in finding this way corresponds to the following set of trial functions:

$$f(\vec{r}) = \exp\left\{-\tfrac{1}{2}(r/d)^2\right\} \tag{5}$$

and

$$\Phi(\vec{r}) = -\tfrac{1}{2}r^2\alpha F(\varphi/\alpha). \tag{6}$$

Here, d is an adjustable constant and F is a function which satisfies $F'(\pm 1) = 1$. Substitution of these expressions into Eq. (3) yields

$$E = Cd^2 + \frac{1}{d^2}, \tag{7}$$

with

$$C = \alpha^2 \int_0^1 F^2(x)dx + \tfrac{1}{4}\int_0^1 \left\{F'(x)-1\right\}^2 dx. \tag{8}$$

The lowest value of E is reached if one selects $d^4 = 1/C$, which leads to $E = 2\sqrt{C}$. In order to find the lowest value of E, we minimize the functional C with respect to F, which gives

$$F = \frac{1}{2\alpha}\frac{\sinh(2\alpha\varphi)}{\cosh(2\alpha)}.$$

Hence, the lowest value of E satisfies

$$E \leq \left\{1-\tanh(2\alpha)/2\alpha\right\}^{1/2}. \tag{9}$$

We have tried to improve this value of E further by letting the range of the trial function $f(\vec{r})$ be dependent on the polar angle φ. Explicitly,

$$d(\varphi) = \mu\left\{1+p(1-\varphi^2/\alpha^2)^2\right\}.$$

It has turned out that the parameter p, which corresponds to the lowest value of E, is very small and that the corresponding reduction of E is less than 1%.

The value of E which corresponds to H_{c3} is

0.59. It follows from Eq. (9) that the nucleation field for superconductivity is certainly <u>larger</u> than H_{c3} if the angle 2α does not exceed 76°. Since the nucleation field H_{c2} corresponds to $E = 1$, it follows from Eq. (9) that nucleation occurs for a value of H_{c4} which satisfies

$$\frac{H_{c4}}{H_{c2}} \geq \left\{1-\frac{\tanh(2\alpha)}{2\alpha}\right\}^{-1/2}. \tag{10}$$

It follows from Eq. (10) that the nucleation field increases towards infinity at least like $\left\{\tfrac{2}{3}\alpha\sqrt{3}\right\}^{-1}$ if $\alpha \to 0$, so that nucleation can in principle occur for any field above H_{c3}, depending on the value of α. Another conclusion is that irregularities of the surface, like scratches, may cause nucleation to occur for fields above H_{c3}.

It has not been proven that a critical angle $\alpha < \pi/2$ exists below which the nucleation field exceeds H_{c3}. This question can only be solved by a rigorous analysis of the Landau-Ginzburg equations for our geometry.

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[1]V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950).

[2]D. Saint-James and P. G. de Gennes, Phys. Letters 7, 306 (1963).

[3]W. E. Druyvesteyn, private communication.

[4]P. G. de Gennes, Superconductivity of Metals and Alloys (W. A. Benjamin, Inc., New York, 1966), p. 199.

MEASUREMENT OF PHOTOABSORPTION OF THE SODIUM HALIDES NEAR THE SODIUM $L_{2,3}$ EDGE

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The optical absorption of the sodium halides (NaF, NaCl, NaBr, NaI) has been studied at energies about 30 to 75 eV, i.e., in the neighborhood of the sodium $L_{2,3}$ edge. The intense continuum of the synchrotron radiation emitted by the 6-GeV electron synchrotron has been used as the light source.

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.[1-3] We have studied photoabsorption due to transi-

tions from the $L_{2,3}$ shell of Na$^+$ in the four sodium halides (NaF, NaCl, NaBr, and NaI) with onset at photon energies of about 32 eV ($\sim$370-Å wavelength). Similar measurements have been performed by O'Bryan.[4] We have obtained improved results by using the synchrotron radia-

tion of the 6-GeV electron synchrotron at Deutsches Electronen-Synchrotron (DESY) as a radiation source with a continuous spectral distribution.[5] 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 $L_{2,3}$ edge at 73 eV). Mg filters were added for measurements in the 32- to 50-eV range (Mg $L_{2,3}$ 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.[6] All measurements were performed at room temperature.

Figure 1 shows the energy dependence of the absorption coefficient derived from our measurements. As the sample thickness has not 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.
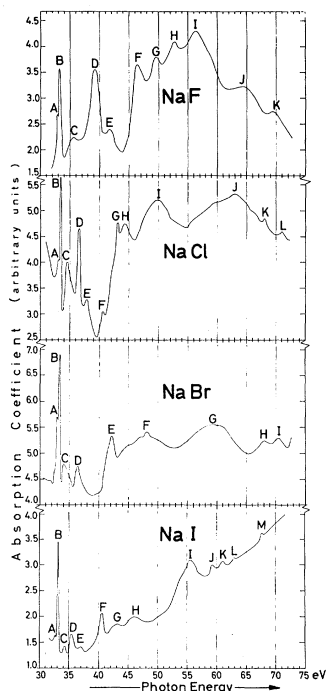

FIG. 1. Spectral dependence of the photoabsorption of the sodium halides near the sodium $L_{2,3}$ edge.

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

Maximum		Present study	O'Bryan[a]	Electron energy loss[b]
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		
NaI	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		

[a]Ref. 4.   [b]Ref. 8.

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[7] in the first, second, and third orders. The calibration is especially good for the most prominent peak B, since it lies 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 easily be 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.[4] 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[8] 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.[9]

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[1]) 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.[10] Our results are in excellent agreement with his.

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[1]K. Teegarden and G. Baldini, Phys. Rev. 155, 896 (1967).

[2]D. M. Roessler and W. C. Walker, Phys. Rev. 166, 599 (1968).

[3]G. Baldini and B. Bosacchi, Phys. Rev. 166, 863 (1968).

[4]H. M. O'Bryan, Phys. Rev. 57, 995 (1940).

[5]R. Haensel and C. Kunz, Z. Angew. Phys. 23, 276 (1967).

[6]R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag, Appl. Opt. 7, 301 (1968).

[7]K. Codling and R. P. Madden, Phys. Rev. Letters 12, 106 (1964).

[8]M. Creuzburg, Z. Physik 196, 433 (1966).

[9]P. E. Best, Proc. Phys. Soc. (London) 79, 133 (1962).

[10]T. Sagawa, in Proceedings of the International Conference on Soft X-Ray Spectroscopy and the Band Structure of Metals and Solids (Academic Press, Inc., New York, to be published).