FINDING A PATH THROUGH A CRYSTAL
THEORETICAL MODELING OF IONIC CONDUCTIVITY

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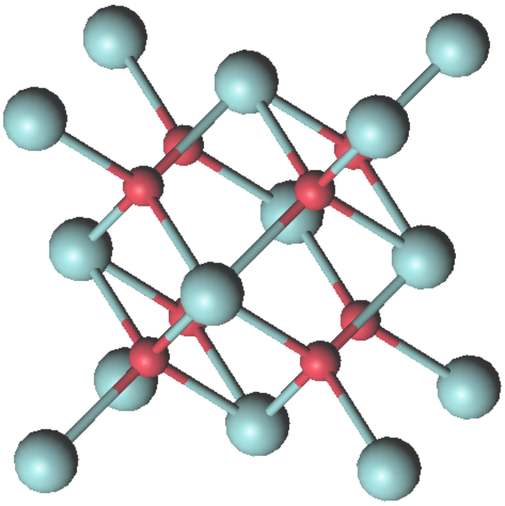

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Introduction

We are more familiar with electrical conductivity caused by the motion of electrons in a material. This can be found almost everywhere from electrical wiring at electrical appliances to advanced computer electronics.

The conductivity of a material is a property that depends on the materials ability to transmit charge carriers giving rise to a current. A current in itself does not have to be confined within a material but can be a stream of free charged particles in space. Examples of this include particle accelerators and streams of charged particles ejected from the sun.

Moving ions also give rise to a current. Ionic conductivity is as the name implies due to ions moving through a material. Ionic conductivity is not as common as electronic conductivity and not as widely understood. It has not been as thoroughly studied as electrical conductivity and is a relatively new concept. Examples of ionic conductivity can be found in ion detectors, such as pH meters, gas detectors, super-capacitors, batteries, and is an important component in fuel cells [1].

One interesting notion of ionic conductors is that they are an intermediate between a crystalline solid and a liquid electrolyte. If melted, any ionic system becomes an ionic conductor, but some systems retain this property at temperatures lower than the melting point.

Electronic conductors depend on the electron configuration. Metals have a “cloud” of free electrons around the nucleus. This is what give metals their distinctive shiny surface. These electrons can be very easily exited giving metals their conductive property. Insulators have a band gap compared to metals which have no band gap. This means that it will require a very high energy to excite an insulator to make it conduct.

Conductivity depends not only on chemical composition, but also on the crystal structure. For example, diamond is an insulator whereas graphite is a weak conductor.

In a similar way ionic conductors depend on the crystal structure. There are a few factors which makes a system to be an ionic conductor:

- it should be ionic, and without any directed bonds (e.g. covalent bonds),
- it should be “porous”, meaning it should be relatively easy to move an ion in a given direction,
- it should contain ions which create a matrix, a “skeleton” building up the overall structure.

A diamond is not an ionic conductor. It has very strong covalent bonds, have a compact structure and is not ionic. Conversely zirconia is a very good ionic conductor. Zirconia has a porous structure and is quite ionic. Another similarity to electronic conductors is that not all ionic compounds have the property as an ionic conductor as all metals are not as conductive. For example, table salt is not an ionic conductor. Calcium fluoride is another example of a very weak ionic conductor. The ionic radius may not have any influence on ionic conductivity. In calcium fluoride both ions are approximately the same size but in table salt the ions differ in size. The crystal structure is very different in salt and calcium fluoride. In zirconia the ions differ in size in a similar manner as in table salt but for lanthanum fluoride, another ionic conductor, the ions are similar in size. However the valence difference may have some effect along with the use of heavier atoms. Zirconium and lanthanum are heavy atoms with a high valence whereas calcium and sodium are light atoms with low valences.

Experimental measurements of ionic conductivity do not give any detailed insight in the ionic motion as it requires a large bulk to measure over. Empirical measurements can only yield information on how conductive a material is, what type of atoms that are moved and the temperature or energy required for conduction. It will not show how or where ions move or which paths they take through the crystal.

There are several approaches in modeling molecular and crystal structures. Some are: Molecular Mechanics, Molecular Dynamics and Quantum Chemistry. Molecular Mechanics and Molecular Dynamics approaches are usual choices for similar studies. The advantage of these methods is the speed of calculations and the ability to consider large clusters for modeling. However, these methods rely on parametrization, which describes interactions between atoms. In the case of ionic conductors, atoms will be put into unusual surroundings, which will change electronic structure of the system. Ab initio, parameter-free, quantum chemical methods seem to be a proper choice in this case. Quantum chemistry deals with charge distributions and chemical bonds.

There are few theoretical studies of super ionic conductors. None of them is made with usage of modern quantum chemical methods.

Structural measurements have been done on ionic conductors but these are more of “snapshots” of a specific structure and does not give any data on specific ionic motions. Studies involving ionic conductivity are about fuel cells, ceramics, lattice defects and super-capacitors [1][2][3][4][5].

Aim

The aim of this study is to find the mechanism that describes the ionic conductivity in several crystal structures and try to explain in detail how these ions move. The method can be used in determining how porous a crystal is, or how mobile an ion is around its equilibrium. By developing a method that successfully describes ionic conduction, the same method can be applied on other more or less known structures. We expect to predict paths for ionic conduction and some properties of the crystal.

The model developed in this work can be used to predict the behavior and properties of ionic conductors.

Model

Pure Crystal Structures

Three different structures has been studied. The first structure was CaF_2, Fluorite, because it has a simple structure and is a poor ionic conductor. The second system was LaF_3 with a more complex structure and it is known as a good fluoride ion conductor [1]. The third system was cubic ZrO_2, zirconia. Zirconia is known to be a very good oxygen ion conductor. The construction of the crystal systems used in the calculations can be described in several steps.

The first step includes analysis of the crystallographic data describing the ideal crystal.

The crystallographic data for the structure was acquired either from a database [8][11] or other literature [9][12][13]. From the literature one can find crystallographic data that contains a space group, a set of Wyckoff positions, or Wyckoff coordinates in partial coordinates and atomic parameters for the structure unit cell [9]. Some databases may even contain a complete unit crystal in Cartesian coordinates [8][11]. In this case the second and third step can be skipped. The crystallographic data can be obtained from own structural measurements as well.

The second step used the space group and Wyckoff coordinates. The space group was used to find a specific set of Wyckoff positions in a table of space groups [15].

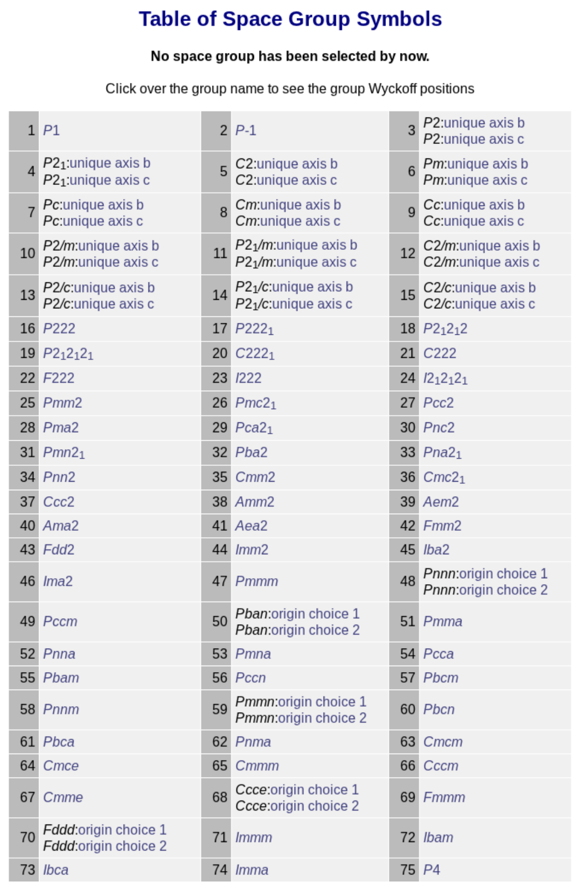


Table of Space Group Symbols

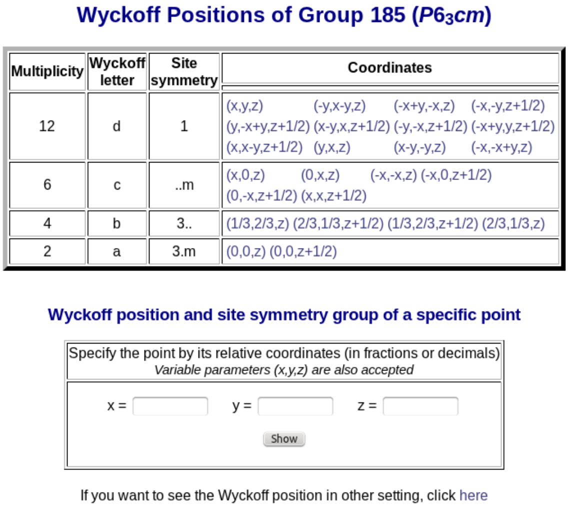
No space group has been selected by now.

Click over the group name to see the group Wyckoff positions

1	*P*1	2	*P*-1	3	*P*2:unique axis b *P*2:unique axis c
4	$P2_1$:unique axis b $P2_1$:unique axis c	5	*C*2:unique axis b *C*2:unique axis c	6	*Pm*:unique axis b *Pm*:unique axis c
7	*Pc*:unique axis b *Pc*:unique axis c	8	*Cm*:unique axis b *Cm*:unique axis c	9	*Cc*:unique axis b *Cc*:unique axis c
10	*P*2/*m*:unique axis b *P*2/*m*:unique axis c	11	$P2_1/m$:unique axis b $P2_1/m$:unique axis c	12	*C*2/*m*:unique axis b *C*2/*m*:unique axis c
13	*P*2/*c*:unique axis b *P*2/*c*:unique axis c	14	$P2_1/c$:unique axis b $P2_1/c$:unique axis c	15	*C*2/*c*:unique axis b *C*2/*c*:unique axis c
16	*P*222	17	$P222_1$	18	$P2_12_12$
19	$P2_12_12_1$	20	$C222_1$	21	*C*222
22	*F*222	23	*I*222	24	$I2_12_12_1$
25	*Pmm*2	26	$Pmc2_1$	27	*Pcc*2
28	*Pma*2	29	$Pca2_1$	30	*Pnc*2
31	$Pmn2_1$	32	*Pba*2	33	$Pna2_1$
34	*Pnn*2	35	*Cmm*2	36	$Cmc2_1$
37	*Ccc*2	38	*Amm*2	39	*Aem*2
40	*Ama*2	41	*Aea*2	42	*Fmm*2
43	*Fdd*2	44	*Imm*2	45	*Iba*2
46	*Ima*2	47	*Pmmm*	48	*Pnnn*:origin choice 1 *Pnnn*:origin choice 2
49	*Pccm*	50	*Pban*:origin choice 1 *Pban*:origin choice 2	51	*Pmma*
52	*Pnna*	53	*Pmna*	54	*Pcca*
55	*Pbam*	56	*Pccn*	57	*Pbcm*
58	*Pnnm*	59	*Pmmn*:origin choice 1 *Pmmn*:origin choice 2	60	*Pbcn*
61	*Pbca*	62	*Pnma*	63	*Cmcm*
64	*Cmce*	65	*Cmmm*	66	*Cccm*
67	*Cmme*	68	*Ccce*:origin choice 1 *Ccce*:origin choice 2	69	*Fmmm*
70	*Fddd*:origin choice 1 *Fddd*:origin choice 2	71	*Immm*	72	*Ibam*
73	*Ibca*	74	*Imma*	75	*P*4

Figure 1. A picture of a part the Wyckoff webpage. Here the space group of the structure can be selected.

When selecting a specific space group on this web page it will show a table of several Wyckoff positions. We can call this a Wyckoff table.


Wyckoff Positions of Group 185 ($P6_3cm$)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
12	d	1	(x,y,z) (-y,x-y,z) (-x+y,-x,z) (-x,-y,z+1/2) (y,-x+y,z+1/2) (x-y,x,z+1/2) (-y,-x,z+1/2) (-x+y,y,z+1/2) (x,x-y,z+1/2) (y,x,z) (x-y,-y,z) (-x,-x+y,z)
6	c	..m	(x,0,z) (0,x,z) (-x,-x,z) (-x,0,z+1/2) (0,-x,z+1/2) (x,x,z+1/2)
4	b	3..	(1/3,2/3,z) (2/3,1/3,z+1/2) (1/3,2/3,z+1/2) (2/3,1/3,z)
2	a	3.m	(0,0,z) (0,0,z+1/2)

Wyckoff position and site symmetry group of a specific point

Specify the point by its relative coordinates (in fractions or decimals)
Variable parameters (x,y,z) are also accepted

If you want to see the Wyckoff position in other setting, click here

Figure 2. The Wyckoff table for the space group 185. LaF_3 is of this group.

Other sources may have different layout of the columns but they will still give the same information. The first column is the multiplicity. It tells how many coordinates will be generated from a single Wyckoff coordinate.

The next is the Wyckoff letter. This is basically used to separate the different Wyckoff positions if they were to have the same multiplicity. The multiplicity together with the letter is what is called the Wyckoff position.

The third column tells the symmetry for that Wyckoff position. This was not important for this work and was not used for the calculations.

The last column contains sets of partial coordinates. The provided coordinates from a source will each fit in one of these sets, same or different. Using this fit the rest of the coordinates in that Wyckoff position could be obtained. The number of coordinates provided from crystallographic data depends on the chemical formula of the substance. At least one of each element should be available. A more detailed description of how these coordinates are derived is written in each part.

The coordinates obtained in this step was in partial coordinates and needed to be converted into Cartesian coordinates for use in the calculations.

The third step now made use of the atomic parameters. These was used when converting the partial or lattice coordinates obtained in the second step into Cartesian coordinates in an Euclidean space. The parameters a , b

and c is the size of the unit cell in each direction. An important note is that these parameters is not necessarily orthogonal. The parameters are related in different way depending on the structure. For example for a cubic lattice they will relate as $a=b=c$. The parameters were used to obtain translation vectors. These as with the parameters depend on the crystal structure. In the cubic example the translation vectors could be obtained by $\bar{A}=a*\bar{X}$, $\bar{B}=b*\bar{Y}$ and $\bar{C}=c*\bar{Z}$ where $\bar{X}=(1,0,0)$, $\bar{Y}=(0,1,0)$ and $\bar{Z}=(0,0,1)$.

The Cartesian coordinates were then obtained as a matrix by matrix multiplying the translation vectors with the partial coordinates.

$$\begin{pmatrix} A_1 & B_1 & C_1 \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{pmatrix} \times \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \\ y_1 & y_2 & y_3 & \cdots & y_N \\ z_1 & z_2 & z_3 & \cdots & z_N \end{pmatrix}$$

where x_1, y_1, z_1 etc. are the partial coordinates obtained from the Wyckoff table. The resulting matrix will be in Cartesian coordinates.

In the fourth step the unit crystal of the substance was used. However this may not be what looks like a “complete” structure with some parts missing. This can be fixed in two ways.

In one way when expanding the structure it will complete the unit cell of the crystal. Points can be added in some corners of the unit crystal i.e. at the coordinates $(0,0,0)$, $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$ to the partial coordinates and then translate these in the same way as the other partial coordinates in step three. These will end up in the corners of the unit cell in the Cartesian coordinates as well. These can be made up by dummy atoms that are easily identified separately from the others and can be removed later. We used a graphical editor, GV, from the Molcas package. In Molcas GV these points can be used to find and apply symmetry, in effect copying a part of the crystal in a direction. E.g. selecting one point, or atom, in one corner and another in one corner will duplicate any unit in between in that direction when applying symmetry. This will use the existing atoms to fill in any “gaps” that may be present. Coordinates are checked at symmetry operation as to avoid any duplicate atoms in the same position. When a satisfying unit crystal is made any “excessive” atoms can then be removed. The added corner points were primarily made as references for use in the fifth step but could additionally serve a use in this way as well.

The second way in getting a more complete crystal is by manually adding more points to the partial coordinates before translation. Eight 3-dimensional coordinates can be generated ($(0,0,0)$, $(0,0,1)$, $(0,1,0)$, $(0,1,1)$ etc.). These are then added to each of the coordinates in one of the sets obtained in the second step creating eight new coordinates for each coordinate in the set. The old coordinate is kept as it is as well. (Identifying which set that seems to be “lacking” may be difficult). This will produce some coordinates that contain components larger than 1. These coordinates can be ignored as these fall outside of the actual unit crystal. Depending on the structure this may be needed for more than one set of coordinates. For the LaF_3 system this was done for one fluoride set and on the lanthanum set. A code for implementation of this algorithm has been written.

The fifth set was about creating the external field surrounding the physical structure. The order of which to do step five and six is not of any consequence. Creating the external field was very straight forward. By applying symmetry operations, in Molcas GV, in each direction the crystal was enlarged. This can be done more than once to get a larger field. Here one layer was used. The coordinates for the atoms outside the original unit cell was converted into point charges.

The sixth step the actual ionic conduction was simulated. Depending on the structure one of the ions are moved a certain path. By examining the structure and the surrounding of the ion that is moved a path towards a position with a same species ion was drawn. If there was no obstruction, such as other ions, the path was deemed worthy of simulation and included for calculation of the energy as the ion changed position along the path.

The other ion in the target position was kept in the first calculations and then removed to simulate a vacancy in the rest of the calculations. This was to examine the mobility of the ion in a “pure” crystal.

During this step the structure was minimized as to contain the surrounding ions around the path only. The removed ions were used as point charges.

Defects

As mentioned in the introduction experimental measurements can only be done over a bulk and will only yield an overall result for the entire crystal. It will not provide any information on how or where individual ions move within the crystal.

A theoretical approach was chosen to develop a method that describes the ionic conductivity. There are several systems that can describe molecular properties. For this work quantum chemistry was chosen to model the system. Quantum chemistry can be used to describe charge distributions and thus changes in charge and chemical bonds.

A limited volume was deemed necessary as large crystals with many atoms would produces too heavy or time consuming calculations.

Making the paths for the ionic motion in the crystal is relatively straight forward. The paths represents the ionic conduction. One conductive ion in a crystal is selected. For example zirconia is conductive for oxygen ions [1] and is used as an example in the three figures below (oxygen is red).

Other conductive ions adjacent to the selected ion and the volume in between should be examined. If there is enough open volume between two ions a path can be formed. Of course conductive ions in other locations should be examined as different paths can be made in different areas of the crystal.

The porosity can be examined by moving an ion from its equilibrium position in various directions as shown in fig. 1. The energy will increase in a similar manner to how two atoms moves closer to each other (see first part of calcium fluoride). Depending on how porous a material is the energy can increase faster or slower. The energy can even vary for other direction in the same crystal.

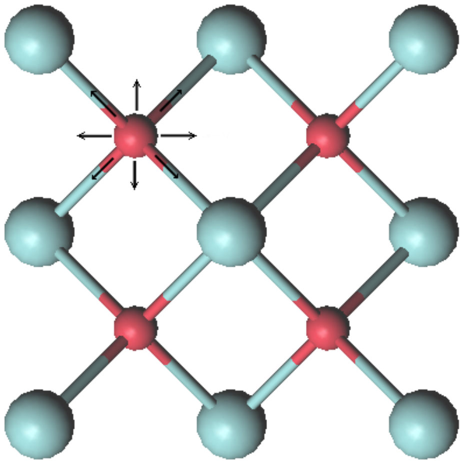


Figure 3. The porousness of the crystal can be examined by moving the ion slightly out of its equilibrium.

The actual ionic conduction can be simulated by introducing imperfections in the crystal in the form of vacancies as other oxygen ions are removed. Fig. 4 shows an example of a simple path in zirconia.

As a vacancy is created an adjacent oxygen ion can be moved to this vacancy. Any adjacent ion can be moved given there is enough space or low enough electron density from surrounding ions along the path. Different paths can be formed depending on the crystal structure. Some paths may even be directly equal. In fig. 4 the shown path will give the same energy results as moving the ion straight down or moving the lower left ion to the right (and introducing vacancies at these locations). This is the model used in all three systems. The path itself was made by moving an ion in several steps toward the vacancy. In each step the energy was calculated. The actual paths for each crystal are shown for each structure.

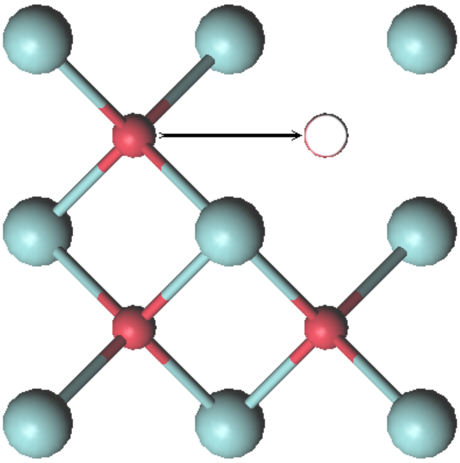


Figure 4. The ion can be moved to an adjacent vacancy as they become available.

Ionic conduction is most likely not limited to a single ion moving one single step when looking at larger systems. It could be seen as a similarity to electronic conduction where ions or electrons move in a cascading pattern through the structure. This modeled is examined in the last system for comparison. However, in that particular model two ions are moved simultaneously.

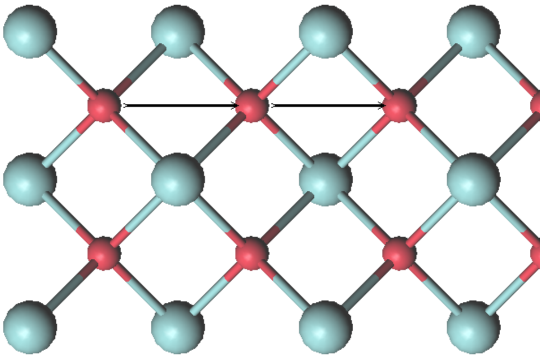


Figure 5. Ionic conduction can be described as a cascading motion of multiple ions.

By observing a single small volume within the crystal, such as a unit cell can give a more detailed result. Ionic conduction as the name implies is about moving ions. Ions are charge carriers and thus a quantum chemical approach is needed.

Method

The Hartree-Fock method can handle a large number of atoms and provide a good accuracy in energy when solving the Schrödinger equations. HF handles atomic orbitals and molecular orbitals as Gaussian functions making calculations more efficient [21].

Density functional theory DFT, in its common implementations for so called hybrid functionals, based on Hartree-Fock theory, but corrects it by adding correlation terms. The results, the geometry and the energy for the ground state, obtained within DFT/B3LYP theory are in a good agreement with experiment [22].

Molcas is a quantum chemical software for use as a computational tool [6]. Molcas makes use of several modules available for calculations. Below is a short description of the code that was used.

The `GATEWAY` program module handles basic molecular parameters [7]. This contains the coordinates for the crystal, the basis set, group symmetry and the command `RICD`.

The coordinates for the crystal is under the command `COORD`. These coordinates can be written directly or as a file name to a separate file containing the coordinates of the crystal.

The basis set used for the calculations was `ANO-RCC-VDZ`.

`ANO` covers the periodic system. `RCC` includes scalar relativistic corrections and correlation of semi-core orbitals. The last part, `VDZ` (valence double zeta) determines the overall quality of the system. `MB` for minimal basis set can be used in place of `VDZ` to simplify the calculations as it uses the minimal basis functions needed for a systems. `MB` is good enough but as Zr and La are heavier atoms containing d- and f-orbitals, `VDZ` was used throughout the calculations for consistency. The higher quality options use more Gaussian functions to describe the orbitals giving a better accuracy. Too high of a quality would make the calculations more complex.

`RICD` is used to generate on-the-fly auxiliary basis sets in an attempt to shorten the calculations by simplifying the calculation of integrals.

The information on the external field is put under the `GATEWAY` module. The purpose of the external field is to lessen the burden of calculations on a huge number of physical atoms by having the atoms further away represented by point charges representing the removed ions. Written as `XFIELD`, this contain the coordinates for the point charges. The size for the external field was one unit crystal around the actual crystal, giving a total size of three units in each dimension.

The size of the crystal that was used in the calculations was consistent with the unit cell of the system. A larger amount of more complex atoms increase calculation time. The size of the actual crystal ranged between 20-30 atoms. The size of the external field was approximately 26 times the amount of the unit cell. The calculation time could range from 45 minutes for simple atoms to 10 hours for the more complex atoms.

The `SEWARD` module computes the one-electron and two-electron integrals for the molecule and basis set provided in the program `GATEWAY`. The module can contain additional commands for more complex integrals if needed. Here `SEWARD` is run without any additions.

The `SCF` module calculates Hartree-Fock and DFT wave functions. It uses Hartree-Fock (HF) Self-Consistent Field (SCF) method to solve the calculations. To include Density Functional Theory (DFT), which deals with the electron density [22], the command `KSDFT` is used under the `SCF` module. The `B3LYP` functional was used for the `KSDFT` calculations. The total charge of the physical crystal is set under the `SCF` module with the `CHARGE` command and a numerical value.

Problems Inherent of the Modeling

It should be noted that this is a model using approximations in many places. This will lead to some limitations. By using quantum mechanical calculations a large number of heavy or complex atoms will take longer time and use more memory. A minimization of the system to reduce time and memory is introduced. This will affect the accuracy of the model. By minimizing the model to the closest and the surrounding atoms around the path less atoms and thus less memory will be used. The paths are assumed as straight lines from starting position to final position. This may not be the case. The other ions within the lattice is set to be completely immobile and is not moved from their equilibrium position.

CaF_2, Calcium Fluoride

Introduction

CaF_2, or Fluorite can be considered to be a poor ionic conductor (as it is not in the list of ionic conductors) [1]. It has a hardness of 4 on Mohs scale of minerals [20]. It was studied first because it has a simple structure of which to build and to get a reference of how a non-conductor behaves.

One property of the ionic conductivity to be studied is to see at what energies are required for the crystal to start conduct.

Due to its simple crystal structure it was easy to model and determine how fluoride ions can move within the lattice with added vacancies.

A single unit crystal of CaF_2 consists of 14 Calcium ions in a face centered cubic pattern surrounding 8 Fluoride ions in a simple cubic pattern. Table 1 shows the atomic parameters for a CaF_2 unit crystal.

Model

CaF_2 is a cubic crystal with the space group $Fm\bar{3}m$ (#225). It has a single lattice parameter of $a=5.462\text{Å}$. All data was taken from a single source [8]. This source contained a complete crystal ready to use. The following tables shows the atomic parameters and Wyckoff positions for CaF_2.

Table 1. Atomic parameters for CaF_2 in $Fm\bar{3}m$ where $a=5.462\text{Å}$.

	x	y	z
Ca	0	0	0
F	¼	¼	¼

Table 2. The three lowest rows of the Wyckoff table for space group $Fm\bar{3}m$ (#225).

Multiplicity	Wyckoff letter	Site symmetry	Coordinates (0,0,0)+(0,½,½)+(½,0,½)+ (½,½,0)+
8	*c*	$\bar{4}3m$	(¼,¼,¼) (¼,¼,¾)
4	*b*	$m\bar{3}m$	(½,½,½)
4	*a*	$m\bar{3}m$	(0,0,0)

As a complete crystal was obtained no further work using the parameters was necessary. The unit cell is shown in fig. 4. using Molcas GV together with the coordinates for the crystal an external field was created. The unit cell was duplicated in each direction. All coordinates outside the original unit cell was replaced with external field points each representing the ion they replaced, i.e. a charge of -1 for fluoride ions and $+2$ for the calcium ions. These points have no actual physical shape. The paths the ions move to represent the ionic conduction was relatively straight forward due to the simple structure.

To have an ionic conductivity the ions in the lattice need some degree of freedom to be able to move far enough to reach any defects that may have formed.

Fig. 6 below shows the unit crystal for CaF_2 and marking which fluoride ion with an “X” that was selected to move. The numbers indicates the direction of the paths the fluoride ion makes in each calculation. If the fluoride ions are considered to be positioned in corners of a cube, then the first path is along an edge line (moving X towards 1), the second is diagonally across a side (X towards 2) and the third is diagonally through the crystal (X towards 3). Paths in opposite directions to other unit crystals are equivalent to the three paths within the unit crystal.

First the energies for a complete crystal with no defects such as removed fluoride ions is studied. Only a part of the paths are followed since the energy increases to infinity as the distance between the ions approaches zero. This can be used as a measurement of the porosity of the crystal.

Then vacancies were introduced, one for each path by removing the numbered atoms. This represents the ionic conduction. The charges were examined along with the energies. The energy difference was studied using the starting point in the path as a reference.

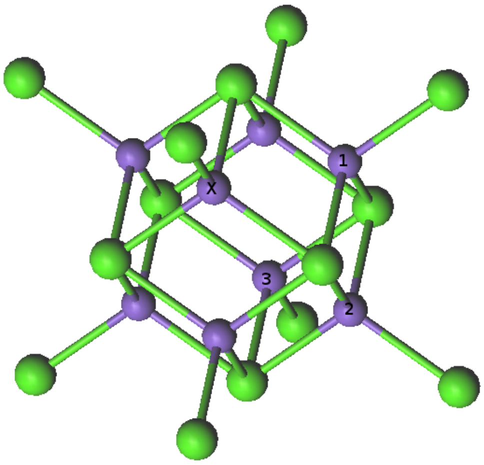


Figure 6. The CaF_2 structure of a single unit cell showing moving and target fluoride ion.

Results and Discussion

The first examined path running along the edge line gives a common and expected repulsion as the moved fluoride ion is getting closer to another fluoride ion (fig. 7). Note that the path of the fluoride ion takes it right between two calcium atoms. The charge of these calcium ions decreases as the fluoride ion approaches the center between them in a way to distribute the charge change in the two fluoride ions.

As seen in fig. 5 in the energy there is a limited degree of freedom for the ion to move. The charge (fig. 8) of the moved fluoride ion is stable at first but as the ionic radius of the two fluoride ions is increasingly overlapping the charge increases rapidly and seems to level of at 0 as forming a covalent bond.

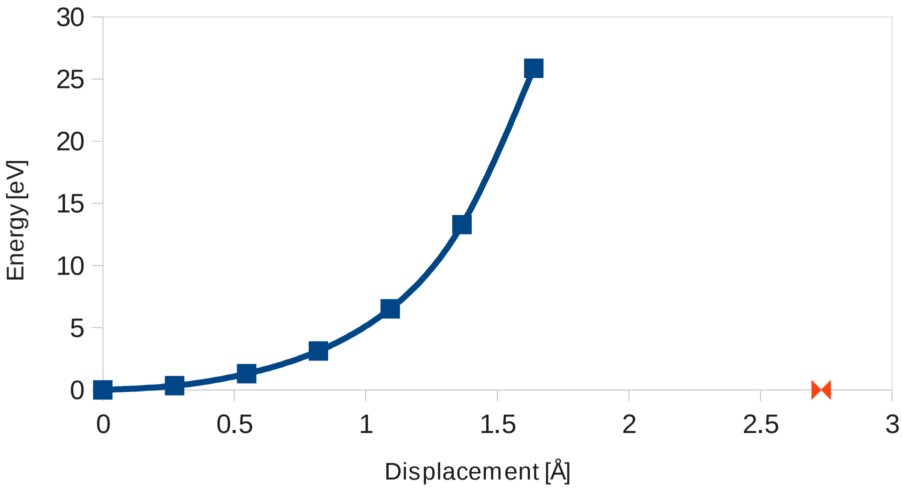


Figure 7. Energy of the crystal as the fluoride ion is moved along the first path. At the last point the fluoride ions are well inside each others ionic radius'. The cross marks the position of the other fluoride ion.

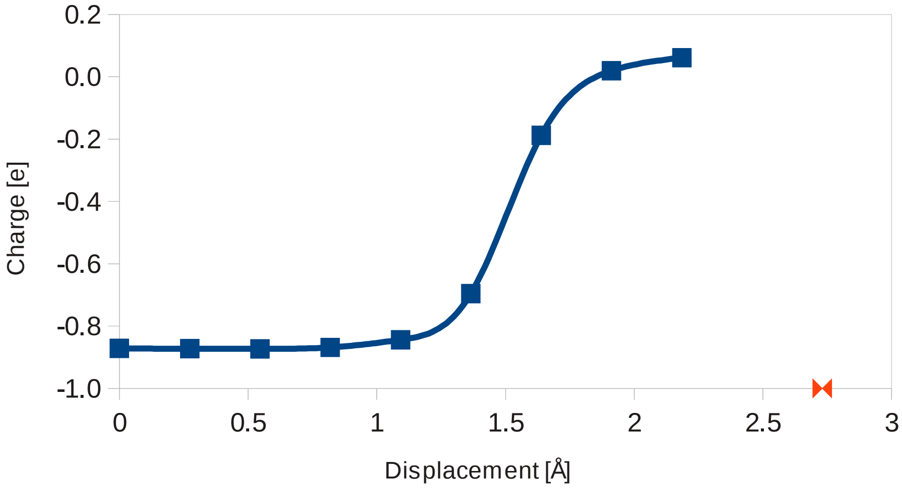


Figure 8. The change in charge over the first path.

The second path of the fluoride ion is diagonally along the side (fig. 9). The repulsion is quite different, most likely due to a calcium ion positioned rather close to the path. The charge behaves similar to the charge in the first path distributing it over the calcium ion. As the fluoride ion is moved along the path it is 'squeezed' between two other fluoride ions and close to a calcium ion half way through. The large increase in energy half way before the hard sphere repulsion from the other fluoride ion is most likely the steric or electrostatic interactions from the two fluoride ions and the calcium ion.

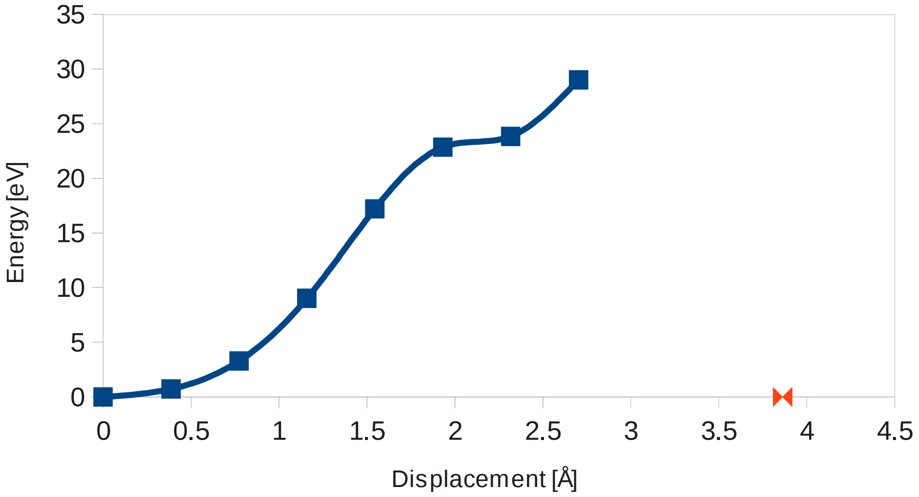


Figure 9. Energy of the crystal as the fluoride ion is moved along the second path.

The third and last path taking the fluoride ion for a journey through the interior of the unit crystal have an energy increase similar to that of the first path (fig. 10). The fluoride ion pass by other fluoride ions but at a larger distance compared to the second path. However it is still close enough to affect the energy as seen as a slow increase until the energy increase from the repulsion of the overlapping ionic radius from the two fluoride ions.

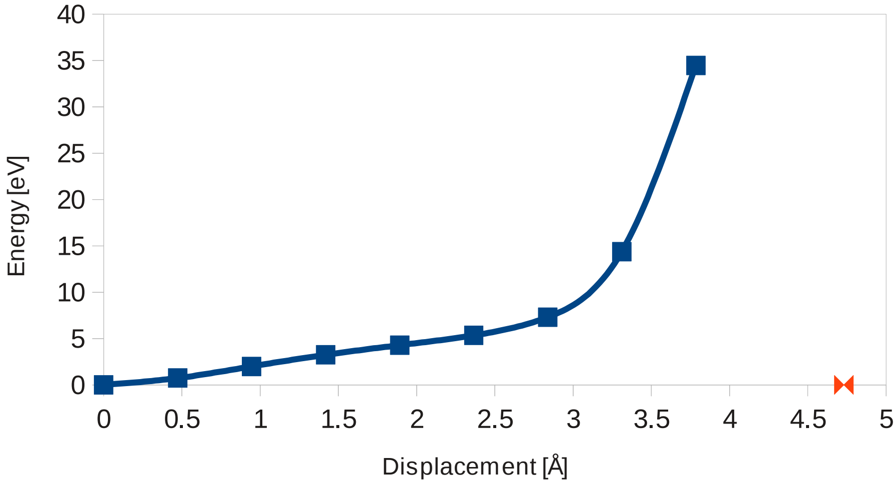


Figure 10. Energy of the crystal as the fluoride ion is moved along the third path through the crystal which is also the longest.

The introduced defects are vacancies in the position of the numbered fluoride ions representing each calculation. One ion is removed in each calculation. Moving the fluoride ion to these locations produces a barrier curve. The energy required to overcome this barrier was examined. The energy can be related to a temperature using $E = kT$.

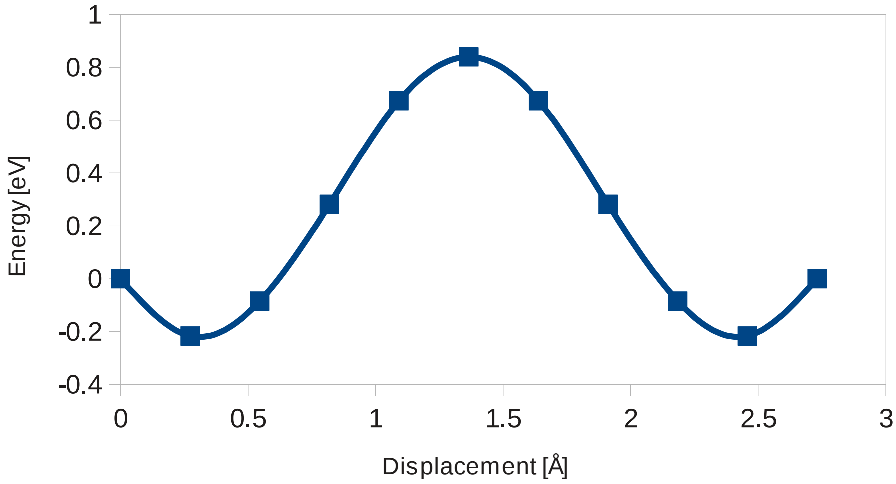


Figure 11. Energy of the crystal for the first path with fluoride ion in the target location removed.

The energy is very different from the case without defects. The degree of freedom seems greatly increased in fig. 11 and it seems to even gain some energy in moving the Fluoride ion. However the energy required to pass the barrier is close to 1 eV. An increase in energy of 1 eV would be equivalent to an increase in temperature of approximately 11600 K. Given the energy to pass the barrier the crystal is most likely in a gaseous state.

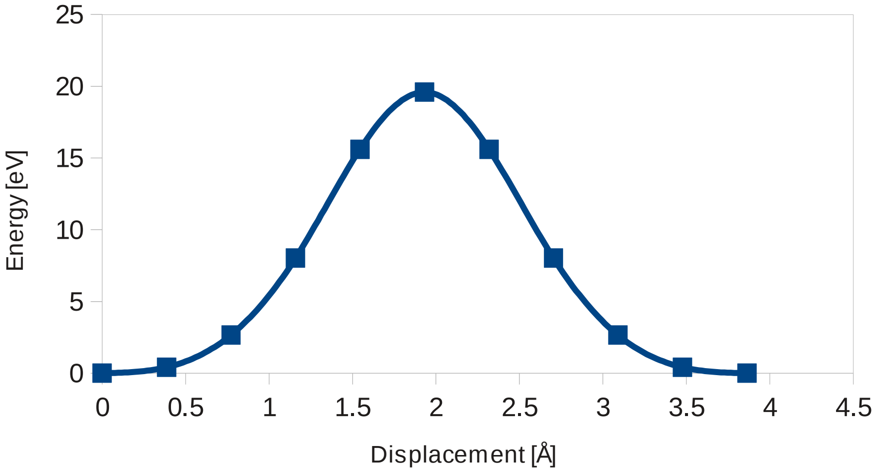


Figure 12. Energy of the crystal for the second path.

In the second path (fig. 12) the degree of freedom is much lower and the barrier is too high to be passed. The high barrier is from where the fluoride ion is in between and very close to two fluoride ions and calcium ion.

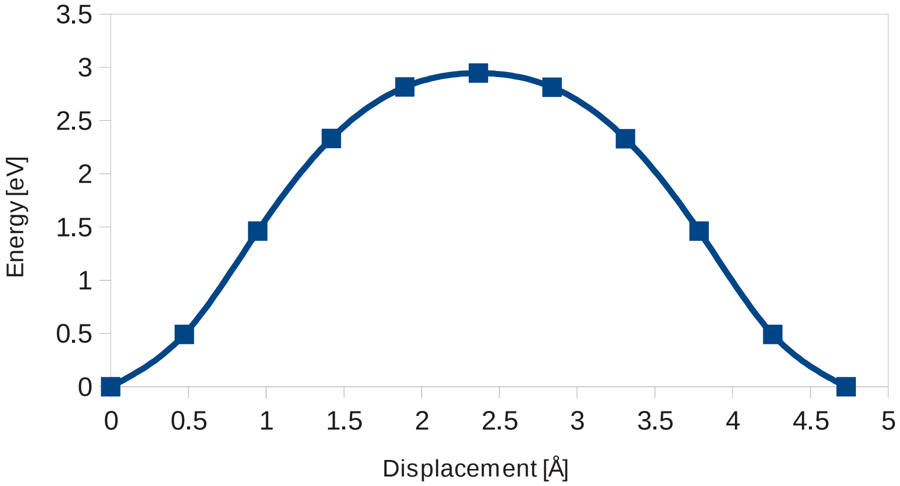


Figure 13. Energy of the crystal for the third path.

In the last path the degree of freedom is even less than that of the second. The barrier is lower but not low enough to be an effective ionic conductor at room temperatures or below the melting point. The third path does not only show the energy for a straight path through the crystal. It can represent a version of the second or even first path. The fluoride ion is first moved towards the center of the crystal and then to another corner.

The ionic radius of Ca^{2+} is 1.14Å and for F^- it is 1.19Å [23]. These values can be used when looking at the graphs below showing the distances between the moved ions and the closest stationary ions. In some cases the distance is smaller than the sum of the radius'. This also explains the large increase in energy.

The following figures shows the distance to the closest neighbors when the fluoride ion is moved along its path.

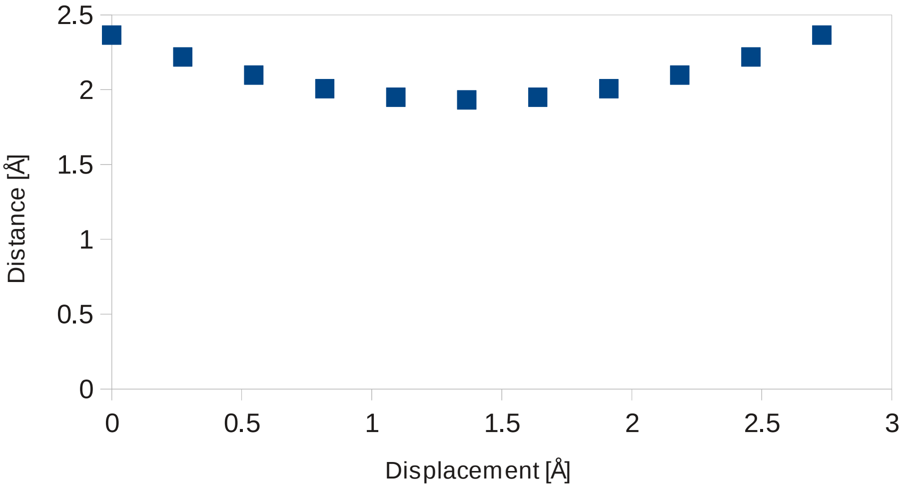


Figure 14. Distance to the closest calcium ions as the fluoride ion is moved along the first path.

In fig. 14 the closest fluoride ion is not needed since the distance increases as the fluoride ion is moved. This shows an expected shape for a particle that passes another particle.

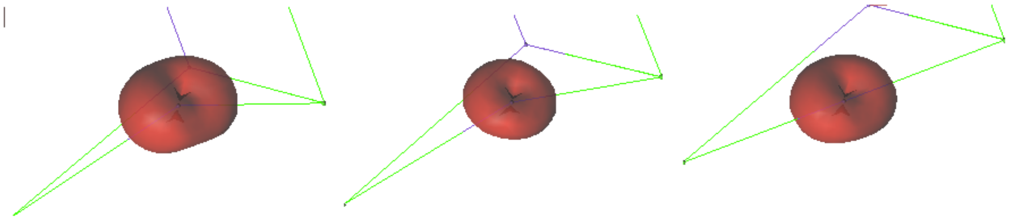


Figure 15. The change in electron density when moving along the first path.

Fig. 15 shows the difference of the electron density at three different points along the first path. The difference was obtained by subtracting the electron density in one point in the path from the electron density in the equilibrium position. The right-most picture shows the density in the half way point. The two left pictures shows the density in points between the midway and the starting point. The difference seems to first decrease and then increase. This is because the energy decreased at the beginning of the path to later increase before halfway.

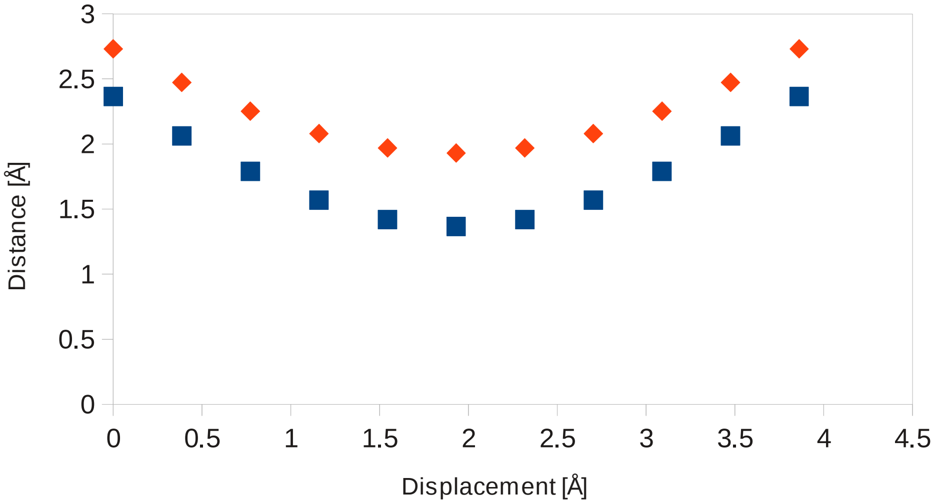


Figure 16. Distance to the closest calcium (squares) and fluoride (diamonds) ions along the second path.

In the second path the fluoride ion is more confined as seen in fig. 16. It is much closer to both calcium ions and fluoride ions which explains the high increase in the energy.

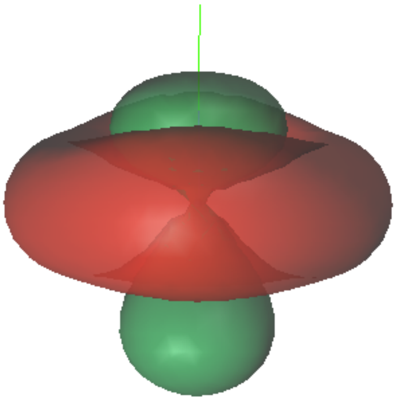


Figure 17. Electron density difference of the fluoride ion when half way along the second path.

In fig. 17 the electron density difference is very different compared to fig. 15. The thinner part of the "donut"-shape points towards the neighboring fluoride ions. The smaller upper part is close to a Calcium ion.

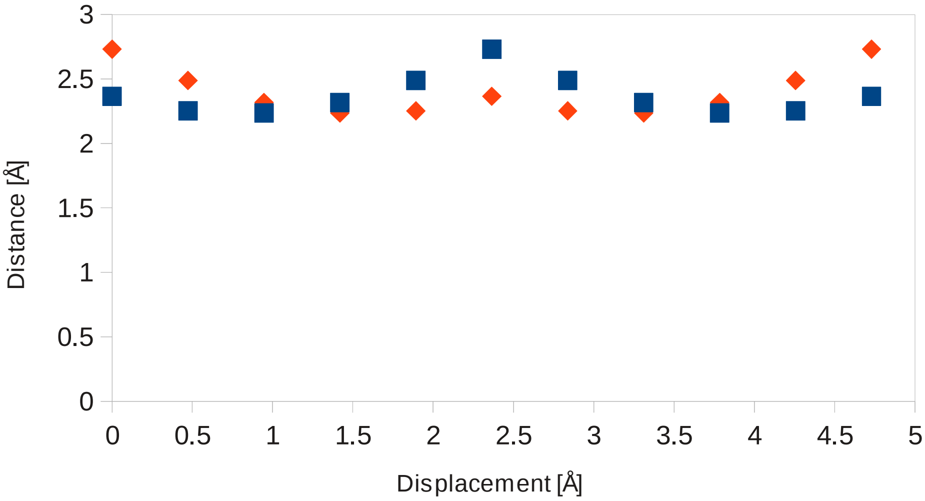


Figure 18. Distance to the closest (not the same ions all the way) neighbors as the fluoride ion moves through the crystal.

In the path through the crystal the closest neighbor changes from fluoride to calcium midway. But the overall distances are larger compared to the second path.

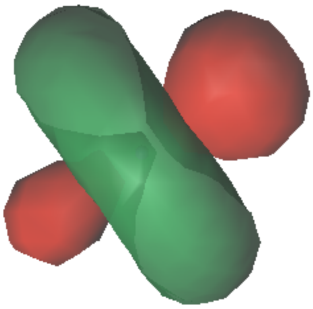


Figure 19. Electron density of the fluoride ion in the center of the crystal.

The electron density difference changes in a similar way as in the second path (fig. 19). Similar to the second path the distance to both calcium ions and fluoride ions become smaller unlike in the first path where the distance to other fluoride ions increases. The thicker upper sphere points to a vacant fluoride position. The “donut” is now lined in between the nearby fluoride ions.

The dips at the beginning and end of fig. 11 indicates that the fluoride ion is more mobile in this direction. Compared to the other directions which seems as mobile with or without vacancies. Looking at fig. 11 and 15 the change in density becomes bigger probably because the distance to other fluoride ions increases. As the energy starts to increase the density difference become larger again due to the closer distance to the calcium ions. In the second path the ionic radius' of the moved fluoride ion and the calcium ion along the path overlap. This can be seen in fig. 17 as the density changes radically. It is affected by both a calcium ion and two fluoride ions compared to the first path where the moved fluoride ion is mainly affected by two calcium ions. In the third path diagonally through the unit crystal the electron density is almost similar in shape to the one from the second path. one difference between the second and third path is the surrounding ions. In the second path the moved fluoride ion has one calcium ion and two fluoride ions in close proximity. In the third path the fluoride ion will be in the center of the crystal putting all other ions at equivalent distances putting the fluoride ions closer.

For fluorite the most likely path for ionic conduction is the first path as it has less energy to overcome compared to the other paths. It is not low enough to be an ionic conductor since the temperature needed is well above the melting point for CaF_2 ($1418^\circ C$).

LaF_3, Lanthanum Fluoride

Introduction

LaF_3 is used as an ionic conductor for fluoride ions [1]. LaF_3 is used among other things as an ion-selective electrode, a transducer or sensor that convert the activity of fluoride ions in solutions to an electric potential [17]. Ion-selective electrodes are used in biochemical and biophysical research measuring the ion concentration in an aqueous solution [16]. LaF_3 can be doped with europium ($\sim 0.3\%$) for use as ion-selective electrode or neodymium for use as a scintillating material [17].

Model

The space group, lattice parameters and Wyckoff positions for LaF_3 was obtained from an article [9]. LaF_3 is a hexagonal close-packed crystal with space group $P6_3cm$ (or #185). The lattice parameters, $a=7.185\text{Å}$ and $c=7.351\text{Å}$, was used from the same paper.

A crystal have three lattice parameters, a , b and c . For cubic systems such as CaF_2 these are related as $a=b=c$ and for hexagonal systems such as for LaF_3 $a=b\neq c$. The parameters are the lengths of the unit crystal on each side and may not necessarily be orthogonal.

The coordinate parameters for LaF_3 was as follows in the table below.

Table 3. Atomic parameters in $P6_3cm$ for LaF_3.

	x	y	z
La	0.6742	0	0.25
F(1)	0	0	0.3209
F(2)	1/3	2/3	0.2187
F(3)	0.2857	0	0.0810
F(4)	0.3724	0	0.4185

This is basically all the crystallographic data that is needed to start creating the unit crystal. Next the Wyckoff positions for this space group was obtained. This can be found in many places, here [15] was used. Looking up the space group P6$_3$cm or number 185 the following table of Wyckoff positions was found.

Table 4. Part of the Wyckoff table for space group $P6_3cm$ (#185).

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
6	c	$..m$	(x,0,z) (0,x,z) (-x,-x,z) (-x,0,z+½) (0,-x,z+½) (x,x,z+½)
4	b	$3..$	(1/3,2/3,z) (2/3,1/3,z+½) (1/3,2/3,z+½) (2/3,1/3,z)
2	a	$3.m$	(0,0,z) (0,0,z+½)

To use the Wyckoff table one atom is taken from table 4 and fitted in one of the coordinates. F(1) can be taken as one example. This only fits in the row where the multiplicity is 2 with Wyckoff letter a, designated as Wyckoff position 2a. This then gives another coordinate for that atom. It may be fitted in Wyckoff position 6c as well. However, this will give the exact same result as for 2a. Same thing is done with the other atoms, La fits in Wyckoff position 6c, F(2) in 4b and F(3) and F(4) in 6c. A total of 24 coordinates was obtained from this. These coordinates were in partial coordinates and needed to be converted to Cartesian coordinates, in Å. To do this a conversion matrix was used. The space group of LaF$_3$ belongs to a family of hexagonal close-packed crystal. The translation vectors for this particular crystal is [10]:

$$\begin{array}{lrcr} A= & \left(1/2\cdot a,-1/2\cdot 3^{1/2}\cdot a,0\right) & = & \left(3.5925,-6.222,0\right) \\ B= & \left(1/2\cdot a,1/2\cdot 3^{1/2}\cdot a,0\right) & = & \left(3.5925,-6.222,0\right) \\ C= & \left(0,0,c\right) & = & \left(0,0,7.351\right) \end{array}$$

In some cases these might be written as A$_1$, A$_2$ and A$_3$ but let's use A, B and C to make it a little easier. These can be used in a matrix multiplication to get the Cartesian coordinates.

$$\begin{pmatrix} A_1 & B_1 & C_1 \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{pmatrix} \times \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \\ y_1 & y_2 & y_3 & \cdots & y_N \\ z_1 & z_2 & z_3 & \cdots & z_N \end{pmatrix}$$

The coordinates x_1, y_1, z_1 etc. are the partial coordinates obtained using the Wyckoff table. The Cartesian coordinates can be calculated using either vector or matrix multiplication depending on the programs capabilities or the programmers skills. In some crystals like this LaF_3 it may not easy to see any borders of the unit cell. An atom of a different type from the rest of the crystal, e.g. Ti, can be put in the partial coordinates of $(0,0,0)$, $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$ giving an atom in four corners of the unit cell. One in origin and one in each crystal axis at the crystal edge. More atoms can be added to fill in any gaps that may appear in the unit cell. In this case more of La and F(2) of the atomic parameters were added. The four atoms in the corners were used in Molcas to enlarge the unit cell in each direction. The large crystal created from this was used for external field points in the same manner as for CaF_2. The unit crystal was used to find potential pathways that a fluoride ion could take. Since the LaF_3 crystal is not cubic it is not as easy to determine possible pathways as it was for CaF_2. A simple outline of how to find the pathways is to look on each fluoride ion and its neighboring fluoride ions. If the distance or line-of-sight between two fluoride ions is clear of obstacles it is a candidate for a pathway. Thus moving the ion from its position towards the position of the other ion no other particle would be in the way. Some pathways can be considered identical, thus reducing the sheer number. When a path was determined the fluoride ion in the end position was removed and another neighboring fluoride ion was moved stepwise toward that position. Each step was saved in a separate position file. These position files were used in input files used for calculations in Molcas.

Results and Discussion

The paths selected to be studied can be seen in the picture below. More paths can be found but these will pass too close to other ions giving a very large energy barrier.

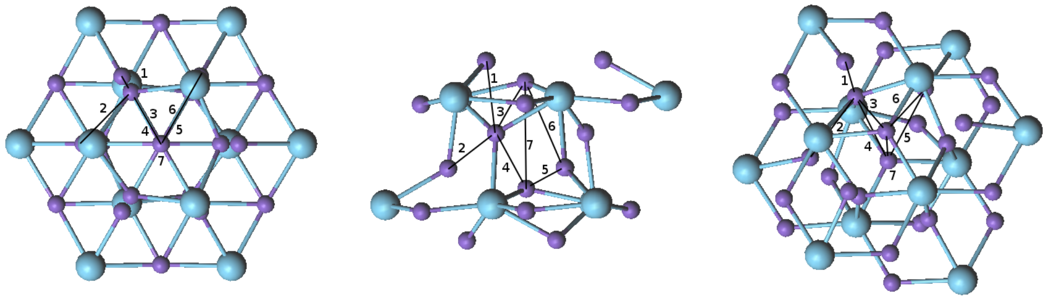


Figure 20. The chosen paths.

The paths are made around the center hexagon. This can be regarded as an approximate unit cell.

The first path is in a corner of the hexagon. This fluoride ion is moved from an upper position down to a vacancy position just underneath. Figure 21 shows the energy as the fluoride ion is moved in the corner.

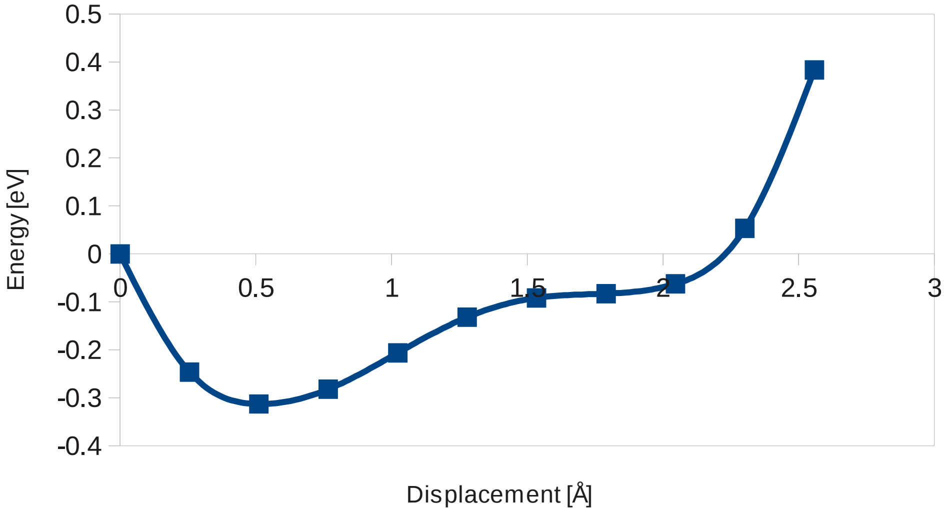


Figure 21. The energy as a fluoride ion is moved along the 1st path in fig. 20.

Figure 22 shows that the charge is almost constant as the ion is moved. A low change in charge could be another indication of a possible path.

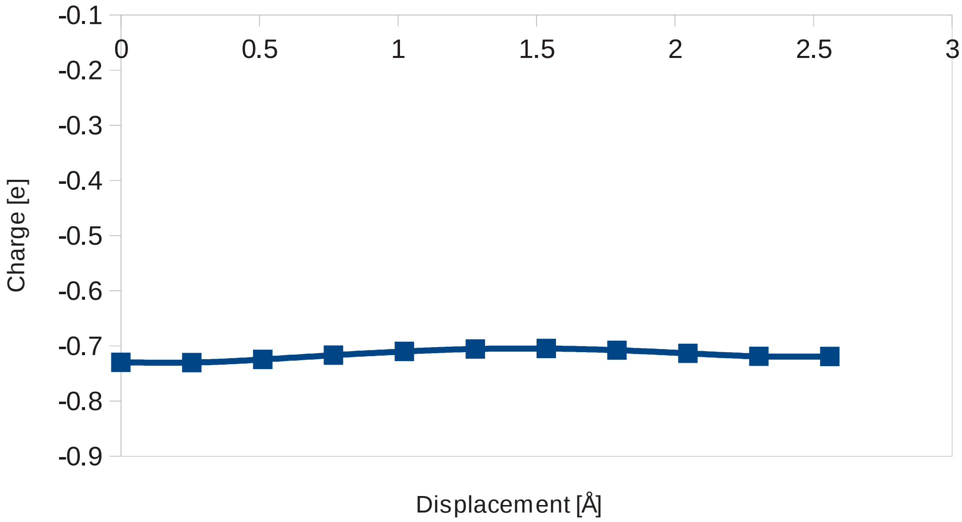


Figure 22. The charge of the fluoride ion along the corner path.

Next is moving a fluoride ion along the side of the hexagonal crystal. Fig. 23 illustrates the energy as the ion is transferred towards the vacancy in another corner, unlike in fig. 21 where it was in the same corner. Here it can be seen that the ion is easily moved in the beginning and have a clear barrier.

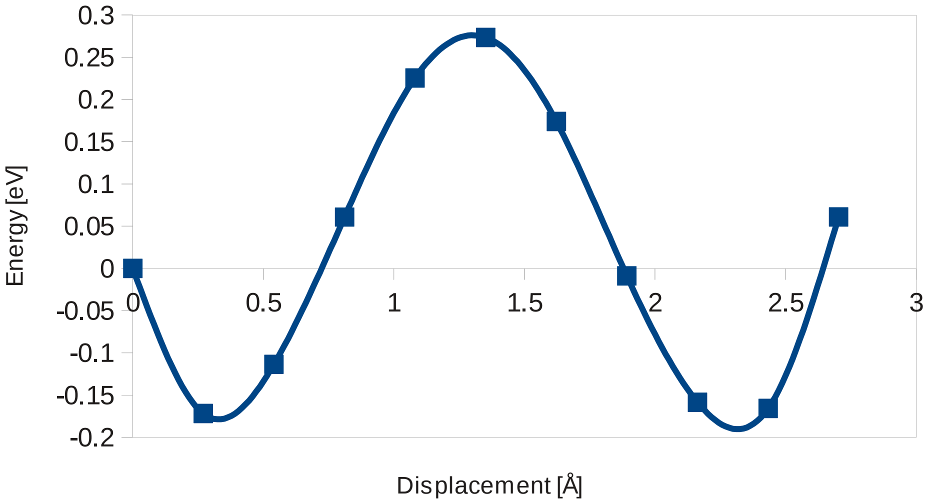


Figure 23. Energy as the fluoride ion moves along the side, the 2^{nd} path in fig. 20.

Fig. 24 shows that there is little change in the charge but it is still larger than in fig. 22.

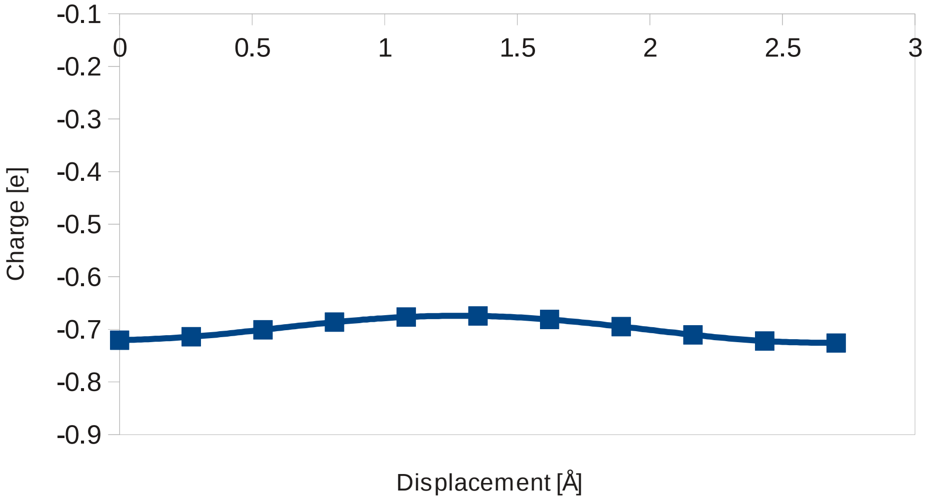


Figure 24. Charge along the side path.

Fig. 25 shows the energy as the central ion in the crystal is moved to a corner. The corner as mentioned earlier contain two fluoride ions. This deals with the lower of these positions.

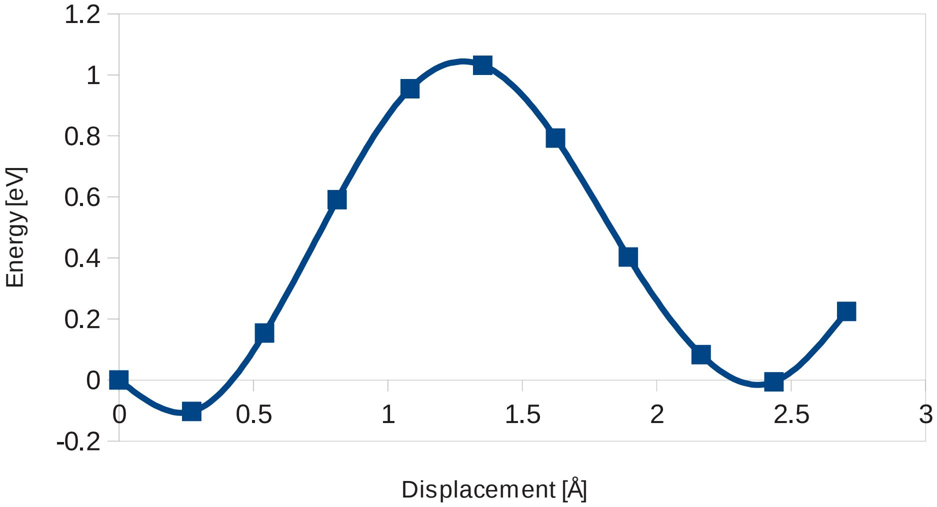


Figure 25. Center ion moving towards a lower corner vacancy, the 3rd path.

The charge in fig. 26 shows a larger change than before but it is still quite small.

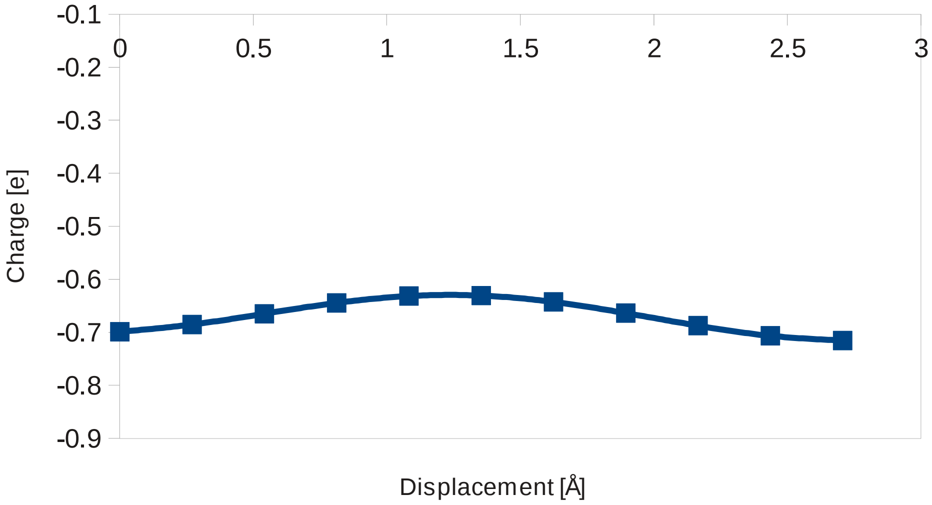


Figure 26. Charge of the central ion.

Fig. 27 is more of a complement to fig. 25. It represents the energy as another ion in the center is moved. Here it is a fluoride ion below the previous one, the 4th path in fig. 20.

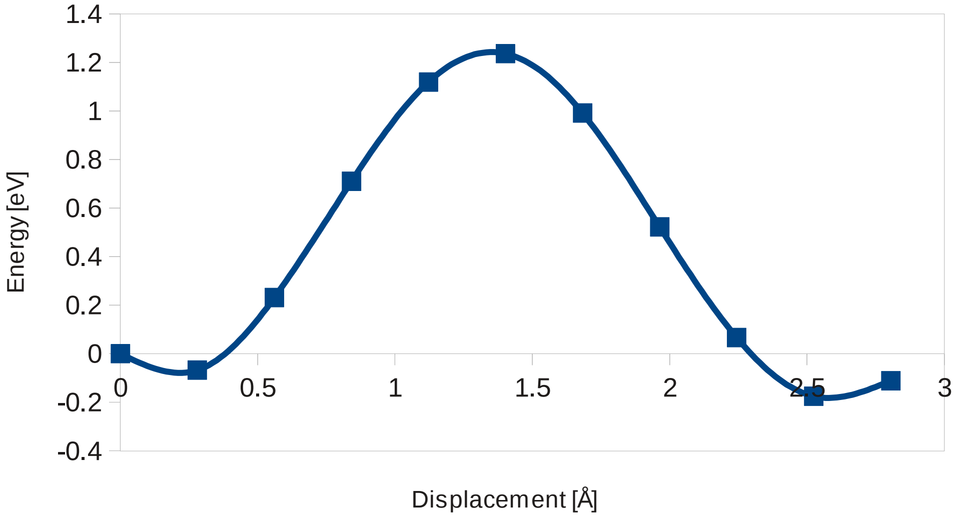


Figure 27. A lower central ion is moved to the same vacancy as in the previous path. This being the 4th path.

Fig. 28 shows little change in the charge once again.

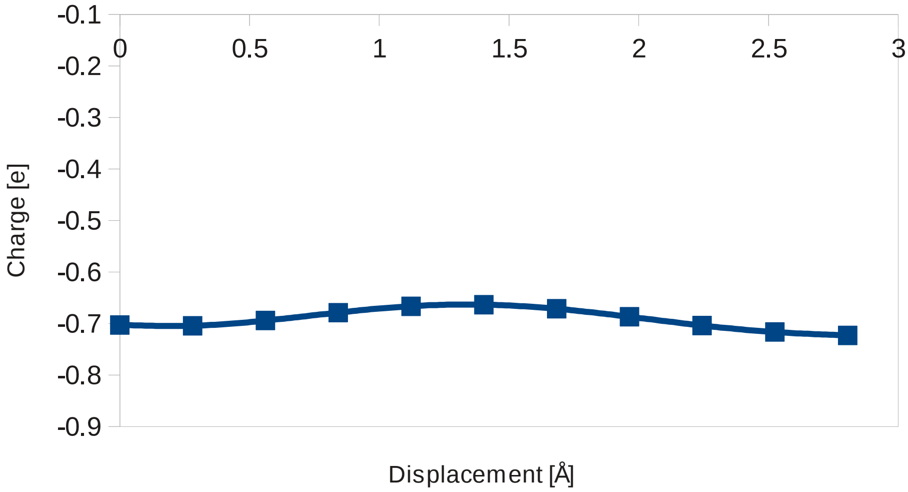


Figure 28. The charge along the 4th path.

In fig. 29 the central ion is now moved to the upper position in the corner, the 5th path.

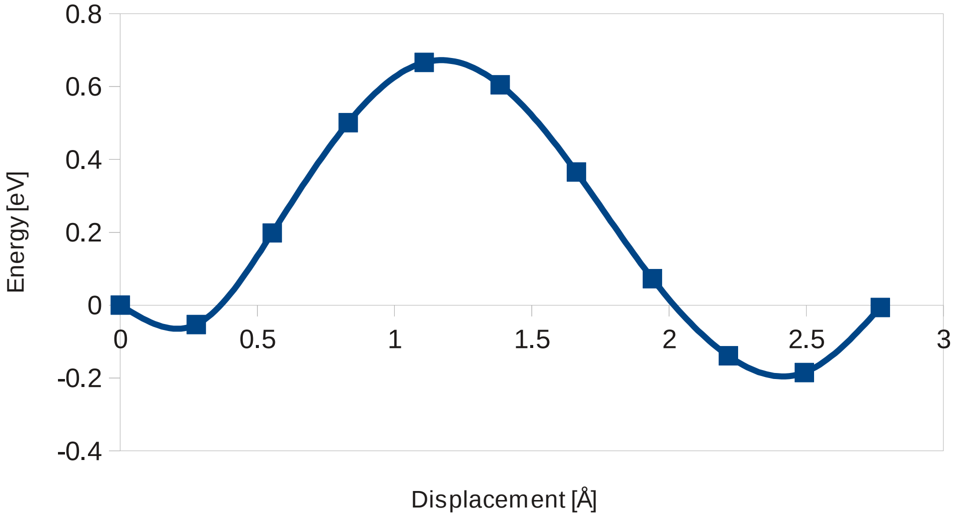


Figure 29. Central ion moved towards the corner upper position, the 5th path.

The charge is still relatively stable as the ion is moved.

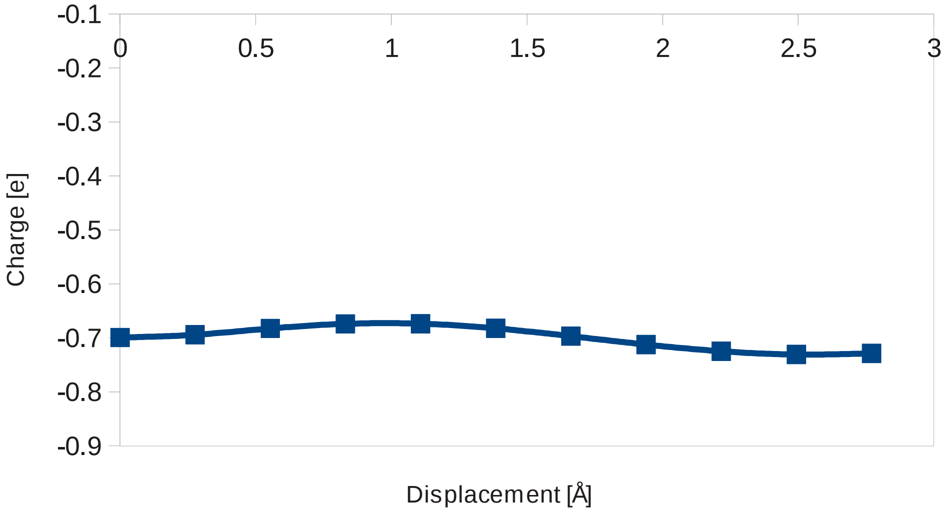


Figure 30. The charge along the 5th path.

In the 6th path, a central ion just above the previous one is moved to the same vacancy. This path brings it very close to a lanthanum ion.

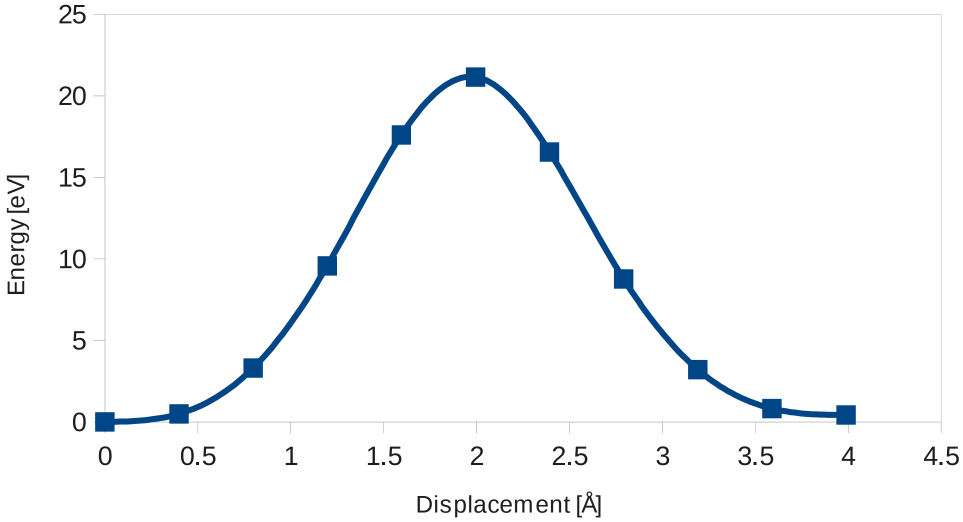


Figure 31. A central ion above the one in the previous path is moved to the same vacancy. This is now the 6th path.

The charge is now tremendously increased as the fluoride ion is moved close to the lanthanum ion.

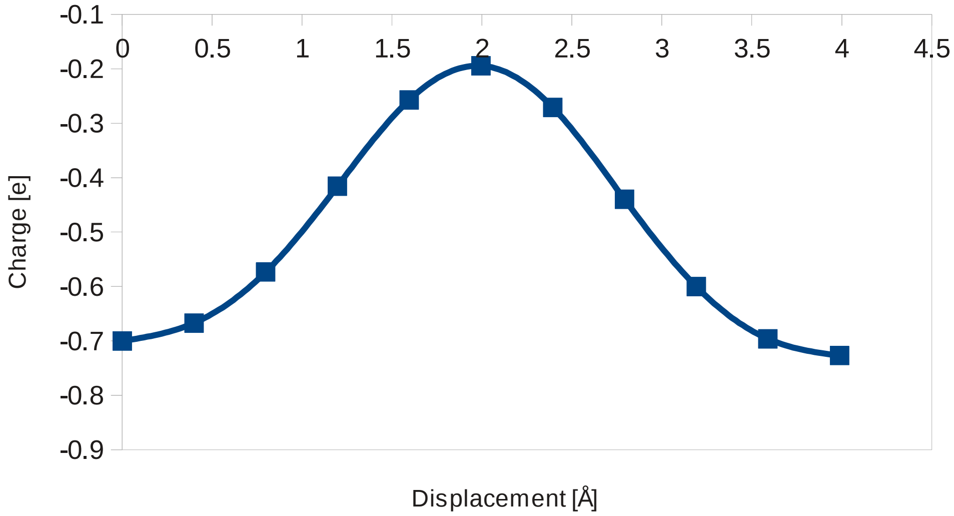


Figure 32. The charge increases as the fluoride ion approaches closely to the lanthanum ion.

The last path is when one atom in the middle of the crystal is moved downwards to a vacancy left by a lower equivalent atom.

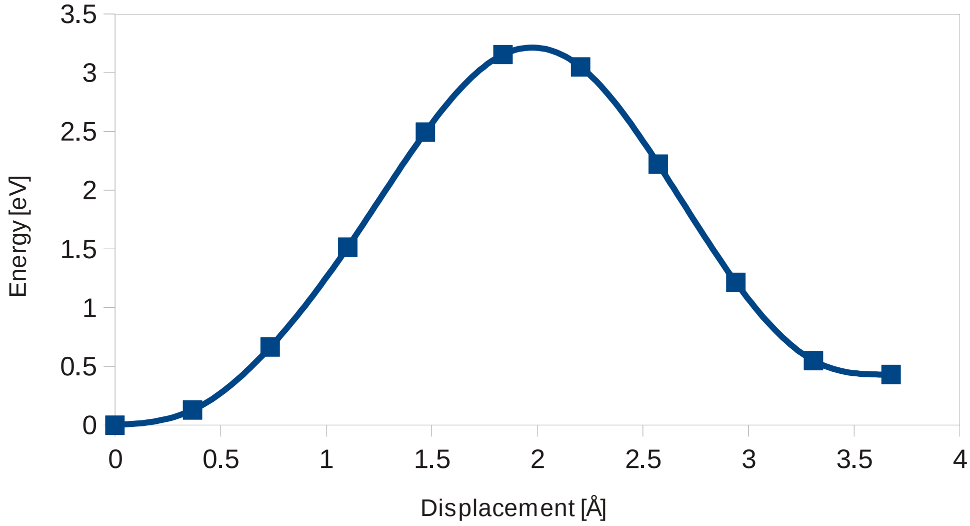


Figure 33. The center Fluoride ion is moved downward. The 7^{th} *path.*

As in the first paths the charge stays relatively unchanged again but with a slight difference in appearance.

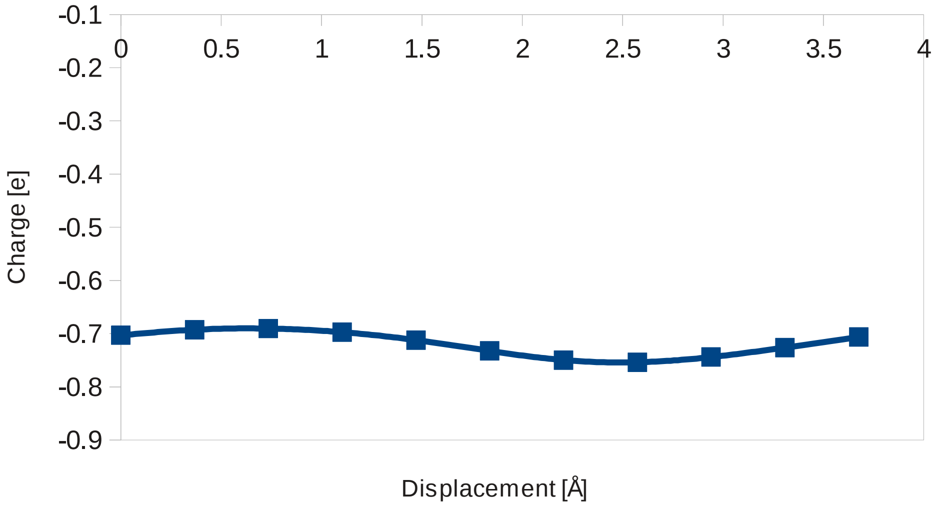


Figure 34. The charge as the center ion is moved down through the crystal.

The fluoride ion can be considered very mobile in the first and second paths. The highest value of the energy in fig. 21 is at $0.38\mathrm{eV}$ and the lowest is at $-0.31\mathrm{eV}$ so there may be a small net gain in energy. There is no clear barrier as was seen for CaF_2. However, the energy in fig. 21 would indicate that moving in the opposite direction would lead to a higher gain in energy. Since the positions would still be the same along the path the calculations are the same, it is only the order that change.

The consistency in the charge may be because the distances to the neighboring ions remains almost the same along the paths. It decreases by as little as $0.1-0.3\text{Å}$ for all paths but the 6th path where the distance decreases by 1Å .

In the calculations the paths are considered strictly linear and so the ions do not deviate from the path. The crystal itself is considered very rigid as no other ion is moved.

This is a pure hexagonal crystal that is simulated. The introduced vacancies are part of this simulation. When producing LaF_3 crystals they are commonly grown with a small amount of a dopant [17]. The dopant will introduce vacancies in the crystal and the dopant material changes the surrounding structure. This could affect the energies for the ionic conduction. Other ions in the crystal may move a little around their equilibrium as some ion moves along a path.

In the first and second path the ion can be seen as very mobile around their equilibrium position, but some mobility can be seen in the third, fourth and fifth paths. In the last path it looks quite rigid around its equilibrium point as there is no lowering in energy as there are in the first paths. Comparing the energies for each path it can be assumed that the ion may not just be moving in a straight line but could also deviate along the path.

There is a clear difference between the poor ionic conductor CaF_2 and LaF_3 in that the energies are much lower. The most likely paths here are the first path but the second path could be included. As mentioned before the paths and even the surrounding can be modified in different ways to lower the energies. Examining each path in detail can give some indication of how these paths could be modified. For example the second path have a barrier that would require an equivalent temperature of $\sim 2700^\circ C$ which is well over the melting point for LaF_3 (boiling point is unknown). Using the above assumptions the barrier could be lowered.

ZrO2, Zirconium Oxide

Introduction

ZrO2 is known as zirconia and is a good oxygen ion conductor [14]. Stabilized zirconia is used in oxygen sensors and solid oxide fuel cells (SOFC) because it allows for free movement of oxygen ions at high temperatures. This is a property that increases with temperature at low dopant concentrations. Its high ionic and low electronic conductivity makes it one of the most useful electro-ceramics [14]. Due to its very low thermal conductivity it sees uses as a thermal barrier between multiple fuel cells and coating in jet and diesel engines [4]. Zirconia go through three different phases at increasing temperature. At temperatures below $1440\,^{\circ}C$ it has a monoclinic structure. Between $1440\,^{\circ}C$ and $2640\,^{\circ}C$ it change phase to a tetragonal structure. At temperatures above $2640\,^{\circ}C$ it attains a cubic structure. The melting point is at $2715\,^{\circ}C$. The different phases can be stabilized by adding impurities such as calcium oxide or yttrium oxide at high temperatures. Cubic zirconia is commonly used as a diamond simulant due to the difficulty in visually discerning it from real diamonds. Having a hardness of 8 on Mohs scale of hardness [20] it finds uses as ceramic blades as well.

Model

The space group for cubic zirconia is $Fm\bar{3}m$, the same as for CaF_2. The same partial coordinates was used from CaF_2 but using the lattice parameter $a=5.086$ for cubic zirconia from the work of G. Jomard *et. al.* [13]. The rest was basically the same as for building and setting up paths in the calcium fluoride system.

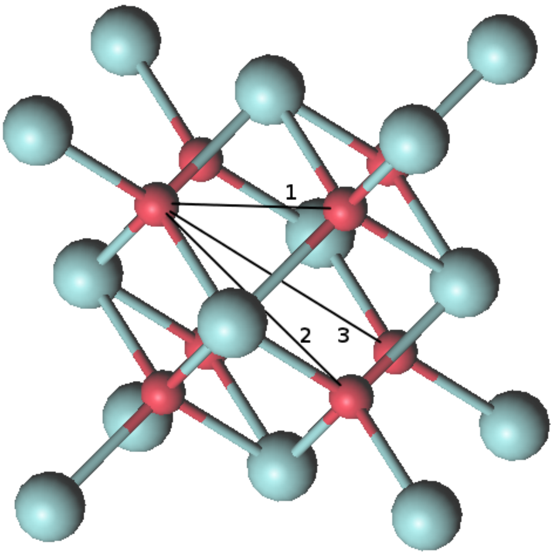


Figure 35. ZrO_2 unit crystal with the paths shown. Zr are blue and O are red.

Results and Discussion

The first graph shows the energy for the first path.

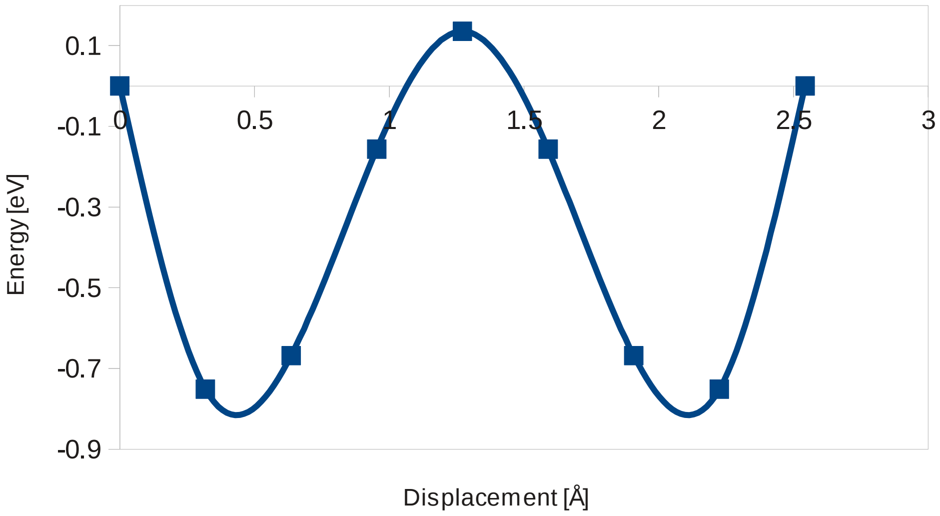


Figure 36. The first path, along the side.

The first path have the same shape as for the CaF_2 system but much lower energies. The oxygen ion can be seen as very mobile in this direction.

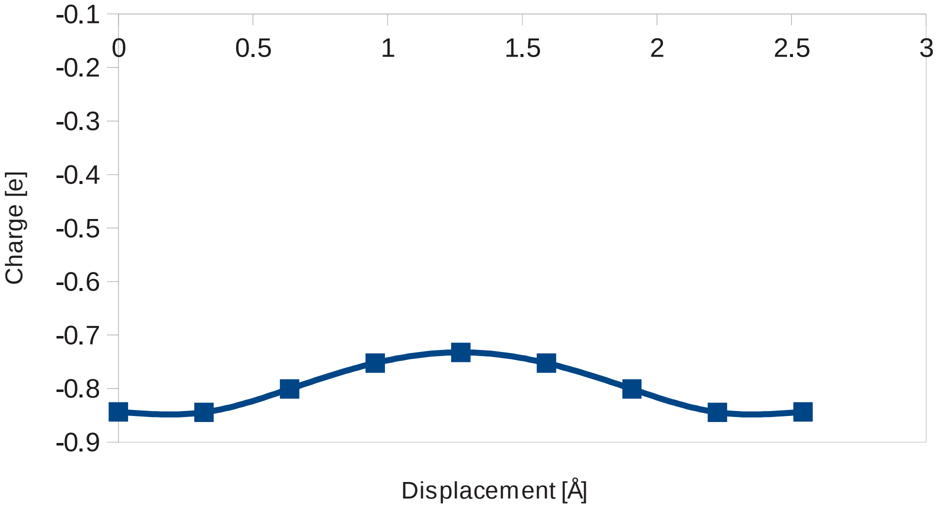


Figure 37. The charge stays relatively constant along the path.

The charge of the ion as it is moved along the path remains quite close to -1 .

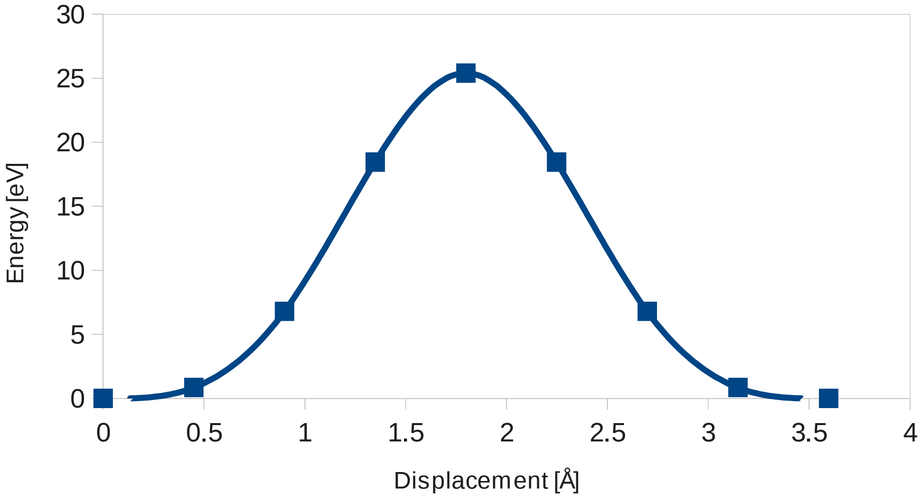


Figure 38. The energy along the second path. The energy barrier is even higher than for the CaF_2 system.

The second path has the highest barrier (fig. 38). This barrier is much higher than the one seen for the same path in the CaF_2 system.

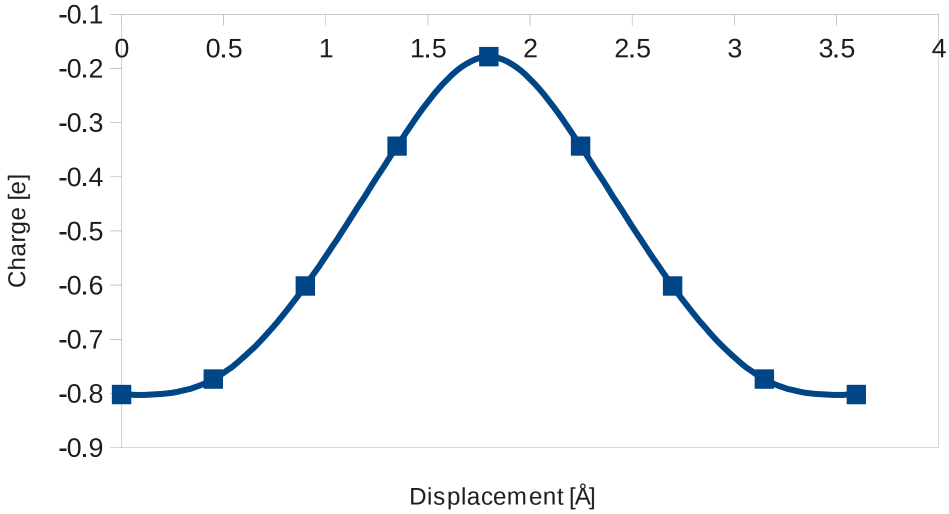


Figure 39. The charge for the second path. As it moves close to another ion the charge approaches that of a covalent bond.

The change in the charge of the oxygen ion is not the same as for CaF_2 in the same path. Here it approaches that of a covalent bond.

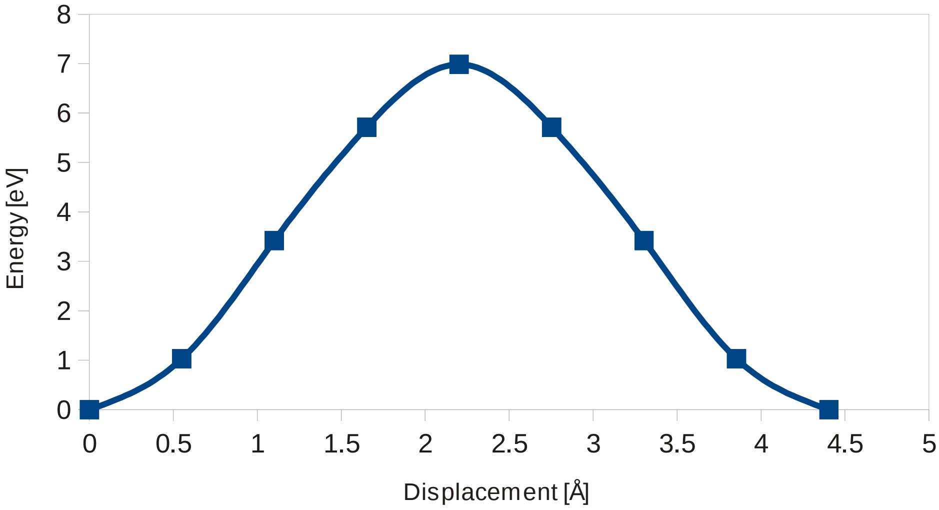


Figure 40. The energy for the path through the crystal. It is higher than for the CaF_2 system.

The path diagonally through the crystal gives a high barrier as well. The charge is relatively constant.

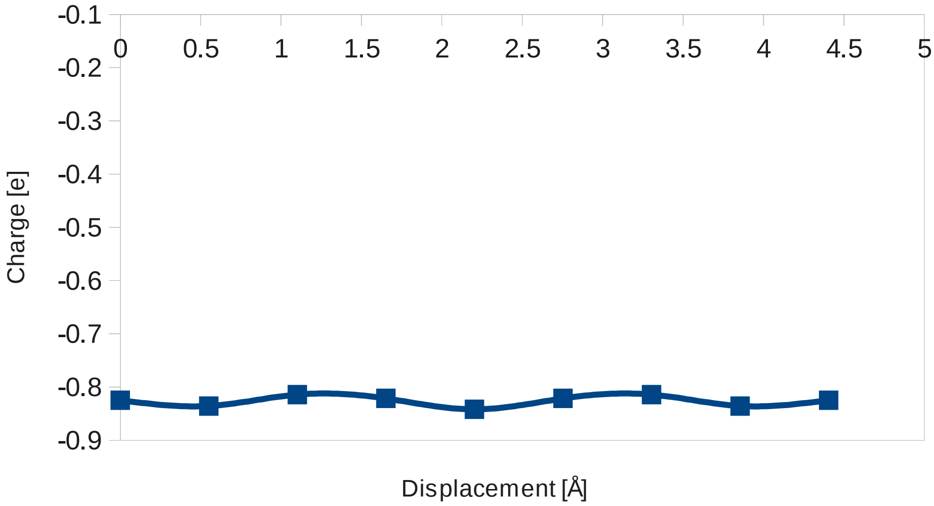


Figure 41. The charge changes very little along the path.

Figure 42 shows the energy as two oxygen ions are moved simultaneously along the first path. The same total number of atoms is retained in the model.

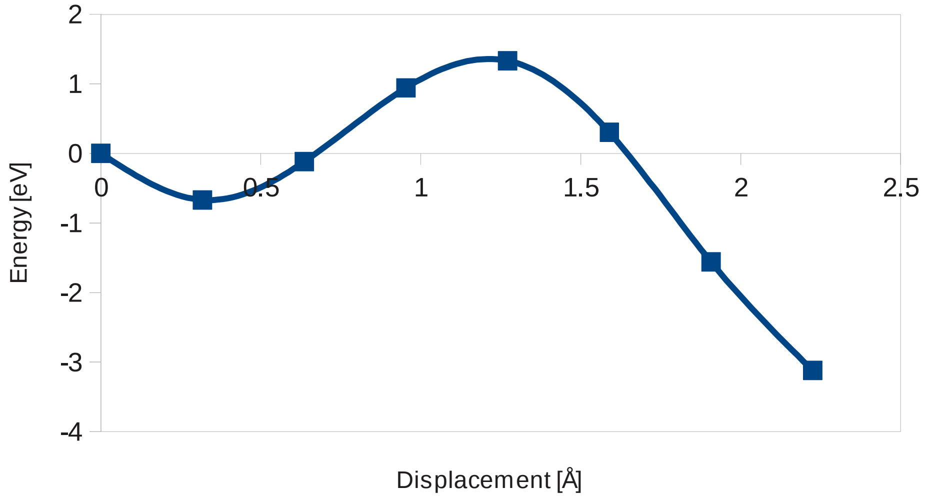


Figure 42. The energy for moving two Oxygen ions along the first path. The energy of the barrier is higher than moving a single ion.

The charges of the two ions have a big resemblance to the charge of the ion in the first path. The collapse in the end of the graphs is because one of the ions is moved outside the physical system.

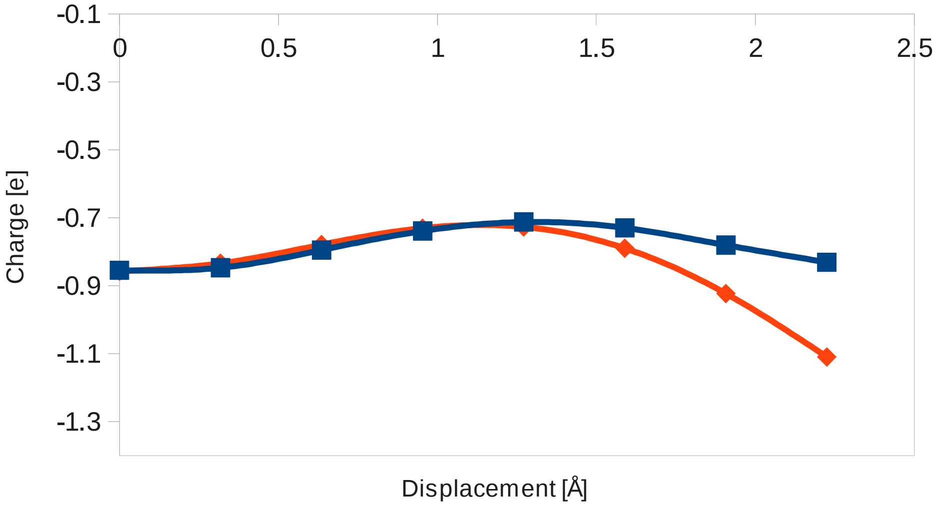


Figure 43. The charges for the two Oxygen ions retains similar values as a single ion.

The energies for the paths resemble the energies for CaF_2 in the way that the first path have the lowest barrier and the second have the highest.

The barrier represents a temperature of $\sim 1200\,^{\circ}C$, well below the melting point for ZrO_2. This is a good sign for a potential ionic conductor. The common operating temperature for zirconia solid oxide fuel cells (SOFC) is between $800-1000\,^{\circ}C$. SOFC use yttria stabilized zirconia in a cubic structure. Other material can be found in the cell components of a SOFC [18]. The added Yttrium can provide one explanation for the difference in temperature. The ionic activity reaches a maximum at concentrations of $15-18\,\%$ yttrium [12]. Another way to produce cubic zirconia is by adding CaO to pure zirconia at high temperatures [19]. This will both stabilize it and add impurities such as vacancies. This simulation is very close to that system except for there are no calcium or yttrium atoms.

When moving two oxygen ions simultaneously the energy for the barrier was increased almost ten-fold. This could mean or support the notion that the system prefer to move a single ion at a time or as a wave through instead of an entire row at the same time. The collapse in fig. 42 and 43 is because of moving one atom outside the physical crystal. The same physical size and borders was used from the system of the first path to try to keep some consistency in the calculations and to retain the small number of atoms.

The first path can be seen as the only possible path but is well enough since this path is available in all three dimensions for the crystal. In this case the theory corresponds well to practical experimentations when comparing temperatures. In this sense it can be considered a good model and it is worth expanding upon. More work could be done on the tetragonal structure and the monoclinic for comparison. Additionally dopants in the form of added yttrium and calcium can be added to compare changes in the energy of the barrier. As mentioned in the LaF_3 part the path is not necessarily straight.

Conclusions

Comparing the results from the poor ionic conductor and ionic conductor there is a distinct difference in energies of the barriers. A good first sign for a model like this. The non-conductor have a high barrier, above the melting point, and the ionic conductors have a lower barrier, well below the melting point. The more complex structure have a more or less complex barrier curve.

For lanthanum fluoride the one possible path is in the corner where there is no real barrier except for the end points. However this path is rather limited to its access to the rest of the crystal. I would like to add the second path along the edge as an additional viable ionic conduction path. The barrier is not low enough for ionic conduction but it might be low enough to have its path modified. All paths in this model are simulated as straight lines from point A to point B. In reality this may not be the case at all. By modifying the path by having it deviate somewhat towards the sides may lower the barrier just enough to have it conduct. The surrounding ions is considered to be completely immobile. By having the surrounding ions move a little away from the path could lower the barrier even further. With this lanthanum fluoride can conduct throughout the structure.

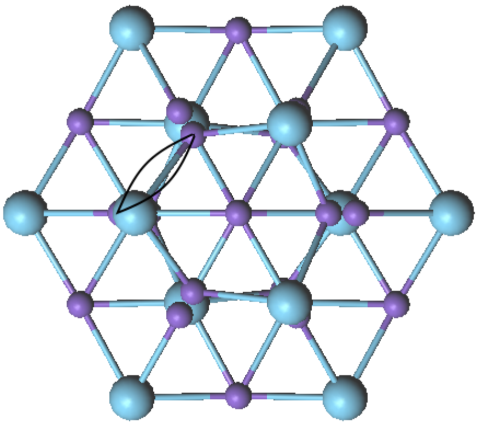


Figure 44. A small deviation from the original path might just do the trick.

Comparing the other paths they have some mobility around their equilibrium even if they have a much too high barrier. The conductive ion could move a little in those directions.

In the case of the zirconium dioxide the only possible path, based on the energy of the other two barriers, is the one along the side. However as this path traverse in all three dimensions it has complete access throughout the structure. The two other paths are quite similar to the two latter paths in the calcium fluoride system. This could mean that in a cubic system like CaF_2 and ZrO_2 the other paths are just not feasible. This may not be surprising since the ion comes very close to both same charge and opposite charge ions.

Moving two ions simultaneously did affect the barrier tremendously. Even more than predicted. The barrier increased almost ten-fold but the mobility remained largely unaffected with an increase of only $0.1\,\mathrm{eV}$.

Ionic conduction can be assumed not to be a motion of an entire row of ions simultaneously. It is most likely more of a cascade of ions moving as a vacancy appears.

One interesting notion is which structures are ionic conductors. Almost all ionic conductors, excluding organic conductors, contain transition metals or heavy atoms [1]. This could be because the electron shells are more easily disrupted by exterior forces as they are more loosely bound to the nucleus.

Future work on this model can include finding an optimal path and to allow the atoms closest to the path to relax during the transit.

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