

## **Animation of Crystal Structure Variations with Pressure, Temperature and Composition**

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### **INTRODUCTION**

The mineralogical literature is full of images of crystal structures. These images provide a satisfying way to understand and interpret the results of a crystal structure analysis. They also provide a visual model for understanding many physical properties. For instance, an atomic-scale understanding of the cleavage in mica is immediately obtained once an image of its structure has been seen.

Now, however, with the advent of personal computers that can compute and display images quickly, it is possible to routinely create dynamic images of crystal structures, not only by simply spinning them about an axis, but also as a function of temperature, pressure and composition. Examples of these animations are found on the cover of this volume and at the edges of the pages of this chapter. Such dynamic images are effective means for presenting papers at meetings using computer projectors, and could have a place in on-line journals. They can be a useful guide for understanding the results of an experiment and are indispensable in the classroom situation. Constructing a series of images, stored as bitmaps, and then displaying these images one after another is an effective way to make the computer animations. This paper presents an outline of the procedures for making these sorts of movies.

It is anticipated that the contents of this chapter will soon be outdated, because computer-generated animation techniques are still rapidly developing. As such, we at least hope to provide a starting point and some motivation for those who would like to present and visualize their data in a new and exciting way.

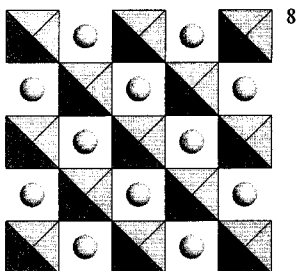
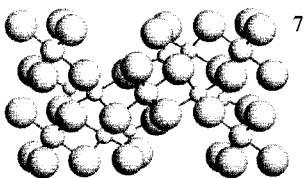
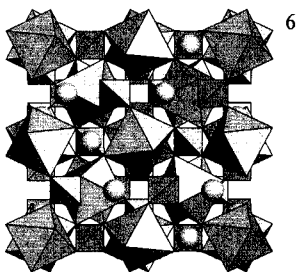
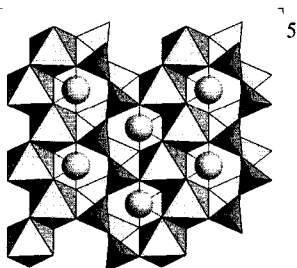
### **DATA SELECTION**

A movie can be easily constructed from a set of data if the data can be characterized by a one-dimensional parameter. Because a movie is a set of images, or frames, displayed as a function of time, we can use the parameter as a proxy for time. For instance, to make a movie of a crystal structure as a function of temperature we make a set of frames with each frame containing an image of the structure at a different temperature. Likewise, combining images of the structure at various pressures can produce animations displaying the effect of pressure.

The change in a structure as a function of composition can be effectively constructed in a variety of ways. The structural changes of a binary solid solution, e.g. diopside-jadeite, can be constructed as a function of the mole fraction, X. Other chemical changes may be more difficult to construct. For instance, constructing an animation of the garnet structure as a function of chemistry is complicated because it is a multicomponent system with more than one chemical parameter. In some cases an alternative parameter can be found, such as cell volume or length of a cell edge.

### MAKING THE IMAGES

Each frame of the movie must be constructed separately, and stored as a bitmap. There are a number of details to keep in mind when making these images. One of the most important is the choice of a color model for storing the bitmaps. Here is some background on the color models used in today's computers. Each pixel is constructed of three components that emit red, green or blue, the so-called RGB model. A given color is obtained by defining the intensity of each of these three components. For instance, the combination of intense red, with low intensity green and blue, produces the color red. The color yellow is constructed by combining intense red and green, with low intensity blue.



Presently, there are three standard choices for a color model on a computer: 8, 16, or 32 bits. The bit sizes are related to the amount of memory required to store the color of a single pixel on the screen. The 8-bit model is smaller than the 32-bit model. With the 8-bit model, one can define the intensity of the red, green or blue component with a resolution of 1 part in 64. This means that there are  $64^3 = 262,144$  possible colors that can be constructed. However, 8-bit video graphic cards are constrained to a choice of only 256 of these colors. The specific 256 colors chosen by a user are known as the "palette." The 8-bit model is also called the 256-color model. VGA video adapters are restricted to the 256-color model. The 16-bit model can display all 262,144 possible colors and it defines the limit of a SVGA video adapter. With the 32-bit model, the intensities can be defined with a resolution of 1 part in 256, so there are  $256^3 = 16.8$  million colors available. The 32-bit model can only be constructed with "true color" video adapters.

Once an image is constructed on the computer, it must be stored as a bitmap. Bitmaps constructed from the 256-color model are small and can be accessed and displayed quickly. The bitmaps constructed with the 16- and 32-bit models take up more storage space and are slower to display.

For this reason, many graphics software packages only accept bitmaps constructed from the 256-color model. Furthermore, many of the video projectors used to display computer images on a screen only accept images constructed with the 256-color model. Therefore, at the time of this writing, it is recommended that movies be constructed from bitmaps made with the 256-color model.

It is important that the choice of the 256 colors be fixed to the same palette for all the frames. If the palette varies, then displaying the movie will require remapping the palette after each frame. This function will constrain the

speed of the movie. Further-more, if the palette is not fixed, and not remapped, then a very disturbing flicker can be observed as the movie progresses between frames. Therefore, choose a single palette of colors for the entire movie.

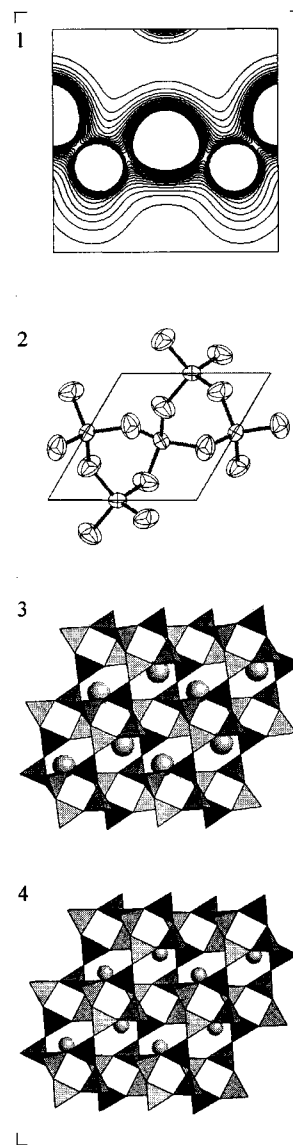
An effective use of color can be obtained by gradually changing the color of an atomic site for movies of changes in site chemistry. For instance, a movie showing the change in structure of the forsterite ( $\text{Mg}_2\text{SiO}_4$ ) to fayalite ( $\text{Fe}_2\text{SiO}_4$ ) solid solution could have the M1 and M2 octahedra change from green to brown, with the exact shade chosen as a function of the composition.

The choice of a background color is arbitrary, but experience has shown that some video projectors have trouble displaying movies constructed with white backgrounds. The projectors may try to automatically refocus, resulting in erratic display.

The size of the bitmap must also be chosen. For movies that will be presented from the computer, the resolution should probably be one of the standard choices:  $640 \times 480$ ,  $800 \times 600$ , or  $1024 \times 768$  pixels. The first number represents the width of the image in pixels, and the second is the height. The  $640 \times 480$  resolution is fast to display, but the borders of spheres and polygons will be ragged. If the animations are to be displayed through a video projector, then its capacity should be investigated. All the video projectors can display the  $640 \times 480$  resolution, but only newer models will display the others. For choices of non-standard resolutions, the only serious consideration should be to maintain the 4:3 ratio between width and height, in order to keep the aspect ratio constant so that spheres remain round. The movies that we make for display on the Internet are usually at a resolution of  $320 \times 240$  pixels. This is large enough to view details on a PC and small enough to load quickly. Problems can occur if the images are made at one resolution and the movie is displayed at another resolution. Lines and edges of polygons become ragged.

For images to be displayed as hard copy the important considerations are the final image size and the resolution of the printer. For instance, the images on the side of the pages in this chapter were made to be  $1\frac{3}{4}$  inches square. Our printer has a 600 dot per inch resolution. Therefore, we chose to make the images  $1.75 \times 600 = 1050$  pixels square.

There are a number of bitmap formats that can be used to store the images. One of the oldest is PCX, which is constructed to match the structure of video memory so they are very fast to load, but large. BMP, GIF and JPG are also popular, but slower to load to the screen. If the movies are to be displayed on the Internet, then it is recommended that



the frames be stored in the GIF format.

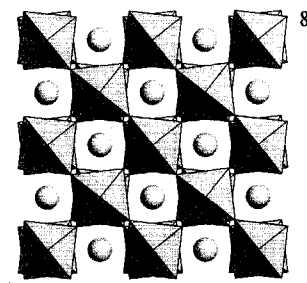
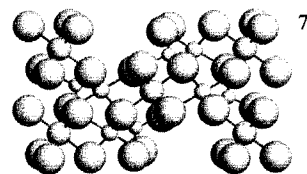
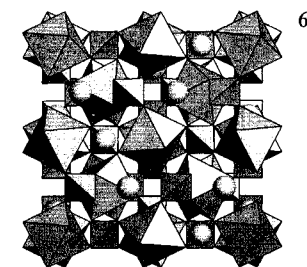
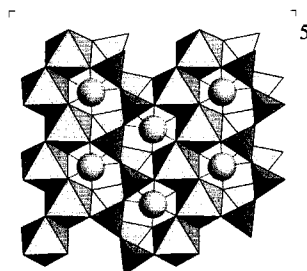
Another important consideration when making images is the choice of scale. The width of an image should be fixed, say to 25 Å, and maintained for each frame. Depending upon the purposes of the animation, the scale should be chosen from the largest image. For instance, if a movie is being made of a structure at pressure, then choose the scale from the image of the room pressure data. If it is being made of a structure at temperature, then choose the scale from the high-temperature image. Of course, this scaling consideration is not necessary for some movies, for instance if you wanted to zoom in on a structure.

Along with scale, the choice of orientation and origin should also be addressed. Keep the center of the image fixed so that expansion or contraction is displayed relative to this point. Usual choices for the fixed point are the origin, [0,0,0], or the mid-point,  $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ , of a unit cell. Animation of phase transitions may require some preliminary considerations in order to translate the origin so that a common point is fixed for both phases. This procedure was required for the pyroxene and perovskite examples.

### SPACING THE FRAMES

In many cases, a movie can be constructed by stringing together images of the crystal structure obtained from an experimental dataset. For instance, suppose that we wanted to make an animation of a crystal structure as a function of pressure from data recorded at 0, 5, 8, and 12 GPa. Then a movie can be constructed with images made at each of these pressures. The progress of the movie may not be smooth however, since the display of the frames is linear but the pressures are not. To get smoother movies, the structural data can be interpolated, say by a least-squares method, and frames constructed at 0, 3, 6, 9, and 12 GPa, for instance. Some datasets do not display enough variation to see the changes. In this case, consider extrapolating the data.

If a movie is being made to show a phase transition, then careful consideration to spacing the images is necessary. Any extrapolation of the data must originate from the transition point. Effective representation of transformations can also be made using only two frames, one from each side of the transition. The movies of the pyroxene and perovskite transitions shown in this chapter were made from three frames, with each image constructed from a different phase.



## DISPLAYING THE MOVIE

Once the frames have been constructed then the movie can be displayed. We have had great success by simply making the images in the PCX format and displaying them one after another with a simple in-house DOS program. This method works well because images in the PCX format are fast to load. However, this will not work in future WINDOWS environments because they will no longer support DOS-based programs. Furthermore, DOS programs cannot display movies over the Internet.

In order to overcome this limitation we have started using the GIF89 format to display animations. This format requires the frames to be processed into a single GIF file that displays the animation when opened. Some sort of software is required to process the frames. We use shareware called "Movie Gear" made by Gamani Productions. Animations made with this format can also be displayed on the Internet, and are readily imported into other software, such as "PowerPoint," for presentation purposes. At this time, the GIF89 format only supports 256 colors.

## SOFTWARE SOURCES

### American Mineralogist Crystal Structure Database

This is a set of all the crystal structure data ever published in the *American Mineralogist*; it is maintained by Robert Downs for the Mineralogical Society of America. It is a source of digital data files used to construct images and can be found at

<http://www.geo.arizona.edu/xtal/cgi/test>

### XTALDRAW

This software, written by R.T. Downs, K. Bartelmehs, and K. Sinnaswamy may be used to make images of crystal structures. It is available with a large set of data files at

<http://www.geo.arizona.edu/xtal/personal.html>

### Movie Gear

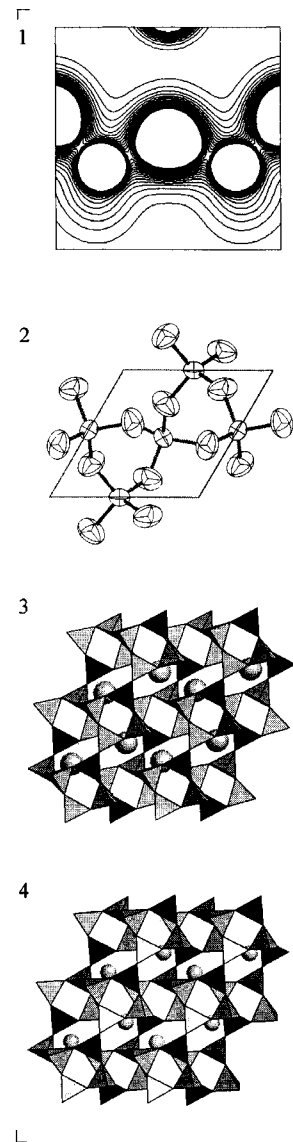
Shareware to construct animated GIF89 files that display the mineral movies on both the PC and on the Internet. We do not control access to this software, but as of this publication date, it can be obtained from

<http://www.gamani.com>

### Summary

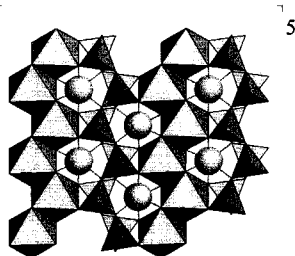
Examples and detailed instructions to make crystal structure movies are at

[http://www.geo.arizona.edu/xtal/movies/crystal\\_movies.html](http://www.geo.arizona.edu/xtal/movies/crystal_movies.html)



## EXAMPLES

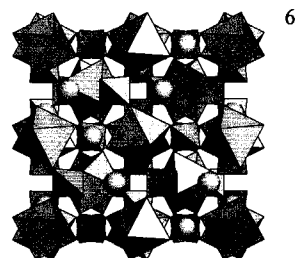
The 14 image-sequences for Examples 1-4 (those on the right margins) may be viewed by flipping through the odd pages 91-117, in that order. The image-sequences for Examples 5-8 (left margins) may be viewed by flipping through the even pages 116-90, in that order.



5

**Example 1: Electron density of Na  $\cdots$  Si-O-Si**

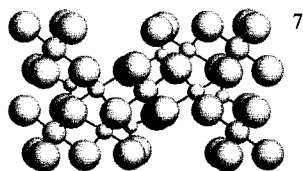
These images show the change in electron density as Na approaches and leaves the bridging  $O_{br}$  atom in an Si-O-Si linkage. The electron density was calculated with the Gaussian program on the molecule  $H_9NaO_5-H_6Si_2O_7$ . The  $H_9NaO_5$  molecule was fixed in shape so that when it was close to the bridging  $O_{br}$  atom it formed a  $NaO_6$  octahedron. The H atoms were used to make the molecule neutral. The data for each frame was constructed by minimizing the energy of the group while holding the Na- $O_{br}$  distance fixed and varying the  $H_6Si_2O_7$  geometry. There are seven unique frames, constructed with  $R(Na-O_{br})$  varying from 3.2 Å to 2.0 Å in steps of 0.2 Å.



6

**Example 2: Displacement ellipsoids of quartz.**

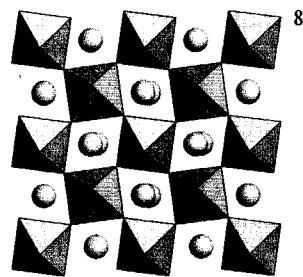
These images show the change in the displacement ellipsoids of quartz ( $SiO_2$ ) as a function of temperature using the experimental data of Kihara (1990). The ellipsoids display 99% of the probability density. Fourteen unique images were constructed at  $T = 298, 398, 498, 597, 697, 773, 813, 838, 848, 859, 891, 972, 1012, 1078$  K without smoothing. The phase transition from the  $\alpha$  to  $\beta$  phase occurs between frames 8 and 9. Each image is constructed with a width of 10 Å using the XTALDRAW software.



7

**Example 3: Microcline at pressure.****Example 4: Albite at pressure.**

These images show the changes in the crystal structures of microcline ( $KAlSi_3O_8$ ) and albite ( $NaAlSi_3O_8$ ) as a function of pressure using data from Allan and Angel (1997) and Downs et al (1994), respectively. The  $SiO_4$  and  $AlO_4$  groups are displayed as tetrahedra while the K and Na atoms are displayed as spheres. The images are constructed from a slice of the structure ( $0.5 \leq y < 1.0$ ), looking down (010) with a width of 26 Å using the XTALDRAW software. The data for each frame were obtained by smoothing the experimental results using least-squares on pressure, and computing the structure at 0, 10 and 20 GPa. The images can be compared in order to see the differences in the compression mechanism of the two structures (Downs et al. 1999).



8

**Example 5: Clino-ferrosilite phase transitions.**

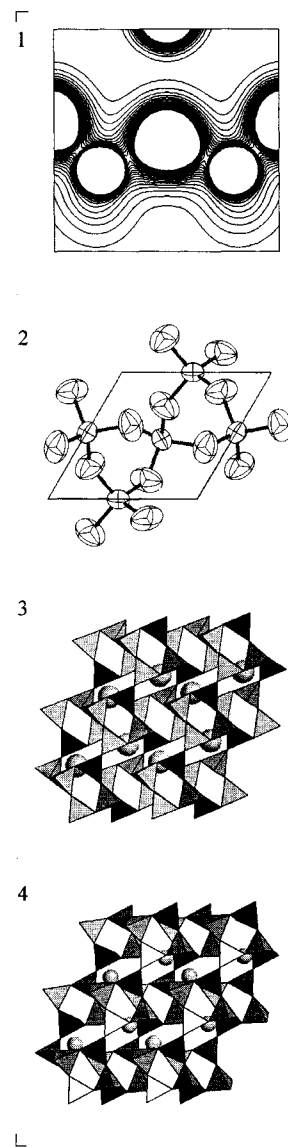
This movie is made of three images, each constructed from data at different pressure and temperature conditions and each representing a different topology. The first image is constructed from the  $C2/c$  data of Sueno et al (1984) at  $T = 1050^\circ\text{C}$ . The second and third images are from the room condition  $P2_1/c$  and the  $P = 1.87$  GPa  $C2/c$  data, respectively, of Hugh-Jones et al (1994). The images were made using the XTALDRAW software with a width of  $20 \text{ \AA}$ , looking down  $(100)$ . The origin was chosen in order to bring  $\text{O}_2$  to the center of each image. The  $\text{M}_2$  cation is displayed as a sphere, while the  $\text{SiO}_4$  and  $\text{M}_1\text{O}_6$  groups are displayed as polyhedra. Electron densities were constructed by Kevin Rosso to determine the bonding topologies of the  $\text{M}_2$  site. The images demonstrate the changes in bonding that are brought about by changes in pressure and temperature (Downs et al. 1999).

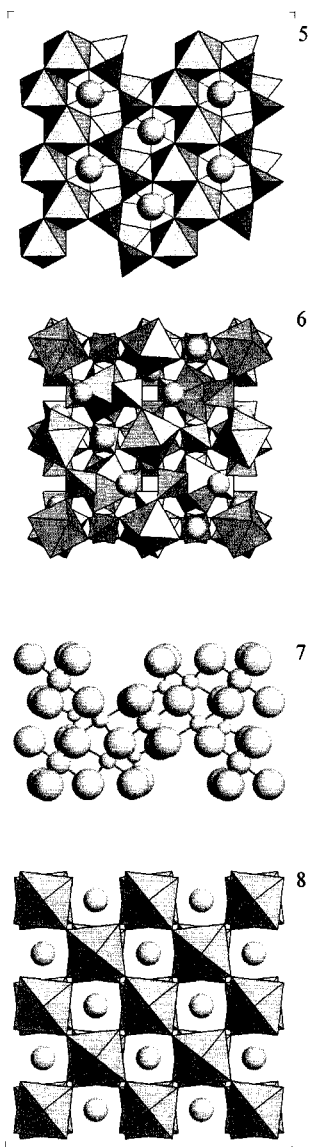
**Example 6: Garnet as a function of chemistry.**

This movie illustrates an attempt to provide an overview of the changes in the silicate garnet structure as a function of chemistry. A total of 31 garnet structures from the literature were chosen for this study. These garnets varied in chemistry and their data were collected at a variety of temperatures and pressures. It was first assumed that we could plot the structural variations as a function of  $a$ -cell edge. The data were subjected to least-squares and a movie was constructed that did not make sense. Upon closer examination it was determined that the  $y$ -coordinate of the  $\text{O}$  atom did not vary linearly with  $a$ -cell edge, but instead formed two distinct linear trends that intercepted at  $a = 11.8 \text{ \AA}$ . Consequently, the data were split into two groups, those structures with  $a \geq 11.8 \text{ \AA}$  and those with  $a < 11.8 \text{ \AA}$ . Both sets were independently subjected to linear least-squares of all crystallographic parameters as a function of the  $a$ -cell edge. Fourteen model structures were then constructed with the  $a$ -cell edge varying from  $13.6$  to  $10.0 \text{ \AA}$  in steps of  $0.3 \text{ \AA}$ . The figures were made using XTALDRAW with the tetrahedral and octahedral sites illustrated as polygons, and the dodecahedral site as a sphere. The figures are  $20 \text{ \AA}$  across and are viewed down  $[001]$ . As the cell edge decreases you should observe that the tetrahedra rotate first in one direction, and then in the reverse direction.

**Example 7: Olivine as a function of pressure.**

This movie illustrates the change in the olivine structure as a function of pressure. The data is from a high-pressure study of the compression of  $\text{LiScSiO}_4$  olivine by Hazen et al (1996). The structural parameters were fit to a linear least-squares model against pressure, and model data





were computed at 0 to 20 GPa in steps of 5 GPa. These five frames are repeated in the sequence 12345432123454 known as the “ping pong model.” The figures were drawn with XTALDRAW at a width of 16 Å, viewed down [001]. The oxygen atoms are the larger spheres. The movie demonstrates that the O atoms become more nearly closest-packed with increasing pressure.

#### Example 8: Perovskite phase transitions.

This movie illustrates some of the changes in symmetry of the perovskite structure. The data is from high-temperature studies of  $\text{SrZrO}_3$  (Ahtee et al. 1976; Ahtee et al. 1978). There are three unique images illustrating the cubic, tetragonal and orthorhombic symmetries. The figures were drawn with XTALDRAW at 16 Å widths. The structures are all viewed down [001]. The cubic structure is translated  $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$  relative to the other two. The  $\text{ZrO}_6$  groups are drawn as octahedra and the Sr atom as a sphere.

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