

for a nuclear charge  $Z$ . For any electron with angular momentum  $l \neq 0$ , the wave function vanishes at the nucleus; therefore, the sum  $A = 0$ . For example, for the  $2p$  level the negative contribution  $A_{1S, 2P}$  balances the positive contributions from all other transitions. For a state with  $l = 0$ , however,

$$\psi_m^2(0) = (Z/na)^3/\pi, \quad (10)$$

where  $n$  is the principal quantum number and  $a$  is the Bohr radius.

Inserting (10) and (9) into (6) and using relations between atomic constants, we get for an  $S$  state

$$W_{ns}' = \frac{8}{3\pi} \left(\frac{e^2}{\hbar c}\right)^3 \text{Ry} \frac{Z^4}{n^3} \ln \frac{K}{\langle E_n - E_m \rangle_{Av}}, \quad (11)$$

where Ry is the ionization energy of the ground state of hydrogen. The shift for the  $2p$  state is negligible; the logarithm in (11) is replaced by a value of about  $-0.04$ . The average excitation energy  $\langle E_n - E_m \rangle_{Av}$  for the  $2s$  state of hydrogen has been calculated numerically<sup>7</sup> and found to be 17.8 Ry, an amazingly high value. Using this figure and  $K = mc^2$ , the logarithm has the value 7.63, and we find

$$W_{ns}' = 136 \ln[K/(E_n - E_m)] \\ = 1040 \text{ megacycles.} \quad (12)$$

<sup>7</sup>I am indebted to Dr. Stehn and Miss Steward for the numerical calculations.

This is in excellent agreement with the observed value of 1000 megacycles.

A relativistic calculation to establish the limit  $K$  is in progress. Even without exact knowledge of  $K$ , however, the agreement is sufficiently good to give confidence in the basic theory. This shows

- (1) that the level shift due to interaction with radiation is a real effect and is of finite magnitude,
- (2) that the effect of the infinite electromagnetic mass of a point electron can be eliminated by proper identification of terms in the Dirac radiation theory,
- (3) that an accurate experimental and theoretical investigation of the level shift may establish relativistic effects (e.g., Dirac hole theory). These effects will be of the order of unity in comparison with the logarithm in Eq. (11).

If the present theory is correct, the level shift should increase roughly as  $Z^4$  but not quite so rapidly, because of the variation of  $\langle E_n - E_m \rangle_{Av}$  in the logarithm. For example, for  $\text{He}^+$ , the shift of the  $2s$  level should be about 13 times its value for hydrogen, giving  $0.43 \text{ cm}^{-1}$ , and that of the  $3s$  level about  $0.13 \text{ cm}^{-1}$ . For the x-ray levels  $LI$  and  $LII$ , this effect should be superposed upon the effect of screening which it partly compensates. An accurate theoretical calculation of the screening is being undertaken to establish this point.

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## Spectral Location of the Absorption Due to Color Centers in Alkali Halide Crystals

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SEITZ<sup>1</sup> has recently published a paper summarizing the properties of the absorption bands arising from electrons trapped in the lattice of alkali halide crystals. The present writer is not aware of the existence of a compilation of data on the spectral location of these various bands. Table I was prepared to collect

this information. The terminology for the bands is that used by Seitz. In this respect it is of interest to point out that the band designated by Seitz as the  $M$ -band (after Molnar) has been called the  $O$ -band (after Ottmer) by Kalabuchov.<sup>2</sup>

In addition to the  $F$ -,  $R_1$ -,  $R_2$ -, and  $M$ -bands occurring in the pure alkali halides, Table I also

<sup>1</sup>F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1946).

<sup>2</sup>N. Kalabuchov, *J. Phys. U.S.S.R.* **9**, 41 (1945).

TABLE I. Spectral location of the absorption in alkali halide crystals.

	Inter-ionic salt distance, <sup>a</sup> <i>d</i> (Angstroms)	Location of absorption peak (Angstroms) (Values in parentheses are calculated)				
		<i>U</i> -Band	<i>F</i> -Band	<i>R</i> <sub>1</sub> -Band	<i>R</i> <sub>2</sub> -Band	<i>M</i> -Band
LiF	2.01	(1320)	(2540) 2570 <sup>c</sup> 2500 <sup>d-f</sup>	(2950)	(3200) 3100 <sup>e</sup> 3060 <sup>d</sup>	(4160) 4440 <sup>e</sup>
LiCl	2.57	(1740)	(3980) 3850 <sup>d, f</sup>	(4620)	(5000) 5800 <sup>d</sup>	(6100) 6500 <sup>d</sup>
LiBr	2.75	(1870)	(4520)	(5250)	(5680)	(6790)
LiI	3.00	(2060)	(5310)	(6160)	(6670)	(7770)
NaF	2.31	(1550)	(3280) 3410 <sup>e</sup> 3350 <sup>d</sup> 3400 <sup>f</sup>	(3810)	(4120) 4150 <sup>d</sup>	(5160) 5050 <sup>e</sup> 5100 <sup>d</sup>
NaCl	2.81	(1920) 1920 <sup>b</sup>	(4710) 4580 <sup>e</sup> 4700 <sup>d</sup> 4650 <sup>f</sup>	(5470) 5450 <sup>*e</sup>	(5920) 5960 <sup>*e</sup>	(7010) 7250 <sup>e</sup> 7200 <sup>d</sup> 7050 <sup>b</sup>
NaBr	2.98	(2040) 2100 <sup>b</sup>	(5250) 5400 <sup>d, f</sup>	(6100)	(6600)	(7700)
NaI	3.23	(2230)	(6090) 5850 <sup>f</sup>	(7070)	(7650)	(8710)
KF	2.67	(1810)	(4280) 4550 <sup>d, f</sup>	(4970)	(5380) 5700 <sup>e</sup>	(6480)
KCl	3.14	(2160) 2140 <sup>b</sup>	(5760) 5560 <sup>e</sup> 5630 <sup>d, f</sup>	(6690) 6580 <sup>*e</sup>	(7250) 7270 <sup>*e</sup>	(8350) 8250 <sup>e</sup> 8200 <sup>d</sup>
KBr	3.29	(2280) 2280 <sup>b</sup>	(6300) 6250 <sup>e</sup> 6300 <sup>d, f</sup>	(7320) 7350 <sup>*e</sup>	(7920) 7900 <sup>*e</sup>	(8970) 8920 <sup>*e</sup> 9200 <sup>b</sup>
KI	3.53	(2460) 2440 <sup>b</sup>	(7180) 6890 <sup>e</sup> 7200 <sup>d</sup> 6850 <sup>f</sup>	(8340)	(9020)	(10,000)
RbF	2.82	(1930)	(4740)	(5500)	(5950)	(7070)
RbCl	3.27	(2260) 2300 <sup>b</sup>	(6230) 6090 <sup>d</sup> 6240 <sup>f</sup>	(7240)	(7830)	(8890)
RbBr	3.43	(2380) 2420 <sup>b</sup>	(6800) 6940 <sup>e</sup> 7200 <sup>b</sup>	(7900) 8050 <sup>*e</sup>	(8550) 8590 <sup>*e</sup>	(9560) 9570 <sup>*e</sup>
RbI	3.66	(2560)	(7630) 7500 <sup>e</sup> 7750 <sup>f</sup>	(8850)	(9590)	(10,600)
CsF	3.00	(2060)	(5310)	(6160)	(6670)	(7770)
CsCl	3.56 (s.c.)		6200 <sup>z</sup>			
CsBr	3.71 (s.c.)					
CsI	3.95 (s.c.)					

<sup>\*</sup> Indicates a measurement at  $-180^{\circ}\text{C}$ .

(s.c.)=simple cubic.

<sup>a</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, Book Company, New York, 1940).

<sup>b</sup> R. Hilsch and R. W. Pohl, as quoted by J. H. de Boer, *Electron Emission and Adsorption Phenomena*, p. 277.

<sup>c</sup> See reference 3 in text.

<sup>d</sup> R. Ottmer, *Zeits. f. Physik* **46**, 798 (1928).

<sup>e</sup> See reference 4 in text.

<sup>f</sup> See reference 6 in text.

<sup>z</sup> This approximate value was taken from a figure given by R. W. Pohl, *Proc. Phys. Soc. London* **49** (extra part, p. 3) (1937).

<sup>b</sup> See reference 2 in text.

includes data for the *U*-band which arises when hydrogen enters into solid solution with the alkali halides, replacing halogen ions. Some of the measurements reported were made at  $-180^{\circ}\text{C}$ , the corresponding values of wave-length at room temperature will be higher by about 100 or 200 Å than those listed. In addition to the bands tabulated, Molnar<sup>3</sup> found an additional band (with properties similar to the *R*-bands) in NaCl at 8230 Å (measured at  $-180^{\circ}\text{C}$ ). Schneider<sup>4</sup> also reported an additional band in LiF at 5200 Å.

Since the location of all the bands has not yet been measured, estimated values of those as yet unmeasured would be of interest. Fröhlich,<sup>5</sup> from theoretical considerations concerning the *F*-band, derived the relation

$$\nu_{\max} d^2 = h/16m = 0.45 \text{ cm}^2\text{-sec.}^{-1}, \quad (1)$$

where  $\nu_{\max}$  is the frequency of maximum absorption,  $d$  is the inter-ionic distance (lattice constant) of the salt considered (in cm),  $h$  is Planck's constant, and  $m$  is the electronic mass. Mollwo<sup>6</sup> reported that his experimental data agreed with an equation of this form with a constant of 0.50  $\text{cm}^2\text{-sec.}^{-1}$ . If Eq. (1) is rewritten in terms of wave-length, one obtains

$$\lambda_{\max} = 667d^2 \text{ Å}, \quad (2)$$

where the value of  $d$  is now given in angstroms. The writer has fitted empirical equations of this same general type to the data compiled in the table and obtained the following relations<sup>7</sup>

$$U: \lambda_{\max} = 615d^{1.10} \text{ Å}, \quad (3)$$

$$F: \lambda_{\max} = 703d^{1.84} \text{ Å}, \quad (4)$$

$$R_1: \lambda_{\max} = 816d^{1.84} \text{ Å}, \quad (5)$$

$$R_2: \lambda_{\max} = 884d^{1.84} \text{ Å}, \quad (6)$$

$$M: \lambda_{\max} = 1400d^{1.56} \text{ Å}. \quad (7)$$

These formulas (and that of Fröhlich above) apply only to those alkali halides crystallizing in the face-centered cubic structure and not to

<sup>3</sup> J. P. Molnar, M.I.T. Ph.D. Thesis, Physics Dept. (October, 1940). The writer is indebted to Dr. Molnar for his kind permission to use his previously unpublished data.

<sup>4</sup> E. G. Schneider, *J. Opt. Soc. Am.* **27**, 72 (1937).

<sup>5</sup> H. Fröhlich, *Zeits. f. Physik*, **80**, 819 (1933).

<sup>6</sup> E. Mollwo, as reported by Pohl in reference (3).

<sup>7</sup> These equations were first presented in a Ph.D. Thesis to the M.I.T. Physics Dept., June, 1944.

CsCl, CsBr, and CsI, which have simple cubic structures.

The values enclosed in parentheses in the table are those calculated from the above equations. In the case of the *F*-band the mean error is 130 angstroms, which is less than that for Mollwo's relation. The most serious point of disagreement is in the case of the *R*- and *M*-bands for LiCl. In the case of LiF, the "secondary maxima" reported lie between the predicted  $R_1$  and  $R_2$  values, possibly indicating that the two separate bands were not resolved. The good agreement in the case of the *U*-band indicates that the claim of Hughes<sup>8</sup> that this band can be represented by an equation of the general type considered here with an exponent of two is certainly in error.

Although no attempt is made to justify the equations presented here on a theoretical basis, the equality of the exponent in the case of the *F*- and *R*-bands seems more than fortuitous. According to the pictures suggested by Seitz,<sup>1</sup> these three bands arise from absorbing centers involving only halogen-ion vacancies in the crystal lattice, while the *M*- and *U*-bands involve an alkali-ion vacancy and a negative hydrogen ion, respectively.

<sup>8</sup> A. L. Hughes, Rev. Mod. Phys. **8**, 294 (1936).

The fact that the spectral location of all the observed absorption bands depends only on the lattice constant (and on the temperature) suggests an interesting possibility. Since solid solutions of the various alkali halides will have lattice constants intermediate to those of the parent salts, it would seem plausible that the position of the absorption peaks could be changed at will, simply by varying the composition of such mixed crystals. This might possibly be of value in the application of this absorption phenomenon to practical problems such as the Siatron.<sup>9</sup> So far as the writer is aware, no work on color centers in solid solutions of the alkali halides has been reported.

Another interesting implication of the empirical relations presented here is that the absorption spectra due to color centers in LiI and CsF, which have identical lattice constants, should be indistinguishable as far as spectral location is concerned. At present very little is known concerning the variation of the relative intensities and the permanency of the various bands from one salt to another.

<sup>9</sup> A. H. Rosenthal, Proc. Inst. Rad. Eng. **28**, 203 (1940). H. W. Leverenz, R.C.A. Review **7**, 199 (1946). See also Vol. V of the M.I.T. Radiation Laboratory Technical Series to be published.