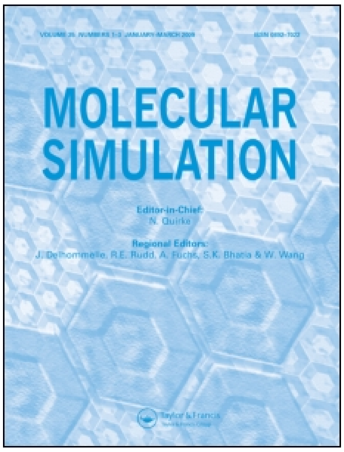

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ATOMISTIC SIMULATION OF NEW MATERIALS: PITFALLS AND PROMISES

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In this paper, we discuss some of the pitfalls that may be encountered using atomistic computer simulations of complex inorganic materials. The examples discussed are intended to illustrate the promising role that computer simulations can play in solid state chemistry, providing the pitfalls are avoided.

KEY WORDS: Inorganic materials; ceramics; solid state chemistry interatomic potentials

INTRODUCTION

In this paper, we discuss some of the pitfalls that may be encountered in the application of atomistic computer simulation methods to "new" inorganic materials. From our discussion, it will, hopefully, be apparent that computer simulations can provide substantial information that both complements and supplements available experimental data, provided that care is taken to avoid the major pitfalls. Firstly, however, it is convenient to define, for our present purposes, what we mean by a new material and how its characteristics may contribute to difficulties in the simulation: what it is, if anything, about new materials that make then hard to model.

In the field of inorganic materials, such as ceramics, a new material may be defined as one whose property set fulfils, or has the potential to fulfil, a contemporary technological requirement. This working definition includes the case where improved properties have been discovered as in, for example, the new high T_c oxide superconductors. Although, in many cases, the compounds have been around for some time, their property sets may not have been determined previously, and thus their technological potential not appreciated.

The characteristics of new materials may be outlined as follows: The most distinctive feature usually is the complexity of the crystal chemistry, both in terms of the atomic structure and of the actual chemistry. Examples here include, on the one hand, the magnetoplombite structured aluminates where the emphasis lies more towards the crystal structure and stoichiometry rather than chemistry, and on the other hand the Bi-Sr-Ca-Cu-O superconductors in which the complex crystal chemistry is coupled with (or perhaps due to) the multi-cation chemistry. Computer simulations, in general, work best when the interatomic potentials used to describe the various interactions in the solid are simplest. Thus whilst the pair potential approach expoused by Born is satisfactory for the alkali halides and other simple compounds with classical ionic-type characteristics, it has not been found to work for SiO_2 in which the bonding is somewhat directional and more akin to the classical notions of covalency.

For reviews, see Catlow and Mackrodt [1] and Catlow and Cormack [2]. Extensions to the Born model have, however, been used successfully to overcome this problem. Indeed, Islam *et al.* [3] have used such a three body bond bending potential addition to the Born potential model to reproduce the structural features of CuO, a necessary prerequisite for the simulation of Cu containing compounds, as we shall argue below.

In the next section we outline the properties of potential models, used in the simulation of inorganic materials, such as ceramics. Here we will list some of the pitfalls that we feel should be avoided; in the subsequent sections we will use case studies to illustrate our theme.

INTERATOMIC POTENTIAL MODELS

The earliest simulations were founded upon the work of Born who used point ion charges and short range repulsive interactions to obtain some properties of solid alkali halides. The pair potential model was very successful and has been used for a wide range of materials usually, but not exclusively, binary compounds such as NaCl, CaF_2, MgO, UO_2 and so on. These materials also have the distinct advantage of high symmetry, relatively simple crystal structures.

Two principal limitations to the Born model have been encountered. Firstly, no description of optical or high frequency dielectric properties is possible, since the use of point ions preclude any electronic contribution to the polarisability, which is purely displacive in this case. This limitation has been overcome in a number of ways, but the most successful has been the Shell Model of Dick and Overhauser [4]. Originally introduced to account for some of the lattice dynamical properties of the alkali halides, it has been applied widely to oxide materials as well. It was found to be crucial in the calculation of the energies of charged defects where electronic polarisation contributions cannot be ignored. The basic model is a simple mechanical one. The ion is treated by means of a core and shell which are coupled by a harmonic spring. The net ionic charge is distributed between the core and the shell in such a manner as to give appropriate values for the polarisability, which is given, for a free ion, by Y^2/k, where Y is the shell charge and k the harmonic spring constant. The short range repulsive potentials are taken to act between the shells; this removes the possibility of a polarisation catastrophe, provided that the shell model parameters give physically reasonable values for the (electronic) polarisability.

The second limitation is one to which we have already alluded and is concerned with the application of the pair potential model to solids in which the bonding is largely directional, such as silica, or in which the coordination is clearly not isotropic such as CuO. In each of these cases, inadequacies in the potential model have been removed by using additional three-body potentials. The effect of these, acting about bond angles, is to introduce directionality into the interatomic forces, thus simulating, if you will, the effects of covalency. It should be stressed that potential models such as these are not meant to represent, or model, in any way the electron density distribution but merely the interatomic forces resulting from it.

The first pitfall that should be pointed out is that use of the shell model will affect the short range repulsive potential parameters. That is to say that for a particular (binary) compound, a shell model potential cannot usually be obtained simply by replacing the unpolarisable ions by cores and shells. Conversely, a rigid ion potential cannot be found just by taking a shell model potential and making the ions unpolarisable. In both cases, one must expect a change in repulsion parameters. A good example here is the potential models of Jacobs and MacDonaill [5] for bismuth oxide. In order to do a molecular dynamics calculation, a rigid ion potential was needed: they found it necessary to refit the short range parameters, because on making their shell model ions unpolarisable, the calculated value of the static dielectric constant fell by an order of magnitude, so making the model rather poor. Thus, the short range parameters were adjusted, slightly, so that both shell model and rigid ion potentials gave the same calculated value for ε_0 in agreement with experiment.

In the discussion on potential models for ceria, we will take this problem further.

The second major pitfall that needs to be considered arises when potential models need to be found for ternary and other compounds with more complicated crystal structures. The principal feature of these compounds is that they contain more than one cation and so the model must contain several cation-anion potentials. It is sometimes tempting to obtain the potential parameters by fitting to the known physical properties and crystal structure. This can lead to problems, in that potentials derived in this way may not be able to reproduce the crystal structure (and other properties) of the relevant binary compounds. This is often because the structure of the tenary compound may exhibit some special features that are not found in the binary structures; especially important here is the question of cation coordination. This may also be true if the potentials are not derived empirically but are calculated in some way for example using electron gas methods. An example of this is La_2CuO_4. This has a fairly high symmetry structure in which Cu is octahedrally coordinated.

A related question here concerns the case when some of the potentials have been determined previously, but others have not. Again La_2CuO_4 may be taken as an example [6]. The La---O and O---O interactions have obtained from fitting to the structure of La_2O_3, but there have been few studies of CuO. The temptation is thus to derive parameters for the Cu---O interaction by using the existing interactions for La---O and O---O and fitting to eg the crystal structure of La_2CuO_4.

This suffers from the same problem just discussed, in that Cu is in an abnormal coordination in La_2CuO_4. The Cu---O potential thus derived will almost certainly not work for CuO.

The point to be taken here is that potential interactions are best transferred from binary compounds to ternary compounds and not vice versa. Only in exceptional circumstances will potentials determined by fitting to ternary compounds be usable in other applications.

In the next section, we discuss some recent examples of atomistic simulations that we feel will illustrate and amplify our discussion in this section.

EXAMPLES

(1) Magnetoplumbite Structured Aluminates

These compounds, with a general chemical formula, $MAl_{12}O_{19}$ (M = Sr, Ca, etc.) display a wide ranging chemistry based on extensive cation replacement and non-stoichiometry. For example, rare earths may be substituted for the divalent alkaline earth ions, being compensated by the additional replacement of Al by Mg or Mn. Such materials are being investigated for applications in a number of areas: substrate materials for their ferrite based counterparts which are used in bubble memory devices and other electronic devices; as laser materials, they are potentially better than

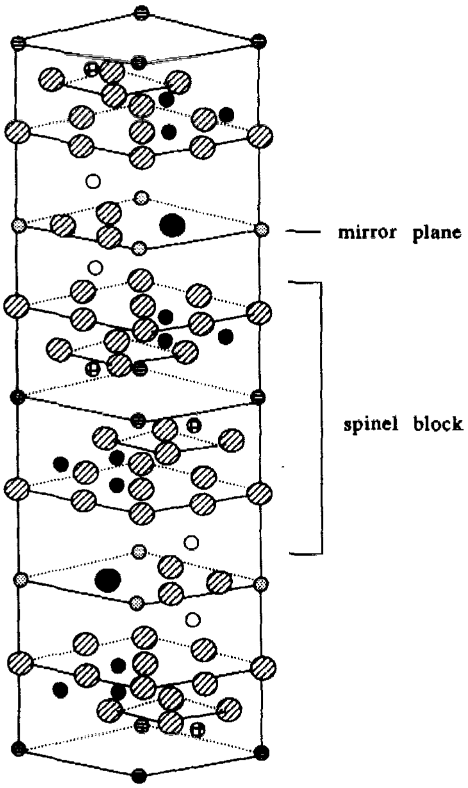

Figure 1 The magnetoplumbite unit cell of $SrAl_{12}O_{19}$. ▨O^{2-} ●Sr^{2+} ⊖Al(1) ○Al(2) ⊖Al(3) ○Al(4) ●(Al(5)

YAG, if some of the point defect related problems can be overcome; and they have been suggested as repository materials for radioactive waste elements such as caesium.

The basic problem which is intrinsic to all of the above possible applications is that point defect behaviour leads to mechanical instability and degradation in optical properties. It is therefore essential to be able to understand how these defects behave, so that some control may be effected to overcome the problems. To this end, we have initiated a study of the point defect properties of these materials, beginning with $SrAl_{12}O_{19}$ [7].

The starting point is, of course, a viable potential model for this material. Despite the complexity of the crystal structure, shown in figure (1), by transfering the interactions, from the appropriate binary compounds SrO and Al_2O_3, we have been able to reproduce the structure, as may be appreciated from Table (1) which compares the x-ray determined structural coordinates with our equilibrated calculated coordinates.

Clearly, by taking advantage of the earlier work on SrO and Al_2O_3, the pitfall of fitting potential parameters to a complicated ternary crystal structure has been avoided. Further use of this model is being made in the calculation of point defect energies.

Table 1 A comparison of the final equilibrated atom positions after starting with conceptually generated atomic coordinates with the data available in X-ray literature for $SrO.6Al_2O_3$.

Atom		*Data from literature (X-ray)*	*From conceptually generated*	Δ*
Sr	x	0.6667	0.6667	0.0000
	z	0.3333	0.3333	0.0000
Al(1)	x	0.0000	0.0000	0.0000
	z	0.0000	0.0000	0.0000
Al(2)	x	0.0000	0.0000	0.0000
	z	0.2500	0.2500	0.0000
Al(3)	x	0.3333	0.3333	0.0000
	z	0.276	0.0310	0.0034
Al(4)	x	0.1685	0.1675	0.0010
	z	−0.1082	−0.1084	0.0002
Al(5)	x	0.3333	0.3333	0.0000
	z	0.1903	0.1890	0.0013
O(1)	x	0.0000	0.0000	0.0000
	z	0.148	0.1492	0.0011
O(2)	x	0.3333	0.3333	0.0000
	z	−0.0538	−0.0536	0.0002
O(3)	x	0.1822	0.1838	0.0016
	z	0.2500	0.2500	0.0000
O(4)	x	0.1552	0.1516	0.0036
	z	0.0523	0.0527	0.0004
O(5)	x	0.5025	0.4995	0.0030
	z	0.1476	0.1447	0.0029

*Difference between predicted and X-ray data.

(2) Aluminium Nitride

This example illustrates the benefits of looking not just at the crystal structure, but also at some other physical properties. AlN has the wurtzite structure and is often classified along with other compounds such as SiC as a covalent semiconductor. One might be hesitant thus to apply the Born model to this material. At the very least,

Table 2 (a) Strains in La_2CuO_4 lattice:

Specie		*Average Strain*					
		X %	*Y %*	*Z %*	*XY %*	*XZ %*	*YZ %*
	La	0.000	0.000	0.300	–	–	–
Internal	Cu	0.000	0.000	0.300	–	–	–
Basis	O	0.000	0.000	0.3000	–	–	–
Bulk Lattice	–	0.623	0.623	0.1100	0.000	0.0000	0.000

Table 2 (b) Strains in CuO lattice:

Specie		*Average Strain*					
		X %	*Y %*	*Z %*	*XY %*	*XZ %*	*YZ %*
Internal	Cu (4c)	0.000	0.000	0.000	–	–	–
Basis	O (4e)	0.000	1.100	0.0000	–	–	–
Bulk Lattice	–	0.025	0.157	0.664	0.000	−5.1780	0.000

Table 3 (a) Potential Parameters for AlN

Interaction	*A/eV*	*ϱ/Å*	*C/eVÅ^{-6}*
Al-N	3074.54	0.27234	0.00
N-N	22134.37	0.29562	193.67

N shell charge: −3.95435 N core-shell spring constant: 54.85058

Table 3 (b) Comparison between some calculated and observed properties for AlN.

Property	*calculated*	*Observed*
a/A	3.1178	3.1114
c/A	5.0013	4.9792
ε_0	9.8	8.8
ε_∞	3.7	4.7

some form of three-body potential might be needed to handle the directionality in the bonding in such a compound. However, if one looks at the band gap (6.2 eV), and the difference between the static and optical dielectric constants (8.8 v. 4.7), there must be a high degree of ionicity involved. Thus a pair potential model is, in fact, not an unreasonable place to start [8]. In this case, the initial trial N···N parameters were taken from the work on Li_3N of Walker and Catlow [9]. The parameters for the Al···N interaction were adjusted by fitting to the structural data, using as trial parameters, those from the Al···O interaction [10].

Once the structure was being reproduced adequately, shell model ions were introduced and the whole fitting procedure repeated until the dielectric constants were also being reasonably well calculated. Some minor adjustments to the N···N potential were necessary. Table (3) compares the properties of the completely equilibrated model for AlN, with those found experimentally. The agreement is good which shows that extensions to the Born pair potential model were not needed. Further, the benefits of looking beyond the basic simple descriptions of bonding often used, are readily seen. This potential model may be expected to find extensive use in a number of AlN containing systems, such as, for example, the Sialons.

On the other hand, an example where the pair potentials seem to work, but in fact may not is provided by La_2CuO_4. This case is discussed in the next section.

(3) La_2CuO_4

It has already been remarked that the apparent success of pair potential models for La_2CuO_4 may be serendipitious because of the unusually regular coordination of copper ions in this structure. The site symmetry of Cu in La_2CuO_4 is much higher than for most, if not all, other Cu containing oxides. This is certainly true for the superconducting ceramic oxides such as $Ba_2YCu_3O_{6+x}$ and the Bi-Sr-Ca-Cu oxides, and is why potentials that appear to work for La_2CuO_4 are not at all successful for these other copper containing compounds. In fact, Cu···O interactions that may be used in models of the structure of La_2CuO_4 do not perform adequately for the binary CuO. This leads to one of the pitfalls described above, as may be seen clearly by examining the residual bulk lattice and basis strains that arise when the potentials are used with the experimentally determined structural parameters. This information is gathered together in Table (2). Note that these strains indicate the extent to which the potential model would change the structural coordinates, if relaxation to equilibrium were allowed. In other words, they are a measure of the difference between the experimental structure and that predicted from the potential model.

In some cases, these strains, especially the basis strains, are zero. This is because of the crystallographic site symmetry: no variation in these coordinates is permitted. Thus the model for La_2CuO_4 may appear to be more successful than it really is. If the strains for CuO are examined, it will be readily appreciated that the Cu· · ·O potential (as used in La_2CuO_4) does not perform at all adequately for the binary oxide. In part, this is due to the square planar coordination of the Cu ions in CuO, which does not lend itself to proper description by pair potentials, unlike the octahedral coordination found in La_2CuO_4.

The low coordination of Cu in CuO may be accounted for through the use of three-body terms, as demonstrated by Islam *et al.* [3]; these models also work in La_2CuO_4.

(4) Defect Energies in Ceria

In this last example, the influence of shell model parameters on defect energies (and other properties) in ceria are discussed. The short range potential model used is basically that of Lewis and Catlow for CeO_2 [10]; only the shell model parameters were altered in this study. The results of varying the shell model parameters are summarised in Table (4), which gives the calculated dielectric constants, Schottky and Frenkel energies (per defect) for various combination of shell charges and spring constants. Figure (2) shows how the binding energy between trivalent dopant cations and the compensating oxygen vacancy varies as a function of dielectric constant. The trends are identical with experiment, at least for dopants with a smaller ionic radius than Ce^{4+}, and a perfect match is found for a model static dielectric constant of 22 – which is in the middle of the measured values [11].

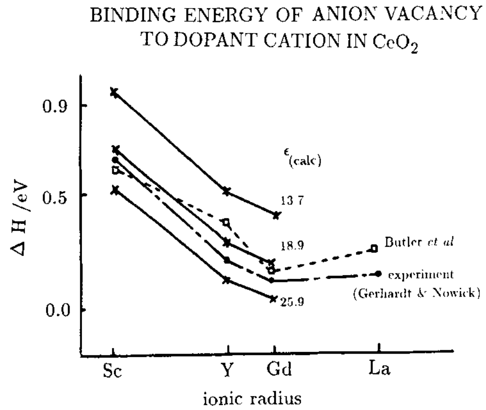

Figure 2 Association energies for dopant cation-oxygen vacancy pairs in ceria as a function of model dielectric constant.

Table 4 Shell Model Parameters and Defect Energies in Ceria

Oxygen *Y*	*k*	*cerium* *Y*	*k*	E_o	ε_∞	*Schottky*	*Anion Frenkel*
−2.07719	10.0	1.35	150.0	19.27	4.35	2.43	2.93
	20.0			19.14	2.77	2.44	2.94
	50.0			19.06	1.76	2.44	2.94
−3.07719	20.0	1.35	150.0	−92.0			
	43.89			45.95	3.83	1.13	2.19
	125.0			24.17	1.79	2.09	2.71
−3.07719	125.0	1.35	250.0	18.97	1.78	2.32	2.87
−3.07719	25.0	1.35	150.0	1571.94	8.71	Did Not Converge	
			350.0	68.57	8.53		
			1100.0	45.41	8.43		
	35.0			26.97	4.98	1.08	2.32

From Table (4), several trends can be inferred. Firstly, changing the oxygen ion polarisability largely affects ε_∞, but not ε_0, and caused no significant changes in the defect energies. On the other hand, changing the cation polarisability alters ε_0, and not ε_∞, but does cause the changes in the defect energies seen in figure (2).

Further, increasing the magnitude of the oxygen shell charge decreases the value of C_{44} (turning it slightly negative), but none of the other elastic constants, which are unchanged by other variations in the shell model parameters. Also, it can be seen that values of Y_{ox} and k_{ox} that give the same free ion polarisability do not give similar dielectric constants, and give wildly different defect energies (when those calculations actually converged). This indicates that the short range potentials have a considerable influence on the polarisability of ions in the lattice and underlines the remarks made earlier about the pitfalls associated with converting shell model potentials to rigid ion and vice versa. One shouldn't be too surprised at this, of course, because a major contribution to the dielectric properties comes from the displacement polarisability of the ions which is governed by the forces acting on the ions.

Perhaps the most important observation, though, comes from considering the validity of the potential model itself. The short range parameters clearly reproduce the structure and give reasonable values for the elastic constants. They can apparently be combined with appropriate shell model parameters to give sensible dielectric properties. Thus, overall one might think one has a good potential for ceria. This conclusion is reinforced by the calculated binding energies for the dopant-vacancy pairs shown in figure (2). However, the model predicts Schottky, instead of anion Frenkel, intrinsic disorder, and is thus at odds with the known experimental evidence on this point. From this point of view, the model must be regarded as unacceptable, especially since it is possible to find potential models (e.g. Butler *et al.*) [12] which do predict the right mode of intrinsic disorder.

How, then, should one view this model and those predictions from it that cannot yet be tested against known experimental data? Does it deserve any further consideration? No answers to these questions are offered here; the questions merely provide a further pitfall into which the unwary simulator may be trapped.

SUMMARY

In this paper, we have offered a discussion of some of the problems that may be encountered in building an interatomic potential model. Our remarks, though general, are aimed at those wishing to attempt simulations of new inorganic materials, in keeping with the theme of the conference. By increasing the awareness of some of the major pitfalls to be avoided, it is hoped that the promising future for atomistic simulations may be promoted.

Acknowledgements

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