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FARADAY EFFECT IN CUBIC CRYSTALS

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ABSTRACT

The magneto-optic rotation has been measured in five cubic crystals KCl, KBr, KI, LiF and MgO for a number of wavelengths from γ 5780 Å to λ 2848 Å. Dispersion formulæ have been proposed for both optical refraction and magnetic gyration. The formula for magnetic gyration fits the experimental data to within $\frac{1}{2}$%. It is found in the case of alkali halides that all the absorption wavelengths, characteristics of the substances, are effective towards the magnetic gyration in the same proportion as in refraction, *i.e.*, the value of the anomaly factor for different absorption frequencies are the same. But the values of anomaly factor are definitely less than unity (which is the value to be expected of atoms and ions having the inert gas structure) and they are ·85, ·85, ·87 and ·84 for KCl, KBr, KI, LiF respectively. In MgO, the value of the anomaly factor for λ 1300 Å is found to be ·96, while that for the other wavelength λ 400 Å is zero.

INTRODUCTION

Although liquids and gases have been the subject of numerous mangeto-optic investigations very little experimental work has been done on the dispersion of magnetic gyration in crystals. Such data are of considerable importance for the understanding of the spectroscopic behaviour of solids. Extensive and accurate measurements of the dispersion of magneto-optic rotation have been made only in CaF_2, NaCl, KCl and some minerals (Meyer, 1909; Landau, 1908; Voigt, 1908). Recently Ramaseshan (1947, 1948) has measured the Faraday rotation for a few wavelengths in the visible region in many cubic crystals but many of the crystals used by him exhibited residual birefringence and no corrections were made to eliminate its effect on the magnitude of Faraday rotations. The present writer was fortunate in getting some optically good quality specimens of alkali halide crystals. In the case of crystals having residual birefringence, the effect of birefringence on the magnetic rotation has been eliminated here by adopting the method developed recently (Ramachandran and Ramaseshan, 1952; Sivaramakrishnan and Ramaseshan, 1956).

Darwin and Watson (1927) have shown that the magnetic gyration in most substances satisfies the modified Becquerel formula $V = \gamma \cdot e/2\, mc^2 \cdot \lambda\, dn/d\lambda$, where γ is the magneto-optic anomaly factor. They found the value of the anomaly factor to lie between ·60 and ·90 in the crystals NaCl, KCl, CaF_2, etc. From the theory on Faraday rotation based on quantum mechanical ideas (Rosenfeld, 1929; Van Vleck, 1932), it is known that for atoms and ions in which the outer electrons are in the S state (*i.e.*, inert gas structure), the value of the anomaly factor should be unity. In the studies of the author (1954) on electrolytic solutions, it is found that the value of the anomaly factor for free ions of halogen and alkali metals are very nearly unity. The crystals of alkali halides are considered to be typically ionic, the ions having an inert gas structure and hence one could expect a value of unity for γ in these crystals also. But earlier studies have revealed that in these crystals the value of the anomaly factor deviates from the theoretical value of unity. The present investigation was undertaken with a view to get more accurate data on the dispersion of Faraday rotation and to see how far the value of anomaly factor deviates from the theoretical value. For this the crystals that have been chosen for study are KCl, KBr, KI, LiF and MgO. The study of these crystals is of interest because of another reason also. From the recent studies on calcite, sodium chlorate and the nitrates of lead, barium and strontium it has been possible to establish definitely that the γ factors for the different absorption frequencies are different (Ramaseshan and Sivaramakrishnan, 1956; Sivaramakrishnan, 1956). It would be of some interest to see whether the values of anomaly factors for the different characteristic absorption frequencies of these crystals are identical or not. The results obtained are presented below.

MATERIALS AND METHODS

The specimens of KCl, KBr, and KI used here were grown from melt in this laboratory by Dr. K. Vedam and Mr. C. P. Gopalakrishnan. The crystals were practically free from any impurity and were respectively of size 3 × 3 × 3 cm., 1 × 1 × 0·5 cm., and 3 × 1 × 1 cm. As the crystals had been annealed for a considerable period, they showed practically no restoration between crossed polaroids. However, the rotations were measured with the incident light polarised at various azimuths and the values were found to be practically identical thereby confirming that the crystals were sensibly free from any birefringence (Ramachandran and Ramaseshan, 1952). The lithium fluoride crystals used here was of size 2 × 2 × 0·5 cm. and was free from any birefringence, and was supplied by the

Harshaw Chemical & Co. The magnesium oxide crystal was grown from melt by National Carbide and Company, and was slighly birefringent. This crystal exhibited a preferred axis of strain. Therefore this crystal was set in the magnetic field such that the incident light vibration was parallel to the principal axis of strain. The apparent magnetic rotation ψ_0 was first determined and then the polariser was rotated through 45° and ψ_{45} was determined. From these the true rotation ρ was evaluated from the formula $3\rho = 2\psi_0 + \psi_{45}$ (Sivaramakrishnan and Ramaseshan, 1956). The magnetic rotations have been measured in all these crystals for a number of wavelengths from λ 5780 Å to λ 2848 Å by employing the photoelectric polarimetry technique described in detail by the author in an earlier publication (Sivaramakrishnan, 1956). The Verdet constants in minutes/cm./oersted are given in Table I. The absolute values of Verdet constant of the author and Ramaseshan (1947) differ by about 3 to 5% in these crystals. This may be due to the birefringence in the specimens studied by Ramaseshan.

DISPERSION FORMULÆ FOR REFRACTION AND MAGNETIC GYRATION

As pointed out in the earlier publications of the author (1956), if the following type of dispersion formula for optical refraction

$$n^2 - 1 = A + \Sigma \frac{A_i\lambda^2}{(\lambda^2 - \lambda_i^2)} \qquad (1)$$

is used, then the magneto-optic rotation can be expressed by a formula

$$Vn = \frac{e}{2mc^2} \sum_i \frac{A_i\gamma_i\lambda_i^2\lambda^2}{(\lambda^2 - \lambda_i^2)^2} \qquad (12),$$

where A_is are constants, λ_is the absorption wavelengths, γ_is the values of magneto-optic anomaly factors for different absorption wavelengths, *e* and *m* the elctronic charge and mass and V the Verdet constant in radians. Therefore for a complete study of the dispersion of magnetic gyration and hence the magneto-optic anomaly factor it is necessary to analyse the data on refractive indices into dispersion formulæ using experimentally known absorption frequencies. It is also necessary to use identical absorption frequencies in both the dispersion formulæ since they are governed by the same absorption frequencies. In the case of KCl and KI (Radhakrishnan, 1948; Ramachandran, 1947) satisfactory dispersion formulæ for refraction of the Drude type, using experimentally known absorption wavelengths, are in existence. However, in KBr, the very recent data on refractive indices (Rodney *et el.*, 1952, 1953) accurate to one unit in the fifth place of decimals, has been made use of by the present writer for constructing a proper dispersion formula. Three experimentally observed absorption wavelengths λ 1800 Å, λ 1460 Å and λ 1100 Å (Hilsch and Pohl, 1930; Schneider and O'Bryan, 1937) have been used in this dispersion formula along with an infrared dispersion frequency at λ 88 μ corresponding to the peak in the infrared absorption band reported by Barnes (1932). This formula fits the experimental data on

TABLE I

Verdet Constant in min./cm./oersted of the crystals

Wavelength	KCl		KBr		KI		LiF		MgO	
	$V_{exp.}$	$V_{cal.}$	$V_{exp.}$	$V_{cal.}$	$V_{exp.}$	$V_{cal.}$	$V_{exp.}$	$V_{cal.}$	$V_{exp.}$	$V_{cal.}$
5780	0·0294	0·0294	0·0442	0·0443	0·0753	0·0751	0·00932	0·00935	0·0377	0·0377
5461	0·0333	0·0334	0·0503	0·0503	0·0864	0·0863	0·01055	0·01055	0·0427	0·0427
4916	0·0424	0·0423	0·0648	0·0645	0·1124	0·1128	0·01313	0·01313	0·0542	0·0541
4358	0·0564	0·0562	0·0869	0·0868	0·1558	0·1554	0·01702	0·01698	0·0712	0·0714
4047	0·0670	0·0674	0·1053	0·1053	0·1926	0·1940	0·01992	0·01993	0·0848	0·0851
3650	0·0872	0·0878	0·1390	0·1392	0·2670	0·2693	0·02485	0·02499	0·1089	0·1096
3342	0·1099	0·1108	0·1803	0·1795	..	..	..	..	..	..
3132	0·1338	0·1334	0·2232	0·2211	..	..	0·0353	0·0353	0·1644	0·1638
3022	0·1490	0·1490	0·2520	0·2496	..	..	0·0384	0·0383	0·1808	0·1808
2970	..	..	..	..	..	..	0·0401	0·0400	..	..
2848	..	..	..	..	..	..	0·0439	0·0440	..	..

refractive indices from λ ·4047 μ to 25·14 μ to one unit in the fifth place of decimals. In the case of LiF a new dispersion formula has been constructed using a constant term, a reasonable hypothetical ultraviolet absorption wavelength λ 865 Å and an infrared wavelength at λ 32 μ corresponding to the peak in the experimentally observed absorption band (Barnes, 1932). This formula is found to fit the experimental data on refractive indices from λ ·1935 μ to 10·82 μ (Gyulai, 1927; Hohls, 1937), better than the one proposed by Radhakrishnan (1948). In the case of MgO, two ultraviolet absorption wavelengths λ 1300 Å and λ 400 Å are used in the dispersion formula, along with an infrared absorption frequency at 18 μ; Here also the calculated values of refractive indices are found to agree with the experimental ones of Strong and Price (1935) very well. Table II gives the values of the constants in the dispersion formulæ (1) and (2) for all the five crystals. By using the same absorption wavelengths the experimental data on Verdet constant has been fitted into dispersion formulæ of the type (2). The calculated values of Verdet constant from these formulæ are given in Table I along with the experimental ones. It can be seen from this table that the calculated and the experimental values agree well within the limits of experimental error of ½%. It may be remarked here that by using the ultraviolet absorption wavelengths λ 902 Å for LiF and λ 1180 Å for MgO suggested by Radhakrishnan in his dispersion formulæ

TABLE II

The values of the constants in the dispersion formulæ

$$n^2 - 1 = A + \Sigma \frac{A_i\lambda^2}{(\lambda^2 - \lambda_i^2)}; \quad Vn = \frac{e}{2mc^2}\,\Sigma\,\frac{A_i\gamma_i\lambda_i^2\lambda^2}{(\lambda^2 - \lambda_i^2)^2}$$

Constants	KCl	KBr	KI	LiF	MgO
A	·24341	·24236	·4532	·2650	..
A_1	·35736	·41169	·2150	·6596	·7537
A_2	·37616	·42657	·8027	..	1·2034
A_3	·19808	·2808	·1780	..	..
A_4	2·5143	2·502	..	6·778	2·32
λ_1	1000* Å	1100* Å	1290* Å	865 Å	400 Å
λ_2	1310* Å	1460* Å	1805* Å	..	1300 Å
λ_3	1620* Å	1800* Å	2190* Å	..	..
λ_4	70·7* μ	88* μ	..	32* μ	18 μ
γ_1	·854	·850	·871	·836	0
γ_2	·854	·850	·871	..	·963
γ_3	·854	·850	·871	..	..

* Experimentally observed absorption wavelengths.

N.B.—The infrared absorption wavelengths are considered to be ineffective towards the dispersion of magnetic gyration.

for refraction (1948, 1950), the experimental data on magnetic gyration could not be fitted into dispersion formulæ and hence new formulæ have been constructed here for both optical refraction and magnetic gyration using same absorption wavelengths in both.

MAGNETO-OPTIC ANOMALY FACTOR

The mean magneto-optic anomaly factor $\bar{\gamma}$ was determined in all these crystals from the experimental data on Verdet constant and the $(dn/d\lambda)$ values obtained from the optical refraction formulæ. Excepting MgO, in all the other crystals the value of $\bar{\gamma}$ was practically constant at all wavelengths, within the limits of experimental error, thereby revealing that all the absorption frequencies are effective towards the magnetic gyration in the same proportion as in refraction. Generally in the optical refraction formulæ the constant term A represents the contribution to refraction by the very far ultraviolet absorption wavelengths. For magnetic gyration their contribution is assumed to be negligible in these crystals. Even in the case of MgO, the value of magneto-optic anomaly factor is constant if it is assumed that the very far ultraviolet absorption wavelength λ 400 Å is inactive, *i.e.*, has its γ value as zero. If it is assumed that λ 400 Å also contributes to magnetic gyration along with λ 1300 Å, the value of mean anomaly factor is found to increase slightly but gradually with the decrease in wavelength from ·91 for λ 5780 to ·93 for λ 3032 Å.

The magnitude of the anomaly factor in these crystals reveal some interesting features. In the alkali halides, the values of γ are in the order $\gamma(\text{KI}) > \gamma(\text{KBr}) \approx \gamma(\text{KCl}) > \gamma(\text{LiF})$ and are ·87, ·85, ·85 and ·84 respectively. Also the values of γ do not vary with wavelength in these crystals contrary to the finding of Darwin and Watson (1927) who have reported that the values increased to some extent with the decrease in wavelength in KCl, NaCl, CaF_2, etc. This may be due to the fact that these authors have not used accurate dispersion formulæ for these substances. It can be easily noticed in all these crystals that the value of the magneto-optic anomaly factor deviates considerably from the theoretical value of unity. According to the theory of Rosenfeld (1929), these crystals should have their anomaly factor value as unity since the ions in them possess the inert gas structure. Therefore this significant deviation in γ may indicate a slight distortion in the electron atmosphere due to the crystalline field. This distortion seems to be greater in LiF than in KI. It can be generally concluded that the larger and heavier the ion the lesser is its electron atmosphere distorted. This is supported from studies on other physical properties like melting point, Debye temperature, thermal expansion, strain polarisability constant, etc., where the values indicate lesser attracting forces between the ions in KI than in KBr and KCl (Burstein and Smith, 1948). The value of the anomaly factor for MgO is found to be ·96. Magnesium oxide is generally known to be less polar than the alkali halides like NaCl. It is definitely known from X-ray scattering (Wollen, 1930) that there is considerable overlapping of neighbouring atoms in the crystal and the valence electrons are shared by both magnesium and oxygen atoms thereby introducing some homopolar binding. But the anomaly factor value of nearly unity in this crystal is rather disturbing.

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