

Symposium Overview Computer Simulation of Inorganic Solids

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SUMMARY

A symposium on 'Computer Simulation of Inorganic Solids', organised by the Applied Solid State Chemistry Group Trust and by the Polar Solids Group of the Royal Society of Chemistry was held in London, in December 1988. Speakers at the forefront of research in computational techniques for simulation of inorganic solid materials reviewed the range of application of these methods and the prospects for future application to a largely non-specialist audience.

The meeting was timely and well supported. The majority of the talks given are presented in this volume. This overview discusses the recent expansion of interest in solid state chemistry and the important role that computer simulation methods have played in this growth. The papers are summarised with especial reference to recent developments in solid state chemistry and materials science.

1. SOLID STATE CHEMISTRY AND COMPUTATIONAL METHODS

Solid State Chemistry was, for many years, a poor relation to other fields such as coordination chemistry and organometallic chemistry when judged by the funding of research, the numbers of researchers in the field and by the attention given in teaching courses. Any casual observation of the environment will immediately reveal that this state of affairs has little to do with the importance of solids either in the natural world or in technology and commerce. Possibly, it had something to do with the relative complexity of many solids, their frequent non-molecular nature, and the difficulty of characterising them in any well-defined manner.

One consequence of this neglect by many chemists of a major branch of their subject has been the growth of 'materials science'. The study and creation of technologically important solids has been driven forward by the commercial pressures of the electronics and communication industries with the development, for example, of semiconductor materials, magnetic materials and optical fibres. Often, the major input has come from physicists, or metallurgists who see their subject broadening into non-traditional materials such as composites and ceramics.

In the last two decades, however, the important role of the chemist in solid state studies has become increasingly appreciated, both by chemists themselves and by their colleagues from other disciplines.

There are two important reasons for this.

Firstly, many important materials are becoming more complex. One example of this complexity is provided by fast-ion conductors. While the existence of fast-ion conductors has been known since the last century, indeed Michael Faraday discovered the effect in lead-fluoride and Nernst demonstrated applications for zirconia around the turn of the century, their study only became fashionable, not to say hectic, in the last two decades, following the invention by Kummer and Weber of the sodium-sulphur battery in the mid-1960s. Fast-ion conductors, whether electronic insulators such as β alumina and lithium nitride, or electronic conductors such as the insertion compounds TiS_2 or V_6O_{13} , are chemically complex and the involvement of chemists was essential in helping to rationalise and push forward this new field. For example, one of the most promising new materials is an ionically conducting polymer electrolyte first announced by Armand in 1978. A chemical appreciation was essential in making the imaginative leap from the information in the published literature to a potential application in advanced batteries.

Another example of such increasing complexity is provided by the high temperature superconductors discovered by Bednorz and Müller only in 1986. Compared to the traditional superconducting elements or alloys which were chemically simple, although a triumph of engineering to manufacture, the high temperature superconductors have real chemistry and a complicated one at that. The chemist is a vital member of the development teams both in attempting to characterise existing materials and, especially, in developing new ones. Whereas the field of fast-ion conductors is now scientifically mature, even if technologically in its infancy — the most recent electric vehicle announcements making the news in December 1989 still utilise lead-acid batteries — a great deal of the high temperature superconductor story has still to be told.

This increasing complexity is a theme which runs through many other fields of materials science. In contrast to the bombshell of the announcement of high temperature superconductors, a prime reason for this increasing complexity of materials is not a sudden discovery but a continual striving for improved properties difficult to achieve with traditional materials. For such reason, the field of molecular electronics has come into being where an ultimate objective may perhaps be the utilisation of chemical function at a molecular level to achieve properties currently exhibited at a much larger, even though impressively small, scale by inorganic semiconductor devices. In such an aim we would, of course, see the final marriage of molecular and solid state chemistry. We are not yet near that dream but the study of, for example, organic materials for non-linear optics or for displays has been spawned on route.

The second reason for the growth in solid state chemistry in the latter two decades has been the spectacular improvement in characterisation methods, especially those based on diffraction techniques. Chemists have made full use of and, indeed, assisted in the development of several of these new experimental tools. In the late 1960s, the first lattice images produced by chemists from materials such as slightly reduced rutile were being greeted with scepticism by those established in electron microscopy. The resolution of electron microscopes was several angstrom units and computational methods for reproducing image patterns were not developed. Today, image resolution is at the 1 angstrom unit level, simple coordination polyhedra may be routinely identified and computational confirmation of the images produced is routine practice. Our understanding of the

real-space defect structures of solids at the basic building block level has been transformed by the application of the electron microscope in recent years, latterly assisted often by recent developments in solid state NMR techniques. The study of non-stoichiometric solids in general, of ionic conductors and of catalyst materials are but selected samples.

Equally important have been the development of neutron and x-ray scattering techniques. The last two decades have seen the development of synchrotron light sources which have transformed our ability to perform x-ray diffraction studies in real time or under varying ambient conditions and other techniques which demand high brightness sources such as EXAFS, which can give important information on atomic environments not available from diffraction methods. There has been the commissioning and application of high-flux neutron sources, notably the Institut Laue Langevin in Grenoble and the ISIS pulsed source in the UK. These major research facilities have transformed neutron scattering from being a difficult, time-consuming and laborious technique usable often only in last resort, generally with reactors designed for other purposes, to a prime tool for the study of solids often giving information inaccessible by any other method. The development of profile refinement methods for powders, although initially pursued by Rietveld on a medium-flux source, has, when applied to data from high-flux sources, transformed our ability to study the crystallography of materials which cannot readily be obtained as single crystals. For many years, the profile refinement method was primarily applied to neutron data but the development of the synchrotron light sources with monochromatic x-ray beams has permitted this method now to be widely applied to x-ray data also.

There has, however, been one further vital development in permitting the advances in solid state studies which have been made in the last two decades. This is the ability to understand and verify through computer modelling the structures and other properties which have been deduced by experiment.

Because of the very complexity of the materials often studied, experimental data are frequently not unequivocal. Or even if they are, the data by themselves do not permit the depth of understanding necessary to understand fully the properties of interest or to extrapolate the findings to related systems. If real progress is to be made, it is frequently essential to be able to model, for example, the energetics of a possible defect structure in a non-stoichiometric material or of a possible diffusion mechanism via atomic potential calculations or molecular dynamics.

The ability to perform realistic calculations of this type demands extensive computing power. For example, techniques and computer codes to perform atomistic lattice simulations were developed by Lidiard, Norgett and colleagues in the 1960s, and applied to increasingly complex defect situations, but necessarily still in solids with simple unit cells, by Catlow and others in the 1970s. Only in the 1980s has the advent of true supercomputers permitted the application of such techniques, and also of methods such as molecular dynamics simulation, to solids of much greater complexity and lower symmetry.

This volume is concerned with the application of computer modelling techniques to materials of the type discussed above. The articles demonstrate how computational methods and experimental methods may often be applied in conjunction with each other to obtain major advances in understanding and how computational methods can rationalise and clarify apparently complex behaviour.

2. BACKGROUND TO THE MEETING

A meeting, held in December 1988, on 'Computer Simulation of Inorganic Solids' was jointly sponsored by the Applied Solid State Chemistry Group Trust and the Polar Solids Group in the UK. Both Groups are subject groups of the Royal Society of Chemistry. The formation of both Groups has reflected the increasing attention being paid to interdisciplinary solid state sciences and, especially, to solid state chemistry in the last two decades. The Applied Solid State Chemistry Group was formed in the early 1980s and the Polar Solids Group a few years earlier. The Polar Solids Group is deliberately interdisciplinary and informal. The Applied Solid State Chemistry Group is run along more formal lines, and maintains significant representation from industry, as well as from academic and government science and technology, both within its Committee and amongst its members. It has grown rapidly since its formation.

Given the important underpinning that computer simulation increasingly plays in the development of solid state chemistry and related solid state sciences, it seemed natural that the two groups should combine to organise the first symposium on this field aimed at the wider solid state community rather than the computational specialist.

The organising committee of Dr. Alan Comyns, Dr. Steven Parker, Dr. Alan Chadwick and the author assembled a programme of speakers who are at the forefront of research in computational techniques in their various fields. However, the talks deliberately addressed not the research aspects of the computational techniques themselves but rather the range of application of the methods and prospects for future application.

Such a meeting was extremely timely because both the computer development and the code development which have been undertaken over the years have now rendered several techniques not only relatively straightforward but also fairly economical to apply. Given an understanding of what such methods can achieve, there is a real promise of their being used effectively and productively on a much wider scale than at present.

The meeting must be judged a considerable success. All the speakers gave clear, timely and enthusiastic presentations and over 100 participants came to listen — far in excess of the organisers' expectations. It was particularly gratifying that nearly half the audience were research students which argues strongly for the health of this field in the UK in the future. It was, indeed, particularly apposite that such a meeting should be held in the UK because many of the methods reviewed have been pioneered in the UK and that country is still one of the leaders in the application of computer modelling to solid state materials.

The reason for this state of affairs lies in the manner in which the research effort of the UK atomic energy programme was set up at Harwell. Although nuclear power is not at all buoyant in the UK as we enter the 1990s, Harwell has been, ever since its establishment in the late 1940s, a beacon of excellence in solid state science and solid state chemistry. The need to understand the properties of complex materials based on uranium dioxide led to the development of a great deal of expertise in and techniques of solid-state chemistry in the 1950s and 1960s which, in considerable measure, laid the groundwork for the revival in solid state chemistry which has taken place in the last two decades.

In a complementary fashion, Harwell's expertise in theoretical physics was the source of the modelling techniques for lattice simulations and molecular dynamics which have, through cooperation with universities and industry, developed into the useful and widely available techniques

of today. Originally, such methods were developed to assist understanding of the behaviour of defects in alkali halides and in uranium dioxide. Now, they are being applied to such complex materials as β -alumina, zeolites and high temperature superconductors.

Five of the papers presented at the meeting are reproduced in this volume. They give an excellent overview of the range of application of computer simulation methods to inorganic systems and to the interplay between computational and experimental methods. The conference was primarily dedicated to the discussion of continuous solid state systems rather than to the modelling of discrete molecular systems, but an opportunity was taken to include, because of its wide interest and complementarity, one paper on non-inorganic materials which deals with computer simulation of liquid crystals. All the papers are complementary to the papers on molecular modelling which most frequently appear in this Journal. It is believed that this contrast will provide the reader with a helpful and stimulating overview of a particularly exciting and still-developing area of solid state research. In the future, as the final paper indicates, there will be increasingly interdisciplinary approaches in computer modelling as in other fields. For example, calculations will combine both solid state potential methods, primarily used in continuous solids to date, with other techniques which take more explicit account of electrons to study more complex but important phenomena such as the interaction of gaseous molecules with inorganic surfaces.

3. REVIEW OF THE PAPERS

The five papers presented in this volume present a comprehensive overview of the diversity of computer modelling methods now applied to solid state chemistry together with a look forward to future opportunities. They also give a most up-to-date insight into several classes of materials of great current interest and how the modelling methods are assisting with the understanding of properties and as a great aid to future research and development.

The first paper by Allan and Mackrodt deals with atomistic lattice simulations of high temperature superconductors. Codes developed from the approach introduced by Lidiard and Norgett are used to calculate properties of complex copper oxides derived from La_2CuO_4 , giving many insights into the factors which may affect the superconducting properties.

The second paper by Thomas and Zendejas combines three topics already discussed above, namely neutron scattering, ion-conductors and molecular dynamics simulation. The conducting-ion distribution in the β'' -aluminas is extremely complex and difficult to elucidate even with the aid of modern single crystal neutron diffractometry. This is especially the case at high temperatures when the conducting ions are extremely delocalised or when more than one conducting ion is present. Molecular dynamics simulation can assist the unravelling of these complexities.

The following paper by Parker reviews molecular dynamics simulations applied to novel glasses based on ZrF_4 . Such glassy phases have been intensely studied in recent years because their extremely low intrinsic scattering at IR frequencies gives the possibility of extremely long optical signal transmission distances (over 1000 km) without amplification. But what are the structural features behind such glasses? Where there is no long range order from a crystallographic repeat unit, diffraction experiments are much more equivocal in providing data which can elucidate structural features. Computer simulation can assist greatly with understanding many aspects of the structure of glasses and provides a link with diffraction and other experiments.

Allen and Wilson review recent progress in the computer simulation of liquid crystals. They show how rather simple models which take into account size and shape can reproduce many of the phases demonstrated by liquid crystals. Unfortunately, in the paper, it is not possible to reproduce the excellent video, presented at the meeting, which demonstrates the transitions between neighbouring phases as the temperature is changed, but, as with the other papers, many excellent diagrams are provided. Even with the computer power available today, modelling such complex materials is only possible using approximate methods and the authors discuss how these can be best addressed to the problems of modelling liquid crystals.

Finally, Stoneham provides a concise overview of future directions which computer modelling may take, noting, however, at the beginning, that it is now 50 years since the paper by Mott and Littleton demonstrated the principles by which effective potentials could be built into calculations, even though it is only relatively recently that sufficient computer power has been available to permit accurate modelling of real systems.

Simulation of high temperature superconductors

Allan and Mackrodt point out that the extremely small energy change at the superconducting transition has a consequence for all superconductors that the normal state properties remain essentially unchanged in the superconducting state. Therefore, insights into the criteria for the observation of high temperature superconductivity may be obtainable from a study of the normal state properties. This paper addresses this issue and uses codes which have been previously successfully exploited in lattice simulations of many other oxide materials.

The authors show the principles behind the codes used and demonstrate initially that they are quite capable of reproducing the correct crystal structures for a series of ternary copper oxides. Indeed, the calculated lattice parameters are within 2% of the measured values.

Phonon densities of states may also be calculated and it is demonstrated that for four superconducting materials there is a strong phonon peak in the vicinity of 10 meV which may be a prerequisite for phonon-mediated high temperature superconducting behaviour.

It is pointed out that, for all high temperature superconductors, the phenomenon involves defect electrons and holes arising via doping. The simulation methods allow defect energies to be calculated. In all the materials studied, the energy difference between Cu 3d holes and O 2p holes is small. This suggests valance band holes of mixed character and strong carrier-lattice coupling, which supports the possibility that carrier-phonon coupling might make some contribution to the phenomenon of high temperature superconductivity.

Furthermore, the calculations find holes to be stable in La_2CuO_4 , Ca_2CuO_3 and Sr_2CuO_3 and electrons to be stable in Nd_2CuO_4 . These results predict hole superconductivity in La_2CuO_4 and electron superconductivity in Nd_2CuO_4 , in agreement with observation.

Finally, the authors demonstrate that it is possible to calculate the location of metal ion substituents of different valency in the various oxides studied. Such effects are extremely important in understanding and modifying superconduction behaviour. For example, strontium doping in La_2CuO_4 leads to superconducting behaviour. It is predicted that the Sr^{2+} will substitute for La^{3+} . On the other hand, smaller ions such as Al^{3+} are predicted to substitute for copper with a potentially deleterious effect on the superconductivity because of the break up of the superconducting CuO_2 planes.

Molecular dynamics simulation and diffraction

Fast ion conductors have a major component which can be described satisfactorily within a given space group. However, there can be minority components with lower symmetry. Frequently, in conventional crystallographic data processing, the consequences of this lower symmetry are ignored. The result is a constrained, time-averaged representation of the lower symmetry minority component on the majority structure. The authors show how a molecular dynamics approach can assist greatly both in determining the correct structural features of the minority lower symmetry component and also in allowing predictions to be made from the data obtained. They review the principles and pitfalls of molecular dynamics calculations and apply them to sodium β'' -alumina and to this material where some sodium ions are substituted by barium ions.

It is the sodium ions in β'' -alumina which form the mobile lower symmetry phase compared to the spinel-like structure of the rest of the unit cell. Although this material has been intensively studied crystallographically for over 20 years and is the essential basis of the sodium-sulphur battery, the fine details of the sodium-ion distribution have, because of the problems associated with unravelling the detailed structure of such materials, remained elusive. It is, however, just such knowledge which is necessary to understand the chemistry and properties of this remarkable material. The problem is further complicated by the non-stoichiometry of the material. Some of the Al^{3+} ions are substituted by Mg^{2+} and the sodium lattice is correspondingly non-stoichiometric.

The calculations demonstrate that the mobility of the Na^+ ions increases dramatically with temperature. Jumps between adjacent crystallographic sites begin to occur around 400 K whereas the oxygen ions also found in the conducting plane behave quite normally. The simulation also demonstrates the sodium ion relaxation towards vacant sites and that the sodium distribution appears to become totally disordered around 500 K.

While it is not possible to provide a quantitative relation between trajectories obtained from molecular dynamics simulation and scattering densities derived from diffraction experiments, the authors demonstrate qualitative similarity which lends support to the conclusions drawn. Of particular interest are features which can be explored by molecular dynamics simulation but which are inaccessible to experiment. The authors demonstrate the possibility of correlated motion of sodium ions at higher temperatures in the non stoichiometric material and also that, in a hypothetical stoichiometric material $\text{Na}_2 \text{MgAl}_{10} \text{O}_{17}$, no sodium mobility is found even at 1200 K. This latter result demonstrates most clearly the important contribution that non-stoichiometry makes to the fast ion behaviour.

Finally, it is shown how the simulations can allow local ordering processes to be isolated even in situations where more than one ion type is found in crystallographically equivalent sites so that their behaviour is indistinguishable experimentally, at least by diffraction techniques. The effect of substituting Ba^{2+} ions on the sodium ion behaviour provides such an example and the simulations show how the sodium ion behaviour is modified at lower temperatures and how it evolves as the temperature is raised. In particular, at lower temperatures, the Na^+ ions form a cluster around the Ba^{2+} substituents.

Molecular dynamics simulations of halide glasses

The glasses based on ZrF_4 were only discovered in the early 1970s. Study and technological in-

vestigation of these materials has been intense in the last 15 years. However, their existence is not easily explained by the normal criteria of glass formation based on cations of small coordination number with associated network formers. The author discusses the choice of potentials for studying these glasses and the limitations which the technique is subject to because of the relatively small structural unit simulated and the possibility for errors in potentials.

The simulation of glasses is necessarily somewhat different from that of crystalline materials, as there are no lattice positions which can be used as starting points for ionic trajectories. In the case of glasses, the approach is to start in the molten state where ions are freely diffusing and to lower the temperature to a supercooled glassy state before continuing the calculation to permit re-equilibration and the determination of the desired properties.

The calculations for the doped zirconium fluorides yield information on the Zr coordination number, which is strongly indicated to be greater than 6, probably 7 or 8. The results also indicate that the fluorines around Zr^{4+} are arranged as triangular dodecahedra (as in $\alpha\text{-ZrF}_4$) rather than as Archimedean antiprisms (as in $\beta\text{-ZrF}_4$). Polyhedra are linked both via edge and corner sharing.

The simulations show that small ions such as Li^+ act as network modifiers and are coordinated by both bridging and non-bridging fluoride ions. In contrast, ions such as Al^{3+} are network formers, being octahedrally coordinated by non-bridging fluoride ions.

The calculations also indicate that, in comparison with silicate glasses, the structure in fluoride melts breaks up quickly with a rising temperature, that the fluoride glass structure does not allow space for diffusion of hydrogen as is the case with silica glasses, and also that the F^- ions are relatively mobile below the glass transition temperature. The author notes that the results obtained are by no means the whole story for these materials and that in the future many other properties may be fruitfully studied by simulation methods.

Computer simulation of liquid crystals

The authors point out that the complex molecules which form liquid crystalline phases cannot yet be modelled realistically. Additionally, the phenomena which characterise liquid crystalline behaviour occur over scales of time and length which are large compared with the times and distances for which molecular dynamics simulations are traditionally evaluated. This entails that, for accurate simulation of properties, extremely lengthy computer simulations are required, a formidable undertaking even with present-day supercomputers. The present approach is therefore to simulate model systems. This review shows the richness of results which can be obtained from hard non-spherical models and compares the results with those using other approximations.

It is pointed out that while atomic hard sphere models provide a sound basis for understanding the properties of simple liquids, it is not self evident that hard non-spherical models can reproduce the properties of liquid crystals. The authors discuss earlier work on hard non-spherical particles. It was only in the mid-1980s that liquid crystal phases were definitely observed using Monte Carlo calculations. The authors then review the molecular dynamics simulations they have performed more recently which demonstrate spontaneous ordering to a nematic phase for hard ellipsoids and a nematic-smectic transition for hard spherocylinders. Interesting ordering properties are also observed in simulations of hard particle systems constructed from spheres with the top and bottom cut off to give disc-like shapes.

The authors go on to discuss work on more sophisticated models, for example where soft bodi-

es are assumed rather than hard bodies. To proceed beyond this more sophisticated model, molecular structure must be included. It is clear from the experimental data that the stability of various liquid crystal phases is extremely sensitive to the fine details of molecular structure and inter-molecular interaction. The authors show how actual molecular structures can be approximated to permit calculations to be attempted in realistic computer time but, although various strategies are discussed, the resulting calculations are so complex that, even with present-day supercomputers, progress is difficult.

Finally, the authors discuss the modelling of films of liquid crystals using Monte Carlo simulations. The results indicate that surface regions are less well-ordered than the interior and that the disordered surface area penetrates the system further as the transition temperature is approached. This area of the subject is a particularly exciting one for further study because of the rich variety of phenomena which may be observed and because of the great technological relevance.

Future directions

Stoneham summarises the achievements of lattice modelling which include predictions of stable phases, of defect energies and of diffusion rates. He points out that metals and semiconductors are less easily studied than ionic materials and that large bio-molecules can also not be studied with similar predictive accuracy.

He also lists interesting new materials which have been studied in recent years and points out that only for a few have reliable quantitative predictions been made and demonstrated. However, in spite of this, the importance of modelling is that it provides a framework for understanding behaviour and experimental result and a focus for looking forward to the development of deeper scientific understanding and to technological improvement.

The study of diffusion, of superconductors and of interfaces is briefly reviewed. It is pointed out that grain boundary structure and surface phenomena can now be modelled successfully for ionic crystals as can metal-oxide interfaces which will permit, it is hoped, great advance in the study, for example, of coatings and of catalysts. Finally, Stoneham reviews how electrons can be explicitly included rather than being taken account of through the use of inter-atomic potentials and, going on from this, how organic materials such as conducting polymers and bio-molecules can be accurately modelled.

A personal list of difficult but important areas for future study is provided by the author to stimulate the modellers of the 1990s.