

# Magnetic properties of solids: Krishnan's contribution

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*K. S. Krishnan and his students developed precise experimental methods to measure magnetic anisotropy of crystals. The work established the usefulness of magnetic methods as a valuable supplement to X-ray methods for determining crystal structure. This led to the organization of the Department of Magnetism in the Indian Association for the Cultivation of Science. Some remarks about the subsequent developments in the field of magnetism will be made to put the work in modern perspective.*

K. S. Krishnan<sup>1</sup> came to Calcutta in 1920. The capital of India in the British empire had been moved to Delhi in 1912. The University College of Science and Technology at Rajabazar in Calcutta was founded in 1914 by the efforts of Asutosh Mookerjee and with munificent contributions from Taraknath Palit and Rashbehary Ghosh. When the aura of political power faded, the stars in Calcutta's science began to shine more brilliantly. C. V. Raman was Palit Professor of Physics and had his research group in the Indian Association for the Cultivation of Science (IACS) at 210 Bowbazar Street. For Krishnan, the star stood over this address. He joined Raman's part, and from 1923 to 1928 he took part in spectroscopic researches, which included the discovery of the Raman Effect.

The other professor at the Calcutta University Physics Department was D. M. Bose, who was working on magnetic materials at that time. Bose's researches led to the 'spin-only' formula for the magnetic moment for the 3-d atoms in salts; this won international recognition<sup>2,3</sup>. The next important contribution in the field of magnetism came from K. S. Krishnan and his students first at the Dacca University (now spelt Dhaka in Bangladesh) and later at IACS. They carried out measurements of magnetic anisotropy in crystals by the elegant oscillation method<sup>4</sup> and the critical couple method<sup>5</sup>.

## Magnetism in crystals

The magnetic energy of a crystalline substance can be written as

$$E = -\frac{1}{2} \int [k_{11}H_x^2 + k_{22}H_y^2 + k_{33}H_z^2 + 2k_{12}H_xH_y + 2k_{23}H_yH_z + 2k_{31}H_zH_x] dv, \quad (1)$$

where  $k_{11}$ ,  $k_{22}$ , etc. represent the susceptibilities of the crystal referred to the coordinates  $x$ ,  $y$ ,  $z$ , and the integral is taken over the whole volume of the crystal, whose shape is not yet specified. When the applied field is in the  $x$ -direction,  $H_y = 0$ ,  $H_z = 0$  and the energy is

$$E = -\frac{1}{2} \int k_H H^2 dv, \quad (2)$$

where  $k_H$  is the susceptibility of the crystal in the  $x$ -direction and depends on the direction  $x$  of  $H$ . The magnetic energy cannot depend on the choice of axes. Hence

$$k_{11}H_x^2 + k_{22}H_y^2 + \dots + 2k_{12}H_xH_y + \dots = k_H H^2. \quad (3)$$

If  $(l_1, m_1, n_1)$  are the direction cosines of  $H$  relative to the coordinates  $(x, y, z)$  we get

$$k_{11}l_1^2 + k_{22}m_1^2 + \dots + 2k_{12}l_1m_1 + \dots = k_H. \quad (4)$$

Now we may refer the magnetic ellipsoid to its principal axes which are defined by  $k_{12} = k_{23} = k_{31} = 0$ ,  $k_{11} = k_1$ ,  $k_{22} = k_2$ ,  $k_{33} = k_3$ .  $k_1$ ,  $k_2$ ,  $k_3$  are termed the principal magnetic susceptibilities. Then if  $H$  is in the direction  $(l, m, n)$  we get

$$k_1l^2 + k_2m^2 + k_3n^2 = k_H. \quad (5)$$

Corresponding to the volume susceptibilities  $k_1$ ,  $k_2$ ,  $k_3$  we have mass susceptibilities  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$ , respectively. Measurement with powdered samples gives us  $\frac{1}{3}(k_1 + k_2 + k_3)$  or  $\frac{1}{3}(\chi_1 + \chi_2 + \chi_3)$ .

On exciting an inhomogeneous magnetic field the force on a small crystal of volume  $v$  is

$$k_H v H (dH/dx). \quad (6)$$

A paramagnetic substance tends to move to a higher field. By measuring the force the susceptibility can be measured.

It often happens that in the case of a monoclinic crystal, the direction of only one principal magnetic axis  $k_3$  is known. If the crystal is mounted with the  $k_3$  axis parallel to the  $z$ -axis and perpendicular to  $H$ , then  $n = 0$ , and

$$k_1l^2 + k_2m^2 = k_H$$

or,

$$k_1 \cos^2 \phi + k_2 \sin^2 \phi = k_H, \quad (7)$$

where  $\phi$  is the angle between the  $k_1$  axis and  $H$ . Hence, a couple (equal to the rate of change of magnetic energy with angle of displacement,  $dE/d\phi$ ) will act on the crystal:

$$\begin{aligned} \frac{dE}{d\phi} &= -\frac{1}{2} \frac{d}{d\phi} (k_H H^2 v) \\ &= \frac{1}{2} (k_1 - k_2) v H^2 \sin 2\phi. \end{aligned} \quad (8)$$

When a circular disc of the crystal is cut with the plane of the disc perpendicular

to the known magnetic axis and suspended with the plane horizontal and parallel to a uniform field  $H$ , the disc will be acted upon by a couple given by eq. (8), which is maximum when  $\phi = 45^\circ$ .

## Experimental methods

### Oscillation experiments

Suppose that a crystal is suspended by a torsion fibre parallel to the  $k_3$  axis and oscillates with a period  $T_0$ . If now a uniform field  $H$  is applied parallel to the  $k_1$  axis, then from eq. (8) on rotating the crystal through an angle  $\delta\phi$  about the axis of the fibre, a restoring couple  $\{C + (k_1 - k_2)H^2v\}\delta\phi$  acts on the crystal instead of the couple  $C\delta\phi$  in the absence of the field, where  $C$  is the torsion constant of the fibre. A new period of oscillation  $T_1$  is observed. Then

$$CT_0^2 = \{C + (k_1 - k_2)H^2v\}T_1^2, \quad (9)$$

so

$$k_1 - k_2 = ((T_0^2 - T_1^2) / T_1^2)(C / H^2)(1 / v), \quad (10)$$

or

$$\chi_1 - \chi_2 = ((T_0^2 - T_1^2) / T_1^2)(C / H^2)(1 / m), \quad (11)$$

where  $m$  is the mass of the crystal. If  $\chi$  is gram molecular susceptibility, the right hand side of eq. (11) is multiplied by the molecular weight  $M$ .

Krishnan and his students attached each crystal to the lower end of a short piece of glass suspended by a vertical quartz fibre from a torsion head and found the periods of oscillation. Complications from the shape of the specimens were attended to. Special attention was required to ensure the uniformity of the magnetic field ( $\sim 5$  kG).

The value of the largest principal susceptibility was found by the Rabi immersion method<sup>6</sup>. A quartz fibre was used; the solution was weak manganese chloride.

### Critical couple method

The crystal is suspended in a uniform horizontal magnetic field at the end of a

calibrated long, thin quartz fibre, the upper end of which is fixed to the axis of a graduated torsion head. The crystal is allowed to take up its equilibrium orientation in the field under zero torsion of the fibre. If the torsion head is now slowly rotated through an angle  $\alpha$ , the crystal will rotate in the same direction but through a smaller angle  $(\alpha - \phi)$ . The couple acting on the crystal tending to restore it to its original orientation would be equal to  $(ml/2M)\Delta\chi H^2 \sin 2\phi$ , according to eq. (6), where  $\Delta\chi$  is the difference between the maximum and minimum gm molar susceptibilities of the crystal in the horizontal plane. This couple is balanced by that due to the torsion fibre, viz.  $C(\alpha - \phi)$ . As the torsion head is rotated further, there comes a stage when  $\phi$  just reaches the value  $\pi/4$  (the corresponding value of  $\alpha$  being  $\alpha_c$ , say), and the couple due to the magnetic field reaches its maximum value. Equating the opposing couples, we get

$$C(\alpha_c - \pi/4) = \frac{m}{2M}\Delta\chi H^2. \quad (12)$$

With the slightest further rotation of the torsion head the crystal will naturally yield and turn around. On this property is based an accurate measurement of  $\alpha_c$  which by eq. (12) enables us to determine  $\Delta\chi$ . In practice  $2\alpha_c$  is measured directly by finding the two critical positions of the torsion head, obtained by clockwise and anticlockwise rotations of the torsion head from its initial position.

We have only described the main experimental methods. The papers of Krishnan and coworkers contain lots of experimental tricks to measure weak anisotropies. They contain enormous amount of data.

These papers established Krishnan's idea that the magnetic anisotropy of a diamagnetic or paramagnetic crystal could be correlated with the anisotropy of the individual molecules and their relative orientations. In favourable cases the precise orientation of molecules in the unit cell could be determined from magneto-crystalline measurements. The work of Krishnan and his students, and of Kathleen Lonsdale established the fruitfulness of magnetic methods as a valuable supplement to the methods of X-ray analysis for determining the architecture of crystals.

Later work on iron group and rare earth salts correlated with theoretical work of Van Vleck and Penney and Schlapp on crystal fields in solids.

Another important work by N. Gan-guli and Krishnan established that electrons in graphite form a two-dimensional electron gas obeying Fermi-Dirac statistics<sup>7</sup>.

### Subsequent developments

We note that Krishnan's measurements were started in a small university department and were done with an apparatus not too expensive. Today a university department can afford the latest version of the apparatus at IACS (ref. 8) which operated between liquid air temperature and a moderately high temperature. But investigations in magnetism subsequently developed in directions well beyond the capacity of university departments<sup>9</sup>.

Firstly, the magnetic phenomena require high fields and liquid helium or even lower - millikelvin - temperatures. Perfect diamagnetism is found in superconductors. Superconducting magnets, based on type-II superconductors, can produce very high, steady fields. These are beyond a university department. Only with the discovery of high temperature (above liquid nitrogen temperature) superconductivity, research in such a subject can be done in university departments. Some departments in universities and IITs have procured rotation magnetometers and carried on research in magnetic materials.

Secondly, magnetic structure determination took a new turn with the introduction of neutron methods. Neutron diffraction and neutron scattering methods can only be done in the vicinity of reactors. Universities or even research institutes could not carry out such experiments. The record of research at Trombay reactors at BARC, Mumbai, has been good. Recently with the establishment of Inter-university Centres for Department of Atomic Energy Facilities (IUC-DAEF) university workers can hope to do neutron-based work.

Thirdly, research on nuclear moments, much smaller than atomic moments, started with atomic and molecular beams and later gave rise to nuclear magnetic resonance (NMR)

methods and other related resonance methods. Only research institutes could afford such facilities in India; in particular, the uniformity of magnetic field in NMR studies required high technology. Still several research groups have procured such facilities and done good work. Only the Mössbauer experiments could be done in many laboratories in universities, provided the source could be obtained from reactors or accelerators.

The style of doing research in magnetism has changed, but the standard set by Krishnan and his students has not been surpassed or equalled.

Some information about Krishnan's students in magnetism may not be out of place. B. C. Guha joined (West) Bengal Educational Service and was a part-time teacher in Physics in Calcutta University when I was a student in the M Sc class (1958–60); he used to lecture on magnetism. A. Mookherjee was (probably) the teacher in St. John's College, Agra (1959) who showed us around his laboratory in magnetism when we, the students of physics from Calcutta University, visited Agra on an educational tour (1959); later he taught at Burdwan (now spelt Bardhawan)

University. Santilal Banerjee also joined (West) Bengal Educational Service and taught in Presidency College, Calcutta, in 1940; his name appeared in the college records<sup>10</sup>. A. Bose stayed in IACS, continued magnetic measurements at low temperature and later built up the Indian Cryogenic Council; he was a Fellow of the Indian National Science Academy, Delhi. S. C. Ganguly taught at Bangabasi College, Calcutta, and later at Jadavpur University. A. C. Guha taught in Berhampur College at Berhampur, West Bengal, and is still alive.

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1. Krishnan, K. S., *Collected Works of K. S. Krishnan*, National Physical Laboratory, New Delhi, 1988.

Two amusing slips in the excellent biographical sketches, one by K. R. Ramanathan and another by K. Lonsdale and H. J. Bhabha, should be noted: S. N. Bose never wrote a thesis for a formal doctoral degree; in Krishnan's days football matches were played not in the Eden Gardens, but in the 'Maidan' or 'Garer Math' (playgrounds outside the Fort).

2. Van Vleck, J. H., *The Theory of Electric and Magnetic Susceptibilities*, Clarendon Press, Oxford, 1932.

3. Bates, L. F., *Modern Magnetism* Cambridge, 1951.
4. Ref. 1, p. 308.
5. Ref. 1, p. 402, also p. 439.
6. Ref. 1, p. 346; also ref. 3.
7. Ref. 1, p. 509.
8. Ref. 1, p. 580 shows a figure of this apparatus. The earlier papers did not give any picture of the apparatus.
9. See e.g. Majumdar, C. K., in *Current Trends in Magnetism* (eds Satya Murthy, N. S. and Madhav Rao, L.), Indian Physics Association, 1980.
10. Presidency College, Calcutta, Centenary Volume 1955 (West Bengal Govt. Press, Alipore, 1955), p. 54 [Teachers in Natural Science – Physics].

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