

# 3D-Printing Crystallographic Unit Cells for Learning Materials Science and Engineering

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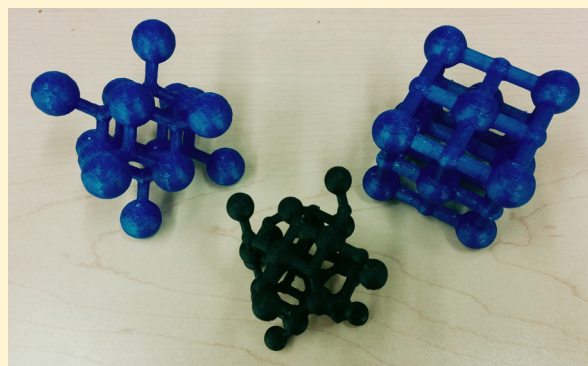
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**ABSTRACT:** Introductory materials science and engineering courses universally include the study of crystal structure and unit cells, which are by their nature highly visual 3D concepts. Traditionally, such topics are explored with 2D drawings or perhaps a limited set of difficult-to-construct 3D models. The rise of 3D printing, coupled with the wealth of freely available crystallographic data online, offers an elegant solution to materials science visualization problems. Here, we report a concise and up-to-date method to easily and rapidly transform actual crystallography files to 3D models of diverse unit cells for use as instructional aids.

**KEYWORDS:** Crystals/Crystallography, Materials Science, X-ray Crystallography, General Public, High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Inorganic Chemistry, Hands-On Learning/Manipulatives, Chemoinformatics



Typical material science and engineering introductory curriculum, as exemplified in the seminal Callister text,<sup>1</sup> includes extended discussion of crystal structures. Such a class in materials science is required as part of the general engineering core courses in many engineering degrees, and the topic is sometimes also included in advanced high school chemistry, first year general chemistry at university, and upper-division inorganic chemistry classes. A firm grasp of 3D crystal structures is essential to understanding important analytical techniques such as X-ray crystallography. The number of degrees granted in materials science has been growing in recent years,<sup>2</sup> and there is active discussion about how it is crucial that materials departments focus on education, including instructional creativity and charisma, to recruit bright students.<sup>3</sup>

3D printing is an emerging technology with applications that span across many disciplines.<sup>4</sup> Its use for creating educational materials is not new, but such endeavors do tend to underestimate the complexity of the task.<sup>5</sup> There are a handful of existing publications on how to 3D print molecules.<sup>6</sup> Many focus on either simple organic molecules or complex metal–organic frameworks. Others are highly technical or, despite being only a couple years old, already out of date in regards to the rapidly upgrading software versions. This report is focused on streamlining the process of 3D printing crystal structures so that a novice instructor can handily print visually attractive models of all seven crystal systems and even any crystalline

material registered on an open database or otherwise available as a cif file.

The advantage of the method reported here is that it focuses on unit cells discussed in materials science and engineering courses, it uses real data in a streamlined manner, it is widely accessible, and it results in visually attractive 3D models. Such 3D models are potentially useful for class discussions, but of course their utility is limited by how well they are integrated into the larger scope of the course by the instructor. 3D models are perhaps most useful to students who are kinesthetic or tactile learners, and such models could be used in conjunction with virtual visualizations, drawings, and verbal descriptions, so that students of all learning styles could have a comprehensive understanding of unit cells in materials science and engineering.

The process reported here takes only a few short steps. A material is first located within the Crystallography Open Database,<sup>7</sup> and the crystallographic data file (cif) is downloaded. The cif file is opened with VESTA,<sup>8</sup> a free chemical visualization software and, after a few quick manipulations, is exported as an wrl file. The wrl file is then opened with Blender, another free software package, and undergoes brief editing before being exported as an stl file.<sup>9</sup> This stl file, with perhaps some scaffolding added, can then be fed directly to 3D printers such as a MakerBot. The 3D crystal structures pictured in this report were all printed on the Columbia University Science

Library 3D MakerBot Replicator 2 printer, but may also be outsourced to general 3D printer companies such as ShapeWays. Although a 3D printer such as the MakerBot 2 Replicator is rather expensive, it is quite affordable to outsource the printing of a few models to companies such as Shapeways. The models presented here were printed using polylactic acid (PLA) filament, which results in sturdy and appealing 3D unit cells for crystallographic systems. Process steps are detailed below.

## ■ PROCESS

### Crystallography Open Database and Material Selection

The Crystallography Open Database (COD) is a great resource.<sup>7</sup> The COD data can be easily searched, perhaps by element, knowing what material is desired to be modeled. A search for Ce and O, for example, returns a few results ( $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ ), with journal references for further details on the entry. Clicking on CIF downloads the cif crystallography file for the indicated entry. The COD boasts over 318 000 entries and of course includes all materials that an introductory student would encounter. Although the COD is the method preferred here, other alternative databases are available.<sup>10</sup>

**Vesta.** Visualization for Electronic and Structural Analysis (VESTA) is freely available software.<sup>8</sup> It is useful for visualizing cif files, as well as many other purposes. It was found to be more intuitive and simple to use, for the purposes here, when compared to Mercury,<sup>11</sup> which is another software platform widely cited in the molecular model 3D printing community. Once the cif file is opened in VESTA (File → Open), the default display is ball-and-stick with invisible bonds. To make the bonds visible, bring up the bonds menu (Edit → Bonds). On the bonds menu, click “New” to create a new set of bonds. The unit cells usually look best with the boundary mode set to not search beyond the boundary, and editing the minimum and maximum bond length such that only neighboring pairs are bonded. Once the appropriate bonds are created and confirmed, the properties menu should be accessed (Properties button under Style tab). To aid the stability of the printed structure, atom and bond sizes should probably be increased. Multiplying the atom sizes by 1.5 and tripling the bond cylinder radius was a successful combination in many cases. This can be done under the atoms tab of the properties menu and the bonds tab, respectively. Finally, the file can be exported (File → Export) as a wrl file.

**Blender.** Blender is a powerful graphic visualization software available for free download.<sup>9</sup> Its ability to visualize molecules is helped by the free plugin ePMV (embedded Python Molecular Viewer<sup>12</sup>). The default structures that appear when opening Blender can be deleted by right-clicking on them, hitting delete, and confirming. The wrls can be imported (File → Import → wrl), and then the ePMV button at the top right of the window should be selected. The whole molecule should be selected (Select → Select All), and then converted to a print object (Object → Convert To → Mesh from Curve/Meta/Surf/Text). Now the file is ready to be exported as an stl (File → Export → stl). This stl file can be uploaded onto sites such as Will It 3D Print<sup>13</sup> to confirm its compatibility with the 3D printing process, which requires 3D model files to have particular characteristics in order for the printer's software to properly interpret them as solid objects.

**Further File Edits and Printing Process.** The analysis carried out by Will It 3D Print<sup>13</sup> is helpful but not always

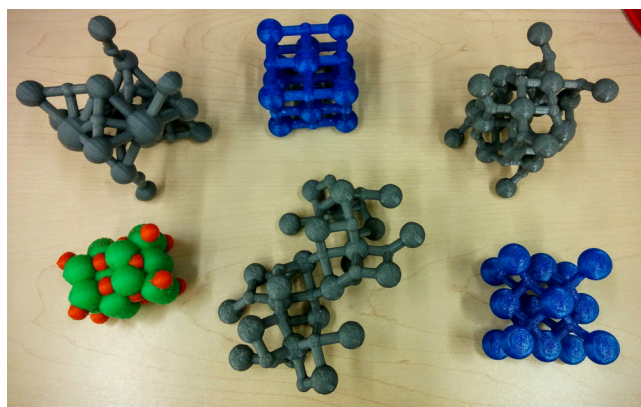
sufficient to ensure a quality print. There are many variables affecting the final product, including the quality and condition of the supplied plastic material, the particular characteristics of the specific printer being used, and occasionally even the ambient temperature. It is likely that the successful production of a finished model will require some iterations of design modification and printer settings adjustments.

The simplest next step is to open the stl file in the Makerbot Desktop software that will prepare the file for printing. With the use of the Change Position dialogue box, the model should ideally be placed at the center of the platform, by clicking both the On Platform and the Center buttons. The Change Rotation dialogue box can be used to change the orientation of the model relative to the printing surface; this can be useful in terms of minimizing the surfaces that will require a support structure to be printed beneath them, thereby using less plastic in the process. Under Settings, standard quality options (0.2 mm layer height, 10% infill, 2 shells, 200 °C extrusion temperature when using PLA) are a good starting point, making sure to check the Raft and Supports boxes. A raft is a flat layer of plastic that is deposited on the platform to serve as an attachment point to the printed model; the supports are extra plastic parts printed to brace parts of the model that would otherwise be extruded into midair. The Makerbot Desktop version of supports are thin sheets of plastic that can be torn off after printing by hand or using tools such as pliers. Supports are particularly important since the ball-and-stick models will have overhanging sections that cannot be printed successfully without an underlying structure. Once the settings are saved, clicking the Export Print File button will produce a preview of the print process, and subsequently, a saved file with printer instructions (in the case of the MakerBot, a file with the extension X3G). This file can then be sent to the printer either through the MakerBot software itself, if the computer is connected to the printer, or it can be saved to a SD card to be inserted into the printer and selected using the MakerBot's built-in menu.

## ■ RESULTS

### 3D Printed Unit Cells

Shown in Figure 1 are examples of 3D printed unit cells.



**Figure 1.** Unit cells, 3-D printed using the process described, of (from top left clockwise): perovskite, rock salt, tetragonal spinel, fluorite, corundum, and space-filling tetragonal spinel featuring dual atom colors. Unit cells pictured here are about 3 in. tall.

## Variations

The process described here is of course only a streamlined and quick guide for beginners. This process can be readily adapted to suit various related purposes, including printing with instruments other than the MakerBot, or using different software to generate the necessary final product. For example, a program called Meshmixer<sup>14</sup> can be used to generate supports that are different from the ones automatically generated by the MakerBot Desktop software. Whereas the MakerBot supports are thin strips of plastic, MeshMixer creates tubular supports with very small attachment points to the model itself, possibly resulting in a cleaner final product once the supports are removed. Meshmixer generates customizable supports and allows for manually placing and removing supports from different parts of the model; experience may suggest that a given section needs more support than calculated by the software. Once the model is finished, it can be exported once again in stl format, to be then opened with MakerBot Desktop for the final preparation.

With the method described here, the easiest way to distinguish between different atom types is by atomic size. The VESTA program easily allows switching between atomic radius or ionic radius or whatever custom radius the user chooses. Other options include painting the atoms different colors by hand after the printing process. 3D printing in multiple colors is challenging because in many cases two different files must be created (one for each color). The space-filling tetragonal spinel featuring dual atom colors pictured in Figure 1 was achieved by alternatively setting atoms of one type to a radius of zero and exporting individually; it was then manufactured using a printer equipped with dual extruders, one for each color. Many more advanced techniques are possible once a foundational familiarity (as described in this report) has been achieved.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Callister, W. D. *Materials Science and Engineering: An Introduction*, 4th ed.; John Wiley & Sons, Inc: New York, 1997.
- (2) Cargil, G. S., III; Van Tyne, C. J. Status and Evolution of Accreditation for Materials Programs in the US. *J. Mater. Educ.* **2009**, *31* (1–2), 99–116.
- (3) A Matter of Survival? *Nat. Mater.* Editorial. **2003**, *2* (1), 1.10.1038/nmat807
- (4) Horvath, J. *Mastering 3D Printing*; Apress: Berkeley, CA, 2014.
- (5) Mercuri, R.; Meredith, K. An Education Venture into 3D Printing. *4th IEEE Integrated STEM Education Conference* **2014**, 1–6.
- (6) (a) Chen, T.-H.; Lee, S.; Flood, A. H.; Miljanić, O. Š. How to print a crystal structure model in 3D. *CrystEngComm* **2014**, *16*, 5488–5493. (b) Scalfani, V. F.; Vaid, T. P. 3D printed molecules and extended solid models for teaching symmetry and point groups. *J.*

- Chem. Educ.* **2014**, *91*, 1174–1180. (c) Stone-Sundberg, J.; Kaminsky, W.; Snyder, T.; Moeck, P. 3D printed models of small and large molecules, structures and morphologies of crystals, as well as their anisotropic physical properties. *Cryst. Res. Technol.* **2015**, *50* (6), 432–441. (d) Moeck, P.; Stone-Sundberg, J.; Snyder, T. J.; Kaminsky, W. Enlivening 300 level general education classes on nanoscience and nanotechnology with 3D printed crystallographic models. *J. Mater. Educ.* **2014**, *36*, 77–96. (e) Kitson, P.; Macdonell, A.; Tsuda, S.; Zang, H.; Long, D.-L.; Cronin, L. Bringing Crystal Structures to Reality by 3D Printing. *Cryst. Growth Des.* **2014**, *14* (6), 2720–2724. Casas, L.; Estop, E. Virtual and Printed 3D Models for Teaching Crystal Symmetry and Point Groups. *J. Chem. Educ.* **2015**, *92*, 1338.
- (7) Crystallography Open Database. <http://www.crystallography.net/> (accessed August 2015).
- (8) Visualization for Electronic and Structural Analysis (VESTA). <http://jp-minerals.org/vesta/en/> (accessed August 2015).
- (9) Blender. <https://www.blender.org/> (accessed August 2015).
- (10) Crystal Structure Databases. [http://serc.carleton.edu/research\\_education/crystallography/xldatabases.html](http://serc.carleton.edu/research_education/crystallography/xldatabases.html) (accessed August 2015).
- (11) Mercury. <http://www.ccdc.cam.ac.uk/Solutions/FreeSoftware/Pages/FreeMercury.aspx> (accessed August 2015).
- (12) Python Molecular Viewer. <http://www.autopack.org/install/blender-installation> (accessed August 2015).
- (13) Will It 3D Print. <http://www.willit3dprint.com/> (accessed August 2015).
- (14) Meshmixer. <http://www.meshmixer.com> (accessed August 2015).