

be studied by allowing the electron stream to effuse through a small orifice. Along with S. C. Jain, a set of investigations were done to confirm these vapour pressure measurement ideas and to estimate the thermionic emission constants of several materials. Krishnan's versatility allowed him to solve a number of mathematical questions concerning the temperature distribution of such systems.

The collected works of K. S. Krishnan were edited by K. Lal and brought out by the National Physical Laboratory in 1988.

In his personal life, Krishnan was one who combined deep scholarship in many areas with high human values of ethics and justice. He was at the same time a model of humility and dignity, with no

trace of arrogance. His mastery of Sanskrit and Tamil literature as well as Indian philosophies made him an unusually rounded personality. He loved tennis and bridge and could be quite witty in conversation. When he died, he left behind his wife, two sons and four daughters as well as numerous other colleagues to mourn the loss.

The scientific stature of Krishnan attracted numerous honours. The fellowships of almost all Indian Academics, and of several Academics/Societies abroad, the Knighthood of the British Government, the first Bhatnagar Memorial Award, the National Professorship at the age of 60 and numerous honorary doctorates rested lightly on his shoulders, making no difference to his humility and

human qualities. In the late forties and fifties, he had to spend considerable time in working with the Council of Scientific and Industrial Research, University Grants Commission, Department of Atomic Energy and several other government agencies. All these he did along with his pursuit of science and culture.

He was perhaps a current day model of the ancient sages or rishis who made India great.

*E. S. Raja Gopal is in the Department of Physics, Indian Institute of Science, Bangalore 560 012, India and National Physical Laboratory, New Delhi 110 012, India.*

## K. S. Krishnan: A pioneer in condensed matter physics

*T. V. Ramakrishnan*

K. S. Krishnan was among the first to explore many interesting phenomena in the solid and liquid states of matter after the birth of quantum mechanics. He was very much at ease with the then new wave mechanics and used its ideas creatively and imaginatively. He developed apparently simple but ingenious experimental techniques for measuring solid state properties. He recognized and exploited connections between phenomena in different fields of physics. He was very perceptive in realizing the significance of many new and old observations concerning condensed matter, often presaging their formal elaboration by decades. It is specially necessary to recall these aspects now, when the prevailing ethos is one of often extreme specialization in form and content. I shall try to briefly summarize here some of Krishnan's contributions to condensed matter physics from the points of view mentioned above. Some of the areas to which he contributed are: molecular arrangement in solids and liquids using magnetic and optical anisotropies, electronic nature of graphite as reflected in its diamagnetism, the Jahn-Teller effect, the essential role of structural disorder-order in the electrical transport properties of elemental solid metals as well as alloys and liquid metals, and finally the determination of work function of metals.

In a series of papers extending over several years, Krishnan and his collaborators, first at Dacca and later in Calcutta, showed how the magnetic properties of many aromatic molecular crystals and of inorganic complexes<sup>3-6</sup> reflect molecular anisotropies, bonding and crystal field effects. Clever techniques such as immersing the crystal in a fluid with the same average magnetic susceptibility so that the small residual crystalline anisotropies stand out and can be accurately measured, and new ways of measuring small torques even for tiny crystals, were some of the tools that enabled them to get the numbers needed. Krishnan and collaborators chose a number of homologous or closely related families. From the values of the diamagnetic susceptibility and its anisotropy, compared with crystal structural (X-ray) information, optical anisotropy, and molecular calculations, they sought to obtain quantitative measures of how different side groups or addition of benzene rings changes molecular size, shape, rigidity and orientation.

An equally impressive achievement is the work on paramagnetic ions in crystals, where using magnetic measurements, many of the crystal field theory-based ideas of van Vleck and coworkers are substantiated<sup>3,4</sup>. For example in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , from the size sign of mag-

netic anisotropy, the actual symmetry of the crystalline electric field as well as the rhombic deviation from cubic symmetry of this field, and the coincidence of crystalline field and magnetic axes are inferred<sup>4</sup>. The small room temperature deviation from Curie law ( $\chi \propto T^{-1}$ ) for the magnetic susceptibility in Tutton salt,  $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is connected with the Final temperature reached in its adiabatic demagnetization<sup>5</sup>.

A study of nearly hundred rare earth and transition metal ion salts is used to 'map out' the systematics of crystalline electric fields at these ion sites as a function of electronic configuration and crystal structure<sup>6</sup>.

This whole effort is remarkable for clarity of physical insight, the cogency of many different types of arguments used, the kinds of evidence marshalled, completeness, sustained effort and even lucid writing! This was one field where quantum mechanical wave function ideas were first applied successfully to crystals, and Krishnan was clearly an imaginative leader in giving substance to this enterprise.

A very interesting anomaly which Krishnan spotted is the diamagnetism of graphite<sup>7</sup>. The diamagnetic susceptibility is much larger for magnetic field perpendicular to the basal plane than for field along the plane, by a factor of forty

The collective way of learning and doing science is very important. This is particularly true when one is a student in a college or a research scholar in a university, a research institute or a laboratory. In our own country there are isolated centers like the Presidency College in Calcutta, which continue to produce first rate students. One of the reasons behind this is the (fast disappearing) tradition of students learning new things on their own in group discussions and in the process going deep and beyond what one learns in the classroom.

I heard this several years ago, but do not remember from whom, that KSK was involved in organizing several group discussions even when he was a student in American College, Madurai. G Venkataraman, in his book *Journey into Light* confirms this in the following passage: 'Krishnan took a master's degree in physics but the only opening then available to him was a Demonstrator in Chemistry in Madras Christian College. During this period, Krishnan ran an informal but highly successful lunch-hour discussion on diverse topics in physics and chemistry which soon began to attract participants from other colleges as well. One beneficiary later remarked that he had learnt more physics from the lunch-break seminars than from regular class-room lectures.'

One cannot explain the power and usefulness of group discussions—it has to be experienced. When I was a student at the Indian Institute of Science, Bangalore, a few of us students of physics from IISc and NAL were introduced to this joyous experience by S. K. Rangarajan, formally a professor of chemistry, in whose house we assembled virtually every evening to discuss such grave issues as amorphous solids and renormalization group. Each one of the discussants has made a mark. Such informal discussions are even more valuable in smaller and isolated institutions.

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or so. The latter has a size typical of other diamagnetic solids. Krishnan and collaborators obtained and made high quality samples of graphite and related derivatives, and experimentally determined the magnetic behaviour as a function of temperature, intercalation, crystallite size, etc. Krishnan then showed that over a wide temperature range  $77 \text{ K} \leq T \leq 1300 \text{ K}$ , the data fit a phenomenological (two dimensional) free electron gas model with *one* electron per unit cell, and a degeneracy temperature of about 500 K. This raises a number of questions which are all mentioned by Krishnan, who also explored possible answers. Each carbon atom contributes four electrons, so why does the high temperature limiting form ( $\chi_{\text{dia}} = -n\mu^2/3k_B T$ ) point to there being only one? If only one, why is there no Pauli paramagnetism? The degeneracy temperature of a free electron gas with the density corresponding to graphite is about  $1 \times 10^5 \text{ K}$ . So what is the cause of an energy scale nearly 200 times lower? Is a semimetallic state the cause? What kind of semimetal is it? While elaborate band structure calculations lit the experiment, there is, as far as I know, no deeper theory that encapsulates the anomalous behaviour so clearly recognized and described phenomenologically by Krishnan.

The third area that I would like to highlight is the work of Krishnan and

Bhatia<sup>8-10</sup> on electrical transport in metals. Here, Krishnan recognized and exploited the analogy between light (electromagnetic wave) and electron wave scattering from dense matter. In a beautifully detailed calculation<sup>10</sup> the resistivity of solid sodium was calculated by finding the current relaxation rate of each electronic state  $\mathbf{k}$  ( $|\mathbf{k}| = k_F$ ), (the Fermi wavevector magnitude) as a result of scattering by anisotropic elastic fluctuations of the lattice. Consequently, the relaxation rate itself is seen to depend on the orientation of (the state)  $k$  with respect to the crystalline lattice. This was a new idea at the time. In a slightly earlier work, Bhatia and Krishnan<sup>8</sup> analysed the resistivity of a binary alloy,  $A_c B_{1-c}$ . They showed that this is the sum of two parts. One arises from the averaged atomic scattering cross-section multiplying the fluctuation of average density, very much as in light scattering from a medium (Einstein and von Smoluchowski). The other is due to the difference in the scattering cross-sections of  $A$  and  $B$  which couples to fluctuations in relative concentration  $c$ . Now near an order-disorder transition in the arrangement of  $A$  and  $B$  atoms on the lattice, the latter is directly related to fluctuations in the order parameter: it can be strongly temperature-dependent. Bhatia and Krishnan used the approaches available for order-disorder transitions (Bragg and Williams, Bethe, . .) both below and above

$T_c$ , and the concentration fluctuations resulting therefrom. They then applied their results to explain the temperature dependence of resistivity  $\rho$  in Cu-Zn alloy which has an order-disorder transition at 742 K. A comprehensive discussion which includes consequences of the Brillouin zone change in the equiatomic ordered phase, possible effects of short range order below  $T_c$ , a more sophisticated approximation (used) for short range order above  $T_c$  and the resulting temperature dependence of  $\rho$ , all together give this work a timeless flavour.

The line of thinking initiated in the work on resistivity of binary alloys led to a short classic paper in *Nature*<sup>9</sup> on the resistivity of liquid metals. The idea, clear to those familiar say with X-ray scattering from liquids, is that the scattering cross-section from such a medium for wavevector transfer (or change)  $\mathbf{q}$  is given by the product of an atomic form factor (atomic scattering cross-section)  $\sigma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$  times a static structure factor  $S(q)$  which depends on the spatial arrangement of the scatterers in the liquid. Precisely the same approach enables one to calculate electron scattering rates from liquids (and solids). In the long wavelength (small  $q$ ) limit, this reduces to scattering from average density fluctuations, determined by compressibility. Bhatia and Krishnan argued that this could be adequate if the Fermi energy electrons have a wavelength that is small as is the

case for first group elements.  $S(q)$  has a peak near the smallest reciprocal lattice vector  $\mathbf{G}_s$  of the solid into which the fluid freezes. So if the elastic scattering events  $|\mathbf{k} + \mathbf{G}_s| \cong |\mathbf{k}|$  are not possible with  $|\mathbf{k}| \cong k_F$ , electron scattering will be low. If they are, the scattering is substantial and the resistivity is high. They argued that this is the essential reason why divalent liquid metals with longer  $k_F$  are much more resistive than monovalent ones [ $S(q \sim 0)$  is typically twenty or more times less than  $S(q \cong G)$ ]. The work anticipates, by almost two decades, that of Ziman<sup>11</sup> on resistivity of liquid metals and that of Greene and Kohn<sup>12</sup> on the electrical resistivity of sodium. The additional crucial idea these authors use is that of a weak pseudo-potential, i.e. the relative weakness of the effective interaction between an electron and an ion (in an *sp* band or simple metal). This pseudo-potential can be calculated and then a low order expansion in it suffices. The lowest order process involves the structure factor (in general the dynamic structure factor  $S(\mathbf{q}, \omega)$ ). For example, Greene and Kohn<sup>12</sup> show how the conventional electron-phonon scattering theory of Bloch, and the liquid metal transport theory of Ziman<sup>11</sup> are contained in a single formalism, and how quantitative resistivity calculations can be made knowing the pseudopotential  $v(q)$ , the phonon spectrum for  $S(\mathbf{q}, \omega)$  and the measured static structure factor  $S(q)$  for the fluid phase. They also remark on the location of the

Fermi wave vector with respect to the peak of the structure factor (or the smallest reciprocal lattice vector  $\mathbf{G}$ ) and made a detailed analysis of the relative importance of umklapp processes.

Perhaps the last major contribution of Krishnan to condensed matter physics was a new approach to determining the work function of a metal<sup>13</sup>. Here again the basic idea is deceptively simple: measure the equilibrium saturation vapour pressure of electrons coming out of the hot metal from a hole in it and in thermal equilibrium with the metal. The actual measurement of this small pressure from the effusion current is a delicate affair, but the approach has obvious advantages, such as independence with respect to surface conditions and partial electron reflection from the surface (which affect thermionic emission rates). The results for graphite, several semiconductors, and transition metals have since been superseded, but it remains an original attempt.

For almost a quarter of a century, Krishnan seems to have been more or less the lone Indian practitioner of the quantum approach to understanding phenomena in condensed matter, doing both theory and experiment as necessary.

The ease of approach, the sure touch, and the freshness of many of Krishnan's contributions coming across a gap of more than half a century are indeed unusual. I am grateful to the editors of the centenary issue for this experience, and invite readers to savour the treat for themselves.

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*T. V. Ramakrishnan is in the Department of Physics, Indian Institute of Science, Bangalore 560 012, India.*

## K. S. Krishnan—the complete physicist

*R. Sundaram*

In the scientific circles abroad C. V. Raman was described as a giant light scatterer, M. N. Saha as a great astrophysicist, S. N. Bose as a great theoretician of boson fame, H. J. Bhabha as a great theoretician of cosmic ray fame and K. S. Krishnan as the complete physicist. Krishnan started his career with Raman and did extensive investigations on the scattering of light in a large number of liquids. He also did original work on the magnetic properties of crystals in relation to their structure. Later he did theoretical investigations on the electrical conduc-

tivities of metals and alloys. He had attained international fame at an early age. He could comment on all areas of physics with a high degree of excellence. He had an uncanny ability to penetrate to the roots of any problem, be it classical or quantum. It is because of his versatile knowledge, we felt, he was chosen to be the founder director of the National Physical Laboratory, India. I had the good fortune to be selected by Krishnan as a scientific assistant from the very inception of the laboratory. In this centenary year of Krishnan I pay my tributes to this

eminent physicist in this brief article describing his passion for physics.

Krishnan or Sir K.S. as he was referred to by his admirers, took over the directorship of the National Physical Laboratory in 1948. He was almost the first to arrive in the laboratory every day and the assistant working on the research problem assigned by Professor was invariably there. Krishnan was a great critic and the assistant will have to face his incisive logic and ruthless criticism. He had always a research problem of his own apart from the general guidance he