# Computational modelling in materials at the University of the North

**Phuti E. Ngoepe[a*] and C. Richard A. Catlow[b]**

**We review computational modelling studies in materials resulting from the National Research Foundation–Royal Society collaboration. Initially, investigations were confined to transport and defect properties in fluorine and oxygen ion conductors used mainly in energy storage devices. Subsequently, the programme was broadened to include the themes of minerals, metal alloys, and polymers. Electronic and structural properties and voltage profiles of lithium battery electrodes with spinel, graphite, and chalcogenide structures were studied on energy storage devices. Similar properties have been investigated in the new magnesium-based chevrel structures. Calculations on the electronic and structural characteristics of precious metal and transition metal sulphides have also been carried out. In particular, new robust interatomic forcefields have been derived, thereby enabling bulk and surface atomistic simulations of large systems including ilmenite, apatite and electrolytic manganese dioxides. Phase stability studies of light metal alloys, such as AlRe and MgLi, have been conducted and transformations followed amongst competing phases of $Pt_3Al$. Cluster expansion methods were applied to Pt alloys for the generation of databases needed in the derivation of phase diagrams. We have also studied surface interactions of $PtAl_2$ with sulphur and oxygen molecules. Semi-empirical potentials of gold were used to investigate the gold nanoclusters, in conjunction with with *ab initio* methods. A fourth theme involved studies of polymers in which transport of small gas molecules and silicone oils in polysiloxanes were investigated. The wetting of nafion membranes and cellulose structures is now being studied for various applications. Spectroscopic methods have been used in part to complement theoretical calculations. We also report on the management and outcomes of the programme to date.**

## Introduction and background

Here we review the research programme on computational modelling of materials at the University of the North (renamed the University of the Limpopo in January 2005) run under the auspices of the National Research Foundation–Royal Society (NRF–RS) initiative. The aims and long-term goals of the NRF–RS science, engineering and technology (SET) programme were to increase the number and quality of black researchers, to provide access to U.K. institutions and to expose black scientists to the international scientific arena, to foster a climate of collaborative research between Britain and South Africa, and to create centres of excellence

Computational modelling of materials is a relatively new field and has been consolidated in the last thirty years. It now covers a wide range of subjects from physics and chemistry to biology. Significant leaps in computational power and its affordability, from systems such as PC clusters, together with current developments in theoretical methods, have now advanced to a point where reliable quantitative computer modelling predictions of many kinds of materials properties are possible. This has further been enabled by a substantial increase in the number of atoms that can be modelled; thousands for quantum mechanical modelling and up to billions using semi-empirical and empirical methods.[1] In addition, the current innovative approaches of working across length scales of modelling and use of hybrid methods have opened new opportunities of handling some of the most complex and highly correlated systems and composites. Consequently, a new scientific approach is evolving where simulations are no longer just compared with the two traditional methods — experiments and theory — for their validation, but are used in conjunction with them in order to solve practical problems.

Several large international companies use computational modelling of materials to optimize their efficiencies and profits. South African companies such as Sasol, the SA Druggist Group, science councils such as the CSIR and Mintek, and universities have established modelling programmes to study materials and their processing, while other institutions have contracted computational modelling services for a similar purpose. The computational modelling community in South Africa is beginning to join hands in sharing experiences and expertise from either the perspective of software development or hardware management. Cooperation is also emerging in attempts to acquire high-performance computing facilities. The Materials Modelling Centre (MMC) at the University of the North (UNIN) was formally established in 1996, although computational modelling began there earlier. The initial aims and objectives of the centre were to:

- Build and strengthen research capacity in computational modelling of materials at the university, in a province (Limpopo) where technological expertise and manufacturing activities involving materials processing are minimal, but where abundant natural resources need to be beneficiated. Limpopo currently receives 1.3% of the national investment in research and development, though it harbours 10% of the population.
- Train postgraduate students to use a combination of a wide array of computational tools, experimental techniques and databases in designing materials with specific characteristics. In this process, appropriately qualified people will be produced to assist South African industry become internationally competitive.
- Collaborate with educational institutions and laboratories, both locally and internationally, to enhance research capacity.
- Liaise closely with industry and national laboratories on materials design, using various types of modelling approaches. This will contribute towards cost-effective development of a variety of commercial products that are materials based.
- Study the beneficiation of minerals and related materials, in order to enhance the value of South Africa's abundant primary resources and to turn such materials into useful products.
- Participate in local and national forums, networks and initiatives that deal with industrial competitiveness based on materials and which lead to the creation of job opportunities.

[a]Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga 0727; and Manufacturing and Materials Technology, CSIR, P.O. Box 395, Pretoria 0001, South Africa.

[b]Davy Faraday Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, W1X 4BS; and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

*Author for correspondence. E-mail: ngoepep@ul.ac.za

The NRF–RS initiative has provided an environment where the intentions of the programme and that of the MMC could be integrated and where participants with related research interests in South Africa (UNIN) and the U.K. were able to collaborate fruitfully. The establishment of this initiative at UNIN significantly enhanced its research profile. The U.K. has several well-established researchers in the area of computational modelling, hence the NRF–RS programme has been an excellent vehicle for facilitating interactions with their South African counterparts.

## Themes of study and their highlights

Prior to the start of the NRF–RS collaboration, the Materials Modelling Centre conducted computational modelling on materials used in energy storage devices. In order to be aligned with broader needs of South African industries, mainly minerals and their downstream applications, three additional research themes were introduced — minerals, metal alloys, and polymers. A wide range of modelling techniques have been used in the collaboration, and these are now being combined to tackle practical problems and to achieve the programme's objectives. We highlight here some of the achievements which, we believe, will provide far-reaching benefits in the future.

### Minerals

Sulphide minerals are abundant in South Africa and accommodate some of the major platinum-bearing compounds such as PtS, $PtAs_2$, and $PtSb_2$. Since most of these compounds are covalent, *ab initio* density functional theory planewave pseudopotential (DFT–PWP) methods were used to investigate the effect of pressure on their electronic, optical and structural properties, where elastic moduli were deduced.[2,3] Some base metal sulphides such as pyrite and pyrrhotite co-exist with precious metal sulphides. *Ab initio* calculations on the electronic and structural properties of $FeS_2$ as pyrite and marcasite[4] have provided an excellent basis for deriving empirical potentials. Large quantities of cobalt, nickel and iron sulphide pentlandite compounds also occur as intergrowths with some of the platinum sulphides. PWP studies provided an explanation as to why $Co_9S_8$ and $Fe_{4.5}Ni_{4.5}S_8$ occur in nature whereas $Fe_9S_8$ and $Ni_9S_8$ do not. The stability of these compounds was evidenced by their heats of formation and the location of their Fermi levels relative to pseudogaps in the electronic density of states.[5]

A recent major breakthrough is the derivation of the first robust empirical interatomic potentials for pyrite and hence for mineral sulphides as a whole. The potentials for $FeS_2$ have accurately predicted ambient and high pressure[6] and high temperature[7] structural and elastic properties. Similar potentials have also contributed to understanding the surface properties of the pyrite[8] and marcasite forms of $FeS_2$. The derivation of potentials has been extended to precious metal compounds possessing the pyrite structure, such as $PtSb_2$ and $PtAs_2$ such that bulk and surface properties were successfully predicted.[9] Preliminary results have been derived for tetragonal precious metal sulphides and the potentials are being further refined. The availability of potentials has opened a new avenue for calculating the bulk and surface properties of metal sulphides, such as ion transport, and point and line defects, flotation behaviour, smelting, crystal growth, dissolution, and nanoparticle formation, involving up to hundreds of thousands of atoms considered in the same way as traditionally performed with metal oxides.

Ilmenite ($FeTiO_3$) is abundant in South Africa and is beneficiated locally in the production of $TiO_2$ pigments and titanium metal. A series of ilmenite-structured $MeTiO_3$ compounds (Me = Fe, Mg, Zn, Mn) has been studied using DFT–PWP methods. Their structural and electronic properties have been explored in terms of Me and pressure.[10] However, the DFT methods alone could not predict the insulator behaviour of the highly correlated $FeTiO_3$; on the contrary, they modelled it as metallic. Consequently, the hybrid unrestricted Hartree-Fock and density functional theory methods were used to model adequately the electronic spin configuration and reproduce the experimental bandgap of 3.0 eV and the correct structure of $FeTiO_3$.[11]

Apatite plays a significant role as a biomaterial and as a mineral source of phosphate. The surface properties of the apatite structure have been studied.[12] Furthermore, the intergrowth of apatite and silica was investigated in detail as a precursor for work on bioglasses.[13] Vanadium dioxide ($VO_2$), which forms rutile and monoclinic structures, has been investigated in order to understand its photochromic properties around the transition temperature of 68°C. Interatomic potentials for the compound have been derived, together with those of dopants that are likely to reduce the transition point to room temperature.

### Energy storage devices

The initial work on energy storage devices involved fluorites, which are model systems for ionic conduction in batteries. A combination of techniques such as static and molecular dynamics calculations and EXAFS measurements elucidated how defect and ion transport mechanisms vary with temperature and composition in the fast-ion phase of mixed-metal fluorites.[14,15] Furthermore, light-scattering techniques and calculations have shed valuable light on ion transport changes in $BaF_2$[16] and $CaF_2$ effected by various types of lanthanide dopants. $LiC_6$ serves as an electrode for lithium batteries, and a comprehensive *ab initio* study on its structural and electronic properties,[17] including associated voltage profiles,[18] have been carried out. Similarly, the first calculations have been conducted to predict structure, energetics and voltage profiles[19] for magnesium-based chevrel-structured ($MgMo_6S_8$) electrodes used in the emerging technology of magnesium batteries, which are less polluting and potentially have a higher energy density than traditional storage batteries.[20]

Cubic stabilized zirconia, $ZrO_2(xY_2O_3)$, is one of the most reliable electrolytes in solid oxide fuelcells. A combination of elastic constants forcefield calculations and experiments at high temperature[21] confirmed the nature of defect clusters in this material.[22] This provides a reliable approximation for modelling oxygen transport, which determines the efficiency of the fuelcells and how it changes with yttria dopant concentration and temperature. Electrolytic manganese dioxides (EMD) are used as electrodes in alkaline batteries; their efficiency could be enhanced by a better understanding their complex structure. We used a combination of surface energy calculations, molecular dynamics and EXAFS to study intergrowths of pyrolusite and ramsdellite polymorphs.[23] Simulated amorphization and recrystallization techniques, based on tens of thousands of atoms, have been employed recently to grow nanoparticles and intergrowths of these polymorphs. The deduced radial distribution functions compare well with EXAFS results.[24] The method has provided a wealth of information on complex defects in EMD including intergrowths, twinning, dislocations and vacancies.

### Metal alloys

Phase diagrams play a crucial role in guiding the manufacture of products from their component materials, since they indicate compositions and temperatures that are suitable for use. Studies

on the phase stability of metal alloys, in particular aluminium-rhenium alloys, using PWP methods has provided heats of formation. Such energies confirm the stabilities of structures for a variety of compositions, and are used as inputs in the prediction of phase diagrams. Similar studies have been carried out on precious metal superalloys, in particular $Pt_3Al$, used in high temperature jet engines. Competing phases, namely, cubic $L1_2$ and tetragonal $DO_C$ structures in these superalloys, render them unsuitable for such applications. Tetragonal distortions and displacements which induce cubic to tetragonal transformation in $Pt_3Al$ have been identified. Electronic bands and density of states structures around the Fermi level were used to explain the causes of instability and were compared with those of $Ni_3Al$ in which competing phases are not observed. In addition, the Connolly-Williams methods have been used to study cluster expansion of $Pt_3Al$ alloys and to determine the associated Hamiltonians, which enable prediction of phase diagrams. $PtAl_2$ is amongst the structures which appear in the platinum-modified bondcoats for nickel-based superalloys. The oxidation and sulphidization on $PtAl_2$ surfaces have been investigated by DFT–PWP calculations and the variation of reactivity of metals with alloying is predicted from electronic and structural properties[25] and agrees with available experimental results.[26]

Studies of light metal alloys based on magnesium and aluminium are expanding owing to their recent extensive use in the manufacturing of automotive components. We have investigated the stabilization of a cubic phase of magnesium by alloying with lithium, which is more ductile than the hexagonal phase. Phase stabilities and elastic properties have been studied[27] and these will be combined with scans from optical and electron micrographs to activate object-orientated finite element modelling, which will provide detailed information on their mechanical properties.

Nanoparticles of gold are used for applications as catalysts. Since nanosystems require a large number of atoms, the semi-empirical Sutton–Chen potentials of gold have been refined to reproduce the surface energy and melting temperature of gold relatively accurately.[27]

### Polymers

An understanding of permeation by small gas molecules in polymers plays a vital role in enhancing insulating properties of protective clothing. The effects of temperature, penetrant size, and the nature of forcefields on penetrant (small molecules such as methane, helium, and oxygen) diffusion and solubility in polysiloxanes has been investigated, using molecular dynamics techniques and the Widom insertion method, respectively.[29] Current work involves studies of the transport of silicone oils in polysiloxanes networks, where the diffusion is reasonably well predicted. Proton exchange membrane fuelcells use nafion as an electrolyte. Studies of diffusion and solubility of water and methanol in nafion membranes have been carried out, together with the impact of temperature on these transport properties.[30] Research on polymers has been extended to natural fibres and their composites, where the impact of the interaction of cellulose and inorganic materials on mechanical properties is being studied in detail. Initial molecular dynamics studies on four types of celluloses have predicted their structures well.

## Impact of the programme

One of the main objectives of the programme is to increase the number of black postgraduate students in science, engineering and technology. In 1997, 4 M.Sc. students participated in the programme at UNIN (there was no Ph.D. student). In 2004, these numbers had increased to 12 (two women) and 7 (including one woman), respectively. These students, who are all African, were recruited by exposing undergraduates to research in computational modelling, and by providing some with vacation employment where they assisted with literature searches and the analysis of experimental results. Approximately 35 students have completed B.Sc. honours degrees, and have carried out projects in computational modelling. An encouraging number have pursued postgraduate studies at UNN and at other universities. Twenty-two students completed their M.Sc. degrees with six obtaining distinctions. Most of the M.Sc. graduates proceed to a Ph.D., and seven doctoral students have now completed their studies. The numbers are significant, bearing in mind the relatively few higher degrees in physics awarded in South Africa. However, the number of women participating in postgraduate studies is too few.

Gratifying reports have been received from the examiners of theses, who are appointed worldwide, on the quality of our students. Workshops on the theoretical basis underpinning computational modelling studies have been offered under the NRF–RS collaboration, and these now accommodate students from other universities in South Africa. Collaboration with the U.K. groups has greatly added to the value of the training and supervision provided in a wide range of projects. Some of the South African participants are staff members at UNIN, hence the programme has supplied well-qualified lecturers who play a valuable role in teaching, mentoring and supervision. However, there is the challenge of retaining competent staff at the university, since they tend to be attracted by other institutions and industry. The University of Limpopo therefore needs to work on planning career paths for its faculty, whilst they undergo staff development training.

Many presentations on work that derive from the programme have been made at local and international conferences. They currently total 152 at conferences in South Africa and 40 at meetings abroad. Some students have won conference prizes; for example, the De Beers award for the best Ph.D. presentation in solid-state physics at the South African Institute of Physics conferences was won by H.M. Sithole and D. Mkhonto in 2000 and 2002, respectively. Furthermore, in the last eight years annual conferences on computational modelling in materials, run under the auspices of the NRF–RS collaboration at UNIN, have been attended by representatives from local universities, science councils and industry; this has significantly enhanced awareness of computational modelling of materials in South Africa. The 14th International Conference on Defects in Insulating Materials, held in Midrand north of Johannesburg in 2000, was co-hosted by the MMC. The number of published papers from the centre was initially modest, but has now reached 35.

### Regional and industrial impact

The choice of the four research themes in the NRF–RS collaboration has enabled the MMC to position itself strategically relative to the mining, minerals, metallurgical and energy industries. Some of the main technology missions of the South African National Research and Development Strategy,[31] particularly the Advanced Manufacturing Technology, and Resource-Based Sustainable Development strategies, are related to these themes. Furthermore, the MMC has been making contributions that support the Limpopo Provincial Development Growth Strategy, with special emphasis on mining, which is one of the three pillars of economic development in the province. The MMC is looking forward to playing a key role in the evolution of platinum- and chemistry-based initiatives, which are seen as

priorities by the province, by developing relevant technologies and training and supplying appropriately qualified people. We also expect that our energy projects will contribute usefully to evolving national energy initiatives.

### Research culture and social aspects

The exposure of postgraduate students to institutions in the U.K.* and to the different ways of living in that country, has enhanced their confidence in computational modelling studies and assertiveness on how they conduct their scientific and personal affairs. This change is noticeable in the way they contribute and engage at seminars and local conferences. Furthermore, the clusters around various themes have engendered a spirit of mutual support amongst students, which significantly benefits new entrants to postgraduate studies and those learning new methods. The assumption of different responsibilities in the MMC, whether in the organization of conferences, the scheduling of talks, or the recording of minutes, has also helped shape their management skills. A critical aspect that is often overlooked is that postgraduate students are young adults faced with family responsibilities. Their families, who nurtured them through their school and undergraduate years, mostly rely on their support after graduation. As they grow older, they start their own families and are under pressure to look for employment. It is thus important to factor this component into their financial support, especially at a time when South Africa is increasingly reliant on ageing researchers and experiences an acute shortage of younger scientists.

## Capacity building

Achievements of the SET objective of the NRF–RS programme and the highlights mentioned above were underpinned by institutional support in a wider sense. Since the start of the collaboration, research capacity on computational modelling at UNIN was strengthened by expansion of the research infrastructure. Silicon Graphics servers and workstations were purchased with the assistance of the university, the NRF (then the Foundation for Research Development) equipment programme, as well as THRIP, the CSIR and Silicon Graphics. The university expanded the computational modelling laboratory, and provided adequate accommodation to researchers. It also installed a standby generator to guarantee uninterrupted supply of electricity in cases of power failure. In line with recommendations from the 1999 mid-term review of the NRF–RS programme, the positions of deputy director and a principal administrative officer were created in the centre.

### Management of the programme

The South African and U.K. project leaders held meetings regularly to review progress and discuss the running of the project in both countries in line with the guidelines provided by the NRF and the Royal Society. Joint annual business meetings, which set targets for the year, have been effective in guiding the programme. These meetings preceded or followed the annual materials modelling conferences held at UNIN. Researchers and students have been divided into four groups in accordance with the chosen themes of the collaboration. The groups discuss common issues in the theme such as methods, preparation of papers, theses and other related matters. The South African coordinator and his deputy managed the running of the centre and the collaboration. A systems manager ensured that hardware and software systems were properly maintained and updated. He was trained by the computer vendor, Silicon Graphics, when it still had a presence in South Africa, to do initial troubleshooting in the case of systems failure; this approach has made the maintenance of hardware and software affordable. An administrator has been essential, with focus on financial management, assistance of students with registration and financial support, liaison with collaborating institutions on administrative matters, travel arrangements for researchers, and organization of conference. The U.K. coordinator was responsible for supporting researchers financially during their stay in Britain, and generally ensured that the junior parties make good progress wherever they were posted. The NRF and Royal Society managements were found to be effective, accessible and involved at about the right level.

The development of research capacity and change of research culture, in an environment where traditional research values have not been nurtured, is a formidable task. However, with interventions of research capacity building spearheaded mainly by the NRF, seeds of a research culture were sown, particularly in the early 1990s. The dawning of the new democratic dispensation in South Africa in 1994 drew a significant number of competent and potential researchers from institutions such as UNIN, to join government, the science councils and others. In addition, the requirements of meeting employment equity targets in various organizations further depleted the university's corps of competent people. Those who remained fairly active in research continued to be visible and at times even appeared odd in the system; they thus required even stronger resolve and motivation to remain committed to the assignment. Since the beginning of the collaboration, the reliability of the computer network within the university and connectivity nationally and internationally remained a major obstacle, since it limited communication and transfer of data between UNIN and institutions in the U.K. Moreover, access to the scientific literature and electronic journals of UNIN has been limited; this situation has been aggravated by the fluctuating rand/dollar exchange rate, and is one of the areas that need serious attention.

## Conclusion

The achievements outlined above could not have been realized without the support of the NRF–RS SET programme. The high standing of the Royal Society and the NRF ensured the involvement of leading U.K. researchers. This has been the most effective way of enhancing modelling expertise at UNIN. Several students, from both UNIN and Britain, have produced first-rate theses. The students, particularly from UNIN were exposed to a wide variety of computational techniques and are developing as confident, independent researchers. The establishment of a centre of excellence at UNIN is being largely achieved. Furthermore, it is beginning to make an impact on aspects of provincial economic development. It is envisaged that the programme will sustain itself to a considerable extent, but this will be further enhanced by the continuation of the collaboration to consolidate some important emerging areas of research. The project was also of benefit to the U.K. partners as it introduced them to a range of new scientific problems.

We gratefully acknowledge the support of the National Research Foundation and The Royal Society and contributions of the South African and United Kingdom participants in the programme.

*Project leaders and institutions in the U.K. participating in the joint programme are: C.R.A. Catlow (The Royal Institution and University College London); A.V. Chadwick (University of Kent, Canterbury); N.H. de Leeuw (University College London); G. Goldbeck-Wood (University of Cambridge, and Accelrys Inc., Cambridge); N.M. Harrison (Imperial College of Science, Technology and Medicine, London, and Daresbury Laboratory, Warrington); S.C. Parker (University of Bath); D.G. Pettifor (University of Oxford); N. Quirke (Imperial College of Science, Technology and Medicine, London); D.C. Sayle (Cranfield University, Swindon); and K.V. Wright (The Royal Institution and University College London).

1. Sharma A., Haas A., Nakano A., Kalia R.K., Vashishta P., Kodiyalam S., Miller P., Zhao W., Liu X. and Campbell T.J. (2003). Immersive and interactive exploration of billion-atom systems. In *Presence: Teleoperators and Virtual Environments,* vol. 12, eds R.B. Loftin and L. Rosenblum, pp. 85–95. MIT Press, Cambridge, MA.
2. Nguyen-Mahn D., Ntoahae P.S., Pettifor D.G. and Ngoepe P.E. (1999). Electronic structure of platinum-group minerals: prediction of semiconductor band gaps. *Mol. Simul.* **22**, 23–30.
3. Mangwejane S.S. (2005). *Atomistic, electronic and optical studies of $PtSb_2$ and $PtBi_2$.* M.Sc. dissertation, University of the North, Sovenga.
4. Nguyen-Mahn D., Pettifor D.G., Sithole H.M. and Ngoepe P.E. (1998). Electronic structure, pressure dependence and optical properties of $FeS_2$. In *Materials Research Society Symposium Proceedings,* vol. 91 (Tight-Binding Approach to Computational Materials Science), eds P.E.A. Turchi, Gonis and L. Colombo, pp. 401–406. Materials Research Society.
5. Chauke H.R., Nguyen-Mahn D., Ngoepe P.E., Pettifor D.G. and Fries S.G. (2002). Electronic structure and stability of pentlandites: $Co_9S_8$ and the related alloys. *Phys. Rev. B* **66**, 155105–155109.
6. Sithole H.M., Ngoepe P.E. and Wright K.W. (2003). Atomistic simulation of the structure and elastic properties of pyrite ($FeS_2$) as a function of pressure. *Phys. Chem. Miner.* **30**, 615–619.
7. Tlali S.B., Mathe B.M., Kotane L.M., Schoning F.R.L., Comins J.D., Every A.G., Sithole H.M., Ngoepe P.E. and Wright K.W. (2004). Brillouin scattering studies and computational simulations of the elastic properties of pyrite ($FeS_2$) at high temperatures. *Phys. Stat. Sol.* **9**(c)**1**, 3073–3076.
8. de Leeuw N.H., Sithole H.M., Parker S.C. and Ngoepe P.E. (2000). Modelling surface stability and reactivity of pyrite: Introduction of the new potential model. *J. Phys. Chem.* **104**, 7969–7976.
9. Ngoepe P.E., Ntoahae P.S., Mangwejane S.S., Sithole H.M., Partker S.C., Wright K.V. and de Leeuw N.H. (2005). Atomistic simulation studies of iron sulphide, platinum antimonide and platinum arsenide. *S. Afr. J. Sci.* **101**, 480–483.
10. Mkhonto D. (2002). *Computer simulation of ilmenite systems.* MSc dissertation, University of the North, Sovenga.
11. Wilson N.C., Muscat J., Mkhonto D., Ngoepe P.E. and Harrison N.M. (2005). The structure and properties of ilmenite from first principles. *Phys. Rev. B.* **71**, 075202-1-9.
12. Mkhonto D. and de Leeuw N.H. (2002). A computer modeling study of the effect of water on the surface structure and morphology of fluorapatite: introducing a $Ca_{10}(PO_4)_6F_2$ potential model. *J. Mater. Chem.* **12**, 2633–2644.
13. de Leeuw N.H., Mkhonto D. and Catlow C.R.A. (2003). A computer modelling study of the adhesion of apatite thin films on silicate surfaces. *J. Phys. Chem. B* **107**, 1–3.
14. Netshisaulu T.T., Ngoepe P.E. and Chadwick A.V. (1999). Computer modelling and EXAFS study of disorder in $CdF_2(xPbF_2)$ mixed systems. *Mol. Simul.* **22**, 1–21.
15. Netshisaulu T.T., Chadwick A.V., Ngoepe P.E. and Catlow C.R.A. (2005). EXAFS and computer modeling studies of lead-cadmium fluoride. *J. Phys. Condens. Matt*. **17**, 6575–6586.
16. Rammutla K.E., Comins J.D., Erasmus R.M., Netshisaulu T.T., Ngoepe P.E. and Chadwick A.V. (2002). Investigation of the superionic behaviour of $BaF_2$(xmol% $LaF_3$) by Raman and Brillouin scattering and molecular dynamics simulations. *Radiat. Eff. Def. Solids* **157**, 783–788.
17. Kganyago K.R., and Ngoepe P.E. (2003). Structural and electronic properties of graphite and lithium intercalated graphite. *Phys. Rev. B* **68**, 205111–205127.
18. Kganyago K.R., Ngoepe P.E. and Catlow C.R.A. (2003). Ab initio calculation of the voltage profile for $LiC_6$. *Solid State Ionics* **159**, 21–23.
19. Kganyago K.R., Ngoepe P.E. and Catlow C.R.A. (2003). Voltage profile, structural prediction and electronic calculations for $Mg_xMo_6S_8$. *Phys. Rev. B* **67**, 104103–104112.
20. Aurbach D., Lu Z., Schechter A., Gofer Y., Gizbar H., Turgeman R., Cohen Y., Moshkovich M. and Levi E. (2000). Prototype systems for rechargeable magnesium batteries. *Nature* **407**, 724–727.
21. Botha J.C., Chiang J., Comins J.D., Mjwara P.M. and Ngoepe P.E. (1993). Behaviour of elastic constants, refractive index and lattice parameter of cubic zirconia at high temperatures. *J. Appl. Phys.* **73**, 7268–7274.
22. Chaba P.J. and Ngoepe P.E. (1998). Computer modelling studies of elastic and transport properties of yttria stabilised zirconia. *Mol. Simul.* **21**, 161–172.
23. Maphanga R.R., Ngoepe P.E., Parker S.C. and Chadwick A.V. (2003). Computational modeling and EXAFS studies of electrolytic manganese dioxide. In *Proc. 2nd International Conference of the African Materials Research Society,* eds Y. Ballim, A.G. Every, S. Luyckx and D.C. Levendis. University of the Witwatersrand, Johannesburg.
24. Sayle T.X.T., Catlow C.R.A., Maphanga R.R., Ngoepe P.E. and Sayle D.C. (2005). Simulating $MnO_2$ nanoparticles using amorphisation and recrystallisation technique. *J. Am. Chem. Soc.* **127**, 12828–12837.
25. Mokagane M.M., Ngoepe P.E., Harrison N.M. and Montanari B. (2003). Adsorption of sulphur on $PtA1_2$. In *Proc. 2nd International Conference of the African Materials Research Society,* eds Y. Ballim, A.G. Every, S. Luyckx and D.C. Levendis. University of the Witwatersrand, Johannesburg.
26. Rodriguez J.A. and Kuhn M (1997). Interactions between sulfur and platinum in bimetallic surfaces: Reaction of $S_2$ with Pt-Al alloys. *J. Vac. Sci.* **A15**, 1608–1612.
27. Phasha M.J. (2005). Ab initio *study of cohesive, electronic and elastic properties of ordered cubic–based Mg–Li alloys.* M.Sc. thesis, University of the North, Sovenga.
28. Mahladisa M.A, Ackermann and Ngoepe P.E (2005). Structural properties of gold clusters at different temperatures. *S. Afr. J. Sci.* **101**, 471–474.
29. Segooa L.R.M., Ngoepe P.E. and Goldbeck-Wood G. (2001). Atomistic simulation of gas phase atoms with small radii through polysiloxanes. *Radiat. Eff. Def. Solids* **156**, 341–346.
30. Dolo J.J., Ackermann L. and Ngoepe P.E. Molecular dynamics simulation studies of water and methanol in nafion membrane. In *Proc. 2nd International Conference of the African Materials Research Society,* eds Y. Ballim, A.G. Every, S. Luyckx, D.C. Levendis, p. 228. University of the Witwatersrand, Johannesburg.
31. *South Africa's National Research and Development Strategy* (2002). The Government of the Republic of South Africa, Pretoria.