

considerations. From DTA (Arend, Hoffmann & Waldner, 1973; Depmeier, Felsche & Wildermuth, 1977), birefringence, X-ray and neutron diffraction (Knorr, Jahn & Heger, 1974) measurements of $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$, the phase transition $I4/mmm = Abma$ at 393 K was shown to be of second order. Under such conditions, the orthorhombic room-temperature space group must be a subgroup of the HTT space group. Among the symmetry groups which satisfy the diffracting conditions of the HTT phase, only $I4/mmm$ (and not $I4/m$) has $Abma$ as a subgroup (Neubüser & Wondratschek, 1969).

(6) The refinement of a structure can always be attempted assuming a subgroup of the actual space-group symmetry, thus increasing the number of variables. With a ratio of number of observations to number of variables of 2.9 for the HTT phase, conclusions from such a refinement should be judged carefully. This ratio would even reduce to 2.6 taking into account the six variables (two positional and four thermal parameters) listed in Table 2 of the HTT phase given without any e.s.d. (Mikhail, 1977*b*). For this refinement also, the same remark concerning the loss of information as mentioned under (4) can be made. Although $I4/m$ requires double the amount of data compared with $I4/mmm$, the new refinement with space-group symmetry $I4/m$ has been performed with the 133 reflections taken from Heger *et al.* (1975).

(7) Mikhail's papers give unusual interatomic distances and angles; e.g. in the HTT phase an octahedral angle of 86.08° for the MnCl_6 group and C-H bond lengths between 0.779 and 1.06 Å are given without interpretation. The corresponding values from Heger *et al.* (1975) are 89.9° and 1.03–1.09 Å. Furthermore, hydrogen bonds of the type C-H...Cl are unusual.

In conclusion, we assert that we have no indication that the space groups $P4_2/nm$ of the low-temperature and

$I4/mmm$ of the high-temperature phases as reported by Heger, Mullen & Knorr (1975, 1976) from neutron diffraction are incorrect. This conclusion is supported by the refinement of the low- and high-temperature phases of the related compound $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ where the same tetragonal space groups had to be adopted (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976). In addition, a recent theoretical study by Blinč, Zeks & Kind (1978) shows that the LTT phase follows logically from a phase-transition model based on the order-disorder of the CH_3NH_3 groups.

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Reactivity of solids. Edited by J. WOOD, O. LINDQVIST, C. HELGESSON and N. G. VANNERBERG. Pp. xx + 810. New York: Plenum, 1977. Price \$71.40.

For three decades, the rapid progress of solid state chemistry had led to many congresses. This book contains the 116 papers presented at the 8th International Symposium on the Reactivity of Solids which was held in Göteborg (Sweden) in June 1976.

It is divided into six topics, each of which is headed by a general introduction to the subject: reaction at surfaces and interfaces, especially at elevated temperatures (33 papers), influence of structural defects on the reactivity of solids (34 papers), solid state reactions in organic materials (6 papers), reactions in vitreous solids (8 papers), new developments in experimental techniques for the study of reactivity of bulk solids and of surfaces (15 papers), solid state reactions in technology (20 papers).

This book is specially intended for solid state chemists who will find a wide coverage of the work in progress in this field of chemistry. The main aims of research, often connected with basic present day problems, are faithfully reflected: catalysis, corrosion, ionic superconductors, reaction selectivity and new materials are the more frequent subjects of papers.

Most of these results, often very different from each other through their aim and through the experimental methods used, underline the prominent part played by all sorts of defects in the common solid. It has been possible to undertake this kind of research into real solids often because of the always increasing efficiency and flexibility of the physical methods which may be used in solid state chemistry (X-ray, electron, neutron diffraction, LEED, IR, Raman, Auger, mass and Mössbauer spectroscopies, ESR, NMR *etc.*). The simultaneous use of diffraction and spectroscopy seems to be more and more frequent and leads to quite interesting results.

Some work on reaction mechanisms is also presented; it demonstrates that a high degree of knowledge exists in certain fields and that the will for better control of reactions, especially when they lead to industrial application, also exists.

The size of this book is a consequence of the extension of the subject dealt with since all the papers are presented. Its high cost may lead to questions about the necessity to produce this kind of book with a less costly appearance, more in harmony with the rather short-lived information it contains.

In spite of this, such collections of original papers are a good thing especially in the case of research areas, such as reactivity of solids, which are located at the fringe of several branches of science. They allow the reader to easily carry out a review of the subject which would be more difficult to do by other means because of the different origins of the papers to be considered.

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Preparation and crystal growth of materials with layered structures. Physics and chemistry of materials with layered structures. Vol. 1. Edited by R. M. A. LIETH. Pp. ix + 280. Dordrecht, Boston: Reidel, 1977. Price Dfl 95.00, US \$38.00.

A book dealing with the preparation and crystal growth of materials with layered structures would appear to be a welcome addition to the literature of solid-state chemistry. Unfortunately, the present volume is likely to prove a disappointment to many of its readers because of the uneven treatment of the subjects encountered in the various chapters. A review on synthesis should have three major features: a discussion of the *details* of the synthesis sufficient to enable the reader to duplicate the material if he chose, an *overview* outlining the extent of the field, the range of composition and alternative synthetic techniques, and a *critical assessment* of the literature which would enable the reader to avoid well known 'pitfalls' in the areas. It is the reviewer's obligation to provide more than a recounting of previous publications.

Hooley's chapter on graphite intercalates is a classic example of a good review. In thirty pages he presents a clear picture of the mechanisms of intercalation in graphite, the range of materials which can be formed, and a critical assessment of areas where conflicting information appears in the literature. Synthetic pathways are described and the basic references are cited for details. Graphite intercalates represent an extremely complex field for the synthetic chemist and to provide such a clear picture in such a brief space is a tribute to Hooley's ability as a reviewer.

The chapter on transition-metal dichalcogenides by Lieth and Terhell provides a counterexample. It is long, over 80 pages, and includes many repetitions, especially in describing

the synthesis of each of the dichalcogenides in a separate section. There are some conspicuous lapses in the general discussion, one example being the reference to the tight binding calculations of Murray, Bromley and Yoffe for electron band structure when a number of APW band-structure calculations dating from 1973 (Mattheiss's and Kasowski's work in particular) provide considerably more detail. The tables are unfortunately formatted and consume more space than necessary. However, the most distressing feature is the lack of *synthesis* of the known data – the absence of an overview and critical assessment of the literature as mentioned above – which is the most important service that the reviewer can render.

Schoonman and Lieth in their discussion of metal halides provide a good feeling for the scope of the field and some excellent examples of specific systems. Synthesis pathways are neatly presented for each member of the series in tabular form and the thermodynamic properties, as inferred from thermal and electrochemical measurements, are also included in tables. The presentation is a little too condensed. For example, it is hard for a reader to carry out a thermodynamic calculation exclusively on the basis of the information presented here.

The other three chapters have much more limited scope: bivalent metal hydroxides (Oswald and Asper), III–VI compounds (Lieth), and IV–VI compounds (Buck). The authors can, and do, devote much more attention to each of the members of the series. The hydroxide study has detailed descriptions of the synthesis routes and the resulting structure. Lieth presents the phase diagram and pressure–composition relationship for the gallium chalcogenides and InSe, although again the synthesis discussion could be condensed by using a parallel instead of a serial format. Buck's discussion of layered oxides, sulfides and selenides of tin, lead and silicon treats the topics in great detail, but a more extended discussion of the general features would be appreciated.

Viewed in terms of the criteria discussed in the first paragraph, this is not a reference book for the synthetic chemist. However, most of the articles present a useful overview of the current synthetic efforts in the various areas. While it is not likely to be a classic reference in the field, these summaries provide a good introduction for new workers in the area.

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Crystal growth and materials. ECCG1, Zürich, 1976. Edited by E. KALDIS and H. J. SCHEEL. Vol. 2 of the series **Current topics in materials science.** Edited by E. KALDIS. Pp. xvi + 916. Amsterdam: North-Holland, 1977. Price \$122.50, Dfl. 300.0.

A review of this book by M. B. Small has been published in the October issue of *Journal of Applied Crystallography*, p. 673.