

the present state of this technique can be compared with that of magnetic resonance in its early days, though it seems unlikely that the instrumentation will ever be as widely available. A nicely illustrated paper by L. Eyring surveys the application of high-resolution transmission electron microscopy to crystals. This technique, potentially able to reveal individual atoms as they undergo reaction in a solid (a resolution of 2 Å has been obtained on instruments using 1 MeV or more), has had a profound impact on solid-state chemistry and shows exciting promise for the future. Shear and other defects are made visible (though a practised eye seems necessary to recognize the calculated pattern in the real image), and crystallographers will be fascinated by these photographs and by those of intergrowth domains. The final paper in this section by a group from Argonne is an interesting progress report on the design of a user-orientated single-crystal neutron diffractometer which ingeniously adapts the Laue technique to structure analysis by using the possibility for time-of-flight analysis inherent in a pulsed source.

In the second section, R. A. Laudise (who sees electronic materials as the 'learning medium' on which the science of solid-state chemistry grows as it helps in their development) presents five examples of research at Bell Laboratories, including intercalation compounds (Li in VS_2) as storage-battery electrodes, barium titanates 'engineered' to dielectric specification, and a study of oxide precipitation in 'perfect' silicon crystals. J. B. Goodenough gives a detailed and authoritative analysis of bulk and surface states of pure and doped rutile in relation to its use as a photoelectrode for solar-energy conversion; his passing remark that 'Chemists trained in the concepts of solid state physics are already in too short a supply for industrial demand, and the problem is destined to become more acute in the near future' deserves attention. Other papers in this section include: Robbins on solar cells employing CdSe and CdTe electrodes and a sulphide-polysulphide electrolyte solution (pressure-sintered materials seem as efficient as single crystals in this system); Wold and Dwight on the use of F^- substitution (rather than O^{2-} deficiency) in TiO_2 photoelectrodes, to give conduction without loss of chemical stability; Miller and Epstein on replacement of the *N*-methylphenazinium ion by the neutral phenazine molecule in $NMP^+ \cdot TCNQ^-$, which enabled them to study electrical properties as a function of band filling, and the role of disorder in one-dimensional conduction; and Street and Clarke on the structures and properties of the conducting polymers $(SN)_x$ and $(CH)_x$ and their derivatives with such electron acceptors as Br_2 , AsF_5 , and Ag^+ . Finally, the storage problems associated with the 'hydrogen economy' are considered by Wallace, Craig and Rao in an article on hydrogen absorption by intermetallic compounds, where the interest lies in speed of absorption and desorption as much as storage capacity: $LaNi_5H_6$ is typical in dehydrogenating in minutes when pressure is reduced. The structural mysteries here are now being resolved – by neutron diffraction, naturally – and are discussed in some detail.

The last (and longest) section covers very varied ground. R. S. Feigelson discusses crystal growth by electrolysis of molten salts, e.g. Si, GaP, and InP from eutectics such as 'Flinak' (LiF–NaF–KF) and 'Pofnak' ($NaPO_3$ –NaF– KPO_3 –KF); M. A. DiGiuseppe describes the difficult techniques used to grow large rare-earth gallium garnet

crystals, needed as substrates for oriented 'magnetic-bubble' films of the Fe analogues (matching of lattice parameters is crucial here); while Milstein discusses methods of growing large crystals of rare-earth intermetallics (Ho/Tb/Dy Fe_2), whose enormous room-temperature magnetostriction directs their use in transducer devices. The 'subtle, but interesting, structural and magnetic properties' of A_xVF_3 systems, described and interpreted by Lee, Williamson and Boo, include superstructures and magnetism–composition discontinuities. J. D. Corbett discusses extended metal–metal interactions in low-valent transition-metal halides, e.g. the remarkable chain structure of Gd_2Cl_3 – 'the so-called eighth wonder of the rare-earth world' – from a structural viewpoint, and H. Steinfink shows how conductance and other properties of $Ba_xFe_xS_z$ compounds can be understood on the basis of the clusters and chains of condensed FeS_4 tetrahedra revealed by X-rays and the Fe valency distribution indicated by Mössbauer spectroscopy. Other papers include one on the hydrothermal stability of simulated radioactive-waste glass by G. J. McCarthy and co-workers ('The record for chemical complexity . . . may well be held by problems involving the stability of radioactive wastes'), and one on phase equilibria in the system K_2O – MgO – Fe_2O_3 – Al_2O_3 – SiO_2 by R. S. Roth.

This was a timely symposium and the authors, editors, printer, and publisher have done a fine job in bringing us their contemporary overview of an important area of research. (My only regret is that no verbal discussion of the papers is included – if it occurred, it was surely fascinating.) Attractive print, few errors, excellent figures, and a good index maintain the high standard of the series, and I think most chemists with an interest in the solid state will want their library to have a copy.

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Mixed-valence compounds. Edited by D. B. BROWN.
Pp. viii + 519. Reidel, 1980. Price Dfl. 115.00, US
\$60.50.

This book comprises the series of lectures which were given at the NATO Advanced Study Institute at Oxford in 1979. It gives an excellent survey of the present state of mixed-valence chemistry and is likewise interesting for chemists, physicists, mineralogists and biologists. The first part, which consists of three introductory, but instructive chapters (P. Day, A. Ludi, D. B. Brown), is an overview of mixed valency and outlines the essential features of mixed-valence behaviour. Classical examples such as Prussian Blue and others, which are thoroughly investigated and well understood, are discussed. In the second part the different theoretical approaches to the understanding of the electronic structure in mixed-valence compounds are presented in three chapters (T. J. Meyer, P. N. Schatz, N. S. Hush). The considerable development and also the controversy in this field are immediately obvious. The third part describes the application of some experimental methods, which are sensitive to the electronic properties of mixed-valence compounds – such as magnetism (W. E. Hatfield),

Mössbauer spectroscopy (D. B. Brown) and other spectroscopic methods (J. H. Clark). Finally, the fourth part is devoted to different classes of mixed-valence materials and their importance for various fields of research. Here the significance of mixed-valency concepts in the chemistry and physics of inorganic and organic linear-chain compounds or of clusters and polymetallic centres, which are also of interest for biologists, is emphasized. The importance of mixed-valence properties with respect to the colour and the electronic spectra is reviewed in two chapters on mixed-valence minerals and heteropoly blues.

The most important aspects of mixed valency in theory and applications are well documented and represented in the four parts of the Proceedings. Though the quality of the articles is not equally high in all cases the reviewer considers the book comprehensive and very useful. It can be warmly recommended not only to those who are directly involved in mixed-valence chemistry but also to those who want to become acquainted with this interesting and promising field of research.

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Fiber diffraction methods. Edited by A. D. FRENCH and K. C. H. GARDNER. Pp. 518. American Chemical Society, 1980. Price US \$35.50.

Although this book is a collection of papers presented at a symposium, *Diffraction Methods for Structural Determination of Fibrous Polymers*, held during the 178th Meeting of the American Chemical Society (September, 1979), it seems to cover most of the current problems in the field making it a state-of-the-art volume. A thorough treatment of fiber diffraction theory by S. Arnott, given in the first chapter, constitutes a good introduction for readers with other backgrounds. Volumes of this kind are particularly welcome since relatively few such publications appear in this field.

While Vainshtein's well known book *Diffraction of X-rays by Chain Molecules* (Elsevier, 1966) mainly dealt with the theoretical aspects, the present volume gives much space to the technological aspects. This seems to be quite relevant since the last 15 years have seen much progress in the methodology (owing to innovations in instrumentation and computers), including the use of the two-dimensional film scanner in assessing the diffraction intensity, the sophisticated simulation of diffraction patterns taking even the disorder of the object into consideration, and various techniques of refining molecular structures against diffraction intensity, all of which are treated in this book. The latter half of this book is devoted to studies on individual polymers. These include poly(*p*-phenylene), cellulose, chitin, poly(tetramethylene terephthalate), α -1,3-D-glucan, curdlan, (bacterial) polysaccharides, amylose and polynucleotides (both synthetic and natural). Another volume dealing with more

biological objects including fibrous organelles is perhaps needed.

Because of the flourishing of protein single-crystal crystallography, the role of fiber crystallography, especially in the field of biopolymers, tends to be underestimated. However, by considering just the recent heated arguments on the extent of the structural variety (including the reversed hand of the screw sense!) that DNA can accommodate (treated by S. Arnott) and dynamical studies of fiber diffraction using synchrotron radiation (not treated), the lasting value of this older field of diffraction is clear and I wish to express my appreciation of the serious and painstaking efforts made by such people as the authors of this volume who remained in this field despite the vogue to escape to other fields. The book is well produced and easy to read, despite being the reproduction of the camera-ready forms submitted by the authors.

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Books Received

The following books have been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Electrical transport in solids, with particular reference to organic semiconductors. By K. C. KAO and W. HWANG. Pp. xx + 663. Oxford: Pergamon Press, 1981. Price £50.00, US\$120.00. A review of this book, by D. D. Eley, has been published in the January 1982 issue of *Acta Crystallographic*, Section A, page 174.

The analytic theory of point systems. By J. D. BERNAL. Pp. xiv + 135. 1923. Published in facsimile and available at £2.50 + postage (30p in the UK) from A. L. Mackay, Dept of Crystallography, Birkbeck College, London WC1E 7HX, England. The name of J. D. Bernal requires no introduction to crystallographers. What is not so well known is that Bernal's first scientific paper was never published. It was written when J. D. was a student – and a rather shy one – at Emmanuel College, Cambridge. Considered to be too long for publication, it did earn him a £30 prize and, more important, a post with Sir W. H. Bragg, which set him on his crystallographic career. This paper, once surviving at Birkbeck College only as a single copy, has now been duplicated and is available, as above, through Dr A. L. Mackay. Introductory notes, by Dr Mackay and by Professor R. Schwarzenberger, are included.