CHAPTER THREE

Crystal Structure Analysis and Editing

3.1 Crystal structure analysis program *Builder*

The *Builder* program is used to analyze structural details of a crystalline solid and edit its structure if necessary. Thus the use of *Builder* may involve the following tasks: (1) to prepare an input file, *filename.CI*, for a crystal under study, (2) to view the crystal structure and analyze spatial relationships between atoms, and (3) to edit the crystal structure to produce a set of atom coordinates needed for electronic structure calculations.

Builder lets the user generate an input file, *filename.CI*, interactively. It allows the user to work with more than one crystal structure at a given time and have multiple views of a given crystal structure. A crystal structure can be viewed in terms of a unit cell or multiple unit cells and can be rotated, translated, and scaled interactively. To facilitate the editing of a current structure on the screen, *Builder* provides various ways of selecting atoms and bonds from the structure and deleting them. It also enables the user to add atoms to the current structure and replace some atoms of the current structure with other atoms.

The *Builder* window has menus *File*, *Build*, *Display*, *Setting*, and *Window* (*Figure 3.1*), and each menu has a set of commands in the drop-down list. The main functions of these menus are as follows:

- ***File***

  To load an existing input file (i.e., *filename.CI*) or the input-making program (i.e., *Define Crystal Structure*) into *Builder*.

- ***Build***

To edit a current structure on the screen to produce a set of atom coordinates for electronic structure calculations.

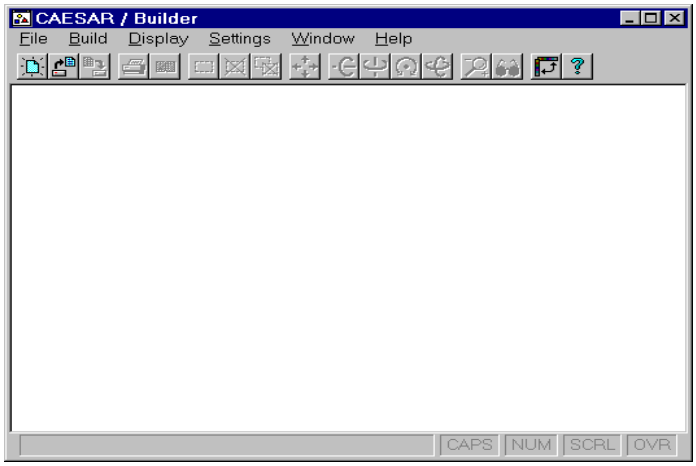

Figure 3.1. Builder window.

- ***Display***
  To display and analyze the geometrical details of a current structure.

- ***Setting*** and ***Window***
  To change the graphic representation of a current structure.

To facilitate the analysis and editing of a current structure on the screen, *Builder* provides the icons for frequently used commands on the tool bar of its window. The user can find the functions of these icons by placing the mouse cursor on top of them. These icons are concerned with:

- opening an existing input file for *Builder*

- creating a new input file for *Builder*

- selecting and unselecting atoms and bonds of a current structure on the screen

- moving, rotating and zooming the current structure

- providing a stereoview of the current structure

Each icon is enabled or disabled when clicked with the mouse.

3.2 Creating a crystal structure

The *File* menu has two commands for creating a crystal structure. If an input file, *filename.CI*, containing the structural information of a crystal already exists, then it is loaded into *Builder* using the *Open* command. If not, the *New* command is used to load the input-making program, *Define Crystal Structure*, and show its dialog box (*Figure 3.2*). The use of this interactive program is self-

explanatory. After the completion of an input-making session, it is recommended to save the resulting file under a file name, *filename.CI*, using the *Save As* command.

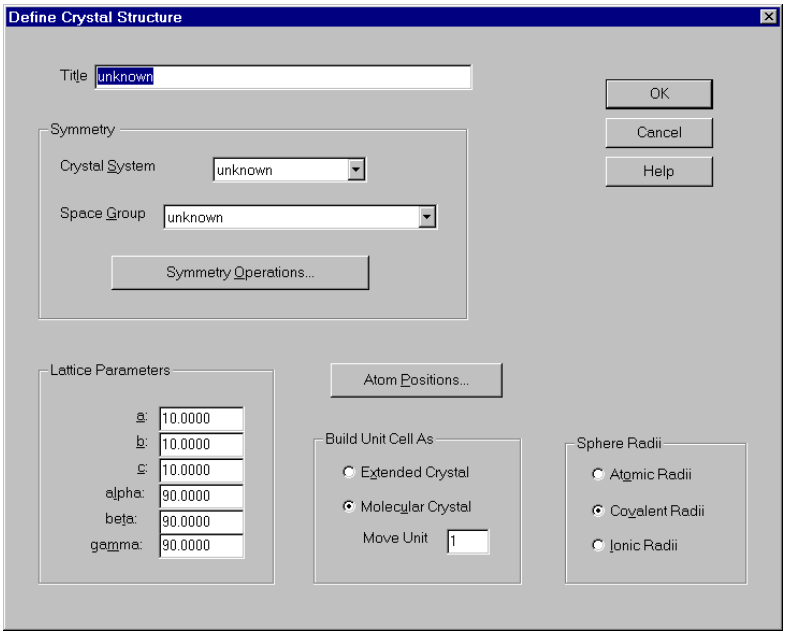

Figure 3.2. Define Crystal Structure dialog box.

3.3 Displaying and analyzing a crystal structure

The *Display* menu has three groups of commands. The contents of a unit cell are not changed by any of these commands. The functions of these commands are as follows:

Show:
To highlight certain atoms selected by the user and to either show or suppress certain atoms and bonds selected by the user, the unit cell box, and the Cartesian axes.

Label Atoms:
To label certain atoms selected by the user. In general, the label of an atom is given by Sy-mm-nn, where "Sy" is the chemical symbol of the atom, "mm" is either a number or a character used to distinguish atoms of different groups, and "nn" is a sequence number used to distinguish different atoms within a group (e.g., C-1-1, C-1-2, C-2-1, C-2-2; C-a-1, C-a-2, C-b-1, C-b-2; etc.).

Rendering As:
To change the style of representing the atoms and bonds of a crystal structure. The four available options are *Wireframe*, *Stick Only*, *Ball and Stick*, and *Space Filled*.

Fit Inside Window:
To resize a current structure to optimally fit the *Builder* window.

New View:
To provide another view of a current structure on the screen.

Move:
To move a current structure to anywhere on the screen. It is necessary to press/hold the left mouse button and drag the mouse in the direction of a new position.

Rotate:

To rotate a current structure around a certain axis the user chooses so as to bring out its three-dimensional perspective and generate a view needed for analyzing the local environment around any given atom. It is necessary to press/hold the left mouse button and drag the mouse in the direction of rotation. Another rotational axis can be specified by clicking the appropriate option of this command.

Zoom:

To zoom-in or zoom-out a current structure. It is necessary to press/hold the left mouse button and drag the mouse to left or right.

Stereo View:

To display a stereoview of a current structure. A stereoview consists of two slightly rotated views of the structure (around a vertical axis in opposite directions). The left-hand-side (LHS) one is for the left eye, and the right-hand-side (RHS) one for the right eye.

Align Crystal:

To change the origin and orientation of the Cartesian coordinate system. This command opens the *Align Molecule* dialog box (*Figure 3.3*), where the coordinates of three points, say, A1, A2 and A3, should be specified. The position of A1 is used as the new origin, and the A1-A2 vector as the new x-axis. The three points A1, A2 and A3 define the new xy-plane. If all three points refer to the positions of the atoms of a current structure, it is convenient to select them before opening the *Align Molecule* dialog box so that their coordinates are copied into the dialog box. In other cases, the user should type in their coordinates one by one.

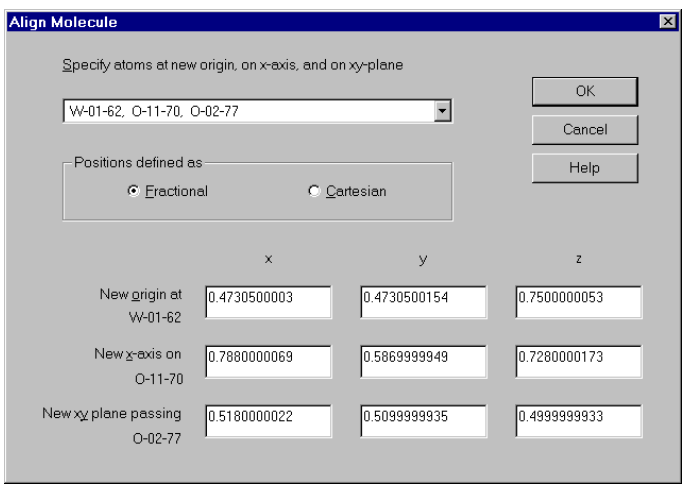

Figure 3.3. Align Molecule dialog box.

Atom Environment:

To describe the local environment around a certain atom selected by the user in terms of the Z-matrix geometry building method. To find the interatomic distances, bond angles, and dihedral angles associated with a specific atom, it is necessary to select the atom plus one, two or three other atoms around it and use the *Atom Environment* command. This opens the *Atom Environment* dialog box (*Figure 3.4*), from which the needed information is found based on the Z-matrix method of geometry building. Selection of only two atoms (A1, A2) is needed to find the A1-A2 bond distance. Selection of three atoms (A1, A2, A3) provides information about the A1-A2 bond distance, the A1-A2-A3 bond angle for each of the 3! combinations of the atom sequence. Selection of four atoms (A1, A2, A3, A4) provides the A1-A2 bond distance, the A1-A2-A3 bond

angle and the A1-A2-A3-A4 dihedral angle (with the middle A2-A3 bond defining the rotational axis) for each of the 4! combinations of the atom sequence.

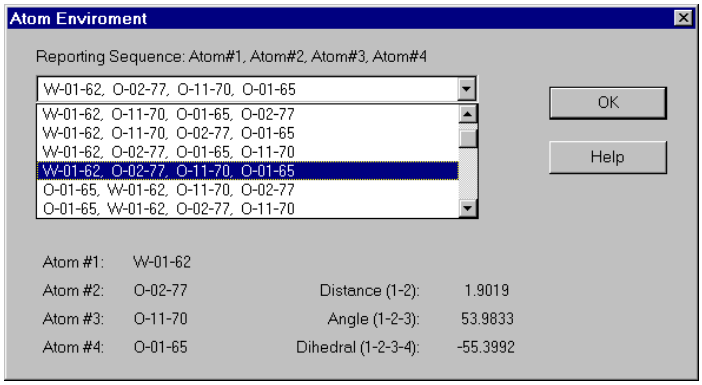

Figure 3.4. Atom Environment dialog box.

Crystal Information...:

To obtain information about a current structure on the screen. This command opens the *Crystal Information* box (*Figure 3.5*).

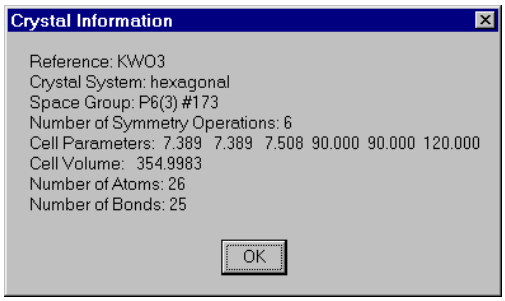

Figure 3.5. Crystal Information box.

3.4 Editing a crystal structure

The *Build* menu has four groups of commands. These commands may alter the contents of a unit cell and have four groups of functions:

Select:

To select atoms and bonds from a current structure. With the mouse the user can quickly select atoms and bonds. For this purpose, the mouse operation must be under one of the several selection modes provided by *Builder*. The mouse is under a selection mode when the user chooses the *Mouse Select* or *Mouse Toggle Select* option of the *Select* or *Unselect* command (see below). The user can also select certain atoms and bonds using other options of the *Select* command. The *Some Atoms...* option opens the *Select Atoms* dialog box (*Figure 3.6*). Likewise, the *Some Bonds...* option opens the *Select Bonds* dialog box (*Figure 3.7*).

Unselect:

To unselect some or all of the atoms and bonds selected by the user. This action can be achieved by either using the mouse or using the options of the *Unselect* command.

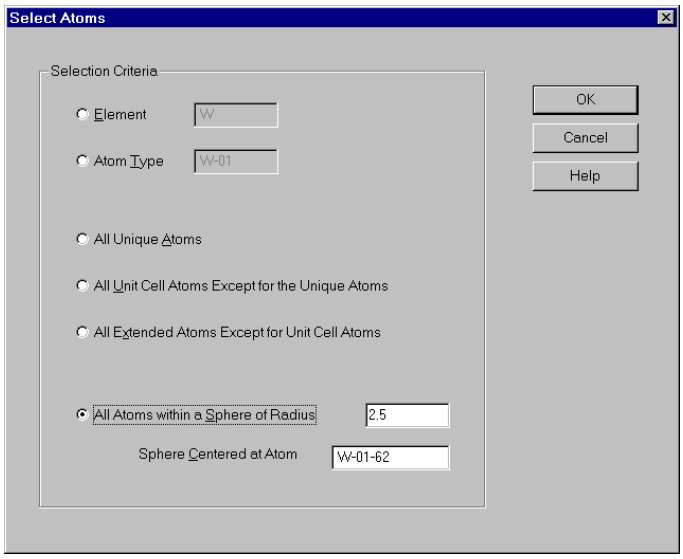

Figure 3.6. Select Atoms dialog box.

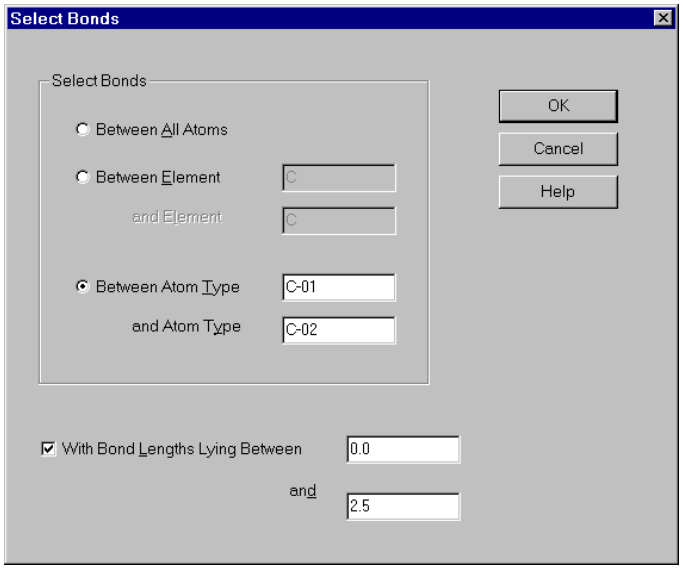

Figure 3.7. Select Bonds dialog box.

Delete:

To delete certain atoms and bonds from a current structure. The user may select either those to be deleted or the rest of the crystal to be kept. To delete objects, it is necessary to choose an appropriate option of the *Delete* menu. When an atom is deleted, all of its bonds with other atoms are automatically deleted. Any deleted objects cannot be restored.

Modify Crystal...:

To open the *Define Crystal Structure* dialog box filled with the information about a current structure. It is used to produce a new input file by modifying the existing input file, *filename.CI*, of a current structure.

Translate Atom Group...:

To translate selected atoms and bonds by a vector, m**a** + n**b** + p**c**, where **a**, **b** and **c** are the repeat vectors of the crystal, and m, n and p are appropriate integers. This command opens the *Place Fragment* dialog box (*Figure 3.8*).

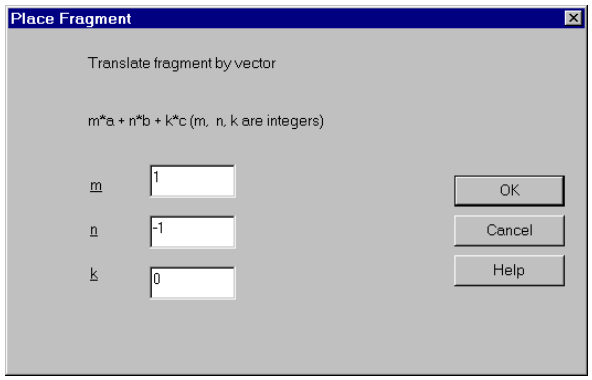

Figure 3.8. Place Fragment dialog box.

Add Atom Group...:

To add selected atoms and bonds to the place translated by a vector, m**a** + n**b** + p**c**. This command opens the *Place Fragment* dialog box and is convenient for extending a crystal structure step by step.

Extend Cells...:

To generate an extended structure of a solid. This command opens the *Extend Unit Cell* dialog box (*Figure 3.9*). To form an extended view of a crystal structure, copies of its unit cell may be placed at the (m**a** + n**b** + p**c**) sites. The command *Extend Cells* opens the *Extend Unit Cell* dialog box, where it is necessary to define the cut-off boundaries along the three axes in units of fractional coordinates. Here non-integer boundaries are allowed.

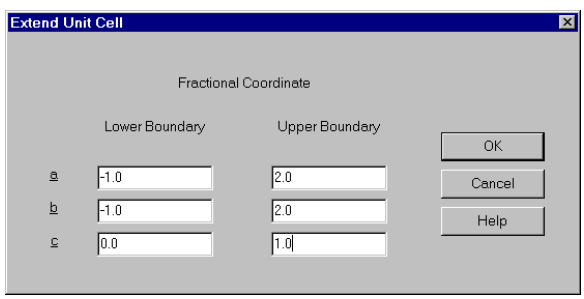

Figure 3.9. Extend Unit Cell dialog box.

Convert Unit Cells:

To convert the space group of a solid to P1 by considering all the atoms of a unit cell as unique. Also to fit all atoms of a unit cell into a unit cell box.

Add Hydrogens...:

To add hydrogen atoms to appropriate atoms of a unit cell when they are missing in a crystal structure report. This command opens the *Add Hydrogens* dialog box (*Figure 3.10*).

Add Atom...:

To add an atom to a position specified by the user in terms of the Z-matrix geometry building method. The atom to add is defined with respect to the three atoms of a current structure the user selects in the Z-matrix method of geometry building. This command opens the *Add Atom* dialog box (*Figure 3.11*).

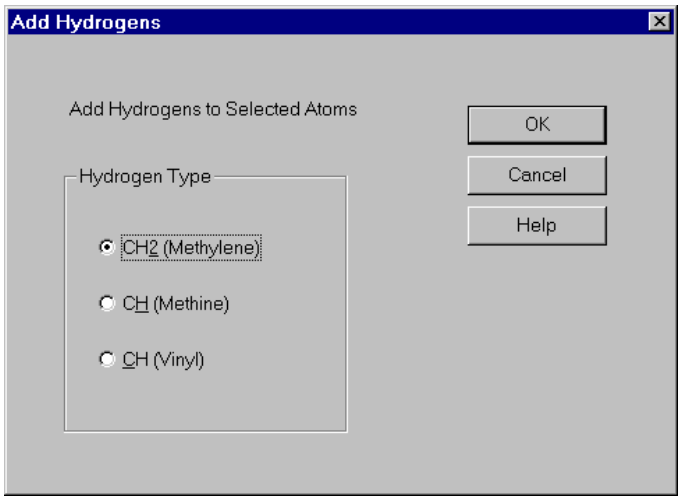

Figure 3.10. Add Hydrogens dialog box.

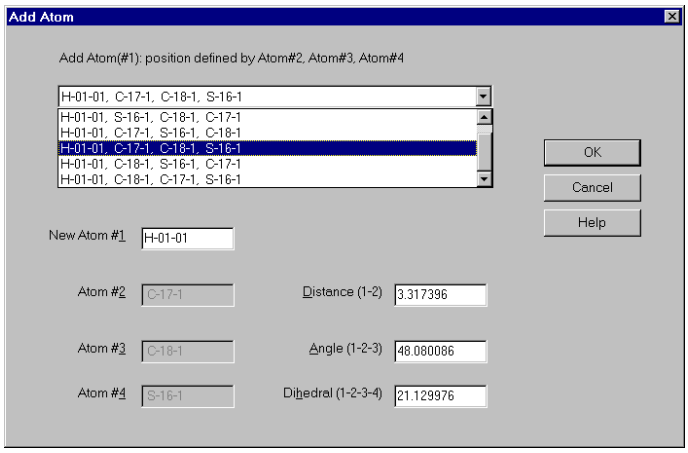

Figure 3.11. Add Atom dialog box.

Replace Atom...:

To replace an atom of a current structure with another in terms of the Z-matrix geometry building method. This command opens the *Replace Atom* dialog box (*Figure 3.12*). The user should select the atom to be replaced plus three other atoms before opening this box.

Bond Two Atoms:

To draw a bond between two atoms selected by the user.

Regenerate All Bonds:

To restore the original bonds of a current structure when some of them are deleted as a consequence of editing the structure.

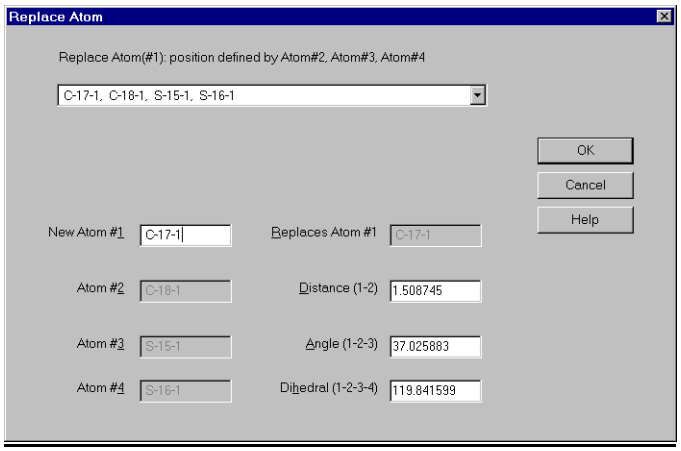

Figure 3.12. Replace Atom dialog box.

3.5 Changing display options

The *Settings* and *Window* menus of the *Builder* window have various commands for changing the display settings. The meanings of these commands are mostly self-explanatory. Several important commands are described below.

Labeling Styles:

To control how the label of an atom, when desired, should appear around each atom the user selects. This command opens the *Labeling Styles* dialog box (*Figure 3.13*).

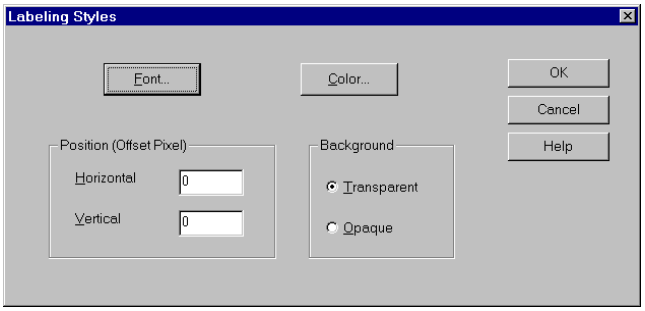

Figure 3.13. Labeling Styles dialog box.

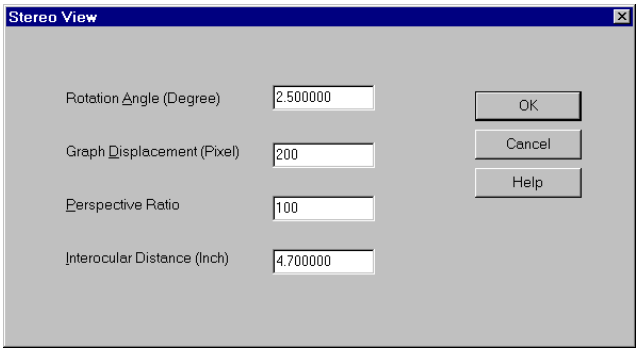

Figure 3.14. Stereo View dialog box.

Stereo View:

To obtain an optimal stereoview. It opens the *Stereo View* dialog box (*Figure 3.14*), the parameters of which can be altered slightly to produce a desired result. Instead of using this command, the user may employ the *Home* and *End* keys to adjust the separation between the LHS and RHS views, and the *Insert* and *Delete* keys to adjust the relative rotation angle between the two views. A stereoview can be translated, rotated, or zoomed as a whole when the mouse is in the translation, rotation or scaling mode.

3.6 Examples

3.6.1 Hexagonal graphite

Hexagonal graphite belongs to a hexagonal crystal system and has the space group symmetry $P6_3/MMC$. Its unit cell parameters are a = b = 2.4612Å, c = 6.7079Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. There are two unique atom positions in a unit cell, type A carbon atom at (0, 0, 1/4), and type B carbon atom at (2/3, 1/3, 1/4).

• ***Entering the crystal structure data***

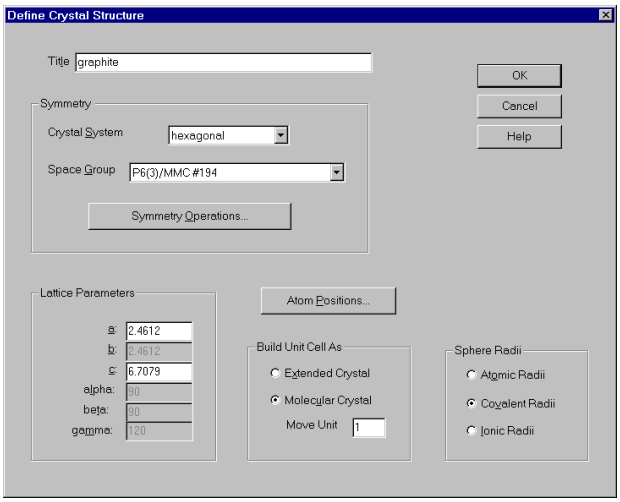

Figure 3.15. Define Crystal Structure dialog box.

To enter the structural information of graphite into *Builder*, use the command *New* command to open the *Define Crystal Structure* dialog box (*Figure 3.15*). One may write any descriptive title (e.g., "graphite") in the *Title* field. Then choose "hexagonal" from the *Crystal System* drop-down list, and select "P6(3)/MMC #194" from the *Space Group* drop-down list. The user may inspect the symmetry operations of this space group by clicking the *Symmetry Operations* button, which opens the *Symmetry Operations* dialog box (*Figure 3.16*). All the edit fields in this dialog box are grayed because they must not be changed. The scroll bar is used to browse through all the symmetry operations. One can exit this box by clicking the *Close* button.

Next enter the cell parameters in the *Lattice Parameters* field, where lengths and angles are in Å and degree units, respectively. Note the values predefined by *Builder*. The lengths of *a* , *b*, and *c* are all predefined to be 10.0 Å, the angles of *alpha*, *beta*, and *gamma* to be 90°, 90°, and 120°, respectively. Only the two edit fields, *a* and *c*, are not grayed, so the user can modify them. The value of *b* is automatically set to be the same as that of *a*, as dictated by the hexagonal crystal symmetry of

graphite. Now change *a* to 2.2456. Upon leaving the *a* edit field, *b* is changed to 2.2456. Change *c* to 6.6943.

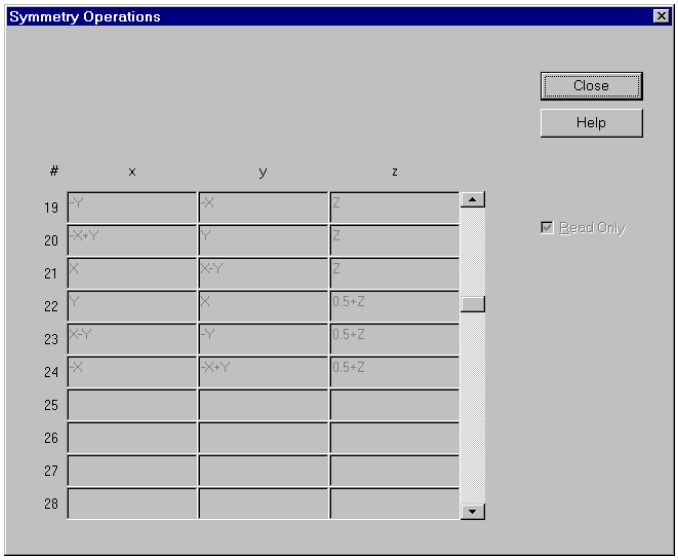

Figure 3.16. Symmetry Operations box.

A crystalline solid may be an extended solid or a molecular solid. The *Build Unit Cell As* field provides two options, *Extended Crystal* and *Molecular Crystal*. For graphite it is proper to choose the former option, but the user may choose the latter option as well. In order to link bonds properly in a molecular crystal, *Builder* searches adjacent unit cells and creates all possible bonds. How many nearest-neighbor unit cells to search along each repeat direction is given in the *Move Unit* field. In the *Ball and Stick* representation of a crystal structure, each atom is represented by a sphere of certain radius. *Builder* provides three different radii ("atomic", "covalent" and "ionic") for each element, and the user may choose any of the them in the *Sphere Radii* field.

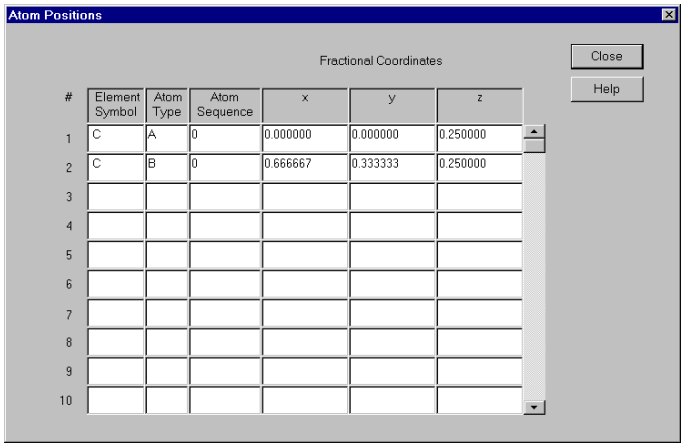

Figure 3.17. Atom Positions dialog box.

To enter the fractional coordinates of the unique atoms of a unit cell, click the *Atom Positions* button to open the *Atom Positions* dialog box (*Figure 3.17*) and type the data as shown there. In

analyzing a crystal structure, it is important to label the unique atoms of its unit cell differently so that the user can easily recognize different groups of atoms (i.e., those not related by space-group symmetry operations) as well as different atoms within each group (i.e., those related by space-group symmetry operations). Given the label of an atom as Sy-mm-nn, the values of "nn" for the atoms generated by space-group symmetry operations are automatically provided by *Builder*. In *Figure 3.17*, the two unique atoms of hexagonal graphite were given the labels C-A-0 and C-B-0. Once all the unique atoms are specified, click the *Close* button and return to the *Define Crystal Structure* dialog box.

By closing the *Define Crystal Structure* dialog box, one should see the structure as shown in *Figure 3.18*. Before proceeding further, it is safe to save the input data just prepared by using the *Save As* command, which opens the *Save As* dialog box (*Figure 3.19*). It is necessary to choose a proper directory (e.g., CAESAR\Examples\Chapter3\Graphite), type a file name (e.g., "*GR.CI*") in the *File Name* field, and save the data under that name.

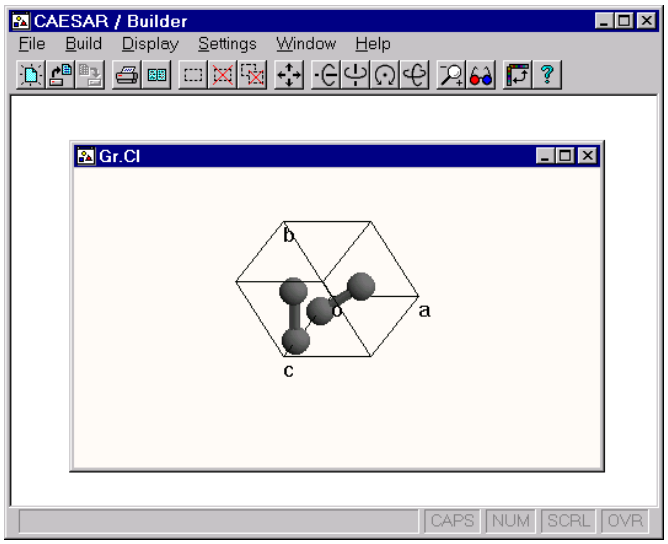

Figure 3.18. Projection view of the unit cell of hexagonal graphite.

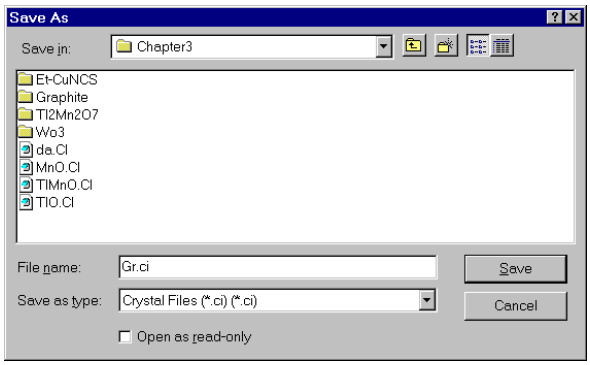

Figure 3.19. *Save As* dialog box.

• *Viewing the structure from different angles and labeling atoms*

To analyze a crystal structure, it is often desirable to view the structure from different angles. This is achieved by rotating the structure. Use the *Rotate: Around Horizontal Axis* command to specify

the horizontal axis as the axis of rotation, press/hold the left mouse button, and drag the mouse in a down direction until the structure resembles the one shown in *Figure 3.20*. If the structure is not centered in the window, use the *Move* command, press/hold the left mouse button, and drag the mouse around until it is centered. To obtain a bigger or smaller structure, use the *Zoom* command, press/hold the left mouse button, and drag the mouse to left or right until the size appears appropriate.

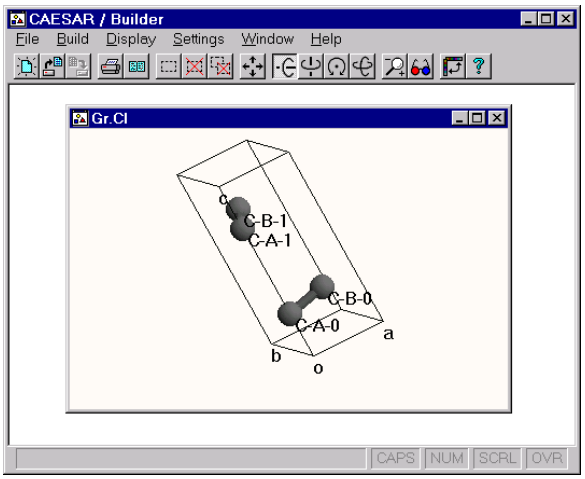

Figure 3.20. Perspective view of the unit cell of hexagonal graphite.

To distinguish atoms, it is necessary to label them. Use the options of the *Label* command to label all the atoms of the crystal structure. In *Figure 3.20* there are four atoms in a unit cell, i.e., two atoms of type A and two atoms of type B. The two original unique atoms (i.e., C-A-0 and C-B-0) are bonded to form one group, and the two symmetry-generated atoms (i.e., C-A-1 and C-B-1) form another group.

By further rotating the structure around the horizontal axis, the user can see that the two groups of C atoms are separated along the c-axis, i.e., there are two graphite sheets per unit cell. To illustrate this point, it is necessary to have an extended view of the structure.

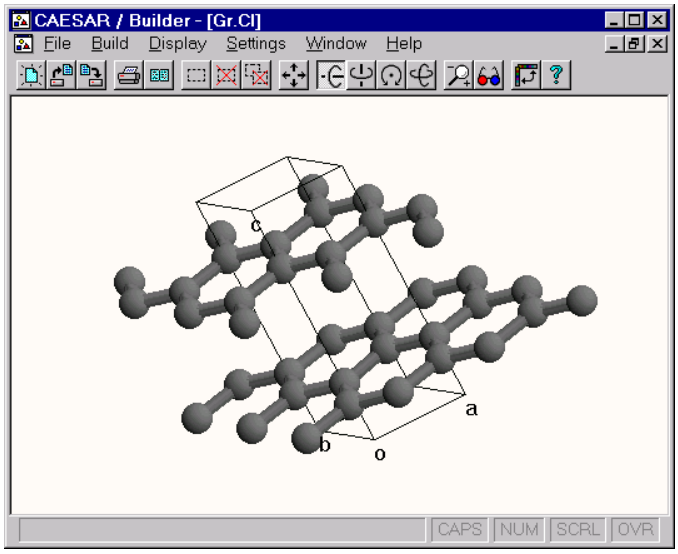

Figure 3.21. Extended perspective view of two graphite layers.

• Making an extended view

To obtain an extended view of the crystal structure, use the *Extend Cells* command to open the *Extend Unit Cell* dialog box (*Figure 3.9*) and define the boundaries of a desired extended crystal structure. For example, the data of *Figure 3.9* extend the structure along the a- and b-axes from -1.0 to 2.0 in fractional coordinate. This leads to three consecutive unit cells along the a- and b-directions thereby generating 3 x 3 unit cells in the ab-plane. There is no extension along the c-axis in this example. Once the dialog box is closed, the extended view of the structure is displayed (*Figure 3.21*). For clarity the displaying of atom labels can be turned off using the command *Label: All Atoms*.

From *Figure 3.21* it is clear that graphite has two layers per unit cell, with each layer parallel to the ab-plane. The user may rotate the structure along different axes to examine the relative arrangement between the two layers.

3.6.2 κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

In this section, we examine the structural features of the organic conducting salt κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Here BEDT-TTF refers to the organic donor molecule, bis(ethylenedithio) tetrathiafulvalene (*Figure 3.22*). This example shows how to load crystal data from files, identify atoms, change representation of atoms and bonds, analyze atom arrangement, hide atoms, extend the crystal, add hydrogen atoms, and calculate interatomic distances, bond angles and dihedral angles.

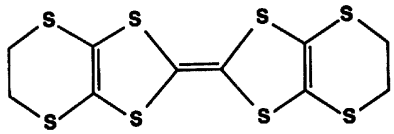

Figure 3.22. Structure of the organic donor molecule BEDT-TTF.

• Loading structure data from file

The loading of the crystal structure data for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ into *Builder* as described in Section 3.7.1 can be tedious, because its unit cell has many unique atoms. The *filename.CI* file for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is *Cu.CI* in the CAESAR\Examples\Chapter3\ET subdirectory. The user may inspect the contents of this file using any text editor. Use the *Open* command to load the *Open* dialog box and find in the CAESAR\Examples\Chapter3\ET subdirectory. The file *Cu.CI* is listed in the *File name* field. Double-click the file *Cu.CI*, then the data are loaded into *Builder*, and the crystal structure is displayed (*Figure 3.23*). The user may inspect and modify the crystal structure data imported into *Builder* by using the *Modify Crystal* command, which opens the *Define Crystal Structure* dialog box loaded with the input information of the *Cu.CI* file.

• Identifying atoms/Changing representations of atoms and bonds

At first glance, the structure of *Figure 3.23* seems complicated. Since there is only one Cu atom in the formula unit, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the user may first find out the Cu atom locations. Use the command *Select: Some Atoms...* command to open the *Select Atoms* dialog box (*Figure 3.6*), check the *Element* option of the box, type "Cu" in the edit field, and close the box by clicking the *OK* button. This will select all the Cu atoms in the unit cell and highlight them in the display. (This is the *dialog box* method of selecting atoms.) Furthermore, the user may label the selected atoms using the

command *Label Atoms: Selected Atoms Only* command. The Cu-01-0 atom is the unique atom, and Cu-01-1 is generated from Cu-01-0 by the symmetry operation. A unit cell of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has two Cu(NCS)$_2$ units.

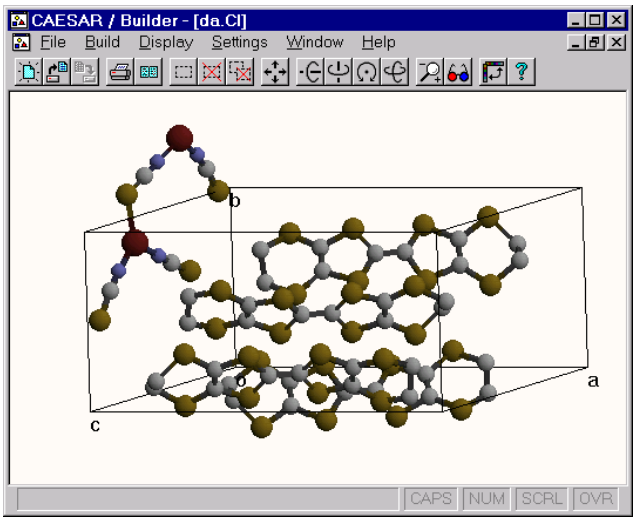

Figure 3.23. Perspective view of the unit cell of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

To find the N, C and S atoms attached to the Cu, the user may repeat a similar procedure to select and label atoms until the desired atoms are all found. However, it is more convenient to select them by using the *Select: Mouse Select* command. Point the mouse cursor on an atom to be selected and click, then the atom is selected and is grayed. Repeat this process until all desired atoms are selected. (This is the *mouse click* method of selecting atoms.) Alternatively, the user may position the mouse cursor at the upper left corner of a rectangular area to be selected, press/hold the left mouse button, drag the mouse in a down and RHS direction to include as many atoms to be selected as possible inside the rectangular area to be swept by the mouse cursor (excluding the atoms not to be selected), and then release mouse button. The selected atoms are grayed and labeled. If this method does not include all the atoms intended for selection, repeat the above procedure. (This is the *mouse drag* method of selecting atoms.)

Since a two-dimensional projection view on the screen is used for the *mouse click* or *mouse drag* method, unintended atoms can be selected accidentally. To avoid such a selection, it is convenient to rotate the structure so that no unintended atoms lie underneath the intended ones. To remove the unintended atoms that are selected, use the command *Unselect: Mouse Unselect* and unselect them using either the *mouse click* or the *mouse drag* method. The V-shaped structures on the left side of *Figure 3.23* represent the two Cu(NCS)$_2$ units.

Let us now consider identifying other atoms. The display may have become crowded due to atom labels. The user can remove them by turning off the *Label Atoms* command. The left-side substructure of *Figure 3.23* must be BEDT-TTF. From the fact that the crystal has two Cu(NCS)$_2$ per unit cell, there should be four BEDT-TTF units per unit cell. However, the left-side substructure of *Figure 3.23* is so entangled that it is unclear how these units are arranged. To understand the relative arrangement of the BEDT-TTF molecules, it is necessary to view the structure from different angles. It is not a problem to decide around which axis or how much to rotate the structure, because the rotation is carried out fast and continuously until one finds a proper view. Use the *Rotate: Around Horizontal Axis* command to specify the horizontal axis, press/hold the left mouse button, and drag the mouse in a down direction until the structure looks as shown in *Figure 3.24*, which clearly shows that there exist four distinct BEDT-TTF units.

The display can be simplified using a less complex display option for atoms and bonds. One may use the *Rendering As: Stick Only* or *Rendering As: Wireframe* command for this purpose.

• Understanding atom arrangements/Hiding some atoms

So far two atom groups of the crystal structure were identified. Let us examine the spatial arrangement of the structure in more detail. *Figure 3.24* suggests that the $Cu(NCS)_2$ units are contained in the bc-plane, and that the BEDT-TTF molecules form a layer parallel to the bc-plane, with the long axis of each BEDT-TTF molecule inclined to the bc-plane.

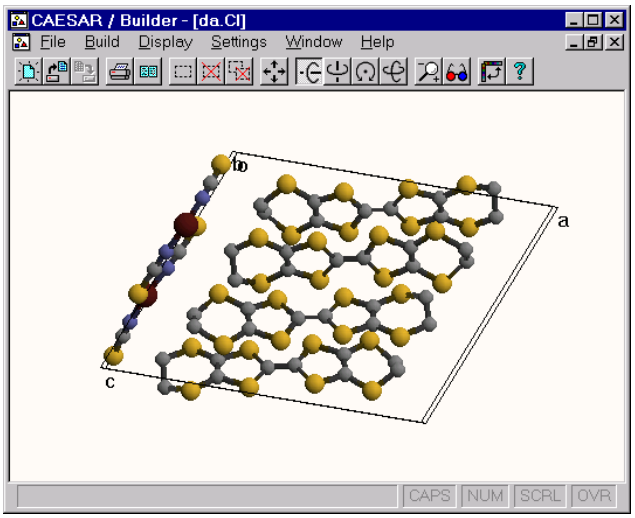

Figure 3.24. View of the unit cell of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ showing four BEDT-TTF molecules.

To confirm the above suggestions, let us first consider the $Cu(NCS)_2$ units. Select only the two $Cu(NCS)_2$ units and use the *Show: Selected Only* command to hide the objects other than $Cu(NCS)_2$. Experiment with rotating the structure around the horizontal axis. It should be clear that the two $Cu(NCS)_2$ units are indeed parallel to the bc-plane.

Now consider the BEDT-TTF units. If the user is unfamiliar with the structure of BEDT-TTF, it is necessary to examine the structure of BEDT-TTF. First unselect the two $Cu(NCS)_2$ units using the *Unselect: All Selected* command. Then select one of the four BEDT-TTF units. Use the command *Label Atoms: Selected Atoms Only* to show the identity of each atom. Rotate the molecule around and inspect its structural feature. It should be clear that BEDT-TTF is largely planar.

Next consider the four BEDT-TTF molecules as a whole. Unselect all selections first using the *Unselect: All Selected* command. Then select the two $Cu(NCS)_2$ units and use the *Show: Unselected Only* command to show only the BEDT-TTF units. Since there are four BEDT-TTF molecules (total 72 atoms excluding the H atoms, which are not included in the structure file *Cu.CI*), the user may simplify the display using the *stick-only* or *wireframe* display. As done for the $Cu(NCS)_2$ units, experiment with rotating the structure around the horizontal axis back and forth. The user should come across a structure similar to *Figure 3.25*, which hints that the four BEDT-TTF molecules are divided into two BEDT-TTF dimers. Each dimer consists of two nearly parallel BEDT-TTF molecules, and the arrangement between two dimers is nearly orthogonal. This can be seen by viewing the BEDT-TTF molecules along the direction of the long molecular axis of BEDT-TTF. Use the *Rotate: Around Vertical Axis* command, press/hold the left mouse button, and drag the mouse in the left or right

direction until the structure resembles the one shown in *Figure 3.26*, which reveals that BEDT-TTF dimers have a near orthogonal arrangement.

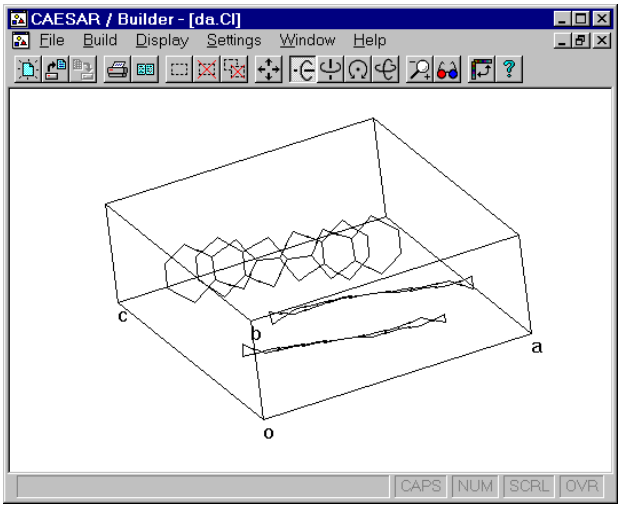

Figure 3.25. Perspective view of the unit cell of κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$ showing that the four BEDT-TTF molecules form two dimers.

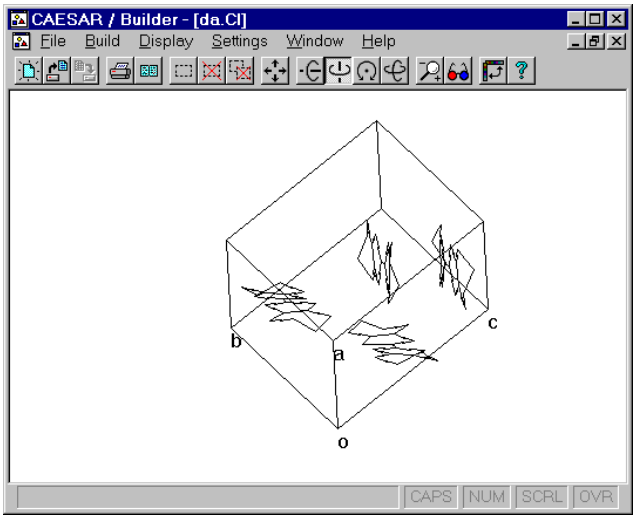

Figure 3.26. Projective view of the cell of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ showing that the four BEDT-TTF molecules form two dimers.

• *Extending the crystal structure*

To obtain an extended view of the crystal structure, use the *Extend Cells* command to open the *Extend Unit Cell* dialog box and define the boundaries of a desired extended crystal structure. For example, the data in *Figure 3.27* specify that the structure is extended along the b- and c-axes from -1.0 to 1.0 in fractional coordinate (i.e., three consecutive unit cells along the b- and c-directions). There is

no extension along the a-axis in this example. On closing the dialog box, the extended view of the structure is displayed. For example, a projection view of the extended structure on the bc-plane is presented in *Figure 3.28*, which shows the relative arrangement between the layer of $Cu(NCS)_2$ units and that of BEDT-TTF molecules. It also shows that the $Cu(NCS)_2$ units form linear chains running along the b-direction.

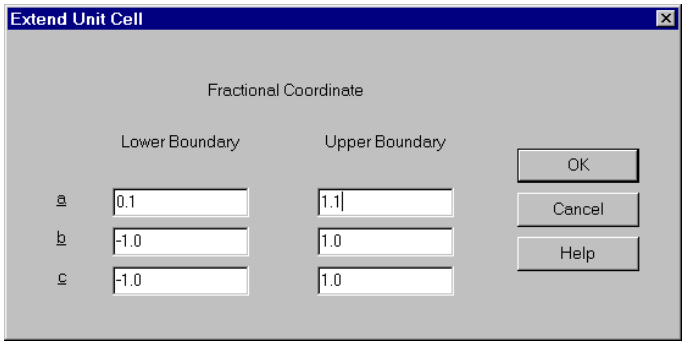

Figure 3.27. Extended Unit Cell dialog box of the *Build:Extend Cells* command.

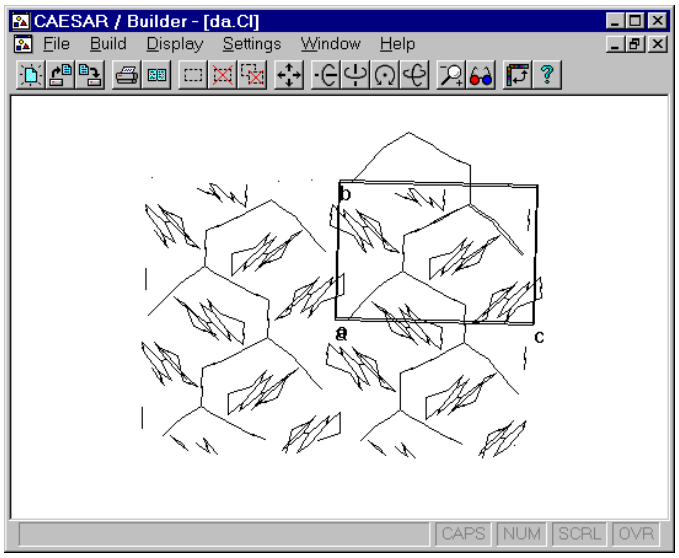

Figure 3.28. Extended projection view of the anion and cation layers of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$.

To obtain an extended view of only the $Cu(NCS)_2$ or the BEDT-TTF layer, it is necessary to separate the BEDT-TTF units from the $Cu(NCS)_2$ units by selecting, for example, the $Cu(NCS)_2$ units according to the procedures described earlier. Since an extended structure is large, it is necessary to consider which selection method, the *dialog box*, *mouse click* or *mouse drag* method, is convenient to use. For this task, the mouse click method will be tedious. The mouse drag method cannot be applied to the structure of *Figure 3.28*, because any mouse dragging will select both $Cu(NCS)_2$ and BEDT-TTF units. However, one can rotate the structure of *Figure 3.28* around a vertical axis to obtain its projection view on the ac-plane, and then rotate the latter around the perpendicular axis so that the

projection view of the $Cu(NCS)_2$ units appears as a vertical line. Then it is easy to select the whole $Cu(NCS)_2$ units using the *mouse drag* method. The use of the *dialog box* method for the same task is cumbersome. This requires first finding the atom attributes of the Cu, N, C and S atoms belonging to the $Cu(NCS)_2$ units, because the use of C and S in the dialog box will select the carbon and sulfur atoms of BEDT-TTF as well as $Cu(NCS)_2$. One can eventually find that the Cu, N, C and S atoms of the $Cu(NCS)_2$ are described by Cu-01, N-21, C-21, S-21, N-22, C-22, and S-22 by following the procedures of identifying selected atoms that are discussed earlier. Then use the command *Select: Some Atoms* to open the *Select Atoms* dialog box (*Figure 3.29*). In the dialog box check *Atom Type*, type "Cu-01", and close the box. Repeat this procedure for "N-21", "C-21", "S-21", "N-22", "C-22" and "S-22". This will select all the atoms of the $Cu(NCS)_2$ units.

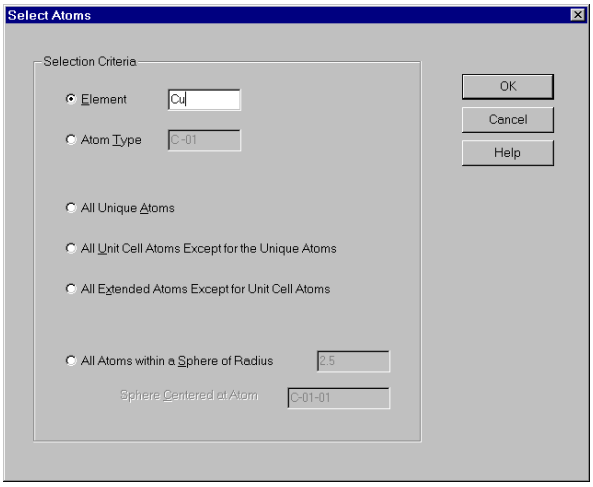

Figure 3.29. Select Atoms dialog box of the *Build:Select:Some Atoms* command.

Now one can use the *Show: Selected Only* command to hide the units other than $Cu(NCS)_2$ or the *Show: Unselected Only* command to hide only the $Cu(NCS)_2$ Units. In this way, one can produce the extended views of the $Cu(NCS)_2$ and the BEDT-TTF layers shown in *Figures 3.30* and *3.31*, respectively.

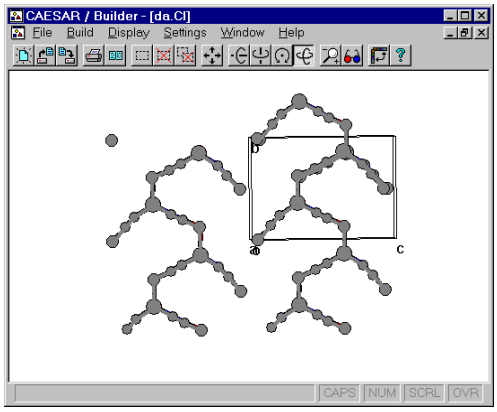

Figure 3.30. Extended projection view of the anion layer of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ showing that the anions form polymetric chains along the b-direction.

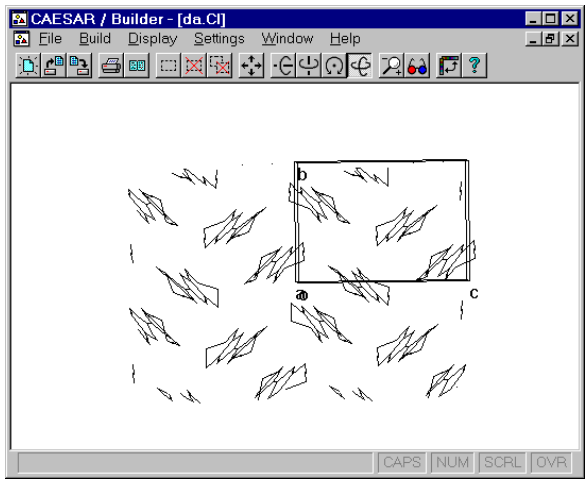

Figure 3.31. Extended projection view of the cation layer of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ showing that the BEDT-TTF dimers have an orthogonal arrangement.

It is possible to delete the atoms used in extending a crystal structure. Use the *Unselect: All Selected* command to clear up all selections. Use the *Select: Some Atoms* command to open the *Select Atoms* dialog box. In the dialog box check *All Extended Atoms Except for Unit Cell Atoms*. This will select all the extended atoms. Use the command *Delete: All Selected* to delete these extended atoms.

•Adding hydrogen atoms/Calculating distances and angles

The user may have noticed that the structural views of the BEDT-TTF molecules do not have hydrogen atoms. It is a common problem with X-ray crystallography that accurate hydrogen positions are mostly unavailable and hence are often not reported. In calculating the electronic structures of organic molecular crystals, it is crucial to make sure that the molecules have no missing hydrogen atoms, although they may not have been reported. *Builder* provides a convenient way to add missing hydrogen atoms.

The user can add hydrogen atoms by using the Z-matrix method of geometry building, in which the position of a new atom A1 is specified using three atoms A2, A3 and A4 whose positions are already known. The essential idea is to consider the atom connectivity A1-A2-A3-A4 and then specify the A1-A2 bond length r, the A1-A2-A3 bond angle θ, and the A1-A2-A3-A4 dihedral angle ϕ. Here the A2-A3 bond serves as the rotational axis for determining the dihedral angle between the A1-A2 and A3-A4 bonds. To add an hydrogen atom (i.e., A1) using the Z-matrix method, it is necessary to first select three atoms (i.e., A2, A3 and A4) from a structure shown on the screen and use the *Add Atom...* command to open the *Add Atom* dialog box (*Figure 3.12*). Then specify the r, θ and ϕ values of this box and exit the box.

For certain types of hydrogen atoms (i.e., *methylene*, *methine*, *vinyl*), the user can add them to appropriate C atoms by specifying their type. For this purpose, select the C atom(s) of a current structure to which hydrogens are to be added, then use the *Add Hydrogens...* command to open the *Add Hydrogens* dialog box (*Figure 3.10*), choose the appropriate hydrogen atom type, and close the box. In the present case, each six-membered ring of BEDT-TTF has an ethylene group, i.e., two methylene groups. Thus for each BEDT-TTF, one first needs to select all four methylene carbon atoms, to which hydrogen atoms are to be added. A unit cell has four BEDT-TTF molecules and hence 16 methylene carbon atoms to select. One may select them using the *mouse click* method. Then use the *Add Hydrogens...* command to open the *Add Hydrogens* dialog box and check the *CH2 (Methylene)* option in the dialog box (*Figure 3.10*), and then exit the box. The exact positions of the hydrogens added in this manner can be examined by using the *Atom Environment* command to calculate the relevant bond

distance, bond angle, and dihedral angle associated with any added hydrogen. For this purpose, one has to select first the hydrogen atom in question and then three other atoms defining the hydrogen position in the sense of the Z-matrix method.

3.6.3 K_xWO_3

In this section the structural features of potassium tungsten bronze K_xWO_3 is examined. The hexagonal potassium tungsten bronze K_xWO_3 has a three-dimensional lattice made up of corner-sharing WO_6 octahedra, and the potassium cations K^+ are located in the hexagonal tunnels of the lattice. When all the K^+ sites are occupied, x = 1/3. In this example we need to repeat the same steps as shown in Section 3.6.2. To avoid redundancy, our description will be brief if it is similar.

• ***Loading structure data from file***

The file for K_xWO_3 is *KW.CI* in the CAESAR\Examples\Chapter3\KxWo3 subdirectory. Use the *Open* command to load the file into *Builder*, and the crystal structure is displayed (*Figure 3.32*).

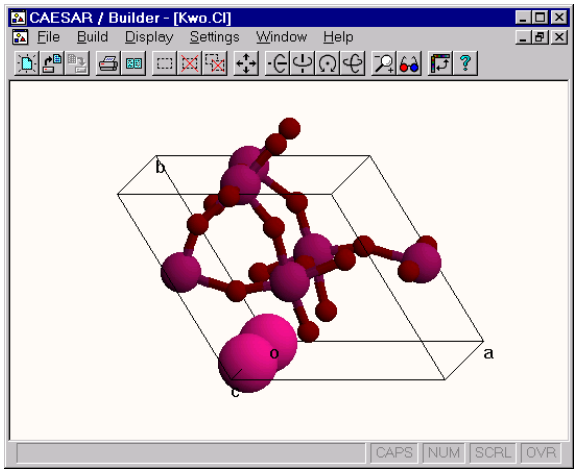

Figure 3.32. Perspective view of the unit cell of K_xWO_3.

• ***Identifying atoms***

In Section 3.6.2 the locations of all atoms were found by selecting atoms by elements and then labeling them. Here we use a quicker way to identify atoms by showing their labels temporarily, i.e., by moving the mouse cursor on top of any atom to identify and then clicking the right mouse button. The labels disappear when the graphic display is refreshed (due to window re-sizing, translation, rotation, etc.). Identify the eight large atoms first using this method in *Figure 3.32*. The two atoms lying along the c-axis are potassium, and the six other large atoms are tungsten. The small atoms (total 18) are oxygen. Thus the crystal structure has the formula $(K_xWO_3)_6$ per unit cell.

• ***Understanding the atom arrangement and extending the crystal structure***

To comprehend the atom arrangements of an unfamiliar crystal structure, it is necessary to view the crystal from several different view angles. Use the *Rotate: Around Horizontal/Vertical Axis* command to carry out a three-dimensional rotation. Then press the arrow keys, *Up*, *Down*, *Left* and *Right*, until the structure looks as presented in *Figure 3.33*, shows a projection view of the structure along the c-axis. Compared with *Figure 3.32*, *Figure 3.33* looks simpler because many atoms are hidden by other atoms. There is a large room around each potassium site (at the unit cell corners), which indicates that the structure has straight tunnels running along the c-direction, and potassium atoms are located there. After experimenting various rotations, it is possible to guess that the structure consists of WO_6 octahedra, and they share their oxygen corners.

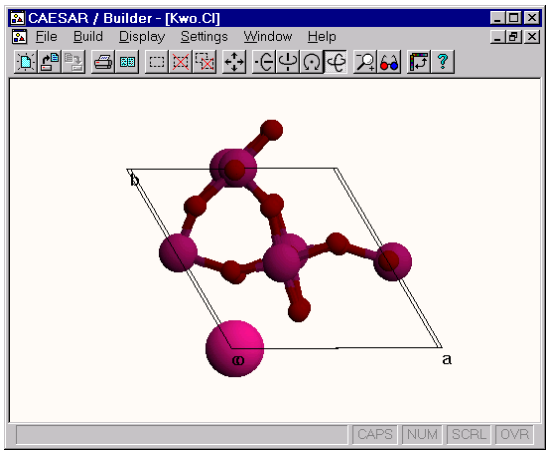

Figure 3.33. Projection view of the unit cell of K_xWO_3 along the c-direction.

To confirm the above suggestions, it is necessary to look beyond a single unit cell. To form an extended view of the crystal, the user should specify the amount of extension along each of the three unit cell axes. In the present case, it is desirable to have an extended structure in which all the tungsten atoms are fully coordinated with oxygen atoms. To generate such a structure, it is needed to guess how much a unit cell should be extended along each unit cell direction and then look at the extended structure in an iterative manner.

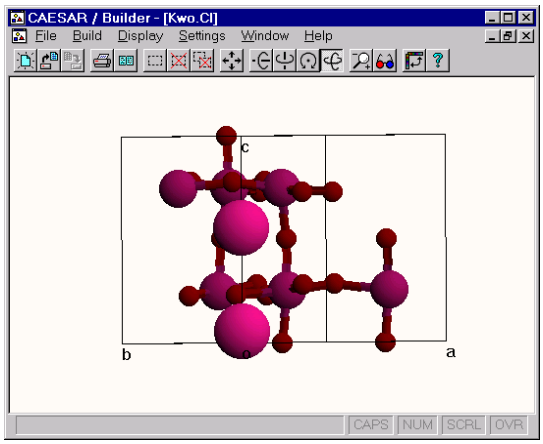

Figure 3.34. Perspective view of the unit cell of K_xWO_3 around the c-axis.

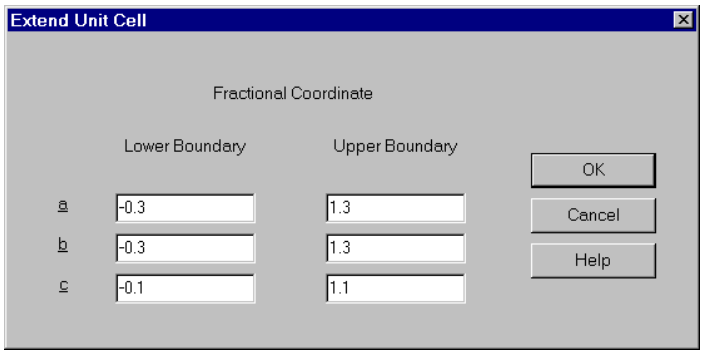

Figure 3.35. Extended Unit Cell dialog box of the *Build:Extend Cells* command.

Figure 3.33 suggests that the tungsten atoms on the unit cell edges parallel to the b-axis can be fully coordinated by extending the cell along the a-axis direction from 0.0 - 1.0 to -0.3 - 1.3 in fractional unit. For the tungsten atoms lying on the upper unit cell edge parallel to the a-axis, the cell extension along the b-axis direction from 0.0 - 1.0 to 0.0 - 1.3 would fully saturate the tungsten coordinates. In *Figure 3.33*, these tungsten atoms appear fully coordinated. However, the structure of *Figure 3.33* is a projection view along the c-axis. This becomes clearer when the structure is rotated around a horizontal axis (*Figure 3.34*). A very little extension is needed along the c-axis, because the higher-lying tungsten atoms will be fully coordinated when the oxygen atoms of the bottom cell edge are repeated along the c-direction. Now use the command *Extend Cells* to open the *Extend Unit Cell* dialog box (*Figure 3.35*) and define the boundaries of a desired extended crystal structure as reasoned above. Specifically the numbers in *Figure 3.35* request an extended structure filling the box having the dimensions of -0.3 - 1.3 along the a- and b-axis directions and -0.1 - 1.1 along the c-axis direction. On closing the dialog box, an extended view of the structure is displayed (*Figure 3.36*). The extension produces several isolated oxygen atoms. The *Rendering As: Stick Only* command to obtain a simpler display (*Figure 3.37*). By rotating the structure of *Figure 3.37* around the horizontal axis, the user can generate a structure similar to the one shown in *Figure 3.38*. From *Figures 3.37* and *3.38*, it is clear that the WO_6 octahedra share their "axial" corners to form WO_5 chain along the c-axis, and three such chains are joined together by sharing their "equatorial" oxygen atoms to form a W_3O_{12} triple-chain.

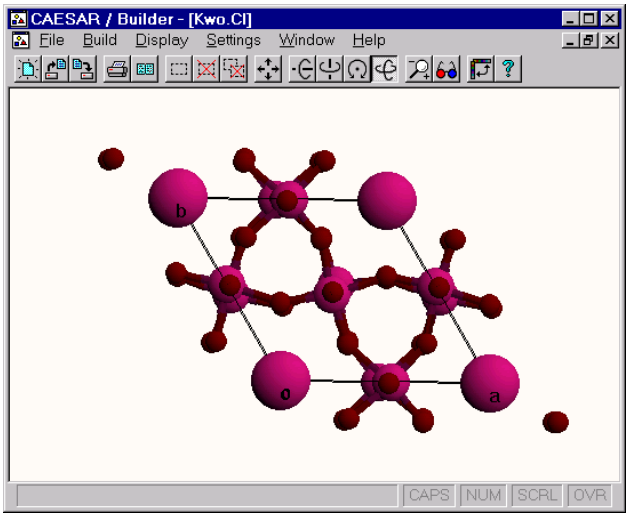

Figure 3.36. Extended projection view of K_xWO_3 along the c-direction.

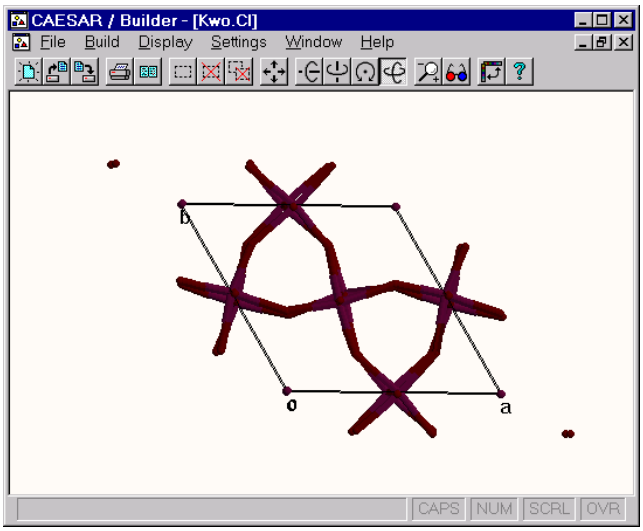

Figure 3.37. *Stick only* representation of the extended projective view of K_xWO_3 along the c-direction.

Figure 3.37 indicates the presence of straight tunnels running along the c-axis at each corner of the unit cell. To visualize this directly, it is necessary to extend the structure further. For this purpose, first delete the atoms added in extending the crystal. Then use the *Select: Some Atoms* command to open the *Select Atoms* dialog box and check the *All Extended Atoms Except for Unit Cell Atoms*. This will select all the extended atoms. Use the *Delete: All Selected* command to delete them. Now use the *Extend Cells* command to open the *Extend Unit Cell* dialog box and extend the structure to -1.3 - 1.3 along the a- and b-axis directions, and to 0.0 - 1.2 along the c-axis direction. This leads to an extended view of the structure shown in *Figure 3.39*. It is obvious that the potassium atoms are located in the hexagonal tunnels running along the c-axis at each corner of the unit cell, and that the W_3O_{12} triple-chains are fused together by sharing their outer "equatorial" oxygen atoms to form the three-dimensional W_3O_9 lattice. These "equatorial" oxygen atoms form hexagonal rings, which further form the hexagonal tunnels along the c-direction.

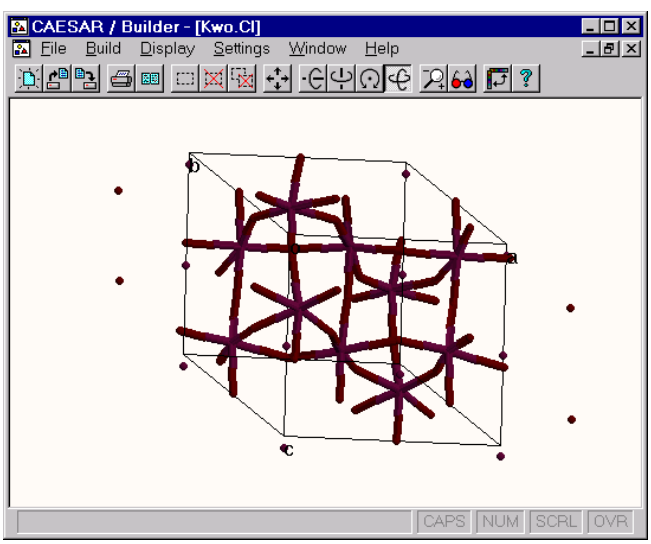

Figure 3.38. Projection view of the extended view of K_xWO_3.

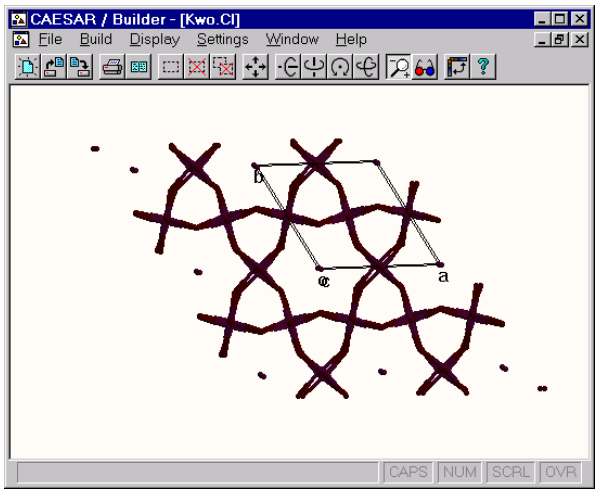

Figure 3.39. Extended projection view K_xWO_3 Showing a hexagonal tunnel running along the c-direction.

•Atom environment/Calculating distances and angles

The WO_6 octahedra of K_xWO_3 octahedra do not seem to have an ideal octahedral structure. To study the arrangement of six oxygen atoms around one W, it is necessary to get an isolated WO_6 first. (If there were several nonequivalent WO_6 octahedra, the user has to examine all of them one by one.) Select the center W atom of one WO_6 octahedron and its surrounding six O atoms. To show only the selected atoms, use the *Show: Selected Only* command. *Figure 3.40* shows a stereoview of these atoms.

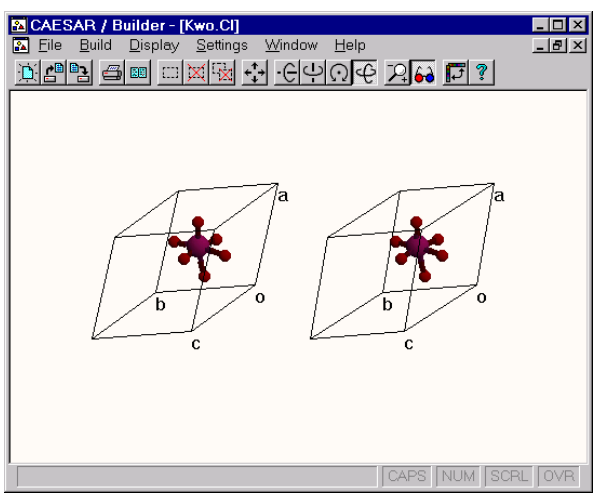

Figure 3.40. Stereoview of one WO_6 octahedron taken from the 3D lattice of K_xWO_3.

The user may wish to calculate bond lengths, bond angles, and dihedral angles associated with some atoms of the chosen octahedron. For this purpose, select appropriate atoms (e.g., W and three O

atoms) from the structure (*Figure 3.39*) and then use the *Atom Environment* command. This opens the *Atom Environment* dialog box (*Figure 3.41*). Calculations of bond length, bond angle and dihedral angle are based on the Z-matrix geometry building method. Since four different atoms were selected, there are 24 ways of arranging their sequence. Choose an appropriate sequence (e.g., A1-A2-A3-A4) from the *Reporting Sequence* drop-down list and exit the box. Then the relevant bond distance, bond angle, and dihedral angle are shown, as depicted in *Figure 3.41*.

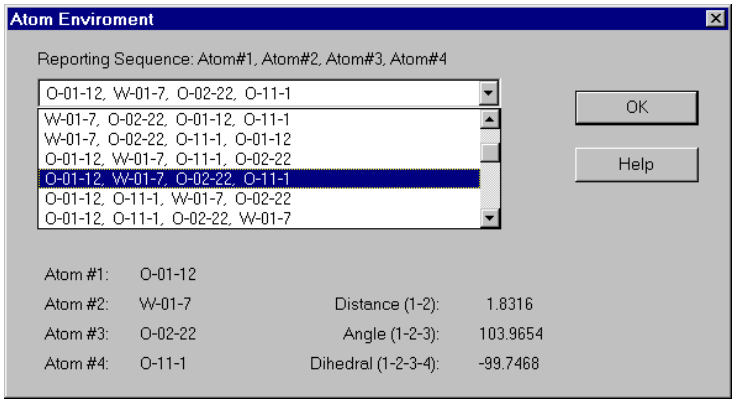

Figure 3.41. *Atom Environment* dialog box of the *Window:Atom Environment* command of *Builder*.

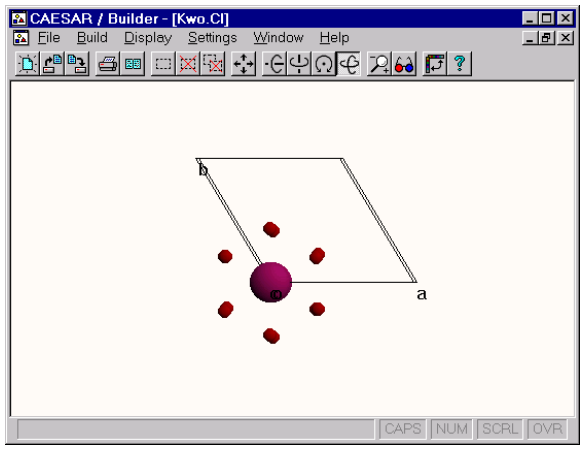

Figure 3.42. Projection view of the nearest-neighbor O atoms around the K atoms in a hexagonal channel of K_xWO_3.

As can be seen from *Figure 3.39*, the potassium atoms are located in the hexagonal tunnels running along the c-axis at each corner of the unit cell. Here we examine the environment of the potassium atoms in more detail. First follow the procedures leading to *Figure 3.39*. Then using the *mouse drag* method, select the nearest-neighbor atoms of the K atoms lying on the c-axis. These atoms are the equatorial oxygen atoms shared by the nearest-neighbor WO_6 octahedra of the K atoms. Select the K atoms on the c-axis as well. Then delete the unselected atoms to obtain the structure shown in *Figure 3.42*. When this is rotated, a perspective view such as shown in *Figure 3.43* is obtained. Select and delete the upper and lower K atoms of the structure in *Figure 3.43*, and then connect adjacent oxygen atoms. For this purpose, first select two adjacent oxygen atoms to connect, use the command *Bond Two Atoms* to connect them. Repeat these steps until all adjacent oxygen atoms are bonded. Then, as shown in a stereoview of *Figure 3.44*, it is found that a K atom is surrounded by two puckered

O_6 rings, and the K atom is closer to one of the two O_6 rings (i.e., the upper one). By calculating the K-O distances as carried out for the WO_6 octahedron, it is found that the K-O distances range from 2.9 Å to 3.6 Å.

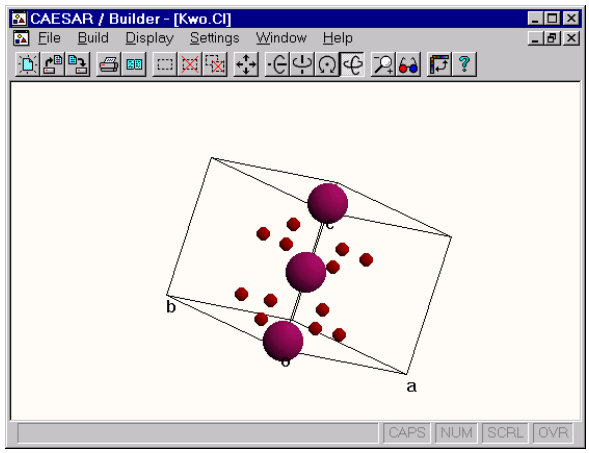

Figure 3.43. Perspective view of the nearest-neighbor O atoms around the K atoms in a hexagonal channel of K_xWO_3.

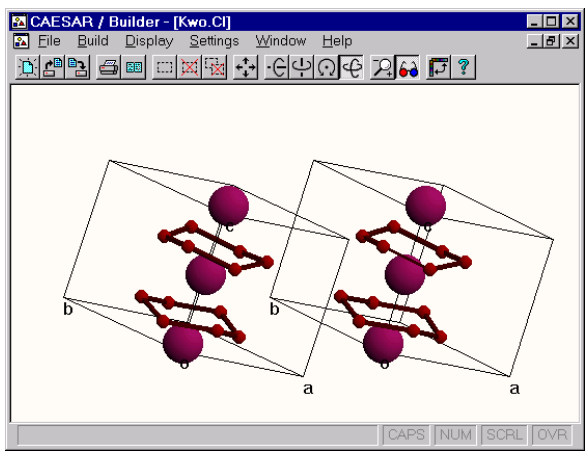

Figure 3.44. Stereoview of the nearest-neighbor O atoms around the K atoms in a hexagonal channel of K_xWO_3, where the adjacent oxygen atoms are linked to emphasize their puckered hexagonal ring shapes.

3.6.4 $Tl_2Mn_2O_7$

$Tl_2Mn_2O_7$ has the pyrochlore structure. This structure (Space Group Fd-3m, #227) contains eight formula units per unit cell. As will be discussed below, $Tl_2Mn_2O_7$ can be written as $(Mn_2O_6)(Tl_2O')$ because its structure can be described in terms of two interpenetrating sublattices, Mn_2O_6 and Tl_2O'. The structure is significantly more complex than the three structures discussed so far. It is convenient to decompose the structure of $Tl_2Mn_2O_7$ into Mn_2O_6 and Tl_2O' sublattices, load sublattice data from files, analyze them separately, and finally examine the whole structure.

• ***Decomposing structural data***

Let us first focus on the sublattices separately by dividing the input file into two separate files, with each file containing the data of one sublattice. These two files, *Tl.CI* and *Mn.CI*, are in the CAESAR\Examples\Chapter3\Tl2Mn2O7 subdirectory. The file *Tl.CI* contains only an Tl atom and an O' atom, the file *Mn.CI* contains only an Mn atom and an O atom, while the file *TlMn.CI* contains all these atoms together.

• ***Understanding the Tl_2O substructure***

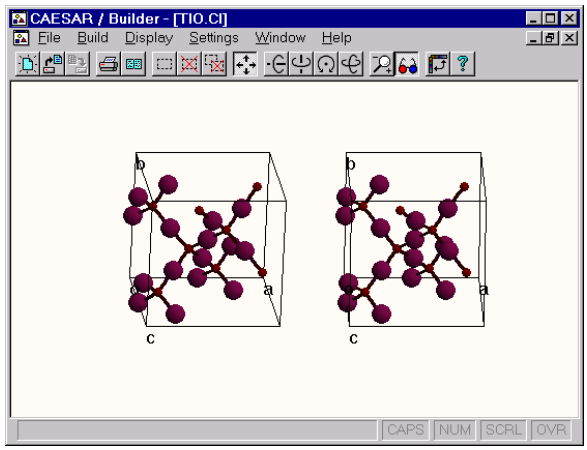

Figure 3.45. Stereoview of the unit cell of the Tl_2O sublattice of $Tl_2Mn_2O_7$.

Use the *Open* command to load the *Tl.CI* file into *Builder* and display the crystal structure as already described. By using the *Into Unit Cell Box* option of the *Convert Unit Cell* command, the user can obtain a perspective view in which all the atoms are contained in a unit cell. From this the user can generate a stereoview of the sublattice shown in *Figure 3.45*. The locations of all the atoms can be found by identifying the atoms. The sublattice has eight Tl_2O units per unit cell. Each Tl atom forms linear O-Tl-O bonds, and each O atom is tetrahedrally surrounded by four Tl atoms.

To show the local environment of only one oxygen atom, the user may select all atoms surrounding one oxygen atom within a certain radius from the oxygen atom such that the selected atoms consist of four O-Tl-O units joined to the central oxygen. (The user can find the O-Tl-O distance of 4.3 Å by using the *Atom Environment* command.) To achieve this, first select the center oxygen (i.e., O-1-0). Then use the *Select: Some Atoms* command to open the *Select Atoms* dialog box, check the *All Atoms within a Sphere of Radius* option, type "4.4" (slightly longer than the O-Tl-O distance of 4.3 Å) in the edit field, and click the *OK* button. Then the central oxygen atom and its four nearest neighbor Tl and four nearest-neighbor O atoms are highlighted. To show only the highlighted atoms, use the command *Show: Selected Only*. *Figure 3.46* shows a stereoview of these atoms.

Because of the long O-Tl-O distance (4.3 Å), the Tl_2O framework has room to accommodate the Mn_2O_6 sublattice. Formally, the Tl_2O sublattice has the cuprite structure Cu_2O, in which two identical frameworks interpenetrate each other. One may also compare the Tl_2O framework with the diamond network. Topologically, the oxygen atoms of Tl_2O correspond to the C atoms of diamond, and the Tl atoms of Tl_2O to the midpoints of the C-C bonds of diamond. This comparison can be

easily visualized when the structure is rendered with the *Stick Only* or *Wireframe* option so that the atoms are hidden.

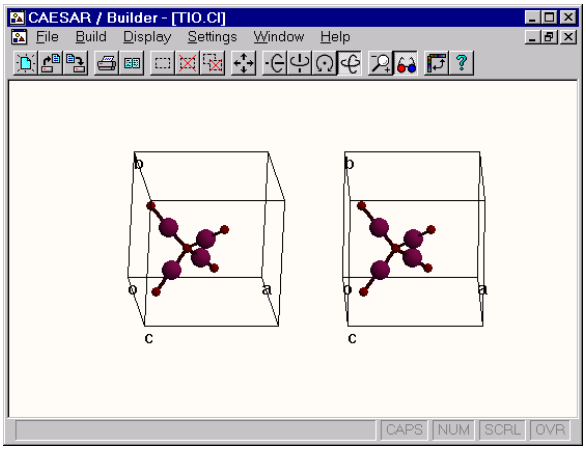

Figure 3.46. Stereoview showing the local environment around the oxygen atom in the Tl_2O sublattice of $Tl_2Mn_2O_7$.

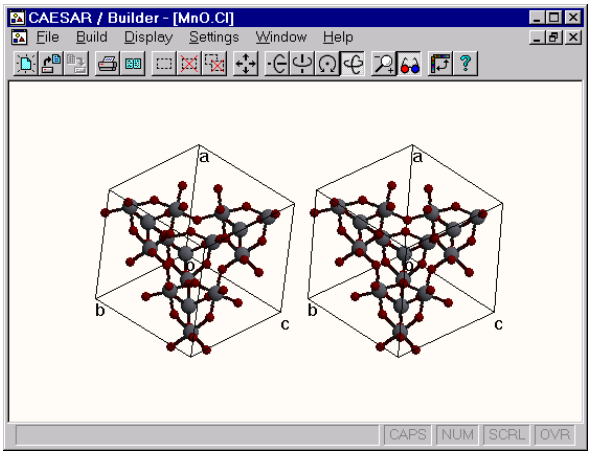

Figure 3.47. Stereoview of the unit cell of the Mn_2O_6 sublattice of $Tl_2Mn_2O_7$.

• *Understanding the Mn_2O_6 substructure*

Load the *Mn.CI* file (in the CAESAR\Examples\Chapter3\Ti2Mn2O7 subdirectory) into *Builder* and display the crystal structure. In order to put the atoms inside the unit cell box, the user may employ the *Into Unit Cell Box* option of the *Convert Unit Cell* command. However, this operation will cut some Mn-O bonds lying outside the box and as a consequence generate unconnected O atoms inside the unit cell box. To avoid such a displeasing structural view, it might be better to employ the following procedure: (1) Select all atoms lying outside the box except for those making bonds with the Mn atoms lying on and inside the unit cell box. (2) Then use the *Translate Atom Group...* command to translate the selected inside the unit cell box. The translation vector can be readily found by rotating

the structure and generating its view along the unit cell vector directions. *Figure 3.47* presents a view of the structure thus obtained. The sublattice has eight Mn_2O_6 units per unit cell.

The user can eventually verify by extending the crystal structure that the Mn_2O_6 substructure is made up of corner-sharing MnO_6 octahedra, that each MnO_6 octahedron shares its corners with six other MnO_6 octahedra, and that the MnO_6 octahedra form a diamond network. Topologically, each MnO_6 octahedron of the Mn_2O_6 sublattice corresponds to the midpoint of each C-C bond of the diamond lattice with a three-fold rotational axis of each MnO_6 octahedron coinciding with the C-C bond axis. As an example of illustrating these points, one might extend the crystal structure and select all the atoms surrounding one Mn atom within a certain radius such that the selected atoms will consist of one MnO_6 octahedron surrounded by its six nearest-neighbor MnO_6 octahedra. For this purpose, first extend the structure in all three directions (e.g., -0.5 - 1.3 in fractional unit), then choose a central Mn atom, identify its atom attribute (e.g., Mn-1-1), and find the radius of the sphere (centered at that Mn) that will exclude all atoms but those belonging to the six nearest-neighbor MnO_6 octahedra surrounding the central Mn atom. These steps are facilitated by zooming-in the central part of the extended structure. The proper radius can be determined in a trial-and-error manner by choosing a radius and looking at the selected atoms until the right value is found. Alternatively, it can be determined by first finding one of the outermost oxygen atoms from one of the six nearest-neighbor MnO_6 octahedra of the central Mn atom and then calculating its distance to the central Mn atom using the command *Atoms Environment*. Either way the proper radius is found to be 5.4 Å. *Figure 3.48* shows a stereoview of the resulting structure, in which the central MnO_6 octahedron share its upper three oxygen atoms with three MnO_6 octahedra lying above, and the lower three oxygen atoms with three MnO_6 octahedra lying below. These octahedra are fused together as in a staggered form of ethane. In the Mn-O-Mn bridges between MnO_6 octahedra, the Mn-O distance is 1.9 Å, and the Mn-O-Mn bond angle is 134°.

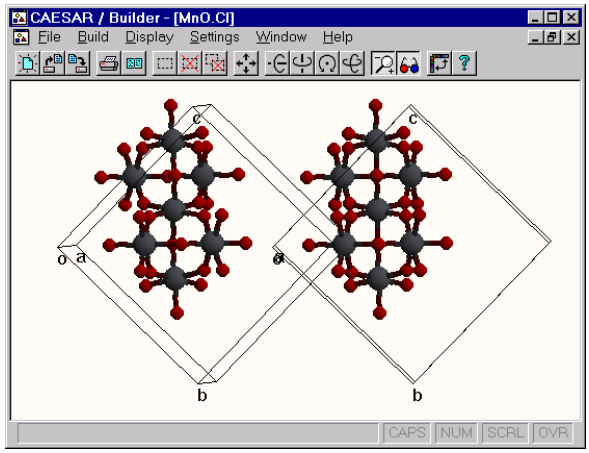

Figure 3.48. Stereoview showing the local environment of one MnO_6 octahedron in the Mn_2O_6 sublattice of $Tl_2Mn_2O_7$. The central MnO_6 octahedron is surrounded by its six nearest-neighbor MnO_6 octahedra.

• ***Putting the sublattices together***

To examine the whole crystal structure, load the *TlMn.CI* file (in the CAESAR\Examples\Chapter3\Ti2Mn2O7 subdirectory) into *Builder*.

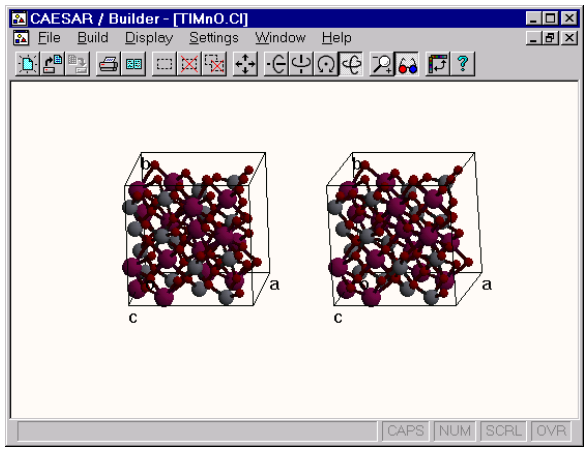

Figure 3.49. Stereoview of the unit cell of $Tl_2Mn_2O_7$.

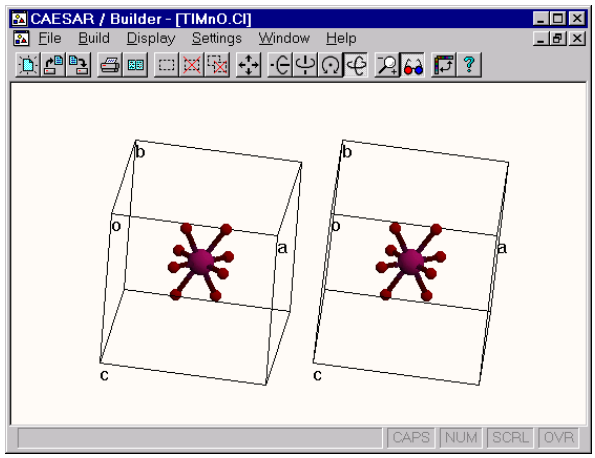

Figure 3.50. Stereoview showing the nearest-neighbor O atoms around one Tl atom in $Tl_2Mn_2O_7$.

As an example, a view of its structure is given in *Figure 3.49*. To understand the relative arrangement of the Tl_2O' and Mn_2O_6 sublattices, it is necessary to examine the local environments of several atoms (e.g., Tl, O) that will contain the atoms of both sublattices. First extend the crystal structure and select the atoms around one Tl within a proper radius such that the selected atoms consist of the Tl atom and its nearest neighbor O' and O atoms. Following the procedures described above, the radius is found to be 2.50 Å, slightly longer than the Tl-O distance 2.46Å. Then, as illustrated by a stereoview in *Figure 3.50*, it is observed that the Tl atom is surrounded by two O' atoms and six O atoms. In order to understand the relative arrangement of the six O atoms, one can make every two adjacent O atoms joined. Then the six O atoms form a puckered O_6 ring as shown in *Figure 3.51*. In diamond the carbon atoms form puckered C_6 rings. The occurrence of puckered O_6 rings in the Mn_2O_6 sublattice is expected, because each MnO_6 octahedron of the Mn_2O_6 sublattice corresponds to the midpoint of each C-C bond of the diamond lattice. Each O-O edge of a puckered O_6 ring represents an O-O edge of an MnO_6 octahedron. Thus, the environment of Tl changes from two oxygen atoms in the sublattice Tl_2O' to eight oxygen atoms in the whole structure, with the additional six atoms coming from the Mn_2O_6 sublattice. In fact the six secondary Tl-O bonds (2.46 Å) are the closest contact between the

Tl_2O' and Mn_2O_6 sublattices, and they are significantly longer than any other bond lengths within each sublattice (e.g., Tl-O = 2.14 Å in the Tl_2O' sublattice, and Mn-O = 1.90 Å in the Mn_2O_6 sublattice).

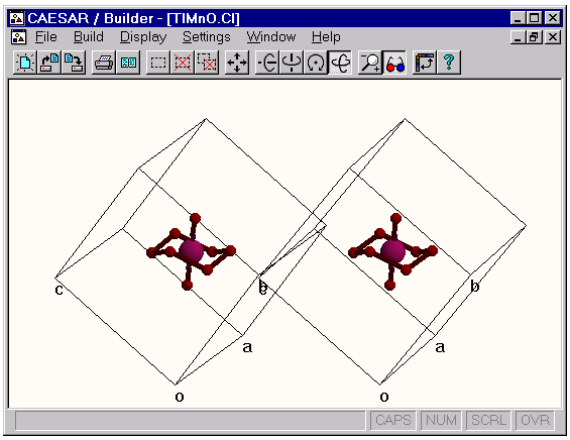

Figure 3.51. Stereoview showing the nearest-neighbor O atoms in $Tl_2Mn_2O_7$, where the ajacent O atoms were linked for clarity.

To examine the environment around one O atom of the Mn_2O_6 sublattice, the user may select the atoms around one such oxygen atom within a certain radius such that the selected atoms include the central oxygen atom and its nearest neighbor Tl and Mn atoms. The proper radius can be found to be 2.5 Å, slightly longer than the Tl-O distance 2.46 Å and Mn-O distance 1.90 Å. Then, as illustrated by a stereoview in *Figure 3.52*, the user will find a distorted tetrahedral arrangement of two Tl and two Mn atoms around the oxygen atom. By rotating this structure, one can find that it has the point group symmetry of C_{2v}.

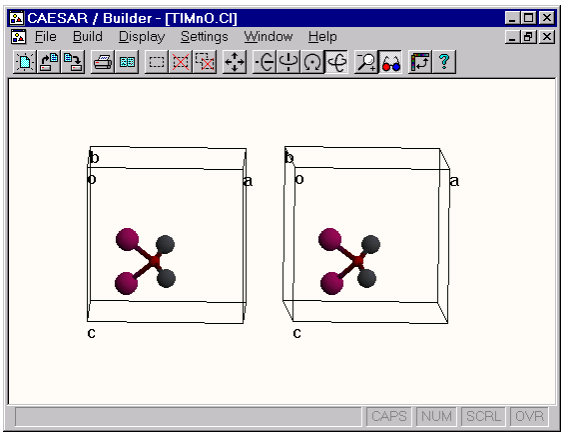

Figure 3.52. Stereoview of the nearest-neighbor atoms around one O atom in $(Mn_2O_6)(Tl_2O')$.