Fine Structure in the Exciton Bands of the Alkali Halides*

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This paper presents new data on the optical absorption spectra of evaporated films of KI, NaI, RbI, NaBr, and KBr in the region between 1700 A and 2500 A. The measurements were made at room temperature and −180°C. The absorption spectra of the iodides reveal hitherto unreported structure in the fundamental-band region of the salts.

I. INTRODUCTION

MANY measurements of the optical absorption of the alkali halides in the ultraviolet have been made in the past. Pohl and his co-workers measured the absorption of thin films in the region from 1600 A to 2600 A at room temperature.[1] Later, Schneider and O'Brien extended these measurements further into the vacuum ultraviolet.[2] Their work was also done at room temperature. Very recently Taft and Philipp, and also Martienssen have observed the absorption spectra of the iodides at low temperatures in the region between about 1850 A and 2600 A.[3] Hartman and his co-workers have given data on the optical absorption spectra of KCl and NaCl.[4]

The data presented in the present paper overlap the results of the aforementioned investigators but also show new features not observed in these investigations. The original contribution of the present work consists of an examination of structure in the fundamental bands of NaI, KI, and RbI at −180°C in the region between 1700 A and 1850 A, and observations on the first fundamental band of NaBr and KBr at −180°C. The experiments on the iodides show some new structure in the so-called exciton bands and may be of interest in connection with recent theoretical work.[5] The work on NaBr and KBr was done in an attempt to clarify some observations made by the Göttingen school. Bauer gives evidence that the first fundamental band of NaBr is a doublet which can be resolved at room temperature.[6] His result, however, appears to depend upon a single experimental point. It was felt that this very interesting doubling should be investigated at low temperature where the splitting should be more pronounced.

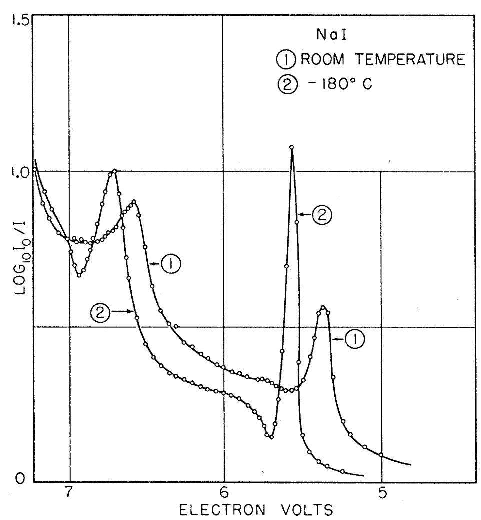

FIG. 1. The optical absorption spectrum of a thin film of NaI on a NaCl substrate at −180°C and room temperature.

II. EXPERIMENTAL

The measurements of optical absorption were made on films of the order of 1000 A thick, evaporated onto a LiF or NaCl substrate in vacuum. Both the evaporation

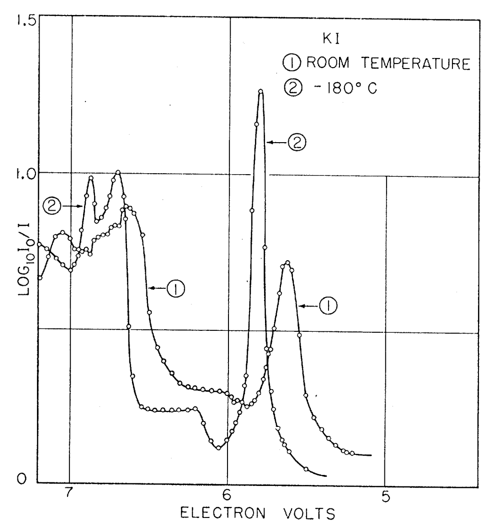

FIG. 2. The optical absorption spectrum of a thin film of KI on a LiF substrate at −180°C and room temperature.

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[1] R. Hilsch and R. W. Pohl, Z. Physik **57**, 145 (1929); **59**, 812 (1930).

[2] E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

[3] W. Martienssen (to be published); E. A. Taft and H. R. Philipp (to be published).

[4] Hartman, Nelson, and Siegfried, Phys. Rev. **105**, 123 (1956).

[5] Albert W. Overhauser, Phys. Rev. **101**, 1702 (1956); T. Muto and S. Oyama, J. Phys. Soc. Japan **12**, 101 (1957); T. Muto and H. Okuno, J. Phys. Soc. Japan **12**, 108 (1957); D. L. Dexter (to be published).

[6] G. Bauer, Ann. Physik **19**, 434 (1934).

TABLE I. Positions of the iodide fundamental bands at room temperature and −180° C.

Crystal	Position of bands at room temperature in ev	Position of bands at −180°C in ev
NaI	5.375 6.575	5.575 6.700
KI	5.625 6.650 7.050	5.800 6.700, 6.875
RbI	5.525 ∼6.50 6.575 6.950	5.700 6.500, ∼6.60 6.650 ∼6.85, 6.975

and the measurements were carried out in the same cryostat so that the films were never removed from the vacuum during the experiment. During evaporation the substrate was held at room temperature and the films were not heated above this temperature. Cooling was done with liquid nitrogen.

A Bausch & Lomb single monochromator equipped with Corning fused-silica prisms and aspheric lenses was used in the experiment. An RCA end-on photomultiplier with a sodium salycilate phosphor was used as detector with a Nester hydrogen lamp as source. It was necessary to surround the monochromator, source, detector, and cryostat with an atmosphere of dry nitrogen since oxygen absorbs strongly in the region below 1950 A.

The cryostat was designed to permit rotation of the inner nitrogen container about the vertical axis so that the film could be turned in and out of the beam from the monochromator between it and the detector. Thus, the optical absorption of the crystal was measured in terms of the quantity $\log_{10}(I_0/I)$, where I is the intensity of the light transmitted by the film and I_0 is the intensity of the incident beam. This quantity is often called the optical density of the sample. Such a measurement cancels out any absorption by the quartz windows of the cryostat. Measurements were made before and after evaporation to correct for absorption or reflection by the substrate but no correction was made for the reflectivity of the films themselves.

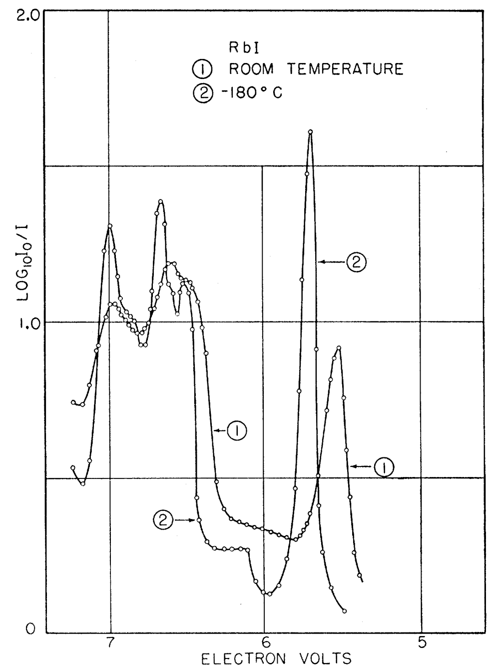

FIG. 3. The optical absorption spectrum of a thin film of RbI on a LiF substrate at −180°C and room temperature.

III. DISCUSSION

1. NaI, KI, and RbI

Figures 1, 2, and 3 show the optical absorption spectra of NaI, KI, and RbI respectively. The spectrum of NaI shows two peaks in the region studied. At room temperature the first fundamental band appears at 5.375 ev and a second hand at 6.575 ev. A third band, observed by Hilsch and Pohl at room temperature, occurs at 7.26 ev, outside the range of the present measurements. Upon cooling to −180°C the two bands sharpen and shift to shorter wavelengths but no splitting is observed. At −180°C the edge which Taft ascribes to band-to-band transition becomes noticeable at about 5.75 ev.

In the spectrum of KI, three distinct bands occur at room temperature. The first fundamental band is at 5.65 ev, a second band at 6.65 ev, and a third at 7.07 ev. Cooling to −180°C produces sharpening and shifting of the bands. In the case of the second band this sharpening reveals that the band is actually a doublet with components at 6.700 ev and 6.875 ev. This fact has not been reported up to now. The first fundamental band, as is well known, remains single with its peak at 5.8 ev at −180°C. The edge occurs at about 6.1 ev.

Three peaks also appear in the absorption spectrum of the RbI film at room temperature. They occur at 5.525 ev, 6.575 ev, and 6.950 ev. Upon cooling to −180°C the band at 6.575 ev splits into two components at 6.500 ev and 6.650 ev. This splitting was first reported in the recent work of Taft and Philipp and Martienssen.[3] The present data indicates that there might be a third component in this group at about 6.575 ev and also shows that the band which occurs at 6.950 ev at room temperature probably consists of two components. At −180°C this latter band resolves into a peak at 6.975 ev and a shoulder at about 6.85 ev.

The positions of the various bands in the iodide absorption spectra are given in Table I.

The data shown in Fig. 4 are presented as an interesting corollary to the observations on the optical absorption of KI discussed above. The curve gives the excitation spectrum of the luminescence of a single crystal of KI at −180°C. This luminescence has been

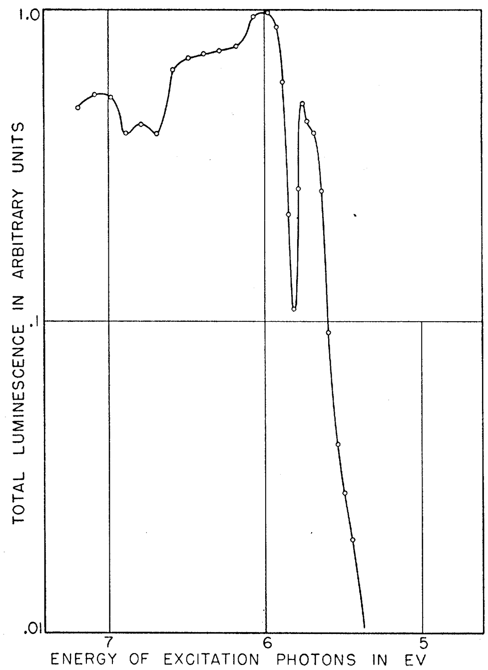

FIG. 4. The excitation spectrum of the luminescence of KI at −180°C.

described in a previous paper.[7] It is sufficient for the present work to note that the curve is a plot of the total intensity of luminescence against quantum energy of the exciting radiation. The intensity of the exciting radiation in number of quanta per second was held constant. Each of the minima in the excitation spectrum corresponds to a maximum in the optical absorption spectrum. In fact, the excitation spectrum bears a faithful impression of the absorption spectrum even to the extent of details like the edge at 6.10 ev.

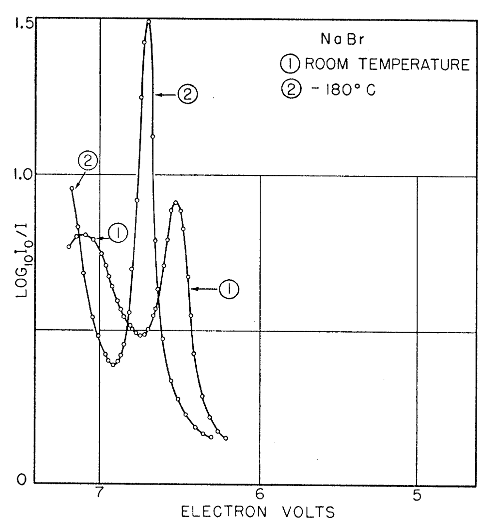

FIG. 5. The optical absorption spectrum of a thin film of NaBr on a LiF substrate at −180°C and room temperature.

[7] K. J. Teegarden, Phys. Rev. **105**, 1222 (1957).

2. NaBr and KBr

As mentioned above, Bauer presented data in which the first fundamental band of NaBr appears to be double at room temperature. In an effort to extend his observations the data given in Fig. 5 was taken. The first and second fundamental bands of NaBr are shown at room temperature while only the first lies in the spectral range investigated at −180°C. No splitting of the first band appears at either temperature. One would expect that a splitting observable at room temperature would be even more easily resolved at −180°C. On the other hand, it is well known that the method used to produce thin alkali-halide films has a marked effect on their optical absorption spectra. Thus, it is possible that the splitting which Bauer observed was related to the fact that he annealed his films at elevated temperatures before measuring their absorption. The films used in the present work were not annealed.

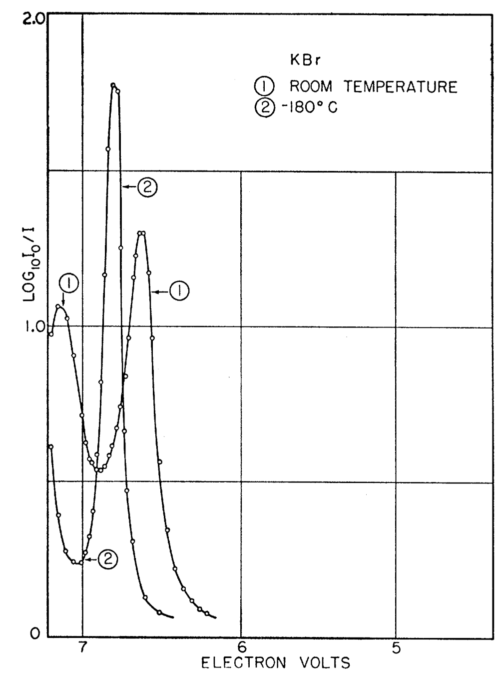

FIG. 6. The optical absorption spectrum of a thin film of KBr on a LiF substrate at −180°C and room temperature.

Figure 6 shows the first fundamental band of KBr at room temperature and −180°C. No splitting is indicated in this case.

IV. ACKNOWLEDGMENTS

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