

Physics. — *On Some Phenomena which are Caused by the Low Indices of Refraction of Alkali Boron Fluorides.* By J. H. DE BOER.
(Communicated by Dr. G. HOLST).

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In the preparation of simple or complex fluorides it may often occur that already a considerable quantity of salt has crystallised or has been formed as a precipitate, the latter not being visible. The explanation is simply that the indices of refraction of most fluorides are so low that they are in the neighbourhood of their saturated solutions. The boundaries of separate crystals are consequently difficult to distinguish; powdery precipitates become transparent.

These phenomena were particularly marked in the preparation of the alkali boron fluorides. When the sparingly soluble potassium salt is precipitated by double transformation of boron fluor hydrogenic acid, HBF_4 , with a solution of potassium chloride, it is possible that the precipitate is hardly visible. It is stated in the literature that the salt is deposited as a gelatin, which does not pass into a crystalline form until later. The precipitate is, however, only apparently a gelatin; this is perceived when the salt is sucked off. The filtration proceeds exceedingly rapidly; as long as the mass is still wet, it is quite transparent; as soon however as the upmost layer of the salt is sucked dry, the filter is suddenly seen to be quite filled with a white crystalline substance.

Now the indices of refraction of the alkali boron fluorides are very low indeed, which was clearly demonstrated in the preparation of the cesium salt, CsBF_4 . A precipitate of the cesium salt, obtained by double transformation of a solution of HBF_4 (from fluor hydrogenic acid and boric acid) with cesiumchloride, was not only perfectly transparent, but displayed besides brilliant colour effects. In a definite solution, in which cesium salt was precipitated, green light was e.g. perfectly transmitted, the other colours being still more or less dispersed in the precipitate. Objects, viewed through the precipitate, were therefore coloured green, being surrounded by a red-violet border. The index of refraction of the cesium salt¹⁾ is, therefore, so low that in the green it is equal to that of the above solution containing hydrochloric acid, the colour effects being caused by the difference in dispersion between salt and solution.

¹⁾ The alkali boron fluorides are orthorhombic, hence they have, strictly speaking, three indices of refraction. This, however, is disregarded, and by index of refraction of the salt only a mean value is meant.

We find here a phenomenon analogous to that in potassium silico fluoride, K_2SiF_6 ¹⁾, of which BERZELIUS already states that during the precipitation rainbow colours are visible, and that the salt is deposited as a gelatin through which colours play.

The dispersion curve of the cesium boron fluoride has a less steep course than that of the solution, which is clear from the fact that by careful dilution of the solution or by gentle heating the colour of the transmitted light changed from green to blue, the dispersed colours changing from red-violet to brownish yellow.

The index of refraction of the above solution at 20° C. for the D-line appeared to be: 1.3502. Hence the "index of refraction" of $CsBF_4$ for the D-line lies somewhat higher than this value.

In another solution, in which the initial substances were brought together in more concentrated form, orange light was transmitted, the scattered light being greenish blue. The index of refraction of $CsBF_4$ for the D-line is, therefore, slightly *smaller* than the index of refraction for the D-line of this latter solution, which appeared to be 1.3563. Hence we know now:

$$1.3563 > n_D \text{ for } CsBF_4 > 1.3502.$$

This low value for the index of refraction of $CsBF_4$ might have been predicted on the ground of FAJANS and JOOS' considerations ²⁾. By the aid of definite suppositions as to the deformation of the electron layers in ions these investigators have succeeded in constructing a table of refractions for the ions, the latter being supposed as gaseous and undeformed. Thus they give as value for the triply charged boron ion 0.05, for the singly negatively charged fluor ion 2.5. Now in $(BF_4)'$ the boron ion will give the same value, the deformation under the influence of the fluor being only small. The fluor ions themselves are, however, strongly onesidedly deformed by the boron ion; their value of refraction is greatly lowered. We can, however, approximately evaluate how great this diminution is. While the free chlorine ion has a refraction 9.0, this value is diminished to 6.97 in BCl_3 , i.e. to 77 % of the original value. Likewise the free bromine ion has a value of 12.67, in BBr_3 9.97, hence only 79 %. Therefore we might say that in the neutral BF_3 the fluor had decreased to about 75 % of its value, and amounts therefore to 1.9. In the $(BF_4)'$ the deformation of the fluor ion will again be somewhat smaller, so that the value there will be > 1.9 . Hence we get a refraction > 7.65 for the $(BF_4)'$.

The free Cs^+ has a refraction 6.24. Contrary to many other salts we may assume that in $CsBF_4$ the ions influence each other only to a small extent. For the $(BF_4)'$ is little deformable (like ClO_4' , an example which FAJANS and JOOS cite), and Cs^+ is little deforming; also the reverse, i.e.

¹⁾ This is fully described by R. W. WOOD, Physical Optics 1921, p. 112.

²⁾ K. FAJANS and G. JOOS. Zeitschr. f. Phys. 23, 1, 1924.

a deformation of Cs' by $(\text{BF}_4)'$ can practically be excluded. We therefore arrive at the conclusion that the refraction of CsBF_4 has a value $> 7.65 + 6.24$, hence > 13.89 .

As therefore

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} > 13.89$$

it is only necessary to know the density d to arrive at a valuation of n . The density proved to be 3.2, hence we find for the index of refraction:

$$n_D > 1.33.$$

On the ground of such considerations it would be expected that the indices of refraction of rubidium and potassium boron fluoride are still lower. We shall see that this is actually the case.

While the appearance of the colour effects in the precipitation of the cesium salt is more or less accidental (because the dispersion curve intersects that of the mother liquid which contains hydrochloric acid) the matter is simpler in the rubidium boron fluoride.

During the precipitation no colour effects are observed, evidently because the index of refraction lies lower than that of the solution. In the recrystallisation of RbBF_4 from pure water brilliant colours make their appearance. A solution of RbBF_4 saturated at room temperature (0.6 gr. in 100 cc.) appears to have the same index of refraction as pure water (1.3332). If solid RbBF_4 is brought into this solution, it again looks gelatinous; it appears that the yellow light is transmitted and that the dispersed colours cause blue borders. The index of refraction of RbBF_4 for the D-line appears, therefore, to be very near 1.33 indeed.

In CsBF_4 the play of colours could be varied at pleasure on dilution with water or on addition of HCl (on dilution of a very concentrated HCl -solution, which contained CsBF_4 and transmitted *red* light, we could pass through the whole spectrum, the complementary colour always appearing as border colour round the objects); this did, of course, not succeed in the case of rubidium salt. It is still possible to vary the colour, namely by heating the system; the indices of refraction of the solution diminish more rapidly than those of the salt, so that at higher temperatures the points of intersection of the curves shift more towards the violet.

It may be seen from the following table that in this salt really pretty well the whole spectrum can be traversed in this way.

The index of refraction of potassium boron fluoride lies still lower than that of the rubidium salt, hence also lower than that of water. A solution of the potassium salt saturated at room temperature (only 0.6 gr. in 100 cc.) had again practically the same index of refraction as that of water. The solid salt brought in this solution displays hardly any colours. Only a blue dispersion is very faintly perceptible; also the separation

between salt and solution is much clearer. Evidently the dispersion curve of the potassium salt does not intersect that of water, but it lies under

RbBF₄ in water

Temperature	Colours of the transmitted light	Colours of the dispersed light
0°	orange	green-blue
10°	orange yellow	blue
20°	yellow	blue
30°	green yellow	blue violet
40°	yellow green	violet with some red
50°	yellow green	faint red violet
55°	green	red violet
60°	green with some blue	violet red
70°	blue	brown orange
80°	indigo blue	orange yellow
90°	violet	yellow with some orange
100°	violet	yellow

the water-curve. On heating, the curve for the solution descends more rapidly than that for the salt; they intersect each other, and this causes again the pronounced colour effects to appear. As appears from the following table the colours are almost the same as those of the rubidium salt at about 30° to 40° lower temperature.

Temperature	Colours of the transmitted light	Colours of the dispersed light
40°	orange yellow	blue
50°	almost yellow	blue
60°	yellow	blue
70°	green yellow	blue violet
80°	yellow green	violet
90°	green	red violet
100°	blue	yellow brown

While the Cs-, Rb-, and K-salts of the boron fluor hydrogenic acid are sparingly soluble, the Na- and Li-salts dissolve readily in water ¹⁾.

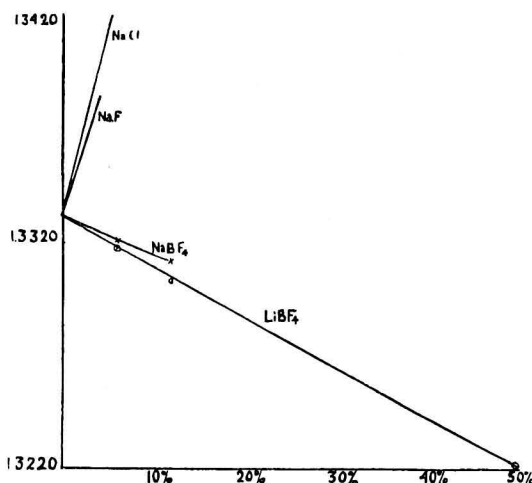
¹⁾ Cf. for the further properties: J. H. DE BOER and J. A. M. V. LIEMPT. Rec. d. tr. chim. des Pays-Bas, **46**, 124 (1927).

It was more or less to be expected that the indices of refraction of these salts should be still lower, and it might also be expected that the solutions of these salts had a lower index of refraction than that of water.

This appeared actually to be the case; thus the following values were found for the *D*-line at 20° C.:

		Water:	1.3332
NaBF ₄	6 ⁰ / ₀	solution:	1.3321
	12 ⁰ / ₀	„	: 1.3312
LiBF ₄	6 ⁰ / ₀	„	: 1.3318
	12 ⁰ / ₀	„	: 1.3303
	50 ⁰ / ₀	„	: 1.3221.

This last value is not so very certain, as the measurement had to be done very rapidly; there were indications that the glass was attacked. As is, however, clear from the adjoined figure, the points lie sufficiently accurately on a straight line.



By way of comparison also the increases of the index of refraction of water on dissolving NaCl or NaF have been drawn.

Also the boron fluor hydrogenic acid itself lowers the index of refraction of water. A solution containing about 20⁰/₀ of this acid gave a value of 1.3284.

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