-like conduction band states should give additional information. We measured fine structure of photoabsorption in LiF, LiCl, LiBr and LiI near the Li K Edge (photon energy  $\sim 60$  eV).

Such measurements have been reported only for LiF by Lukirskii et al.<sup>2</sup>. For all Li halides some of the most prominent structure has been measured in electron energy-loss experiments by Creuzburg<sup>3</sup>.

We used the continuous spectrum of synchrotron radiation at the 6 GeV electron synchrotron DESY as a light source<sup>4</sup>. The samples were mounted between the synchrotron and a grazing incidence scanning type spectrometer with a resolution of 0.1 eV at 60 eV photon energy. The samples were evaporated in situ from molybdenum boats onto Al films of 1000 to 2000 Å thickness. For measurements at energies below the Al L<sub>2,3</sub> edge (73 eV) these Al films serve not only as substrates but also as filters to reduce the influence of higher order reflections of the grating.

Figure 1 shows the spectral dependence of the absorption coefficient of the lithium halides. As film thickness was not determined no absolute values are given. The peaks are labeled with capital letters beginning at the onset of absorption. The positions of the maxima are given in Table I. The values are compared with the optical measurements in LiF by Lukirskii et al.<sup>2</sup>. The agreement is excellent for the most prominent peak (B), but less ideal for the others. The peaks found in electron energy-loss experiments on all the halides by Creuzburg<sup>3</sup> are in good agreement with our measurements with

the exception of peak C in LiF.

There are some especially prominent peaks (Fig. 1) with a half width of 0.5 to 1 eV at the onset of absorption. By analogy to transitions from the valence band at the onset of the fundamental absorption region<sup>1</sup> we interpret these peaks as the result of exciton excitation. To each of these excitons there should belong an edge at higher energy which marks the onset of transitions into the respective band. We are not able to identify such edges in an unambiguous way.

Above the first prominent peaks we see a rich structure which might be related to the density of p-like states in the conduction band. The peaks labeled E in LiF, LiCl, and LiBr are especially characteristic. They are quite narrow and shift systematically from halide to halide. An unexpected feature is the anomalous structure at the lower energy side of peak A in LiI. This may be caused by the  $N_{4,5}$  absorption of the iodine ion (see Bearden<sup>5</sup>), but another possibility is that it is caused by decomposition products, since LiI is known to decompose with irradiation.

The three exciton peaks (A, B, C) of LiCl and LiBr show a remarkable similarity in the two materials, while there is only one prominent peak (B) in LiF and LiI. In both LiF and LiI there is a shoulder structure, which might be another hidden peak (A) at the low energy side of the main peak.

Notice that the lack of resolution is not an effect of our apparatus since the resolving power is 0.1 eV. The shape of this structure in LiF has been already observed<sup>2</sup>. We have also measured the LiF absorption spectrum with the film at liquid N<sub>2</sub> temperature but no essential change in the structure was observed. The only change was a shift of the peaks by 0.2 eV to higher energies.

There are several possibilities to explain the width of the exciton peaks such as for example lifetime broadening due to exciton decay into continuum states and transitions from other states into the empty K level. To obtain some information about the contribution of the latter decay mechanism, we measured the spectrum of metallic lithium. Lithium was evaporated in normal high vacuum by surrounding the substrate film by a liquid nitrogen cold trap. This retards oxidation, which is mainly due to the water vapour pressure as had been observed formerly<sup>6</sup>. The width of the observed edge (Fig. 1) is about 0.3 eV. This is in qualitative agreement with older results by Skinner et al.<sup>7</sup>, who have also remarked the final width of the edge. We thus believe that at least part of the width of the exciton peaks may be due to the limited lifetime of the empty K level, modified by the halogen ions.

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Table I. Position of the peaks in the absorption spectra of the lithium halides. The position is given in eV.

Maximum	present study	Lukirskii et al. <sup>2</sup>	electron energy-loss <sup>3</sup>
LiF	A	61.13±0.07	
	B	61.91±0.07	61.9
	C	64.9 ±0.15	65.1
	D	67.4 ±0.15	68.4
	E	69.6 ±0.15	70.1
LiCl	A	60.75±0.07	60.65
	B	62.27±0.07	62.1
	C	63.54±0.07	63.5
	D	65.4 ±0.15	
	E	68.8 ±0.15	
LiBr	A	60.44±0.07	60.30
	B	61.68±0.07	61.5
	C	62.96±0.07	62.8
	D	64.8 ±0.15	
	E	67.7 ±0.15	
	F	70.2 ±0.15	
LiI	A	59.42±0.07	
	B	59.82±0.07	59.4
	C	61.5 ±0.2	61.3
	D	65.6 ±0.2	
	E	71.4 ±0.2	



Fig. 1 Spectral dependence of the photoabsorption of the lithium halides. The absorption of metallic lithium is given near the K edge.



