PREDICTING NEW STRUCTURES: THE SIMPLE CUBIC AND PEROVSKITE CASE

by

Matthew Lords
advisor
Dr. Gus Hart

Physics 492R Capstone Project Report
Department of Physics and Astronomy
Brigham Young University
March 2009

Copyright (*c*) 2008 Matthew Lords
All Rights Reserved

Abstract

Many structures have an underlying motif such as an fcc, bcc, or hcp *parent lattice* with different chemical orderings on the lattice. Among seemingly infinite possibilities for these orderings, why does nature only choose the few that it does? **Purpose** To predict new simple cubic and perovskite structures which can be observed experimentally. **Method** Using a *combinatorial* approach, generate all unique binary simple cubic structures with 2 to 8 atoms in the unit cell. Calculate the *likelihood* that each of these structures can be observed in nature, and plot their likelihood as a function of the structure's concentration. Through this list we will be able to predict new structures. **Results** Through this method we have been able to generate a list which is ordered by a structure's likelihood. We know this because observed structures tend to have a higher calculated likelihood than non-observed structures at a given concentration. Using this information we now have predictions for new simple cubic structures which we can also apply to new perovskites.

1 Introduction

1.1 Crystal Background

A crystalline structure is a material where the atoms are arranged in such a way that a repeating pattern can be found throughout the structure. Fig. 1(A) is an example of a 2D square lattice. In the structure we see two different atoms represented by white and black dots. The unit cell represents the smallest repeating pattern found in the structure and is represented by the rectangle [1]. In fig. 1(A) the smallest cell has 2 lattice sites inside: 1 white atom (consisting of the 4 white quarters inside the rectangle) and 1 black atom (consisting of the 2 halves). A lattice site refers to a unique position inside the structure. In other words you would not be able to tell the difference between equivalent lattice sites based solely on the surrounding atoms. This structure is a derivative *superstructure* of the simple square case shown in fig. 1(B). A *derivative superstructure* is a structure that has lattice points that correspond to some *parent lattice*. In this example if we made all the dots in fig. 1(A) white then they would correspond to the lattice points in the right image making fig. 1(B) the parent lattice [2].

In 3 dimensions these same ideas apply. Many structures that are found in nature have a parent lattice which is simple cubic (SC), face-centered cubic(FCC), body-centered cubic(BCC), or some other base structure. Figure 2 shows an SC parent lattice with a derivative superstructure. In my research I focused primarily on the simple cubic structure which is, as its name implies, the simplest structure.

Figure 1 A(left) 2D example with 2 different atoms and with 2 lattice sites in the unit cell. **B(right)** Square lattice which is the parent lattice of the left example.

$$
\begin{aligned}
\tilde{\mathbf{a}}_{\mathbf{1}} &= a\hat{x} \\
\tilde{\mathbf{a}}_{\mathbf{2}} &= a\hat{y} \\
\tilde{\mathbf{a}}_{\mathbf{3}} &= a\hat{z}
\end{aligned} \tag{1}
$$

The simple cubic structure is interesting for many reasons. It is the parent lattice of many interesting materials found in nature. NaCl, or rock salt, is a derivative superlattice of the simple cubic structure (Fig. 2(B)).

1.2 Motivation for my work

It can cost a lot of time and money to attempt to create a new structure. Researchers prefer to have a starting point rather than randomly mixing elements together. This starting point involves intensive computational work to simulate and predict whether a certain structure or mix of elements at a certain concentration is energetically favorable.

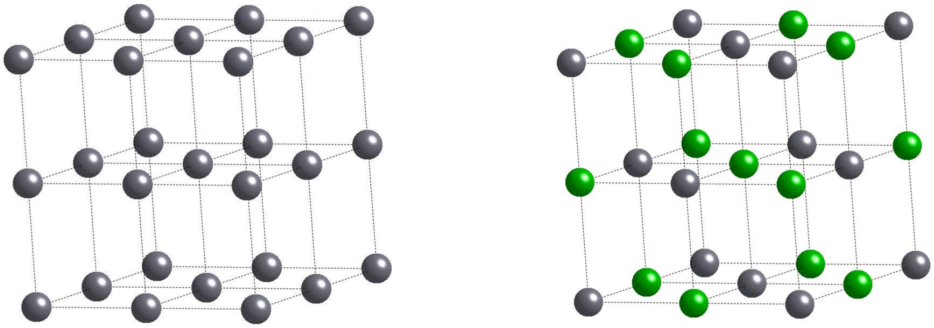

Figure 2 **A(left)** Simple cubic parent lattice with lattice parameter *a*. Contains only one unique lattice site.**B(right)** NaCl structure which is a derivative superlattice of the SC crystal. Contains 2 unique lattice sites.

This process can also be time-consuming especially when considering the seemingly limitless number of structures that can exist.

My research is a means of getting a starting point for eventually synthesizing new crystal structures. In my research, I take a combinatorial approach to generating all unique structures which are available (1) given a certain number of lattice points in the unit cell, and (2) a certain parent lattice. After generating this list, I create a chart that gives the likelihood of each structure as a function of its concentration. With this list, one can see which structures are more likely to be observed experimentally.

1.3 What does this mean?

There has already been some work in this area of research [2]. This work focused on generating a list of structures for the fcc and bcc cases. Through this research a

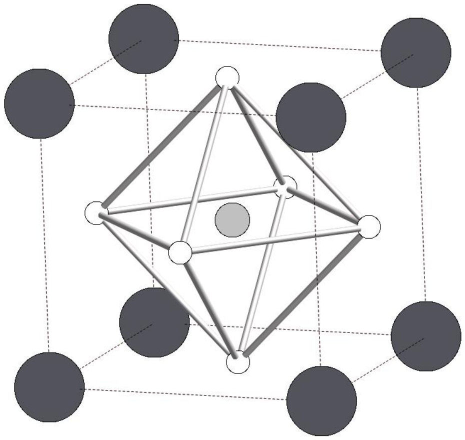

Figure 3 Simple perovskite with the A site, B site and oxygen site labeled.

new fcc structure has been predicted, $CdPt_3$ or $L1_3$. Work is currently being done to synthesize this new structure [4].

I am working with the simple cubic case to predict new perovskite structures (Fig. 3). The perovskite is a simple cubic structure consisting of 3 atomic sites: an A site, a B site and the oxygen sites. The oxygen forms an octahedron around the B-site while the A site sits on the corners just outside this octahedron. The chemical formula for the perovskite is ABO_3.

The method used in predicting new structures looks at the differences in bond types (bonds between like and unlike atoms). Often times perovskites are alloyed at either the A site or the B site so that the chemical formula becomes either $A(B_xB'_{1-x})O_3$ or $(A_xA'_{1-x})BO_3$. Since we are looking at the differences throughout the structure we only need to focus on the site where the alloying occurs. Fig. **??** shows how the perovskite is simple cubic when looking at only the A site or the B site.

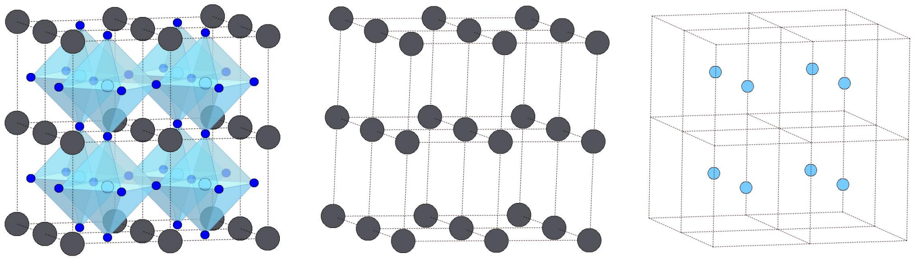

Figure 4 **A(left)** Perovskite structure showing the A, B and oxygen sites. **B(middle)** Simple cubic structure that represents only the A-sites. **C(right)** Simple cubic structure that represents only the B-sites.

2 Method

2.1 Enumerating all structures

We first need to answer the combinatorial question of how many structures are possible. In a structure, each unit cell has a finite number of possible configurations. Figure 5 illustrates the 2-dimensional case of a structure with 2 lattice sites in the unit cell. The first two structures (A and B) are unique while the far right structure (C) is equivalent to the first(A) by a 90 degree rotation. There are cleary only two unique structures for a square parent lattice with a unit cell of size 2. Any other structure is equivalent to one of these two by translations or rotations. [2]

This same idea applies to the 3-dimensional case. There is a finite number of unique configurations for a structure with a given number of lattice sites in its unit cell. For our list we decided to generate all unique structures with 2 to 8 lattices sites in the unit cell. We could extend this to include more structures, but for the scope of this project we decided to keep it simple. In order to generate this set of unique simple cubic structures I used an algorithm based on the group-theoretic properties of the superstructure and its parent lattice. I will give a brief review of how this algorithm

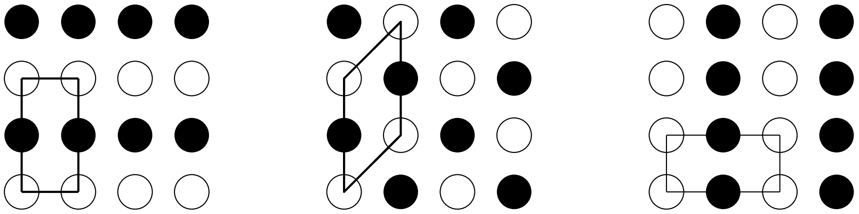

Figure 5 **A(left)** Square lattice with vertical stacking atomic sites. **B(middle)** Square lattice with diagonal stacking. **C(right)** Lattice with horizontal stacking, and which is equivalent under symmetry operations to the left figure. [2]

works over the next few pages.

This method looks at the relationship between the derivative superstructure and its parent lattice in order to generate a set of unique superstructures . Because the derivative superstructure is an integer combination of the parent lattice, we can obtain the superstructure by multiplying the parent lattice by a matrix of integers. This equation can be written in the form $\mathbf{B} = \mathbf{AH}$. In this equation, $\mathbf{A}$ is the parent lattice, $\mathbf{B}$ is the derivative superstructure, and $\mathbf{H}$ is an integer matrix. The matrix $\mathbf{H}$ has a determinant which is equal to the number of lattice sites in the unit cell. [2]

In order to generate all the unique derivative superstructures $\mathbf{B}$ we need to generate all unique $\mathbf{H}$ matrices for a given number of lattice sites in the unit cell. There are a seemingly infinite number of $\mathbf{H}$ matrices, but by putting $\mathbf{H}$ into Hermite Normal Form (HNF) we can generate a finite set of $\mathbf{H}$ matrices:

$$\begin{pmatrix} a & 0 & 0 \\ b & c & 0 \\ d & e & f \end{pmatrix} \quad \begin{array}{c} 0 \leq b \leq c \\ 0 \leq d \leq f \\ 0 \leq e \leq f \end{array} \tag{2}$$

In this form we can generate all unique **H**, by first setting the diagonals of the matrix to have a product equal to the number of lattice sites in the superstructure's unit cell. We then generate a finite set of HNFs using the rules listed above. Once these HNFs have been generated we reduce this list by removing the HNFs that are symmetrically equivalent. This is done by comparing each HNF by the symmetry operations of the parent lattice. This will give us a set of unique HNFs which correspond to unique superstructures. [2]

We then generate all unique configurations of atoms for each superstructure. To do this we first generate all possible *labelings* for a given number of lattice sites in the superstructure. The number of labelings that is generated for a binary structure is 2^N, where N represents the number of lattice sites in the unit cell. For a binary structure with 4 lattice sites, we would generate the following 16 labelings with a and b representing the different atoms or labels:

aaaa	*baaa*	*abaa*	*aaba*
aaab	*bbaa*	*baba*	*baab*
abba	*abab*	*aabb*	*bbba*
bbab	*babb*	*abbb*	*bbbb*

Table 1 List of all possible labelings for a binary structure with 4 lattice sites in the unit cell.

This list of labelings needs to be reduced to only contain symmetrically inequivalent labelings. The first step in reducing this list is to remove the labelings that don't contain all the labels. In this example we would remove the labelings *aaaa* and *bbbb*. These labelings would correspond to the case with only one lattice site in the unit cell. [2]

We then compare the labelings under the translations of the parent lattice to see which are equivalent. In order to do this we first put the **H** matrix into its Smith Normal Form(SNF):

$$\begin{pmatrix} d_1 & 0 & 0 \\ 0 & d_2 & 0 \\ 0 & 0 & d_3 \end{pmatrix} d_3 \text{ is divisible by } d_2 \text{ and } d_2 \text{ is divisible by } d_1 \tag{3}$$

The diagonals of the SNF tell us how we can permute the labelings, and these permutations correspond to the translational symmetry operations of the parent lattice. Each labeling consists of d_1 sets, each set has d_2 subsets, and each subset has d_3 labels. The labeling is then permuted over each set, subset, and label configuration. If the SNF diagonals were $d_1 = 1$, $d_2 = 2$, and $d_2 = 2$ then the labeling *abba* would be permuted to the labelings *abba*, *baab*, *baab*, and *abba*. [2]

The next reduction to this list involves removing the labelings that are equivalent under an exchange of labels (i.e. $aaab \rightleftharpoons bbba$). For our final list of structures we omitted this step except in the case of a 1:1 ratio of *a* to *b* labels. This allows us to generate a complete plot based on the concentration of *a* atoms. [2]

The list is further reduced by removing the labelings that are superperiodic. This is done by seeing which permutations leave the labeling unchanged. For the labeling *abab* it can be permuted 4 ways (derived from the SNF). These four permutations change the

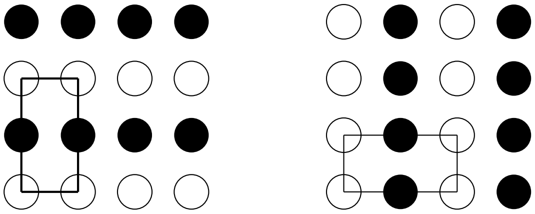

Figure 6 **A(left)** Square lattice with vertical stacking atomic sites. **B(middle)** Square lattice with diagonal stacking. **C(right)** Lattice with horizontal stacking, and which is equivalent under symmetry operations to the left figure. [2]

label to (1)*abab*, (2)*baba*, (3)*abab*, and (4)*baba*. The first permutation is the identity and can be omitted, but the third permutation leaves the labeling unchanged from the original. This means that *abab* is superperiodic and that it was already generated for the case with 2 lattice sites in the unit cell. [2]

The final step is to remove labelings that are equivalent by the parent lattice rotations. Figure 6 shows an example of this in the 2-dimensional case with 2 lattice sites in the unit cell. In this example the two structures are equivalent by a 90 degree rotation. A more detailed explanation of how each of these steps is carried can be found in the paper by Hart and Forcade. [2]

For the SC case, I generated all the unique structures with 2 to 8 atoms in the unit cell. Table 2 shows the number of unique structures that are possible, given a certain number of lattice sites in the unit cell. This table was created using the steps listed above, including the exchange of label step. Figure 7 shows the 3 unique simple cubic structures with 2 lattice sites in the unit cell. This means that any structure that has 2 lattice sites in the unit cell, and that has a SC parent lattice, is equivalent to one of these structures.

Lattice Sites	Unique Structures	Running Total
2	3	3
3	3	6
4	15	21
5	14	35
6	65	100
7	52	150
8	291	443

Table 2 This table represents the number of unique structures found in the simple cubic case for a given number of lattice points in the unit cell.

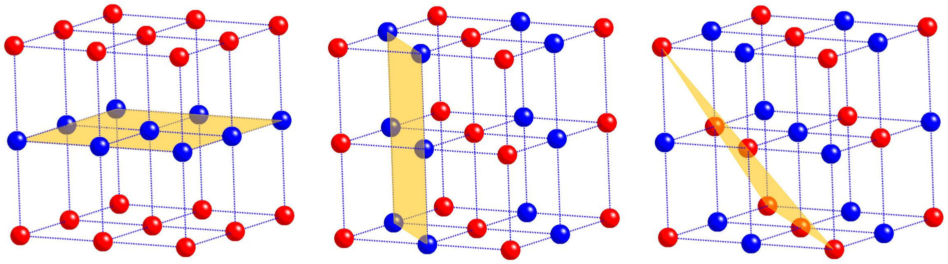

Figure 7 All the unique SC structures with 2 lattice sites in the unit cell. Stacking shown for each structures (100), (110), and (111)

2.2 Calculating the Likelihood index

In the SC case we have calculated a total of 443 structures with 2 to 8 atoms in the unit cell, and out of all these structures only a small percentage has actually been observed experimentally. What is it that makes these observed structures more likely than those structures not found? Do some of the structures that have not been observed actually exist?

The solution to this problem lies in the bond-type distribution of a structure. For a given binary structure there exists a configuration of atoms that is more energetically favorable than another. This is because either the bonds between like atoms, or the

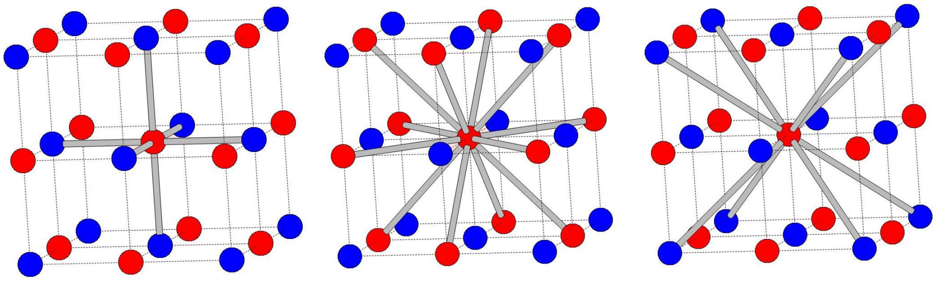

Figure 8 Generating Likelihood Index: Example showing the bond types of the first 3 nearest neighbors for the simple cubic case with 2 lattice sites in the unit cell. **A(left)** 1st NN, **B(middle)** 2nd NN, and **C(right)** 3rd NN.

bonds between unlike atoms are more energetically favorable at each bond legnth. For example, in some structures like-atom bonds at the first nearest neighbor bond length are lower in energy than unlike-atom bonds, and bonds between unlike atoms is lower in energy at the second nearest neighbor. So a structure that maximizes the number of like atom bonds at the first nearest neighbor bond length and unlike atom bonds at the second nearest neighbor would be more likely than a 'random' configuration of bond-types. The likelihood index that we generate compares each structure by looking at how they maximize the number of like-atom and unlike-atom bonds at each bond length when compared with the random case [3].

The first step in calculating the likelihood index is to measure how far each site in the structure deviates from the 'random' case. This is done by calculating the average bond type at each bond length for a given site and then subtracting this value from the average bond type for the 'random' case. The average bond type for the random case is $(2x-1)^2$ where x is the fraction of a sites. We then sum over the number of lattice sites in the structure: [3]

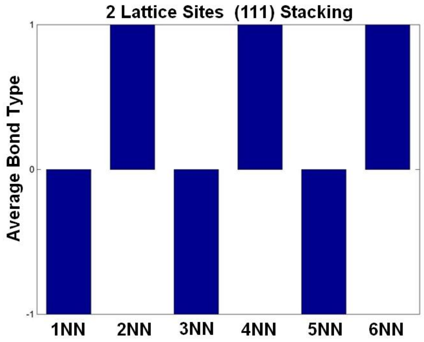

Figure 9 The average bond type for the simple cubic structure with 2 lattice sites in the unit cell and with 111 stacking. Calculated up to the 6th nearest neighbor.

$$\sum_{\text{pairs}} \left|\text{Avg. Bond Type} - (2x-1)^2\right| \tag{4}$$

Figure 8 shows how we would calculate the average bond type for the first 3 nearest neighbors for a simple cubic structure with 2 lattice sites in the unit cell. For the 1st NN there are 6 unlike atom bonds and 0 like atoms bonds. This gives us an average bond type of $(0-6)/6 = -1$ for the 1st NN(Fig. 8(A)). The 2nd NN has an average bond type of $(+12-0)/12 = +1$ (Fig. 8(B)), and the 3rd NN is $(0-4)/4 = -1$ (Fig. 8(C)). In this example the fraction of a sites is 1/2 and so the average bond type of the 'random' case is 0. This example gives us the highest possible average bond type at each level alternating between purely like atom bonds and purely unlike atom bonds (Fig. 9), and it has the lowest possible value for the random 'random' case. Overall this structure will give us the highest likelihood index possible.

This particular structure has already been observed in many perovskites, most alkaline halides (including NaCl), and many other structures. The reason this structure is so common is because it optimizes the number of unlike atom bonds at the nearest neighbor bond length, and unlike atom bonds at the second nearest neighbor bond length. For example in the case of Na and Cl, Na prefers have the negatively charged Cl atoms at the nearest neighbor bond length and vice versa. This simple cubic structure with (111) stacking maximizes this layout and so it is the most stable structure for NaCl, and many other similar structures. This structure's abundance is accurately predicted by its likelihood index.

Once the likelihood index has been calculated for each structure, the next step is to match the structures that have already been observed experimentally with those in our list. This is done by comparing the observed structure with each structure in our list to see if they are equivalent. The algorithm used to compare these structures is the same as the method used to generate the list of unique structures. We first derived the HNF and the labeling from each structure that we compared. Once the HNF and labeling of each structure has been derived it is just a matter of comparing them using the same methods mentioned earlier.

The final step is to see which structures have a high relative likelihood that have not been observed experimentally. Figure 10 shows the likelihood index for each structure and we can see that the observed structures tend to have a higher likelihood index at each concentration. By further analyzing this plot we see that there are structures with a high relative likelihood that have not been observed. In particular at the $x = 1/3$ concentration the observed structure does not have the highest likelihood. With this information we can predict a new structure. This structure is presented in Fig. 11, and its basis vectors and primitive vectors are:

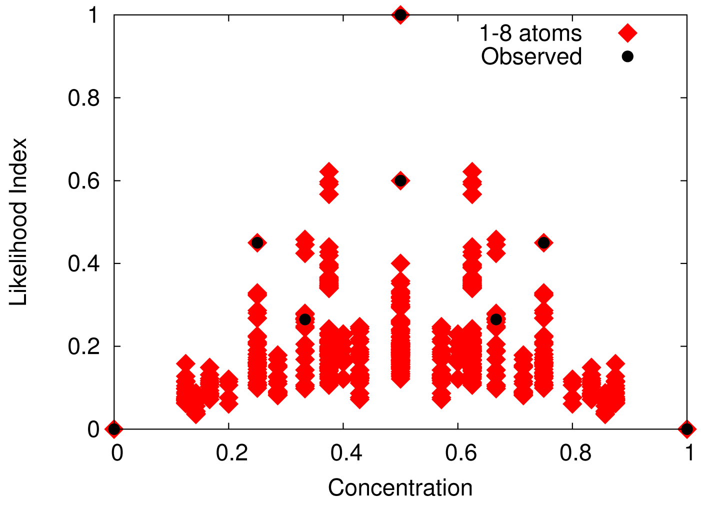

Figure 10 Plot of the likelihood index for binary simple cubic superlattices. Plots the concentration for A_xB_{x-1} with x from 0 to 1 so for each structure on the left of center there is a structure on the right which is equivalent by site swapping A⇔B

$$
\begin{array}{cc}
\text{Primitive Vectors:} & \text{Basis Vectors:} \\
\begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 1 & 3 \end{pmatrix} &
\begin{array}{lclllc}
\mathbf{A_1} & = & 0\vec{x} & 0\vec{y} & 0\vec{z} & \mathrm{A} \\
\mathbf{A_2} & = & 0\vec{x} & 1\vec{y} & 1\vec{z} & \mathrm{A} \\
\mathbf{A_3} & = & 0\vec{x} & 1\vec{y} & 0\vec{z} & \mathrm{B} \\
\mathbf{A_4} & = & 0\vec{x} & 1\vec{y} & 2\vec{z} & \mathrm{B} \\
\mathbf{A_5} & = & 0\vec{x} & 0\vec{y} & 1\vec{z} & \mathrm{B} \\
\mathbf{A_6} & = & 0\vec{x} & 0\vec{y} & 2\vec{z} & \mathrm{B}
\end{array}
\end{array}
\qquad (5)
$$

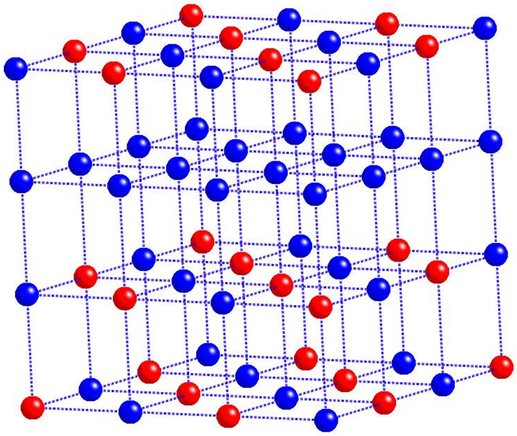

Figure 11 Possible binary structure with 6 atoms in the unit cell.

3 Conclusion

This work is important for multiple reasons. First of all, it gives further evidence that this method for calculating the likelihood of a structure is accurate. It also has given us possibilities for new simple cubic structures which we can use to predict new perovskites.

Now that we have these new possibilities the next step is to use VASP, or some other first principles code, to verify our findings. This method predicts new structures, not new compounds so will need to look further into which atoms tend to be perovskites. We can then run simulations using these atoms and this structure to see if it is energetically favorable.

References

[1] Harold T. Stokes, *Solid State Physics for Advanced Undergraduate Students*, 4th ed. (Provo, Utah, 2007), p. 5.

[2] Gus L. W. Hart and Rodney Forcade, ”Algorithm for generating derivative structures,” Phys. Rev. B **77,** 224115 (26 June 2008).

[3] Gus L. W. Hart, ”Where are Nature’s missing structures?,” Nature Materials **6,** 941-945 (Dec. 2007).

[4] Gus L. W. Hart, ”A new intermetallic prototype? Verifying predictions in CdPt and PdPt by exhaustive enumeration,” Phys. Rev. B (submitted Dec. 2008).

[5] U.S. Naval Research Laboratory, “Crystal Lattice Structures,” http://cst-www.nrl.navy.mil/lattic/ (Accessed October 29, 2006).