**Defect statistics:**

1. **Definitions**

Crystal has crystallographic sites *S*, and *S* can be a defect substituted with an atom/vacancy *A* with the charge state *q*, *ASq*. For example, in ZnO, {*S*} = {Zn, O, *i1, i2*}, {*A*} = {O, Zn, Ga, *V*}, {*q*} = {-2, -1, 0, +1, +2}, then the defects can be GaZn+, GaZn0, VO2+, VO+, VO0 etc.

As derived in Section 1, canonical statics is applied to each site, that is, the defect densities are

 **(1-10)**

, where is the density (number) of the S site, is the formation energy of *ASq* with respect to the energy of the ideal crystal, and is the partition function for the site *S*.

 **(1-11)**

, where the first term of the right-hand equation corresponds to of the ideal site ().

 Here we define partial partition functions, which do not include the ideal site case,

 **(i-1)**

 **(i-2)**

From eq. (1-10), the total density of the *AS* defects is given by

 **(i-3)**

, and the total density of the defects for site *S* is

 **(i-4)**

Then, the density of the ideal sites for site *S* is

 **(i-5)**

1. **Defects frozen at *T*def**

The total defect density at site *S* is

 **(ii-1)**

 **(ii-2)**

1. **Charge states at *T* for the defects frozen at *T*def: Perfect freeze case**

Upon the condition the defects created at *T*def in (ii) are maintained and no extra defects are created at lower temperatures, *T*, the *q* charge states of the defect *AS* are given by

 **(iii-1)**

Note that the partition function in (iii-1) does not include the ideal site as this site *S* is supposed to be a defect, so the partition function is the partial partition function .

1. **Check the case *T*def = *T***

 From eq. (iii-1),

 **(iv-1)**

is obtained, being consistent with eq. (1-10).

**======================================================================================**

1. **Statistics at given *T***

Defects at a *S* site can take different states like: *SS*0 (no defect), *VS*2-, *VS*-, *VS*0, *VS*+, *VS*2+, Ga*S*2+ etc, which are expressed by

{*i*} = {*AS*q} (i = ) (1-1)

. Therefore following constraints should be applied in the scheme of canonical ensemble. i.e.,

The total site number:

 (1-2)

, where denote the number of the sites with the *i* state,

For the entire system, the total energy should be

 (1-3)

, where denote the formation energy of the site with the *i* state.

The total configuration numbers is expressed as

 (1-4)

, where is the configuration number of the ideal sites, and denote the configuration numbers of the site *S*.

 (1-5)

. To obtain maximally probable configuration, the following function *F* should be maximized with the constraint parameters of the Lagrange’s multiplier method (for eqs. (2) and (3)),

 (1-6)

Using the Stirling’s approximation

 (1-7)

eq. (6) will be approximated by

 (1-6’)

To minimize *F* with respect to ,

 (1-8)

Then

 (1-9)

As explained in textbooks of statistical physics,

and is determined by eq. (2). Then,

 **(1-10)**

, where is the partition function for the site *S*.

 **(1-11)**

**This result means that we should apply the canonical statistics to each site independently.**

Note that *i* includes the ideal model, which is normalized to 0 and  **is approximated to ~1 if all satisfy**

 **(1-12)**

Then usual expression

 **(1-13)**

is obtained.

**Ignore below =============================================================================**

1. **Defect densities at *T*def**

Given by

 **(2-1)**

 **(2-2)**

, giving the total defect densities at the site *S*:

 **(2-3)**

1. **Charged states of defects at *T* for the defect densities frozen at *Tdef*: Consider only the frozen defects**

We here consider only remain and are formed at *T* lower than *T*def. The atomic defect structures are frozen and therefore those can take different charge states only, where the ideal state must be exclude. I.e., the defect states are expressed only by the charge states *q*..

{*q*} = {-2, -1, 0, +1, +2 etc} (3-1)

Then, we obtain

 **(3-2)**

 **(3-3)**

Note that does not include the ideal state and cannot be approximated to 1.

If one (*q* = *q’*) is satisfactory smaller than the other , and

 **(4-2)**

This result would be consistent with our intuitive conclusion, where all the defects take the lowest energy state.

1. **What happens if *T* = *T*def**

In principle, eq. (3-2) must be identical to eq. (1-10) if *T* = *T*def.

 **(1-10)**

 **(1-11)**

**=**

 **(3-2’)**

 **(3-3’)**

 **(4-1)**

1. **Charged states of defect at *T* for the defect densities frozen at *Tdef*: More realistic case. Additional formation of thermal equilibrium defects at *T***

We need to consider and separately for the site *S* because the former sites cannot change structure and can change charged state only, while the latter can produce/change defect states by thermal equilibrium. Therefore, former counts only different charge states and must exclude the ideal state.

{*q*} = {-2, -1, 0, +1, +2 etc} (16)

and

 **(17)**

 **(18)**

Note that does not include the ideal state and can not be approximated to 1.

Whil

1. **Charged states of defect at *T* for the defect densities frozen at *Tdef***

We need to consider and separately for the site *S* because the former sites cannot change structure and can change charged state only, while the latter can produce/change defect states by thermal equilibrium. Therefore, former counts only different charge states and must exclude the ideal state.

{*q*} = {-2, -1, 0, +1, +2 etc} (16)

and

 **(17)**

 **(18)**

Note that does not include the ideal state and can not be approximated to 1.

while the latter follows the discussion in Section 1.

 **(18)**

 **(19)**

Then total defect states at *T* for the defects frozen at *T*def are given by

 **(20)**

1. **Consistency check.**

One requirement for eq. (20) is that the case *T*def = *T* must be equal to eq. (10).

 **(21)**

for *i* is not the ideal state.

 **This condition is satisfied only if .**