Reprinted from "The Proceedings of the Indian Academy of Sciences,
Vol. XXVIII, No. 5, Sec. A, 1948

THE FARADAY EFFECT AND MAGNETO-OPTIC ANOMALY OF SOME CUBIC CRYSTALS

BY S. RAMASESHAN
(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received November 20, 1948
(Communicated by Prof. R. S. Krishnan, F.A.SC.)

THE magnitude of the Faraday rotation in most transparent substances is expressible by a formula of the Becquerel type, *viz.*,

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

where V is the Verdet constant, e and m are the electronic charge and mass respectively, c the velocity of light, λ the wavelength and n the refractive index. γ is a multiplying factor (called the magneto-optic anomaly) which is approximately constant throughout the visible and the ultra-violet regions, provided the contribution made to the dispersive power by the infra-red absorption bands is eliminated from the formula. Becquerel (1897) arrived at his original formula, in which the factor γ had a value of unity, purely from classical considerations. Van Vleck (1932) has considered the derivation of the Becquerel formula from quantum mechanical ideas and arrives at a conclusion that the value of γ depends on the state of the electrons of an atom and it need not necessarily have a value equal to one. He also found that for atoms and ions in which the electrons have an inert gas configuration (*viz.*, when the outer electrons are in the s state), the value of γ must be equal to unity, *i.e.*, the anomaly disappears. Surprisingly enough, (as has been remarked by Darwin and Watson (1927), such crystals like NaCl and KCl which are reputed to be of the ionic type have a value of γ of about 0·8. This decrease in γ must obviously be due to the distortion of the electron atmospheres of the atoms due to the crystal structure. The value of γ may be therefore tentatively assumed to be an indication of the departure of the binding from the true ionic type. A study of the magneto-optic rotation and anomaly in crystals would throw considerable light on the nature of the binding in the crystalline state. Accordingly the present writer made some measurements in diamond, zinc blende, and other crystals (Ramaseshan, 1946, 1947). The present work was undertaken with a view to get more accurate data in the case of the crystals already investigated and to extend the studies to other crystals. The Faraday rotation measurements were made in a series of cubic crystals (NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, KAl $(SO_4)_2$ 12 H_2O and NH_4Al $(SO_4)_2$ 12 H_2O and the magneto-optic anomaly has been calculated in each case. To get a clearer insight into the meaning of the magneto-optic anomaly, the Verdet constant and γ for concentrated solutions of these crystals in water have also been determined and the results are reported in this paper.

2. EXPERIMENTAL METHODS

For measurements of the Faraday effect, a polarimeter made by Franz Schmidt and Haench and Co., Berlin, was used. The analyser was mounted on a divided circle that could read upto 0·01°. The polarimeter was fitted with a Lippich double field polariser in which the half shadow angle could be varied from 0° to 20°. When this angle was between 3° and 4° most accurate and satisfactory results were obtained. With clear transparent crystals or solutions repeated settings of the match-point do not vary by more than 0·02°. While taking measurements, the usual precautions that are necessary to eliminate instrumental errors were taken. Each value given in the tables is a mean of ten settings. The sources of light used in these visual measurements were a sodium lamp with a light yellow filter for λ 5893 and a mercury point-o-lite lamp with suitable filters for isolating λ 5461 λ 4358.

On account of the low sensitivity of the eye to the region below λ 4358, visual observations could not be extended below this wavelength. Instead a spectrographic method was resorted to. With the same polarimeter arrangement as mentioned above, the light coming out of the analyser was focussed by means of an achromatic lens on the widened slit of a Hilger baby quartz spectrograph. A series of photographs was taken with different settings of the analyser. Each line in the spectrum being an image of the half shade, the match-point for different wavelengths could be easily determined. It was found that with a half shadow angle of 6° and with a point-o-lite mercury lamp running at 2·4 amps. as the source, an exposure of 30 seconds was sufficient to record the spectral line at the match-point when it is least intense. The analyser was rotated by 0·05° between successive photographs and the match point could be placed within 0·05° to 0·10°; and as the magnetic rotation was usually above 10° the accuracy obtained was quite satisfactory. The extinction positions for the wavelengths λ 5780, λ 5461, λ 4358, λ 4046 and λ 3665 were determined for each crystal without the magnetic field and with the magnetic field on and reversed. The values obtained for the first three wavelengths did not differ by more than ½ to 1% from the values obtained by visual measurements.

These measurements could not be extended beyond λ 3665, since the absorption of the film of canada balsam in the double field polariser became considerable below this wavelength. It is proposed to extend these studies to the far ultraviolet (at least upto λ 2537) by using ultra-violet polarising prisms.

The magnet used in these experiments was of the Rutherford type fitted with special pole-pieces. With currents upto 6 amps. the magnet could be run continuously for an hour without much heating. The refractive indices of the crystals and solutions were measured with a Pulfrich refractometer. The measurements were always made at room temperature (25 ± 1° C.).

3. MATERIALS STUDIED

The crystals whose Verdet constants are to be measured by the above method must be absolutely free from birefringence, since irregular birefringence induced by residual strain would make it impossible to match the two halves of the double field polariser. Further, magnetic rotation as measured by the usual method is known to diminish in the presence of a small amount of birefringence. Therefore, great care was taken to see that only isotropic crystals were chosen for these measurements. A piece of rock-salt about 2 cm. × 2 cm. × 0·8 cm. was cleaved from a larger specimen. The potassium chloride, sodium chlorate, potassium alum and ammonium alum were grown by the method of slow evaporation from saturated solutions. Crystals of ammonium chloride and bromide were grown from saturated solutions in which urea was introduced as an impurity catalyst. Refractive index measurements show that the urea present in the crystals obtained in this way could not be more than 1%. A large crystal of potassium bromide 7·5 cm. × 6·10 cm. × 3·05 cm. in size was used. Although the crystal was full of irregular birefringence there was a small region 3 mm. × 3 mm. where the light was always extinguished when observed between crossed nicols. The surfaces of all the crystals were polished with rouge and putty powder so that the half-shade could be seen through them very clearly.

The solutions were prepared from the purest chemicals manufactured by either Kahlbaum or Merck. In the measurement of the Faraday rotations in solutions, the same glass cell was used for all the solutions.

4. RESULTS

Tables I to IX give the values of the Verdet constant determined for different wavelengths for crystals of NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, $KAl(SO_4)_2\,12H_2O$ and $NH_4Al(SO_4)_2\,12H_2O$. The thickness of the crystal used, the magnetic field and the specific gravity of the crystal are

TABLE I

Magneto-optic data for NaCl crystal

Thickness 2·231 cm. Magnetic field 8450 oersteds
Specific gravity 2·163

Wavelength in Angstroms	2ρ Magnetic rotation in degrees	V Verdet constant in min./cm. oersted		γ%
		Author	Mayer & Landau	
5893	21·68	0·0345	0·0328	89·0
5780	23·06	0·0367	··	89·8
5461	25·76	0·0410	0·0390	90·1
4358	43·00	0·0685	0·0655	88·0
4046	50·80	0·0809	0·0775	89·0
3665	69·70	0·111	0·106	90·0

TABLE II

Magneto-optic data for KCl crystal

Thickness 0·965 cm. Magnetic field 9780 oersteds.
Specific gravity 1·988

λ	2ρ	V		γ%
		Author	Mayer	
5893	8·64	0·0275	0·0267	82·1
5780	9·08	0·0289	··	82·1
5461	10·32	0·0328	0·0316	82·2
4358	17·30	0·0551	0·0534	82·7
4046	21·40	0·0680	··	83·1
3665	27·40	0·0870	··	83·2

TABLE III

Magneto-optic data for KBr crystal

Magnetic field 3540 oersteds Specific gravity 2·75

λ	2ρ		V	γ%
	Thickness 6·10 cm.	Thickness 3·05 cm.		
5893	30·60	15·40	0·0425	78·5
5461	36·00	18·10	0·0500	79·5
4358	60·4	30·15	0·0840	78·2
4046	··	38·00	0·106	79·4
3665	··	48·20	0·134	79·1

TABLE IV

Magneto-optic data for KI crystal

Thickness 1·070 cm. Magnetic field 8450 oersteds

Specific gravity 3·13

λ	2ρ	V	$\gamma\%$
5893	21·10	0·070	78·2
5461	25·00	0·083	78·9
4358	45·50	0·151	78·3

TABLE V

Magneto-optic data for NH_4Cl crystal

Thickness 0·906 cm. Magnetic field 9780 oersteds

Specific gravity 1·529

λ	2ρ	V	$\gamma\%$
5893	10·62	0·0362	71·9
5461	12·61	0·0430	72·7
4358	21·68	0·0739	72·9

TABLE VI

Magneto-optic data for NH_4Br crystal

Thickness 0·746 cm. Magnetic field 9780 oersteds

Specific gravity 2·325

λ	2ρ	V	$\gamma\%$
5893	12·28	0·0504	69·0
5461	14·61	0·0601	69·8
4358	25·29	0·1040	69·5

TABLE VII

Magneto-optic data for $NaClO_3$ crystal

Thickness 2·054 cm. Magnetic field 8450 oersteds
Specific gravity 2·490

λ	2ρ	V		γ%
		Author	Voigt	
5893	4·68	0·0081	..	31·0
5780	5·02	0·0087	0·0088	31·2
5461	6·08	0·0105	0·0106	31·5
4358	9·40	0·0163	..	31·2
4046	11·60	0·0201	..	32·0
3665	15·80	0·0272	..	33·0

TABLE VIII

Magneto-optic data for potassium alum

Thickness 0·931 cm. Magnetic field 9940 oersteds
Specific gravity 1·76

λ	2ρ	V	γ%
5893	3·82	0·0124	53·3
5780	4·01	0·0130	54·2
5461	4·44	0·0144	55·1
4358	6·78	0·0220	55·5

TABLE IX

Magneto-optic data for ammonium alum

Thickness 0·895 cm. Magnetic field 9940 oersteds
Specific gravity 1·64

λ	2ρ	V	γ%
5893	3·79	0·0128	54·3
5780	3·97	0·0134	54·7
5461	4·48	0·0151	55·2
4358	6·87	0·0232	55·4

also given at the top of each table. The values of the Verdet constant determined by other authors (Mayer, 1909; Landau, 1908; Voigt, 1908) have also been included in the tables. The refractive index data are not given here as they correspond to the values determined by previous workers (Soret, 1884; Haase, 1927; Ramaseshan, 1947). The last column in each table gives the value of γ, the magneto-optic anomaly, expressed as a percentage. Table X gives the natural and magnetic rotations in $NaClO_3$ crystal as also the ratio of the two for different wave-lengths. Table XI gives the concentration, specific gravity, Verdet constant and the magneto-optic anomaly for all the solutions that were studied and Table XII gives their dispersion data.

TABLE X

Natural and magnetic rotations in $NaClO_3$

Thickness of the crystal 2·054

λ	ρ (natural) in degrees/cm.	$\rho\times 10^4$ in degrees/cm. oersted	$\frac{\rho_n}{\rho_m}\times 10^{-4}$
5893	31·4	1·35	23·3
5780	33·2	1·45	23·0
5461	37·0	1·75	21·1
4358	59·2	2·71	21·9
4046	68·2	3·35	20·4
3665	86·0	4·53	18·9

TABLE XI

Magneto-optic data for solutions

Magnetic field 8450 oersteds $\lambda = 5461$ A

Thickness of the column 1·767 cm.

Substance	No. of gms. in 100 gms. water	Sp. Gr.	2ρ	V	γ %
Water ..	..	1·00	7·71	0·0155	76·3
KCl ..	21·2	1·114	9·12	0·0183	79·1
KBr ..	48·78	1·288	11·30	0·0227	85·4
KI ..	88·10	1·476	17·08	0·0343	85·4
NaCl ..	24·12	1·136	9·72	0·0195	79·4
NH_4Cl ..	27·20	1·061	9·98	0·0200	78·8
NH_4Br ..	75·08	1·297	13·68	0·0275	83·2
$NaClO_3$ ..	106·3	1·442	8·61	0·0173	72·9
$KAl(SO_4)_2\,12H_2O$ ..	12·68	1·051	7·86	0·0158	75·5

TABLE XII

Dispersion data for solutions

Substance	n_{5893}	n_{5461}	n_{4358}	$\lambda \frac{dn}{d\lambda}(5461)$
Water ..	1·33239	1·33381	1·33940	2011
KCl ..	1·35594	1·35756	1·36411	2294
KBr ..	1·37771	1·37957	1·38764	2634
KI ..	1·41660	1·41941	1·43159	3979
NaCl ..	1·36462	1·36634	1·37335	2435
NH_4Cl ..	1·37230	1·37408	1·38138	2520
NH_4Br ..	1·40915	1·41146	1·42127	3271
$NaClO_3$ ..	1·38739	1·38905	1·39593	2351
$KAl(SO_4)_2 12H_2O$	1·34304	1·34447	1·35036	2048

5. DISCUSSION OF RESULTS

The tabulated results reveal many interesting features. For instance, one notices that the modified Becquerel formula is very nearly obeyed by all the crystals in the wavelength region between λ 5893 and λ 3665 and the values of γ for each crystal is approximately constant in this region of the spectrum. It is significant that in the case of crystals, $\gamma(NaCl) > \gamma(KCl)$ and $\gamma(KCl) > \gamma(KBr) > \gamma(KI)$ and similarly $\gamma(NH_4Cl) > \gamma(NH_4Br)$. If it is assumed that the reduction in the value of γ is an indication of the distortion of the electron atmospheres of the ions in the crystal, then heavier ions distort the electron atmospheres more than the lighter ones. The low value of γ for $NaClO_3$ and the alums is probably due to the fact that the covalent linkages in ClO_3 and SO_4 ions produce a very great distortion in the electron atmospheres of the atoms. The comparatively lower values of γ for NH_4Cl and NH_4Br may also be due to the covalent nature of the N–H bond.

Table XIII gives the γ values for the different crystals and solutions.

TABLE XIII

Magneto-optic anomaly in crystals and solutions

Substance	Concentration No gm./100 gm. solution	γ (solution)%	γ (crystal)%
Water ..	100·0	76·3	..
NaCl ..	19·4	79·4	89
KCl ..	17·5	79·1	82
KBr ..	32·8	85·4	79
KI ..	46·8	85·4	78
NH_4Cl ..	21·4	78·8	72
NH_4Br ..	42·9	83·2	69
$NaClO_3$ ..	51·5	72·9	32
$KAl(SO_4)_2 12H_2O$	11·3	75·5	54

Excepting in the case of $NaClO_3$ and potassium alum (the two crystals having very low γ values), the γ for the solutions is always greater than that for water. Of special significance is the fact that γ values for KBr, KI, NH_4Cl and NH_4Br solutions are greater than the corresponding values for the crystals. This indicates that the γ for the ions in solution is greater than that for the ions in the crystal. Tentative calculations show that γ for the ions in solution is between 95% and 100%, *i.e.*, they approach the value suggested by Van Vleck for free ions with inert gas configurations. These calculations and conclusions are purely tentative, as the effects of the ions in solution on the dispersive power of water have not been taken into consideration.

The results obtained with $NaClO_3$ solution are very striking. While the γ in the crystal is only 33%, the γ for a 50% solution shoots upto 72%, *i.e.*, only 4% less than that for water. In fact, if the γ value for the ions in solution were the same as that for the ions in the crystal, then γ for a 50% solution should be of the order of 50%. On the other hand, if the γ for Na ion is assumed to be 100%, then approximate calculations show that γ for ClO_3 ion is of the order of 50 or 60%. The low value of 33% obtained in the $NaClO_3$ crystal is most probably due to partial covalent forces that come into play in the crystal.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman and Prof. R. S. Krishnan for the keen interest they took in these investigations.

SUMMARY

Using a Lippich double field polarimeter together with a spectrograph, the Faraday rotation for crystals of NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, $KAl(SO_4)_2\ 12\,H_2O$ and $NH_4Al(SO_4)_2\ 12\,H_2O$ have been measured for the wavelengths, λ 5893, λ 5780, λ 5461, λ 4358, λ 4046 and λ 3665. The magnetic rotation for concentrated solutions of these crystals in water were also measured. The magneto-optic anomaly for the crystals and solutions has been calculated from the measurements of the dispersion values. It is found that in the case of crystals, $\gamma(NaCl) > \gamma(KCl) > \gamma(KBr) > \gamma(KI)$ and $\gamma(NH_4Cl) > \gamma(NH_4Br)$. The γ for the solutions except in the case of $NaClO_3$ and the alums is always greater than that for water. The γ values for the ions in solution are higher than those for the ions in the crystal. The presence of covalent bonds tends to diminish the value of γ [$\gamma(NaClO_3$ crystal$) = 33\%$ and $\gamma(\text{Alum}) = 52\%$]. The γ value for a 50% solution of $NaClO_3$ is 72%.

REFERENCES

Becquerel, H.	.. *Comptes Rendus*, 1897, **125**, 679.
Darwin and Watson	.. *Proc. Roy. Soc.*, London, A, 1927, **114**, 474.
Haase	.. *Zeit. f. Kryst*, 1927, **65**, 509.
Landau, S.	.. *Phys. Z. S.*, 1908, **9**, 417.
Mayer, V.	.. *Ann. d. Phys.* (4), 1909, **30**, 622.
Ramaseshan	.. *Proc. Ind. Acad. Sc.*, A, 1946, **24**, 104.
Soret	.. *Arch. Sc. Phys.* (3), 1884, **12**, 554.
Van Vleck	.. *Theory of Electric and Magnetic Susceptibility, Oxford*, 1932, 367.
Voigt	.. *Phys. Z. S.*, 1908, **9**, 589.