THE MAGNETIC ANISOTROPY OF RHOMBIC SULPHUR.

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1. Introduction.

THE structure of rhombic sulphur has been recently investigated by B. E. Warren and J. T. Burwell[1] by the method of X-Ray analysis. They found that their results could be satisfactorily interpreted by assuming a symmetrical puckered ring-shaped molecule, consisting of 8 atoms, with a bond angle of 105° and an S–S distance of 2·12 Å. From intensity considerations they deduced the orientation of the molecule in the crystal, and found that the plane of the ring is parallel to the *c* crystallographic axis and makes an angle of about 50° with the *a*-axis.

The magnetic anisotropy of rhombic sulphur has been studied by K. S. Krishnan and his collaborators.[2] At the time of their investigation, however, the necessary data concerning the molecular structure and arrangement were not available for any interpretation of the results to be possible.[3] But in the light of the recently proposed model, the magne-crystallic data assume considerable importance. We can test the general validity of the X-ray analysis by examining whether the results obtained from the magnetic experiments fit in with the suggested scheme of molecular arrangement and structure. And if so, we should also be in a position to get valuable information regarding the magnetic properties of the S_8 molecule.

A careful determination of the magnetic anisotropy of rhombic sulphur has been made with the above object in view, and the results are presented in this paper.

2. Experimental.

The magnetic anisotropy of the crystal was determined by the torsional method developed by Krishnan.[4] The details of experimental arrangement and procedure have been given in an earlier paper by the author.[5] Since the crystal system is orthorhombic, the orientation in the field could be conveniently observed by noting the setting of the crystal edges.

1 B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, 1935, **8**, 6.

2 K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans.*, 1933, **231**, 235.

3 For chemical evidence, see Ephraim, *Anorganische Chemie*, Dresden and Leipzig, 1934.

4 K. S. Krishnan and S. Banerjee, *Phil. Trans.*, 1935, **234**, 267.

5 P. Nilakantan, *Proc. Ind. Acad. Sci.*, 1935, **2A**, 622.

The direct determination of the torsional constant of the fibre by the oscillating disc method was found to be unsatisfactory in the case of the fine fibres that were used. The modulus of torsion was therefore indirectly evaluated from experiments on a single crystal of calcite suspended with the trigonal axis horizontal, the anisotropy of which in the plane concerned being known with some accuracy.

Special care was taken to prepare sulphur crystals free from impurities. A saturated solution of recrystallised sulphur in Kahlbaum's pure carbon disulphide was allowed to evaporate slowly inside a large bell-jar. Beautiful crystals with well-developed (111) faces were obtained. Experiments were performed on six different crystals.

3. Results.

The results are shown in Table I below. The mean values of the specific anisotropy, as well as the gram molecular anisotropy for the S_8 molecule

TABLE I.

Mode of suspension	Orientation	Specific Anisotropy $\times 10^8$	Gram molecular Anisotropy (S_8) $\times 10^6$
a–axis vertical	c–axis along the field	$\chi_c - \chi_b = 0.31$	$\chi_{c_M} - \chi_{b_M} = 0.79$
b ,, ,,	c ,, ,,	$\chi_c - \chi_a = 2.56$	$\chi_{c_M} - \chi_{a_M} = 6.57$
c ,, ,,	b ,, ,,	$\chi_b - \chi_a = 2.27$	$\chi_{b_M} - \chi_{a_M} = 5.82$

are given. The usual notation has been adopted χ_a, χ_b, χ_c standing for the specific susceptibilities along the respective axes. The susceptibilities along the different axes have been computed from a knowledge of the mean susceptibility of rhombic sulphur with the help of the anisotropy data. The calculated values are presented in Table II.

TABLE II.

Specific susceptibility $-\chi \times 10^8$	Gram molecular susceptibility (S_8) $-\chi_M \times 10^6$
$\chi_a = 0.500$	$\chi_{a_M} = 128.2$
$\chi_b = 0.478$	$\chi_{b_M} = 122.4$
$\chi_c = 0.474$	$\chi_{c_M} = 121.6$

Mean susceptibility of rhombic sulphur $\chi = -0.484 \times 10^{-6}$.[6]

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[6] R. N. Mathur and M. B. Nevgi, *Zeit. Phys.*, 1936, 9–10, 617.

4. Discussion.

The results obtained are found to disagree with those of Krishnan. According to him, $\chi_b - \chi_c = 0 \cdot 22$, $\chi_c - \chi_a = 0 \cdot 78$ and $\chi_b - \chi_a = 0 \cdot 94$ (unit 10^{-8}) which gives $\chi_a > \chi_c > \chi_b$ numerically.[7] But actually we find that $\chi_a > \chi_b > \chi_c$.

In view of the symmetry possessed by the molecule the molecular magnetic constants are evidently the susceptibility in the plane of the ring and that in a direction perpendicular to it. We can also reasonably presume that in such a ring-shaped molecule the diamagnetic susceptibility perpendicular to the plane, should be greater than that in the plane. Then the c-crystallographic axis will be the direction of least diamagnetic susceptibility, since, according to X-ray analysis the plane of the ring contains the c-axis. Besides, the normal to the plane is given to be nearer to the a-axis than the b-axis and, therefore, we should have the maximum diamagnetic susceptibility along the a-axis. These conclusions are all verified by experiment. Thus it is seen that the general scheme of molecular arrangement suggested by X-ray analysis finds support in the magne-crystallic data. The angle which the plane of the ring makes with the a-axis, however, can be independently evaluated from the following relations :

$$K_1 = \chi_{c\text{M}}$$
$$K_1 \cos^2\theta + K_2 \sin^2\theta = \chi_{b\text{M}}$$
$$K_1 \sin^2\theta + K_2 \cos^2\theta = \chi_{a\text{M}}$$

Where K_1 and K_2 are the magnetic moments induced in the molecule along and perpendicular to the plane, respectively, by unit field, referred to a gram-molecule (S_8).

θ = the angle which the normal to the plane makes with the a-axis. On calculation we find,

$$K_1 = -121 \cdot 6 \times 10^{-6},$$
$$K_2 = -129 \cdot 0 \times 10^{-6},$$
$$\theta = 19° \text{ nearly.}$$

It is seen that the plane of the ring makes an angle of 70° nearly with the a-axis instead of 50° as given by X-ray analysis.

The feeble anisotropy of the sulphur molecule as compared with that of say, graphite or naphthalene, is no doubt, partly, due to the puckered shape which gives the molecule considerable thickness ($1 \cdot 15$ Å). The effective projected mean square radius for the electron charge distribution is only

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[7] The actual values given in their paper are 0.07, 0.25 and 0.30 (unit 10^{-6}) referred to a gram atom (?). The specific anisotropy has been calculated therefrom.

slightly greater in the plane than at right angles to it.   In fact, the feebleness of the anisotropy lends support to the idea of a puckered ring.

In conclusion, I wish to express my thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his encouragement in the course of the work, and valuable criticism.

Summary.

The magnetic anisotropy of rhombic sulphur has been determined.   The magne-crystallic data are in general agreement with the results of X-ray analysis and support the idea of a puckered ring-shaped molecule consisting of 8 atoms, orientated with the plane parallel to the c-axis of the crystal. The magnetic data, however, give the inclination of the plane of the ring to the a-axis to be about 70° instead of 50° as suggested by X-ray analysis.