Density Functional Theory and the Calculation of $TcMg_2O_4$ Spinel Lattice Parameters

A Senior Project
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Summary of Results

Table 1 The Results for the pure Mg and Tc crystals and $TcMg_2O_4$ Spinel.

Crystals Property	Mg		Tc		$TcMg_2O_4$	
	DFT	Experiment	DFT	Experiment	DFT	Experiment
Lattice Constant (Å)	3.2	3.21	2.78	2.74	8.6	8.498
Cohesive Energy (eV/atom)	1.47	1.51	6.72	6.85	0.6288	NA
Bulk Modulus (GPa)	34.2	35.4	264	297	146	NA

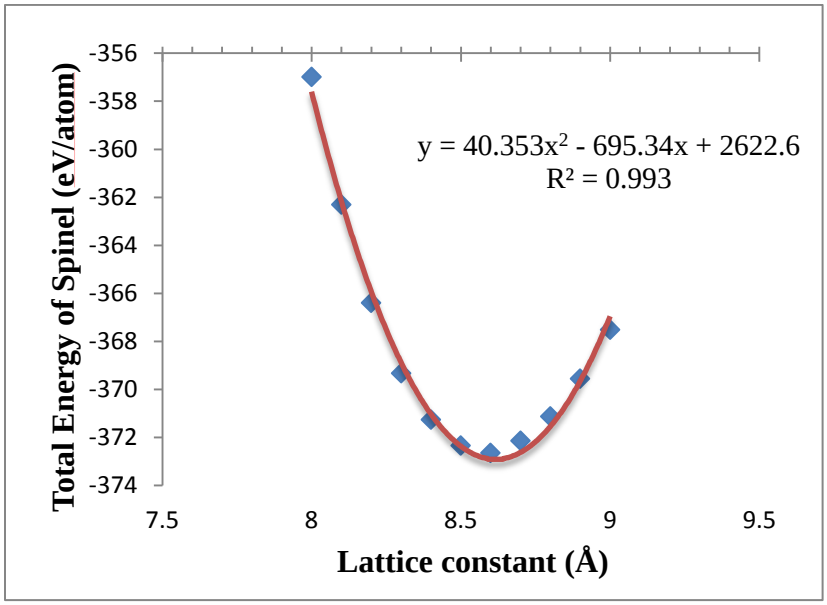

Figure 1 Shows the minimum total energy and lattice constant of the spinel calculated by DFT. These results were subsequently used to determine the cohesive energy and bulk modulus of the spinel.

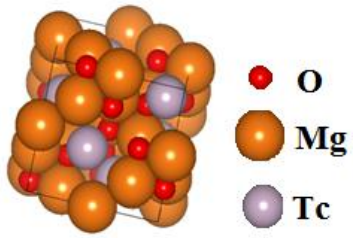

Figure 3 Shows a 3-D model of $TcMg_2O_4$ Spinel in an FCC crystal.

Introduction

Background

Nuclear energy has the potential to meet future electricity demand and provide a cleaner alternative of energy as opposed to burning coal. Burning coal produces about 4eV of energy per reaction. Nuclear reactors produce about 2.5 million times more energy per pound than coal. The problem lies in the fact that many people have lost confidence in the operation of nuclear power plants (NPP) after historical accidents such as the Chernobyl disaster and most recently the Fukushima accident.[1] However, it has been confirmed that countries with NPPs plan to continue developing their nuclear capacity in the future. First, the public must be convinced that scientists are working on ways to develop peaceful use of nuclear energy and incorporate safety, security and safeguards into NPPs.

There are two types of nuclear fuel cycles. A closed fuel cycle, represented in Figure 3, is used in France where they reprocess their waste. The uranium makes a full circle from fuel pellet to reprocessing back to another fuel pellet.[2]

Figure 3 An illustration of a closed nuclear fuel cycle.

Currently, the United States has an open fuel cycle which means all the waste generated from our NPPs will not be reprocessed and needs to be stored in some type of long term storage. Spent fuel is 96% recyclable where the last 4% of fission products would need to be put into long term storage. Figure 4 illustrates the fission products from spent nuclear fuel.

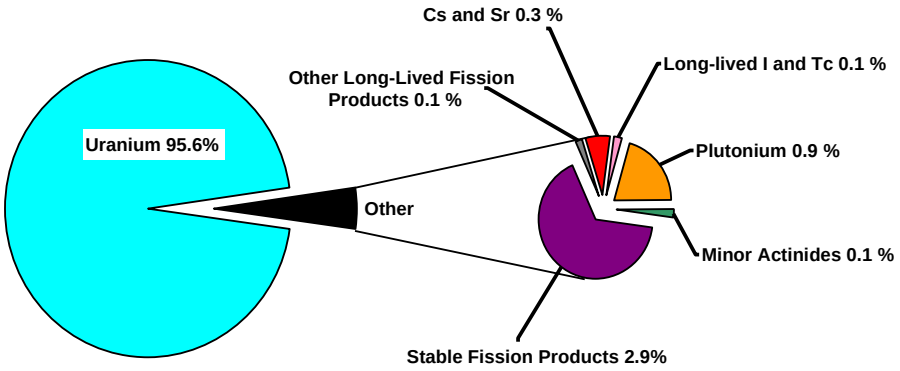

Figure 4 Radioactive fission products.

There is a small contribution from radioactive Technetium (^{99}Tc) that needs to be neutralized for long-term storage. This paper focuses on addressing one aspect of the nuclear repository phase and uses Density Functional Theory to model $TcMg_2O_4$ spinel as a potential candidate for the long-term storage of ^{99}Tc. Spinel's are attractive candidates to store the ^{99}Tc waste because they are chemically stable and physically hard which enables them to withstand degradation in the environment.[3]

Density Functional Theory

Density functional theory (DFT) has found application in many areas of science. It has been most widely used in the area of solid-state physics.[4] Technological advances, primarily in computer memory, have allowed DFT to become more powerful with additions of more accurate functionals and computation times. Even with all the improvements that have been made there are still significant errors found in the results especially when the atoms have large intermolecular interactions, for example, van der Waals

forces in gases. However, DFT has proved to be quite accurate when comparing the results to experimental data in bulk materials. The application of DFT to calculate the ground state properties of materials is highly valuable. Not only can unbiased results be determined but substantial amount of time and money can be saved by providing theoretical results without actually having to go into the lab and do the experiment.

DFT applies the laws of quantum mechanics and models the ground state electronic structure of many-body systems. The theory uses functionals to determine the properties of a system. In this case the functionals approximate the electron density of a system which greatly reduces the number of degrees of freedom when solving the Schrödinger equation. A crucial development to DFT was made by describing a "sea" of electrons in a bulk material by its density and not the many-body wave function. This means that the variable of the system is reduced to the three spatial coordinates x, y, and z, for example, instead of the 3N degrees of freedom.[5][6] There are many types of functionals that exist and corrections or approximations that make the calculations better but the main idea is that it can never be perfect and it only maps an approximate density to the real density so that we can ultimately find the correct energy.

The ground state energy of the atoms in a crystal can be found by solving, in this case, the time-independent Schrödinger equation. This analysis uses the time-independent non-relativistic version known as the Born-Oppenheimer approximation shown below.

$$\widehat{H}\Psi(\vec{r}_N) = E\Psi(\vec{r}_N) \quad [1]$$

The Hamiltonian $\widehat{H}$ in equation 1 consists of a sum of three terms: the kinetic energy, the interaction with the external potential, and the electron-electron interaction and are shown in equation 2.

$$\widehat{H} = -\frac{1}{2}\sum_i^N \nabla_i^2 + V_{ext} + \sum_{i<j}^N \frac{1}{|r_i + r_j|} \quad [2]$$

The Schrödinger equation is solved for a set of anti-symmetric wavefunctions. Once the lowest energy eigenvalue is determined you have obtained the ground state energy of the system. It is important to

understand that DFT is highly dependent on approximations to exchange correlation interaction. The ground state wave function and energy may be found by searching all possible wavefunctions for the one that minimizes the total energy. From this, many properties of a material can be determined.

The lattice constant of a crystal structure is one property that can be determined using DFT. It can be found by the corresponding minimum total energy in a plot of the total energy versus the various lattice constants of the atom or molecule under investigation. Also, by plotting the energy versus volume of the crystal lattice to create a best fit line gives an equation whose second derivative is proportional to the bulk modulus of the system, as shown in the equation 3. The bulk modulus is a compounds resistance to compression.

$$B_o = V\frac{d^2E}{dV^2} \quad [3]$$

Another structural property that can be determined is the cohesive energy. The cohesive energy of the molecule is the energy required to break the atoms in a crystal apart into their isolated components. This parameter can be found by calculating the total energy of an isolated atom and then subtracting the total energy of the solid crystal from the energy of the isolated atom as shown in equation 4,

$$E_{cohesive} = (n)(E_{isolated\ atom}) - E_{solid\ crystal} \quad [4]$$

where *n* is the total number of atoms in the crystal.

VASP

Calculating the total energy of the crystal under investigation means solving the Schrödinger equation, which is no easy task. This requires many computations which can take up to several hours even by a supercomputer. In order to compute this total minimum energy a highly sophisticated program, whose foundation is based on DFT, is utilized for accurate and fast results. The program approaches solving the Schrödinger equation by simulated quantum mechanical molecular dynamics. It uses first principles, that is *ab initio,* and hence is named the Vienna *ab initio* simulation package (VASP). The

approach is based on the local density approximation (LDA) which simplifies the many-body problem by approximations to the exchange-correlation energy functional in DFT. The local density approximation locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density.[2] While this approach overestimates some constants it is successful in many ground state properties such as the lattice constant, and bulk moduli. The operating system used by VASP is Linux which makes running the program fairly easy and quick to learn even for beginners.[7] A simplified road-map of the actions VASP performs begins by solving the time-independent Schrödinger equation. The complete wavefunction, probability density and total energy are then known. If the change in total energy is not less than 10^{-6} eV then the potential is reconstructed and the process is done again until the change in energy is less than 10^{-6} eV. From there, the total energy and vectors, that is the position of the atoms, are used to calculate the force between atoms and once this change in force is less than 10^{-3} eV/Å the calculations stop. The reason we want to minimize the force is to get the minimum total energy of the crystal structure, thus, giving the molecules ground state conformation. The basic method VASP uses is DFT. The complete wavefunction is given as a linear combination of basis wavefunctions or the known set of wavefunctions to begin the process. The total wavefunctions linear combination of wavefunctions have coefficients that give the contribution of each basis wavefunction.[5][6][7]

All of the physical parameters can be calculated if the relevant electronic ground states are known. VASP can compute the ground state wavefunction and energy by searching all possible wavefunctions for the one that minimizes the total energy. Once this has been done, other modeling programs such as VESTA, for example, can be used to create 3-D images of what the crystal structure might look like.

The potential of DFT is highly valuable. A lot of time and money can be saved by simulating the crystal structure of unknown compounds using VASP. Many structural properties can be determined without ever actually having to step into the lab. Of course, the program is not perfect but the accuracy of

the results can be used as a starting place for an experiment and then compared to observation. This incredible theory has been utilized in the nuclear fuel cycle by exploring various spinel's for long-term storage of ^{99}Tc. Exploring the possible technetium containing spinel's that are most energetically favorable, or most stable, efficient to make and cost productive would be an invaluable contribution to nuclear energy research. The radioactive ^{99}Tc can be safely stored in a repository for a long time and bring peace-of-mind to the public.

Instrumentation

A supercomputer running 12 processors was used to perform calculations using the *ab initio* simulation package (VASP). The interaction between ions and electrons is described by the ultra-soft Vanderbilt pseudopotentials (US-PP). The approach taken by VASP is based on the local density approximation (LDA). A kinetic-energy cutoff of 400 eV is chosen for the plane wave basis set. The k-point coordinates were set at 5x5x5 to create the k-point grid for the Tc and Mg crystals and $TcMg_2O_4$ spinel.

Before the calculations could be performed some basic programming skills were developed in Linux. Basic commands such as copying and transferring files, changing directories, logging in and out of the server, and various scripts were written and used to setup or modify the files prior to running the individual jobs. The four primary files modified were the POSCAR, INCAR, POTCAR, and KPOINTS files.

The POSCAR file contained the information for the lattice cell shape and size as well as initial atom positions including the primitive and basis vectors. The POTCAR file contained information of the potentials for each atom used. The INCAR file contained the algorithm choices and parameters and the KPOINTS file contained the information for the integration grid over k-space.

Once these four main files had been modified for each of the crystal structures under investigation they were copied into 10 different files with 10 different lattice constants. The lattice

constant was changed in increments of 1/10 on each side of the observed experimental value. The POSCAR file was changed accordingly in order to obtain data to create a symmetric plot. Literature was used to find experimental results for the lattice constant observed. VASP then calculated the total energy of the crystal which would be used for subsequent calculation of the bulk modulus and cohesive energy or the crystal structure. Ten jobs each were run for the Mg and Tc crystals and the $TcMg_2O_4$ spinel.

Results

Magnesium Crystal

A plot of the total energy versus lattice constant of the Mg crystal structure was used to determine the minimum total energy of the crystal. VASP was used to compute the total energy of the crystal at various lattice constants. The lattice constant with the minimum total energy was determined to be the crystals theoretical lattice constant using DFT. The data used to create the plot, shown in Figure 5, can be found in Table A1 in the Appendix.

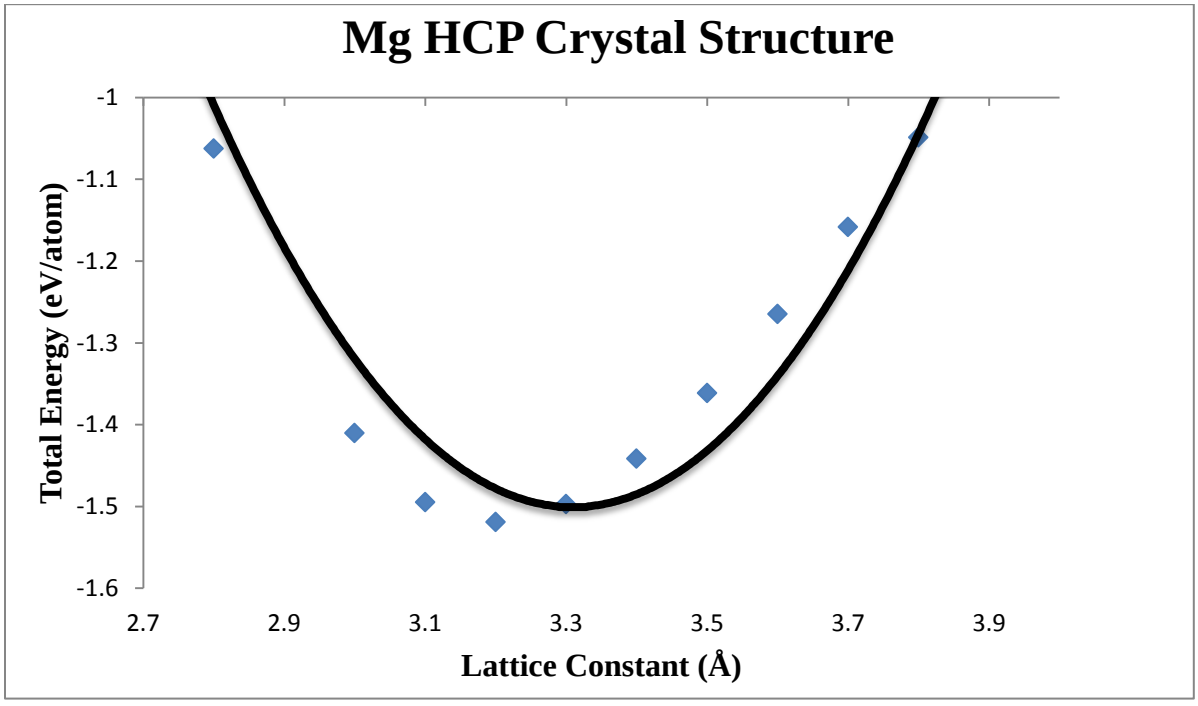

Figure 5 The total energy of the Mg crystal calculated for 10 different lattice constants. The plot was used to determine the theoretical value of the lattice constant.

The literature value for the lattice constant is observed to be about 3.21 Å. [8][9] Using the approximations (LDA) implemented in VASP, DFT calculated this value to be 3.2 Å. This is in excellent agreement with the experimentally observed value corresponding to a difference of less than 1%. Table 2 shows the results calculated from DFT compared to those observed experimentally.

Table 2 Results of DFT Compared to Experimental Observation for the Mg Crystal.

Parameter	DFT	Experimental*	Relative Error (%)
Lattice Constant (Å)	3.2	3.21	< 1
Total Energy (eV/atom)	1.52	1.47	3
* See Reference 8			

Once the lattice constant was determined the volume of the crystal lattice was calculated and plotted against the total energy of the crystal structure, shown in Figure 6. A second order polynomial was fit through the data points and the first coefficient of this quadratic was used to calculate the bulk modulus using equation 5.

$$B_o = V\frac{d^2E}{dV^2} \qquad [5]$$

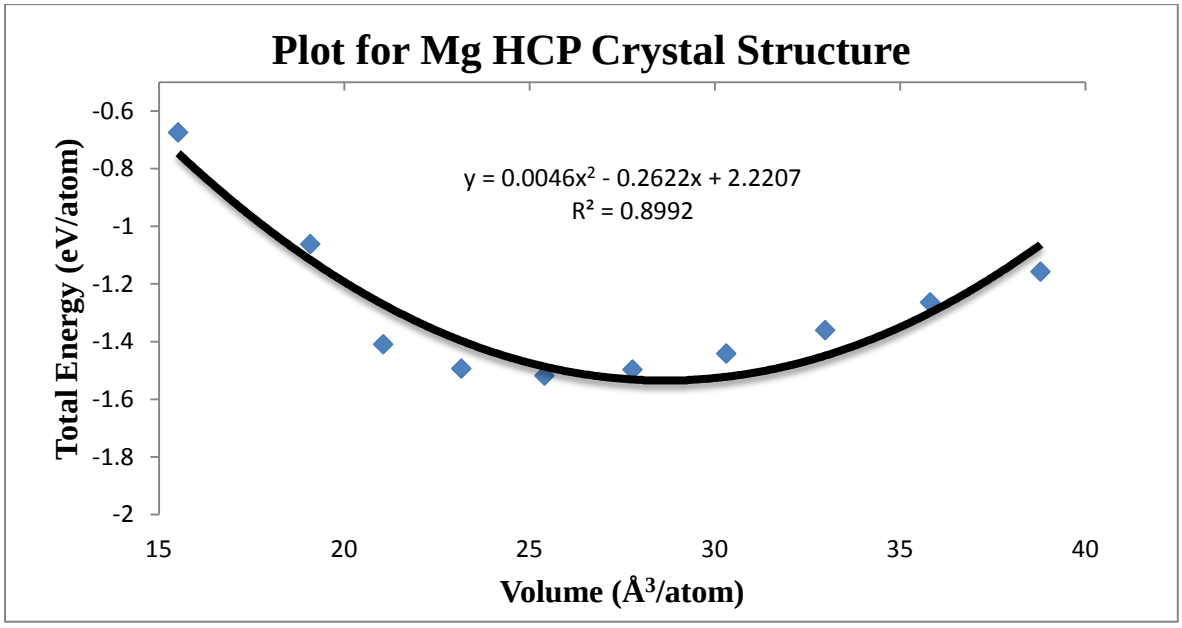

Figure 6 Shows the volume of the Mg crystal plotted against the total energy of the lattice. The highest order coefficient of the equation through the data was used to calculate the bulk modulus.

Using equation 5 the bulk modulus was determined to be,

$$B_o = V\frac{d^2E}{dV^2} = (2\ atoms)(23.17\ Å^3/atom)(0.0046\ eV/Å^6)(160.2\ GPa/eV/Å^3) = \mathbf{34.2\ GPa}$$

The values used in this calculation come from the following: the data used to create the plot, shown in Table A1 in the Appendix, in Figure 6 (*23.17 Å^3/atom*), the highest order coefficient from the best fit line (*0.0046 eV/Å^6*), and the last term is a conversion factor into GPa (*160.2 GPa/eV/Å^3*). The theoretical value calculated using DFT was 34.2 GPa, this is in excellent agreement with the experimentally observed value of 35.4 GPa.[3] corresponding to a difference of about 3%.

The cohesive energy was also calculated. The energy of the isolated magnesium atom first had to be calculated and then subtracted from the energy of the solid crystal. Equation 6 was used to determine the cohesive energy as,

$$E_{cohesive} = (n)(E_{isolated}\ atom) - E_{solid\ crystal} = (2\ atom)(-0.02664\ eV) - (-3.2\ eV)/2\ atom = \mathbf{1.55\ eV/atom} \quad [6]$$

where *n* is the number of atoms in the lattice, for magnesium this is two. The value for the energy of the isolated atom was provided by previous work on Mg crystal. The energy of the solid crystal was that calculated by VASP earlier. Using Equation 6 the cohesive energy for the HCP crystal structure of magnesium was calculated to be 1.55 eV/atom. The experimentally observed value is 1.51 eV/atom.[3] This corresponds to a difference of less than 3%.

Technetium Crystal

The total energy for the crystal lattice of technetium was also calculated using various lattice constants. The lattice constant was determined to be 2.78 Å. The value observed experimentally is said to be 2.74 Å [3]. This corresponds to a difference of about 1%. Again, excellent agreement was found between the results calculated by DFT and experimental observation. The data used to create the plot in Figure 7 can be found in Table A2 in the Appendix.

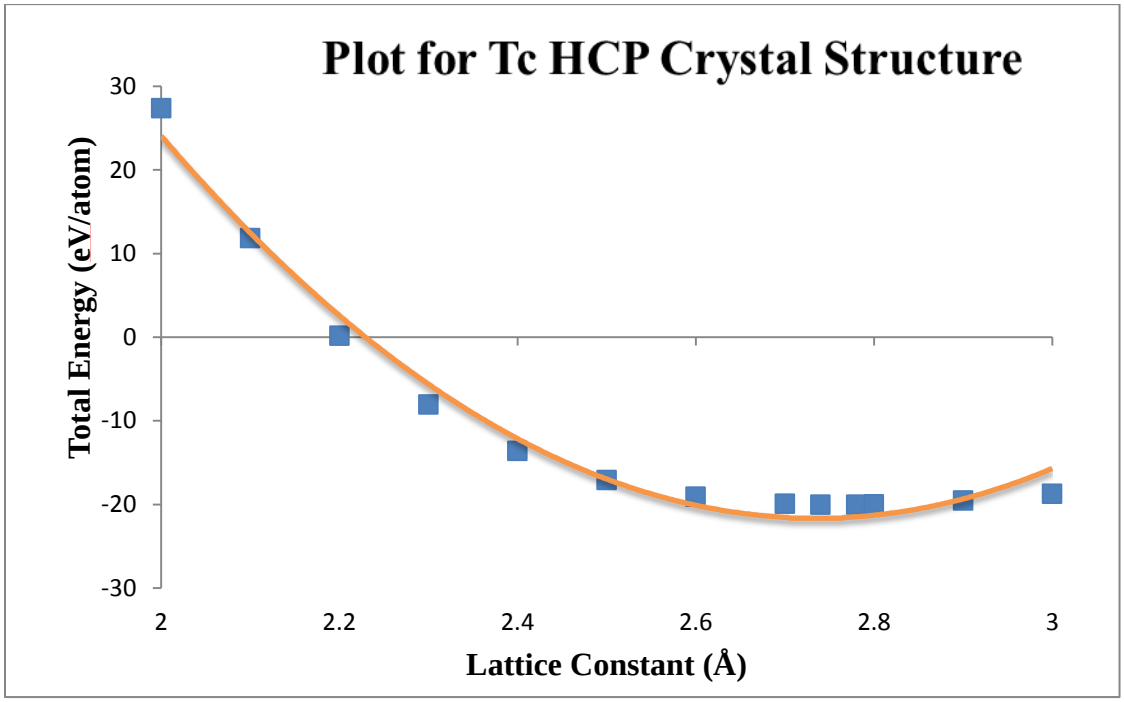

Figure 7 The total energy of the Tc crystal structure was calculated for 13 different lattice constants and the minimum value in the plot was determined to be the theoretical value for the lattice constant.

The volume of the crystal lattice at various lattice constants was calculated and plotted against the total energy to determine the bulk modulus. The data used to create the plot in Figure 8 can be found in Table A2 in the Appendix. Figure 8 shows the relationship between the volume of the Tc crystal and the total energy. Using Equation 3 the bulk modulus was determined to be 264 GPa. The experimental value is observed to be 297 GPa. This gives an error of about 11%.

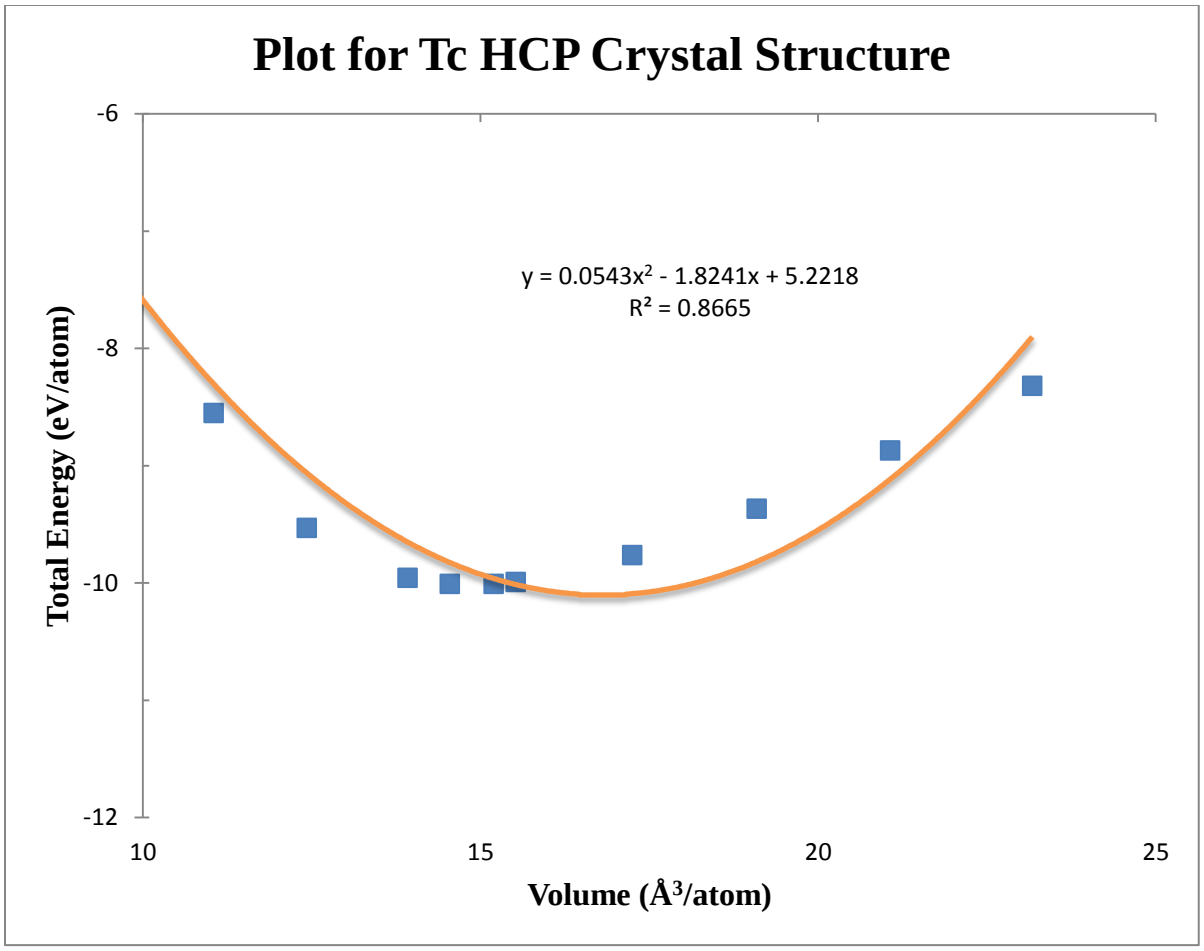

Figure 8 The volume versus total energy of the crystal structure was used to determine the bulk modulus for Technetium.

It is worth mentioning that the large discrepancy between the results from DFT and those experimentally observed is due to human error. When modifying the POSCAR file that contains the lattice cell shape, size and initial atom positions I made an incorrect assumption that the c/a ratio (lattice constant/height) was the same for all elements. Ideally, the c/a ratio should be 1.633 so this is the number I used for both the Mg and Tc crystals. However, in reality each element has its own respective c/a ratio. Most importantly, the c/a ratio was input correctly for the $TcMg_2O_4$ Spinel which gave excellent results as you will soon see.

The cohesive energy for technetium was calculated using equation 4. Its value was determined to be 6.72 eV/atom. The experimental value is observed to be 6.85 eV/atom [8]. This corresponds to a difference of less than 2%. Once again DFT has proved to be exceptionally accurate. Table 3 summarizes all the calculated parameters for the Tc crystal.

Table 3 Results of DFT Compared to Experimental Observation for the Tc Crystal.

Parameter	DFT	Experimental*	Difference (%)
Lattice Constant (Å)	2.78	2.74	1
Cohesive Energy (eV/atom)	6.72	6.85	2
Bulk Modulus (GPa)	264	297	11
* See Reference 8			

$TcMg_2O_4$ Spinel

Now that the energy for the isolated atoms of Technetium and Magnesium have been calculated, analysis of the $TcMg_2O_4$ spinel was done. The same method was repeated for determining the lattice constant of the Spinel. Using DFT the value was calculated as 8.6 Å. The experimental value is observed to be 8.498 Å.[3] This is in excellent agreement with a difference of less than 2%. The graph of the total energy versus lattice constant of the spinel is shown in Figure 9. The data used to create this plot can be found in Table A5 in the Appendix. This specific type of Spinel was a novel candidate for storing the Tc^{99} waste and as such we knew that comparison of the results from DFT to experimental observation would be limited. Nonetheless, the calculations were performed with the intentions of guiding future experimental synthesis.

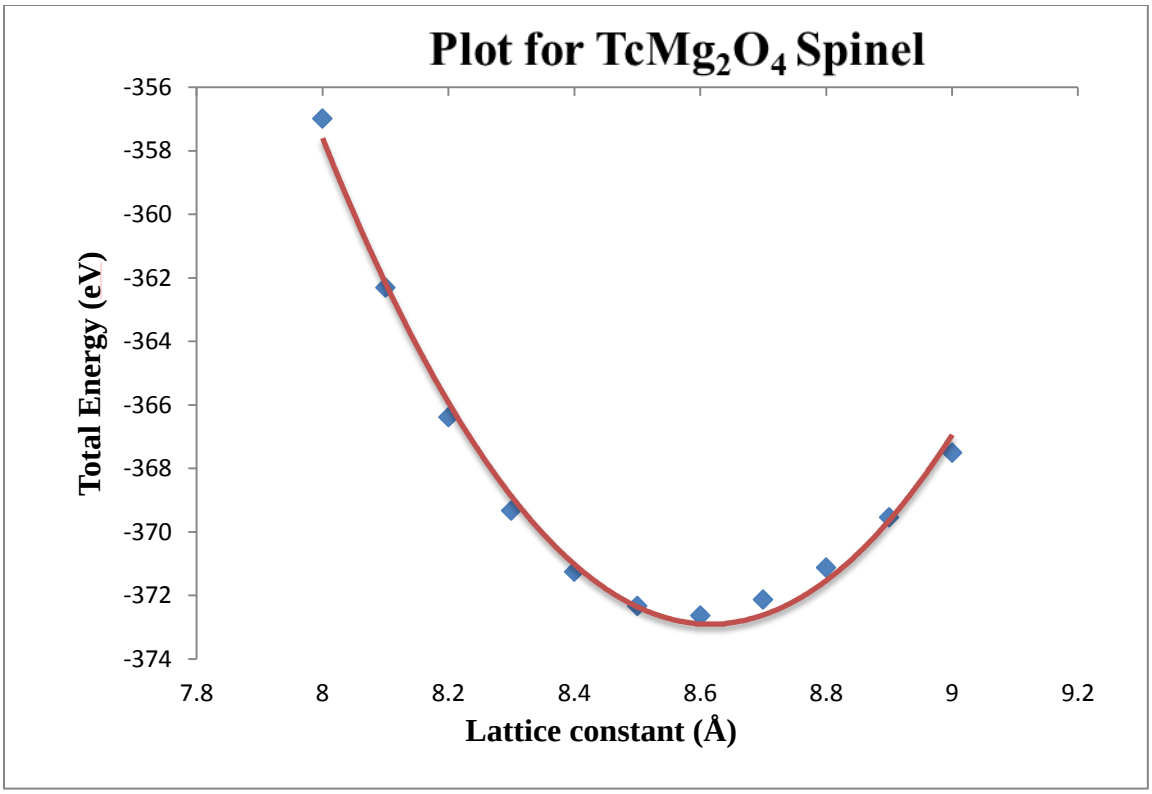

Figure 9 The total energy of the Tc crystal structure was calculated for 11 different lattice constants and was plotted to determine the theoretical value for the lattice constant.

A plot of the volume versus total energy of the spinel was created to determine the bulk modulus. The plot is shown in Figure 10 below. The data used to create this plot can be found in Table A6 in the Appendix. Using Equation 3, the bulk modulus was calculated as 146 GPa. The cohesive energy was also calculated, however, a slight modification was made to the original equation for the cohesive energy to account for the different constituents of the spinel (i.e. Technetium Magnesium and Oxygen). The equation used to calculate the bulk modulus of the spinel is given as,

$$E_{cohesive\ spinel} = [\, n_{Tc}E_{Tc\ crystal} + n_{Mg}E_{Mg\ crystal} + n_{O}E_{O\ crystal}\,] - E_{solid\ spinel\ crystal} \qquad [7]$$

$$= \frac{[\,(4\ atom)(-3.2\ eV/atom) + (8\ atom)(-22.24\ eV/atom) + (16\ atom)(10.32\ eV/atom)\,] - (-372.64\ eV)}{56\ atoms}$$

$$= +\ 0.3\ \text{eV/atom}$$

where n_{Tc} is the number of Tc atoms, n_{Mg} is the number of Mg atoms, and n_O is the number of oxygen atoms 4, 8, and 16 respectively. There are a total of 56 atoms within the crystal lattice. The values in this equation come from previous values calculated earlier for Mg (3.2 eV/atom), Tc (22.24 ev/atom ÷ 8 = 2.78 ev/atom), and the energy for the oxygen atom was provided to me due to lack of time (10.32 eV/atom). The minimum total energy (-372.64 ev/atom) comes from the theoretically determined lattice constant shown from the data in Table A3 in the Appendix. Using Equation 7 the cohesive energy was calculated to be 0.3 eV/atom. The most significant result in this part of the experiment was the result of the cohesive energy. A positive value of 0.3 eV/atom not only indicates that the synthesis is experimentally possible but also that it is energetically favorable. This is because the total energy of the bulk crystal is greater than the total energy for the isolated components of the spinel. Although, these calculated properties could not be compared to any experimental observations they can be used as a guide line to future synthesis. The results of the Spinel are summarized in Table 4.

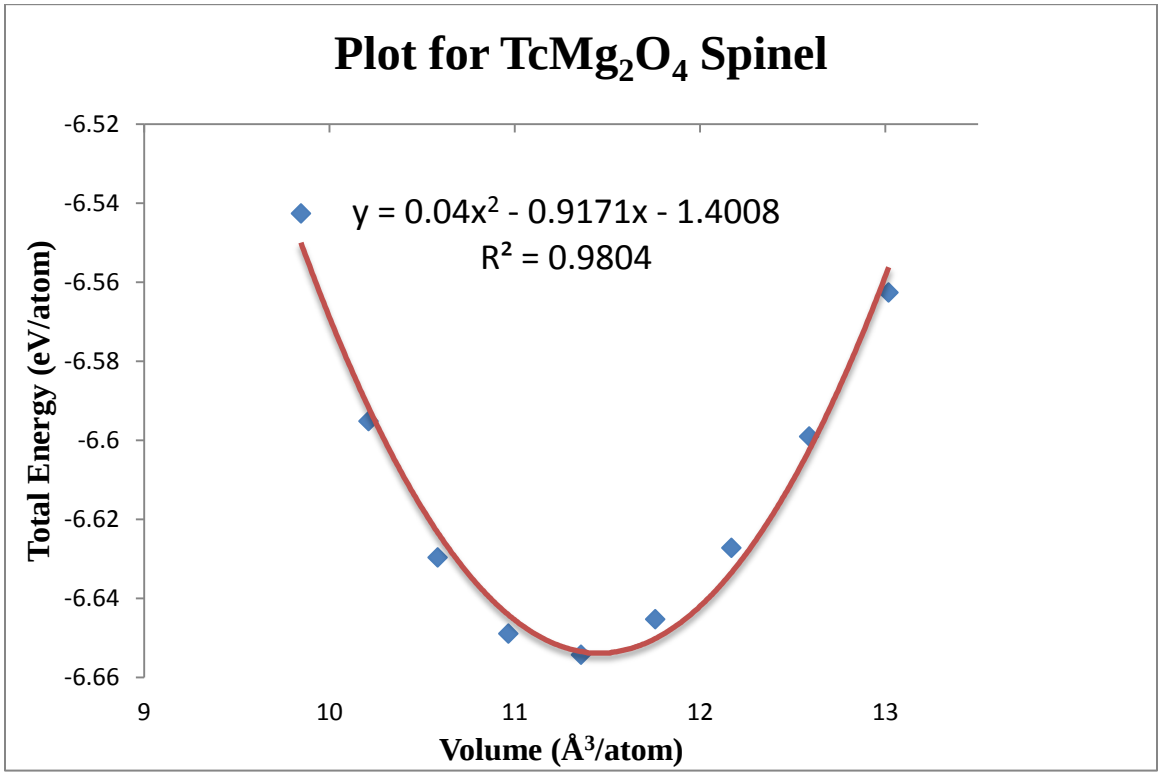

Figure 10 Shows the volume versus total energy of the crystal structure that was used to determine the bulk modulus for $TcMg_2O_4$ spinel.

Table 4 Results of DFT Compared to Experimental Observation for the $TcMg_2O_4$ Spinel.

Results	DFT	Experimental*	Difference (%)
Lattice Constant (Å)	8.6	8.498	1
Total Energy (eV/atom)	0.3	NA	-
Bulk Modulus (GPa)	146	NA	-
* See Reference 8			

Conclusion

Discussion

A summary of all the results for each of the pure Mg and Tc crystals as well as the $TcMg_2O_4$ Spinel are shown in Table 5. Where there was literature available, it was found that DFT and experimental observation were in excellent agreement; especially in determining the lattice constant. The relative error in all cases was less than 2%. There was a larger discrepancy between theory and experimental observation in the bulk modulus of Tc. This is because of human error. When I modified the POSCAR file I did not input one of the primitive vectors correctly. Specifically, the c/a ratio was not correct. Ideally the c/a ratio is about 1.63 for an HCP crystal structure. However, I realized that each element actually varies slightly form this value and for Tc it's closer to 1.603. This was significant enough to throw off the calculated value and an error of about 11% was found between DFT and experimental observation.

Table 5 Summary of the Physical Properties for Mg and Tc Crystals and $TcMg_2O_4$ Spinel.

Crystals Property	Mg		Tc		$TcMg_2O_4$	
	DFT	**Experiment**	**DFT**	**Experiment**	**DFT**	**Experiment**
Lattice Constant (Å)	3.2	3.21	2.78	2.74	8.6	8.498
Cohesive Energy (eV/atom)	1.55	1.51	6.72	6.85	0.3	NA
Bulk Modulus (GPa)	34.2	35.4	264	297	146	NA

The results proved that DFT can be used to predict properties of systems that have not been synthesized, as well as guide future synthesis. Also, the fact that this spinel has a positive cohesive energy indicates this specific spinel is a promising candidate as it is energetically favorable. If synthesized, the spinel will be hold together as a stable complex.

The results for the lattice constant of $TcMg_2O_4$ spinel were in excellent agreement with XRD data by Muller et al.[3] Depending on the results from alternative technetium spinel's, such as the inverse spinel, the one that provides the greatest binding energy, least amount of time and money to make will be the best candidate for providing a habitable environment for the ^{99}Tc nuclear waste.

Future Work

As always, there is more work to be done. In the future, calculations of the inverse spinel may be explored. It might be possible that technetium is more likely to occupy octahedral sites within the crystal lattice which suggests the inverse spinel as an alternate, more favorable, form. The normal spinel has Tc in tetrahedral sites of the crystal lattice. It might benefit to examine Tc oxides as well. For example, a perovskite mineral with the general stoichiometry ABO_3. The x-ray diffraction analysis can be observed via VESTA to help guide the synthesis. One could also explore simulations of metallic Tc alloys such as a Tc-Ni binary system or a Tc-Ni-Mo tertiary system. Overall, DFT proves to be a rigorous theoretical framework for investigating future materials yet to be synthesized. Through this theory it is only a matter of time before a habitable environment will be synthesized to store ^{99}Tc safely for a long time without any hazardous concern.

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References

[1] M. Kroenin, D Sednev, D Chumak. "Nondestructive testing at nuclear facilities as basis for the 3S synergy implementation." The 7th International Forum on Strategic Technology. 2012: pg. 1

[2] D. D. Sood, S. K. Patil, "Chemistry of Nuclear Fuel Reprocessing: Current Status" *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 203, No. 2 (1996), pg. 547-73

[3] O. Muller, W.B. White, R. Roy. "Crystal chemistry of some technetium-containing oxides" *Journal of Inorganic and Nuclear Chemistry, 26:12*(1964)*: 2075-2086.*

[4] C. Kittel, "Introduction to Solid State Physics" 5th ed., Wiley, New York, 1976.

[5] P. Hohenberg and W. Kohn, "DFT Theory" *Phys. Rev. 136*, B864 (1964).

[6] R. K. Nesbet. "Reference-State Density Functional Theory" *J. Phys. Chem. 100 (1996): 6104-6106*

[7] Introduction to VASP 4.6. *(GIST)* Super Computing and Collaboration Environment Technology Center. Tutorial.

[8] J. Wang, L. A. Eriksson, B Johnson, R. J. Boyd. "Electron Densities of Homonuclear Diatomic Molecules as Calculated from Density Functional Theory" *J. Phys. Chem. 100 (1996): 5274-5280*

Appendix

Table A1 Calculated Values by VASP Used to Determine the Lattice Constant and Bulk Modulus of the Mg Crystal (Figure 5 and 6).

Lattice Constant (Å)	Minimum Total Energy (eV)	Minimum Total Energy (eV/atom)	Volume (Å^3/atom)
2.7	-1.34946098	-0.67473049	13.91804613
2.8	-2.12486521	-1.062432605	15.52247872
3	-2.82039189	-1.410195945	19.09197
3.1	-2.98954365	-1.494771825	21.06551401
3.2	**-3.0380939**	**-1.51904695**	**23.17058**
3.3	-2.99483028	-1.49741514	25.41141207
3.4	-2.88327862	-1.44163931	27.79225144
3.5	-2.72268555	-1.361342775	30.31734125
3.6	-2.52928466	-1.26464233	32.99092416
3.7	-2.31685272	-1.15842636	35.81724283
3.8	-2.09739542	-1.04869771	38.80053992
3.9	-1.87860242	-0.93930121	41.94505809
4	-1.66661916	-0.83330958	45.25504

Table A2 Calculated Values by VASP Used to Determine the Lattice Constant and Bulk Modulus for the Tc Crystal (Figure 7 and 8).

Lattice Constant (Å)	Minimum Total Energy (eV)	Minimum Total Energy (eV/atom)	Volume ($Å^3$/atom)
1.8	71.04719824	35.52359912	4.123864015
1.9	46.93050356	23.46525178	4.85006572
2	27.36173707	13.68086854	5.656877936
2.1	11.83339774	5.91669887	6.548543321
2.2	0.17883977	0.089419885	7.529304533
2.3	-8.07734329	-4.038671645	8.603404231
2.4	-13.60192503	-6.800962515	9.775085073
2.5	-17.10200693	-8.551003465	11.04858972
2.6	-19.06280075	-9.531400375	12.42816083
2.7	-19.91232862	-9.95616431	13.91804105
2.74	-20.01900403	-10.00950202	14.54583005
2.78	**-20.019349**	**-10.0096745**	**15.19221887**
2.8	-19.98467888	-9.99233944	15.52247306
2.9	-19.52986483	-9.764932415	17.2456995
3.0	-18.73525908	-9.36762954	19.09196303
3.1	-17.74072394	-8.87036197	21.06550632
3.2	-16.63936237	-8.319681185	23.17057203
3.4	-14.43307994	-7.21653997	27.7922413
3.6	-12.6636704	-6.3318352	32.99091212

Table A3 Calculated Values by VASP used to Determine the Lattice Constant and Bulk Modulus for $TcMg_2O_4$ Spinel (Figure 9 and 10).

Lattice Constant (Å)	Minimum Total Energy (eV)	Minimum Total Energy (eV/atom)	Volume ($Å^3$/atom)
8	-356.9893705	-6.374810187	9.142857143
8.1	-362.3036765	-6.469708508	9.490017857
8.2	-366.3878501	-6.542640181	9.845857143
8.3	-369.3280655	-6.595144028	10.21048214
8.4	-371.2608241	-6.629657574	10.584
8.5	-372.3403245	-6.648934366	10.96651786
8.6	**-372.6390961**	**-6.654269572**	**11.358**
8.7	-372.1382566	-6.64532601	11.75898214
8.8	-371.1249201	-6.627230716	12.16914286
8.9	-369.5464941	-6.599044537	12.58873214
9	-367.5095993	-6.562671416	13.01785714