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## Short Communication

# Photometric study of manganese and potassium dichromate reaction in strong sulphuric acid medium

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### Abstract

The versatility of chromium(VI) as an oxidant in high sulphuric acid medium for the oxidation of manganese(II) to manganese(III) is discussed. The effective oxidizing power of chromium(VI) depended on the concentration of the acid. The reaction between manganese(II) and chromium(VI) in an acid concentration of 11·0–12·0 M was found to be rapid to start with, but the oxidation is quantitative and complete only after 4 hours time. The wine-red coloured manganese(III)-sulphate complex is stable for over a week.

Key words : Photometry, manganese(II), chromium(VI), sulphuric acid, oxidation, manganese(III)–sulphate complex.

Purdy and Hume[1] used bromate in 8 M sulphuric acid for the oxidation of Mn(II) to Mn(III). The difficulty in this reaction is the use of potassium cyanide for destroying liberated bromine. No one employed chromium(VI) in high sulphuric acid for the oxidation of manganese(II). Hence photometric study of the oxidation of manganese(II) with potassium dichromate in high sulphuric acid was undertaken.

Oxidation of manganese(II) to manganese(III) by potassium dichromate was observed in the sulphuric acid medium in the acid concentration range 2–16 M. However, quantitative oxidation of manganese(II) was possible only when the sulphuric acid concentration was maintained at 11·0–12·0 M. In this concentration of acid the wine-red manganese(III)–sulphate complex formed showed maximum absorbance at 520 nm. The absorption spectrum obtained for this complex is similar to that of Purdy and Hume[1]. To begin with oxidation of manganese(II) will be quite rapid but the complete oxidation, however, takes 4 hours time. Order of mixing of the reagents had no effect. Three fold excess of chromium(VI) is required for the total oxidation of manganese(II) to manganese(III). The wine-red complex formed is stable for over a week. The system obeyed Beer's law when the Mn(II) concentration was 1–10 mg per 25 ml of the solution and when the dichromate concentration was 0·004 M.

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# Progress of research on the Raman effect : A statistical analysis

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## Abstract

The progress of research on the Raman effect is very briefly reviewed from 1928, the year of the discovery, to the present day. The total number of publications which exceeds 23,600 up to the end of 1978 has been statistically analysed year-wise, country-wise and subject-wise. The two Raman revolutions that have taken place in the Sixties and Seventies have been satisfactorily accounted for. A glossary of different types of Raman excitations is appended.

**Key words :** Raman effect, statistical analysis of trends in research.

## 1. Introduction

While working in the Indian Association for the Cultivation of Science in Calcutta Prof. C. V. Raman discovered[1] a new scattering phenomenon in 1928 which was later designated as " Raman Effect ", in which any scattering medium could simultaneously absorb one photon and emit another of higher or lower frequency compared to that of the absorbed one. The energies of the incident (absorbed) and scattered photons differed by an amount corresponding to the energy difference between two quantum mechanical states or levels of the scattering medium. Such a process was first envisaged by an Austrian Physicist, A. Smekal[2], in a theoretical paper entitled " On the quantum theory of dispersion " published in 1923. He could not, however, foresee the far reaching significance of his conclusions till Raman discovered the phenomenon independently as a culminating event of a series of experiments carried over a period of seven years by himself and his students, particularly K. R. Ramanathan, K. S. Krishnan and S. Venkateswaran.

The fundamental and most important aspect of Raman scattering is that it provided an easily accessible tool for the spectroscopic investigation of energy levels of systems not easily accessible by the usual absorption and emission techniques. Depending on the range of energy levels and the agencies responsible for this mechanism, the Raman scattering process can now be classified under the following categories : vibrational, rotational, anisotropic (wing), electronic, second order, resonance, scattering by phonons, polaritons, magnons, plasmons, plasmaritons, Landau levels, excitons, soft modes and spin flip transitions, and non-linear effects such as Stimulated, Hyper, Inverse, Coherent anti-Stokes and Coherent Stokes Raman Scattering, Raman Induced Kerr Effect (RIKE) and Higher Order Raman Spectral Excitation Studies (HORSES), etc. These different Raman excitations are defined and explained more clearly in Appendix I.

Although the techniques used for recording and measuring Raman spectra data have undergone many changes during the last fifty years, the principal components for recording the spectra have remained the same throughout. They are: (1) a source of monochromatic radiation, (2) a container with a suitable gadget for varying the temperature and pressure of sample, (3) a dispersing instrument and (4) a detecting-*cum*-recording system. For the first thirty-five years Raman effect studies were confined to vibrational, rotational and anisotropic spectra of molecules in the gaseous and liquid states and to the internal and lattice spectra of crystals. These studies were more concerned with the establishment of quantum mechanical principles and supplying information about the structure and other fundamental parameters of molecules and crystals than with practical applications except in chemical analysis. The highlight of this era lay in the fact that there was very little innovation in the technique of study. It was extremely simple and comparatively cheap, but was exotic and laborious involving the use of 404·6 and 435·8 nm mercury radiations for excitation, ordinary spectrographs and prolonged photographic exposures. Even the technique of excitation by 253·66 nm mercury resonance radiation together with a mercury vapour filter in the path of the scattered beam extensively used by the group at Bangalore in the Forties and Fifties which gave some fillip to the work on Raman spectra of crystals and their interpretation in terms of lattice dynamics, had its own limitations[3]. In the early Sixties, Raman effect studies got a boost with the use of photoelectric photon counting techniques and the developmen of commercial Raman monochromaters. Since 1963, the rapid development of gas lasers (helium-neon, argon ion, helium-cadmium), photo multiplier scanning monochromaters with or without computer interface revolutionalized the practice of Raman spectroscopy. With the progressive development of the techniques of excitation and detection using lasers of different power. all the different types of Raman excitations (which are enumerated in the second paragraph of this paper) were discovered and recorded. Raman spectra of coloured and even opaque substances were recorded. Scattering from very small samples could now be measured with ease and as lasers allow for front scattering as well as transmitted scattering, the optical quality of the sample becomes less important. The volume of samples required for study shrank from cc's to milli cc's and it became easy to record the spectra of solutions, single crystals, powders, films, fibres, etc., maintained at any desired temperature and pressure. The introduction of spinning or flowing sample arrangements extended the utility of Raman spectroscopy still further by minimizing sample heating and consequent decomposition. This quantum jump in the applicability of the technique constituted the first laser Raman revolution and thereby the studies on Raman effect increased by leaps and bounds with regard to the range of coverage and versatility of its applications. This was the first renaissance in the history of Raman spectroscopy. Continued technological innovation and the development of more powerful lasers, tunable dye lasers, time-resolved and space-resolved Raman spectrometers and multichannel analysers and Raman microprobes have brought about a second renaissance in Raman effect studies in the Seventies.

Since the discovery in 1928 more than 25,000 papers (original articles and reviews) on various aspects of Raman effect have been published up to the end of 1979 in scientific journals, proceedings of international conferences, monographs and reports. A statistical analysis of the progress in research on the Raman effect has been carried out and the results are presented below.

## 2. Statistical analysis

Table I gives an year-wise distribution of the number of papers published arising from research on the Raman effect. The same is shown graphically in Fig. 1. The number of publications in the year of the discovery was 58, while in 1978 it is over 2,000. The diagram illustrates the very rapid rise in interest in the subject during the first few years. This is mainly due to the fact that work on similar lines was going on in France[4] and Russia[5] and with the wide publicity to Raman's first lecture[1] on March 16, 1928, giving

**Table I**

**Number of papers published**

| Year | No. | Year | No. | Year | No. |
|---|---|---|---|---|---|
| 1928 | 58 | 1945 | 77 | 1962 | 275 |
| 1929 | 175 | 1946 | 108 | 1963 | 298 |
| 1930 | 183 | 1947 | 130 | 1964 | 362 |
| 1931 | 187 | 1948 | 181 | 1965 | 403 |
| 1932 | 175 | 1949 | 155 | 1966 | 454 |
| 1933 | 129 | 1950 | 237 | 1967 | 528 |
| 1934 | 177 | 1951 | 146 | 1968 | 736 |
| 1935 | 239 | 1952 | 158 | 1969 | 756 |
| 1936 | 245 | 1953 | 212 | 1970 | 911 |
| 1937 | 217 | 1954 | 198 | 1971 | 1249 |
| 1938 | 207 | 1955 | 185 | 1972 | 1354 |
| 1939 | 159 | 1956 | 212 | 1973 | 1362 |
| 1940 | 150 | 1957 | 233 | 1974 | 1516 |
| 1941 | 150 | 1958 | 216 | 1975 | 1616 |
| 1942 | 129 | 1959 | 195 | 1976 | 2182 |
| 1943 | 86 | 1960 | 202 | 1977 | 1722 |
| 1944 | 90 | 1961 | 186 | 1978 | 2136 |

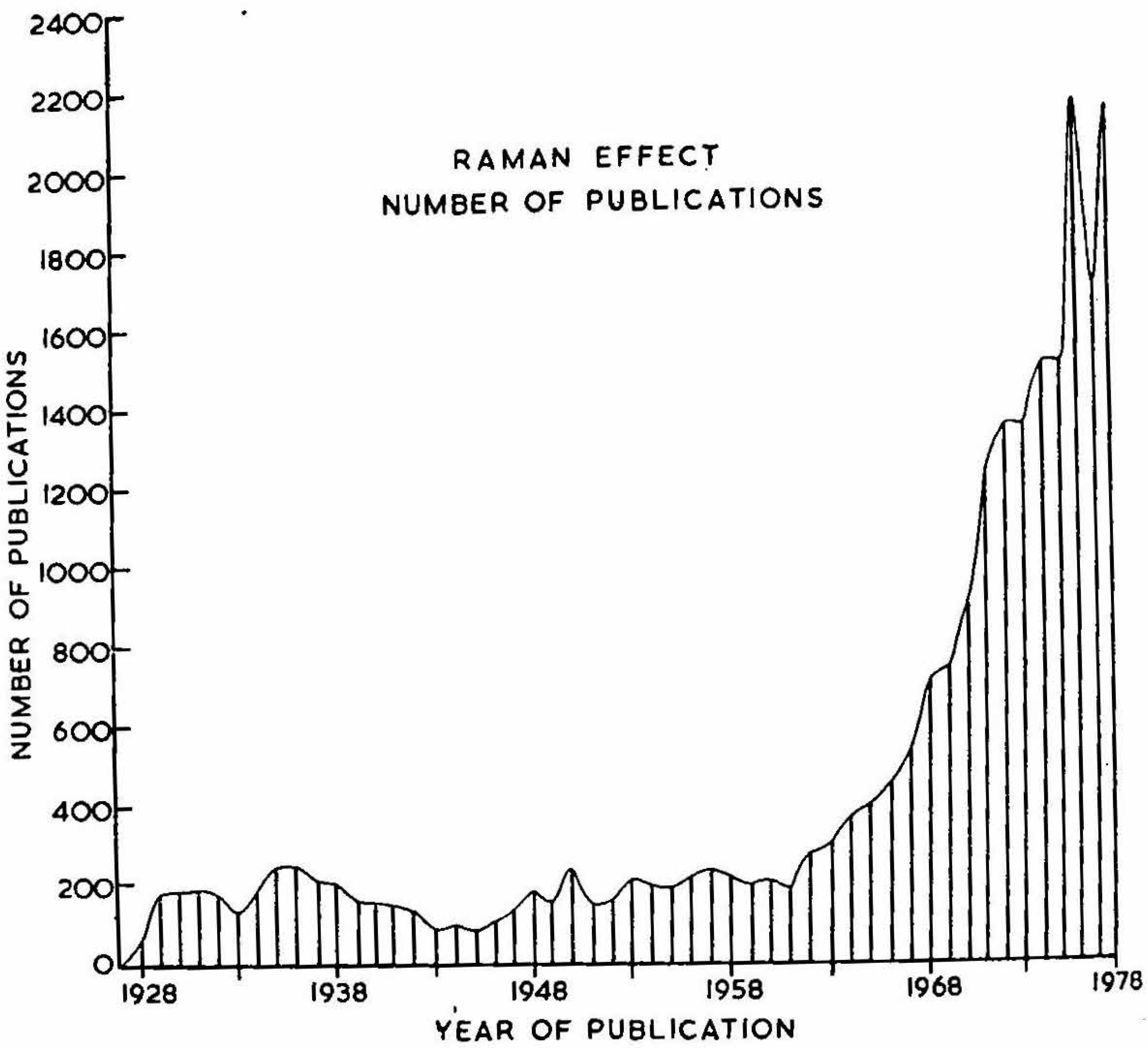

Fig. 1

details of the effect, numerous investigations were carried out in these countries and also in Germany and America. The trend exhibits a prominent dip in 1933. This is mainly due to a steep fall in the publications from India, *i.e.*, from Raman's Laboratory which was leading in the first four years. The work on Raman effect at Calcutta was practically wound up in the middle of 1932 in anticipation of Raman's shifting to the Indian Institute of Science, Bangalore, which took place in March 1933. The work on Raman, effect was started in Raman's Laboratory in Bangalore only in 1934 and went on full steam from 1935 onwards. The number of Indian publications for the years 1931, 1932 1933, 1934 and 1935 were 41, 23, 14, 25 and 43 respectively. During the year 1933, the contributions from Germany and Austria were also reduced by 47%. This should be attributed to the known reduction of funds for fundamental research in Germany at that time. Research on Raman effect in the United States had also a setback during that period. After 1934 publications picked up again. It was during this period that the Placzek's classical paper[6] on the theory of Rayleigh scattering and Raman effect appeared and with this the purely theoretical emphasis changed from an explanation of the origin of the Raman effect to the correlation of that effect with the modes of atomic vibrations. There was also an increased realisation of the applicability of the Raman effect to structural and constitutional problems. In 1939 one finds again a sudden drop in the number of publications. This should be attributed to the outbreak of the Second World War. In the subsequent years there was a progressive decrease in the number which reached a minimum in 1945 at the end of the hostilities. After the war, research on Raman effect began to pick up and the number of publications again increased steadily reaching normalcy in 1950. From 1950 to 1960 the output was more or less steady with a tendency for the curve to fall off in 1961 showing thereby that the older techniques of study of Raman effect had outlived their usefulness. The development of photoelectric recording for Raman spectroscopy and recording Raman spectrometers becoming available commercially after 1961 gave a fillip to studies of Raman spectroscopy especially in the hands of chemists and the output of publications began to rise steadily. It was during this period that lasers were developed. The first successful adoption of a laser as a Raman source by Porto and Wood[7] (1962) and by Stoicheff[8] (1963) led to the progressive use of laser sources for Raman effect studies and consequent proportional increase in the number of publications. Studies using laser excitation accounted for only about 10, 40, 60, 100 and 155 papers out of 298, 362, 403, 454 and 528 papers respectively in the first five years of its use. A major portion of these dealt with stimulated Raman effect, studies on which picked up rapidly in the early stages of laser excitation. The sudden spurt in the number of publications from 1968 onwards should be attributed to the availability of laser Raman monochromaters with photon counting and recording with the added facility of computerisation of data.

A second renaissance started during the period 1972–74 with the development of tunable dye lasers and the time-resolved and space-resolved Raman spectroscopy which opened up a new vista of research on resonance Raman scattering in coloured substances and biomolecules and on nonlinear phenomena such as CARS, HRE, IRE, etc.

International Conferences on Light Scattering Spectra of Solids held in 1968 and 1971 were also partly responsible for the increase in the number of publications in 1968 and 1971. In the subsequent years International Conferences on Raman Spectroscopy held in 1969, 1970, 1972, 1974, 1976 and 1978 were responsible for the abrupt jumps in the number of publications in these years. International Conferences on Raman Spectroscopy held at Freiburg in 1976 and in Bangalore in 1978 where about 300 papers and review articles were presented, and the simultaneous publication of the proceedings in the same years are mainly responsible for the number of publications reaching peak values in these two years. There is now a wide and sustained interest in the Raman effect which is expected to continue for many more years to come.

Another aspect of interest is the geographical distribution of research on Raman effect. Starting from nine countries in 1928 which continue to lead, the work is now carried out in not less than sixty countries. The percentage of publications from the first ten countries topping the list are given in Table II. As is to be expected the United States of America is far ahead of others in the matter of research work in this field. This is because lasers and Raman spectrometers were developed and manufactured in that country in a big way. The modern laser Raman spectrometers are rather costly now-a-days. In the pre-laser era, France and Russia were occupying the second and third places. Now the position is reversed. India was leading the countries in the first few years as regards research on Raman effect was concerned, but it was reduced to the second place in the latter part of Thirties, to the fourth in the Fifties, the sixth in the Sixties and the eighth in the Seventies. There is a progressive decline in output of research in this field. During the fifty years, India contributed over 1,200 papers, *i.e.*, 5·75% of the total publications. Of these, the contribution from the Department of Physics at the Indian Institute of Science accounted for a fourth. India which was one of the leading countries doing work on Raman effect before the laser era and was responsible for many innovations, lagged behind after the introduction of laser excitation. This is mainly due to the non-availability of costly lasers and recording Raman spectrometers in the Sixties. But in the Seventies such facilities have become available in a few laboratories; but not much of work on Raman effect has been carried out there.

From a statistical point of view the next aspect to be considered is the nature of the subjects covered by investigations using Raman spectroscopy. The subject-wise distribution of papers through the years is documented in Table III. Before the advent of lasers the subjects covered by Raman effect studies could be broadly classified under twenty heads. In 1978 this number has increased by six fold. The use of powerful laser beams for excitation paved the way for unexpected expansion of the scope for studies on Raman spectroscopy. Many new types of Raman excitations and nonlinear effects were discovered mainly by scientists from the USA along with the development of lasers and instrumentation for Raman spectroscopy. In the field of resonance Raman spectroscopy, leading theoretical and experimental contributions were from German and Russian scientists. The extensive application of RRS to biomolecules was also initiated by American scientists.

The present exciting fields are surface scattering and scattering from adsorbed molecules. Work on these topics and also on resonance Raman spectra of biomolecules and polymers and on technological applications such as temperature and concentration measurements in combustion chambers, in jet flows and in polluted atmospheres, etc., are expected to increase rapidly in the near future. The nonlinear coherent scattering phenomena such as CARS (Coherent anti-Stokes Raman Spectroscopy), CSRS (Coherent Stokes Raman Spectroscopy), RIKES (Raman Induced Kerr Effect) and HORES (Higher Order Raman Excitation Studies) which involve basic four photon parametric mixing processes are expected to get increasing attention. Of these, work on CARS and its application would open up a new vista of investigations. Time-resolved and space-resolved Raman spectroscopy with the pulsed sources of pico second

**Table II**

**Counry-wise distribution in percentage**

| Sl. No. | | Year | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1928 | 1962 | 1965 | 1968 | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978 |
| 1. | USA | 10·3 | 15·3 | 33·0 | 35·4 | 36·4 | 39·4 | 33·8 | 32·3 | 29·4 | 27·8 | 29·1 | 28·1 | 27·0 |
| 2. | USSR | 8·6 | 33·0 | 22·3 | 17·2 | 11·6 | 10·9 | 11·2 | 14·9 | 19·3 | 17·4 | 13·0 | 15·5 | 13·3 |
| 3. | FRANCE | 24·0 | 5·8 | 8·0 | 7·4 | 11·1 | 11·6 | 10·2 | 8·0 | 8·1 | 10·7 | 10·6 | 8·4 | 11·4 |
| 4. | FRG* | 14·0 | 12·4 | 8·0 | 7·2 | 6·6 | 6·0 | 7·5 | 8·4 | 9·2 | 8·9 | 10·6 | 9·6 | 9·0 |
| 5. | UK | 1·6 | 7·6 | 8·3 | 15·0 | 10·4 | 10·9 | 13·0 | 9·0 | 8·4 | 9·9 | 10·1 | 9·3 | 8·9 |
| 6. | JAPAN | 1·7 | 7·3 | 3·8 | 3·0 | 3·1 | 2·8 | 3·8 | 4·7 | 5·7 | 5·2 | 5·8 | 7·4 | 6·5 |
| 7. | CANADA | 3·4 | 6·6 | 1·8 | 4·6 | 8·4 | 6·9 | 5·1 | 5·1 | 5·5 | 4·0 | 4·3 | 3·9 | 4·3 |
| 8. | INDIA | 33·0 | 7·3 | 7·0 | 3·3 | 2·6 | 3·7 | 3·6 | 3·6 | 2·7 | 2·1 | 1·8 | 1·9 | 3·4 |
| 9. | ITALY | 3·4 | 1·1 | 0·5 | 1·6 | 1·2 | 1·0 | 1·6 | 1·5 | 1·2 | 1·7 | 2·0 | 1·7 | 1·8 |
| 10. | HOLLAND | .. | 0·7 | 0·5 | 0·4 | 1·2 | 1·0 | 1·1 | 1·5 | 1·3 | 1·3 | 1·2 | 1·6 | 1·4 |
| 11. | OTHERS | .. | 2·9 | 6·8 | 4·9 | 7·4 | 5·8 | 9·3 | 11·0 | 9·2 | 11·0 | 14·5 | 12·6 | 13·0 |

*FRG includes the whole of Germany and Austria.

### Table III

**Broad classification**

| Subject | Year | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978 |
| INORG. | 410 | 400 | 440 | 497 | 485 | 505 | 735 | 565 | 675 |
| ORG. | 295 | 328 | 398 | 391 | 395 | 435 | 551 | 515 | 612 |
| SEMI COND. | 28 | 65 | 57 | 56 | 81 | 68 | 131 | 65 | 86 |
| RRS | 24 | 32 | 52 | 70 | 89 | 126 | 235 | 141 | 211 |
| SRS | 51 | 60 | 59 | 46 | 59 | 72 | 64 | 75 | 42 |
| ERS | 11 | 4 | 12 | 10 | 12 | 13 | 16 | 17 | 22 |
| HRE | ... | 3 | 8 | 1 | 5 | 6 | 11 | 12 | 16 |
| SORS | 9 | 9 | 9 | 20 | 24 | 19 | 52 | 24 | 26 |
| CARS | ... | ... | 4 | 3 | 13 | 8 | 39 | 46 | 64 |
| BIOMOL. | 20 | 19 | 36 | 75 | 52 | 84 | 129 | 93 | 140 |
| PHASE TRANS. | 15 | 27 | 19 | 24 | 27 | 45 | 110 | 58 | 61 |
| POLARITON | 12 | 14 | 28 | 19 | 30 | 33 | 46 | 21 | 21 |
| MAGNON | 14 | 19 | 13 | 16 | 13 | 9 | 29 | 15 | 9 |
| FERROELEC. | 20 | 33 | 28 | 32 | 35 | 39 | 65 | 28 | 52 |
| SOFT MODE | 5 | ... | ... | ... | 17 | 20 | 30 | 13 | 21 |
| SPIN FLIP | 5 | 16 | 20 | 10 | 16 | 13 | 17 | 6 | 10 |
| MATRIX ISO. | 2 | 14 | 18 | 14 | 8 | 15 | 31 | 18 | 25 |
| APPLICATIONS | 5 | 8 | 29 | 27 | 60 | 44 | 51 | 56 | 60 |
| REVIEW | 33 | 62 | 70 | 65 | 43 | 61 | 91 | 102 | 121 |
| THEORY | 56 | 83 | 74 | 79 | 100 | 89 | 152 | 90 | 120 |
| OPT. ACT. | ... | 3 | 4 | 6 | 3 | 5 | 5 | 11 | 3 |

RRS : Resonance Raman Spectra; SRS: Stimulated Raman Scattering; ERS : Electronic Raman Spectra; HRE : Hyper Raman Effect; SORS : Second Order Raman Spectra, CARS : Coherent anti-Stokes Raman Spectra.

Under the broad title 'Organic' the following are included: aliphatic compounds, aromatic compounds, organic molecular crystals, organic hydrogen bonds, organic halides, organic boron, silicon, germanium, phosphorus, sulphur and selenium compounds, organic metal halide complexes and other organic metal complexes.

Under 'Inorganic.' the following categories of compounds are covered: inorganic general, inorganic crystals (pure, doped, defect and irradiated), inorganic halides, mixed and complex crystals, crystal melts (simple and complex), inorganic ions, alkali halides (pure, doped, defect, and irradiated), superconducting crystals, minerals, inorganic molecular crystals, elements and hydrogen-bonded crystals. The number of investigations on polaritons and stimulated Raman scattering has remained nearly stationary over a period of eight years from 1970.

Under the heading 'Applications' in the table are included papers on gas diagnostics in flow and combustion chambers, atmospheric pollution, remote sensing, Raman lidar, etc. Water and ice continue to be of special interest of study using Raman effect. At least a dozen papers appear every year. It is the nearest known universal solvent and it exhibits a high degree of intermolecular coupling due to hydrogen bonding and plays an important role in biological systems.

duration and the Raman microprobe developed by the French group are expected to play an important role in the study of fast chemical reactions, photochemical processes, phase transitions in solids, analysis of heterogeneous samples, biological processes, medical diagnostics, etc.

The number of journals in which papers on Raman effect appeared in 1928 was 15 covering mainly physics and chemical physics. Now it is well over 140 covering all branches of science. In 1928 *Nature* topped the list of journals which published the maximum number of contributions. Now-a-days specialised journals such as *Journal of Raman Spectroscopy* and *Spectrochimica Acta* top the list. But none of them can beat the *Proceedings of Raman Conferences*. More than eighty books have been published so far.

On the monetary side, it is interesting to note that the total cost of the equipment used by Raman to discover the effect was about Rs. 200 (50 US dollars at the then exchange rate). In the Thirties the total cost of the equipment inclusive of a spectrograph of moderate dispersion was well under Rs. 10,000 ($ 2,500 ). With the development of recording spectrometers and Toronto type lamps the cost went up to Rs. 30,000 in the early Sixties. Now a modern laser Raman spectrometer system with lasers and other accessories would cost nearly Rs. 10,00,000 ($ 1,25,000 at the current rate of exchange). Although Raman spectroscopy has become an important and essential tool for solving problems in many branches of science and technology, one finds that studies using modern Raman spectroscopic techniques have become very costly over the years and are therefore beyond the means of most laboratories in the developing countries.

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## APPENDIX I

### Glossary of Raman excitations

Different types of Raman excitations are enumerated and explained below :

### 1. *Spontaneous or normal Raman effect*

This is an inelastic light scattering phenomenon which is normally exhibited by any medium. Light of frequency $\nu_i$ incident on a medium produces scattered light of weak intensity. When the latter is analysed spectroscopically, it is found to consist of a radiation with the same frequency (Rayleigh scattering) and additional weak spectral lines (Raman scattering) with frequencies $\nu_i \pm \nu_R$, where $\nu_R$ is any one of the eigen-frequencies of the scattering medium (*e.g.*, vibrational and/or rotational frequency in a molecule or phonon in a crystal). The process is called linear because of the linear relationship between induced dipole moment and the applied electric field ($P = \alpha E$). This process is also called first order Raman scattering. Russian scientists used to call this as 'Combination Scattering' instead of Raman effect.

## 2. *Vibrational Raman effect*

This process is spontaneous Raman effect where the transition takes place between two vibrational quantum levels of the system. The frequency shifts of the Raman lines give us directly the vibrational frequencies of the molecule. Frequency shifts vary from a few hundreds to 4,400 wave numbers.

## 3. *Rotational Raman effect*

The transition is between two rotational energy levels of the molecule. Rotational Raman lines are obtained discretely only in the case of molecules having a relatively small moment of inertia. In heavier gases and vapours the lines are much closer and nstruments of greater resolving power are required to separate them. Frequency shifts vary from a few to about 400 wavenumbers.

## 4. *Anisotropic scattering (Wing accompanying Rayleigh line)*

In liquids and highly compressed gases there is hindrance to molecular rotations. The rotational scattering therefore appears as a continuous wing starting from the Rayleigh line and extending somewhat unsymmetrically on either side. The intensity and extent of the wing are related to the anisotropy of the molecules of the liquid.

## 5. *Electronic Raman effect*

In this scattering process the transition takes place between two electronic levels. This is usually observed in gases and also in solids having low-lying electronic levels. Hougen and Singh[9] observed electronic Raman scattering in $PrCl_3$ in 1963.

## 6. *Second order Raman scattering*

The scattering process in which the polarizability is modulated by a frequency corresponding to the vibrational overtones or combinations in liquids or gases or by two phonon frequencies in crystals. The frequency shifts of the observed Raman lines in the second order spectrum which is generally weak correspond roughly to the octaves or combinations of the fundamental vibration frequencies.

### 7. *Resonance Raman scattering*

It is observed experimentally that as the incident laser photon energy used for exciting Raman spectra approaches that of an electronic transition, a marked resonant increase in the intensity of scattering occurs. Since the polarizability $\alpha$ from which the intensity is derived contains a term $1/(\nu_e - \nu_i)$ where $\nu_i$ is the incident frequency and $\nu_e$ is the electronic absorption frequency of the medium. This phenomenon is now termed as resonance Raman scattering. Placzek[6] himself predicted interesting resonance effects in the region where the polarizability theory does not apply in his theoretical article on light scattering as early as 1934. Ornstein and Went[10] were the first to observe abnormal increase in the intensity of the Raman lines of calcite when the frequency of the exciting radiation approached the region of electronic absorption in the ultraviolet, not accountable by the $(\nu_i - \nu_R)^4$ law. But pioneering work in the field of resonance Raman spectroscopy (both theoretical and experimental) were carried out by Shorygin[11] in Russia and Behringer[12] in Germany in the pre-laser days. With the availability of tunable dye lasers, the wavelength of whose output could be varied over a wide range, resonant Raman spectroscopy has become an important tool to the practising chemists and biochemists as it offers a major increase in both sensitivity and selectivity.

### 8. *Raman scattering by phonons*

This process is due to scattering by waves propagating in a crystal. These waves are quantised and are termed phonons or normal modes of a crystal. Each phonon is characterised by a discrete phase velocity $v$ a frequency $\nu$ and a wave propagation vector $k$. Since $|k| \neq 0$, one has to take into consideration momentum conservation. In the case of crystals only those phonons with $|k| = 0$ take part in the first order Raman scattering.

### 9. *Raman scattering by polaritons*

This arises from light scattering by elementary excitations corresponding to mixed states of mechanical and electromagnetic energy. Hopfield[13] christened these coupled excitation states as " polaritons " in 1958. Born and Huang[14] also claimed the existence of such excitation states theoretically (1968). The first experimental confirmation was by Henry and Hopfield[15] in the Raman scattering from cubic GaP in 1965. These coupled polariton states exist only for very small value of $|k|$. Polariton scattering can therefore be observed only in the forward or near forward directions.

### 10. *Raman scattering by magnons*

In ferromagnetic materials the spins of all atoms have the same orientation as the magnetic field, while in antiferro-magnetic materials the spins are oriented anti-parallel. In ferrimagnets the spins are also oriented antiparallel but of different magnitude. Oriented spins are coupled and disturbance by a photon in a crystal creates a spin wave which travels through all spins. Quantised states of spin waves are called magnons. Raman scattering by magnons was first predicted by Elliott and Loudon[16] in 1963 and observed by Fleury and Porto[17] in the antiferromagnetic crystals $MnF_2$ and $FeF_2$ in 1966. Second order Raman scattering or two magnon scattering has also been observed.

### 11. *Raman scattering by plasmons*

Light scattering is by quantised plasma oscillations especially in semiconducting materials. The electrons in a plasma congregate around configuration of minimum energy and normal oscillations around this equilibrium are possible. Interaction by a photon creates a wave propagating through the plasma which is called a plasmon. Raman scattering by plasmons in GaAs was demonstrated experimentally by Mooradian and Wright[18] in 1966.

### 12. *Raman scattering by plasmaritons*

Light scattering takes place by coupled photon–phonon states (polariton-plasmon). When a conductor or semiconductor containing free electrons is placed in a magnetic field, the circular trajectories of the electrons are the quantised cyclotron orbits known as Landau levels. If the effective mass of the electron is small in the crystal, the splittings are large enough to be observed by Raman spectroscopy. Raman scattering from such levels in InSb was first proposed by Woolf *et al*[19]. Slusher, Patel and Fleury[20] experimentally demonstrated such Raman scattering in InSb in 1967.

### 13. *Raman scattering by excitons*

Light scattering takes place by quantised states in electron systems (semiconductors and insulators) which are connected with the formation of a bound electron hole pair. These excitons are mobile excited states that propagate as waves through the crystal when excited by photons.

### 14. *Raman scattering by soft modes*

Light scattering is due to an unstable or 'soft' optical phonon whose frequency decreases substantially as the transition temperature of a structural phase transition is approached. The existence of such a mode was first demonstrated by Raman and Nedungadi[21] in the $\alpha - \beta$ transformation of quartz in 1940. Its existence was predicted theoretically by Cochran[22] while developing the lattice dynamical theory of structural phase transitions.

### 15. *Spin-flip scattering*

This process arises from a transition between Landau levels with a change of quantum number by two. In this process under the action of the photon, the spin of the electron state flips between two opposite directions and the Raman frequency is twice the cyclotron frequency of the electrons. Slusher *et al*[20] were the first to record the spin-flip Raman scattering in InSb with the $10 \cdot 6\,\mu$ $CO_2$ laser in a magnetic field.

### 16. *Spin-flip Raman laser*

Stimulated spin-flip Raman scattering leads to coherent, tunable Raman laser source in the infrared region of the spectrum. The tuning is achieved by a change in the magnetic field strength.

### 17. *Nonlinear Raman effect*

The assumption that the polarization depends linearly upon the electric field is only a first approximation and is not valid for large field strengths. The polarisation may be expressed as $P = \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 \ldots$. For high electric field strengths, which can be achieved with powerful laser sources, the higher order terms in the above series will become comparable to the linear term and have to be taken into consideration for calculating the intensity of scattering. Raman scattering taking place under these conditions is called nonlinear effects. (Examples: Hyper Raman effect, Stimulated Raman effect, Inverse Raman effect, CARS, etc.).

### 18. *Stimulated Raman effect*

With giant pulses of short duration and high peak power obtainable from *Q*-switched ruby or Nd YAG lasers, nonlinear phenomena are observed and one such phenomenon is stimulated Raman scattering. The observation of SRE was first made by Woodbury and Ng[23] rather accidentally in 1962. The correct interpretation was given by Eckard *et al*[24] in 1963. In contrast to the spontaneous or linear Raman effect, only very few lines of a medium and their harmonics are generated. The stimulated Raman radiation has the properties of an ordinary laser radiation. Its main applications lie in the field of light sources and vibrational excitation.

### 19. *Hyper Raman effect*

When large electric field strengths produced by the radiations from giant lasers are used for excitation, a nonlinear inelastic light scattering called hyper Raman scattering appears at $2\nu_i \pm \nu_R$, *i.e.*, in the vicinity of twice the frequency of the exciting line with frequency shifts corresponding to the vibrational, rotational or phonon frequencies. This is an extremely weak scattering process and was first reported by Terhune *et al*[25] in 1965.

### 20. *Inverse Raman effect*

When a medium is illuminated simultaneously by intense monochromatic light and by a continuum, sharp absorption lines can be observed on the anti-Stokes side corresponding to anti-Stokes Raman transitions of the medium. Under the influence of the continuum and the laser radiation, vibrational quanta are absorbed from the continuum which leads to Raman spectrum in absorption. This was first discovered by Jones and Stoicheff[26] in 1964 and is also called " Stoicheff Absorption ".

## 21. *Coherent anti-Stokes Raman scattering* (CARS)

A nonlinear Raman process is generated *via* the third order nonlinear susceptibility of the material by simultaneous excitation with two lasers of frequencies $\nu_1$ and $\nu_2$. Coherent radiation is produced at the frequency $\nu_3 = 2\nu_1 - \nu_2$ whenever $(\nu_1 - \nu_2)$ coincides with the frequency $\nu_R$ of a Raman active mode between two quantised states of the medium. ($\nu_3 = \nu_1 + \nu_R$, *i.e.*, anti-Stokes radiation with respect to $\nu_1$). This phenomenon was first observed by Maker and Terhune[27] in 1965. In CARS the generated wave at $\nu_3$ is produced because of parametric interaction and the two photon processes lead to absorption of this wave; the pump induces a transition of the medium from the ground state to an excited state and the parametric process returns the medium to the initial state. CARS is superior to normal Raman scattering because much larger scattered intensities are available and also because the signal is coherent and restricted to a very small solid angle. The interaction is a nonlinear effect and is parametric in character. CARS has potential for precision spectroscopy.

## 22. *Coherent Stokes Raman scattering* (*CSRS*)

In the process described above if $\nu_2 - \nu_1 = \nu_R$, one observes coherent scattering at $\nu_3 = 2\nu_1 - \nu_2 = \nu_1 - \nu_R$, *i.e.*, as a Stokes Raman radiation. This is less useful compared to CARS because of interference from fluorescence, etc. In this process, the generated wave at $\nu_3$ is increased both by the Raman and by the parametric interaction of the fields. This process is coherent emission at Stokes frequencies by two photon excitation in which case the medium finally goes to an excited state[28].

## 23. *Raman-induced Kerr effect spectroscopy* (*RIKES*)

When a medium is illuminated simultaneously with a circularly polarised pump beam of frequency $\nu_1$ from a powerful laser and a weak linearly polarised probe beam of frequency $\nu_2$, the nonlinear interaction gives rise to a generation of a new beam of frequency $\nu_2$ which is perpendicularly polarised with respect to the original one. The generation of this new component exhibits resonance when $\nu_1 - \nu_2$ is near the frequency of a Raman active vibration in the medium. This nonlinear optical effect is called 'Raman Induced Kerr Effect' (RIKE). This was first discussed by Heiman *et al*[29] in 1976, as a spectroscopic method which can give information about the complete Raman spectrum in a very short time (*i.e.*, nanoseconds). This effect has been experimentally tested in organic liquids. In crystals there are two main effects, the optical activity and the anisotropy affect RIKE. Unlike CARS, RIKES has the advantages of (1) no phase-matching requirements, (2) no nonresonant nonlinear background signal and (3) constant frequency signal. Its signal intensity is quadratic in Raman cross-section and hence weak.

A complete bibliography of the 25,000 and odd papers published during the fifty years after the discovery, *i.e.*, till the end of 1979 has been prepared. This is expected to be published in due course along with a comprehensive author and subject indices.

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# BOOK REVIEWS

**The common sense of science** by J. Bronowski. Published by Heineman, London, 1978, Pp. 159, Price £ 1·50.

This is a reprint of the book first published in 1951 by a distinguished scientist, broadcaster and a great intellectual. It is remarkable that it maintains its freshness and appeal even now.

The book essentially deals with the evolution of scientific thought in the West, particularly in England and Europe. The author makes a brilliant analysis, and considers some deep questions often asked about science as has evolved and as to where we are heading. And I believe, he succeeded in exploding some common misconceptions about science. For example, it has been a well-known modern prejudice that art and science are mutually incompatible. He finds eloquent retort in Greek scientists and philosophers and in the example par excellence of Leonardo Da Vinci of the Renaissance Period. Thus the thesis of his chapter I is concerned with science and sensibility and the underlying connection between arts, culture and science. Chapters 2 to 4 analyse the scientific revolution in the 17th century and the development of Newton's mechanistic model, its enormous success from terrestrial to celestial phenomena and leading to the concept of machine like order in the physical world.

In Chapter 5, the author discusses the central problem of the nineteenth century scientific methods culminating in the concept that all laws must be framed in casual form so much so that the idea and effect has a powerful hold on our minds. It seemed to unify both the physical and biological sciences. This became the guiding common sense principle.

The revolution of the twentieth century science has, however, radically altered our common sense view of the world. Thus Einstein discarded the Newtonian assumption of absolute space and absolute time common to all observers. There is no universal ' now ' and the state of motion of observers plays a very important role. The space and time get intricately mixed up and cannot be distinguished from matters and their motion. The birth of quantum physics led to complete abandonment of the common sense view of the world at the microscopic level, wherein there is inherent uncertainty in the description of nature. At this level we can have only a statistical or probabilistic view of the microscopic world. Even in the life science, determinism had to give way to probability of things happening as exemplified by Mendel's law of the random coupling among the genes.

One is thus naturally led to the idea of chance in Chapter 6, which is discussed at length from various angles—trend and fluctuations, effect and chance, etc., and the unifying principle becomes the probability of occurrences of certain phenomena under some specific conditions.

In chapters 7 to 9 the author turns to deeper philosophical questions and humanism. We are faced with the question whether science plays the role of destroyer or creator Are science and society out of step with each other? The author ends with an optimistic note. He feels that 'science will create values and discover virtues when it looks into man'. Let us hope that his feelings are justified by future course of human society.

In short, this is an extremely stimulating book and it will satisfy readers having passionate thirst for knowing the evolution of scientific thinking. My only regret is that the author has not made any reference to Eastern thoughts as done by other scientists on such subject, *e.g.*, Schrödinger and recently F. Capra.

K. P. SINHA

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**Problems of Linear Electron (Polaron) Transport Theory in Semiconductors** by M. I. Klinger, translated by J. B. Sykes. Volume 87 in the *International Series in National Philosophy* edited by D. Ter Haar, First Edition, 1979. Published by Pergamon Press, Pp. xv + 931. Price $ 125.

Right from the beginnings of the electron theory of electrical conduction in matter, h theory of electrical conductivity has rivetted the attention of many able physicists. Apparently the last word is not yet uttered. The book under review deals with an account of the recent theories of electron transport in semiconductors. This book is a translation of the Russian version published in 1973 and deals mainly with electron (polaron) transport theory in three-dimensional solids under the single particle approximation and excludes discussion of many electron correlation effects. The approach is wholly theoretical and does not deal with high frequency effects. The first part has a very useful account of the general dynamical theory of linear transport according Kubo formalism. The second part is an account of the theory of polaron transport in crystalline semiconductors. The third part is devoted to the topic of electron transport in disordered systems. The book makes rather heavy reading and the references concentrate very much on the Russian literature on the topic. Considerable familiarity with quantum mechanics, statistical physics, and electro-dynamics of continuous media along with knowledge of introductory solid state theory is essential for an intelligent reading of this book.

The book makes very little contact with experimental results and one is likely to get lost in elaborate formulae spread over nearly 900 pages of text. By and large, the first portion of the book is easier to assimilate than the latter two. It is also a bit difficult to find the direction in which this subject is moving. However, it is a useful addition to the existing literature because it brings them together in one place. The book has been reproduced from type script and there are only a few figures. There is a list of additional references, some of them up to 1978. There is also a fairly short index.

G. SURYAN

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**The Observer's Book of Rocks and Minerals** by Richard and Francis Atkinson. Published by Frederick Warne (Publishers) Ltd., 40, Bedford Square, London, WC1B 3HE, 1979, Pp. 184, Price £ 1·50.

Nothing is as important in the natural world as our own earth and the rocks beneath ur feet. *The Observer's Book of Rocks and Minerals* is written by the well-known authors in a clear, readable style and contain many colourful photographs and instructive illustrations to identify minerals and rocks by simple field tests. . The two main parts of the book are the " Description of Rocks " and the " Description of Minerals " with brief sections on the formation of rocks and on the origin of mineral deposits.

Thumb through this book before you go on hikes, trips and vacation. Read nd become familiar with the pictures of minerals and rocks. This may enable you to identify some common rocks and minerals at sight. Visit collecting places, examine specimens and try simple field tests. You will find how useful this Observer's Book on Rocks and Minerals is going to be.

G. V. ANANTHA IYER

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**'A' Level Physics, Volume 1, Mechanics and Heat** by M. Chapple. Published by Macdonald and Evans, Estover Road, Plymouth PL6 7PZ, UK, Second Edition 1979, Pp xiv + 318, Price £ 1·75, ISBN number : 0 7121 0154 3.

This is a good book, obviously written by an experienced teacher and suitable for the PUC or First Year B.Sc. students of our universities. In a way, it is similar to our school and college text books, which give a brief account of the basic principles, follow it up with a few worked examples and give a number of exercises for the students to solve. About 115 carefully drawn figures illustrate the principles and the exercises. Four pages of mathematical tables and a comprehensive index add to the utility of the book.

The book is divided into two parts, the first part dealing with mechanics and properties of matter and the second part dealing with heat. Part one covers units and measurements, statics and hydrostatics, Newton's laws of motion, simple harmonic motion, gravity, elasticity, viscosity and surface tension, these being the sequence in which the topics are discussed. Part two covers the measurement of temperature, heat energy and its transformations, properties of ideal gases, vapours and vapour pressures and the various methods of heat transfer.

Each of the 12 chapters has about a dozen worked examples and about 30 problems and exercises. Hints for the answers are given at the end of the book. The traditional topics are refreshingly interspaced with the ideas of the current status of the subjects. The exercises are also a blend of the traditional problems with the questions based on current day practical experience. The reviewer found Appendix 1, entitled 'Examination Techniques' to be a sound piece of advice to every student serious about an examination. His task of correcting the answer papers of generations of students would have been a lot more pleasant if the student had access to this type of common-sense advice.

In summary, the book is heartily recommended. The only disappointing feature is that the price of £ 1·75 would take the book beyond the reach of most Indian students.

E. S. R. Gopal

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