

derivation of the crystal orientation from the angles between the lines of spots in the spot groups may be arduous.

It may be noted that, if spot groups can be obtained for which the Bragg condition is exactly satisfied, the values of V_{hkl} , relative to V_0 , can be derived from equation (4) in the absence of any information as to the habit or orientation of the crystals concerned. In order to obtain the V_{hkl} values on an absolute basis, however, it is necessary to know the angles between the crystal faces and the orientation of the crystal for at least one reflexion. The potential distribution within the crystal lattice may then be determined on an absolute basis except that, until a satisfactory explanation for the discrepancy between the calculated and observed V_0 values and for the variations in the observed V_0 values is found, the potential must be considered uncertain to the extent of a small additive constant.

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Magnetic Anisotropy and Crystal Structure of Barium Chlorate Monohydrate, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

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The magnetic anisotropy of single crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ has been measured, and the result has been correlated with the fine-structure study of the crystal by X-ray methods.

Introduction

Raman & Krishnan (1927) have correlated magnetic birefringence, optical and magnetic properties of ions in crystals. Chinchalkar (1932) observed that the magnetic birefringence of the chlorate ion is negative. Representing the gram molecular diamagnetic susceptibility along the directions normal to the plane of the oxygen triangle of the ClO_3 ions by K_{\parallel} and that along directions in the plane of oxygens by K_{\perp} , one finds that K_{\perp} is greater than K_{\parallel} , since $R_c - R_o = -2.12$ for the ClO_3 ion in KClO_3 crystals (*International Critical Tables*, 1926). (R_c is the gram molecular refractivity for the direction normal to the plane of the oxygens, and R_o is that in the plane of the oxygens.)

In the following we correlate our magnetic anisotropy results with the fine-structure analysis of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ by X-ray methods (Karth, 1952).

Experimental and results

The magnetic anisotropy was measured by the method of Krishnan & Banerji (1935). The absolute susceptibility in a convenient direction was measured with a Dutta balance (1944). In order to get information

Table 1. *Measured susceptibilities*

χ_3 is the gram molecular susceptibility along the b crystallographic axis of the monoclinic crystals; the algebraically greater of the two values in the symmetry plane (010) is denoted by χ_1 and the smaller by χ_2 ; φ is the angle which the χ_1 direction makes with the c crystallographic axis, taken positive from c towards a through the obtuse β .

Crystal	$\chi_1 - \chi_2$	$\chi_1 - \chi_3$	φ (°)	$\bar{\chi} =$
	(c.g.s.e.m.u.)	(c.g.s.e.m.u.)		$\frac{1}{3}(\chi_1 + \chi_2 + \chi_3)$ (c.g.s.e.m.u.)
KClO_3	5.41×10^{-6}	5.66×10^{-6}	59.2	-48.7×10^{-6}
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	5.54	0.57	60.9	-104.3

which would be helpful in our analysis we have also included a KClO_3 single crystal in our measurements. The results are shown in Table 1.

Discussion

KClO_3 crystallizes in the monoclinic system with two molecules in the unit cell (Zachariasen, 1929). The chlorate groups have the usual pyramidal structure, the three oxygens forming approximately an equilateral triangle; these oxygen triangles are parallel to one another and to the b axis. So $K_{\perp} = \chi_3$. From the table we have $\chi_2 - \chi_3 = 0.25$, hence the plane containing χ_2 and the b axis is a plane of approximate magnetic symmetry.

Krishnan, Guha & Banerji (1932), as a result of measurements on a number of single crystals of nitrates and carbonates, found that the planes of CO_3 and NO_3 ions, i.e. the planes containing the oxygen triangles, are planes of approximate magnetic symmetry. Mookherji (1934) also found the same result with bicarbonate crystals. Hence one may infer, in view of magnetic symmetry in the plane containing the χ_2 and χ_3 direction in KClO_3 crystals, that the oxygen triangles must be lying very close to the plane containing the χ_2 and χ_3 directions. Actually χ_3 lies in the plane of the oxygen triangle while the χ_2 axis makes an angle of about 5.3° with it.

Evidently

$$\begin{aligned}\chi_1 &= K_{\parallel} \cos^2 5.3^\circ + K_{\perp} \sin^2 5.3^\circ, \\ \chi_2 &= K_{\parallel} \sin^2 5.3^\circ + K_{\perp} \cos^2 5.3^\circ, \\ \chi_3 &= K_{\perp}.\end{aligned}$$

Hence the value $K_{\parallel} - K_{\perp} = (\chi_1 - \chi_3) + (\chi_2 - \chi_3) = 5.9$, for each ClO_3 group may be adopted.

$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic system, space group $C_{2h}^6 - C2/c$ (Kartha, 1952), with four molecules per unit cell. Let the plane containing the oxygen triangle make angles $+\psi$ and $-\psi$ with (010). Consequently

$$\begin{aligned}\chi_2 &= K_{\perp}, \\ \chi_3 &= K_{\parallel} \cos^2 \psi + K_{\perp} \sin^2 \psi, \\ \chi_1 &= K_{\parallel} \sin^2 \psi + K_{\perp} \cos^2 \psi,\end{aligned}$$

i.e.

$$K_{\parallel} - K_{\perp} = (\chi_1 - \chi_2) + (\chi_3 - \chi_2).$$

Using the values of $(\chi_1 - \chi_2)$ and $(\chi_3 - \chi_2)$ for a single ClO_3 group in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, as given in Table 1, we have

$$K_{\parallel} - K_{\perp} = 5.3.$$

This may be compared with the value $K_{\parallel} - K_{\perp} = 5.9$ obtained in KClO_3 crystals. In view of the close agreement between the two, it may be concluded that the plane of all the molecules in the unit cell should intersect (010) along the same direction, namely the magnetic axis, in agreement with Kartha's findings.

The inclination of the normal to the molecular planes is given by

$$\cos 2\psi = \frac{\chi_3 - \chi_1}{K_{\parallel} - K_{\perp}} = \frac{-0.29}{5.9},$$

i.e.

$$2\psi = 93^\circ.$$

Thus the angle which the molecular planes make with (010) is $\pm 43.5^\circ$ and the inclination between the two sets of ions is 87° , which compares favourably with 81.3° , the value calculated from the direction cosines given by Kartha. Further, the normal to the oxygen triangle makes an angle of 46.5° with the b axis whereas Kartha's value for this angle is 49.3° .

The magnetic birefringence is negative, hence, according to Bhagavantam (1929), the direction of numerically maximum susceptibility should correspond to that of maximum optical polarizability. Our measurements show that the χ_2 axis, the direction of numerically maximum susceptibility, makes an angle 57.5° with the a crystallographic axis. According to Groth (1908), the largest refractive index is found in a direction making an angle 61.7° with the a axis.

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