

The Magnetic Anisotropy of Crystalline Nitrates and Carbonates.

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1. *Introduction.*

Recent work in the field of magnetism emphasises the relation between the crystal structure and magnetic properties of solids. Such relations exist in all crystals whether ferromagnetic, paramagnetic or diamagnetic. We propose in this paper to discuss the explanation of the anisotropy of diamagnetic crystals, particularly some nitrates and carbonates with regard to which we have data from the measurements of Voigt and Kinoshita* and very recently of Rabi.† These substances are especially simple because, as is well-known from the work of Kossel, Bragg and others, they consist of charged ions held together by electrostatic forces, so that we can attribute the magnetic anisotropy of the crystal to that of the individual ions. Thus, for instance, in the case of sodium and potassium nitrates we may reasonably look for the explanation of observed magnetic anisotropy of the crystal in the structure of the nitrate ion, since presumably the metallic ions are more or less isotropic. It is significant in this connection that nitric acid solution has been found by Cotton and Mouton‡ to exhibit a measurable magnetic birefringence, thus indicating that the NO_3^- ion has a pronounced magnetic anisotropy even in the liquid state. It is possible to estimate this anisotropy in a purely optical way by combining the data for magnetic double-refraction with the measurements of the depolarisation of the light scattered in nitric acid. It is found that the magnetic anisotropy of the NO_3 group thus found, practically agrees with that necessary, as remarked above, to explain the magnetic properties of the crystalline nitrates.

2. *Relation between Structure and Magnetic Properties.*

The crystal structures of sodium nitrate and calcite have been investigated by X-ray methods and the two crystals are found to be homœomorphous. They have an axis of trigonal symmetry. The NO_3 or CO_3 groups are built up of three oxygen atoms at the corners of an equilateral triangle with the nitrogen or carbon atom at the centre, the plane of the triangle being perpendicular to

* 'Ann. d. Physik,' vol. 24, p. 492 (1907).

† 'Phys. Rev.,' vol. 29, p. 174 (Jan., 1927).

‡ 'Ann. Chim. et Phys.,' vol. 28, p. 209 (1913).

the trigonal axis. Potassium nitrate and aragonite, on the other hand, belong to the rhombic system; but here also the three oxygen atoms are arranged symmetrically round the nitrogen or carbon atoms in a plane perpendicular to the "c" axis.

In the following table are given the principal diamagnetic susceptibilities for these crystals:—

| Compound. | Crystal system. | Axis along which susceptibility is measured. | Susceptibility per gm. molec. $\times -10^6$. | Average susceptibility per gm. molec. $\times -10^6$. |
|----------------------------------|-----------------|--|--|--|
| NaNO ₃ | trigonal | \parallel trig. axis \perp trig. axis | 29.5 | } 25.9 |
| | | | 24.1 | |
| CaCO ₃ (calcite) | } trigonal | \parallel trig. axis \perp trig. axis | 40.6 | } 37.8 |
| | | | 36.4 | |
| KNO ₃ | } rhombic | \parallel "c" axis \parallel "b" axis \parallel "a" axis | 35.6 | } 31.7, |
| | | | 29.7 | |
| | | | 29.9 | |
| CaCO ₃ (aragonite) | } rhombic | \parallel "c" axis \parallel "b" axis \parallel "a" axis | 44.4 | } 40.8 |
| | | | 38.7 | |
| | | | 39.2 | |

Sodium nitrate and calcite are magnetically uniaxial owing to the possession of an axis of trigonal symmetry. For potassium nitrate and aragonite, however, the susceptibilities along the "b" and "a" axes are different. But the difference is very small, so that for all practical purposes we may treat them also as magnetically uniaxial crystals. In all the cases quoted in the table, the susceptibility along the axis, which we shall denote by χ_{\parallel} , is numerically greater than the susceptibility, χ_{\perp} , perpendicular to the axis. It is also significant that $\chi_{\parallel} - \chi_{\perp}$ is very nearly the same for the two nitrates, and not very different for the two forms of calcium carbonate. It suggests immediately that the nitrate and carbonate ions are, at least in a very large measure, responsible for the magnetic anisotropy of the respective crystals.

3. Relation to Magnetic Birefringence.

Before proceeding to connect the magnetic anisotropy of the NO₃⁻ ion in the crystals with its anisotropy as deduced from observations on magnetic double-refraction of nitric acid (liquid), we may point out that we would not be justified in assuming that the NO₃⁻ ion is necessarily identical in the two cases. For instance, it is well-known from the investigations of Oxley* that many dia-

* 'Phil. Trans.,' A, vol. 214, p. 109 (1914).

magnetic substances show an appreciable change of susceptibility on crystallisation, suggesting a re-adjustment of the electron-orbits as we pass from the liquid to the crystalline state. We cannot therefore expect any exact numerical agreement between the values of the anisotropy of the NO_3^- ion calculated from the two states.

The constant of magnetic birefringence (Cotton-Mouton constant) of nitric acid has been measured by Cotton and Mouton and $= 6.3 \times 10^{-14}$ at about 16°C . for light of wave-length $\lambda = 5.78 \times 10^{-5} \text{ cm}$. They, however, used acid of density 1.49, which corresponds to a concentration of about 90 per cent. Since the magnetic birefringence of water is negligibly small, we will not be far out if we estimate the value of the constant for 100 per cent. acid at

$$6.3 \times 10^{-14} \times \frac{10}{9} = 7.0 \times 10^{-14}.$$

In order to evaluate the magnetic anisotropy of the molecule from the Cotton-Mouton constant, we require to know the optical constants of the molecule. From the recent work of Bragg* on the birefringence of crystalline nitrates, we have very strong reasons to believe that HNO_3 molecule possesses an axis of optical symmetry, which is perpendicular to the plane of the NO_3^- ion; the moment induced in the molecule by unit field of the incident light-waves, acting along this axis, equal to C, say, being less than when it is acting perpendicular to it ($= A$). On actual calculation from Bragg's data, the ratio of these moments C/A comes out equal to 0.60. However, since the Cotton-Mouton constant refers to the liquid state it is only proper that we should use the value of the optical anisotropy calculated from measurements under the same conditions. Recently careful measurements have been made in the authors' laboratory by Mr. S. Venkateswaran† on the depolarisation of the light scattered by nitric acid of different concentrations. The value of the depolarisation factor extrapolated for 100 per cent. acid $= 0.64$. Calculating from this value we get

$$C/A = 0.38 \text{ or } = 0.50,$$

according to the two hypotheses that have been proposed for light-scattering. Even though the experimental data at present available are not sufficient to decide definitely which of the two hypotheses is correct, the data are more in accord with the hypothesis which gives the latter value of C/A, viz., 0.50.‡

* 'Roy. Soc. Proc.,' A, vol. 106, p. 346 (1924).

† 'Indian Journal of Physics,' vol. 1, p. 235 (1927).

‡ See K. S. Krishnan, 'Proc. Indian Ass. Sci.,' vol. 9, p. 251 (1926).

Now the magnetic anisotropy of HNO_3 molecule can be calculated from the Cotton-Mouton constant, C_m of liquid nitric acid, with the help of the relation

$$C_m = - \frac{(n_0^2 - 1)(n_0^2 + 2)}{30n_0 \lambda k T} \cdot \frac{A - C}{2A + C} \cdot (C' - A'),$$

where n_0 is the refractive index of the liquid outside the field, k is Boltzmann's constant, C' and A' are the susceptibilities of the molecule along and perpendicular to the axis respectively. A being greater than C , it is evident from the above expression that in order to get a positive value for magnetic birefringence, as is actually observed, C' should be numerically greater than A' , *i.e.*, the diamagnetic susceptibility of the NO_3^- ion along its axis should be numerically greater than for perpendicular directions—in conformity with the observations on crystals.

Actually substituting values for C_m and C/A in the expression, we obtain

$$C' - A' = - 6.7 \times 10^{-30}$$

$$\text{or } - 8.8 \times 10^{-30}$$

corresponding to the two values of C/A .

Now according to the assumptions we have made

$$\chi_{\parallel} = N C'$$

and

$$\chi_{\perp} = N A'$$

where N is the Avogadro number per gram molecule.

Therefore $\chi_{\parallel} - \chi_{\perp} = - 4.1 \times 10^{-6}$

or $- 5.3 \times 10^{-6}$,

which may be compared with the observed values

$$- 5.4 \times 10^{-6} \text{ for } \text{NaNO}_3$$

and

$$- 5.8 \times 10^{-6} \text{ for } \text{KNO}_3.$$

It may also be mentioned incidentally that the absolute value of the susceptibility of NO_3^- ion is the same in the crystals and in nitric acid. If from the average susceptibilities of NaNO_3 and KNO_3 we deduct the contributions from the Na^+ and K^+ ions as given by Joos,* we get for the average susceptibility of NO_3^- ion respectively the values—

$$\chi = - (25.9 - 6.5) \times 10^{-6} = - 19.4 \times 10^{-6}$$

and

$$\chi = - (31.7 - 14.5) \times 10^{-6} = - 17.2 \times 10^{-6}$$

per gram molecule.

* G. Joos, 'Z. f. Physik,' vol. 32, p. 885 (1925).

The value calculated from Quincke's results for nitric acid of about 63 per cent. concentration

$$= -17 \times 10^{-6} \text{ per gm. molecule.}^*$$

4. *Relation to the Structure of Ions.*

We have to look for the explanation of the observed magnetic anisotropy of the NO_3^- ion in its peculiar electronic structure. The three O-atoms are distributed symmetrically round the N-atom as centre, all of them lying in the same plane. Pauling† has recently suggested a dynamical model from entirely independent considerations, where he assumes six of the electrons to move in pairs in orbits connecting the central N-atom in turn with the three O-atoms, the other eighteen electrons being distributed about the three O-atoms. (Of course we exclude the K-electrons as contributing negligibly to the susceptibility.) If we now assume that the electron-orbits connecting the N- and O-atoms are in the plane of the atoms, and the other orbits are orientated more or less isotropically, the diamagnetic susceptibility perpendicular to the plane of NO_3^- ion will be numerically greater than for directions in the plane by an amount equal to the contribution from the six binuclear orbits. Taking the other electron-orbits to be all of equal size, it is found on calculation, from the assumption made above, that the susceptibility of a binuclear orbit should be much less than that of one of the other orbits. Too little is known at present regarding multinuclear electron-orbits to enable us to verify how far this conclusion is in accord with the general theory of diamagnetism. The results seem to suggest that these binuclear orbits, if elliptical, should have a large eccentricity.

However, the main conclusion that the anisotropy arises from the six binuclear orbits, seems to gain a further support from the fact that the CO_3^- ion, which has an essentially similar structure, exhibits a magnetic anisotropy (defined by $\chi_{\parallel} - \chi_{\perp}$) almost the same as for the NO_3^- ion. In this connection it need hardly be emphasised that further data on the magnetic susceptibilities of a number of crystals of this type, *e.g.*, nitrates, silicates, carbonates and borates, would be highly desirable and we have initiated experimental work in this direction.

* The susceptibility of nitric acid is assumed, consistently with our assumptions, to be entirely due to the NO_2 ion, the hydrogen atom, having lost its electron, contributing nothing to it.

† L. Pauling, 'J. Am. Chem. Soc.', vol. 48, p. 1139 (1926).

5. *Summary.*

Crystals of sodium and potassium nitrates exhibit a marked diamagnetic anisotropy, the susceptibility perpendicular to the plane of the NO_3^- ion being greater than for directions in the plane; the difference of susceptibility in the two directions is the same for the two crystals.

Attributing this anisotropy to that of the NO_3^- ion, it is found that its magnitude is exactly what we should expect from the known value of the magnetic birefringence (Cotton-Mouton effect) of nitric acid liquid.

An explanation is suggested on the basis of its electronic structure; CO_3^- ion which has essentially the same structure, gives almost the same anisotropy.

A New Differential Dilatometer for the Determination of Volume Changes during Solidification.

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In recent years, the practical requirements of the metal industries have made it necessary to study the factors which govern the production of good castings. One of the most important of these factors is the change of volume which accompanies solidification. The experimental methods which have hitherto been used to determine this change have given discordant results, and it has seemed desirable to devise a new method, less liable to error. The new form of volumometer which is the subject of this paper is intended to eliminate most of the errors inherent in the older methods. It has been applied to the measurement of the volume changes of two eutectic alloys, those of lead and tin and of tin and bismuth, the former of which contracts during solidification, whilst the latter shows a distinct expansion. The results indicate that the method is trustworthy.

Previous Methods of Measurement.

The older methods, which have been used for the experimental determination of the changes in volume, associated with the change in state of bodies, may be divided into the following classes:—

(a) The coefficients of expansion of the solid and liquid, over limited ranges