

D. Deformation of Silver Lattice by Interstitial Boron and Fluorine Impurities

The insertion of interstitial impurities in a host lattice causes local deformations of the lattice. The purpose of this case study is the comparison of such deformations caused by boron and fluorine impurities in a silver lattice.

Outline of Computational Approach

The computational procedure involves the following steps

- Retrieve and optimize structure of silver
- Build supercell and insert boron and fluorine, respectively
- Relax structures
- Compare the two optimized structures

1. Retrieve Structure of Silver

In the INFOMATICA tool, perform a search “**Require that Formula is Ag**” and “**Require that Structural Completeness Complete**” and run the search. Select structure ICSD.64996, which is a low temperature measurement with a reported lattice parameter of $a_0=4.071\text{\AA}$. Load the structure in the MEDEA window (in the database window, select the line with the entry ICSD.64996, right-click and “**view**”).

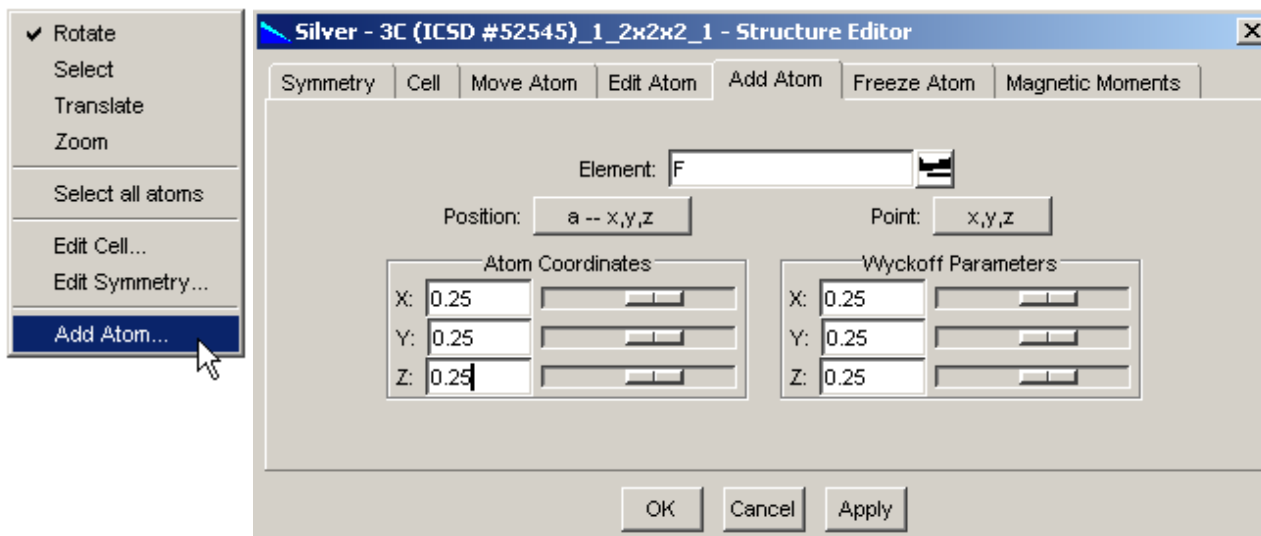
2. Compute Lattice Parameter of Silver

With the crystal structure of Ag in the MEDEA window as the active window (dark blue top bar), we now compute the lattice parameters using VASP. From **Tools** in the MEDEA menu bar, select **VASP 4.6** and invoke the VASP 4.6 graphical user interface by selecting **VASP 4.6 >> Run** from the MEDEA tool bar. From the first panel (“**Calculation**”), select **Structure Optimization** as type of calculation, check **Relax atom positions**, **Allow cell volume to change**, **Allow cell shape to change**. In other words, a full cell optimizations and relaxation of the atom positions is selected. The calculations are performed with the precision “**Accurate**”. All other parameters are left at their defaults. In the SCF tab, the k-spacing is set to 0.2\AA^{-1} , which results in a $14\times 14\times 14$ k-mesh.

The cell optimization increases the original experimental lattice parameter of 4.071\AA by 0.8% to 4.1038\AA . The latter value is used in the subsequent calculations.

3. Build Supercell with Impurity

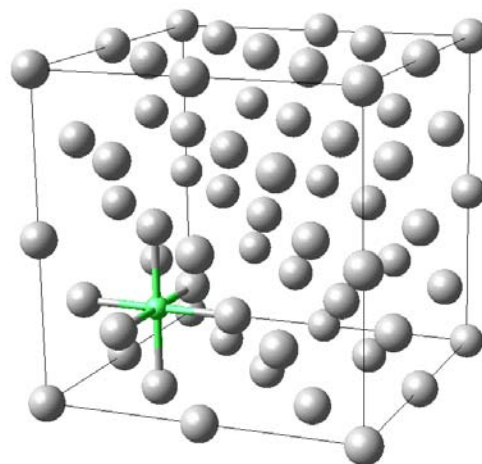
Load the optimized structure of Ag ($a=4.1038 \text{ \AA}$) using **File**>>**Open**>>**Previous Calculation**. Create a 2x2x2 supercell using the command **Edit**>>**Build supercells...** The resulting structure has P1 symmetry. Move the cursor into the white area of the window with the supercell and right-click the mouse button. A dialog comes up. Move the cursor to **Add Atom...** and left-click. A dialog of MEDEA's Structure Editor appears. Insert a fluorine



atom at position (0.25,0.25,0.25) as shown below. Then click **Apply** and **OK**.

Rotate the structure to see the inserted atom. Choose **Edit**>>**Edit bonds...** with a bond factor of 1.05. This shows only bonds around the impurity atom.

If desired, the color of the Ag atoms can be changed by the commands **View**>>**Options**>>**Change colors...** The resulting structure should look as shown on the right.

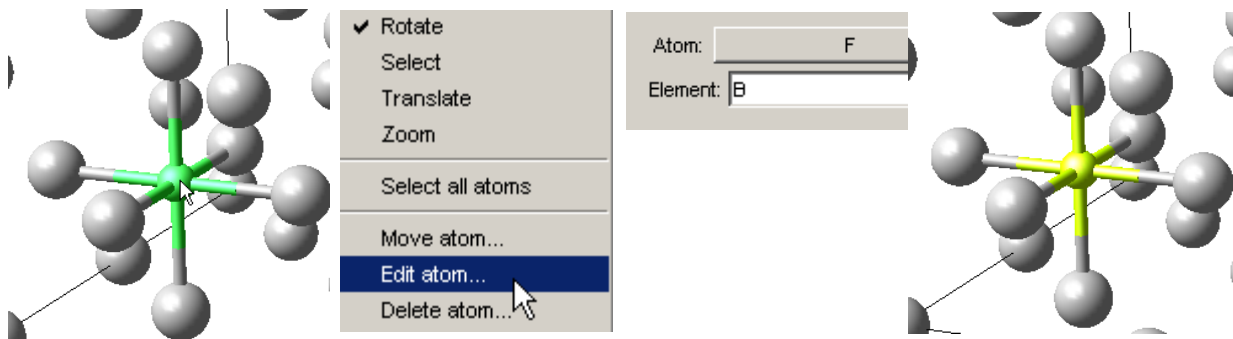


4. Relax Structures

In the following relaxation with VASP, **Normal** precision is sufficient, since only the atomic positions are changed and not the cell parameters. With the system Ag_{32}F in the active window, choose **VASP 4.6**>>**Run** from the Tools. As VASP input parameters, choose **Structure Optimization**>> **Relax atom positions**. The choice for magnetism is **Non-magnetic**. One can also keep the default "**Defined by model**". In either case, the same

non-spin-polarized calculation will be executed. Leave all other parameters at their default values and submit the job.

To perform the same calculation for the boron impurity, activate the supercell structure with the F impurity. Move the cursor over the F atom and right-click the mouse button. A menu should come up with an **Edit atom...** option. (If for some reason a menu without the **Edit atom...** option appears, move the cursor into the white area of the active structure window and just left-click. Then try again.) Replace the Fluor atom by a Boron atom.



Invoke the **VASP 4.6** >> **Run** menu. Leave all parameters the same, but you may want to change the title of the calculations. Then submit the job.

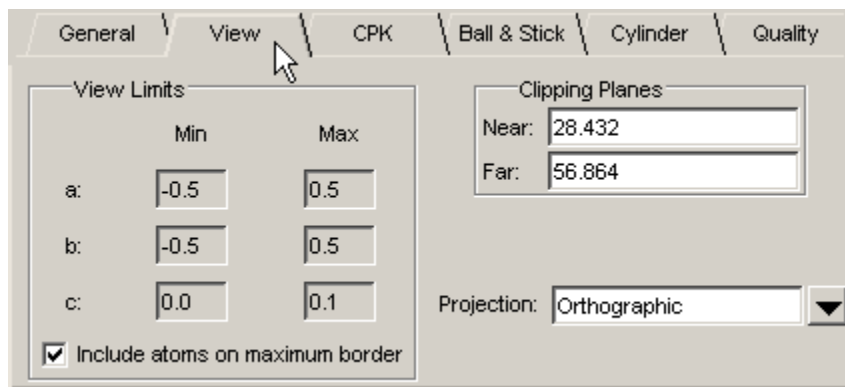
Analyze Results

After completion of the job, the structures are retrieved with

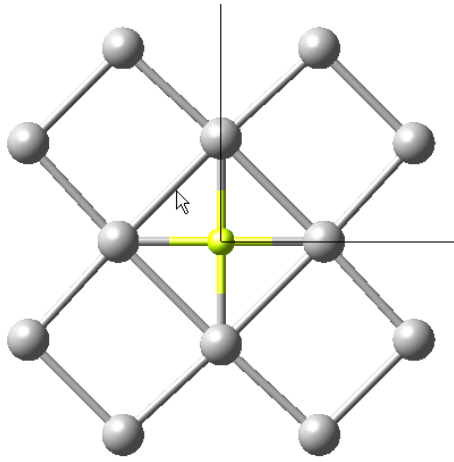
File >> **Open** >> **Previous Calculation**. Use **Edit** >> **Edit Bonds...** to recompute the bonds (they

tend to get scrambled during the optimization). For the present purpose, it is convenient to display only a part of the supercell. This is done using the

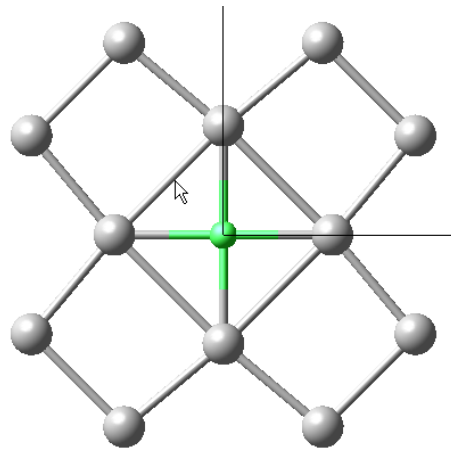
View >> **Options...** command, which brings up a dialog box as shown to the left. Choose the **Min** and **Max** parameters as indicated.



The resulting displays show very clearly that in both cases, the impurity pushes the nearest neighbor Ag atoms away. The distortions are significantly more pronounced for the F impurity than for B, as can be monitored by the distance between two Ag atoms adjacent to the impurity.



Bond Ag/1 - Ag/6, 3.0944 Ang



Bond Ag/1 - Ag/6, 3.2954 Ang