Bhagawati Charan Guha and discovery of the molecular magnet

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The discovery of molecular magnet by Bhagawati Charan Guha is not well-discussed in the history of Indian science. On studying a series of inorganic crystals, Guha found some anomalous magnetic behaviour of copper(II) acetate which was not structurally characterized then. After the discovery of the structure, copper(II) acetate appeared as a dimeric dihydrate molecule rather than an inorganic solid. Guha then put a structure-function correlation between the newly discovered structure of copper(II) acetate and its low-temperature magnetic data. This dimeric copper(II) acetate dihydrate is now regarded as the first reported molecular magnet.

Many of the contributions to the basic sciences by a number of Indian scientists unfortunately have not been well-explored. In a very tough situation, particularly in British-ruled India, several fundamental inventions by a few Indian scientists are noteworthy. Bhagawati Charan Guha is among those scientists, whose discovery of the molecular magnet remains almost unknown among the present generation. Being a graduate student of the celebrated Indian physicist K. S. Krishnan, Guha made a number of significant contributions in magnetism. Before his findings, different transition metal ion salt crystal lattices, where the paramagnetic centres (transition metal ions) are infinitely distributed, were studied to find various magnetic interactions. Guha worked with dimeric copper(II) acetate dihydrate and was the first to establish that similar kind of magnetic interactions can be present inside a molecule[1]. Interestingly, the molecular structure of dimeric copper(II) acetate dihydrate was not known then[2]. This work is now universally accepted, and the Cu(II) molecule is considered as the first[3] and probably the simplest transition metal molecular magnet invented so far. The classical Werner-type coordination molecule (where clearly metal and ligand exist) tris(N,N-diethyldithiocarbamato)iron(III) chloride, to the best of my knowledge, may be regarded as the molecular magnet discovered after copper(II) acetate dihydrate[4].

The discovery

In 1951, during the study of a series of transition metal ion salt crystals, Guha[1] found some anomalous behaviour of copper(II) acetate. The salt was supposed to have mononuclear structure (copper acetate monohydrate). The X-ray structure of copper acetate was not known then. According to Guha[1], '...copper acetate monohydrate, in which both the principal susceptibilities and anisotropies, after a slight rise, decrease very quickly with the lowering of temperature. At room temperature all the p^2's are considerably below the spin-only value, the highest being 2.385, and they fall off very rapidly with the fall of temperature. At 82.8°K, the p_1^2, p_2^2 and p_3^2 are (p_1, p_2 and p_3 are effective Bohr Magneton values along the three principal magnetic axes of the crystal) 0.280, 0.228 and 0.248 respectively, corresponding to an extremely low mean value 0.252. Indeed, the trend of their temperature variation curves suggests that by a further lowering of temperature by 20° or 30°, all the p^2 may completely vanish'. This important finding of Guha was supported by the electron paramagnetic resonance spectral studies of Bleaney and Bowers[5] in the following year. The anomalous behaviour of copper(II) acetate was explained by Guha[1]: 'In the acetate, the non-cubic part of the field should have less symmetry and its magnitude should be greater than in the previous class, so as to make the spin and orbital moment oppose, and practically neutralize each other's effects. This will naturally be particularly marked at low temperatures; whereas, owing to thermal agitation, this neutralization will not be so effective at high temperatures. We do not know enough of the structure of the acetate to verify the existence of such a strong asymmetric field, but from the composition of the molecule one can see that there are not enough atoms of the same kind to build up a symmetrical surrounding for the copper ion.' As stated earlier, the crystal structure of copper(II) acetate was determined in 1953 (ref. 2), that is, two year after the publication of Guha's work[1]. Thereafter Guha[6] explained that the shorter distance between the two Cu(II) centres in the dimeric structure of copper(II) acetate dihydrate than other common copper salts is the reason for the actual interaction (antiferromagnetic) in copper(II) acetate dihydrate, resulting in quenching of the magnetic susceptibility value with decreasing temperature.

Each Cu(II) centre in the Cu(II) acetate dihydrate is assumed to have distorted octahedral geometry with Cu…Cu distance as 2.64 Å (ref. 2). Considering the crystal field splitting of Cu(II) ([Ar]$3d^9$), the only unpaired electron remains in the antibonding orbital (e_g*). The magnetic orbitals, which may be considered as d_{xy} or $d_{x^2-y^2}$ (d_{xy} may be converted to $d_{x^2-y^2}$ only by changing the position of *x* and *y* axes), interact weakly (magnetic exchange) at low temperature to make the electronic spin of the magnetic orbital at one Cu(II) centre antiparallel with respect to the other Cu(II) in the molecule, resulting in antiferromagnetism.

In 1973, the molecular structure of copper(II) acetate was re-determined using neutron-diffraction analysis[7] and its magnetic behaviour was re-explained. The results were in agreement with previous reports.

About this fundamental discovery of the molecular magnet, Olivier Kahn wrote in his famous book *Molecular Magnetism*[8], that 'The magnetic interaction phenomenon within a molecule was discovered in 1951 by Guha and then by Bleaney and Bowers, on a compound known at that time as copper(II) acetate monohydrate. Guha found that the magnetic susceptibility exhibits a maximum as a function of temperature; Bleaney and Bowers observed that the EPR spectra resemble those of triplet states rather than doublets expected for non-interacting copper(II) ions'.

The scientist

Guha came from a well-educated family in Dhaka (presently in Bangladesh) of undivided Bengal. He was born on 21 February 1907 (ref. 9). He studied physics and stood first class first in his post-graduation from Dacca University (presently Dhaka University, Bangladesh). Then he started his research career initially under the supervision of Satyendra Nath Bose in Dhaka. One day Guha met with serious accident in the laboratory while working with X-rays. Both his eyes were injured and he had to take rest and medication for about six months. His elder brother Bhabani Charan Guha was then a lecturer at the Physics Department of Dacca University and a colleague of Bose. According to the advice of Bose and his elder brother, Guha then joined the research group of K. S. Krishnan in the same department in the field of crystal magnetism. During his doctoral study, he not only worked in Dhaka, but also in Indian Association for the Cultivation of Science, Kolkata and Allahabad University as his mentor subsequently moved to those institutions one after another. After having his D Sc degree, Guha joined Midnapore College in West Bengal, as a lecturer and then worked consecutively in Rajshahi College (presently in Bangladesh) and Presidency College, Kolkata. In the 1960s, he also worked part-time at the Department of Physics, Calcutta University[9]. Besides teaching and research, Guha could play the esraj very well. This stalwart of Indian science passed away in November 1996 in Kolkata[9].

Conclusion

It is obvious that during the British rule, there was no support for Indian scientists. Post-independence too, the situation remained almost the same as the economic condition of the country was not good to encourage research in the basic sciences. Guha worked in this very situation of stringency in all respects. His devotion, sincerity and tireless efforts towards reaching his scientific goal will be iconic to the teachers and students of science forever. With advancement in the field, Guha must be saluted for his basic discovery of the molecular magnet, which is proving increasingly important in modern times.

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