

## FARADAY EFFECT IN SOME CUBIC CRYSTALS

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### 1. INTRODUCTION

It is well known that the magnitude of the Faraday rotation in solids or liquids is generally less than that given by the celebrated Becquerel formula which connects it with the optical dispersive power. The percentage ratio of the observed magnetic rotation to that theoretically predicted is called the magneto-optic anomaly. An examination of the available data, especially those obtained in some recent studies by the author (1946) indicate that the magneto-optic anomaly is related to the nature of the electronic binding between the atoms in the solid. In particular, a comparison of the Faraday rotations in diamond and in zinc-blende (Ramaseshan, 1946) disclosed the remarkable result that in spite of the apparent similarity in their structures, the magneto-optic anomaly for diamond is only 28% while that in zinc-blende is 91%. This suggested that the determination of the magneto-optic anomaly of a series of crystals of simple constitution and structure might succeed in giving an insight into the state of the electron atmosphere in crystals. With this object in view, the present investigation was undertaken. It describes measurements made with five cubic crystals, viz., LiF, NH<sub>4</sub>Cl, KBr, NH<sub>4</sub>Br and MgO for which no record of Faraday effect measurements could be traced in the literature. As a check on the accuracy of the work, measurements have also been made with three crystals, NaCl, KCl and CaF<sub>2</sub>, for which data are already available.

### 2. MATERIALS STUDIED

In the determination of the Verdet constant, it is absolutely essential that the crystal to be used should have no residual birefringence. Birefringence induced by strain is known to affect Faraday effect measurements in two ways. Firstly, the restoration of light due to birefringence when the crystal is observed between crossed nicols makes it difficult to observe the restoration produced by the magnetic field. Consequently, the accurate determination of the extinction position becomes difficult. Secondly, the Faraday effect in isotropic substances is known to diminish in the presence of small amounts of birefringence. However, all the crystals

excepting those of MgO and NH<sub>4</sub>Br used in the present investigation were free from this defect.

A large crystal of lithium fluoride of size approximately 3 × 2 × 2 cm., purchased from Harshaw Chemical Co., Ltd., U.S.A., was employed. All its faces were well polished and it proved ideal for Faraday effect measurements. Five crystals of synthetic periclase presented to Sir C. V. Raman by Messrs. Norton & Co., Worcester, U.S.A., were found suitable for the measurement of the Verdet constant in MgO. All the crystals had a small amount of residual birefringence but in four of them this was so small that it did not affect the measurements. Two fine crystals of fluorspar with polished faces, one colourless and the other showing a violet fluorescence, which were originally in possession of Fizeau and now form part of Sir C. V. Raman's crystallographic collection, were available for these studies. Large clear cleavage plates of rocksalt from Baluchistan were used. The ammonium chloride and bromide crystals were grown by Mr. K. G. Ramanathan in this laboratory for some spectroscopic studies. The crystals were 1 × 1 × 0.5 cm. in size. The potassium bromide and chloride crystals were grown by the author by the method of slow evaporation of a saturated solution.

### 3. EXPERIMENTAL PROCEDURE

The Verdet constant  $V$  of a substance can be expressed by the modified Becquerel formula

$$V = \gamma (e/2mc^2) \lambda dn/d\lambda,$$

where  $e$  and  $m$  are the electronic charge and mass respectively,  $\lambda$  and  $c$  the wavelength and velocity of light and  $n$  is the refractive index of the substance. The factor  $\gamma$  in many substances remains constant over the visible and the near ultraviolet provided the dispersion due to the infra-red terms is eliminated from the formula (Darwin and Watson, 1927). To calculate the value of  $\lambda dn/d\lambda$  of a substance, fairly accurate measurements of the refractive indices for a few wavelengths in the visible region are necessary.

The refractive indices of these crystals were determined with the aid of a Pulfrich refractometer made by Carl Zeiss & Co. As most crystals had the form of rectangular parallelepipeds with polished faces, there was not much difficulty in the measurements. Monobromonaphthalene, methylene iodide and a solution of sulphur in methylene iodide were the liquids used to cement the solids to the Pulfrich prism. The refractive indices were determined for the wavelengths  $\lambda$  5893,  $\lambda$  5461 and  $\lambda$  4358. The refractive index measurements were accurate to one unit in the fourth place of decimals for MgO, NH<sub>4</sub>Cl, NH<sub>4</sub>Br and KBr and to two units in

the fifth place for LiF. The dispersion is accurate to 1% or 2%. The dispersion of fluorspar has been determined from the values of refractive indices given in Landolt and Bornstein tables.

An electromagnet of the Rutherford type with its polepieces 28 mm. apart was used. In the earlier determination with LiF the polepieces were kept 32 mm. apart, but later this was reduced to 28 mm. A sodium lamp and a mercury pointolite lamp with suitable filters were used as the sources of light. A wide-angle nicol was used to polarise the light. The magnetic rotation of the light was determined by means of a Laurents polarimeter consisting of a sugar half-shade and a small analysing nicol. The sugar half-shade (Rayleigh, 1884) consists of a cell containing sugar solution arranged such that the two halves of the cell in the field of view are subjected to small rotations, differing by about 2°. The difference in the thickness in the path is obtained by introducing a piece of unstrained glass inside the cell such that the upper edge of the glass divides the field of view into two parts. With this half-shade it is possible to determine the position of equal intensity within 1' or 2' of arc. In each measurement the position of equal intensity was determined first without the magnetic field and then with the field on and reversed. A mean of twenty readings was usually taken. The accuracy of measurement was between  $\frac{1}{2}$ % and 1%. It must be mentioned here that the half-shade could only be used in the case of crystals without any trace of birefringence. It was used for the measurement of the magnetic rotation in LiF, KBr, NH<sub>4</sub>Cl, CaF<sub>2</sub>, NaCl and KCl. For NH<sub>4</sub>Br and MgO which had small amounts of birefringence, the half-shade was dispensed with and the approximate extinction position was determined with the aid of the analyser.

The effective field used was determined by measuring the rotation produced in conductivity water. The Verdet constant for water for  $\lambda$  5893 at 25° was taken to be 0.01307 min. per cm. per gauss. The temperature at which the measurements were taken was always between 23.5° C. and 26° C.

Table I gives the rotation observed for  $\lambda$  5893,  $\lambda$  5461 and  $\lambda$  4358 with water columns of different thicknesses. Table II to IX give the optical and magneto-optic constants of NaCl, KCl, CaF<sub>2</sub>, LiF, KBr, NH<sub>4</sub>Cl, NH<sub>4</sub>Br and MgO. In these tables,  $n$  is the refractive index,  $\rho$  the actual rotation due to the magnetic field,  $V$  the Verdet constant and  $\gamma$  the magneto-optic anomaly.

The values obtained for KCl and NaCl agree closely with those obtained by Becquerel (1885) and Landau (1908). These values are about 5% higher than those obtained by Mayer (1909). The Verdet constant of

CaF<sub>2</sub> agrees closely with the values obtained by different workers (1908, 1909, 1885). The magnetic rotation for  $\lambda$  4358 could not be determined

TABLE I

$V_{5893}$  for water = 0.1307' per cm. per gauss

Distance between polepieces in mm.	Thickness in cm.	Wavelength in Angstroms	Rotation in minutes	Field in gau.
32	1.504	5893	141	7170
32	1.210	5893	113	7150
28	1.504	5893	159	8060
do	do	5461	138	8090
do	do	4358	305	8070
do	1.210	5893	128	8100
do	do	5461	151	8080
do	do	4358	243	8060

$$\frac{V_{5461}}{V_{5893}} = 1.184 \text{ (I.C.T.)}$$

$$\frac{V_{5893}}{V_{5893}} = 1.180 \text{ (Observed)}$$

$$\frac{V_{4358}}{V_{5893}} = 1.916 \text{ (I.C.T.)}$$

$$\frac{V_{4358}}{V_{5893}} = 1.92 \text{ (Observed)}$$

TABLE II

Rock Salt (NaCl)

Crystal No.	Thickness in mm.	Field in gauss		$\lambda$ 5893	$\lambda$ 5461	$\lambda$ 4358
1	4.18	8080	$2\rho$	238'	280'	470'
2	9.05	7160	$2\rho$	464'	546'	915'
			V	0.0355	0.0418	0.0795
			n	1.5443	1.5475	1.5602
			$\lambda \frac{dn}{d\lambda}$	0.0287	0.0454	0.0774
			$\gamma$	91.6%	92.1%	91%

TABLE III

Sylvine (KCl)

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5893	$\lambda$ 5461	$\lambda$ 4358
1	3.55	$2\rho$	162'	192'	321'
2	6.96	$2\rho$	278'	334'	550'
		V	0.0282	0.0334	0.0561
		n	1.4904	1.4932	1.5046
		$\lambda \frac{dn}{d\lambda}$	0.0321	0.0392	0.0662
		$\gamma$	84.6%	84.5%	84.7%

TABLE IV  
Fluorspar ( $\text{CaF}_2$ )

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5893	$\lambda$ 5461	$\lambda$ 4358
1	10.32	$2\rho$	150'	176'	285'
2 (violet)	7.44	$2\rho$	108'	126'	
		V	0.00898	0.01049	0.01710
		n	1.43383	1.43495	1.43949
		$\lambda \frac{dn}{d\lambda}$	0.0140	0.0165	0.0260
		$\gamma$	63.6%	63.6%	65.2%

TABLE V  
Lithium Fluoride ( $\text{LiF}$ )

Thickness in mm.	Field in gauss		$\lambda$ 5893	$\lambda$ 5461	$\lambda$ 4358
27.27	7160	$2\rho$	343'	400'	635'
27.27	8080	$2\rho$	384'	450'	712'
		V	0.00878	0.01023	0.01620
		n	1.39260	1.39341	1.39724
		$\lambda \frac{dn}{d\lambda}$	0.01153	0.01341	0.02110
		$\gamma$	76.1%	76.3%	77.0%

TABLE VI  
Potassium Bromide ( $\text{KBr}$ )

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5893	$\lambda$ 5461	$\lambda$ 4358
1	5.35	$2\rho$	343'	407'	696'
2	5.27	$2\rho$	338'	398'	693'
3	4.56	$2\rho$	295'	348'	601'
		V	0.0398	0.0469	0.0813
		n	1.5585	1.5631	1.5813
		$\lambda \frac{dn}{d\lambda}$	0.0538	0.0633	0.1104
		$\gamma$	73.5%	73.5%	73.2%

TABLE VII  
Ammonium Chloride ( $NH_4Cl$ )

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5393	$\lambda$ 5461	$\lambda$ 4358
1	9.05	2p	544'	641'	1088'
2	3.16	2p	190'	223'	381'
3	2.52	2p	114'	134'	232'
		V	0.0367	0.0432	0.0743
		n	1.6397	1.6439	1.6621
		$\lambda \frac{dn}{d\lambda}$	0.0507	0.0595	0.1070
		$\gamma$	72.3%	72.7%	73.1%

TABLE VIII  
Ammonium Bromide ( $NH_4Br$ )

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5398	$\lambda$ 5461	$\lambda$ 4358
1	4.11	2p	334'	397'	693'
2	2.67	2p	212'	250'	443'
		V	0.0499	0.0589	0.1045
		n	1.7157	1.7217	1.7478
		$\lambda \frac{dn}{d\lambda}$	0.0727	0.0857	0.1505
		$\gamma$	68.6%	68.8%	69.5%

TABLE IX  
Periclase ( $MgO$ )

Field 8080 gauss

Crystal No.	Thickness in mm.		$\lambda$ 5393	$\lambda$ 5461	$\lambda$ 4358
1	7.45	2p	403'	475'	778'
2	7.75	2p	421'	495'	816'
3	11.91	2p	660'	774'	1247'
4	13.35	2p	735'	867'	1418'
		V	0.0344	0.0405	0.0670
		n	1.7375	1.7410	1.7560
		$\lambda \frac{dn}{d\lambda}$	0.0426	0.0500	0.0847
		$\gamma$	80.8%	81%	79.1%

with sufficient accuracy in the fluorspar crystal having a violet fluorescence. This was due to the feeble transmission by the crystal towards the violet end of the spectrum.

#### 4. COLLECTION OF RESULTS AND DISCUSSION

The Verdet constant, refractive index and the magneto-optic anomaly of the eight crystals studied in this paper, together with the values for diamond and zinblende previously obtained by the author, are given in Table X.

TABLE X

Substance	$n_{5893}$	$V_{5893}$	$\gamma\%$
ZnS ..	2.3683	0.226	91
NaCl ..	1.5443	0.0358	91
KCl ..	1.4904	0.0286	86
MgO ..	1.7375	0.0344	81
LiF ..	1.3926	0.00876	76
KBr ..	1.5580	0.0398	74
NH <sub>4</sub> Cl ..	1.6397	0.0367	73
NH <sub>4</sub> Br ..	1.7157	0.0499	69
CaF <sub>2</sub> ..	1.4338	0.00893	65
Diamond ..	2.4172	0.0233	28

Van Vleck (1932) has shown that atoms having the inert gas configuration must obey the unmodified Becquerel formula, *i.e.*, they should have a  $\gamma$  value of 100%. The lower value of  $\gamma$  for the well-known ionic substances NaCl and KCl may be attributed to the deviation of the electron atmospheres of the ions in the crystal from the inert gas configuration. It is natural to expect, on this basis, that in diamond which is completely a covalent crystal, the  $\gamma$  value should be very low. The low values of  $\gamma$  for NH<sub>4</sub>Cl and NH<sub>4</sub>Br may also be attributed to the covalent N-H bond. But a careful study of Table X shows that this elementary hypothesis cannot explain many of the facts observed. For instance, CaF<sub>2</sub> which is usually considered to be an ionic crystal has a value of  $\gamma$  considerably lower than the values for other ionic crystals. At the present stage it has not been possible to correlate any other physical property with the magneto-optic anomaly. Indeed to effect such a correlation, more data on the magneto-optic anomaly in crystals are necessary. Investigations on the determination of the values of  $\gamma$  in other ionic cubic crystals and their solutions are in progress, and it is expected that the results of these studies will throw some light on the meaning of the magneto-optic anomaly.

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gation and for the loan of the crystals. Thanks are also due to Dr. R. S. Krishnan and Mr. K. G. Ramanathan for the loan of the crystals of ammonium chloride and bromide.

#### 5. SUMMARY

The paper records the Verdet constant, refractive index, dispersion and the magneto-optic anomaly of eight cubic crystals, *viz.*, NaCl, KCl, CaF<sub>2</sub>, LiF, KBr, NH<sub>4</sub>Cl, NH<sub>4</sub>Br and MgO for the wavelengths,  $\lambda$  5893,  $\lambda$  5461 and  $\lambda$  4358. The magneto-optic constants for the last five crystals mentioned above have been determined for the first time. The values of the Verdet constant for  $\lambda$  5893 and the magneto-optic anomaly for these crystals are as follows:—LiF 0.00876, 76%; KBr 0.0398, 74%; NH<sub>4</sub>Cl 0.0367, 73%; NH<sub>4</sub>Br 0.0499, 69%; MgO 0.0344, 81%.

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