The Defect Analysis Package manual addendum

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Overview

This manual details the methods used to operate the new features available in DefAP 2.0. It should be used in conjunction with DefAP2_manual.pdf.

Defect 'contour' plots

Summary

This new feature enables the plotting of a material's defect chemistry — and optionally, the accommodation mechanism of dopant element(s) — as a function of two environmental conditions. Figure 1 illustrates the features and mechanisms of the new feature that is operated with two new `tasks`: `defect_phase` and `dopant`.

`filename.input`: new parameters

Each line in this input file consists of a 'tag' or 'parameter' (i.e. a string), a colon sign ':', followed by the entered value. There are some exceptions to this rule, detailed in the list of

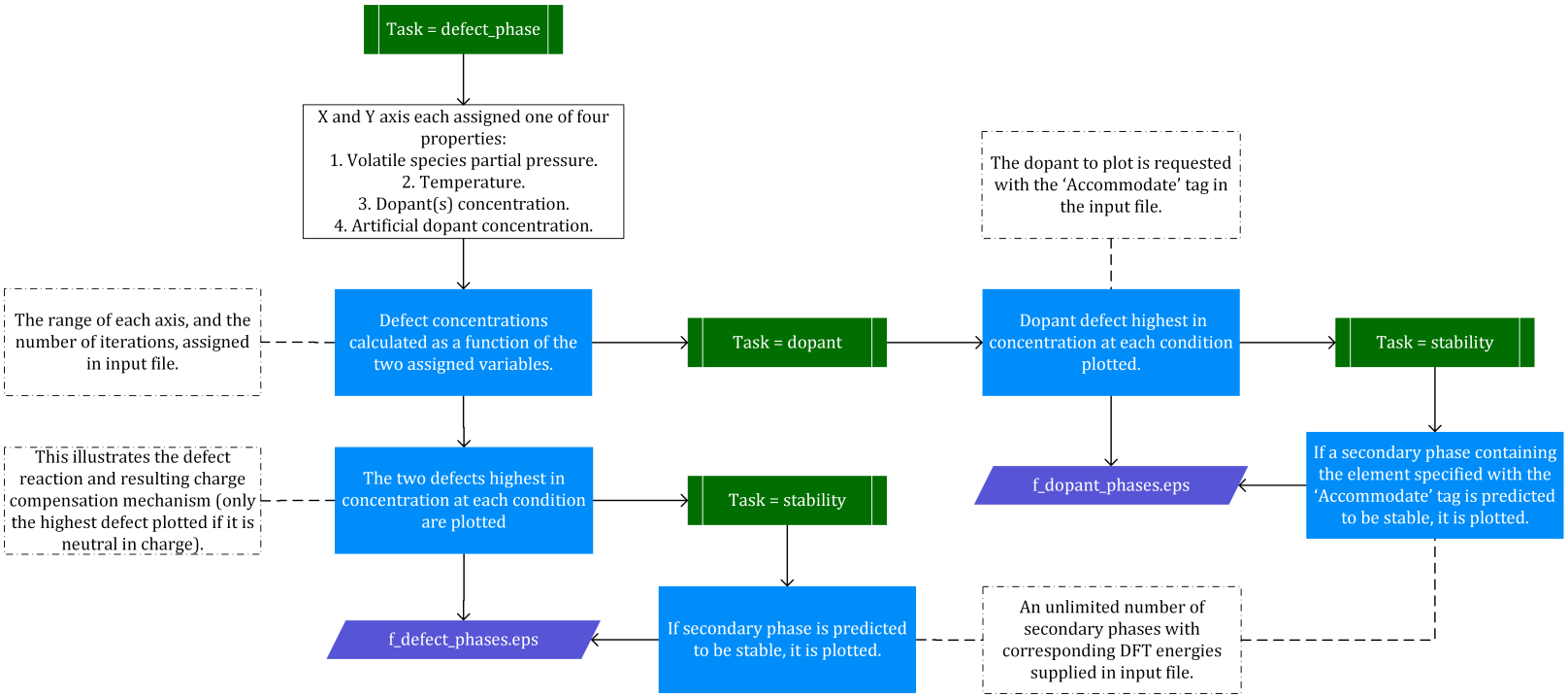

Figure 1: DefAP flow diagram for `defect_phase` task.

optional parameters that follows:

Parameter	Explanation
`tasks`	Instruct what operation you want DefAP to perform. Can provide multiple tasks at once, simply separate with a space. Tasks: • `defect_phase`: Calculate and plot the dominant defect reaction as a function of two properties defined with `loop` (defined in DefAP2_manual.pdf) and `loop2`. At each condition the two defects highest in concentration at each condition are plotted; this illustrates the defect reaction and resulting charge compensation mechanism (only the highest defect plotted if it is neutral in charge). • `dopant`: Dopant defect highest in concentration at each condition plotted, i.e. the dopant accommodation mechanism plotted. The dopant to plot is requested with the `Accommodate` tag. *Requires* `defect_phase` in `tasks`.
`loop2`	Assignment of property on y-axis: • `0`: Volatile species partial pressure. • `1`: Temperature. • `2`: Dopant concentration. • `3`: Artificial dopant concentration.
`min_value_y`	Minimum volatile species partial pressure (10^(`min_value`) atm), temperature (K), or dopant concentration (10^(`min_value`) pfu), depending on loop2 chosen.

`max_value_y`	Maximum volatile species partial pressure (10^(`max_value`) atm), temperature (K), or dopant concentration (10^(`max_value`) pfu), depending on loop2 chosen.
`iterator_y`	Step taken between `min_value_y` and `max_value_y`.
`Accommodate`	Selection of dopant element: the accommodation mechanism of this element is then plotted if `dopant` selected as a `task`.

`filename.output` updates

This file acts as a record of the tasks and processes DefAP is asked to perform. The parameters used to perform the calculations are catalogued, allowing the user to check that the input files have been correctly set up. Additionally:

- If `defect_phase` selected as a `task`, the calculated defect concentrations, chemical potentials for each element, and Fermi level are tabulated at each condition.

- If `stability` selected as a `task`, the results of the stability check are tabulated in this file. When `defect_phase` is selected as the `task`, the stability check is performed and printed at each condition. If DefAP finds any conditions of instability, a message will also be displayed in the main terminal.

`defect.dat`

The `defect_phase` task generates several data files used to create the plots described in the next section.

`filename_defect_phases.p` and `filename_defect_phases.eps`

When `defect_phase` is selected as a `task` DefAP prepares a gnuplot script (`filename_defect_phases.p`) which is automatically run to create an .eps file containing the 'contour' plot

described in Figure 1 (`filename_defect_phases.eps`). The values on the x-axis of the plot are determined by `min_value` and `max_value` in the `filename.input` file; The values on the y-axis of the plot are determined by `min_value_y` and `max_value_y`. The plot can be further customised by modifying the `filename_defect_phases.p` file: this plot is effectively a scatter plot, so the resolution can be increased by reducing the size of `increment` and `increment_y` — this is at the expense of increasing the time to complete the task. Each (`increment`,`increment_y`) coordinate is plotted as a circle with a default radius of `increment`/2. This can be modified in `filename_defect_phases.p`. Labels of defects are based on the defect names given in the `filename.defects` input file.

`filename_dopant_phases.p` and `filename_dopant_phases.eps`

When `dopant` is selected in combination with `defect_phase` as a `task`, DefAP prepares a gnuplot script (`filename_dopant_phases.p`) which is automatically run to create an .eps file containing the 'contour' plot described in Figure 1 (`filename_dopant_phases.eps`). Again, the values on the x-axis of the plot are determined by `min_value` and `max_value` in the `filename.input` file; The values on the y-axis of the plot are determined by `min_value_y` and `max_value_y`. The plot can be further customised by modifying the `filename_dopant_phases.p` file: this plot is effectively a scatter plot, so the resolution can be increased by reducing the size of `increment` and `increment_y` — this is at the expense of increasing the time to complete the task. Each (`increment`,`increment_y`) coordinate is plotted as a circle with a default radius of `increment`/2. This can be modified in `filename_dopant_phases.p`. Labels of dopant defects are based on the dopant defect names given in the `filename.defects` input file.

Gibbs free energy of constituent compounds.

In the original version of DefAP, an option existed to consider the impact of vibrational entropy when calculating the formation energy of each defect. Operation of this method required the calculation of entropy data over a range of temperatures; this was done using empirical methods in the studies to date. The combination of data from DFT and empirical methods is not ideal and represents a weakness in the method.

In this update, the method used to study Li_8PbO_6 by Davies *et al.* has been implemented. This method considers the temperature effects on the constituent compounds by directly calculating their Gibbs free energies within DFT. Specifically, Davies *et al.* used Density Functional Perturbation Theory (DFPT) with the software Phonopy. The information gathered constructs a new input file, `filename.gibbs`.

`filename.input`: new parameters

Each line in this input file consists of a 'tag' or 'parameter' (i.e. a string), a colon sign ':', followed by the entered value. There are some exceptions to this rule, detailed in the list of optional parameters that follows:

Parameter	Explanation
`Gibbs`	Implement the Gibbs free energy of the constituent compounds at the current operating temperature, using the data compiled in `filename.gibbs`. • `0`: Don't apply (default). • `1`: Apply

`filename.gibbs`

The externally calculated Gibbs free energy values are compiled in this file with units: eV/ per functional unit. The input file, `filename.gibbs`, should be constructed as follows:

T	host	constituent	..
T_1	$G_{T_1}^{host}$	$G_{T_1}^{constituent}$	..
T_2	$G_{T_2}^{host}$	$G_{T_2}^{constituent}$	..
:			

The first row is a space-separated list of headings. The heading names of the first two columns are fixed, the remaining must be changed. Beginning at the third column, a column is required for each constituent entered at `constituents`, with the exception of the volatile constituent. The order of the constituent columns in `filename.gibbs` should correspond to the order of the rows entered at `constituents`. On row 1, enter the element/compound name, using the exact same format the name is entered in `constituents`. The input of constituent Gibbs free energies only applies if `chem_pot_method` = `Volatile-Rich-Poor`, otherwise other host data required.

Each row succeeding row 1 is where the Gibbs free energies values are entered at a temperature entered in the first column (K). Temperatures should increase per row added, $T_1 < T_2$. For example, $G_{T_1}^{host}$ is the Gibbs free energy of the host compound at a temperature, T_1. DefAP uses interpolation to obtain the Gibbs free energy values at the temperature it requires. Testing shows that a minimum of four temperatures (4 rows) are required and the temperatures studied must fall within the range of temperature entered in `filename.gibbs`.