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K. S. Krishnan and early experimental evidences for the Jahn–Teller theorem

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Jahn–Teller theorem, proposed in 1937, predicts a distortional instability for a molecule that has symmetry based electronic degeneracy. In 1939, Krishnan emphasized the importance of this theorem for the arrangement of water molecules around the transition metal or rare earth ions in aqueous solutions and hydrated salts, in a short and interesting paper published in *Nature* by pointing out at least four existing experimental results in support of the theorem. This paper of Krishnan has remained essentially unknown to the practitioners of Jahn–Teller effect, even though it pointed to the best experimental results that were available, in the thirties and forties, in support of Jahn–Teller theorem. Some of the modern day experiments are also in conformity with some specific suggestions of Krishnan.

JAHN–TELLER effect¹ is a beautiful and simple quantum phenomenon that occurs in molecules, transition metal complexes as well as solids containing transition metal

or rare earth ions. It states roughly that ‘a localized electronic system that has a symmetry-based orbital degeneracy, will tend to lift the degeneracy by a distortion that results in the reduction of the symmetry on which the degeneracy is based’. In isolated systems such as a molecule or a transition metal complex it is a dynamical or quasi static phenomenon. They are called dynamic and static Jahn–Teller effects². When it occurs co-operatively in crystals it is a spontaneous symmetry breaking phenomenon and a crystal structure change. This is called a co-operative Jahn–Teller effect.

Even before Jahn–Teller theorem appeared, Krishnan and collaborators³ performed a series of pioneering magneto crystalline anisotropy study of families of paramagnetic salts containing transition metal and rare earth ions lending good support to various new quantum mechanical ideas including those of Bethe, Kramers and Van Vleck on crystal field splitting and magneto crystalline anisotropy. In the biographical Memoirs of the Royal Society of London, K. Lonsdale and H. J. Bhaba⁴ wrote:

'The papers published by Krishnan during this period (30s) in collaboration with B. C. Guha, S. Banerjee and N. C. Chakravarty were the foundation stones of the modern fields of crystal magnetism and magnetochemistry'.

In the paramagnetic salts that Krishnan and collaborators studied the magnetic ions are well separated from each other by the intervening water molecules and also anion groups. As a result, any direct or superexchange or dipolar interactions between the magnetic moments are weak; consequently any cooperative magnetic order such as antiferromagnetic order is pushed down to very low temperatures below 1 K. This enabled Krishnan and others to study in detail the magnetic properties of essentially isolated paramagnetic ions in various crystal field environments.

Jahn–Teller theorem and its experimental consequences have been studied in great detail in chemistry and physics, particularly in the context of electron spin resonance experiments⁵. In the simplest of transition metal complexes there is a cubic (octahedral) environment around the transition metal ion such as Cu^{2+} . The octahedral environment leads to a crystal field splitting of the five fold degenerate d level into an orbital doublet (e_g) and a triplet (t_{2g}).

In the work of Krishnan and collaborators, one notices repeated reference to deviation from cubic electric field at the centre of rare earth ions in several cases and transition metal ions in some cases as inferred from their own anisotropic magnetic susceptibility measurements. The most obvious causes for departure from regular cubic symmetry of the coordination clusters are inequivalence of the ligand atoms in the first or second co-ordination shell and forces of crystal packing. No one suspected that electronic orbital degeneracy can lead to an asymmetry such as a distortion of the octahedra with equivalent ligand atoms.

It is at this juncture that theoretical papers of Jahn and Teller appeared, which suggested another important cause for molecular asymmetry. And Krishnan readily appreciated the importance of this theorem for crystal field splitting and arrangement of water molecules around paramagnetic ions in aqueous solutions and wrote an interesting short paper in *Nature*⁶ in 1939 that we reproduce here. It is interesting that Van Vleck⁷, who very much admired⁸ Krishnan, also developed his theory of Jahn–Teller effect for orbital doublets in paramagnetic ions in the same year.

In his paper Krishnan quotes at least four existing experimental results that support the Jahn–Teller theorem: i) X-ray data that is consistent with a small deviation of the perfect H_2O octahedra around the paramagnetic ion in hydrated salts; ii) magnetic data, mostly from his group, that exhibits strong magnetic anisotropy that is similar in magnitudes in various salts, suggesting that

the cause for any distortion arises from the electronic state of the paramagnetic ions rather than the surrounding atoms; iii) asymmetry inferred from electronic absorption spectra of cation surrounded by water molecules in aqueous solutions studied by Freed *et al.*; iv) magnetic double refraction exhibited by the aqueous solution of these salts, as observed experimentally by Raman and Chinchalkar and Haenny, and v) the experimental observation of Chinchalkar that double refraction is absent experimentally when the paramagnetic ion is in an S-state (for example Gd^{3+} or Mn^{2+} which are orbital singlets).

Krishnan's paper contained important suggestions and also looked at a slightly more complex system namely rare earth ions in aqueous solutions than the relatively simpler case of transition metal ions in solids. What Krishnan was looking for was perhaps static Jahn–Teller distortion at room temperature. The issue of timescale associated with the distortion dynamics and the nature of the experimental probe becomes important here. The Jahn–Teller cluster being a finite system, will either quantum mechanically tunnel among equivalent distorted configurations in a phase coherent manner with a short time period, or will hop to various equivalent distorted configurations incoherently through thermal fluctuations. Optical absorption, for example, is a short time scale measurement: it will see even dynamic distortions as a static one. The static susceptibility measurement on the other hand is a low frequency probe. Any indication of distortion through this experiment will mean a nearly frozen distortion.

The choice of paramagnetic salts dissolved in water offers some special advantage too. A paramagnetic ion is typically surrounded by six water molecules forming a rigid octahedral complex. A coordination complex such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, is loosely coupled to the environment namely water. This makes the restoring force against the Jahn–Teller distortion weaker, making a nearly static Jahn–Teller distortion feasible even at room temperatures. On the other hand, in the case of solids, the Jahn–Teller distortion has to work against the packing forces of the crystal, thereby reducing the Jahn–Teller stabilization energy.

Many of Krishnan's experiments involved rare earth ions. In view of the larger degeneracy and also the compactness of the *f*-orbitals, rare earth ions have some advantages as well as disadvantages. The compactness of the wave functions makes the crystal field splitting smaller and also the quenching of orbital angular momentum less important. On the other hand, the spin orbit coupling, which can make the magnetic anisotropy stronger, is larger in the case of rare earths. The larger degeneracy of the *f*-orbitals also leads to a proliferation of low lying multiplets making the theory as well the interpretations of the spectra hard. Perhaps because of these difficulties most of the classic studies of Jahn–Teller

effect seems to be confined to transition metal ion systems.

I will try to put some of Krishnan's suggestions in the modern context. Now it is well known that the dynamic to static Jahn-Teller distortion cross over temperature, as measured by ESR measurements, ranges from 1 K to more than 300 K in a variety of systems¹⁰. Some of these room temperature systems include Cu^{2+} ion that

Krishnan was referring to based presumably on room temperature measurements. What I mean to say is that static Jahn-Teller distortion is not a very low temperature luxury that Krishnan could have missed. Secondly, Krishnan was referring to some X-ray structural data as evidence for octahedral distortion. Some modern EXAFS measurements¹¹ on Cu^{2+} and Cr^{2+} ions in aqueous solutions at room temperatures show the presence of a

Jahn-Teller Theorem and the Arrangement of Water Molecules around Paramagnetic Ions in Aqueous Solutions*

It is well known from X-ray studies that in many of the highly hydrated salts of the iron and the rare earth groups the cation is surrounded by an octahedron of water molecules. This distribution fits well with the observed magnetic properties of these salts; first, it gives an electric field of predominantly cubic symmetry about the central cation, as required by the magnetic data, and secondly, it gives the potential of the electric field the proper sign demanded by the magnetic data. The magnetic data, however, further require (1) that the field, though predominantly cubic in symmetry, should deviate from it considerably, since the cation in these crystals exhibits, in general, a strong magnetic anisotropy, and (2) that for a given cation the magnitude and the asymmetry of the electric field about it should be nearly the same in the different hydrated salts containing the ion, since the magnetic anisotropy of the ion is found to be of the same order of magnitude in all these salts. These requirements will be satisfied in a simple manner if the octahedron, instead of being regular, deviates from it slightly—a small deviation is permitted by the available X-ray data—and the deviation is determined by the nature of the cation in the centre. This arrangement appears very probable in view of the important theoretical result obtained recently by Jahn and Teller¹, namely, that if the electronic state of the central ion is degenerate, the system will be stable only if there is enough asymmetry in the system to remove the degeneracy (except, of course, the special two-fold degeneracy of Kramers). This minimum asymmetry required for stability supplies then the mechanism by which the cation can in a manner determine the geometry of distribution of the water molecules around it.

Such an asymmetric arrangement of the water molecules about the cation seems to persist even in the aqueous solutions of these salts. Freed and his collaborators² have found in the observed multiplicity of the absorption lines of the rare earth ions in aqueous solutions evidence for asymmetric electric fields, nearly the same as in the corresponding hydrated crystals. A comparison of the magnetic behaviour of some of the paramagnetic ions, both of the rare earth and the iron groups, in aqueous solutions, with the ideal free-ion behaviour on one side, and with the behaviour of the ions in the hydrated crystals on the other, also leads to the same conclusion.

The large magnetic double-refraction exhibited by aqueous solutions of these salts³ follows as a natural result. Owing to the asymmetry in the distribution of the water molecules about the paramagnetic ion, and the consequent asymmetry of the electric field about the ion, the group as a whole will be magnetically anisotropic, and will tend to orient in the magnetic field. Since the group will also be optically anisotropic, the solution will exhibit double-refraction. Now these anisotropies, according to the views presented here, should depend indirectly on the incipient degeneracy of the electronic state of the central paramagnetic ion, and in particular on the orbital degeneracy. The observation by Chinchalkar⁴ that the double refraction depends on the orbital angular momentum of the paramagnetic ion, and that in particular the double refraction is almost nothing when the ion is in the S-state, (for example, Gd^{3+}) is significant. Indeed, from the known magnetic anisotropy of the group in the crystal state, and its birefringence, a rough estimate can be made of the magnetic double refraction of the solution, and it is found to be of the right order of magnitude.

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*Reproduced from *Nature*, 1939, **143**, 600.

distorted octahedra with two copper–oxygen distances of about 2.00 Å and 2.3 Å.

Krishnan's suggestion that the large magnetic double refraction observed by Raman and Chinchalkar and Haenny in aqueous solutions of paramagnetic ions is very interesting. This seems to be a compelling evidence for the Jahn–Teller distortion, as explained by Krishnan: the distorted octahedral complex, in view of the magnetic anisotropy arising from the large spin-orbit coupling, tend to align themselves in water along the magnetic fields causing double refraction. The absence of solid state effects and diluteness of the paramagnetic ions makes this argument very important: the system resembles somewhat an ideal gas of 'octahedral molecules' as far as the double refraction is concerned. I should also point out that I have not been able to find out in my short literature survey any later study of Jahn–Teller effect in aqueous solutions using the magnetic double refraction as a probe.

After this one paper on Jahn–Teller effect, Krishnan essentially left the field of crystal paramagnetism. Further, he also never wrote any paper on the issue of Jahn–Teller effect.

The insightful suggestions of Krishnan, that came soon after the Jahn–Teller theorem, was never taken up for further study as far as I can see in the literature.

This paper has remained unknown. One wonders why. One possible reason is the choice of rare earth ions, which as we mentioned earlier is complicated theoretically and also hard when it comes to interpretation of the experimental spectra. Another possible non scientific reason is as follows: a detailed followup paper or some further works by Krishnan⁹ could have made Krishnan's work known more and opened up the field of Jahn–Teller effect much earlier, making Krishnan a pioneer in one more beautiful field.

Detailed experimental confirmation of Jahn–Teller theorem became possible only after the ESR experiments of Bleaney and Bowers¹² in 1952 in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and related family of paramagnetic salts, about 15 years after the enunciation of the theorem and Krishnan's supporting suggestions. The milestones included careful observation of the split ESR line below about 50 K (indicating frozen distortion in the ESR time scales) and motional narrowed unsplit line above about 50 K (indicating a dynamic distortion) for the copper salts.

Nearly half a century of experimental work on Jahn–Teller effect in the modern era is broadly consistent with the sixty year old suggestion of Krishnan. The practically unknown suggestions of Krishnan, however, remains as the only experimental support for the Jahn–Teller theorem covering a period of more than ten years,

Making of a young scientist

Several factors can influence the making of a scientist at various stages in his life. The formative young years are important, of course. Krishnan, in one of his articles in Tamil says: 'my first love for science came in my 4th form (class 9) in my high school in 1911. Even though my teacher was not a professional scientist, he was good at explaining science in a clear and captivating fashion. His lessons not only sunk deep into our mind but also made us crave for more science. Whether it is physics, geography or chemistry, his teaching style was unique. He did not simply reproduce the lessons from the book. He demonstrated many simple experiments for us and also encouraged us to do experiments ourselves. Very few teachers I know are of this type, and I feel fortunate to have had him as my first science teacher. This master teacher's name is Sri A. Subramanya Iyer and he did not stay too long in my school.'

'My real involvement in science came after an year, when my physics teacher asked us to write an "essay" about Archimedes principle. At that time we had just learned the proof of this principle. But, in my article I wrote about an instrument that I constructed, on my own, for measuring the density of solids. A few days later I learned that my instrument is nothing new and it was invented by Nicholas many years ago – "the Nicholas hydrometer", by then text book material.'

'My whole hearted involvement in science came only after seven or eight years, when I got opportunities to read copies of research articles of Prof. C. V. Raman, then Palit Professor at Calcutta University, which appeared in *Nature*, *Philosophical Magazine* and other journals. This whole culture of eminent scientists publishing their work in "Science Journals" and that some of our own scientists like Ramanujan, Raman are contributing first rate articles which are very much appreciated by the world came to me as an eye opener. This gave me a new feeling for science, scientists and the new world of science.'

KSK finishes his article by saying: 'I relinquished the small job I had and decided to do research in physics and went to Prof. C. V. Raman at Calcutta. But, he did not agree for my starting research immediately. Only after learning various aspects of physics properly at Calcutta University for two years was I able to join his research group. I had the good fortune of having a five year "Gurukula vasam" there. These five years turned out to be a festive season in my science life.'

– GB

Speaking of science and for science

Conveying the essence of science and its excitement in an understandable way to a layman or a non-expert is an art that few scientists have mastered. This has its very important role and value in society; it is also an important duty of the science community, that is being neglected in modern times. KSK had this skill as it is clear from his many articles on science and related issues in Tamil and English as well as the talks that he has given in All India Radio. He was also an ardent spokesman for science.

KSK strongly believed that one can convey even very complicated scientific facts in his mother tongue – in this case, Tamil. His scholarship and appreciation of Tamil literature must have given him the gift to perform this task with ease. In one of his articles he speaks of his school science teacher Thirumalai Kozhunthu Pillai, who enthused the students by teaching science in an understandable way in chaste Tamil. Listening to him he got the conviction that difficult scientific concepts could be conveyed in Tamil.

Those of us whose spirit is strong but flesh is weak can gain strength to write science in our mother tongue by studying the works of people like KSK and modern scientists like Narlikar and others.

Through his own first rate scientific work and also through his scholarly personality he was a spokesman for Indian science. One hears that KSK was in many committees and held many responsible scientific administrative positions: he was President of the National Academy of Sciences and also Member of Atomic Energy Commission. It is said that whenever Pandit Jawaharlal Nehru found time (or wanted to get away from politics) he would rush to NPL to listen to KSK of the latest in science. Apparently he always enjoyed listening to KSK, but at the end never forgot to ask KSK 'how this is going to help my countrymen'. I really do not know what KSK's reply was.

– GB

before the beginning of the modern era. As I mentioned earlier, the suggestion of magnetic double refraction by Krishnan may still be useful in the modern context for Jahn–Teller effect study in the rich variety of new and old coordination complexes involving transition metal and rare earth metal ions.

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3. Starting from 1933 Krishnan and collaborators wrote more than a dozen important papers on exhaustive study of magneto crystalline anisotropy in paramagnetic salts.
4. Lonsdale, K. and Bhabha, H. J., in *Biographical Memoirs of the Royal Society of London*, 1962.
5. Abragam, A. and Bleaney, B., *Electron Paramagnetic Resonance of Transition Metal Ions*, Clarendon Press, Oxford, 1970.
6. Krishnan, K. S., *Nature*, 1939, **143**, 600.
7. Van Vleck, J. H., *J. Chem. Phys.*, 1939, **7**, 72.
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(Ph D supervisor of P. W. Anderson) admiration for K. S. Krishnan. Another such instance involving Van Vleck is quoted in the article by K. Lonsdale and H. J. Bhabha (ref. 4).

9. A close look at K. S. Krishnan's style of paper writing shows that typically he starts with a short letter style paper and ends with a series of long papers presenting the details of his experimental investigations. Roughly in each five, six years he goes for new pastures.
10. See for example, Kundu, T. K. and Manoharan, P. T., *Chem. Phys. Lett.*, 1997, **241**, 627; 1997, **264**, 338; Kundu, T. K., Ph D thesis, Chemistry Department, IIT, Madras, 1997; Kundu notes that in solutions the counter ions can affect (renormalize) the cross over temperature considerably in some cases.
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