Part IV

Appendix

"Parting with people is a sadness;

a place is only a place."

–the words of Thufir Hawat

Appendix A

The $^c/_a$ ratio in Rutile Structures

A.1 Abstract

The difficulty in correctly simulating the $^c/_a$ ratio of NiF_2 was reported in chapter 4. The hypothesis, that this may be due to unreproduced anisotropic charge distribution around ions was investigated for a range of rutile materials. Both fluorides (NiF_2, MgF_2, CoF_2, FeF_2 and MnF_2) and oxides (RuO_2, TiO_2, MoO_2 and SnO_2) were investigated so that a range of cation size and electronic structure were considered.

Important crystallographic observables in the rutile structure are the lattice constants (a, c and u). Experimental values are taken from the literature [53], theoretical values are calculated by assuming ideal packing based on ion sizes from Shannon [35], and values are also reported from energy minimisation simulations. Results from all three sources are presented in graphical form as a function of cation radius. Additionally, intrinsic defect equilibria energies are calculated and compared for all structures.

Failure to exactly reproduce the $^c/_a$ ratio is widespread and so unlikely to be due to anisotropic charge distribution. Instead, the balance between energy contributions from the short and long range interaction may not be optimised for this structure.

A.2 Perfect Packing in Rutile

The lattice parameters in this appendix are all compared to those calculated by assuming the ideal packing of hard spheres. This is achieved by deriving crystallographic relationships for a, c and u in terms of the ionic radii. The derivation of these relationships in the rutile structure are detailed below with reference to figures A.1-A.3.

The a parameter can be calculated by considering the basal plane of the rutile unit cell (see figure A.1). The diagonal $\underline{AC}$ in the basal plane is dictated by the cation and anion radii, r_c and r_a respectively. Thus, constructing a right angle triangle and using Pythagoras [121],

$$
\begin{aligned}
\underline{AC}^2 &= \underline{AB}^2 + \underline{BC}^2 \\
(2r_c + 4r_a)^2 &= 2a^2 \\
a &= \sqrt{2}(r_c + 2r_a)
\end{aligned}
\tag{A.1}
$$

There are two conceivable packing arrangements permitted in the rutile structure. Neither alternative will effect the calculation of the ideal a parameter but will effect calculation of the ideal c parameter. The two alternatives are shown schematically in figures A.2 and A.3. Atoms can pack in such a way that either the cation at $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ rests against the anions below (case 1, figure A.2) or the anions rest against each other (case 2, figure A.3). In case 1 c is twice $\underline{ID}$ which can be found by again considering the ionic radii and some simple geometry. With reference to figure A.2,

$$
\underline{ED}^2 = \underline{EI}^2 + \underline{ID}^2
\tag{A.2}
$$

realising that $\underline{ED} = (r_c + r_a)$ and $\underline{EI} = r_a$

$$
\begin{aligned}
\underline{ID} &= \sqrt{(r_c + r_a)^2 - r_c^2} \\
\therefore c &= 2\sqrt{(r_c + r_a)^2 - r_c^2}
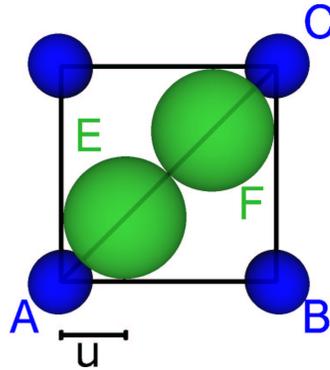\end{aligned}
\tag{A.3}
$$

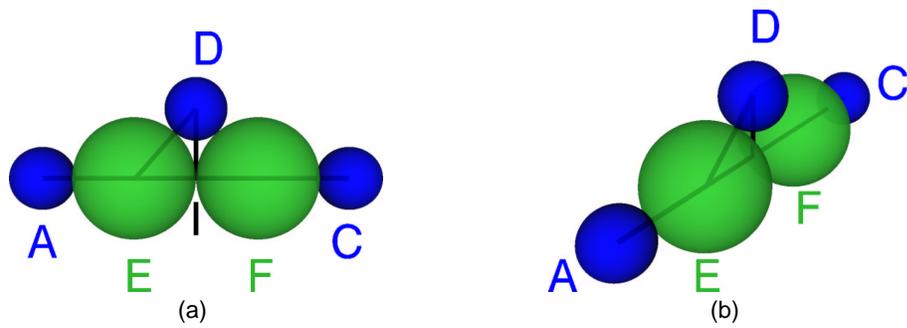**Figure A.1:** Basal plane of the rutile unit cell.

(a)

(b)

Figure A.2: Crystallographic packing in the rutile structure for case 1, assuming anion-cation contact in the c-direction.
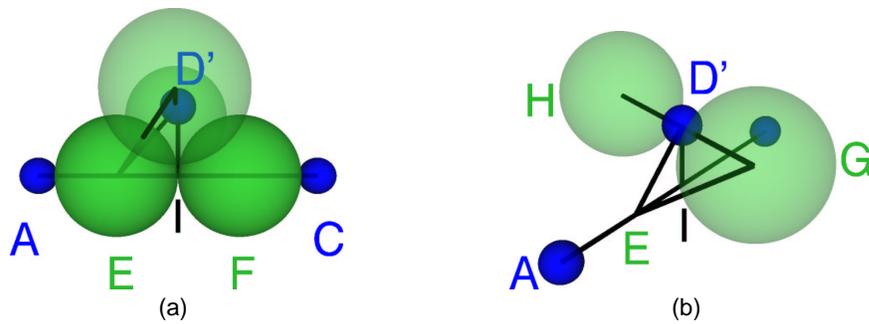

(a)

(b)

Figure A.3: Crystallographic packing in the rutile structure for case 2, assuming anion-anion contact in the c-direction.

In case 2 c' is twice $\underline{ID'}$ which can be found in a similar manner to case 1. With reference to figure A.3,

$$\underline{ED'^2} \;=\; \underline{EI^2} + \underline{ID'^2} \tag{A.4}$$

however, $\underline{ED'^2}$ is unknown and first found by solving,

$$\underline{GE^2} \;=\; \underline{GD'^2} + ED'^2$$

realising that $\underline{GE} = 2r_a$ and $\underline{GD'} = (r_c + r_a)$

$$\underline{ED'} \;=\; \sqrt{4r_a^2 - (r_c + r_a)^2} \tag{A.5}$$

substituting A.5 into A.4,

$$
\begin{aligned}
\underline{ID'} &= \sqrt{3r_a^2 - (r_c + r_a)^2} \\
\therefore c' &= 2\sqrt{3r_a^2 - (r_c + r_a)^2}
\end{aligned}
\tag{A.6}
$$

The issue of which packing scheme to apply can be resolved by considering the relative size of r_a and r_c. There will be a critical ratio where both packing regimes can be applied. Above or below this critical ratio alternate packing schemes are applicable. Thus equating, A.3 and A.6,

$$
\begin{aligned}
2\sqrt{(r_c + r_a)^2 - r_c^2} &= 2\sqrt{3r_a^2 - (r_c + r_a)^2} \\
r_c^2 + 4r_c r_a &= r_a^2
\end{aligned}
$$

dividing by r_a^2 and rearranging to make equal to zero,

$$\left(\frac{r_c}{r_a}\right)^2 + 4\left(\frac{r_c}{r_a}\right) - 1 = 0$$

this is a quadratic which can be solved by the general formula,

$$\left(\frac{r_c}{r_a}\right) = \frac{-4 \pm \sqrt{4^2 - (4 \cdot 1 \cdot^- 1)}}{2 \cdot 1}$$

$$\left(\frac{r_c}{r_a}\right) =^- 2 \pm \sqrt{5}$$

which has two solutions,

$$\left(\frac{r_c}{r_a}\right) = \begin{cases} ^-2 + 2.236 = & 0.236 \\ \\ ^-2 - 2.236 = & ^-4.236 \end{cases} \tag{A.7}$$

a negative solution implies a negative radius which is unphysical hence the critical ratio is,

$$\left(\frac{r_c}{r_a}\right) = 0.414$$

if $\left(\frac{r_c}{r_a}\right) > 0.236$ case 1 is valid

if $\left(\frac{r_c}{r_a}\right) < 0.236$ case 2 is valid

After calculating $\left(\frac{r_c}{r_a}\right)$, for all structures, it is apparent that case 1 always applies. This is intuitively sensible since case 2 would imply that similarly charged anions are touching in the structure which is obviously unfavourable, even with this simple model.

The positional parameter u is somewhat easier to calculate. With reference to figure A.1,

$$\begin{aligned} 2u^2 &= \underline{AE}^2 \\ u &= \frac{\underline{AE}}{\sqrt{2}} \\ u &= \frac{r_c + r_a}{\sqrt{2}} \end{aligned}$$

A.3   Results and Discussion

Figure A.4 compares the a and c parameters for the fluorides (figure A.4a) and oxides (figure A.4b). The results are colour coded such that experimental values are in red, values from the simulation are in blue and values from the above ideal packing description are in black. Figures A.5, A.6 and A.7 show similar graphs except the positional parameter, u, the $^c/_a$ ratio, and the unit cell volume are plotted respectively. Simulations were also used to calculate the intrinsic defect energies and the results are shown in figure A.8.

A.3.1   Fluoride Structural Parameters

The fluoride rutile systems appear to be quite well behaved in that the simplistic ideal packing model gives reasonable agreement with experiment (see figures A.4a, A.5a and A.6a). Generally experimental data gives unit cell volumes smaller than predicted from ideal packing, typically by 5% (see figure A.7a). Simulation volumes naturally follow the experimental results as the volume was used to fit the potential parameters. Deviations from the highly symmetric ideal packing model suggest that the main deviation seems to be in the a parameter which is too small (see figure A.4a). This leads to a larger experimental $^c/_a$ ratio than expected from ideal packing (see figure A.6a).

Interestingly, the ideal packing model deviates from the experimental lattice constants in the opposite direction compared to the simulation. Typically ideal packing is closer to the experimental $^c/_a$ value than the simulated results.

A.3.2   Oxide Structural Parameters

The oxides are far less well behaved rutile systems than the fluorides (see figures A.4b, A.5b and A.6b). Experimental unit cell volumes are between 7% and 15% smaller than
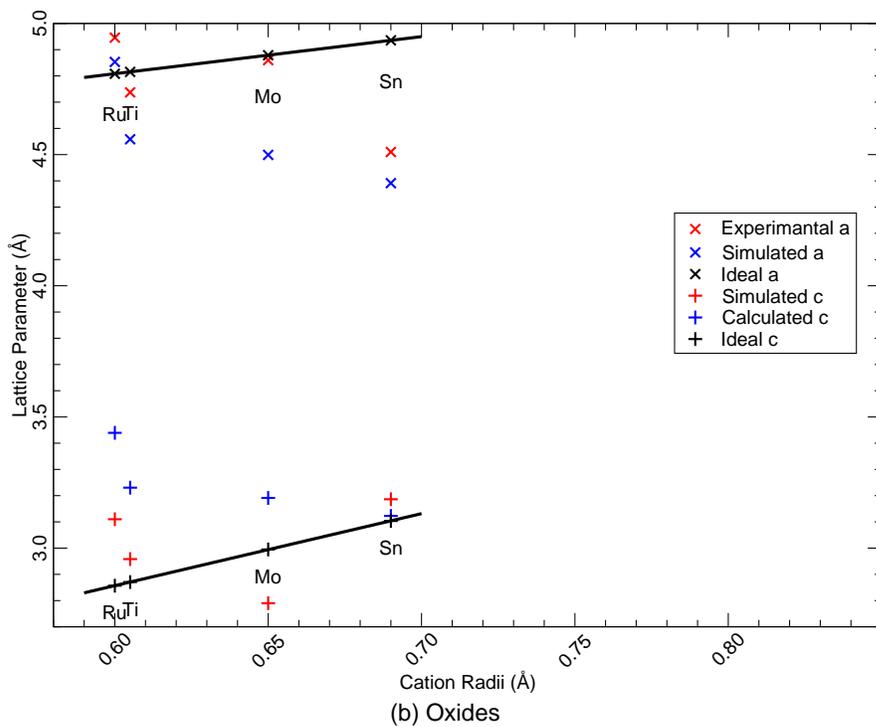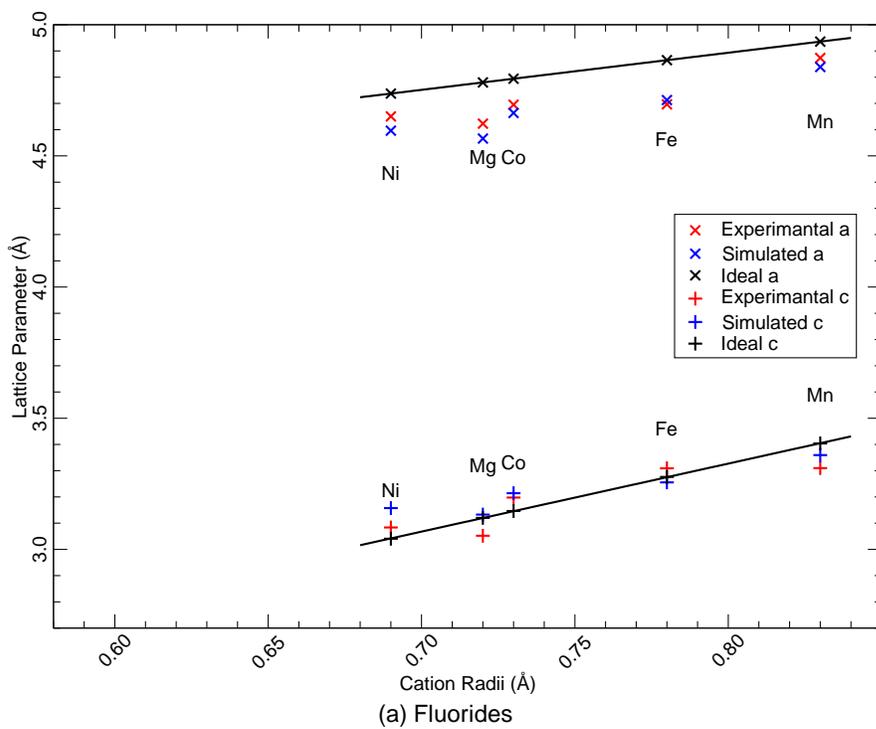
Figure A.4: Experimental (red), simulated (blue), and ideal (black) a ($\times$) and c ($+$) lattice constants for (a) fluorides and (b) oxides with the rutile structure.
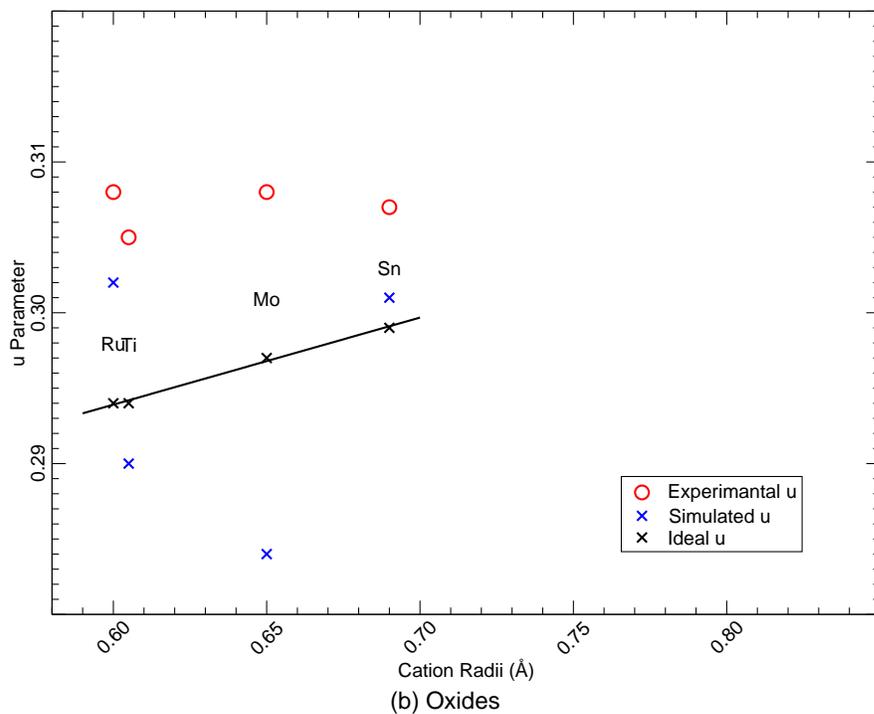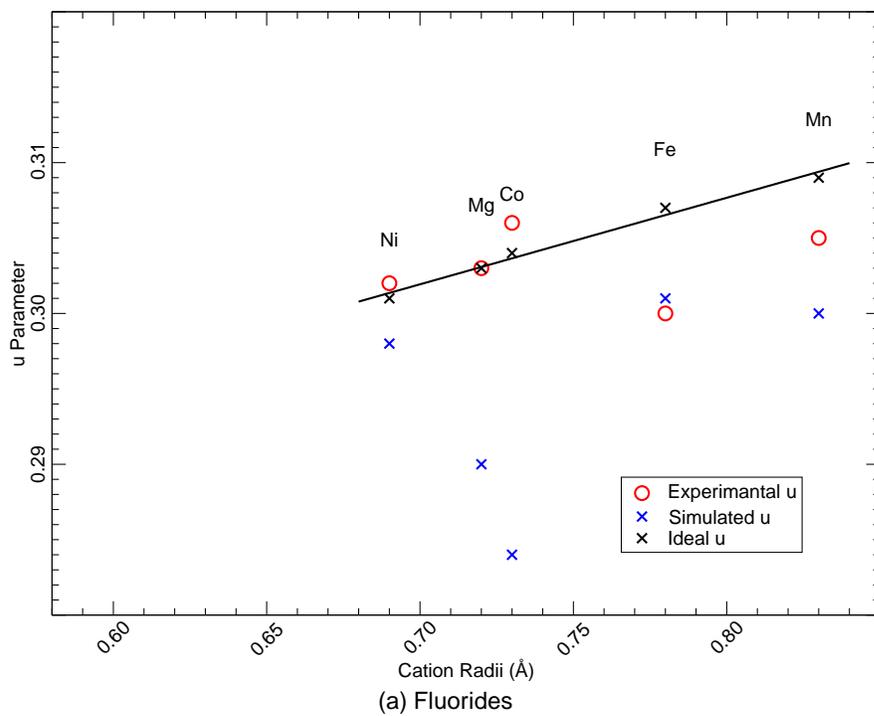
Figure A.5: Experimental (red ◯), simulated (blue ×), and ideal (black ×) u lattice constant for (a) fluorides and (b) oxides with the rutile structure.
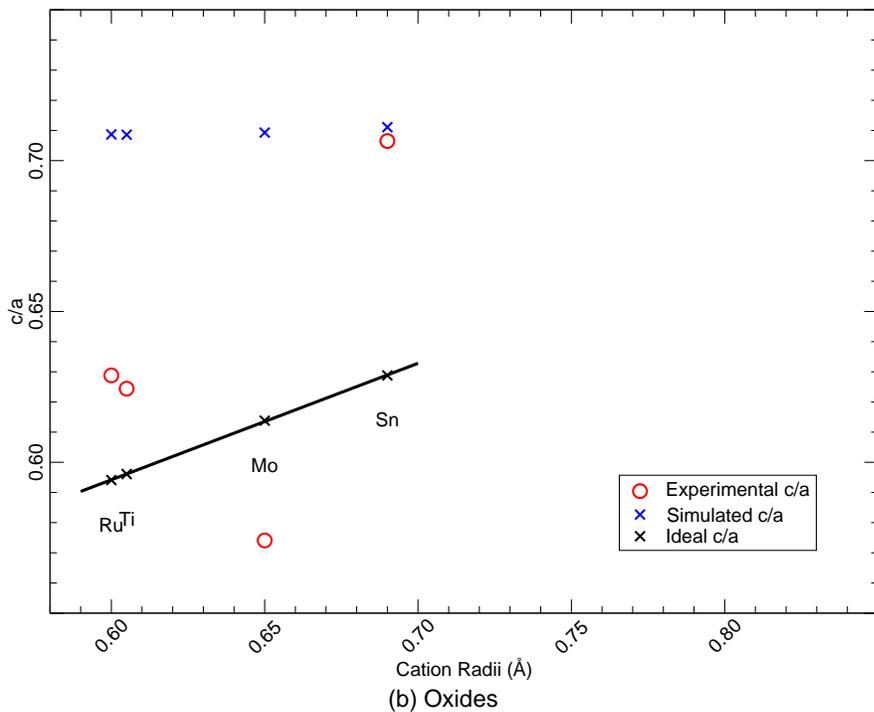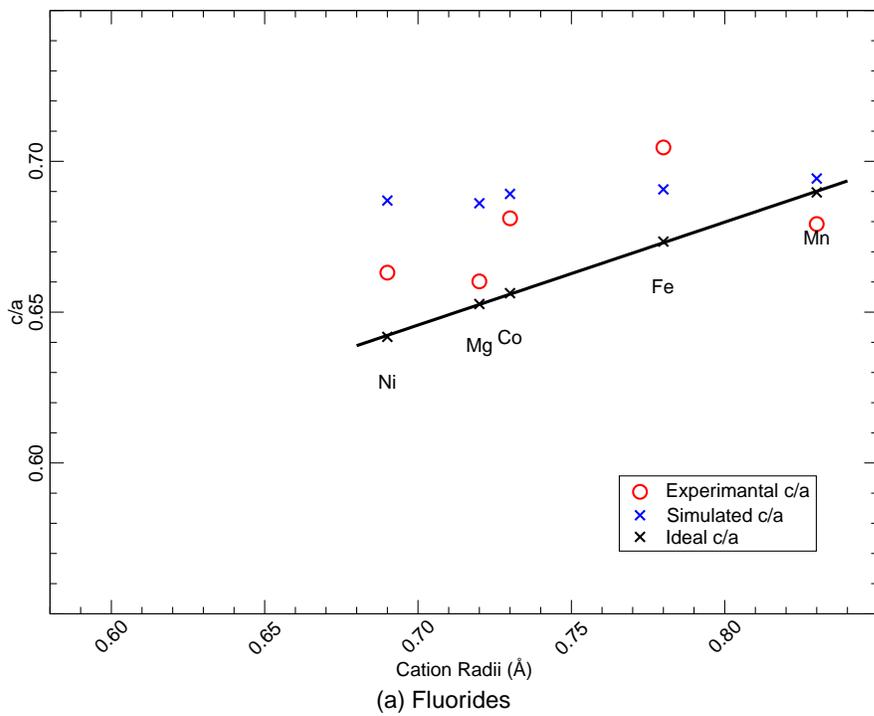
(a) Fluorides

(b) Oxides

Figure A.6: Experimental (red $\circ$), simulated (blue $\times$), and ideal (black $\times$) $^{c}/_{a}$ lattice constants for (a) fluorides and (b) oxides with the rutile structure.

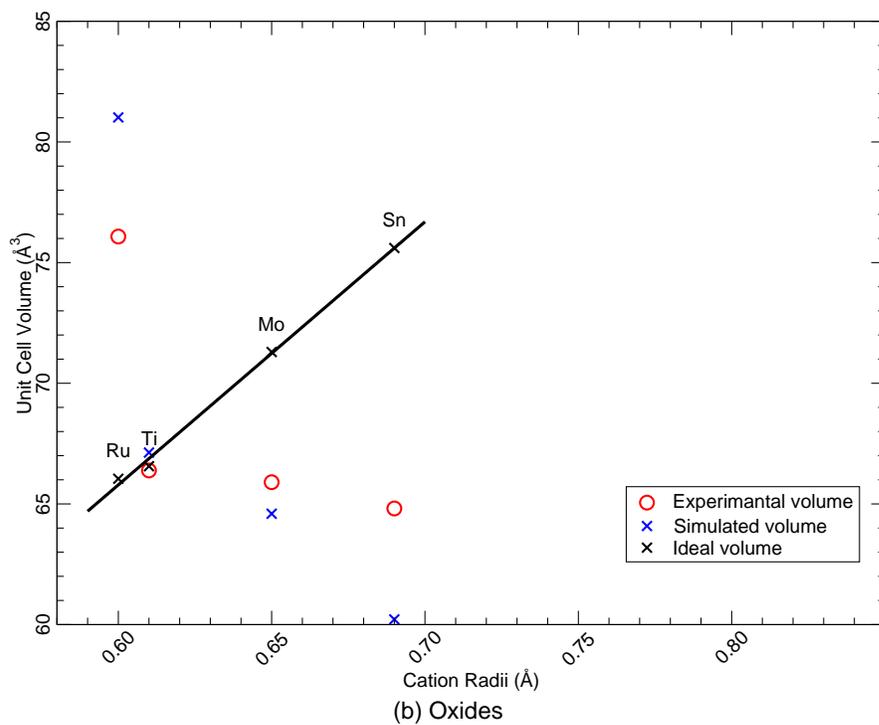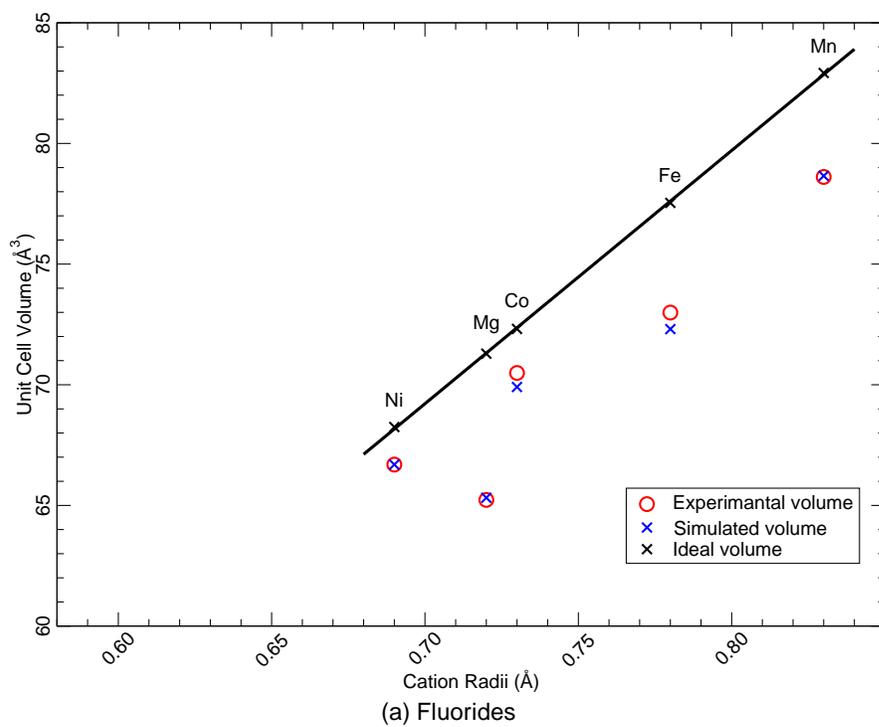**Figure A.7:** Experimental (red ○), simulated (blue ×), and ideal (black ×) unit cell volume for (a) fluorides and (b) oxides with the rutile structure.

ideal packing values (see A.7b) with the obvious exception of TiO_2 which is remarkably close to the ideal volume (within 0.3%). Again $^{c}/_{a}$ ratios are typically too large by up to 12%, with the exception of MoO_2 which is too small by 6%. Unlike the fluorides this is not mainly due to a deviation in a but a more general mismatch between theoretical and experimental results for both c and a.

Simulated results are poor at reproducing experimental data. This is due to the interatomic potential parameters which were not developed for primary use in these rutile crystals. This illustrates the dilemma facing the development of interatomic potentials. A potential that works very well in one crystal system may not be fully transferable to another, while a more transferable potential may not give sufficiently accurate results. This is why it is important to consider trends rather than absolute values. With this is mind the simulated oxide results are much worse at reproducing the experimental $^{c}/_{a}$ ratios. Again, the perfect packing is surprisingly better than the simulation but errors are in the opposite direction.

A.3.3   Intrinsic Defect Energies

Calculated intrinsic defect energies (figure A.8) give a consistent trend with cation radii. Both fluorides and oxides are predicted to be anion Frenkel dominated. Defect energies in the fluorides are significantly lower than in the oxides (compare 2.0eV - 2.3eV in fluoride systems to 6.0 - 6.5eV in oxide systems). The dominant minor defect equilibria also exhibit lower energies in the fluorides than the oxides. This is not surprising due to the 2+ cation valence state in oxides compared to the 1+ valence state in the fluorides. This reflects the point made in chapter 2 that the coulombic contribution to the interaction energy is much greater than the short range interaction. This data also suggests that intrinsic defect energies in this system are not particularly sensitive to cation radii.
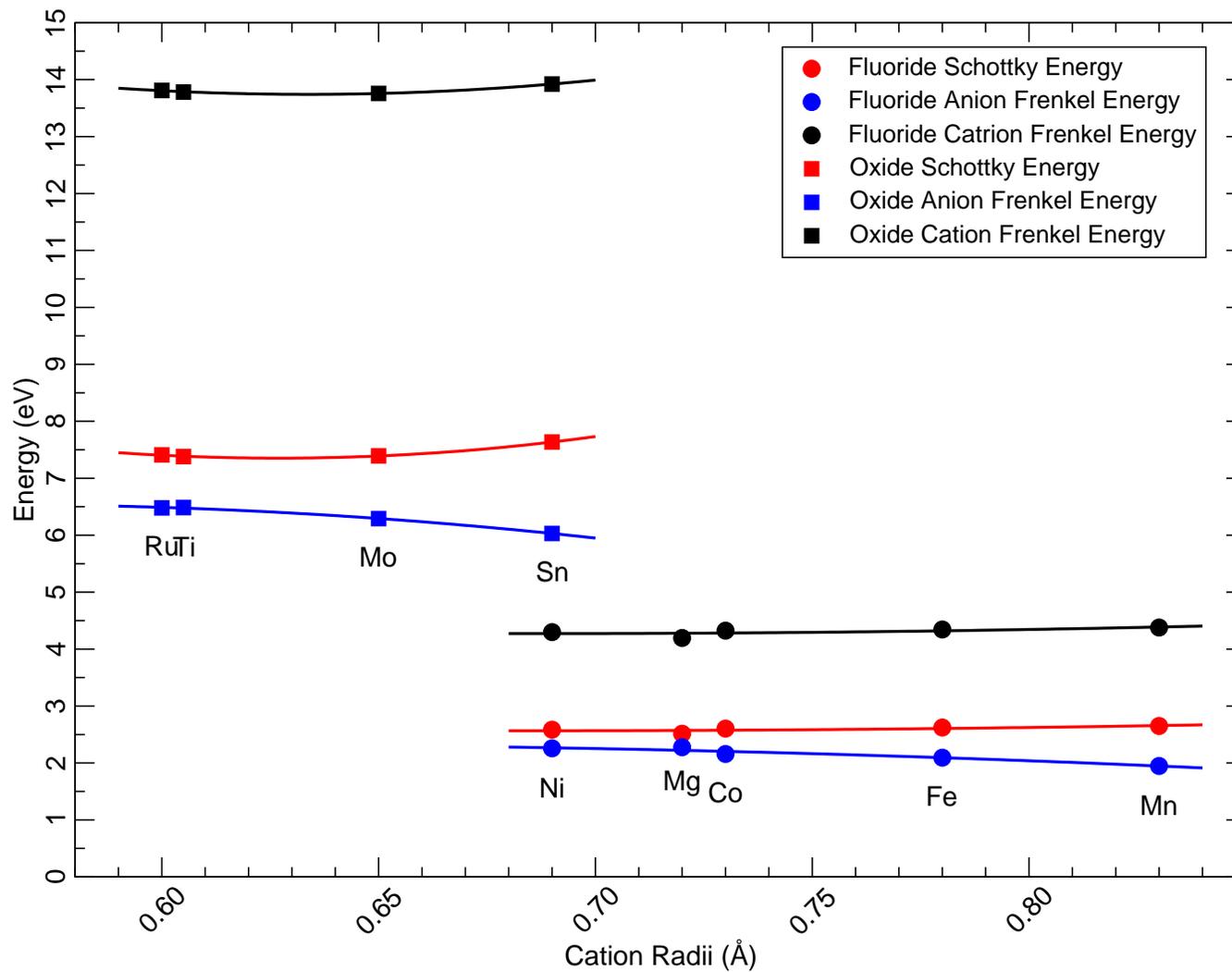
Figure A.8: Simulated intrinsic defect energies for fluorides (●) and oxides (■) with the rutile structure.

A.4 General Discussion

The above comments demonstrate the usefulness and success of a simple ideal packing model. The quality of the packing model depends on the assumed ionic radii, full ionic bonding and a short range bonding. Nevertheless, it serves as a consistent reference for the experimental and simulated results. The results also illustrate that, although the simulation model is based on isotropic forces, it can give different results to a purely isotropic packing model. This is because the forces operate over a longer range.

The tetragonal rutile unit cell predicted from an ideal packing of spheres is not reproduced by either experiment or computer simulation. Both of these tend to prefer a more cubic arrangement indicated by a smaller a and larger c which gives a larger $^c/_a$ ratio. Interestingly, the computer simulation, which is regarded as highly symmetric in its approximation of charge distribution around ions, is further from the ideal prediction than experiment. This perhaps indicates that the balance between short range and long range forces is not optimised in the simulation for this structure. As such, a partial charge model (where less than formal charge states is assumed) may provide better results.

The speculation in this appendix is that, since deviation from experiment is seen more in the a parameter than the c parameter, the atomic interactions in the basal plane are critical. A detailed study of the crystallography of rutile reveals that there are two different anion-cation and cation-cation distances imposed by the symmetry. This is clearly a problem for a classical interatomic potential model that generally has only one minimum in the interaction energy.

Given the deviation from ideal isotropy in the rutile unit cell, it is remarkable that simulations are actually capable in matching experimental data as well as they do. Clearly the atomic interactions in rutile materials could be better described. However, the obvious suggestion that this is due to anisotropic charge distribution can be ruled out since all rutile

systems seem to deviate from an ideal packing prediction. Indeed even the MgF_2 system, which may be expected to be highly symmetric and ionic, showed significant deviations.

Some additional calculations were run with a very repulsive anion-anion pair potential which will reproduce the $^{c}/_{a}$ ratio of rutile materials correctly. However, this was abandoned because this potential clearly gave incorrect defect energies when used in lower symmetry systems (e.g.CaF_2 and NaF).

A.5   Further Work

The interatomic potentials for the oxides could be better tailored to the rutile systems. An adjustment of these potentials could be undertaken and the simulations repeated to see if any different or more precise trends emerge.

The Shannon radii used may not truly represent the ionic radii of the species in these materials. As an extension of this work, simple adjustments could be made which may provide a better match to the experimental data. Here the cation radii is assumed constant for all materials, however, the local environment in the crystal may mean this is not the case. A refined fit to rutile experimental data could provide an alternative radii for the ions in these systems.

The current methodology allows for the use of partial charges, which would alter the balance between short and long range forces, and an extension to the simulation methodology allows the use of a breathing shell. Both of these features may provide better simulation results and should be applied in a self consistent manner; such results would ideally compliment those presented here.