some of the aspects in which I have played a role, and have projected the usefulness of high pressure as a tool in elucidating the spin density wave state of Cr and Cr-alloys.

1. Arrott, A., *Magnetism* (eds Rado, G. T. and Suhl, H.), Academic Press, New York, 1966, vol. 2B.
2. Bacon, G. E., *Acta Crystallogr.*, 1961, 14, 823.
3. Lomer, W. M., *Proc. Phys. Soc. (London)*, 1962, 80, 489.
4. Overhauser, A. W., *Phys. Rev.*, 1962, 128, 1437.
5. Fedders, P. A. and Martin, P. C., *Phys. Rev.*, 1965, 143, 245.
6. Rice, T. M., Jayaraman, A. and McWhan, D. B., *J. Phys. Colloq.*, 1971, 32, C1–39.
7. Fawcett, E., *Rev. Mod. Phys.*, 1988, 60, 209, and references cited therein.
8. Fawcett, E., Alberts, H. L., Galkin, V. ru., Noakes, D. R. and Yakhmi, J. V., *Rev. Mod. Phys.*, 1994, 66, 25.
9. Ramesh, T. G. and Shuba, V., Proceedings of the Kalapakkam IGCAR Conference, 1997.
10. Endoh, Y. E., Mizuki, J. and Ishikawa, Y., *J. Phys. Soc. Japan*, 1982, 51, 2826.
11. Iida, S., Kawara Zaki, S. and Kunitomi, N., *J. Phys. Soc. Japan*, 1981, 50, 3612.
12. Nakanishi, K. and Kasuya, T., *J. Phys. Soc. Japan*, 1977, 42, 833.
13. Teraoka, Y. and Kanamori, J., *Inst. Phys. Conf. Ser.*, 1978, No. 39, 588.
14. Arajs, S., Aidun, R. and Moyer, C. A., *Phys. Rev. B.*, 1980, 5366.

Modern magnetism and the pioneering experiments of K. S. Krishnan

A. K. Raychaudhuri

National Physical Laboratory, K. S. Krishnan Road, New Delhi 110 012, India

In this article we relook at the pioneering experimental contributions of K. S. Krishnan in the area of magnetism. In the early days of quantum mechanics when it was applied to understand magnetism, the precise experiments of his on magnetic anisotropy of diamagnetic as well as paramagnetic crystals provided the much needed experimental foundation for our understanding of an important component of modern magnetism. Classic was his experiment on the Landau diamagnetism of graphite which was shown for the first time as a model of 2-d free electron gas. He was current and much ahead of his peers. He combined most recent physical concepts with precise experiments.

THOSE were the days in twenties when the physics of solids was getting its foundations built on the newly discovered wave mechanics. From atoms and molecules to solids—the basic concepts were developed and many unanswered questions were settled. For the pioneers, magnetism in solids was the frontier that needed to be explored.

Theoretical work of Bethe[1], Van Vleck[2] and others had set the frame work in which one could understand magnetism in solids. The period 1925–1935 saw some of the basic concepts developed. New experiments were done to give support to these theories. It is in this period K. S. Krishnan and his colleagues did some of the most precision experiments in magnetism that gave the much required quantitative base to the new theories. The experiments started when K. S. Krishnan joined C. V. Raman as a research scholar in 1922 at the Indian Association for the Cultivation of Science (IACS) at Bowbazar, Calcutta. He followed it up as a Reader in Physics at Dacca University (1929–1933) and then again as a Professor (occupant of the prestigious Mahendra Lal Sircar Chair) at IACS till he left for Allahabad. During his stay in IACS between 1933 and 1942, Krishnan made two pioneering contributions. (C. V. Raman who occupied the M. L. Sircar chair prior to Krishnan left for IISc, Bangalore in 1933.) Through a series of magnetic susceptibility measurements down to liquid air temperature he established experimentally the role of crystalline electric field on the energy levels of transition metal ions in a solid and particularly the role of crystal symmetry. The second was even more fascinating. From a measurement of magnetic susceptibility of crystalline graphite from 1250 K to 90 K he showed how the theory of Landau diamagnetism of free electron gas can be used to explain the results. He bravely made the suggestion that the electrons in the basal planes of graphite form a 2-d free electron gas. Needless to say the work on graphite received instant recognition from the international scientific body. The Royal Society had to invite yet another Professor from Bowbazar to London. The experiment on graphite was so advanced both in techniques and physical analysis of the data that it was nearly a decade after this that experimenters in other parts of the world started achieving this level of sophisti-

e-mail: arup@csnpl.ren.nic.in

cation. It will be not be an overstatement to say that the M. L. Sircar Professor of 210, Bowbazar Street was the leader on these experiments and remained so till he left for Allahabad to take over the chair left vacant by M. N. Saha. (Note: It is not clear to me, however, why Krishnan did not continue to do experiments on magnetism in Allahabad (1942–1947) or in the National Physical Laboratory 1947–1961. I leave the problem to the historians of science to throw some light on).

Between 1926 and 1941, Krishnan published 43 papers on magnetism covering essentially four broad themes: (1) the magnetic double refraction in liquids, (2) diamagnetic anisotropy and orientation of molecules in crystals, (3) paramagnetic anisotropy – in particular the crystal field effects and (4) the susceptibility of graphite and Landau diamagnetism. It is impossible to review the colossal contribution of Krishnan in this field in a short review article. I will rather try to bring out the essential themes and the highlights.

Experiments on diamagnetic anisotropy

Can the electronic orbits in an atom in a solid (which are supposed to be spatially quantized in a magnetic field) be oriented in a magnetic field? Can the magnetic measurements find out orientation of these orbits in a solid? These two basic questions formed the theme of Krishnan's work on measurements of diamagnetic anisotropy in a solid. It was known from the work of Cotton and Mouton[3] as well as previous work of Raman and Krishnan[4] that certain liquids become double refracting in a magnetic field. (Note: This implies that the refractive index of the isotropic liquid becomes anisotropic in the magnetic field.) The reason being that the diamagnetic molecules of these liquids are magnetically anisotropic which arises due to alignment of orbitals in a magnetic field. Krishnan argued that molecules will preserve this aniosotropy in a crystal. If these molecules are arranged in a crystal in a regular manner, 'the crystal as whole, will usually exhibit differences in magnetic susceptibility in different directions. The magnitude of the differences (i.e. value of the anisotropy) will evidently depend on the relative orientations of the molecule in a unit cell'. In 1929 he proposed that a correlation of magnetic anisotropy of molecules (measured from magnetic double refraction measurements in solution) and the magnetic anisotropy of the crystal can be used to find the molecular orientation in the latter. Krishnan et al.[5] showed in 1933 on inorganic crystal, organic solids and fused crystals that this indeed is the case[5]. They used a torsion method (working at room temperature) and were able to measure a diamagnetic susceptibility anisotropy as small as 0.1×10^{-6} cgs units and were able to use X-ray determined structural data to correlate with their experiment.

The precise measurement of diamagnetic anisotropy of crystals was indeed difficult experiments in those days. It is only with the advent of sensitive SQUID magnetometers that these experiments can be done today regularly. It laid the foundation of quantum mechanical calculation of these quantities in future and probably it was also the place from which the modern topics of magnetism in organic and polymeric solids began.

Magnetic anisotropy of paramagnetic salts and the crystal field effects

For ions belonging to the transition metal series in the periodic table there is a permanent magnetic moment originating from the spins of the electrons which are unpaired. These ions when they exist in a solid make the solid paramagnetic by overcoming the weak diamagnetism coming from the orbital effects. These moments can interact with each other and can align below a certain temperature giving rise to magnetic order like the ferromagnetism and antiferromagnetism. In these phenomena the crystal structure and symmetry in which the ions sit play a very crucial role. For an isolated ion the five d-levels are degenerate although the symmetry of the orbits is distinct. When the ion is placed in a crystal the different orbits of the d-levels see different electric fields arising from the neighboring ions of the crystals due to different spatial extent of the orbits. Bethe[1] in 1929–1930 formulated the theory of 'Stark-splitting of energy levels of paramagnetic ions in crystal'. In this theory the 5-fold degenerate d-levels are split into a group of three and two levels. The group of two levels (two-fold degenerate) form the ground state when the magnetic cation in question sits in an octahedral coordination with 6 nearest neighbour ions. When the coordination is tetrahedral the group of 3 levels (3-fold degenerate) forms the ground state. In 1932 Van Vleck[2,6] and also Penney and Schlapp[7] formulated the basic theory and they found that in a crystal the magnetic behaviour of paramagnetic ions will get substantially affected by the crystalline electric field. In the ground state the ions will show magnetic moments arising from the spins only – a phenomena which we now call the quenching of the orbital moments.

Within a year Krishnan et al.[8] published a comprehensive work on the measurement of anisotropy in the magnetic susceptibilies on a large number of hydrated and unhydrated salts of transition metal elements Mn, Fe, Co, Ni and Cu. They showed that the salt $MnSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ has the least magnetic anisotropy (close to the diamagnetic susceptibility) and correctly correlated that to the fact that the Mn^{2+} ions are in the S-state. They also found that the magnetic moment of the ion

is what one gets from the spin only value. Similar behaviour was also found for the Ni^{2+} ions in nickel salts that the magnetic moment arises from only the spins. These experiments put the theoretical work of Bethe, Van Vleck and others on a firm ground and this formed one of the most complete works in this field. After decades these ideas have become such a common place (and are found in all texts of magnetism) that we forget that it took some of the best minds of that time to make such a complete work of both theory and experiment. Krishnan was not only current but he was also immensely competitive. He did all these experiments within a year or two of the publication of the theoretical works. Krishnan followed up this seminal work with more experiments. He soon realized that measurement of susceptibility at room temperature alone will not suffice. In his own words in 1932: 'Measurements on the susceptibilities of these crystals at low temperatures have been started; detailed discussion of the Curie and Weiss constants of the crystals in relation to their structure will be attempted when these measurements are completed'. Krishnan along with Mookherjee and Bose[9] published in 1939 the measurements of susceptibilities of paramagnetic salts down to 90 K. This work was done at IACS. This time the study extended even to the rare-earth salts which Krishnan envisaged will be somewhat different from the iron-group transition metal salts. The apparatus made by Krishnan and his co-worker could measure the magnetic anisotropy with temperature and the cryostat had automatic temperature control. (I am told that the apparatus still exists.) It was a high precision apparatus. In Figure 1 the schematic is reproduced.
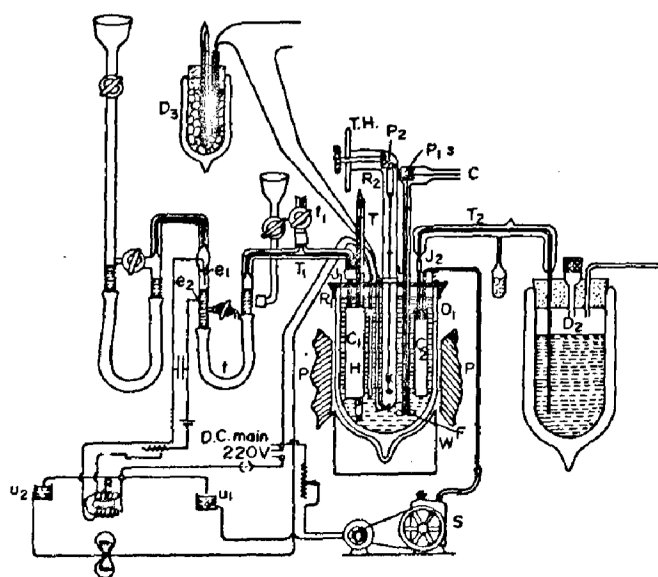

Figure 1. The experimental apparatus of Krishnan to measure anisotropic susceptibility down to 90 K (ref. 9).

From the temperature dependence of the anisotropy of the susceptibility $\Delta\chi$ they could measure the spin orbit coupling constant λ using the relation[7]

$$\Delta\chi = (8N_A \mu_B^2/3k_BT)[8\lambda - 2(\lambda^2/k_BT) - 3k_BT]\Delta\alpha. \quad (1)$$

Here $\Delta\chi$ is the anisotropy in the susceptibility (χ) in the plane of a crystal per g molecule. N_A is the Avogadro's number, μ_B is the Bohr magnetron and $\Delta\alpha$ is a temperature independent factor which depends on the symmetry of the crystal. Krishnan and his co-workers were able to measure a value of $\lambda \approx -330\ cm^{-1}$ from their experiments on measurement of $\Delta\chi$ as a function of T on the Ni^{2+} ion containing solid $NiSeO_4 \cdot 6H_2O$. This matches very well with value of $\lambda \approx -335\ cm^{-1}$ obtained from spectroscopic experiments. This is yet another example of the completeness of the work of Krishnan which used to clinch an issue with quantitative correctness of his experiments. The experiments of Krishnan on the temperature dependence of magnetic anisotropy of rare-earth containing salts $Pr_2(C_2H_5SO_4) \cdot 18H_2O$ and $Sm_2(C_2H_5SO_4) \cdot 18H_2O$ produced some fascinating results where it was shown that the magnetic anisotropy $\Delta\chi$ as function of T shows a maximum and is not a monotonous function of T. Krishnan realized that this has to do with the higher multiplet levels which may lie not too far away from the ground level in these ions. A proper theoretical explanation of this observation came much later but it only confirmed the great intuition of Krishnan.

Magnetic anisotropy of S-state ions in certain crystals and implication on adiabatic demagnetization

Debye[10] and Giauque[11] suggested that paramagnetic salts will produce cooling when they are demagnetized adiabatically and this will enable to attend temperatures well below 1 K. The basic concepts of adiabatic cooling is easy to comprehend. The magnetic field by aligning the spins will produce a system of lower entropy. When the magnetic field is removed adiabatically (so that it cannot exchange entropy with the surrounding) a system of effective lower temperature is produced which then acts as a sink of heat energy for the lattice and the solid cools. The important issue of adiabatic demagnetization is that the magnetic entropy which arises from the moment carrying ions can be substantially lowered by a magnetic field. In 1935 Kurti and Simon performed the land mark experiment on adiabatic cooling[12]. In their experiment they used salts containing Gd^{3+} ions which have zero orbital moments, i.e. the ions are in the S-state. The orbital moment being zero, the spin orbit coupling will be zero and there will be no internal field to align the spins – so that the external magnetic field will have complete control on the magnetic entropy. This is a desirable feature for a salt used for magnetic

1209

cooling. This can be expressed as the ratio of initial temperature T_i and the final temperature T_f after removal of the applied field of magnitude H and is given by:

$$T_f / T_i = E_m / E_i = k_B \theta_m / g \mu_B H, \qquad (2)$$

where g is the Lande g-factor. Thus the final temperature depends on the ratio of the small crystal field energy characterized by the temperature θ_m and the Zeeman energy in the field H. For an S-state ion like Gd^{2+} the expectation was that $\theta_m = 0$. But experimentally it was found that θ_m is small but $\neq 0$. This appeared as a puzzle. It was the experiments of Krishnan and his co-workers done on salts containing S-state ions which solved the puzzle[13]. Krishnan argued that these S-state ions (following an idea of Kramers, Bethe and Van Vleck[14]) will show a 'feebly' separated multiplet structure in zero magnetic field due to higher order crystal field effect and this will lead to a feeble magnetic anisotropy in χ even at room temperature. (In absence of this an S-state ion will show an anisotropy only from the diamagnetic contribution). The IACS team then did an extensive work of measurement of the anisotropy in χ on salts containing S-state ions (like Mn^{2+} ions). They separated out the ordinary diamagnetic contribution by measurements on isostructural solids with non-magnetic ions like Mg and Zn and found that there is indeed a feeble anisotropy which arises from this S-state paramagnetic ions. From their experiments they were able to find the magnitude of $\theta_m \approx = 0.1$ K, which is the same as found from the adiabatic demagnetization experiments done at $T < 1$ K. One should appreciate the vast knowledge of Krishnan and his intuition that he could immediately establish connection between these two phenomena and did the experiment within a year of Kurti and Simon experiment. We should also gauge the extent of precision that he was able to detect an energy scale of 0.1 K from an experiment done at 300 K. (The story goes that Krishnan did not have a good electromagnet needed to carry out the work. He borrowed it from P. C. Mahalanobis, who was then Professor of physics at the Presidency College. Krishnan got the good gadolinium sulphate crystals from Giaque on which he did the magnetic cooling experiments. An outstanding example of resource networking when there was no e-mail or internet!)

Magnetic anisotropy of graphite – A model of 2-d free electron gas

In 1937 Krishnan (along with N. Ganguly[15]) published a very interesting observation that the diamagnetic susceptibility of graphite single crystal is abnormally large at room temperature when the susceptibility is measured along the hexagonal c-axis (see Figure 2). Not only that the diamagnetic χ increases as T is decreased! On the other hand the χ in the basal plane is small (close to what one expects from the orbital contribution) and is temperature independent. The result was puzzling indeed. It was also a difficult experiment since it was done over a wide temperature range from 1250 K to 90 K. In 1941 Krishnan and Ganguly came up with a brilliant explanation of this effect[16]. They argued that the diamagnetic contribution seen along the c-axis arises from the electrons confined to the basal plane. (It is known now that the bonding in graphite is of 2-dimensional type which creates a two-dimensional free electron gas confined to the basal plane.) From their analysis they concluded that the 2-d electron gas has a rather low degeneracy temperature of 520 K and the susceptibility is the Landau diamagnetism. Since the degeneracy temperature is low χ is so strongly temperature-dependent (Note: Degeneracy temperature T_F is a measure of a temperature which roughly divides the classical behaviour from the quantum behaviour which follows Pauli's exclusion principle. At $T \gg T_F$ the gas is like a gas of electrons following the classical Boltzman statistics and at $T \ll T_F$ the electron gas follows the Fermi–Dirac statistics. For ordinary metals $T_F \geq 10^4$ K. As a result, even at a very high temperature the electron gas is still degenerate). This explanation needed few questions to be sorted out: (1) why is the degeneracy temperature so low? (2) why is the graphite electron gas like a 2-d system? and (3) why is the Pauli paramagnetism of electrons (which generally masks the Landau diamagnetism) not seen here?

Krishnan and co-workers had the following explanations:

(1) They argued that in the presence of a lattice when the free electron mass can be replaced by some effective mass the degeneracy temperature T_{FG} is given as

$$T_{FG} / T_F = (\alpha_1 \alpha_2 \alpha_3)^{1/3}, \qquad (3)$$

where the αs arise come from the energy ellipsoid $E = (\hbar^2 / 2\ m)\ (\alpha_1 k_x^2 + \alpha_2 k_y^2 + \alpha_3 k_z^2)$, $k s$ being the wave vector of electrons. For graphite with one electron per atom
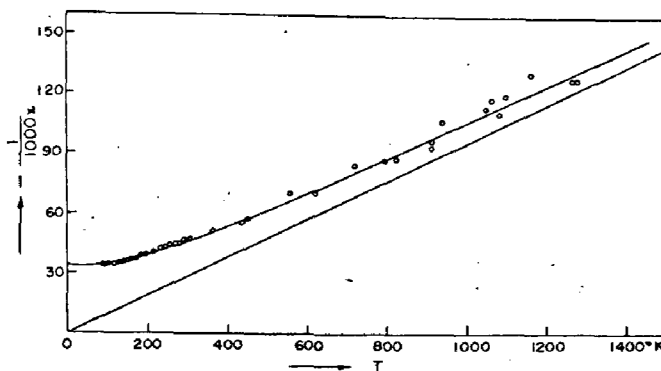

Figure 2. Diamagnetic susceptibility of graphite from 1200 K to 100 K measured by Krishnan and Ganguly (refs 15 and 16).

1210

the free electron (without lattice effects) $T_F \approx 98,000$ K. Observed T_{FG} is 520 K. So they concluded that α_3 is about $(1/190)^3$ of α_1 and α_2 both of which are nearly 1. This implies that the electron mass in the basal plane is like a free electron but the effective mass in the c-axis is $(190)^3$ times larger!

(2) The 2-d nature of graphite has its origin in the bonding as well as in the special structure of the Brillouin zone. The first zone which is a flat hexagonal prism with its axis along the c- axis, contains 3 electrons. They form a closed group and do not contribute to the free-electron gas under consideration. The second zone separated from the first by large energy discontinuity can accommodate one electron. It is this electron that exhibits the 2-d behaviour.

(3) The Pauli paramagnetism arises because of the unpaired spins near the Fermi surface whose energies lie within an energy scale $k_B T$ of the degeneracy energy $k_B T_F$. However, if there is a coupling of opposite spins (due to some reason) and the coupling energy is much larger than $k_B T$ then the unpaired spins will not exist and the Pauli paramagnetism will be not observable! Krishnan predicted that like many aromatic molecule there will exist in graphite a quantum mechanical reason to have spin pairing.

The work on graphite done by Krishnan and co-workers is of great interest. Not only was it modern then, it also has implications in many recently discovered phenomena in physics!

What do we learn from the life and work of Krishnan?

The experimentalists today (and specially those who would dare to win working in India) can learn six very important lessons from the works of Krishnan which I think made him one of the most successful experimentalists of his time. The lessons are: (1) Be current, pay attention to evolving modern concepts and work on problems of current interest. (2) Care for precision and do high precision experiments. (3) Pay attention to quantitative details and try to attend to the underlying physics quantitatively. (4) Have a broad perspective and intuition and do not confine only to a narrow area. (5) Try to network resources. (6) Be quick to produce results and be competitive enough to remain in the forefront.

1. Bethe, H., *Ann. Physik.*, 1929, **3**, 133.
2. Van Vleck, J. H., *Phys. Rev.*, 1932, **41**, 208.
3. Van Vleck, J. H., *Phys. Rev.*, 1932, **41**, 208.
4. Raman, C. V. and Krishnan, K. S., *Proc. R. Soc*, 1927, **A113**, 511.
5. Krishnan, K. S., Guha, B. C. and Bannerjee, S., *Philos. Trans.*, 1933, **A231**, 235.
6. Van Vleck, J. H., *The Theory of Electric and Magnetic Susceptibilities*, Oxford.
7. Schlapp, R. and Penney, W. G., *Phys. Rev.*, 1932, **42**, 666. and Penney, W. G., Schlapp, R., *Phys. Rev.*, 1932, **41**, 194.
8. Krishnan, K. S., Chakravorty, N. C. and Bannerjee, S., *Philos. Trans.*, 1933, **A232**, 99.
9. Krishnan, K. S., Mookherjee, A. and Bose, A., *Philos. Trans.*, 1939, **A238**, 125.
10. Debye, P., *Ann. Physik.*, 1926, **81**, 1154.
11. Giaque, A., *J. Am Chem. Soc.*, 1927, **49**, 1864.
12. Kurti and Simon, *Proc. R. Soc.*, 1935, **A149**, 135.
13. Krishnan, K. S. and Bannerjee, S., *Philos. Trans.*, 1936, **A235**, 343.
14. Kramers, S., Bethe, H. and Van Vleck, J. H., *Philos. Mag.*, 1934, **17**, 961.
15. Krishnan, K. S. and Ganguly, N., *Nature*, 1937, **139**, 155.
16. Ganguly, N. and Krishnan, K. S., *Proc. R. Soc.*, 1941, **A177**, 168.