

HOW TO PREPARE AN INPUT FILE FOR SURFACE CALCULATIONS

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ABSTRACT. This how-to is intended to guide the reader during the preparation of the input file for an intended surface calculation study. Mainly VESTA software is used to manipulate and transform initial structure file along with some home brewed scripts to do simple operations such as translations.

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1. DESCRIPTION

One of the questions I'm frequently being asked by the students is the preparation of input files for surface calculations (or more accurately, "a practical way" for the purpose). In this text, starting from a structural data file for bulk, the methods to obtain the input file fit for structure calculations will be dealt.

2. TOOLS

VESTA¹ is a free 3D visualization program for structural models that also allows editing to some extent. It is available for Windows, MacOS and Linux operating systems.

STRCONVERT² is a tool hosted on the Bilbao Crystallographic [Server](#)[1, 2, 3] (BCS) that offers visualization and also basic editing as well as conversion between various common structural data formats.

TRANSTRU³ is an another BCS tool that transforms a given structure via the designated transformation matrix.

¹<http://jp-minerals.org/vesta/en/>

²<http://www.cryst.ehu.es/cgi-bin/cryst/programs/mcif2vesta/index.php>

³<http://www.cryst.ehu.es/cryst/transtru.html>

225

4.50 4.50 4.50 90. 90. 90.

2

C 1 4a 0 0 0

Pt 1 4b 0.5 0.5 0.5

TABLE 1. Structural data of $Fm\bar{3}m$ PtC

The screenshot shows the 'New Data' dialog box in VESTA, specifically the 'Unit cell' tab. The 'Phase' dropdown is set to 'PtC'. The 'Symmetry' section has 'Crystal system' set to 'Cubic', 'Space group' set to '225', and 'Setting' set to '1'. The 'Lattice parameters' section shows 'a (Å)' as 4.50000, 'b (Å)' as 4.50000, 'c (Å)' as 4.50000, 'α (°)' as 90.0000, 'β (°)' as 90.0000, and 'γ (°)' as 90.0000. The 's.u.' row shows all zeros. A 'Remove symmetry' button is at the bottom. The 'Phase' dropdown is set to 'PtC'.

FIGURE 3.1. VESTA’s “Unit cell” interface

3. PROCEDURE

3.1. Initial structural data. We start by obtaining the structural data for the unit cell of the material we are interested in. It should contain the unit cell dimensions and the atomic positions. Some common formats in use are: CIF[4], VASP[5], VESTA[6] and BCS formats. Throughout this text, we will be operating on the $Fm\bar{3}m$ phase of the platinum carbide (PtC), reported by Zaoui & Ferhat[7] as reproduced in BCS format in Table 1.

These data can be entered directly into VESTA from the form accessed by selecting the “File→New Structure” menu items and then filling the necessary information into the “Unit cell” and “Structure parameters” tabs, as shown in Figures 3.1 and 3.2.

As a result, we have now defined the $Fm\bar{3}m$ PtC (Figure 3.3).

An alternative way to introduce the structure would be to directly open its structural data file (obtained from various structure databases such as COD[8], ICSD[9] or Landolt-Bornstein[10] into VESTA.

3.2. Constructing the Supercell. A supercell is a collection of unit cells extending in the a,b,c directions. It can easily be constructed using VESTA’s transformation tool. For demonstration purposes, let’s build a 3x3x3 supercell from our cubic PtC cell. Open the “Edit→Edit Data→Unit Cell...” dialog, then click the “Option...” button in the “Setting” row. Then define the transformation matrix as “3a,3b,3c” as shown in Figure 3.4.

New Data

Phase: 1

Phase Unit cell Structure parameters Volumetric data Crystal shape

Atomic displacement parameter Anisotropic: None Isotropic: B

No.: Symbol... Label: Charge:

x: y: z: Occ.:

s.u.(x): s.u.(y): s.u.(z): B:

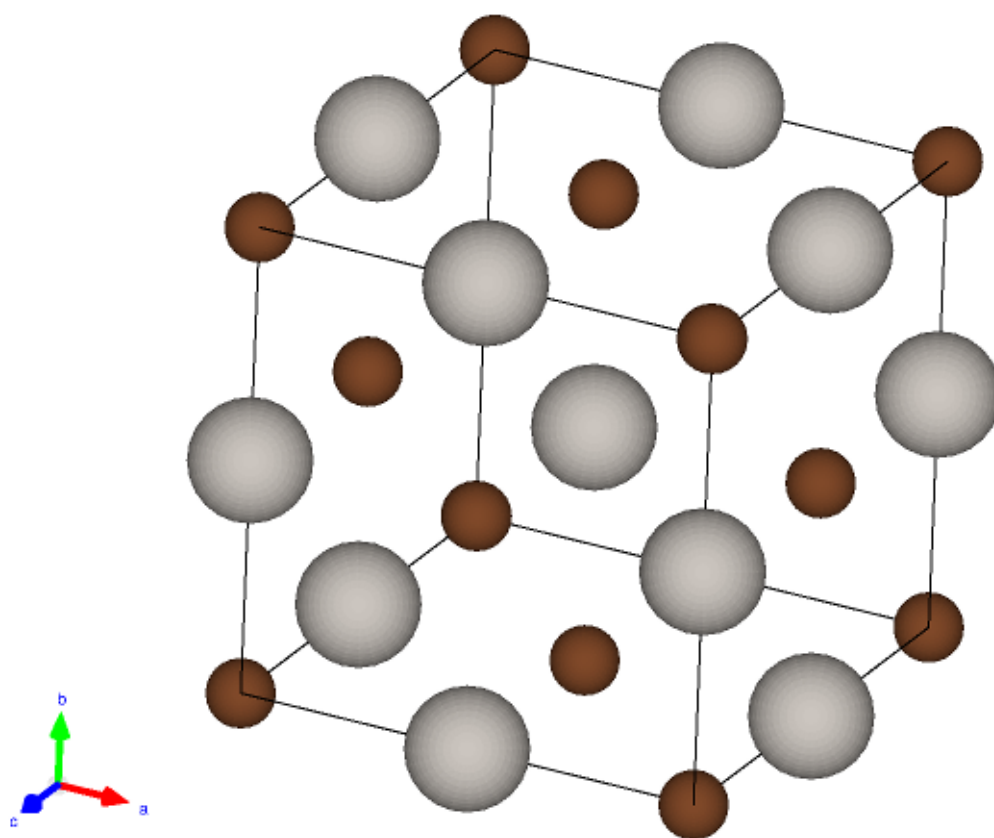
U11: U22: U33:

U12: U13: U23:

NoAtom	Label	x	y	z	Occ.	B
1	C	0.000000	0.000000	0.000000	1	1
2	Pt	0.500000	0.500000	0.500000	1	1

☐ Link

FIGURE 3.2. VESTA's "Structure parameters" interface

FIGURE 3.3. $Fm\bar{3}m$ platinum carbide

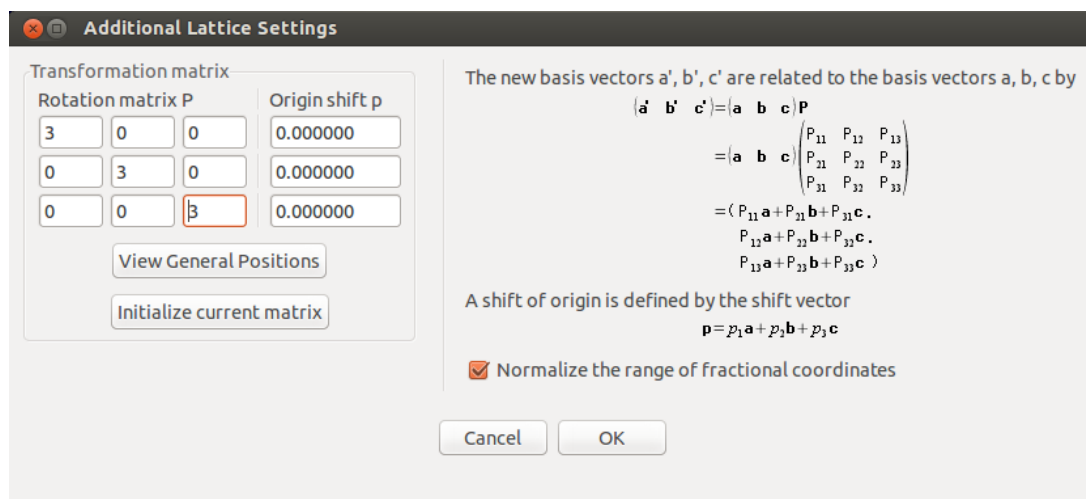


FIGURE 3.4. Transformation matrix for the supercell

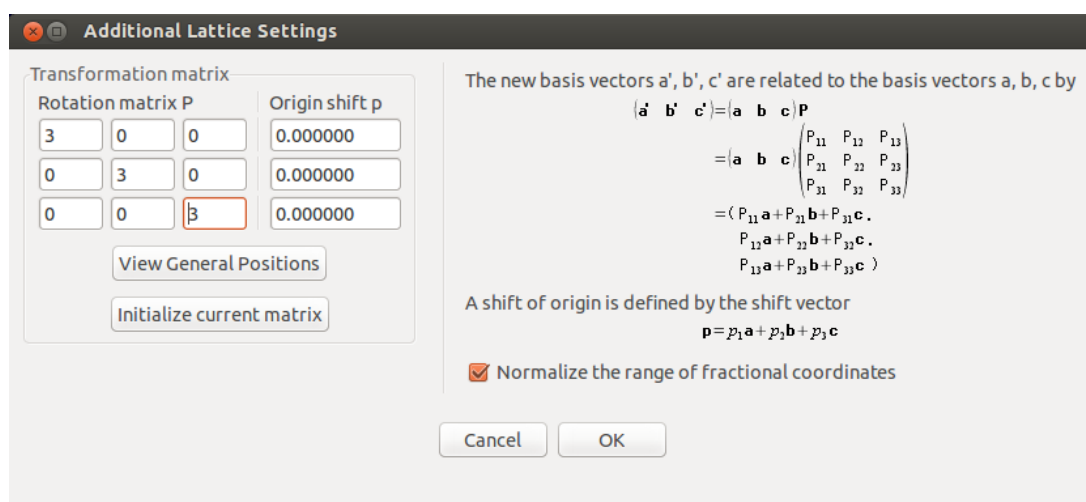


FIGURE 3.5. A 3x3x3 supercell

Answer “yes” when the warning for the change of the volume of the unit cell appears, and again click “Yes” to search for additional atoms. After this, click “OK” to exit the dialog. This way we have constructed a supercell of 3x3x3 unit cells as shown in Figure 3.5.

We have built the supercell for a general task but at this stage, it’s not convenient for preparing the surface since we first need to cleave with respect to the necessary lattice plane. So, revert to the conventional unit cell (either by reopening the data file or undoing (CTRL-z) our last action).

Now, populate the space with the conventional cell using the “Boundary” setting under the “Style” tool palette (Figure 3.6). In this case, we are building a 3x3x3 supercell by including the atoms within the -fractional- coordinate range of [0,3] along all the 3 directions (Figure 3.7).

At this stage, the supercell formed is just a mode of display - we haven’t made any solid changes yet. Also, if preferred one can choose how the unit cells will be displayed from the “Properties” setting’s “General” tab.

3.3. Lattice Planes. To visualize a given plane with respect to the designated hkl values, open the dialog shown in Figure 3.8 by selecting “Edit→Lattice Planes...” from the menu, then clicking on “New” and entering the intended hkl values, in our example (111) plane.

The plane’s distance to the origin can be specified in terms of Å or interplane distance, as well as selecting 3 or more atoms lying on the plane (multiple selections can be realised by holding down

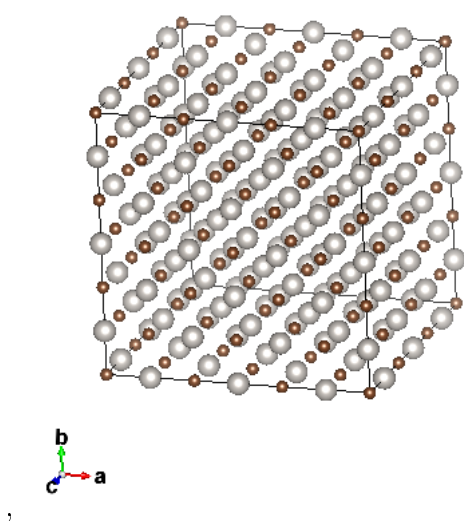


FIGURE 3.6. Designating the boundaries for the construction of the supercell.

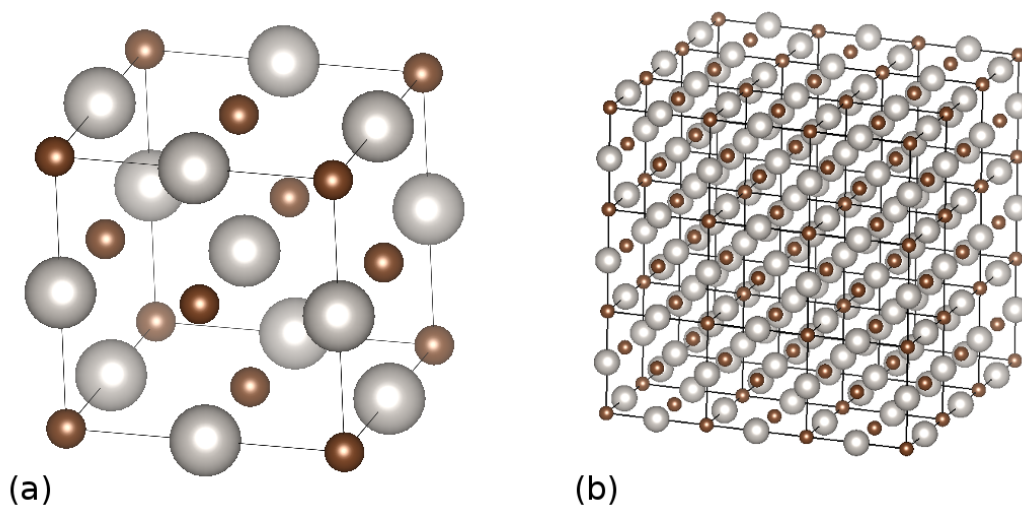


FIGURE 3.7. (a) Single unit cell (conventional); (b) 3x3x3 supercell

Lattice Planes - PtC_225.vesta

Phase: 1 New structure

Material

Specular: 255 255 255 Shininess (%): 100

Edges

☒ Show edges Line width: 1.0

Add lattice planes

Miller indices (hkl): 1 1 1

Distance from origin: 3.89711 Å (1.5 x d)

Color (RGBA): 255 0 255 192

Calculate the best plane for the selected atoms

No.	h	k	l	d (Å)	color
1	1	1	1	3.89711	255 0 255 192

New Delete Clear

PtC_225.vesta

FIGURE 3.8. Selecting the (111) lattice plane

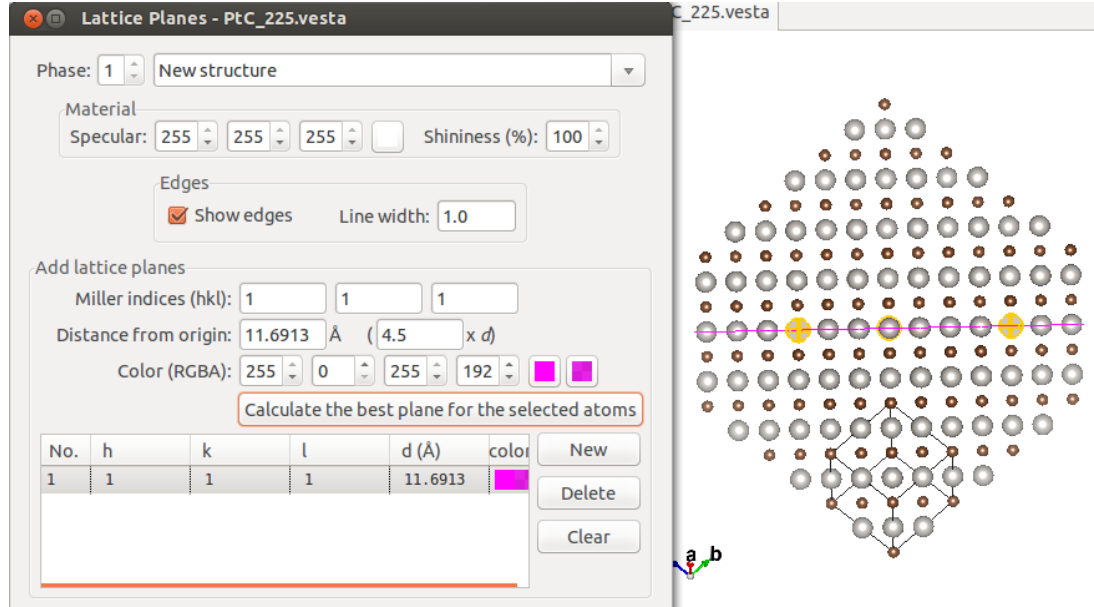


FIGURE 3.9. Selecting the (111) lattice plane in the 3x3x3 supercell

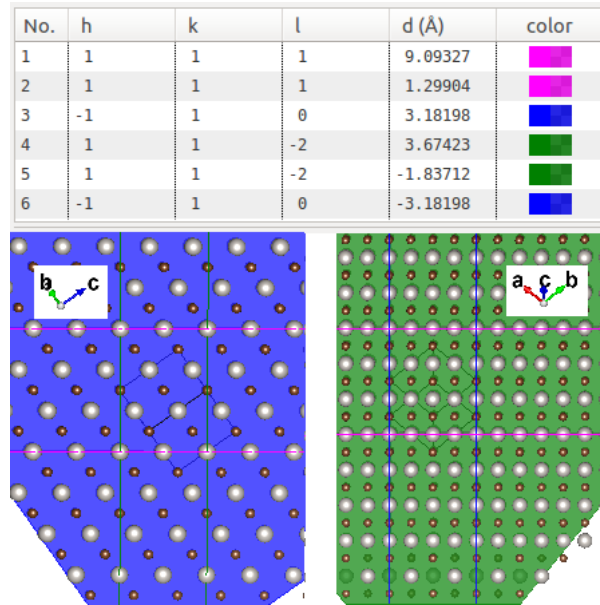


FIGURE 3.10. The new unit cell marked out by the lattice plane “boundaries”

SHIFT while clicking on the atoms) and then clicking on the “Calculate the best plane for the selected atoms” button to have the plane passing from those positions to appear. This is shown in Figure 3.9, done within a 3x3x3 supercell.

The reason we have oriented our system so that the normal to the (111) plane is pointing up is to designate this lattice plane as the surface, aligning it with the new c axis for convenience. Therefore we also need to reassign a and b axes, as well. This all comes down to defining a new unit cell. Preserving the periodicities, the new unit cell is traced out by introducing additional lattice planes. These new unit cells are not unique, *as long as one preserves the periodicities in the 3 axial directions*, they can be taken as large and in any convenient shape as allowed. A rectangular shaped such a unit cell, along with the outlying lattice plane parameters is presented in Figure 3.10 (the boundaries have been increased to $[-2,5]$ in each direction for practicality).

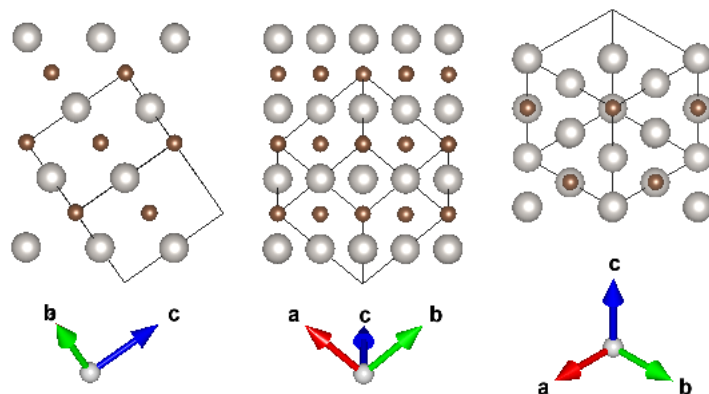


FIGURE 3.11. Filtered new unit cell with the original cell's lattice vectors

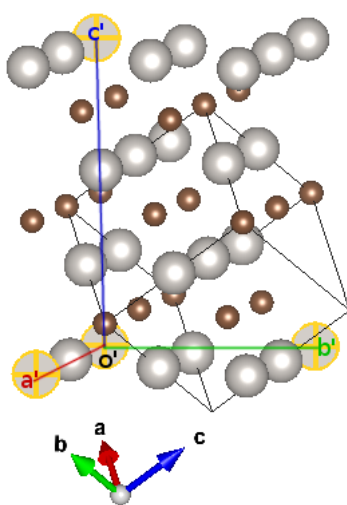


FIGURE 3.12. The reference points for the new axes

3.4. Trimming the new unit cell. The next procedure is simple and direct: remove all the atoms outside the new unit cell. You can use the “Select” tool from the icons on the left (the 2nd from top) or the shortcut key “s”. The “trimmed” new unit cell is shown in Figure 3.11, take note of the periodicity in each section. It should be noted that, this procedure is only for deducing the transformation matrix, which we’ll be deriving in the next subsection: other than that, since it’s still defined by the “old” lattice vectors, it’s not stackable to yield the correct periodicity so we’ll be fixing that.

3.5. Transforming into the new unit cell. Now that we have the new unit cell, it is time to transform the unit cell vectors to comply with the new unit cell. For the purpose of obtaining the transformation matrix (which actually is the matrix that relates the new ones with the old ones), we will need the coordinates of the 4 atoms on the edges. Such a set of 4 selected atoms are shown in Figure 3.12. These atoms’ fractional coordinates are as listed in Table 2 (upon selecting an atom, VESTA displays its coordinates in the information panel below the visualization).

Taking o' as our new origin, the new lattice vectors in terms of the previous ones become (as we subtract the “origin’s” coordinates):

$$a' = -a + b$$

$$b' = -1/2a - 1/2b + c$$

$$c' = a + b + c$$

Therefore our transformation matrix is:

Label	a'	b'	c'	o'
a	0	1/2	2	1
b	1	-1/2	1	0
c	-1/2	1/2	1/2	-1/2

TABLE 2. Reference atoms' fractional coordinates

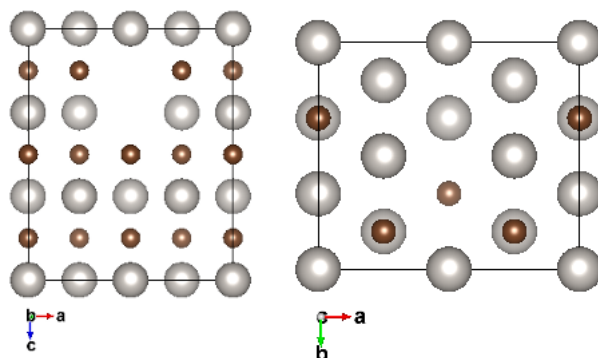


FIGURE 3.13. The transformed structure with missing atoms

$$\begin{bmatrix} -1 & -\frac{1}{2} & 1 \\ 1 & -\frac{1}{2} & 1 \\ 0 & 1 & 1 \end{bmatrix}$$

(i.e., “ $-a+b, -1/2a-1/2b+c, a+b+c$ ” – the coefficients are read in columns)

Transforming the initial cell with respect to this matrix is pretty straight forward, in the same manner we exercised in subsection 3.2, “Constructing the supercell”, i.e., “Edit→Edit Data→Unit Cell..”, then “Remove symmetry” and “Option...” and introducing the transformation matrix. A further translation (origin shift) of $(0,0,1/2)$ is necessary (the transformation matrix being “ $-a+b, -1/2a-1/2b+c, a+b+c+1/2$ ”) if you want the transformed structure look exactly like the one shown in Figure 3.11.

3.5.1. A Word of caution. Due to a bug, present in VESTA, you might end with a transformed matrix with missing atoms (as shown in Figure - compare it to the middle and rightmost segments of Figure 3.11). For this reason, always make sure you check your resulting unit cell thoroughly! (This bug has recently been fixed and will be patched in the next version (3.1.7)⁴)

To overcome this problem, one can conduct the transformation via the TRANSTRU⁵ tool of the Bilbao Crystallographic Server. Enter your structural data (either as a CIF or by definition into the text box), select “Transform structure to a subgroup basis”, in the next window enter “1” as the “Low symmetry Space Group ITA number” (1 corresponding to the P1 symmetry group) and the transformation matrix either in abc notation (“ $-a+b, -1/2a-1/2b+c, a+b+c+1/2$ ”) or by directly entering the matrix form (both are filled in the screenshot taken in Figure 3.14).

In the result page export the transformed structure data (“Low symmetry structure data”) to CIF format by clicking on the corresponding button and open it in VESTA. This way all the atoms in the new unit cell will have been included.

3.6. Final Touch. The last thing remains is introducing a vacuum area above the surface. For this purpose we switch from fractional coordinates to Cartesian coordinates, so when the cell boundaries are altered, the atomic positions will *not* change as a side result. VASP format supports both

⁴Personal communication with K. Momma

⁵<http://www.cryst.ehu.es/cryst/transtru.html>

Structure

```

225
4.50 4.50 4.50 90. 90. 90.
2
C      1      4a      0.000000      0.000000      0.000000
Pt     1      4b      0.500000      0.500000      0.500000

```

Low symmetry
Space Group
/TA number

Transformation
Matrix:

Rotational part

Origin Shift

In matrix form:

-1	-1/2	1
1	-1/2	1
0	1	1

0	0	1/2
---	---	-----

FIGURE 3.14. TRANSTRU input form

notations so we export our structural data into VASP format (“File→Export Data...”, select “VASP” as the file format, then opt for “Write atomic coordinates as: Cartesian coordinates”).

After the VASP file with the atomic coordinates written in Cartesian format is formed, open it with an editor (the contents are displayed in Table 3).

Directly edit and increase the c-lattice length from the given value (7.7942 Å in our case) to a sufficiently high value (e.g., 25.0000 Å) and save it. Now when you open it back in VESTA, the surface with its vacuum should be there as in Figure 3.15.

At this point, there might be a couple of questions that come to mind: What are those Pt atoms doing at the top of the unit cell? Why are the C atoms positioned above the batch instead of the Pt atoms?

The answer to these kind of questions is simple: Periodicity. By tiling the unit cell in the c-direction using the “Boundary...” option and designating our range of coordinates for the {x,y,z}-directions from 0 to 3, we obtain the system shown in Figure 3.16.

From the periodicity, in fractional coordinates, $f|_{z=0} = f|_{z=1}$, meaning the atoms at the base and at the very top of the unit cell are the same (or “equivalent” from the interpretational side). If we had wanted the Pt atoms to be the ones forming the surface, then we would have made the transformation with the “-a+b,-1/2a-1/2b+c,a+b+c” matrix instead of “-a+b,-1/2a-1/2b+c,a+b+c+1/2”, so the half shift would amount the change in the order, and *then* increase the c-lattice parameter size in the Cartesian coordinates notation (i.e., in the VASP file). The result of such a transformation is given in Figure 3.17.

4. ALTERNATIVE WAYS

In this work, a complete treatment of preparing a surface *in silico* is proposed. There are surely more direct and automated tools that achieve the same task. It has been brought to our attention

```

generated_by_bilbao_crystallographic_server
1.0
6.3639612198 0.0000000000 0.0000000000
0.0000000000 5.5113520622 0.0000000000
0.0000000000 0.0000000000 7.7942290306
C Pt
12 12
Cartesian
0.0000000000 3.674253214 6.495164688
0.0000000000 1.837099013 1.299064110
3.181980610 1.837099013 1.299064110
1.590990305 0.918577018 6.495164688
4.772970915 4.592774880 1.299064110
1.590990305 4.592774880 1.299064110
4.772970915 0.918577018 6.495164688
0.0000000000 0.0000000000 3.897114515
3.181980610 0.0000000000 3.897114515
4.772970915 2.755676031 3.897114515
1.590990305 2.755676031 3.897114515
3.181980610 3.674253214 6.495164688
0.0000000000 3.674253214 2.598050405
1.590990305 0.918577018 2.598050405
4.772970915 0.918577018 2.598050405
1.590990305 4.592774880 5.196178858
3.181980610 1.837099013 5.196178858
0.0000000000 1.837099013 5.196178858
4.772970915 4.592774880 5.196178858
0.0000000000 0.0000000000 0.0000000000
3.181980610 3.674253214 2.598050405
3.181980610 0.0000000000 0.0000000000
4.772970915 2.755676031 0.0000000000
1.590990305 2.755676031 0.0000000000

```

TABLE 3. The constructed (111) oriented VASP file’s contents

that the commercial software package Accelrys Materials Studio⁶ has an integrated tool called “Cleave Surface” which exactly serves for the same purpose discussed in this work. Since it is propriety software, it will not be further described here and we encourage the user to benefit from freely accessible software whenever possible.

Also, it is always to compare your resulting surface with that of an alternate one obtained using another tool. In this sense, Surface Explorer⁷ is very useful in visualizing how the surface will look, eventhough its export capabilities are limited.

Chapter 4 (“DFT Calculations for Solid Surfaces”) of Zhang’s Ph.D. thesis^[11] contains very fruitful discussions on possible ways to incorporate the surfaces in computations.

It is the author’s intention to soon implement such an automated tool for constructing surfaces from bulk data, integrated within the Bilbao Crystallographic Server’s framework of tools.

⁶<http://accelrys.com/products/materials-studio/>

⁷<http://surfexp.fhi-berlin.mpg.de>

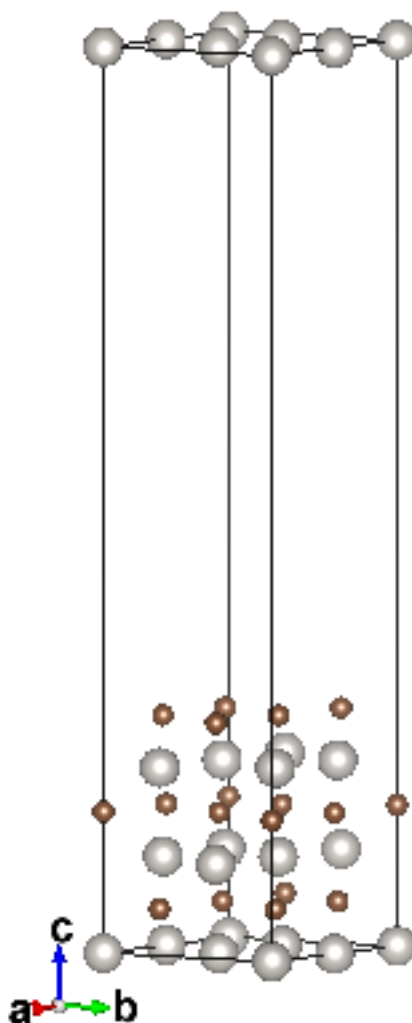


FIGURE 3.15. Prepared surface with vacuum

5. CONCLUSION

Preparing a surface fit for atomic & molecular calculations can be tedious and tiresome. In this work, we have tried to guide the reader in a step-by-step procedure, sometimes wandering off from the direct path to show the mechanisms and reasons behind the usually taken on an “as-it-is” basis, without being pondered upon. This way, we hope that the techniques acquired throughout the text will be used in conjunction with other related problems in the future. A “walkthru” for the case studied ((111) PtC surface preparation) is included as Appendix to provide a quick consultation in the future.

6. ACKNOWLEDGEMENTS

This work is the result of the inquiries by the Ph.D. students M. Gökhan Şensoy and O. Karaca Orhan. If they hadn’t asked a “practical way” to construct surfaces, I wouldn’t have sought a way. Since I don’t have much experience with surfaces, I turned to my dear friends Rengin Peköz and O. Barış Malcıoğlu for help, whom enlightened me with their experiences on the issue.

7. APPENDIX: WALKTHRU FOR PTC (111) SURFACE

- (1) Open VESTA, (“File→New Structure”)

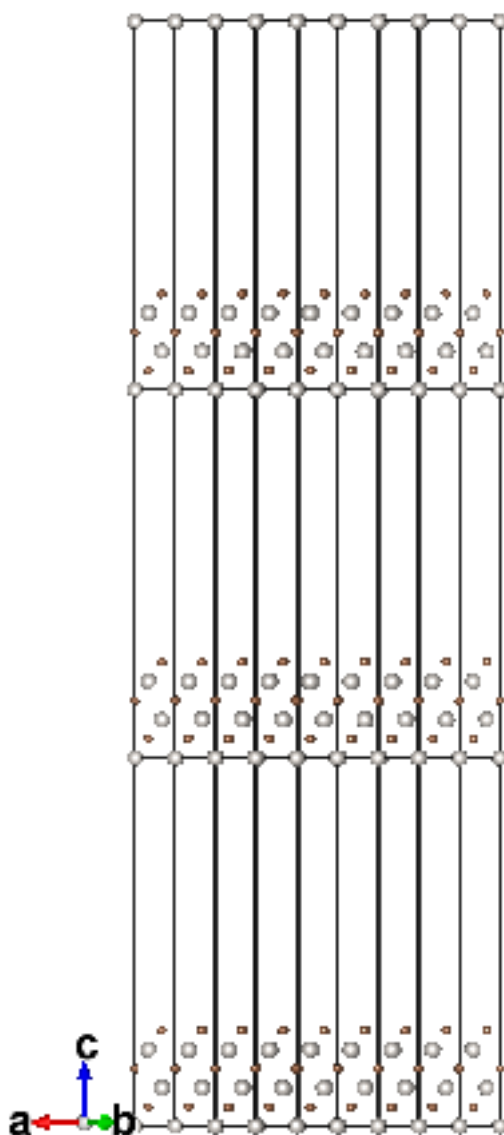


FIGURE 3.16. New unit cell with periodicity applied

- (a) “Unit Cell”:
 - (i) Space Group: 225 (F m -3 m)
 - (ii) Lattice parameter a: 4.5 Å
- (b) “Structure Parameters”:
 - (i) New→Symbol:C; Label:C; x,y,z=0.0
 - (ii) New→Symbol:Pt; Label:Pt; x,y,z=0.5
- (c) “Boundary..”
 - (i) x(min)=y(min)=z(min)=-2
 - (ii) x(max)=y(max)=z(max)=5
- (d) “Edit→Lattice Planes...”
 - (i) (hkl)=(111); d(Å)=9.09327
 - (ii) (hkl)=(111); d(Å)=1.29904
 - (iii) (hkl)=(-110); d(Å)=3.18198
 - (iv) (hkl)=(-110); d(Å)=-3.18198
 - (v) (hkl)=(11-2); d(Å)=3.67423
 - (vi) (hkl)=(11-2); d(Å)=-4.59279

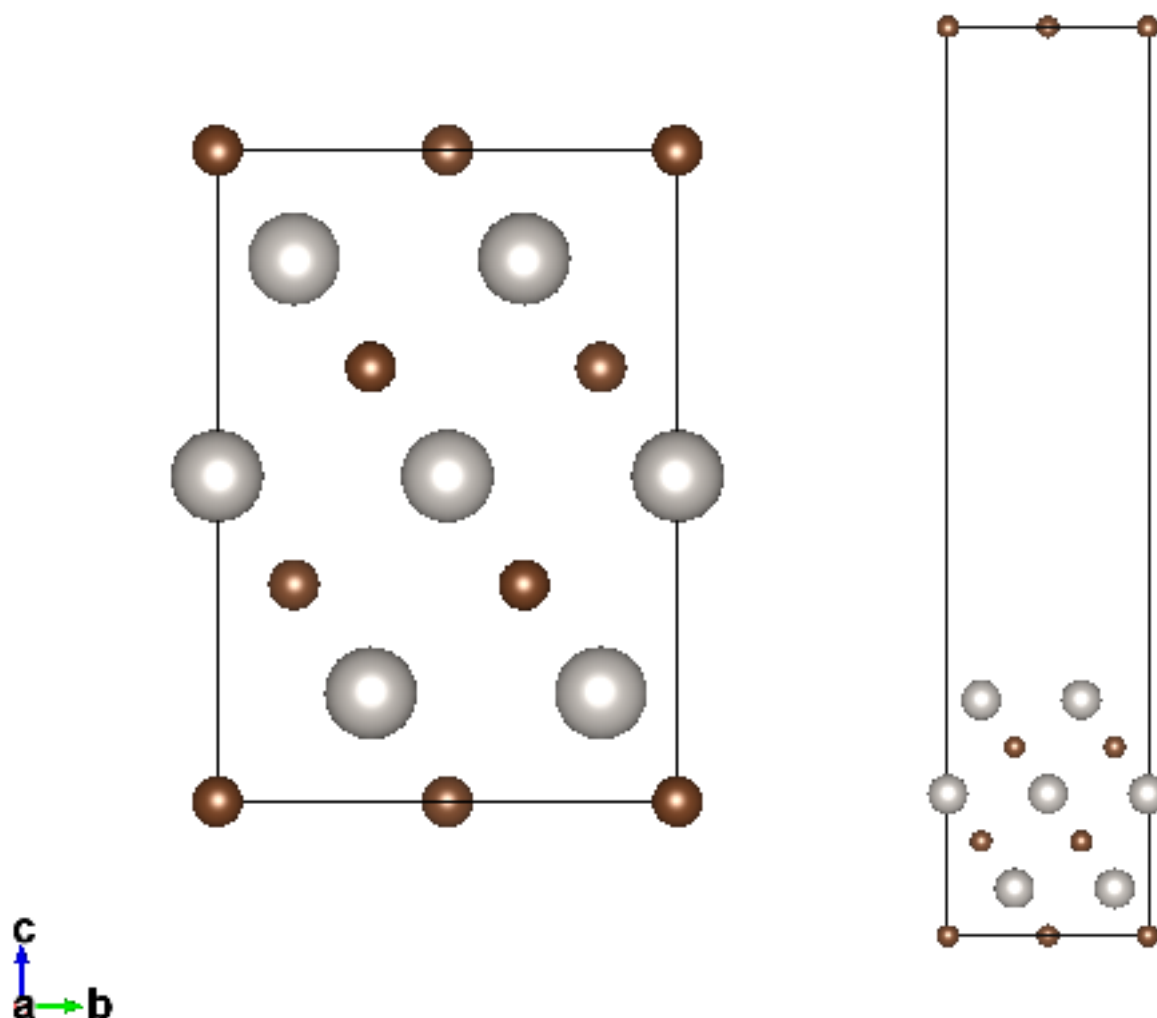


FIGURE 3.17. Alternative surface with the Pt atoms on the top (Left: prior to vacuum introduction; Center: with vacuum; Right: tiled in periodicity)

- (compare with Figure 3.10)
- (e) Select (“Select tool” - shortcut “s” key) and delete (shortcut “Del” key) all the atoms lying out of the area designated by the lattice planes.
 - (f) Select an “origin-atom” of a corner and the 3 “axe-atoms” in the edge of each direction of the unit cell, write down their fractional coordinates
 - (i) o(1,0,-1/2)
 - (ii) a(0,1,-1/2)
 - (iii) b(1/2,-1/2,1/2)
 - (iv) c(2,1,1/2)
 - (g) Subtract the origin-atom coordinates from the rest and construct the transformation matrix accordingly

$$P = \begin{bmatrix} -1 & -\frac{1}{2} & 1 \\ 1 & -\frac{1}{2} & 1 \\ 0 & 1 & 1 \end{bmatrix}$$

- (h) Transform the initial unit cell with this matrix via TRANSTRU (<http://www.cryst.ehu.es/cryst/t>) (Figure 3.14)
- (i) Save the resulting (low symmetry) structure as CIF, open it in VESTA, export it to VASP, select “Cartesian coordinates”
- (j) Open the VASP file in an editor, increase the c-lattice parameter to a big value (e.g. 25.000) to introduce vacuum. Save it and open it in VESTA.

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