but $\Delta_{\mathbf{k}}$ itself may be negative. It includes, along with the electron-hole exchange interaction and other lattice interactions, a term approximately equal to twice the Heller-Marcus term for transverse excitons (at $\mathbf{k}\approx 0$)[26]

$$-2(\tfrac{4}{3}\pi n_0|\boldsymbol{\mu}|^2),$$

where n_0 is the atomic density and $\boldsymbol{\mu}$ is the dipole moment of the optical transition involved. This term, which is present in singlet exciton states only, may easily cause $E_{1\mathbf{k}}$ to lie below $E_{3\mathbf{k}}$ in the vicinity of $\mathbf{k}=0$.

If $\Delta_{\mathbf{k}}$ is large compared to ζ, the "*LS* coupling" limit is reached and very little of $^1\Phi_{\mathbf{k}}$ is mixed into $^3\Phi_{\mathbf{k}}$ by the spin-orbit interaction. In this case only one absorption line (N_1) will be strong.

The formalism of this appendix is rigorous only in the case of a "pure" $p^5\gamma_1$ configuration, i.e., one which is unperturbed by nearby configurations, and in which the electron contributes nothing to the spin-orbit matrix element. These restrictions are discussed briefly in Sec. III(a) of the text.

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[26] W. R. Heller and A. Marcus, Phys. Rev. 84, 809 (1951).

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Ultraviolet Absorption of Alkali Halides*

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The absorption spectra of evaporated films of the alkali halides, with the exception of LiF, have been measured at room temperature and 80°K in the region from 1100 A to 2500 A. The spectra are rather complex at low temperature, but agree fairly well with current theory concerning the multiplicity and grouping of the exciton peaks. In addition, a shoulder has been found in many of the spectra, similar to the ones previously seen and associated with the band-to-band transition in the alkali iodides.

INTRODUCTION

THE optical absorption spectra of the alkali halides in the vacuum ultraviolet region have been investigated by several authors.[1,2] As a necessary experimental background for proposed work on the low-temperature luminescence of these materials and in view of recent interest in exciton absorption,[3–5] some of these measurements have been repeated and extended to liquid nitrogen temperature, using an instrument capable of rather high wavelength resolution. The results show a complexity of structure in the absorption spectra which had not been indicated by the earlier work.

EXPERIMENTAL APPARATUS

The monochromator used was very similar to that described by Tousey and Johnson.[6] Its useful range for this experiment was from 1100 A to 2500 A, and band widths of from 0.5 to 5.0 A were employed. The light source was a modified Hanovia hydrogen arc lamp with one end window removed, operated on direct current. This source was very stable after being allowed to warm up, and provided a continuum down to about 1650 A, with a line spectrum from there on to the 1100 A limit imposed by the lithium fluoride substrates upon which the thin films were deposited. The detection system employed a sodium salycilate phosphor,[7] the luminescence of which was detected by a 6199 end-on photomultiplier. The output of this photomultiplier was recorded on a Brown recording potentiometer.

The samples were mounted in a metal cryostat of double Dewar construction, provided with a rotating seal which allowed either of two symmetrical substrate holders to be placed in the beam of radiation from the monochromator. This cryostat also contained a small electric oven which was used to evaporate the samples. A lithium fluoride window was placed at the exit slit of the monochromator to exclude hydrogen from the cryostat, and thus the cryostat formed a separate vacuum system.

Initially this system was evacuated by a small oil diffusion pump, but it was found that in spite of the baffling provided by the outer Dewar of the cryostat, deposition on the sample of condensible vapors from the pumps interfered seriously with the low-temperature absorption measurements. Quite satisfactory results

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* Sponsored by the Office of Ordnance Research, U. S. Army.

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[1] R. Hilsch and R. W. Pohl, Z. Physik 59, 812 (1930); E. G. Schneider and H. M. O'Bryan, Phys. Rev. 51, 293 (1937).

[2] Hartman, Nelson, and Siegfried, Phys. Rev. 105, 123 (1957).

[3] A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

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[5] R. S. Knox and N. Inchauspé, preceding paper, Phys. Rev. 116, 1093 (1959).

[6] Tousey, Johnson, Richardson, and Toran, J. Opt. Soc. Am. 41, 696 (1951).

[7] K. Watanabe and E. Inn, J. Opt. Soc. Am. 43, 32 (1953).

were obtained, however, by the following procedure. The cryostat was exhausted to a good fore-pump vacuum and then sealed off from the pumps completely while the outer Dewar was maintained continuously at liquid nitrogen temperature. Under these conditions the rate of deposition of condensible vapors was negligibly small (amounting to a decrease in transmission of a cooled blank substrate of about ten percent over a period of an hour).

MEASUREMENTS

For each material studied two films were prepared by evaporation from a platinum boat, the thicker film having an optical density of about one in an absorption peak, and the thinner having about one tenth this density. These films were formed on two substrates of Harshaw single-crystal LiF about one third millimeter in thickness, one of which contained a thermocouple. The material to be evaporated consisted of small fragments of Harshaw single crystals where available, powdered reagent grade material being used otherwise.

Measurements were made by recording 100 A segments of the hydrogen spectrum, first as seen through one of the films and then through the other. These measurements on any particular segment required about five minutes to complete, the light source and detection system being stable to better than one percent over this period of time. After running through the complete spectrum, the substrates were cooled to liquid nitrogen temperature and the measurements repeated.

In the portion of the hydrogen spectrum which contains many sharp lines, the transmission of the sample could be found by considering the height above the background of a particular line. The ratio of this height as seen through the thick film to that seen through the thin film would then give the transmission of the sample for radiation of that wavelength. In this method one ignores the background, composed of scattered light, photomultiplier dark current, and any continuum that may be present.

In practice this rather cumbersome method was used to compute the contribution of scattered light and dark current at several points in the spectrum. This contribution was found to be fairly constant as a function of time and wavelength, and was then used as a correction to be subtracted from the photomultiplier readings at any given wavelength.

No attempt was made to measure film thicknesses, but it was estimated from the results of Bauer[8] that the thick films were on the order of 1000 A while the thin films were about 100 A thick.

The LiF used in the substrates was found to have very little absorption in the spectral range considered. Thus a slight mismatch in substrate thicknesses would have a negligible effect on the absorption structure measured. The deposition of condensible vapors at low temperature was approximately the same on both films, and its effects were thus effectively cancelled. With the exception of reflection effects, then, the results show the absorption of a film of material whose thickness was equal to the difference between the thin and thick films.

The possible importance of reflection corrections in measurements of this type has been pointed out by Hartman, Nelson, and Siegfried.[2] Our measurement technique incorporated these corrections only to the approximation that assumes the reflectivities of thick and thin films to be the same.

RESULTS

Figures 1 (a)–(t) show the absorption spectra which were measured. The data taken at room temperature are shown in dashed lines, while those taken at liquid nitrogen temperature (80°±2°K) are plotted as individual points connected by a solid curve. The room temperature results agree in general with those of Hilsch and Pohl and Schneider and O'Bryan,[1] while at the lower temperature is seen the expected narrowing of the peaks, accompanied, in some of the lower energy bands, by a shift to higher energies.

In our earlier measurements the long wavelength limit of the monochromator was about 1950 A, and the long wavelength structure of the iodides could not be covered. As a result, Teegarden's earlier data[9] for NaI, KI, and RbI were matched to the curves obtained in this work. Later investigation confirmed the appearance of these curves, and they were not replotted.

In the case of CsCl two absorption spectra were found, one (curve I) for a freshly evaporated film, and the other (curve II) for the same film after annealing at room temperature for about ten hours. Measurements were also made on a film of this material which had been evaporated onto a fused silica substrate. In this case a spectrum similar to that found in curve II was found at once, annealing of the film not being required for this result.

A suggested interpretation of these results is that CsCl, when evaporated onto an amorphous surface, crystallizes in its normal CsCl type lattice structure. When evaporated onto the NaCl type crystal structure of LiF, however, it is suggested that epitaxial effects occur, similar to those found by Shultz.[10] The CsCl then crystallizes in the NaCl type structure, reverting to its normal form after annealing. Evidence for this interpretation is afforded by the similarity of curve I to the curves found for the NaCl type chlorides. Attempts were made to find similar annealing effects in the other cesium salts having the CsCl type structure, but with no success.

Another case of interest is that of CsF, where at nitrogen temperature the thicker film was more trans-

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

[9] K. Teegarden, Phys. Rev. **108**, 660 (1957).

[10] L. G. Shultz, Acta Cryst. **4**, 487 (1951).

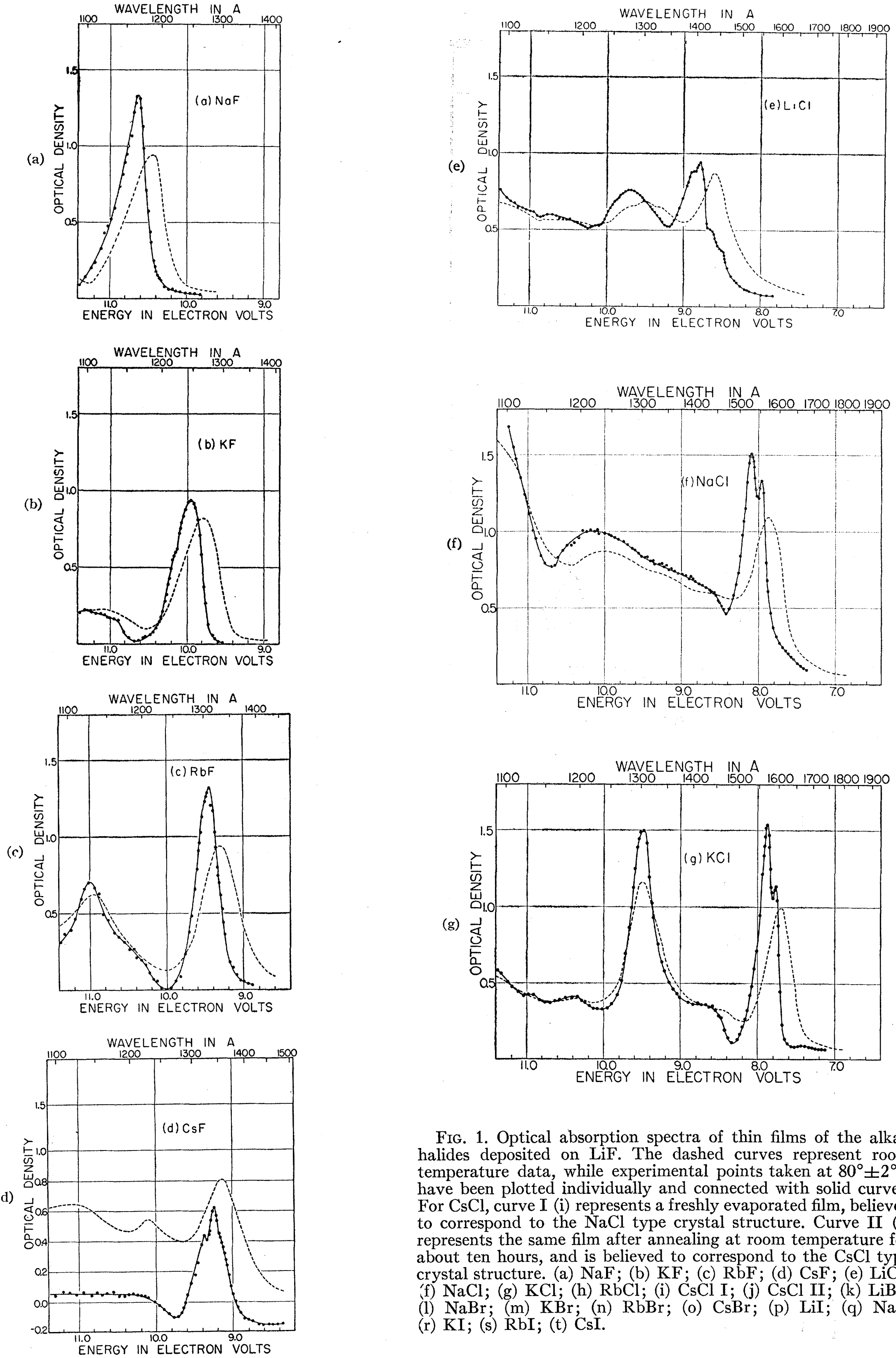


FIG. 1. Optical absorption spectra of thin films of the alkali halides deposited on LiF. The dashed curves represent room temperature data, while experimental points taken at 80°±2°K have been plotted individually and connected with solid curves. For CsCl, curve I (i) represents a freshly evaporated film, believed to correspond to the NaCl type crystal structure. Curve II (j) represents the same film after annealing at room temperature for about ten hours, and is believed to correspond to the CsCl type crystal structure. (a) NaF; (b) KF; (c) RbF; (d) CsF; (e) LiCl; (f) NaCl; (g) KCl; (h) RbCl; (i) CsCl I; (j) CsCl II; (k) LiBr; (l) NaBr; (m) KBr; (n) RbBr; (o) CsBr; (p) LiI; (q) NaI; (r) KI; (s) RbI; (t) CsI.

Fig. 1.—*Continued*

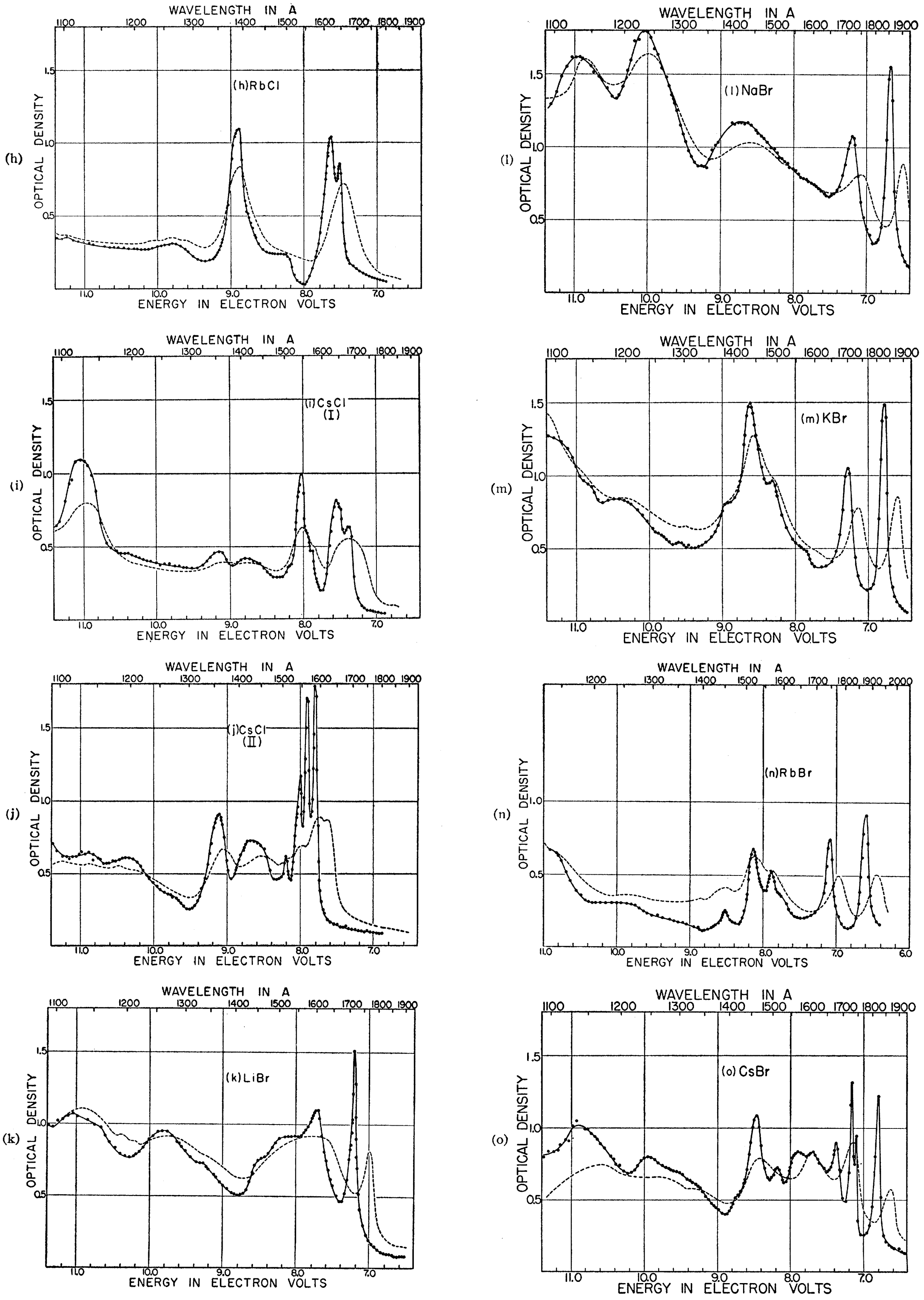
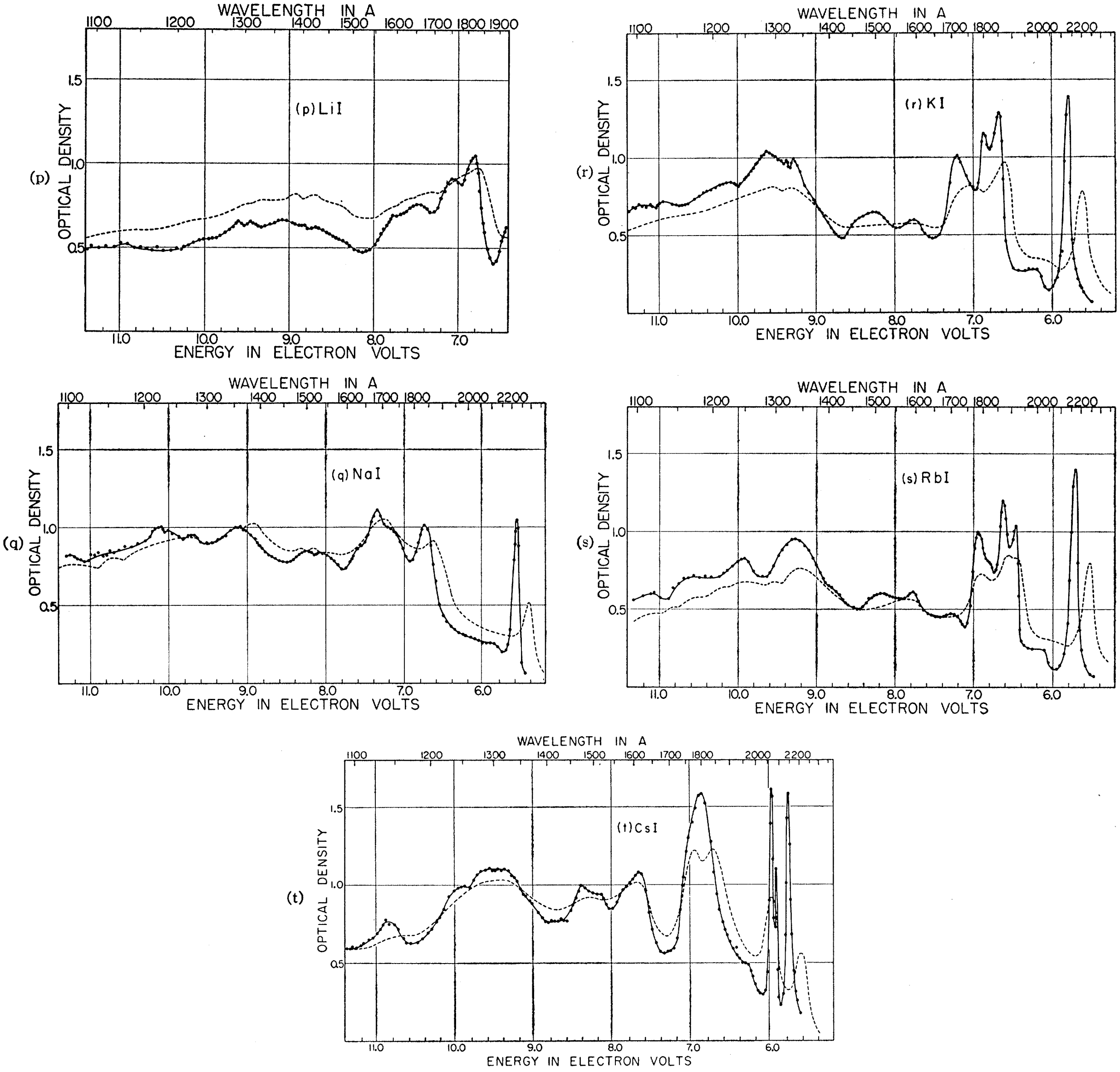


Fig. 1.—*Continued*



parent in the regions of low absorption than was the thinner film, thus resulting in apparent negative densities. The effect was quite reproducible, but no satisfactory explanation has been found.

CONCLUSIONS

Recent theoretical work with excitons in these materials has been based on one of two models. In the "excitation" model the exciton is formed by raising an electron to an excited state of a halide ion, while in the "charge transfer" model an electron from a halide ion is shared by its nearest neighbors. Knox and Inchauspé have however pointed out[5] that the two models are essentially equivalent regarding predictions for the multiplicity of the exciton absorption structure. Accord, ing to these authors there might be, among others- nine bands in the low-energy structure, associated with the halogen doublet, arising from the transitions to the $p^5\gamma_1$ configuration, and a triplet and quartet, from the transitions to $p^5\gamma_3$ and $p^5\gamma_5$ configurations, respectively. In addition, a minimum splitting for the doublet has been calculated under certain restrictions, giving the values of 0.047 ev for the fluorides, 0.103 ev for the chlorides, 0.432 ev for the bromides and 0.889 ev for the iodides.

Overhauser's prediction of five exciton lines for the NaCl structure and six lines for the CsCl structure can be interpreted on either model as a combination of the doublet and triplet in the first case, and the doublet

TABLE I. Splittings of the halogen doublets at 80°K.

Salt	First peak	Second peak	Difference	Predicted minimum splitting[a]
LiCl	uncertain	⋯	⋯	0.103 ev
NaCl	7.96 ev	8.09 ev	0.13 ev	0.103 ev
KCl	7.76 ev	7.87 ev	0.11 ev	0.103 ev
RbCl	7.51 ev	7.64 ev	0.13 ev	0.103 ev
CsCl (I)	7.37 ev	7.54 ev	0.17 ev	0.103 ev
CsCl (II)	7.80 ev	7.91 ev	0.11 ev[b]	0.103 ev
LiBr	7.20 ev	7.72 ev	0.52 ev[b]	0.432 ev
NaBr	6.68 ev	7.20 ev	0.52 ev	0.432 ev
KBr	6.77 ev	7.26 ev	0.49 ev	0.432 ev
RbBr	6.60 ev	7.08 ev	0.48 ev	0.432 ev
CsBr	6.80 ev	7.10 ev	0.30 ev[b]	0.432 ev
LiI	uncertain	⋯	⋯	0.889 ev
NaI	5.56 ev	6.73 ev	1.17 ev	0.889 ev
KI	5.80 ev	6.68 ev	0.88 ev[b]	0.889 ev
RbI	5.70 ev	6.47 ev	0.77 ev[b]	0.889 ev
CsI	5.76 ev	5.91 ev	0.15 ev[b]	0.889 ev

[a] After Knox and Inchauspé (reference 5).

[b] In these cases the probability of configuration interaction makes the computation of the doublet splitting either questionable or invalid.

and quartet in the second. This ordering appears reasonable, since the transition involving nearest neighbors in the charge transfer model gives rise to $p^5\gamma_1$ and $p^5\gamma_3$ configurations in the NaCl lattice, but results in $p^5\gamma_1$ and $p^5\gamma_5$ configurations in the CsCl lattice. The transfer to next nearest neighbors, which presumably requires more energy, results in a $p^5\gamma_5$ configuration in NaCl.

This type of analysis is not in disagreement with the present data. If the doublet is assumed to consist of the two lowest energy bands in each salt, then at 80°K the bands at 7.96 and 8.09 ev in NaCl, 7.76 and 7.87 ev in KCl, 7.51 and 7.64 ev in RbCl, and 7.37 and 7.54 ev in CsCl (curve I) all exceed the predicted minimum splitting for the chlorides. For LiCl no clear splitting is seen, and even the identification of the first strong band as a doublet is uncertain. The splittings are summarized in Table I.

In the case of CsCl in the CsCl lattice structure (curve II) the first two lines, at 7.80 and 7.91 ev, are separated by more than the predicted minimum splitting. But here, as will also be seen in the other CsCl type crystals, the close proximity of other lines indicates that configuration interaction may have become appreciable. Under these conditions the minimum splitting rule for the doublet breaks down and the identification of the groups becomes uncertain. The splitting of the doublet in the cases of NaCl and KCl had been seen earlier in the reflection spectra[2] of these salts, and in the case of NaCl, in the absorption spectrum at 140°K.

Similarly, the bands of 7.20 and 7.72 ev in LiBr, 6.68 and 7.20 ev in NaBr, 6.77 and 7.26 ev in KBr and at 6.60 and 7.08 ev in RbBr exceed the predicted minimum splitting for the bromides. The presence of other nearby peaks in the cases of LiBr and CsBr again indicates the possibility that configuration interaction is present, although the minimum splitting rule is still satisfied in LiBr.

In the iodides the only reasonably well isolated doublet at nitrogen temperature is found in NaI, with lines at 5.56 and 6.73 ev, this separation exceeding the predicted minimum value. It might be suggested that the lines at 5.80 and 6.68 ev in KI, and 5.70 and 6.47 ev in RbI might correspond to "doublets," although the splittings here are too small, the presence of closely adjacent lines again indicating that configuration interactions have become strong enough to invalidate the computation of the doublet splitting. A similar result is seen in the case of LiI, but the experimental results here are of dubious worth, since the absorption curve could not be reproduced. The curve shown is from some of our earlier work, extending only to 1950 A, and is presented as being merely representative of the results obtained for this salt. In CsI, as was the case in CsBr, no pair of lines identifiable as the doublet can be found.

No doublet structure could be resolved in the fluorides, where the minimum predicted splitting is 0.047 ev. This result is not surprising in view of the broadening of the lines through temperature and zero-point energy effects. Some structure is found in CsF, but it seems unrealistic to assign this to the doublet splitting.

It would be interesting to find the relative oscillator strengths associated with the bands of these halogen doublets. A rough graphical analysis finds the second peak to have about twice the area of the first in the bromides, and about three times the area of the first in the chlorides. It seems unwise to attempt to specify the relative areas with any greater precision, since for a given material the peak heights and widths are found to vary slightly from one film to another. In addition, the absorption spectra of thin films have low-energy structure, associated with lattice disorder, which may be extending back into the region of the exciton absorption and affecting the areas of these peaks.

A shoulder in the absorption spectrum, of the type which has been associated with the onset of band-to-band transitions by Taft and Philipp,[11] has been found in many cases. In the fluorides, shoulders are found at about 10.0 ev in CsF and 10.9 ev in KF. A vague indication of a shoulder was found in RbF at about 10.4 ev, and in NaF the shoulder, if present, was outside the spectral range covered. The shoulder found in KF falls at an energy in the rising portion of the photoemission curve measured by Taft and Philipp. The positions of the absorption shoulder at 80°K are summarized in Table II.

In the chlorides, shoulders were found at about 8.6 ev in NaCl, 8.5 ev in KCl, and 8.2 ev in RbCl. In LiCl, as mentioned above, identification of the structure in general is uncertain, and in both of the CsCl curves a

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[11] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1959).

TABLE II. Positions of the absorption shoulder at 80°K.

Salt	1[a]	2[b]	3[c]
KF	10.9 ev	10.4 ev[d]	−0.5 ev
RbF	10.4 ev[e]	...	...
CsF	10.0 ev	...	...
NaCl	8.6 ev	8.5 ev[f]	−0.1 ev
KCl	8.5 ev	8.7 ev[d]	0.2 ev
RbCl	8.2 ev	...	...
NaBr	7.7 ev[e]	...	...
KBr	7.8 ev	8.1 ev[d]	0.3 ev
RbBr	7.7 ev[e]	...	...
LiI	5.9 ev[d,e]	7.3 ev[d]	1.4 ev
NaI	5.8 ev	7.3 ev[d]	1.5 ev
KI	6.2 ev	7.3 ev[d]	1.1 ev
RbI	6.1 ev	7.3 ev[d]	1.2 ev
CsI	6.3 ev	6.4 ev[d]	0.1 ev

[a] Position of absorption shoulder at 80°K.
[b] Energy at which photoelectric quantum efficiency reaches 10^{-3} at 300°K.
[c] (Column 2 − Column 1) Electron affinity (after Taft and Philipp, reference 11).
[d] After Taft and Philipp, reference 11.
[e] Approximate value.
[f] After Taylor and Hartman, reference 12.

shoulder, if present, is apparently obscured by other structure. The positions of the shoulders in NaCl and KCl agree fairly well with those found in the absorption and reflectivity spectra by Hartman *et al.*,[2] and occur just about at the energy where the photoemissive yields seen by Taft and Philipp[11] and Taylor and Hartman[12] are rising steeply.

A shoulder was found at 7.8 ev in KBr, and rather vague indications of shoulders at about 7.7 ev in both NaBr and RbBr. In LiBr and CsBr similar shoulders, if present, are again obscured by other structure. Taft and Philipp find the photoemissive yield strongly rising in the vicinity of about 8.0 ev in KBr.

For the iodides, the appearance of these shoulders was found to be the same as that previously reported and discussed by Taft and Philipp and others.[9,13] In general, there is about one electron volt difference between the point where the shoulder appears and the onset of photoemission.

Assigning interpretations to the other high-energy structure is a rather speculative process, at best. Peaks are seen in KCl, RbCl, and CsCl (curve I) that might be considered to be unresolved triplets of the type found in RbBr and KBr. Similar triplets might be found in the structure just above the doublet in NaI and, possibly, in KI and RbI. One could associate these triplets with the $p^5\gamma_3$ type configuration mentioned by Knox and Inchauspé, but since one has no idea of the splittings to be expected, such an assignment would indeed by speculative at the present.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Dr. R. S. Knox and Dr. N. Inchauspé for their extremely helpful conversations concerning both this work and their own.

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[12] J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).

[13] F. Fischer, Z. Physik **139**, 328 (1954); H. Fesefeldt, Z. Physik **64**, 626 (1930); W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957); Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. (II A) **11**, 257 (1955).