

THERMO-OPTIC BEHAVIOUR OF SOLIDS

V. Alkali Halides

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1. INTRODUCTION

THE halides of the alkali metals form a class of crystalline solids which, on account of the simplicity of their structure, have been the subject of a great many investigations, both theoretical and experimental. In particular, we have a wealth of data on their refractive indices and dispersion. Besides, the work of Hilsch and Pohl (1930) and of Schneider and O'Bryan (1937) have revealed the actual existence of a number of dispersion frequencies in the remote ultra-violet, and in two particular cases, *viz.*, potassium iodide and rubidium bromide, the actual shifting down of these frequencies towards longer wavelengths with rise of temperature has been observed and quantitatively measured (Fesefeldt, 1930). The last mentioned phenomenon is the basis of our theory of thermo-optic behaviour. So far, it had a direct observational basis only for diamond. In this case, although the actual dispersion frequencies have not been observed spectroscopically, the shifts of various other electronic frequencies have been measured, and the proportional rate of change of frequency calculated from these agree with the value for the dispersion frequency deduced from measurements of dn/dt . Fesefeldt's data are therefore of great interest in relation to the present theory as they form a direct confirmation of the ideas developed in it. As will be seen from a later section, it is found that the rate of change of the dispersion frequency calculated from the refractive index data is in agreement with the actually measured value for KI.

With regard to the thermo-optic behaviour of the alkali halides in general, the data are not as plentiful as could be desired. dn/dt has been measured for rock-salt (NaCl), the most familiar of these, between 0.185 and 0.671 μ by Micheli (1902) and from 0.589 to 8.85 μ by Liebreich (1911). For sylvine (KCl), there are data in the visible for wavelengths above 0.434 μ measured by Pulfrich (1892) and in the infra-red by Liebreich (*loc. cit.*) but none at all in the ultra-violet. Among the rest, the following are the only measurements of dn/dt available: for KBr and KI for only

TABLE I

Compound	Reference	Wavelengths for which measurements are available (in microns)
LiF	Gyulai (1927)	0.193 to 0.578
	Hohls (1937)	0.546 to 55.0
	Ramaseshan (1947)	0.436, 0.546, 0.589
NaF	Kublitzky (1934)	0.186 to 0.578
	Hohls (1937)	0.546 to 55.0
KF	Kublitzky (1934)	0.214 to 0.578
RbF	Winchell (1931)	F (0.486), D (0.589), C (0.656)
α CsF	Posnjak and Wyckoff (1922)	F, D, C
β CsF	Winchell (1931)	F, D, C
LiCl		
NaCl*	Martens (1901)	0.185 to 0.589
	Paschen (1908)	0.589 to 15.9
	Rubens and Trowbridge (1897)	9.95 to 17.93
	Rubens and Nichols (1897)	20.57, 22.3
KCl*	Martens (1901)	0.185 to 0.768
	Paschen (1908)	0.589 to 17.68
	Trowbridge (1898)	0.98 to 11.2
	Rubens and Nichols (1897)	20.6, 22.3
RbCl	Sprockhoff (1903)	F, D, C
	Gyulai (1927)	0.193 to 0.577
α CsCl	Winchell (1931)	F, D, C
	Wulff and Schaller (1934)	0.480, 0.546, 0.589, 0.671
	Wulff and Anderson (1935)	0.226 to 0.538
β CsCl	Sprockhoff (1903)	F, D, C
LiBr		
NaBr	Spangenberg (1923)	0.436, 0.447, 0.501, 0.588, 0.608
	Gyulai (1927)	0.206 to 0.615
KBr	Topsoe and Christiansen (1874)	Hy (0.434), F, D, C
	Sprockhoff (1903)	F, D, C
	Winchell (1931)	F, D, C
	Gyulai (1927)	0.206 to 0.615
	Gundelach (1930)	0.768 to 28.5
	Korth (1933)	14 to 26.7
	Forrest (1942)	0.405 to 0.770
	Ramaseshan (1947)	0.436, 0.546, 0.589
RbBr	Sprockhoff (1903)	F, D, C
	Kublitzky (1934)	0.219 to 0.578
α CsBr	Winchell (1931)	F, D, C
LiI		
NaI		
KI	Topsoe and Christiansen (1874)	F, D, C
	Sprockhoff (1903)	F, D, C
	Winchell (1931)	F, D, C
	Gyulai (1927)	0.254 to 0.615
	Korth (1933)	0.546 to 29.0
RbI	Sprockhoff (1903)	F, D, C
	Kublitzky (1934)	0.253 to 0.578
α CsI	Winchell (1931)	F, D, C
β CsI	Sprockhoff (1903)	F, D, C

* For NaCl and KCl, only a few references are given covering the whole wavelength range. For a fuller list, see Herzfeld and Wolf (1925).

one wavelength, the 5461 Å.U. radiation of mercury (Korth, 1934) and for LiF for λ 0.546 and 3.5 μ and for NaF for λ 0.546, 3.5 and 8.5 μ (Hohls, 1937). In this paper, the cases of rocksalt and sylvine have been worked out in detail which lead to some interesting results. Potassium iodide has also been considered somewhat in detail on account of the special considerations mentioned above.

2. SOME GENERAL CONSIDERATIONS

As has been mentioned in the earlier papers of this series, a prerequisite to the theoretical explanation of the thermo-optic properties of a solid is the derivation of a dispersion formula. For both rocksalt and sylvine, various dispersion formulæ have been suggested (Paschen, 1908; Martens, 1901; Goldhammer, 1913; Herzfeld and Wolf, 1925; Fuchs and Wolf, 1928), while for the other alkali halides none have been proposed to the knowledge of the author. All these formulæ should however be considered empirical, since the dispersion frequencies have been taken only so as to fit the refractive index data and have no experimental basis. Since 1930, the ultra-violet absorption frequencies of all the alkali halides (except LiF) and various other crystals have been determined down to about 1000 Å.U. (Hilsch and Pohl, 1930; Schneider and O'Bryan, 1937). In the infra-red also, the absorption frequencies of most of the alkali halides have been directly determined (Barnes and Czerny, 1931; Barnes, 1932). All the measurements have been listed in Barnes' paper (1932). Apart from their importance in other fields, these measurements both in the ultra-violet and in the infra-red are very valuable since they can be directly incorporated in the dispersion formulæ and thus place these formulæ on a sounder theoretical basis. In the present paper such a calculation has been carried out for rocksalt and potassium iodide, for which such an investigation seemed desirable prior to the calculation of the thermo-optic phenomena. There is no doubt that dispersion formulæ embodying the actual absorption frequencies can be obtained for the other salts as well, for many of which extensive data are available for the refractive indices at various wavelengths. In Table I below, a list of references is given of the various published investigations on the refractive indices of alkali halides. Only those in which refractive indices for at least 3 wavelengths have been measured are included in the list.

An important question that has to be considered in this connection is whether the proper form of the dispersion formula is of the Drude type, *viz.*,

$$n^2 - 1 = \sum_r a_r \lambda_r^2 / (\lambda^2 - \lambda_r^2), \quad (1)$$

or of the Lorentz-Lorenz type, *viz.*,

$$\frac{n^2 - 1}{n^2 + 2} = \sum_r a_r' \lambda_r'^2 / (\lambda^2 - \lambda_r'^2). \quad (2)$$

As has been shown by Herzfeld and Wolf (1925), these two forms are algebraically interconvertible into each other. It is therefore necessary to understand precisely what the significance of the quantities λ_r and λ_r' is in the expressions (1) and (2) respectively. It is obvious that if those in (1) are really the wavelengths corresponding to the dispersion frequencies, those in (2) are not, and *vice versa*. To decide which is true, we have on the one hand, the purely theoretical approach to the problem of the dispersion of crystalline bodies, based on lattice theory and considering the interaction of electromagnetic radiation with the regular array of atoms in the crystal. Such theories have been developed by Ewald (1916) and Born (1918, 1922) and their results show that the resultant expression does not take the Lorentz-Lorenz form, but the $(n^2 - 1)$ form. On the other hand, one could actually compute dispersion formulæ of both types and see in which case the assumed dispersion frequencies agree with the observed absorption frequencies. The alkali halides form suitable materials in which to make such critical calculations.

For rocksalt and sylvine, calculations of this type have already been carried out by Wolf and his collaborators (Herzfeld and Wolf, 1925; Fuchs and Wolf, 1928), although not with this specific purpose. They have obtained dispersion formulæ for these substances both in the Lorentz-Lorenz and the Drude forms. In both cases, four dispersion frequencies are used, one in the infra-red, two in the ultra-violet above 1000 Å.U. and one in the still remote ultra-violet. In Table II, the wavelengths of the frequencies employed in the two forms for both NaCl and KCl are given, together with the actually observed values. These measurements have been made, after the publication of the dispersion formulæ, by Barnes and Czerny (1930) in the infra-red and by Schneider and O'Bryan (1937) in the ultra-violet. It will be seen that the dispersion frequencies used in the Drude form agree remarkably well with the infra-red and the nearest ultra-violet frequency. In fact, even the second ultra-violet dispersion frequency is reasonably correct, since it can be supposed to represent both the second and the third absorption frequencies. No such agreement is found with the Lorentz-Lorenz form. There is thus strong reason to believe that the Drude form is really the more appropriate one for the alkali halides and probably for cubic crystals in general. In this connection, it may be mentioned that the author (1947) has succeeded in constructing a Drude dispersion formula for fluorspar, in which the observed absorption maxima

in the ultra-violet are employed. In view of the above considerations, we shall only make use of the (n^2-1) form of the dispersion formula in the succeeding discussions in this paper.

TABLE II
Wavelengths of the Dispersion Frequencies

Rocksalt			Sylvine		
L-L. Form	Drude form	Observed	L-L. Form	Drude form	Observed
343.9 Å.U.	347 Å.U.		514.6 Å.U.	529.1 Å.U.	
		1000 Å.U.			1000 Å.U.
935.9 „	1085 „		966.9 „	1082.8 „	
		1280 „			1310 „
1543.4 „	1584 „	1580 „	1582.9 „	1621.4 „	1620 „
45.75 μ	61.67 μ	61.1 μ	55.09 μ	70.23 μ	70.7 μ

3. DISPERSION FORMULAE OF ROCKSALT AND SYLVINE

As already mentioned, rocksalt is the only alkali halide for which dn/dt measurements are available over the whole spectral range from 0.2 to 9 μ . It will be therefore interesting to apply the theory of thermo-optic behaviour developed by the author (1947 *a*) and consider its various consequences. For this purpose, it is desirable to have an accurate dispersion formula containing the observed frequencies. Such a formula has been constructed by the author and is given below.

Various dispersion formulæ have been suggested for rocksalt which are listed below. They have all been reduced wherever possible to the standard forms

$$n^2 - 1 \text{ or } \frac{n^2 - 1}{n^2 + 2} = C + \sum_r \frac{a_r \lambda^2}{\lambda^2 - \lambda_r^2} \quad (3)$$

Paschen (1908)

$$n^2 - 1 = 0.2807 + \frac{0.8397\lambda^2}{\lambda^2 - (0.1219)^2} + \frac{0.2098 \lambda^2}{\lambda^2 - (0.1596)^2} + \frac{3.350 \lambda^2}{\lambda^2 - (60.0)^2} \quad (4)$$

Martens (1901)

$$n^2 - 1 = 0.155992 + \frac{0.855461 \lambda^2}{\lambda^2 - (0.110725)^2} + \frac{0.317791 \lambda^2}{\lambda^2 - (0.156320)^2} + \frac{1.620760 \lambda^2}{\lambda^2 - (51.2)^2} - 0.000309178 \lambda^2 \quad (5)$$

Herzfeld and Wolf (1925)

$$\frac{n^2-1}{n^2+2} = \frac{0.018619 \lambda^2}{\lambda^2 - (0.03439)^2} + \frac{0.25898 \lambda^2}{\lambda^2 - (0.09359)^2} + \frac{0.029763 \lambda^2}{\lambda^2 - (0.15434)^2} + \frac{0.31207 \lambda^2}{\lambda^2 - (45.75)^2} \quad (6)$$

Fuchs and Wolf (1928)

$$n^2-1 = \frac{0.05225 \lambda^2}{\lambda^2 - (0.0347)^2} + \frac{1.0059 \lambda^2}{\lambda^2 - (0.1085)^2} + \frac{0.2713 \lambda^2}{\lambda^2 - (0.1584)^2} + \frac{3.5417 \lambda^2}{\lambda^2 - (61.67)^2} \quad (7)$$

The author's new formula using the observed frequencies is

$$n^2-1 = \frac{0.187895 \lambda^2}{\lambda^2 - (0.0500)^2} + \frac{0.497649 \lambda^2}{\lambda^2 - (0.1000)^2} + \frac{0.384897 \lambda^2}{\lambda^2 - (0.1280)^2} + \frac{0.259500 \lambda^2}{\lambda^2 - (0.1580)^2} + \frac{3.4740 \lambda^2}{\lambda^2 - (61.1)^2} \quad (8)$$

Paschen has suggested many formulæ. The one given here is his latest. It may be mentioned that Paschen was particularly interested in the infra-red, where from 0.6μ to nearly 22μ , his formula fits well, but it is rather poor in the visible and the ultra-violet, as is revealed by a check made by the author. Martens' formula fits his earlier measurements (1901) remarkably well but not so well with his later measurements (1902), which are more accurate, as judged by the fact that only these are given by Martens himself in the Landolt-Bornstein Tables (1923). Herzfeld and Wolf's formula is of the Lorentz-Lorenz type and the dispersion frequencies used in it do not agree with experimental values. Fuchs and Wolf's formula is perhaps the best suggested so far, in view of the various considerations mentioned earlier. There is however room for improvement in this formula as well. Firstly, the numerical agreement with the refractive index data is not as good as could be expected. Fuchs and Wolf have represented the errors (theoretical—experimental) not in n itself, but in $(n^2-1)/(n^2+2)$, which often comes to 3 units in the fourth decimal place. This means that in (n^2-1) they come to nearly 15 units. Besides, the second and third ultra-violet frequencies have been put together in a single term. In the new formula suggested by the author, the frequencies are all those that have been observed, except the one at 500 \AA.U. This stands for a group of frequencies in the very remote ultra-violet, of which no definite further details are known. It is found that the new formula fits the experimental data much better than Fuchs and Wolf's formula, as may be seen from an examination of Table III. Here, the errors in (n^2-1) (theoretical—experimental) are given in units of the fourth decimal place both with the Fuchs-Wolf formula and the

author's formula. It will be seen that with the new formula, the error is scarcely above 5 units, except for the extreme values in the ultra-violet and the infra-red, while in the middle of the table, it is rarely more than 2 units. In the Fuchs-Wolf formula, on the other hand, the errors appear to be systematic, being often above 10 units and sometimes larger than 15 units. The experimental data for comparison have been taken from the tables compiled by Martens (1923) in the Landolt-Bornstein Tables.

TABLE III

Wavelength in microns	Refractive index		(n^2-1) (th. - exp.) $\times 10^4$	
	Experimental	From author's formula	Author's formula	Fuchs-Wolf's formula
0.185467	1.89332	1.89350	+ 7.0	+ 16.2
0.186290	1.88558	1.88555	- 1.1	+ 10.5
0.193583	1.82809	1.82793	- 5.8	+ 0.7
0.19898	1.79580	1.79591	+ 3.8	..
0.20006	1.79016	1.79028	+ 4.2	0.0
0.214439	1.73221	1.73211	- 3.2	+ 8.0
0.219462	1.71711	1.71705	- 2.2	+ 12.4
0.231288	1.68840	1.68835	- 1.8	+ 15.0
0.257304	1.64604	1.64604	0.0	+ 16.5
0.274869	1.62687	1.62692	+ 1.5	+ 18.1
0.340365	1.58601	1.58609	+ 2.4	+ 12.7
0.441568	1.55962	1.55965	+ 1.0	+ 7.5
0.486133	1.55338	1.55340	+ 0.5	+ 4.0
0.546072	1.54745	1.54745	+ 0.1	+ 3.0
0.58932	1.54431	1.54431	0.0	0.0
0.656278	1.54067	1.54067	- 0.1	- 1.7
0.78576	1.53614	1.53615	+ 0.2	- 2.1
0.88396	1.53401	1.53398	- 1.1	- 5.7
1.1786	1.53037	1.53034	- 0.9	- 6.9
4.1252	1.52165	1.52155	- 3.1	- 11.2
8.8398	1.50204	1.50197	- 2.2	- 10.2
12.9650	1.47172	1.47182	+ 3.0	- 5.0
22.3	1.3405	1.3402	- 8.5	- 2.2

For sylvine also, a number of dispersion formulæ have been suggested which are given below.

Paschen (1908)

$$n^2 - 1 = 0.200970 + \frac{0.700711 \lambda^2}{\lambda^2 - (0.109125)^2} + \frac{0.273286 \lambda^2}{\lambda^2 - (0.159859)^2} + \frac{1.691652 \lambda^2}{\lambda^2 - (57.380)^2} \tag{9}$$

Martens (1901)

$$n^2 - 1 = 0.25841 + \frac{0.672011 \lambda^2}{\lambda^2 - (0.115265)^2} + \frac{0.244603 \lambda^2}{\lambda^2 - (0.160730)^2} + \frac{1.93343 \lambda^2}{\lambda^2 - (61.1)^2} \tag{10}$$

Goldhammer (1913)

$$\frac{n^2-1}{n^2+2} = 0.084232 + \frac{0.169065 \lambda^2}{\lambda^2 - (0.106673)^2} + \frac{0.0281324 \lambda^2}{\lambda^2 - (0.157500)^2} + \frac{0.232735 \lambda^2}{\lambda^2 - (51.009)^2} \quad (11)$$

Herzfeld and Wolf (1925)

$$\frac{n^2-1}{n^2+2} = \frac{0.059064 \lambda^2}{\lambda^2 - (0.05146)^2} + \frac{0.19277 \lambda^2}{\lambda^2 - (0.09669)^2} + \frac{0.029883 \lambda^2}{\lambda^2 - (0.15829)^2} + \frac{0.27700}{\lambda^2 - (55.09)^2} \quad (12)$$

Fuchs and Wolf (1928)

$$n^2-1 = \frac{0.15779 \lambda^2}{\lambda^2 - (0.05291)^2} + \frac{0.78836 \lambda^2}{\lambda^2 - (0.10828)^2} + \frac{0.22971 \lambda^2}{\lambda^2 - (0.16214)^2} + \frac{2.6149 \lambda^2}{\lambda^2 - (70.23)^2} \quad (13)$$

The comments made on Paschen's and Marten's formulæ for rocksalt also hold in this case. Goldhammer's formula was available to the author only through the paper of Herzfeld and Wolf (*loc. cit.*), who criticise it on the ground that it does not give a reasonable value for the dielectric constant. This, as well as Herzfeld and Wolf's formulæ, are of the Lorentz-Lorenz type. Once again, Fuchs and Wolf's formula is the most acceptable for the same reasons as mentioned before, but the errors are as large as with rocksalt in this case also. The author is of the opinion that the general fit of the dispersion formula can be improved as with rocksalt by using the observed frequencies. This was not however attempted as it was unnecessary for the present investigation, *viz.*, the study of the thermo-optical properties. Measurements of dn/dt for sylvine are available only for wavelengths above 0.45μ and in this region the exact location of the ultra-violet frequencies is relatively unimportant. Consequently the Fuchs-Wolf formula was used in the calculations.

3. CALCULATION OF THE SPECTRAL VARIATION OF dn/dt FOR ROCKSALT AND SYLVINE

(a) *Rocksalt*.—The calculation of dn/dt was carried out in the same way as with the other solids studied earlier. Taking a dispersion formula of the Drude form (Eq. 1) one has

$$2n \, dn/dt = -\gamma (n^2-1) + \Sigma 2a_r \lambda^4 \chi_r / (\lambda^2 - \lambda_r^2)^2, \quad (14)$$

where

$$\chi_r = d(\log \lambda_r)/dt = -d(\log \nu_r)/dt. \quad (15)$$

The available data for rocksalt are all at 60° C. for which temperature the coefficient of cubical expansion $\gamma = 1.20 \times 10^{-4}$ (*International Critical Tables*, Vol. 3, p. 43) from which the first term on the right hand side, viz., the contribution due to change in density can be calculated. It now remains to determine only the χ 's of the various frequencies. Now, in the visible and ultra-violet regions, the contribution due to changes in the infra-red frequency is very small. Neglecting this, it is found that the experimental data are fitted with the following values of χ_r :

Fuchs-Wolf formula (Eq. 7):

$$\chi(347 \text{ \AA}) = 0, \chi(1085 \text{ \AA}) = -9.7 \times 10^{-6}, \chi(1584 \text{ \AA}) = 113 \times 10^{-6} \quad (16)$$

Author's formula (Eq. 8):

$$\begin{aligned} \chi(500 \text{ \AA}) = 0, \chi(1000 \text{ \AA}) = -33.3 \times 10^{-6}, \chi(1280 \text{ \AA}) = 23.5 \times 10^{-6}, \\ \chi(1580 \text{ \AA}) = 110 \times 10^{-6}. \end{aligned} \quad (17)$$

In Table IV, the experimental values of dn/dt together with the values calculated from the two formulæ are given for a few selected wavelengths. The data up to 0.5893 is due to Micheli (1902) and those in the infra-red to Liebreich (1911). In the infra-red, the calculations have been carried out with the assumption that the χ for the infra-red frequency is 150×10^{-6} . This value is not unreasonable, since it is of the same order as the χ for the first ultra-violet frequency (at 1580 Å) and also as that for the infra-red frequency in fluorspar. Besides, it may be mentioned that the contribution to dn/dt due to the infra-red frequency shift is small even at 8μ , so that any error in the assumed value of χ is unimportant.

TABLE IV

Wavelength in microns	$dn/dt \times 10^6$		
	From experiment	From author's formula	From Fuchs-Wolf formula
0.2026	+ 29.87	+ 29.5	+ 30.7
0.2145	+ 7.12	+ 6.6	+ 6.3
0.2574	- 21.05	- 19.9	- 20.3
0.3405	- 31.84	- 32.6	- 30.8
0.4680	- 35.66	- 36.5	- 36.6
0.5893	- 37.33	- 37.3	- 36.9
1.6	- 36.64	- 38.6	- 38.6
4.96	- 32.81	- 37.8	- 37.8
6.4	- 32.41	- 37.3	- 37.3
8.85	- 25.23	- 36.1	- 36.1

It may be noticed from the table that in the ultra-violet and visible, the agreement with dn/dt data is equally good with Fuchs and Wolf's and author's formulæ. In the infra-red, both theories agree, but both give an algebraically lower value for dn/dt than the experimental value, the difference between theory and experiment becoming greater with increase of wavelength. Precisely the same type of discrepancy is found with sylvine also. Its significance will be discussed in a later section.

(b) *Sylvine*.—Fuchs and Wolf's formula (Eq. 13) was used for the calculation of the thermo-optic properties. It is found that good agreement with experiment is obtained with the following values of χ for the ultra-violet frequencies:

$$\chi (529 \text{ \AA}) = 0, \chi (1083 \text{ \AA}) = -13 \times 10^{-6}, \chi (1621 \text{ \AA}) = 90 \times 10^{-6} \quad (18)$$

As with rocksalt, a trial value of $\chi (70.7 \mu) = 150 \times 10^{-6}$ was used for the infra-red frequency. This did not affect any of the dn/dt values except the one at 21μ . In Table V, the calculated and experimental values of dn/dt are given. It will be seen that just as with rocksalt, the agreement between the two is good upto about 2μ after which it progressively worsens. The values of dn/dt in the ultra-violet calculated from theory are also included in the Table. They show variations similar to those exhibited by rocksalt. It can be confidently predicted that the trend of the dn/dt -wavelength curve would be verified, and that dn/dt would be found to reverse sign and become positive near about 2000 \AA.U.

TABLE V

Wavelength in microns	$dn/dt \times 10^6$	
	From theory	From experiment
0.200	+ 29.8	..
0.215	0.0	..
0.257	- 24.7	..
0.340	- 32.3	..
0.434	- 35.7	- 35.57
0.589	- 36.1	- 36.41
1.4	- 36.6	- 36.46
5.0	- 36.5	- 35.72
8.85	- 35.7	- 31.14
21.0	- 25.8	- 6.3

4. APPLICATION OF THE THEORY TO POTASSIUM IODIDE

Unlike for rocksalt and sylvine, no dispersion formulæ have previously been suggested for potassium iodide, and so a formula was constructed by the author. Detailed dispersion data for potassium iodide are available

from the work of Gyulai (1927) from 0.254 to 0.615μ and from that of Korth (1933) from 0.546 to 29μ . The latter has also determined dn/dt for $\lambda 5461 \text{ \AA.U.}$ between 38° and 90° C. The refractive index determinations of Gyulai and Korth are not at the same temperature, the former being at 66° and the latter at 38° C. Since dn/dt is known for only one wavelength, it is not possible to reduce both measurements to the same temperature. The difficulty has been overcome by developing two separate dispersion formulæ, one valid for the infra-red above 5μ at 38° C. and the other valid for the ultra-violet and the visible at 66° C. The two are however related as will be clear later. From the work of Hilsch and Pohl and of Schneider and O'Bryan quoted earlier, it is known that the ultra-violet frequencies are at wavelengths 0.2190μ , 0.1875μ , 0.1745μ and 0.1290μ . In the dispersion formula for shorter wavelengths given below, the second and third ultra-violet frequencies which form a relatively close doublet have been replaced by a single frequency in the mean position 0.1805μ . The infra-red frequency is at 102.0 . In the infra-red, beyond about 5μ the contribution to refractive index due to the ultra-violet frequencies is practically a constant and the variations in refractive index are entirely due to the infra-red frequency. Thus, from about 5μ to 29μ , the data of Korth (*loc. cit.*) at 38° C. can be represented by the formula

$$n^2 - 1 = C + a_R \lambda^2 / (\lambda^2 - \lambda_R^2) \quad (18)$$

with $\lambda_R = 102.0 \mu$, $C = 1.6499$, $a_R = 2.530$. The agreement of this formula with experiment can be seen from Table VI. It will be noticed that the difference between the calculated and experimental values of refractive index scarcely exceeds one unit in the fourth decimal place.

TABLE VI

Wavelength in microns	Refractive index		$(n_{cal} - n_{exp}) \times 10^4$
	Calculated	Measured	
4.125	1.6266	1.6269	- 3
8.840	1.6220	1.6219	+ 1
10.02	1.6202	1.6201	+ 1
11.79	1.6171	1.6172	- 1
14	1.6128	1.6128	0
18	1.6026	1.6027	- 1
22	1.5894	1.5895	- 1
26	1.5728	1.5729	- 1
28	1.5632	1.5629	+ 3
29	1.5579	1.5571	+ 8

In the ultra-violet and visible upto 0.615μ , for which range the data of Gyulai (*loc. cit.*) are available, the contribution to $(n^2 - 1)$ of the infra-red term has been calculated and found to be less than one unit in the fifth decimal place. The data are correct only to one unit in the third decimal place, and are given only to four decimal places. One can thus completely neglect the infra-red term in this region of the spectrum. The data are fitted well by a formula of the type

$$n^2 - 1 = A + \sum_{r=1}^3 a_r \lambda^2 / (\lambda^2 - \lambda_r^2) \quad (19)$$

with the three dispersion frequencies mentioned above. The numerical formula is

$$n^2 - 1 = 0.4532 + \frac{0.1780 \lambda^2}{\lambda^2 - (0.2190)^2} + \frac{0.8027 \lambda^2}{\lambda^2 - (0.1805)^2} + \frac{0.2150 \lambda^2}{\lambda^2 - (0.1290)^2} \quad (20)$$

The fit of the formula can be judged from Table VII, where the errors are given in units of the third decimal place. It will be seen that the error is nowhere larger than one unit, which is the limit of experimental error.

TABLE VII

Wavelength in microns	Refractive Index		$(n_{cal} - n_{exp}) \times 10^3$
	Calculated	Measured	
0.2536	2.0172	2.0169	+ 0.3
0.26520	1.9454	1.9452	+ 0.2
0.28035	1.8848	1.8847	+ 0.1
0.29673	1.8391	1.8393	- 0.2
0.31318	1.8060	1.8070	- 1.0
0.33415	1.7749	1.7754	- 0.5
0.36502	1.7431	1.7434	- 0.3
0.40466	1.7162	1.7169	- 0.7
0.43583	1.7013	1.7018	- 0.5
0.49160	1.6831	1.6832	- 0.1
0.54607	1.6713	1.6711	+ 0.2
0.57907	1.6659	1.6656	+ 0.3

From Eq. (20) the value of $(n^2 - 1)$ for very large wavelengths, which we may denote by $(n_{\infty}^2 - 1)$ comes out to be 1.6479 at 66°C . It is obvious that this must correspond to C of Eq. (18) which holds for 38°C . It is not surprising that the value of $(n_{\infty}^2 - 1)$, *i.e.*, the portion of $(n_{\infty}^2 - 1)$ due to the ultra-violet frequencies alone should be larger at 38° than at 66°C . This is because dn/dt at 5461 \AA.U. is negative, and since the infra-red contribution at this wavelength is negligible, dn_{∞}'/dt would also be expected to negative,

We shall now apply these formulæ for calculating the thermo-optic properties. Since at 5461 Å.U. the contribution due to the infra-red frequency is negligibly small, Eq. (19) can be used. Differentiating this and using the usual notation.

$$2n \, dn/dt = -\gamma(n^2 - 1) + \frac{dA}{dt} + \sum_1^3 \frac{2a_r \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r \quad (21)$$

Substituting the values $dn/dt = 5 \times 10^{-5}$ and $\gamma = 1.27 \times 10^{-4}$ (from Fizeau's data quoted in Liebisch, 1891) and also the values of a_r and λ_r , one gets

$$80.6 \times 10^{-6} = 0.5114 \chi_1 + 1.970 \chi_2 + 0.4821 \chi_3 + dA/dt \quad (22)$$

It is clear that the term $-\gamma(n^2 - 1)$ is the part due to density changes, so that 80.6×10^{-6} is the total contribution due to changes of frequency. Now, from the measurements of Fesefeldt quoted above, χ_1 the proportional change of the ultra-violet frequency at 2190 Å.U. comes out to be 163×10^{-6} , so that the term $0.5114 \chi_1 = 82.4 \times 10^{-6}$. It will be noticed that this is of the same order as the total contribution due to frequency changes, but slightly larger. Since further data on dn/dt or on the other χ 's are not available, one is not in a position to make a more exact verification of our theory. Fesefeldt has actually measured the shift of the longer wavelength component of the doublet at 1805 Å.U.; but its peak intensity also diminishes, so that one cannot say how the mean position of the doublet changes. However, by analogy with rocksalt and sylvine, the result obtained here is reasonable. In these cases, it was found that the contribution due to the shift of nearest ultra-violet frequency formed the bulk of the contribution due to frequency shifts towards dn/dt . It was in fact slightly larger than the total contribution, the resultant of those from the rest being slightly negative. The above figures for potassium iodide, taking the actually observed value of χ_1 , exhibit exactly the same behaviour, thus providing a direct experimental verification of our theory.

5. DISCUSSION OF THE RESULTS

The most interesting result that emerges from the present studies is with regard to the values of χ for the different ultra-violet absorption frequencies. In all the three cases studied, a certain amount of similarity has been observed. The nearest absorption has a large positive χ which is of the order of 100×10^{-6} , and the contribution of all the others taken together is slightly negative. In rocksalt the second absorption has a relatively small positive χ (25×10^{-6}), while the next one to this has a negative value (-30×10^{-6}). In other words, while the first two move towards longer wavelengths, the third shifts towards shorter wavelengths. We have not

encountered negative values for χ in the previous cases studied. However, they seem to be the rule for the deeper levels in the alkali halides. It is not possible to conjecture a definite reason for this. A probable explanation may be suggested on the following lines. It is generally supposed that the characteristic absorptions at longer wavelengths are due to the negative ions and those at shorter wavelengths are due to the positive ions. In fact, attempts have been made to interpret the actual transitions corresponding to those at longer wavelengths on these lines (see Mott and Gurney, 1940). Also, it is a fairly well established fact that the ionic character of these salts increases with rise of temperature. For example, Cauchy's relations between the elastic constants are not true for rocksalt at low temperatures, but become more and more nearly valid as the temperature is raised (Seitz, 1944), which is attributed to the increasing accuracy with which one may consider the binding in the crystal to be due to purely ionic central forces. An increase in ionic character means that the charges on the individual ions increase with temperature. The effect of this on the positive ions will be to decrease the screening effect of the outer electrons, and thus in effect to increase the nuclear charge. Thus, the frequencies would be increased. The reverse is to be expected for the negative ions. Besides, there is a general expansion of the lattice with increase of temperature which would tend to decrease the energies of all the levels. As a result one would expect the energy levels of the negative ion to be appreciably diminished and those of the positive ions to be either diminished to a much smaller extent, or to be increased, the alternative being determined by the particular conditions.

Another interesting fact is with regard to the values of dn/dt in the infra-red. In Section 3 it was mentioned that the calculated values were algebraically less than the experimental values and that the difference between the two progressively increased for longer wavelengths in the infra-red. This is the case both for rocksalt and sylvine. Such a situation would arise, if the infra-red frequency varied much more rapidly with temperature than was assumed to be the case. This explanation is not upheld by a closer scrutiny of the facts. We know from Eq. (14) that the contribution to $2n \, dn/dt$ due to the variation of the infra-red frequency is equal to $2a_R \chi_R \lambda^4 / (\lambda^2 - \lambda_R^2)^2$, where λ_R is the wavelength of this frequency. If we attribute the whole discrepancy to the cause mentioned just now, χ_R will have to be of the order of 2 to 5×10^{-3} , which is altogether too large. It means that the frequency would be halved by a rise in temperature of a few hundred degrees, which is certainly not true. Further, the discrepancy between the calculated and observed values is not proportional to

$\lambda^4/(\lambda^2 - \lambda_R^2)^2$, but roughly to $\lambda^2/(\lambda^2 - \lambda_R^2)$. The coefficient of proportionality with the latter type of variation is roughly equal to 1.6×10^{-3} with rocksalt and 0.54×10^{-3} with sylvine. A variation of this type means that the quantity a_R in the numerator of the infra-red dispersion term diminishes at these rates. Dividing by a_R , one obtains the proportional rates of change of a_R in the two cases to be roughly -4.5×10^{-4} and -2.0×10^{-4} .

Now, a_R is proportional to $N_R f_R$ where N_R is the number of dispersion centres and f_R the transition probability. We have already allowed for the decrease due to change in the number arising from thermal expansion. Since we find a further diminution, it must be due to a decrease of f_R , the transition probability. Now,

$$\frac{1}{a_R} \frac{da_R}{dt} = \frac{1}{N_R} \frac{dN_R}{dt} + \frac{1}{f_R} \frac{df_R}{dt} \quad (23)$$

$$= -\gamma - \eta, \text{ (say)} \quad (24)$$

where γ is the coefficient of cubical expansion and η the proportional change of the transition probability. Previously, we had always put $da_R/dt = -\gamma a_R$, assuming the transition probability not to alter with temperature (*cf.* Ramachandran, 1947 *a*). The case of the alkali halides shows that one has also to take the latter effect into consideration. In fact, from the rough calculations given above, η is of the same order as γ , being four times as much in rocksalt and double in sylvine.

The above discussion is, of course, based on the supposition that the experimental results are correct. One should not overlook the possibility of these being wrong. This is particularly so since the data both for rocksalt and sylvine in the infra-red are due to the same worker (Liebreich, *loc. cit.*) and some systematic errors could have crept into the measurements. It would be useful to check Liebreich's data for some wavelengths in the infra-red.

The possibility of experimental errors should not be disposed of lightly because it is not at all clear on theoretical grounds as to why the transition probability should diminish with increase of temperature. In fact, one would suppose that the reverse would be the case, considering the behaviour of its classical analogue, the oscillating dipole moment. On account of the larger lattice spacing and also because of the increasing ionic character of the crystal, one would expect the dipole moment to increase with temperature. Here again, experiment must decide the issue. For quartz it has been found that the peak absorption diminishes with increasing temperatures (Parlin, 1929), but the band also becomes broader. It

is not known what happens to the integrated value of the absorption coefficient. It may be mentioned that a test of our theory in this direction is not difficult; for the diminution of the total strength of the term ($a_R = N_R f_R$) due to thermal expansion alone will be only a small fraction (1/5 in rocksalt and 1/3 in sylvine) of what it would be if the transition probability also changed to the extent required by the dn/dt data.

In conclusion, I wish to sincerely thank Prof. Sir C. V. Raman for the kind and encouraging interest he took in this investigation.

SUMMARY

A direct verification of the general theory of thermo-optic behaviour has been obtained by applying it to the alkali halides. Rocksalt, sylvine and potassium iodide have been considered in detail. For this purpose, new dispersion formulæ embodying observed absorption frequencies have been developed for NaCl and KI. With KI, it is found that the proportionate variation χ [$= -d(\log \nu)/dt$] of the first ultra-violet frequency at 2190 Å.U. measured by Fesefeldt agrees with what is calculated from the dn/dt data, thus verifying the fundamental basis of the author's theory. The theory successfully explains the whole course of the variation of dn/dt with wavelength in the case of rocksalt, and in particular the positive values of dn/dt near about 2000 Å.U. and its reversal in sign with increase of wavelength. The first three ultra-violet frequencies have χ 's of the order of $+100 \times 10^{-6}$, $+25 \times 10^{-6}$ and -30×10^{-6} respectively, the last one near 500 Å.U. not varying with temperature. With sylvine, dn/dt measurements in the visible and near infra-red are satisfactorily explained with similar values of χ as in rocksalt. The paper also contains a general review of the dispersion data for the alkali halides. It is shown that a dispersion formula of the Drude form is more appropriate for these salts than one of the Lorentz-Lorenz form.

REFERENCES

1. Barnes .. *Zeits. f. Phys.*, 1932, 75, 723.
2. ——— and Czerny .. *Ibid.*, 1931, 72, 447.
3. Born .. *Ann. d. Phys.*, 1918, 55, 177.
 Enz. d. Math. Wiss., 1922, 5, pt. 3, 529.
4. Ewald .. *Ann. d. Phys.*, 1916, 49, 1, 117.
5. Fesefeldt .. *Zeits. f. Phys.*, 1930, 64, 623.
6. Forrest .. *Journ. Opt. Soc. Am.*, 1942, 32, 382.
7. Fuchs and Wolf .. *Zeits. f. Phys.*, 1928, 46, 506.
8. Goldhammer .. *Dispersion and Absorption of Light, Leipzig*, 1913, 65.
9. Gundelach .. *Zeits. f. Phys.*, 1931, 66, 775.
10. Gyulai .. *Ibid.*, 1927, 46, 80.

11. Herzfeld and Wolf .. *Ann. d. Phys.*, 1925, **78**, 35.
12. Hilsch and Pohl .. *Zeits. f. Phys.*, 1930, **59**, 812.
13. Hohls .. *Ann. d. Phys.*, 1937, **29**, 433.
14. Korth .. *Zeits. f. Phys.*, 1934, **84**, 677.
15. Kublitzky .. *Ann. d. Phys.*, 1934, **20**, 793.
16. Liebisch .. *Physikalische Krystallographie*, Leipzig, 1891, 91.
17. Liebreich .. *Verh. d. Deutsch. Phys. Ges.*, 1911, **9**, 1.
18. Martens .. *Ann. d. Phys.*; 1901, **6**, 603; 1902, **8**, 459;
Landolt-Bornstein Tables, Hauptwerke, II, 1923, 912.
19. Micheli .. *Ann. d. Phys.*, 1902, **7**, 772.
20. Mott and Gurney .. *Electronic Processes in Ionic Crystals*, Oxford, 1940, 95.
21. Parlin .. *Phys. Rev.*, 1929, **34**, 81.
22. Paschen .. *Ann. d. Phys.*, 1908, **26**, 120.
23. Posnjak and Wyckoff .. *J. Wash. Acad.*, 1922, **52**, 245.
24. Pulfrich .. *Wied. Ann.*, 1892, **45**, 609.
25. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci., A.*, 1947*a*, **25**, 266; 1947*b*, **25**, 280;
1947*c*, **25**, 286.
26. Ramaseshan, S. .. *Ibid.*, 1947, **25**.
27. Rubens and Nichols .. *Wied. Ann.*, 1897, **60**, 45.
28. ——— and Trowbridge .. *Ibid.*, 1897, **60**, 733; **61**, 224.
29. Schneider and O'Bryan .. *Phys. Rev.*, 1937, **51**, 293.
30. Seitz .. *Physics of Crystals*, Mc Graw-Hill, 1940.
31. Spangenberg .. *Zeits. f. Krys.*, 1923, **57**, 494.
32. Sprockhoff .. *N. Jahrb. Min.*, 1903, **18**, 120.
33. Topsoe and .. *Ann. d. Chem. Phys.*, 1874, **1**, 21, 30.
Christiansen .. *Ann. d. Phys. Erg.*, 1874, **6**, 578.
34. Trowbridge .. *Wied. Ann.*, 1898, **65**, 612.
35. Winchell .. "The microscopic characters of artificial inorganic substances and of artificial minerals," 2 Ed. New York, 1931. "See Landolt-Bornstein Tables", III Erg., 1935, p. 1501.
36. Wulff and Anderson .. *Zeits. f. Phys.*, 1935, **94**, 28.
37. ——— and Schaller .. *Zeits. f. Kryst.*, 1934, **87**, 43.