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## Electrogyration Effect in Alums

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The electrogyration effect in 31 alums has been measured within the range 350 to 700 nm. The coefficients of electrogyration show an unexpectedly wide variation in alums of different composition and structural type. The effect is obviously related to the symmetry of the constituents and to their bonding interaction with water molecules. The dispersion of the electrogyration can be described by a formula which is also valid for natural optical activity. In contrast to other electro-optical effects Miller's rule does not apply for the electrogyration of the alums.

### Introduction

In an earlier paper we reported on electric field induced optical activity (electrogyration) and circular dichroism in chromium-doped  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  crystals (Weber & Haussühl, 1974). In continuation of that investigation we now have studied the electrogyration in 30 other pure alums in order to obtain an insight into the general behaviour of the effect within a large number of chemically and structurally related crystals. It should be mentioned that the effect of electrogyration only occurs in crystals of symmetry  $m3$ , without the disturbing influence of birefringence and linear electro-optical effects.

In this point symmetry group the alums crystallize in three different types, called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -alums. Structurally they all are closely related (Lipson, 1935). The three modifications possess surprisingly large differences in certain properties, such as morphology, elasticity, thermoelasticity, and thermal expansion

(Haussühl, 1961). We expected different behaviour of these three types with respect to the electrogyration effect too.

### Measurements

The electrogyration in the crystals under investigation consists of a rotation  $\Delta\varrho$  of the plane of polarization of the incident, linearly polarized light. It is optimally observable in the directions of electric field  $\mathbf{E}$  and wave vector  $\mathbf{k}$  as noted in Table 1. The corresponding  $\Delta\varrho$  is connected with the only independently existing component, named  $s_{123}$ , of the axial third rank tensor of the electrogyration, by

$$\Delta\varrho = (\pi l / \lambda n) \Delta g \quad (1)$$

In this formula  $\lambda$  is the wavelength,  $l$  the length of the specimen parallel to the light path,  $n$  the index of refraction and  $\Delta g$  the change of the scalar product  $g = \mathbf{G} \cdot \mathbf{s} = g_{ij} s_i s_j$ .  $\mathbf{G}$  is the gyration vector with compo-

nents  $G_i = g_{ij}s_j$ ;  $s_i$  are the components of the unit wave vector. The relation between  $\Delta g_{ij}$  and electric field is

$$\Delta g_{ij} = s_{ijk}E_k.$$

The measurements were carried out within the range 350 to 750 nm by employing the dynamic method earlier described (Weber & Haussühl, 1974).

Table 1. *Optimal directions for measuring electrogyration effects in crystals of point symmetry group m3*

*E* direction of electric field, *k* direction of wave vector, *s* effective tensor constant measured.

| <i>E</i>        | <i>k</i>        | <i>s</i>       |
|-----------------|-----------------|----------------|
| [001]           | [110]           | $s_{123}$      |
| [111]           | [1 $\bar{1}$ 0] | $-s_{123}/3/3$ |
| [111]           | [111]           | $2s_{123}/3/3$ |
| [11 $\bar{2}$ ] | [1 $\bar{1}$ 0] | $s_{123}/6/3$  |

The specimens were cut in the form of rectangular prisms of dimensions *ca* 1 cm. All crystals were investigated in at least two of the different directions quoted in Table 1. The values for  $s_{123}$  obtained in different orientations agreed in all cases to within 10%. In several crystals other directions of electric field and wave vector, in which no effect should occur, were also tried. All results confirmed the tensor character of the electrogyration in these crystals.

The setting of the crystallographic axes has been chosen in such a way that the only pentagonal dodecahedron which is observable is labelled {201}. This works with the  $\beta$ -alums where the form {210} occurs during natural growth, but not with the  $\alpha$ -alums. In the case of  $\alpha$ -alums the {210} faces can be developed during a slow growth process on spheres which are cut and ground from large crystals.

Another control of the setting is possible by means of Laue patterns, in which the reflexions ( $h_1h_20$ ) with  $h_1$  being odd are forbidden, provided the correct setting corresponding to space group *Pa3* is used. If the voltage applied to the X-ray generator is small enough, no disturbing higher-order reflexions occur amongst the low-indexed ones. The X-ray setting and the morphological setting coincided in all  $\beta$ -alums, and in the case of  $\alpha$ -alums where sphere growth experiments were carried out.

The meaning of a positive tensor component  $s_{123}$  is that an electric field *E* applied in positive [001] direction induces an anticlockwise rotation of a linearly polarized wave travelling in direction [110], when looking towards the light source.

## Results

Table 2 presents the measured values  $\Delta\varrho$  and  $s_{123}$  for 31 different alums. They are valid for 20°C and a wavelength of 550 nm. In some cases the measure-

ments have been performed at lower temperature in order to avoid dehydration. In the table the composition of an alum  $AB(CO_4)_2 \cdot 12H_2O$  is expressed as ABC. In most cases the relative probable errors are estimated to be smaller than 10%.

Table 2. *Electrogyration of alums*

Units used are  $\Delta\varrho$   $10^{-7}$  deg  $V^{-1}$ ,  $s_{123}$   $10^{-14}$  cm  $V^{-1}$ ,  $\Delta\varrho_{123}^g$   $10^{-12}$  cm  $V^{-1}$ .  $\lambda = 550$  nm, temperature 20°C, or 10°C when marked by an asterisk. Values of  $\Delta\varrho$  refer to  $l = 1$  cm,  $E = 1$  V  $cm^{-1}$ ,  $E \parallel [001]$ ,  $k \parallel [110]$ .

| Alum, modification                             | $\Delta\varrho$ | $s_{123}$ | $\Delta\varrho_{123}^g$ |
|--|-----------------|-----------|-------------------------|
| KAlS, $\alpha$                                 | 1.84            | 8.20      | 1.8                     |
| KAlS, deut., $\alpha$                          | 2.04            | 9.09      |                         |
| RbAlS, $\alpha$                                | 0.71            | 3.16      | 0.8                     |
| NH <sub>4</sub> AlS, $\alpha$                  | 0.03            | 0.14      | 0.03                    |
| TlAlS, $\alpha$                                | 3.60            | 16.5      | 2.5                     |
| CsAlS, $\beta$                                 | 2.95            | 13.2      | 3.6                     |
| CsAlS, deut., $\beta$                          | 2.70            | 12.0      |                         |
| NH <sub>3</sub> CH <sub>3</sub> AlS, $\beta$   | -15.2           | -67.4     | -11.1                   |
| KAlSe, $\alpha$                                | 2.56            | 11.6      | 2.2                     |
| RbAlSe, $\alpha$                               | 1.13            | 5.12      | 1.1                     |
| NH <sub>4</sub> AlSe, $\alpha$                 | 0.45            | 2.03      | 0.4                     |
| CsAlSe, $\alpha$                               | -0.12           | -0.54     | -0.1                    |
| TlAlSe, $\alpha$                               | 1.35            | 6.29      |                         |
| NH <sub>3</sub> CH <sub>3</sub> AlSe, $\beta$  | -33.2           | -150.0    | -17.0                   |
| KGaS, $\alpha$                                 | -0.06           | -0.25     | -0.05                   |
| RbGaS, $\alpha$                                | -0.96           | -4.30     | -0.09                   |
| NH <sub>4</sub> GaS, $\alpha$                  | -1.14           | -5.12     | -1.0                    |
| TlGaS, $\alpha$                                | 1.60            | 7.36      |                         |
| CsGaS, $\beta$                                 | 3.24            | 14.5      | 3.6                     |
| NH <sub>3</sub> CH <sub>3</sub> GaS, $\beta$   | -13.4           | -59.9     | -9.5                    |
| RbGaSe, $\alpha$                               | -0.60           | -2.74     | -0.5                    |
| CsGaSe, $\alpha$                               | -1.87           | -8.54     | -1.8                    |
| RbFeS, $\alpha^*$                              | 11.1            | 50.4      |                         |
| NH <sub>4</sub> FeS, $\alpha^*$                | 10.7            | 48.6      |                         |
| CsFeS, $\beta$                                 | 11.8            | 53.6      | 11.5                    |
| NH <sub>3</sub> CH <sub>3</sub> FeS, $\beta^*$ | -6.95           | -31.4     |                         |
| RbInS, $\alpha^*$                              | -1.82           | -8.17     |                         |
| CsInS, $\beta^*$                               | 3.01            | 13.6      | 3.0                     |
| NH <sub>3</sub> OHAlS, $\alpha^*$              | -2.70           | -12.1     | -1.3                    |
| NH <sub>3</sub> NH <sub>2</sub> AlS, $\beta$   | 3.61            | 16.2      | 1.5                     |
| NaAlS, $\gamma$                                | -0.83           | -3.65     | -1.0                    |

Highly surprising is the wide variation of the electrogyration effect within this group of crystals which are so strongly related in chemical and structural respects. In particular, the methylammonium alums, all of which possess a transition to a ferroelectric phase at lower temperature, show strong negative effects. Comparatively large effects, but with opposite sign, can be observed in all iron alums, too. In NH<sub>3</sub>CH<sub>3</sub>FeS both effects seem to be superimposed yielding a value between those of the methylammonium and iron groups. This is also confirmed by the dispersion behaviour shown in Fig. 1. Iron alums and methylammonium alums show different slopes, whereas the slope of NH<sub>3</sub>CH<sub>3</sub>FeS lies between these two. These high effects of both groups of alums are apparently due to the deviation from spherical symmetry of the electron distribution in the NH<sub>3</sub>CH<sub>3</sub><sup>+</sup> ion as well as in the Fe<sup>3+</sup> ion.

In order to elucidate the relation between the groups with fixed A, B, or C constituents, the differences as shown in Table 3 may be considered. We find nearly constant increments for all types of substitutions within the group of  $\alpha$ -alums with the exception of thallium alums. Therefore we must postulate the existence of a quasi-additivity of the contributions arising from the single constituents. The increments are negative if substitution takes place by cations of higher polarizability. Only in iron, thallium, and selenate alums is the behaviour contrary, and in the case of  $\text{NH}_4^+$  and  $\text{NH}_3\text{OH}^+$  the electrogyration effect is significantly shifted towards negative values compared with alums possessing symmetric monovalent ions. From this behaviour we conclude that ions with low symmetry give an intrinsic contribution to the whole effect, whereas the highly symmetric ions mainly indirectly affect the electrogyration effect by their effect on the water molecules.

Another important result is the monotony of the  $\beta$ -alums  $\text{CsAlS}$ ,  $\text{CsGaS}$ ,  $\text{CsInS}$  all of which possess nearly the same  $s_{123}$  values. This is in strong contrast to the behaviour of  $s_{123}$  in the corresponding series of Rb alums. We suggest that this effect results from the higher stability of the hydration frame in the  $\beta$ -alums compared with that of  $\alpha$ -alums. Similar phenomena are observed in many other properties, such as elasticity, thermoelasticity, thermal expansion (Haussühl, 1961), and thermal stability (Spangenberg, 1949).

The dispersion of the electrogyration is similar in most alums. The dependence on wavelength is approximately described by

$$\Delta\varrho = K\lambda^2\lambda_0^2/(\lambda^2 - \lambda_0^2)^2 \quad (2)$$

with  $\lambda_0 = 88$  nm and  $K = 37.1\Delta\varrho^{\text{ref}}$ .  $\Delta\varrho^{\text{ref}}$  is the induced rotation at 550 nm, reduced to unity of electric field and 1 cm beam length with  $\mathbf{E}$  parallel to [001], and  $\mathbf{k}$  parallel to [110]. Equation (2) is of a form developed by Chandrasekhar (1960) on the basis of a compound oscillator model for natural optical activity. Examples of  $\alpha$ -aluminium and  $\alpha$ -gallium sulphates are presented in Fig. 2. The values of  $\text{NH}_3\text{NH}_2\text{AlS}$  are added. They show a small deviation from the above formula.

A significantly stronger influence on  $\Delta\varrho$  with decreasing wavelength than is indicated by (2) was found in the iron alums, as already shown in Fig. 1. Their behaviour should be seen in connexion with the strong optical absorption of the  $\text{Fe}^{3+}$  ion below a wavelength of ca 400 nm.

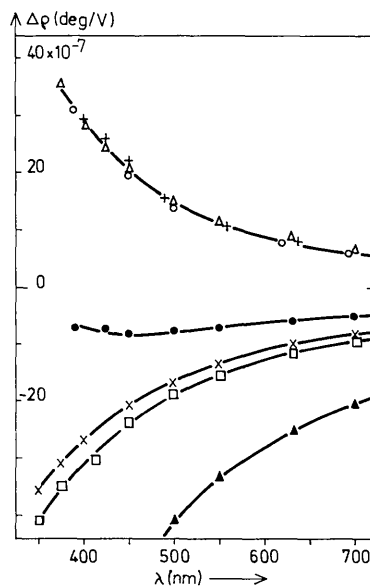


Fig. 1. Electrogyration  $\Delta\varrho$  of methylammonium and iron alums versus wavelength, for  $\mathbf{E} \parallel [001]$ ,  $\mathbf{k} \parallel [110]$ ,  $l = 1$  cm,  $|\mathbf{E}| = 1$  V  $\text{cm}^{-1}$ . + RbFeS, o  $\text{NH}_4\text{FeS}$ ,  $\Delta$  CsFeS, ●  $\text{NH}_3\text{CH}_3\text{FeS}$ , x  $\text{NH}_3\text{CH}_3\text{GaS}$ , □  $\text{NH}_3\text{CH}_3\text{AlS}$ , ▲  $\text{NH}_3\text{CH}_3\text{AlSe}$ .

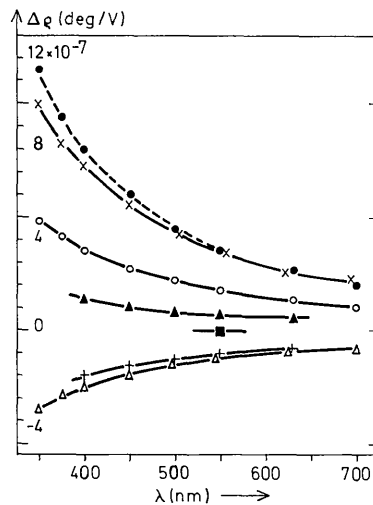


Fig. 2. Electrogyration  $\Delta\varrho$  of Al and Ga sulphates versus wavelength, for  $\mathbf{E} \parallel [001]$ ,  $\mathbf{k} \parallel [110]$ ,  $l = 1$  cm,  $|\mathbf{E}| = 1$  V  $\text{cm}^{-1}$ . ●  $\text{NH}_3\text{NH}_2\text{AlS}$ , x TlAlS, o KAlS, ▲ RbAlS, ■  $\text{NH}_4\text{AlS}$  and KGaS, + RbGaS,  $\Delta$   $\text{NH}_4\text{GaS}$ .

Table 3. Increments of  $s_{123}$  in  $\alpha$ -alums ( $10^{-14}$  cm  $\text{V}^{-1}$ )

|         | K, Rb | Rb, $\text{NH}_4$ | Rb, Cs | Rb, Tl | Al, Ga                | Al, Fe | KAl                    | S, Se |
|---------|-------|-------------------|--------|--------|-----------------------|--------|------------------------|-------|
| AlS     | 5.1   | 3.0               |        | -13.3  | KS                    | 8.5    | RbAl                   | -3.4  |
| AlSe    | 6.5   | 3.1               | 5.4    | -1.2   | RbS                   | 7.5    | $\text{NH}_4\text{Al}$ | -2.0  |
| GaS     | 4.1   | 0.8               |        | -11.7  | $\text{NH}_4\text{S}$ | 5.2    | RbGa                   | -1.9  |
| GaSe    |       |                   | 5.8    |        | TlS                   | 9.1    |                        | -1.6  |
| FeS     |       | 1.8               |        |        | RbSe                  | 7.8    |                        |       |
| Average | 5.2   | 2.2               | 5.7    |        | CsSe                  | 8.0    |                        |       |
|         |       |                   |        |        |                       | 7.7    | -47.7                  | -2.2  |

Finally we discuss the relation between the electrogyration and dielectric properties of the alums by considering the rule of Miller (1964), who defined a quantity  $\Delta$ , applicable to non-linear optical properties and valid for all materials. In the case of the electrogyration of alums this magnitude is defined by (Miller, 1973)

$$\Delta_{123}^q = s_{123} / [4\pi\chi^2(\omega)\chi(0)] .$$

The susceptibility  $\chi(\omega)$  at frequency  $\omega$  is related to the index of refraction  $n$  by the relation

$$\chi(\omega) = (n^2 - 1) / 4\pi ,$$

and the value of  $\chi(0)$  is equal to  $(\epsilon - 1) / 4\pi$ , where  $\epsilon$  is the dielectric constant. The reduced constants  $\Delta_{123}^q$  are listed in Table 2.

Contrary to the second-harmonic generation and the linear electro-optical effect of many materials, where  $\Delta$  is nearly a constant, Miller's rule does not explain the differences in the electrogyration properties of the alums.

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## Rigid-Body Constraints and the Least-Squares Refinement of Crystal Structures\*

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To refine the orientation and location of a rigid group of atoms in a crystal it is not necessary to store the atom coordinates relative to a localized axial system. All atoms in the asymmetric unit are defined relative to a single orthonormal axial system. A local axial system is created by taking an atom in the rigid group as origin and defining the local axes as parallel to these orthonormal axes. The evaluation of the required derivatives is then very easy. The replacement of approximate atom positions by idealized atom positions is described.

### Introduction

Rigid group refinement has previously been performed in a somewhat awkward manner (Scheringer, 1963; La Placa & Ibers, 1965; Doedens, 1970). The awkwardness occurs because the orientation of the rigid group of atoms is described by rotations about fixed axial directions whereas the atoms are described by fixed coordinates in a refineable local axial system.

There are two ways of simplifying the evaluation of an incremental change in orientation and location of a rigid group of atoms.

(i) If fixed local coordinates are used, rotate the rigid group about the initial directions of the refineable axial system.

(ii) If fixed rotation axial directions are used, redefine the local coordinates each cycle so that the initial axial directions of the local axial system are parallel to the rotation axes.

The first method requires the redefinition of the scattering vector relative to the local coordinate system for easy implementation (Rae, 1975). It has an advantage if the group is not truly rigid (symmetry constraints and equal object constraints). It also has an advantage for a linear rigid group in that rotation about the linear direction is easily omitted from the refinement. However, it does require the storage of both the local coordinates and the local axial system. For a strictly rigid, non-linear group the second method is more advantageous and is described in detail.

### Theory

We can describe the position vector of the  $n$ th atom in the rigid group relative to standard orthonormal reference axes  $\mathbf{A}_i$  as

$$\sum_i X_n^i \mathbf{A}_i = \sum_i X_o^i \mathbf{A}_i + \sum_{ij} V_{ij} (Y_n^j - Y_o^j) \mathbf{A}_j \quad (1)$$

where the  $X_n^i$  are orthonormal crystal coordinates of the  $n$ th atom in the group and the  $X_o^i$  are orthonormal crystal coordinates of the local origin after refinement. The  $Y_n^j$  and  $Y_o^j$  are the corresponding values of these

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