
Prof. K S Krishnan and Crystal Magnetism

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The article presents a brief discussion of the two most important contributions in crystal magnetism by Prof. K S Krishnan.

Introduction

K S Krishnan was one of the pioneer scientists who initiated research in crystal magnetism in India. His contributions to the experimental as well as theoretical methods in crystal magnetism were so important and useful that even now his methods find direct or indirect relevance in the latest research in this field. Krishnan carried out extensive measurements on magnetic susceptibility and anisotropy of single crystals of a large number of diamagnetic and paramagnetic substances. In the following, we shall describe two major contributions of Krishnan in the field of magnetism. Firstly, he developed an ingenious technique for the accurate measurement of magnetic anisotropy of single crystals and fabricated a very simple instrument for the purpose. This method is known as critical torque method [1]. The static torque method of Stout and Griffel which is at present used for anisotropy measurement is basically a useful modification of Krishnan's critical torque method. Secondly, he also solved the theoretical problem of correlating magnetic susceptibilities and the anisotropies of crystals with those of their constituent ions or molecules.

Krishnan's Critical Torque Method of Anisotropy Measurement

In this method a crystal is vertically suspended at the end of a calibrated quartz fibre in a horizontal uniform magnetic field (see *Figure 1*). The upper end of the quartz fibre is fixed to the centre of a circular and graduated torsion head, which can be rotated about the axis of suspension of the fibre over a fixed

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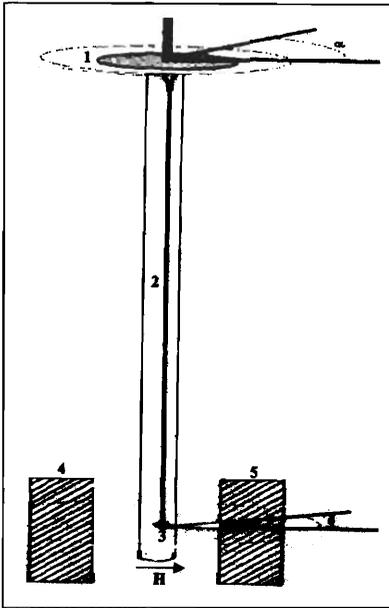


Figure 1. Krishnan's anisotropy balance (schematic diagram)

1. Torsion head, 2. Quartz fibre, 3. Crystal, 4,5. Poles of electromagnet, H-- magnetic field

α = angle through which torsion head is rotated from setting position.

ϕ = a much smaller angle through which crystal rotates from setting position.

For $\alpha = \alpha_c$, $\pi = \pi/4$, α_c may involve a number of full rotation of torsion head.

circular vernier scale. When the magnetic field is switched on, the torque on the crystal will tend to set the direction of maximum susceptibility χ_{\max} in the horizontal plane parallel to the direction of magnetic field. As a result, the crystal will rotate till the torque is balanced by the restoring couple due to the torsion produced in the suspension fibre. With the magnetic field on, the torsion head is suitably rotated so that twist in the suspension fibre is released and the crystal is in equilibrium orientation with zero torsion in the suspension fibre. This is ensured by switching on and off the magnetic field when there will be no rotation of the crystal. This equilibrium orientation of the crystal is also known as the setting position when the χ_{\max} direction in the horizontal plane is parallel to the field. After allowing the crystal to orient in the setting position and with the field switched on if the torsion head

is slowly rotated by an angle α from the setting position the crystal will also rotate in the same direction by a smaller angle ϕ , smaller because the restoring couple due to the magnetic field opposes any deviation of the crystal from the original (setting) position. The couple acting on the crystal tending to restore it to its original orientation is $1/2 (m/M) (\chi_{\max} - \chi_{\min}) H^2 \sin 2\phi$, where m and M are the mass and molecular weight of the crystal and $(\chi_{\max} - \chi_{\min})$ is the molar anisotropy in the horizontal plane of the suspended crystal. This couple is balanced by that due to the torsion of the fibre, the couple due to torsion being $C (\alpha - \phi)$, where C is the torsion constant. Thus we have

$$C (\alpha - \phi) = \frac{1}{2} (m/M) (\chi_{\max} - \chi_{\min}) H^2 \sin 2\phi. \quad (1)$$

If the rotation of the torsion head is continued slowly, a stage will be reached when the angle ϕ just assumes the value $\pi/4$ for which the restoring couple due to magnetic field is maximum, the corresponding value of α is then denoted by a critical value α_c . For further slight rotation of the torsion head, α just exceeds α_c , ϕ will tend to exceed $\pi/4$ and the restoring couple due to

magnetic field will tend to diminish and the torsional couple due to twist of the fibre will be more than sufficient to compensate the restoring couple. As a result the crystal will turn round over a large angle if the fibre is thin. Thus α_C will be critical angle of rotation of the torsion head from the original setting position such that a slight further rotation of the torsion head will be just sufficient to make the crystal suddenly turn round. This critical angle α_C can be measured accurately. Thus we have

$$C(\alpha_C - \pi/4) = \frac{1}{2}(m/M)(\chi_{\max} - \chi_{\min})H^2.$$

$$(\chi_{\max} - \chi_{\min}) = \frac{MC}{mH^2}(2\alpha_C - \pi/2) \quad (2)$$

Hence knowing α_C the anisotropy $(\chi_{\max} - \chi_{\min})$ in the horizontal plane of the crystal can be obtained. In actual practice, the ratio C/H^2 in (2) can be eliminated by comparing the result with that of a standard crystal of known anisotropy in a plane. This is the famous critical torque method of Krishnan for measuring magnetic anisotropy.

Correlation between Principal Crystalline and Molecular Susceptibilities

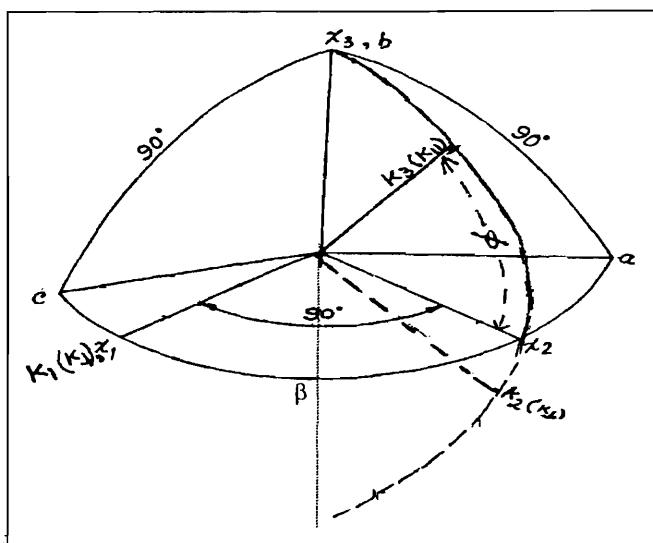
We shall now deal with another important contribution [2] that Krishnan made in collaboration with Kathlene Lonsdale. The work gives, in favourable cases, very useful information regarding the orientation of the principal magnetic axes of the crystal relative to the crystal axes and also the relation of principal susceptibilities of the crystal with those of the constituting ions or molecules.

Lonsdale and Krishnan carried out the mathematical formulation of the components of the resultant crystalline tensor in terms of those of the molecular tensors. From such mathematical formulation useful informations as stated above were derived for different crystal systems under certain approximation but the most useful and interesting conclusions were drawn for

monoclinic crystals. Krishnan and his group carried out magnetic measurements on a large number of diamagnetic organic crystal and also paramagnetic inorganic crystals belonging to monoclinic system. The diamagnetic crystals consisted of planer molecules. Denoting the principal crystalline and molecular susceptibilities by χ_1, χ_2, χ_3 and K_1, K_2, K_3 , respectively, for diamagnetic planer molecules $K_1 = K_2 = K_{\perp}$, and $K_3 = K_{\parallel}$, where K_{\parallel} is the principal molecular susceptibility along the normal to the molecular plane and K_{\perp} is along any direction in the plane. For the paramagnetic monoclinic crystals containing coordination complexes, the ionic cluster was assumed to possess uniaxial symmetry such that $K_1, K_2 = K_{\perp}$ and $K_3 = K_{\parallel}$. The mathematical relations between the crystalline and molecular tensor that Lonsdale and Krishnan derived in a monoclinic crystal led to the important results summarized in *Box 1*. See also *Figure 2*.

The most interesting feature is that with the assumption of uniaxial symmetry, ionic anisotropy can be very easily obtained from the experiments on crystalline anisotropies even without the knowledge of relative orientation of the ionic and crystalline tensors. Further, an idea of orientation of the symmetry axis of the ion can be obtained from the crystalline anisotropy data alone.

Figure 2. Location of the principal crystalline and molecular susceptibility axes in a monoclinic crystal. The figure refers to a paramagnetic monoclinic crystal for $K_{\perp} > K_{\parallel}$. When $K_{\parallel} > K_{\perp}$, χ_1, χ_2 and should be interchanged. The above figure is also valid for diamagnetic monoclinic crystal consisting of planer molecule for which $K_{\parallel} > K_{\perp}$ numerically (i.e. algebraically $K_{\perp} > K_{\parallel}$). a, b, c , – crystallographic axes and β obtuse monoclinic angle.



Box 1

1. One of the three principal crystalline susceptibility axes (which is taken as χ_3 axis) coincides with the symmetry axis 'b' of the monoclinic crystal and the other two principal susceptibility axes (χ_1 and χ_2) lie in the symmetry plane (a-c) i.e., (010) plane.

2. For a diamagnetic crystal consisting of planer molecule $K_3 \gg K_1$ or K_2 (numerically) i.e. $K_{\parallel} \gg K_{\perp}$ numerically and χ_1 is taken to be numerically smaller than χ_2 i.e. $|\chi_1| < |\chi_2|$.

$$\chi_1 = K_{\parallel} \gg K_{\perp}$$

$$\chi_2 = K_3 - (K_3 - K_1) \sin^2 \phi = K_{\parallel} \cos^2 \phi + K_{\perp} \sin^2 \phi \quad (3)$$

$$\chi_3 = K_1 - (K_3 - K_1) \sin^2 \phi = K_{\parallel} \sin^2 \phi + K_{\perp} \cos^2 \phi,$$

where ϕ is the angle that K_{\parallel} axis makes with the reflection plane (ac) i.e. $(90 - \phi)$ is the angle between K_{\parallel} and 'b' axes.

The above relations given in (3) indicate that the plane of the molecule cuts the (a-c) i.e. (010) plane along a line which is the χ_1 axis lying in the (010) plane. Further, $|K_{\parallel} - K_{\perp}| = (\chi_1 - \chi_2) + (\chi_1 - \chi_3)$. Moreover, ϕ can also be evaluated from (3). Thus some useful information about the orientation of molecular plane can be obtained from magnetic investigations.

3. For a paramagnetic monoclinic crystal $\chi_1 > \chi_2$ by convention. With the assumption of uniaxial symmetry of the ion, $K_1 = K_2 = K_{\perp}$ and $K_3 = K_{\parallel}$, the equations in (3) also hold good in a paramagnetic monoclinic crystal if $K_{\perp} > K_{\parallel}$. For $K_{\parallel} > K_{\perp}$, χ_1 and χ_2 in the equations in (3) should be interchanged. From these two sets of equation for the two cases we summarize the conclusion as follows:

(a) The symmetry axis of the ion i.e. K_{\parallel} axis lies either in the $\chi_1\chi_3$ plane or in the $\chi_2\chi_3$ plane depending on whether $K_{\parallel} > K_{\perp}$, or $K_{\perp} > K_{\parallel}$, respectively.

(b) When $K_{\parallel} > K_{\perp}$

$$\begin{aligned} K_{\parallel} - K_{\perp} &= 2(\chi_1 - \chi_2) - (\chi_1 - \chi_3) \\ \cos 2\phi &= (\chi_1 - \chi_3) / [2(\chi_1 - \chi_2) - (\chi_1 - \chi_3)]. \end{aligned} \quad (4)$$

(c) When $K_{\perp} > K_{\parallel}$

$$\begin{aligned} K_{\perp} - K_{\parallel} &= (\chi_1 - \chi_2) - (\chi_1 - \chi_3) \\ \cos 2\phi &= (\chi_3 - \chi_2) / [(\chi_1 - \chi_2) - (\chi_1 - \chi_3)]. \end{aligned} \quad (5)$$

It is to be noted that 2ϕ is the angle between the symmetry axes of the two ions related to each other by reflection in the (a-c) plane. The magnitude of $\cos 2\phi$ cannot exceed unity and (4) and (5) may be used to test whether $K_{\parallel} > K_{\perp}$.



During the period when Krishnan was carrying on magnetic investigation on a number of crystals, the sophisticated techniques for the determination of fine structure in the structural analysis of crystals with which we are acquainted at present were unknown. Any independent method, which indicated the molecular or ionic orientation in the crystal even approximately was considered to be highly useful and therefore greatly welcomed. Krishnan's magnetic investigations thus provided such useful data for structural works at that time.

Indeed Krishnan and his group gave some structural informations, particularly the molecular orientations in a number of organic crystals using the results obtained from magnetic investigations. To quote a few of them we mention the following crystals.

1,2,4,5 – Tetrachloro benzene; *p*-dichloro and *p* – dibromo benzene;

1,3,5 – Triphenyl benzene and Triphenyl carbinol; 4, 4'– dichloro diphenyl

4, 4' – dibromo diphenyl; 1,4 – Naptho quinone; Pyrene, etc.

Further accurate values of ionic anisotropy ($K_{||} - K_{\perp}$) determined easily and directly from crystalline anisotropies ($\chi_1 - \chi_2$) and ($\chi_1 - \chi_3$) using the relations described above for monoclinic crystals (even without the knowledge of the relative orientations of crystalline and ionic susceptibility axes) were extremely helpful to later workers to interpret the magnetic and optical behaviour of a large number of paramagnetic crystals in terms of the ligand field theory.

Suggested Reading

- [1] K S Krishnan and S Banerjee, *Phil. Trans. A*, Vol. 234, pp. 265-298, 1935.
- [2] K Lonsdale and K S Krishnan, *Proc. R. Soc. A*, Vol. 156, pp. 597-613, 1936.
- [3] R Gupta, U S Ghosh and C Basu, *Physics Education*, October-December, pp. 269-278, 1996.

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