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Two-Dimensional Magnets

Finding New Two Dimensional Magnets by Evolutionary Structure Search Algorithms and Ab initio Theory

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Abstract

The structure search software USPEX is used to find stable ground states of two-dimensional metals that are known to exhibit ferromagnetic properties in their three-dimensional bulk states, namely iron, cobalt and nickel. The aim is to find single or double atomic layered magnets. Lattices of interest from the structure search results are examined more closely with higher order of accuracy in the materials modelling program VASP. Limiting the atoms to collinear magnetisation, that is each atom assumes a parallel or anti-parallel spin-up or spin-down orientation, all possible magnetic configurations are examined in order to find the lowest possible energy state that still exhibits magnetic properties. The final results describe the most stable species' compositions along with their respective magnetic moments.

Keywords: scientific computing, USPEX, VASP, structure search, two-dimensional magnets, ab initio, first principles.

1 Background

1.1 Introduction

Magnetism is a highly useful material property which allows for a plethora of practical applications. As technology calls for components of an ever decreasing size it is of interest to see what happens to the magnetic property of certain materials at a smaller scale, namely structures with a mono-atomic thickness. Bringing magnetism into a two-dimensional realm can pave the way for a multitude of technological developments within the field of micro-electronics and sensors.

For the greater part of its history the field of material science has been heavily dependent on empirical experiments where compounds have had to be synthesised in order to be experimented on. The study of material physics has progressed rapidly in the last few decades with the development of increasingly powerful computers. These advances allow for inexpensive yet accurate approximations of material properties in a purely digital manner without having to produce physical specimens.

The purpose of this project is primarily to do an initial computational investigation using numerical methods to find out whether stable two-dimensional ferromagnetic structures can exist. We focus only on a very small subset of materials, sticking purely to the three elements that are known for their ferromagnetic properties in their 3D bulk state, iron (Fe), cobalt (Co), and nickel (Ni) [1]. In their bulk states the magnetic properties of these elements are well known. Physical attributes such as their crystal structure, electron spin configuration and Curie temperature have been studied extensively through empirical methods.

Experimentalists have already managed to produce certain mixed metallic monolayers in laboratories through methods such as chemical vapour deposition, and some of these structures have even been found to have magnetic properties [2]. What sets this investigation apart is the fact that pure iron, nickel and cobalt will be examined. The existence of pure metal monolayers with magnetic properties could potentially pave the way to

finding even stronger magnets through doping. Assuming monolayers of these elements do exist the next step is then to find their physical properties. Hopefully the findings can be used in future studies where the compounds might even be synthesised.

1.2 Ab initio theory

“From the beginning” - in quantum physics the term ab initio entails a process that requires nothing but the fundamental laws of physics that govern many-body electron structures for the prediction of material properties in larger systems. This is in comparison to empirical methods where extensive laboratory testing of materials is performed in order to build a database of properties and interactions such that predictions can be made about new compositions. For this project, ab initio theory was for the most part not looked into on a deeper level. It is, however, the foundational theory on which our two main programs USPEX and VASP base their algorithms, and as such it is of great importance to us here.

Ab initio theory is, based on the above description, in essence a highly broad subject, but here we focus on the concepts of relevance to our project. The process on which the ab initio algorithms are based is the following. The first step of the algorithm is to numerically approximate the solution to the time-independent Schrödinger equation of which we are familiar with, for reference shown in equation (1),

$$\hat{H} |\Psi\rangle = E |\Psi\rangle, \tag{1}$$

for the simplest particle system containing only one electron.

Using this result, the algorithm will then aim to do the same again but for a system of several electrons. This process is then repeated, using a result from the previous step to find the solution of a larger system in every new iteration until the algorithm can model a full atom. This process is intentionally described vaguely, as it is already integrated into both USPEX and VASP, both of which are mostly treated as black boxes in the project. These programs instead work based on certain input files, one of which already describes an atom of an element of choice, and uses that to build larger structures of atoms.

The main characteristic of ab initio theory is however that instead of extrapolating results from empirical data the programs built with ab initio are built solely upon fundamental laws of physics (allowing for some simplifications and assumptions), performing only first principles calculations. This tremendously facilitates the exploration of new materials.

1.3 USPEX

USPEX stands for Universal Structure Predictor: Evolutionary Xtallography [3, 4, 5] and is a MATLAB Runtime software for predicting structures of atoms. It requires interfacing with one of several compatible material property modelling programs¹, in this case

¹USPEX is interfaced with VASP, SIESTA, GULP, DMACRYS, CP2k, QuantumEspresso, LAMMPS, ATK, MOPAC, FHI-aims and Gaussian codes.

the Vienna Ab initio Simulation Package (VASP, described further in the next section), relying on these third party programs ability to perform atomic energy calculations.

USPEX performs an evolutionary structure search, i.e. predicts stable molecular so-called unit cells that can be replicated in a contiguous lattice to form larger structures, as demonstrated in Figure 1. In this case the unit cells consist purely of iron, cobalt, and nickel, respectively, and the number of atoms within the unit cell is allowed to range between one and eight - varying this number can lead to different symmetries in the unit cells which then produce different results. Through a process that iterates through several generations USPEX re-configures individual atoms' positions within the unit cell, striving to find a configuration that yields the lowest possible enthalpy (also referred to as the energy) which would correspond to the most stable structure. In the first generation USPEX creates a batch of random unit cells. From then on it is able to rank individual cells by their enthalpies, and a successive generation can be created partially by keeping the top performers but also by introducing new species through mutations to these as well as some new random configurations in a process that emulates genetic evolution. For each generated structure USPEX depends on VASP to calculate what are the main quantities of interest for this project: the energies of the atoms, as well as their magnetic moment and as such the spin configurations of their electrons. Unless it is unable to converge towards a ground state, USPEX will terminate after a predefined number of generations in which one structure consecutively outperforms the others. The output from a computation is a list of structures of interest along with their predicted material properties and structural information. Ultimately, a single USPEX run for each of the three elements yields all data for us to visualise and interpret. Further processing of these structures however turns out to be necessary.

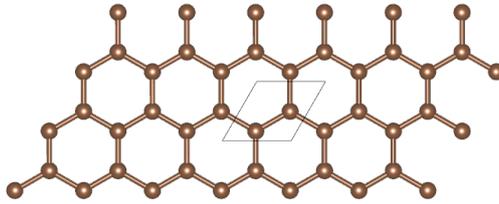


Figure 1: An example of a unit cell highlighted within a contiguous graphene lattice.

USPEX itself requires three types of input files in order to run a calculation. The `INPUT.txt`-file, further shown in Appendix B, contains the parameters that define constraints on the generated structures along with sizes of generations and stopping criteria, among others. It is also here we define the element(s) used, the number of atoms in a unit cell, as well as the desired thickness of the outcome.

The two input files, `INCARs` and `POTCARs` given in Appendix B, are required by the interfaced VASP program in order for it to perform structure relaxation and energy calculations. These are described under the VASP section.

USPEX is run through a submission script in the relevant directory, containing information about the submission to Tetralith (further explained in the Tetralith section), such

as how many cores the computation will use, and the maximal allowed time for the run.

The output of an USPEX run is, in essence, different so called POSCAR-files. These describe mainly the positional data of the atoms in the different resulting unit cells, however they also contain several other pieces of data about the unit cell. Examples of this include the enthalpy, volume, density, magnetic moments of the atoms and whether or not the structure is ferromagnetic/anti-ferromagnetic or not. USPEX also intelligently gathers the "best" POSCARs of different structures, "best" here referring to structures with lower enthalpy. All of this makes it relatively straight-forward to analyse the USPEX results.

1.4 VASP

The Vienna Ab initio Simulation Package [6, 7] is used to evaluate material properties and is what allows for a study of this manner to be conducted. It is written in Fortran and built on the aforementioned ab initio concepts, and more specifically implementing density-functional theory (DFT) to simplify and solve the time-independent Schrödinger equation (now expanded from equation (1) into the following equation (2)) for multiple (N) electrons,

$$\hat{H}\Psi = \left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i<j}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi = E\Psi. \quad (2)$$

Here the DFT simplification applies to the U term that describes the mutual interaction energy that occurs between all electrons. Calculating this term analytically gets convoluted as the number of electrons in the system increases and so the system is instead cleverly reduced to a single-body problem.

The potential energy V is a result of the system's electrons interacting with the electric field created by the nuclei's protons. This term is also subject to one of VASP's simplifications. True potentials are difficult to find so, instead, *pseudopotentials* are used, approximate functionals that take into account that it is mostly the valence electrons that contribute to interatomic interactions and then allowing the core electron states to be considered as fixed [8]. This term is system dependent, meaning each element has its own unique potential that can be calculated once and saved or distributed for use in future calculations.

VASP has a plethora of functions but of interest for this project is the program's ability to perform ionic relaxations, enthalpy calculations and approximations of collinear magnetic properties. As mentioned earlier, USPEX is interfaced with VASP in order to perform its material property calculations during the structure search. Wanting to streamline the search USPEX omits calculating a lot of material properties. Once the structures of interest have been found they can be further investigated individually by feeding the structural information back into VASP.

The input files required to perform a calculation are dependent on what the user wants to compute. If a structure relaxation, approximation of enthalpy or magnetic moment calculation is to be performed then the user has to provide the initial positions of the unit

cell atoms in a POSCAR file, their pseudopotentials in a POTCAR file, a specification of how the computation space is to be discretised in a KPOINTS file and an INCAR file defining calculation parameters. Examples of the specific inputs used in this project can be found in Appendix A.

1.5 Supercomputer calculations - Tetralith

Both USPEX and VASP are run in a Linux environment and are highly parallelised. Despite this, the performed calculations are computationally demanding. A typical USPEX run performs a vast amount of complex calculations and is therefore run exclusively on high performance computers. Pure VASP calculations can be simple enough to run on a regular PC, however not in our case where the input contains an USPEX unit cell.

As a result of this, we have had access to NSC's largest supercomputer cluster Tetralith at Linköping University for our project. Uppsala University has access to Tetralith as a part of a larger material science project [9]. An INCAR-file as well as a KPOINT-file with default parameters defined were introduced to us through this larger project, taken from USPEX's example files collection.

Tetralith consists of 1832 so-called "thin" nodes of 96 GiB RAM and 200 GiB SSD each, as well as 60 "fat" nodes of 384 GiB RAM and 900 GiB SSD each. Each node is also equipped with two Intel Xeon Gold 6130 CPUs, resulting in about 61000 cores in total, all resulting in a performance of about 3 Pflop/s. All computational software and respective licenses required for USPEX and VASP are installed on this machine. For some perspective on the computational demands, our USPEX runs for example while using 32 cores took somewhere in between 8-24h, and our VASP runs using 128 cores took 2-8h.

The cluster could be accessed remotely and calculations were submitted with the SLURM queuing system, a standard within the Swedish National Infrastructure for Computing, SNIC.

1.6 VESTA

The POSCAR-files that were yielded by USPEX, used in VASP, and in general very common throughout the project, contains as previously mentioned the positional data (among other data) of the atoms in a unit cell structure. In addition to the numerical analysis and comparison of output files, a visualisation of these unit cells was of interest due to being able to simply classify the main characteristics of each structure. Two main points of interest was the amount of layers in the structure, as well as whether the structure was buckled or flat. For this visualisation process we were recommended a software called VESTA, Visualisation for Electronic Structural Analysis, by our supervisors (however other visualisation tools were possible as well). VESTA allowed for a smooth overview of the structure, as well as copying the unit cell in all three dimensions. This latter feature made it possible to essentially place several unit cells beside each other in both the x- and y-axes, and as such render a sheet of the material. Examples of this process are found in Figures 2a, 2b, and 2c.

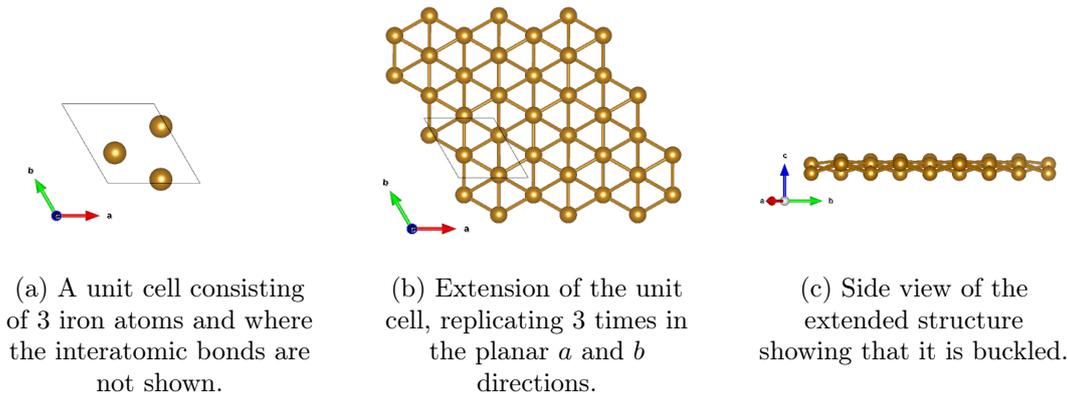


Figure 2: Visual analysis of structures in VESTA.

2 Execution

2.1 USPEX on non-magnetic elements and compounds

At the first stage of the project, practical familiarisation with the above infrastructure is necessary, and as such we first try to recreate structures of more known elements and compounds. The results of these are not of interest in the scope of the rest of the project (as long as they corresponded to known results), however, the process in which we *procure* them is. Through an iterative evolutionary process USPEX creates hundreds of different structures for each metal, over several generations. Between generations USPEX will keep some well performing structures, generate some new ones randomly and mutates old ones.

For the calculations, as mentioned earlier, we first create a directory for the structure in question in the workspace of our Tetralith account. Here we create (or copy from elsewhere and modify) an `INPUT.txt`-file, as well as a sub-directory titled *Specific*, which in turn contains five `INCAR`-files specifying how the interfaced VASP program should perform ionic relaxations and enthalpy calculations along with a corresponding `POTCAR`-file containing pseudopotentials of the constituent element(s). The reason for the five `INCAR`-files is that USPEX can achieve a higher order of accuracy in a shorter amount of time if it gradually relaxes generated structures in several steps instead of making one high-accuracy relaxation in one go. The precision argument in the first relaxation step is set to 'low' and the result from this calculation is then progressively piped into further VASP relaxations with increasing precision. Next, we create (or once again, copy and modify) a *sub*-file in order to queue the calculation on Tetralith.

The `INPUT.txt`-file allows us to define for example stopping criteria, in our case it is decided that if the same crystal has the lowest energy through eight consecutive generations then the computation can be terminated. Each and every structure has its energy and magnetic moment approximated to a 'normal' degree of accuracy.

To gain initial experience, some non-magnetic compounds are trialled as they are less

intricate in terms of input parameters and expected outputs. Black phosphorus, graphene, and monolayered sodium chloride are all experimented with.

```

Current_ORG.mat      POSCAR_order  results1
Current_ORG.mat.backup Seeds          slurm-10841132.out
Current_POP.mat      Specific      sub
Current_POP.mat.backup Submission
INPUT.txt            USPEX_IS_DONE
POSCAR               log

```

Figure 3: Showcasing the files needed for an USPEX calculation (among others created after the run).

2.1.1 Black phosphorus

To start off we were encouraged to perform structure search using USPEX for black phosphorus. This crystalline form of the element is the most stable allotrope at room temperature and is known to be made up of stacked 2D phosphorene sheets, much like how graphite is in principle multi-layered graphene. Phosphorus is generally a volatile element so it is not found naturally in its pure form, instead it tends to be found mixed in with other elements in more stable compounds. The white phosphorus allotrope has made a name for itself in the weapon industry and is therefore more well known than the black phosphorus variant even though it is less thermodynamically stable.

The structure of black phosphorus is easily recognizable, and the lowest energy structure from USPEX shown in Figure 4 can be compared with independent studies [10] of the material to show that the results are consistent.

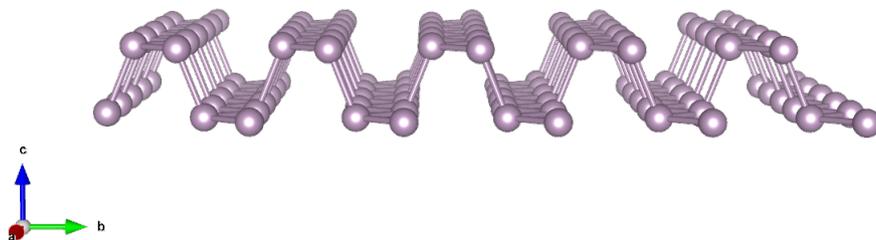


Figure 4: USPEX’s lowest enthalpy output from a phosphorus structure search. The results visually match the findings in an independent study on black phosphorus.

For “discovering” black phosphorous through USPEX, the only thing necessary is to change a single parameter in a template `INPUT.txt`-file for surface calculations, namely the `atomType` to phosphorous (P). All other parameters remain unchanged. The only thing left to do is then to copy the regular phosphorous `POTCAR` from a shared library on the supercomputer, along with the default `INCARs` and the now slightly modified `INPUT.txt` into a new directory, and creating a submission script to queue the run.

Not only does USPEX produce the expected black phosphorus, it lives up to its name of being a universal structure search algorithm. The third best structure among the results is white phosphorus, despite it being a tetrahedral molecular structure instead of a surface and us making an attempt to limit generated structures to two dimensions.

This showcases USPEX ability to find not only the lowest energy configuration within set limitations, it is flexible and can find multiple structures of interest.

2.1.2 Graphene

Graphene is principally the separate layers of which graphite consists, and is built solely of carbon atoms in a hexagonal, two-dimensional layer. Its existence and properties are well known since the 2010 Nobel Prize Awards, and both the relative simplicity of the structure, consisting only of one element, together with its 2D nature relevant to the project make it a good choice for learning how to perform structure search with USPEX.

For “discovering” graphene through USPEX, we go through mostly the same procedure as for black phosphorous. However, this time we are also interested in another parameter in the `INPUT.txt`-file, the `numSpecies`. This parameter is what fixes the amount of atoms in the resulting unit cell, with default value 1. To investigate what effect this has on the computed structures, we run five different instances of carbon structure search (aiming for graphene) with USPEX, each with a different `INPUT.txt`-file with the `numSpecies` set to 1, 2, 4, 6, and 7, respectively. These specific numbers are chosen since we already know that the graphene structure is hexagonal, and as such fixing the amount of atoms in the unit cells to something that cannot divide 6, we figure those runs will not yield the graphene structure. Viewing the results in VESTA we can confirm that this is the case, with an example shown in Figure 5 where Figure 5a shows the expected outcome and Figure 5b demonstrates how a poor choice of the `numSpecies` can lead to unexpected results. This insight is transferred over to the magnetic element searches where a range of different `numSpecies` are examined for each metal.

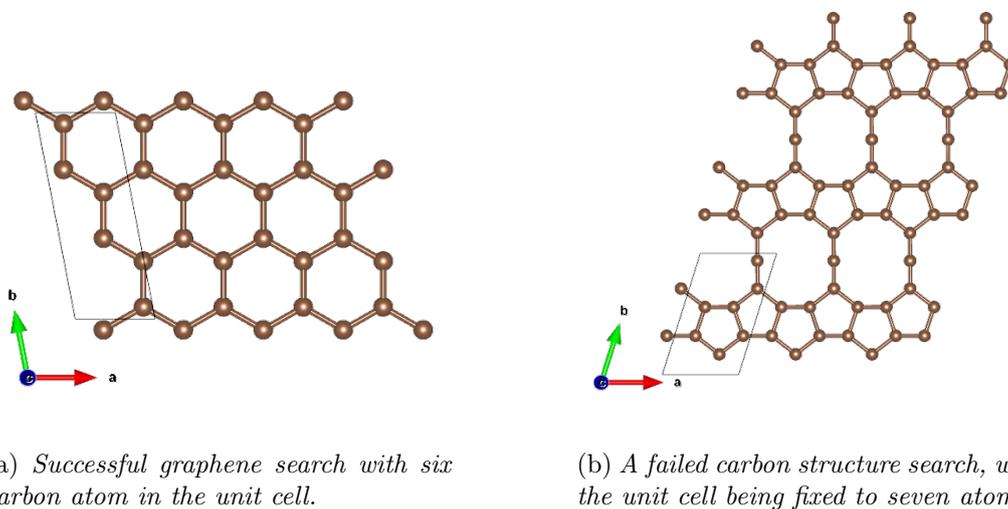


Figure 5: The effects of altering the number of atoms in the generated structures’ unit cells. Not all input parameters were able to produce the desired results.

2.1.3 Sodium Chloride

Out of our own interest and to solidify our understanding of the calculation process, we decide to structure search for two-dimensional sodium chloride, a substance with two constituent elements. It has only recently been proven to exist [11], having been found with the very same software that we are using, USPEX. This 2D variant of sodium chloride also exhibits a hexagonal structure, much like the one of graphene.

In this case we are now investigating a compound species, and as such we have to include two different atoms in the `atomType` parameter in the `INPUT.txt` as well as providing the two respective POTCARs for sodium (Na) and chlorine (Cl). Here we try two different `numSpecies`, one run fixing the unit cell to one sodium and one chlorine, and another with two of each elements. In general, the results are the same in both cases with the hexagonal structure (seen in Figure 6) being found as the second lowest enthalpy structure for both trial runs. The lowest enthalpy structures appear to be very similar to a single ‘slice’ of the normal bulk crystal configuration and is not of interest.

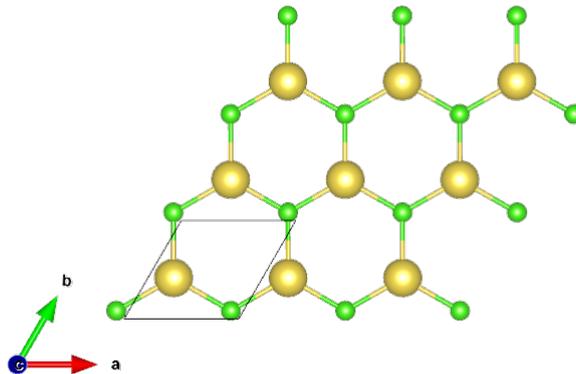


Figure 6: An USPEX output from a sodium and chlorine structure search. The recently reported hexagonal structure of NaCl is recreated successfully.

2.2 USPEX on magnetic elements

The next step is to move on to the project’s focal point, performing structure searches on our three transition metals - finding 2D materials that may not previously have been produced or documented. For these elements, we now have to include the fact that they are magnetic in the input files. This is done by adding (or changing) the `ISPIN` parameter in the five `INCAR`-files. In the `INPUT.txt`-files we have a new `MagRatio` parameter which defines how many (ratio-wise) of the generated structures are to be either non-magnetic, ferromagnetic low-spin, antiferromagnetic low-spin, ferromagnetic high-spin, antiferromagnetic high-spin, ferromagnetic low-high-spin, or antiferromagnetic, i.e. seven different ratios. This also yields an especially interesting part of the results, the

magnetic moment of each individual atom in the generated unit cells. More on this is to be found in Section 3.

Once the computation is complete the 20 ‘best’ species are collated into an easily read file. Looking through these top results we pick out at least 4 structures that are of particular interest to this project: best overall species along with the lowest energy bilayer, monolayer and completely 2D structure.

The only practical differences between the runs of the three elements are the different POTCAR files for each element, as well as the `atomType` parameter in each of the `INPUT.txt`-files. Having seen in the trial computations for graphene that the `numSpecies` parameter can result in different outputs, the number of atoms in the unit cells are allowed to vary between one and eight. Numbers greater than eight are more likely to end up just producing the same structures only with a bigger ‘chunk’ of the lattice in the unit cell. Cells with more atoms in them also require more time in order to be relaxed and taking our allocated amount of computation hours on the supercomputer into account the upper limit is about 16 atoms per unit cell anyway.

Apart from specifying a surface structure search (instead of bulk or nanoparticle), the main parameter that is of importance in the `INPUT.txt`-file for these USPEX computations in an attempt to limit the algorithm to produce two dimensional lattices is the surface thickness, `thicknessS`. According to the documentation this variable defines the maximum permissible difference between *z*-axis coordinates of unit cell atoms in the *randomly* generated structures, measured in Ångström (Å). Previously unbeknownst to us, it is possible for structures to rearrange into bulkier formations that extend beyond this thickness limitation after ionic relaxation. In initial trials the thickness is set to 1, not realising that the unit is Å instead of the number of atomic layers and hence believing this to be the minimum. Upon finding this out it also becomes apparent that 0 Å is a permissible input here. As a result, we end up running calculations with `thicknessS` set to both 0 and 1, for each of the elements. Similar results are found in both cases but the `thicknessS=0` runs produce fewer bulky (several atomic layers) results when compared to the `thicknessS=1` runs. Essentially, greater restrictions on the allowed thickness make it easier for the structure search to converge towards structures that are of interest to us, even though it is still prone to relax some of the structures into a more bulky form.

2.3 VASP on USPEX structures

Having chosen a handful of iron, cobalt, and nickel structures (17 to be specific, more on this is given in Results under Section 3) that are promising candidates we want to investigate whether there exists some permutations of their constituent atoms’ magnetic moments that produce even better magnetisation whilst hopefully retaining a similar energy and shape.

USPEX is very powerful and has been shown to be dependable when working with non-magnetic crystals, but with its capability of performing magnetic property calculations being a new addition it is not certain that the results can be trusted. If a unit cell consists of 6 atoms and each atom can be in a spin-up or spin-down state (corresponding to a positive or negative magnetic moment) then there are $2^6 = 64$ possible configurations

of that species alone. It feels unreasonable that USPEX is able to take all of these permutations into account.

Taking the positional information of the structures of interest from the USPEX search we proceed with pure VASP calculations for a more thorough analysis. Creating individual calculations for each possible permutation we re-relax the structures and re-calculate material properties with greater precision as well as calculating some additional properties that USPEX omits. In total we test 552 different permutations of our chosen iron, nickel and cobalt structures. With a script we can quickly compare the fitness of all the new configurations and cross-reference with what USPEX predicts to be the optimal structure.

3 Results and Discussion

The results in their entirety form somewhat of a library of structure POSCARS and material properties which are most easily viewed in their respective files. The files are freely available at our [GitHub](#) [12].

3.1 Results from USPEX

One caveat to the `thicknessS` parameter is that it does not directly limit the output to the defined thickness, instead it is the initial configuration of atoms in the structure. After ionic relaxation some species revert into what can almost be likened to the metal's bulk centred cubic form. Unfortunately this suggests that the two-dimensional structures might be unstable, with the atoms much rather rearranging into their natural lattice.

3.1.1 Iron

Among the iron structures we choose to focus on as much as seven of the 20 given "best" structures.

- ID 206 - lowest enthalpy, two-layer buckled structure
- ID 252 - 2nd lowest enthalpy, two-layer buckled structure
- ID 280 - 3rd lowest enthalpy, lowest enthalpy two-layer flat structure
- ID 207 - 7th lowest enthalpy, several layers but the lowest structure to display a "triangular" bonding, which would come to be the same as the lowest enthalpy pure 2D structure
- ID 88 - 8th lowest enthalpy, an almost monolayered structure with two "spikes"
- ID 111 - 11th lowest enthalpy, lowest enthalpy monolayer structure
- ID 142 - 13th lowest enthalpy, lowest enthalpy 2D structure

These seven structures along with the other 300 or so generated structures can be quickly compared with each other in a simple graph, Figure 7, that plots individual structures' fitness against their corresponding IDs. This results in a seemingly random scattering of points, but some trends stick out in the randomness. One can see that a lot of structures

converge to the same energy levels, forming horizontal lines in the figure. These lines suggest that there exists stable configurations at those energy levels. Worth noting is that due to USPEX’s evolutionary algorithm, some of the structures might be exact duplicates where a well performing structure is carried over into a subsequent generation. This is not to say that all points along the horizontal lines are duplicates though, it is also possible, if not expected, for slightly different structures to relax into the same configuration. The plot also demonstrates how the `thicknessS` parameter only affects the initial 30 randomly generated structures as these all lie above the horizontal line that we later find out marks the purely 2D structures. After the first generation of 30 structures some mutations relax into more stable bulky structures that then continue to outperform the 2D species.

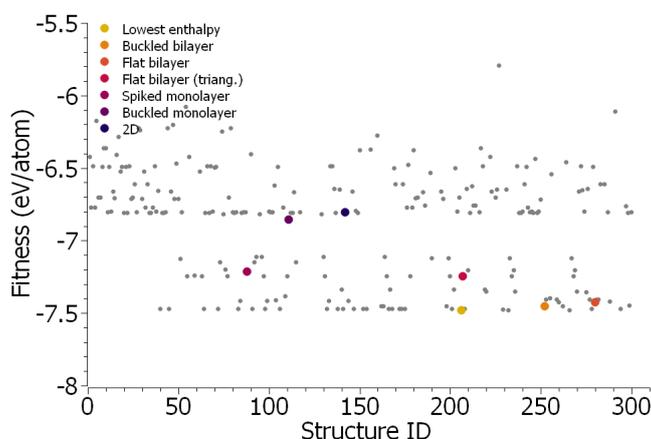


Figure 7: All iron structures found by USPEX structure search. Lower fitness suggests a more stable structure.

3.1.2 Cobalt

Among the cobalt structures we choose five structures of interest.

- ID 53 - lowest enthalpy and two-layer flat structure, has a triangular structure
- ID 140 - 2nd lowest enthalpy, two-layer buckled structure
- ID 221 - 7th lowest enthalpy, two-layer flat structure, has a square bonding (but possibly too many bonds for it to be physically feasible)
- ID 52 - 12th lowest enthalpy, lowest enthalpy monolayer structure
- ID 299 - 15th lowest enthalpy, lowest enthalpy 2D structure

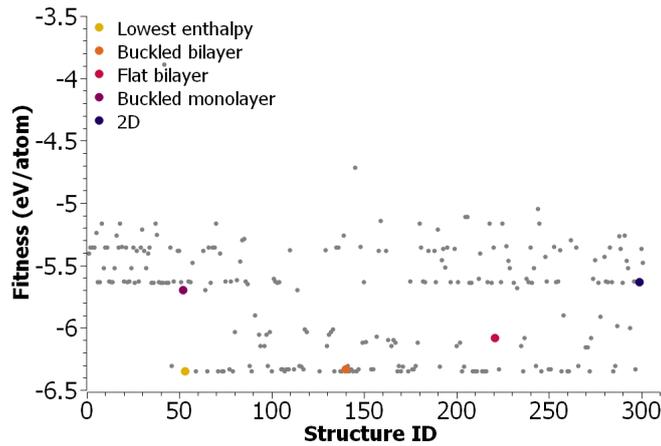


Figure 8: All cobalt structures found by USPEX structure search.

3.1.3 Nickel

Even among the nickel structures we choose five structures of interest to focus on.

- ID 145 - lowest enthalpy, two layer flat structure
- ID 80 - 2nd lowest enthalpy, two layer buckled structure
- ID 138 - 12th lowest enthalpy, an almost monolayered structure with one "spike"
- ID 239 - 13th lowest enthalpy, lowest enthalpy monolayer structure
- ID 213 - 15th lowest enthalpy, lowest enthalpy 2D structure

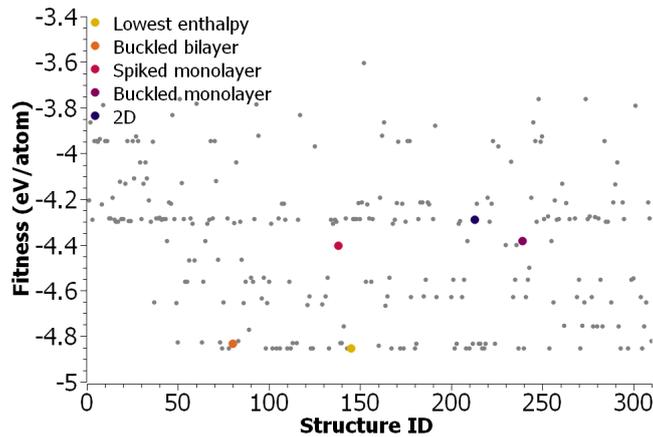


Figure 9: All nickel structures found by USPEX structure search.

The USPEX results in general were relatively simple to produce and interpret, once again a consequence of the strength and versatility of the program. It was only when putting the results to test in VASP that doubts started to appear in regards to the goals of this project in particular.

3.2 Results from VASP

What we ultimately have ended up with is a library of 552 possible nigh 2D magnets. All 552 structures have not been investigated so we cannot say this with 100% certainty yet but just looking at the iron structures the trend has been that USPEX’s results were indeed of the optimal configurations. Some of these results are slightly questionable however. During the ionic relaxation step of our VASP calculations a lot of structures revert into lattices that resemble the metals’ usual 3D bulk formations, suggesting that some USPEX results are not stable states after all. These inconsistencies continue if we look at the enthalpies of the structures. As we would expect, the structures in which we have deliberately changed the magnetic configuration of the atoms do not have the same enthalpy as their USPEX “parent” structure. We would however expect the enthalpies to be the same in the 17 cases where the magnetic moments of the atoms are unchanged, and this is rarely the case. The difference in enthalpy between the USPEX results and the corresponding VASP results are in the best case less than 1 eV, and this can be due to the increased accuracy of the VASP calculations. In many other cases though, this difference could be several eV, so that the accuracy shift can no longer be the sole reason. In these cases we can assume that the re-relaxation has altered the shape of the structure significantly, to a point where it no longer can rightfully be compared to the original USPEX output. It can be said that looking across all cases of ionic relaxation of the structures, they do in general tend to want to bulk up, and an educated guess would be that the structures with higher enthalpy, i.e. the more two-dimensional ones, are somewhat unlikely to be stable enough in practise.

3.3 Future developments

This investigation focuses on homogeneous iron, cobalt and nickel structures. Whilst these metals are undoubtedly ferromagnetic there are other metals and compounds that are known to be more magnetic, at least in their three-dimensional states. There exists a great multitude of such compounds and choosing which ones to investigate in 2D is a project in itself, but it is quite possible that such compounds would produce even more magnetic substrates. This investigation will hopefully provide a basis for future studies in 2D magnets. Magnetic iron, nickel or cobalt substrates might be able to be doped with rare earth metals to produce even stronger magnetic properties.

As a continuation of the project, one may delve deeper into the different calculations VASP is able to perform on the structures found by USPEX. These include for example band structure calculation, magnetic anisotropic calculation, Curie temperature, and the exploration of non-collinear magnetic structures.

Hopefully our findings as well as continued work into the topics above can be used in future studies where the compounds might even be synthesised.

4 Summary and conclusions

In total, 17 different iron, nickel and cobalt structures of interest were found from the USPEX evolutionary structure search. They were selected to be investigated further

in VASP. For these structures all 552 possible magnetic configurations were examined. These structures were ionically relaxed and then enthalpies and density of states (DOS) were calculated in two separate stages.

Theoretically, our USPEX calculations predict that purely two dimensional structures of the three metals are indeed possible, however these structures are not among the most stable of the structures found. The refined VASP calculations bring uncertainty to the results seeing as some ionic relaxations caused bulking of previously mono- or bilayered structures, suggesting that they may in fact not have been stable states. With this said, there still exists some magnetic configurations that yielded 2-dimensional structures that may very well be candidates for actual synthesis.

References

- [1] Moskowitz B.M. *Classes of Magnetic Materials*. Accessed: 2021-01-22. Online [http://www.irm.umn.edu/hg2m/hg2m_b/hg2m_b.html#ferrimagnetism], 1991.
- [2] Rule K.C. Fritzsche H. Kreuzpaintner W. Cortie D.L. Causer G.L. and Klose F. “Two-Dimensional Magnets: Forgotten History and Recent Progress towards Spintronic Applications”. In: *Advanced Functional Materials* 30.18 (2020), p. 1901414. DOI: <https://doi.org/10.1002/adfm.201901414>.
- [3] Glass C.W. Oganov A.R. “Crystal structure prediction using ab initio evolutionary techniques: principles and applications”. In: *J. Chem. Phys.* 124.244704 (2006).
- [4] Valle M. Oganov A.R. Lyakov A.O. “How evolutionary crystal structure prediction works - and why”. In: *Acc. Chem. Res.* 44 (2011), pp. 227–237.
- [5] Stokes H.T. Zhu Q. Lyakov A.O. Oganov A.R. “New developments in evolutionary structure prediction algorithm USPEX”. In: *Comp. Phys. Comm.* 184 (2013), pp. 1172–1182.
- [6] Kresse G. and Furthmüller J. “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”. In: *Phys. Rev. B* 54 (16 1996), pp. 11169–11186. DOI: [10.1103/PhysRevB.54.11169](https://doi.org/10.1103/PhysRevB.54.11169).
- [7] Kresse G. and Joubert D. “From ultrasoft pseudopotentials to the projector augmented-wave method”. In: *Phys. Rev. B* 59 (3 1999), pp. 1758–1775. DOI: [10.1103/PhysRevB.59.1758](https://doi.org/10.1103/PhysRevB.59.1758).
- [8] Segall M. *Pseudopotentials*. Online [<https://www.tcm.phy.cam.ac.uk/~mds21/thesis/node16.html#SECTION00760000000000000000>]. Accessed: 2021-01-26. 1997.
- [9] Sanyal B. *Dynamical phenomena in functional materials*. Online [<https://supr.snic.se/public/project/16828/>]. Accessed: 2021-01-06. 2021.
- [10] Xu Z. Du H. Lin X. and Chu D. “Recent Development in Black Phosphorus Transistors”. In: *J. Mater. Chem. C* 3 (July 2015). DOI: [10.1039/C5TC01484K](https://doi.org/10.1039/C5TC01484K).
- [11] Sukhanova E.V. Popov Z.I. Evlashin S.A. Tarkhov M.A. Zhdanov V.L. Dudin A.A. Oganov A.R. Kvashnin D.G. Tikhomirova K.A. Tantardini C. and Kvashnin A.G. “Exotic Two-Dimensional Structure: The First Case of Hexagonal NaCl”. In: *The Journal of Physical Chemistry Letters* 11.10 (2020). PMID: 32330050, pp. 3821–3827.

- [12] Zdansky Cottle L. and Beas Petersson P. *2D Magnet GitHub Repository*. Online [<https://github.com/Lao140/2DMagnets>]. Accessed: 2021-01-06. 2021.

Appendices

A VASP Inputs

Here we can see some examples of the, POSCAR, KPOINTS and INCAR files. POTCARs are extraordinarily long files that are difficult for humans to interpret.

POSCAR:

```
EA140    3.951    2.437    19.922    90.01    90.39    90.00    Sym.group:    1
1.0
    3.951223    -0.000090    -0.013302
    -0.000004    2.437429    -0.000152
    -0.067487    -0.001253    19.921653
Co
4
Direct
    0.160056    0.590540    0.536438
    0.156720    0.090443    0.430191
    0.657593    0.590488    0.463556
    0.660941    0.090567    0.569815
```

KPOINTS:

```
15x15x15
0
Monkhorst
8 13 1
0 0 0
```

INCAR:

```
SYSTEM = Co
PREC = LOW
EDIFF = 2e-3
IBRION = 2
ISIF = 4
NSW = 85
ISMEAR = 1 ; SIGMA = 0.20
POTIM = 0.020
ISTART = 0
#Crude optimisation
EDIFFG = -2e-1
LCHARG = FALSE
LWAVE = FALSE
```

B USPEX INPUT.txt

INPUT.txt:

```
*****
*           TYPE OF RUN AND SYSTEM           *
*****
USPEX : calculationMethod (USPEX, VCNEB, META)
s-200  : calculationType (dimension: 0-3; molecule: 0/1; varcomp: 0/1)
0.0    : thicknessS
1      : AutoFrac

% vacuumSize
12 12 15 20 20
% endVacuumSize

% optType
1
% EndOptType

% numSpecies
1
% EndNumSpecies

% atomType
Co
% EndAtomType

*****
*           SINGLE BLOCK SETTING           *
*****
1  : minAt
8  : maxAt

*****
*           Magnetic Structures           *
*****
% magRatio
1/20 1/6 1/6 1/6 1/6 1/6 1/6
% EndMagRatio

*****
*           POPULATION                     *
*****
30  : populationSize
30  : initialPopSize
60  : numGenerations
8   : stopCrit
0   : reoptOld

*****
*           VARIATION OPERATORS           *
*****
0.50 : fracGene
0.30 : fracRand
0.00 : fracPerm
0.00 : fracLatMut
0.20 : fracAtomsMut
```

```
*****
*   DETAILS OF AB INITIO CALCULATIONS   *
*****
% abinitioCode
1 1 1 1 1
% ENDabinit

% KresolStart
0.1 0.07 0.06 0.05 0.033
% Kresolend

% commandExecutable
mpprun -np 16 vasp\_std > log
% EndExecutable

30      : numParallelCalcs (how many parallel calculations shall be ...
        : performed)
1       : whichCluster (0: no-job-script, 1: local submission, 2: ...
        : remote submission)
```