



# Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. I. Theoretical background

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## Abstract

The Gibbs adsorption isotherm and Wagner's definition of excess solute at surfaces and grain boundaries are both extended to include other crystalline defects, like dislocations and vacancies. By using a thermodynamic state function which is suitable for a partially open system, open with respect to solvent and closed with respect to solute atoms, a generalized Gibbs adsorption isotherm can be derived. Thus solute segregation to dislocations and vacancies gives rise to a reduction of their formation energies, too. The results of the presented treatment are compared with results stemming from statistical mechanics or computer simulations. Special attention is paid to the question whether defect energies might become zero or negative.

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**Keywords:** Grain boundary energy; Dislocation line energy; Vacancy formation energy; Solute segregation

## 1. Introduction

It is a well-known fact in elemental solids that point defects are thermodynamically stable because the investment in energy of formation  $U_f$  can be compensated for at elevated temperatures  $T$  by an equal contribution  $TS_f$  to the free energy. The latter mainly arise from the gain in configurational entropy  $S_f$ . Extended defects like grain boundaries, stacking faults and dislocations change the configurational entropy of a perfect crystal to a much lesser extent and, therefore, will not be thermodynamically stable below the melting point of the elemental crystal.

In binary or multi-component systems the formation of a defect is accompanied by a more or less pronounced redistribution of the component atoms or molecules around the defect. If solute atoms segregate at the defect, the total free energy is reduced. The corresponding decrease can be assigned to either (i) a decrease in the energy of the trapped solute atom or (ii) a decrease in the formation

energy of the defect. For the latter case, a well-known example from daily life is the formation of foams on liquids. In this case, the free surface is the “defect” and the “alloying” with surfactant molecules reduces the surface energy to an appreciable extent which is sufficient to create rather stable foams. Thus coarsening, driven by a decrease in the overall surface area, is retarded in the presence of solute molecules. A quantitative treatment of the change in surface energy was first provided by Gibbs [1], leading to the following famous relation called adsorption isotherm

$$d\gamma = -\Gamma_A d\mu_A \quad \text{or} \quad \left. \frac{\partial \gamma}{\partial \mu_A} \right|_{n_B, T, a} = -\Gamma_A \quad (1)$$

where  $\gamma$  is the surface energy and  $\mu_A$  is the chemical potential of molecules of type A dissolved in a material of molecules of type B with a constant number  $n_B$ . The surface area  $a$  is maintained constant, too, and  $\Gamma_A$  is the excess amount of molecules of type A in the neighbourhood of the defect as compared with the defect-free crystal. Although mainly used for surface adsorption, Eq. (1) has been applied successfully to grain- and phase boundaries, and has been extended recently to other defects interacting with hydrogen [2].

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In the case of grain boundaries the definition of  $\Gamma_A$  is straightforward, because the concentration of A in the adjacent grains is the same on both sides of the boundary. Although the distribution may not be symmetrical, the excess solute as defined as the integral over the concentration difference between the actual concentration distribution across the boundary and the constant concentration far away from the boundary is independent of the exact position of the grain boundary. For boundaries between two different phases the evaluation of the excess of A is complicated by the fact that the exact position of the dividing interface has to be known [3–5]. In order to avoid this difficulty, Cahn [4] and Wagner [5] introduced new definitions of  $\Gamma_A$ . The latter one has a clear-cut operational meaning and allows pertinent measurements of the interface excess concentration.

It is the main purpose of the present paper to extend Wagner's definition to other defects, like vacancies and dislocations, as well as surfaces and grain boundaries as used in the original work by Gibbs [1]. Thus a generalized Gibbs adsorption equation will be derived describing the decrease in defect energies for a positive excess and an increasing chemical potential of A. The possibility and consequences of whether the decrease in the defect energy predicted by Eq. (1) may lead to zero or even negative values will be discussed. This special discussion of Gibbs adsorption equation has been restricted to grain boundaries [6–10], in order to understand the exceptional thermal stability of nanocrystalline materials.

Experimental evidence for the generalized treatment of all defects and resulting conclusion for the various defects are provided in a subsequent paper [11]. The impact of the extended concept regarding materials science is manifold. Thus the stability or instability of nanostructured materials depends on solute segregation to phase and grain boundaries, solute softening could be due to a reduction of the formation energies of dislocations and/or kinks, and superabundant vacancies [12] are naturally explained by a reduction of their formation energy in the presence of hydrogen. Minor parts of the present work have been published in Ref. [2].

## 2. Wagner's definition of surface excess

Wagner [5] proposed a *Gedankenexperiment*, as schematically shown in Fig. 1. By changing the orientation of a container, which is filled with both gaseous HCl and liquid mercury, the surface of Hg is increased by an amount  $\delta a$ . Then HCl molecules from the gas phase will be adsorbed on the newly generated surface, if the surface excess of HCl is positive. In order to maintain the partial pressure or the chemical potential of HCl, respectively, at constant values, the amount of HCl molecules in the container has to be increased by  $\delta n_A$ . Wagner [5] defines the ratio of  $\delta n_A$  and  $\delta a$  or the corresponding partial derivative as the surface excess of HCl according to the following equation:

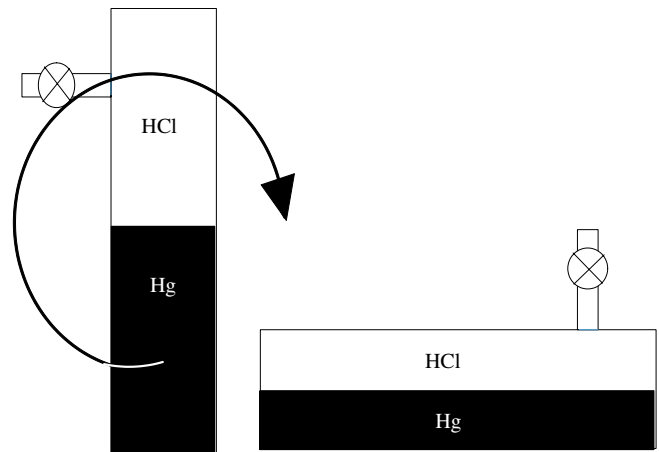


Fig. 1. Schematic presentation of Wagner's *Gedankenversuch*. A vessel with a closed valve contains liquid Hg and gaseous HCl. By turning it into a horizontal position the surface area of the Hg is enlarged and the HCl adsorbs onto the freshly produced area. Thus the partial pressure of HCl is reduced and the number of moles of HCl per additional surface area, which have to be introduced via the valve in order to establish the initial HCl pressure, is defined as excess HCl.

$$\Gamma_A = \left. \frac{\partial n_A}{\partial a} \right|_{T, V, \mu_A, n_B} \quad (2)$$

This definition does not require the correct positioning of a dividing interface and it is equivalent with the excess defined by Gibbs via a dividing interface. In Ref. [5] Wagner uses the pressure,  $P$ , as an intensive variable instead of the chemical potential,  $\mu_A$ . However, holding  $P$  constant is equivalent with keeping  $\mu_A$  constant in the context of Wagner's *Gedankenexperiment* and for binary alloys. In addition, the following derivation reveals that the variable  $\mu_A$  is more appropriate in defining the excess  $\Gamma_A$ .

Wagner also introduced a new thermodynamic potential,  $\Phi$ , defined as [5]

$$\Phi = F - \mu_A n_A \quad (3)$$

where  $F$  is Helmholtz free energy. Eq. (3) has the differential

$$d\Phi = pdV - SdT + \gamma da + \mu_B dn_B - n_A d\mu_A \quad (4)$$

containing a work term  $\gamma da$  due to the surface with a surface energy  $\gamma$ . The function  $\Phi$  is appropriate for measurements with constant volume and constant temperature, and in a closed system with respect to solvent atoms B but open under constant chemical potential with respect to solute atom A. Therefore,  $\Phi$  is the thermodynamic state function which has to be used for the experiment depicted in Fig. 1. As second derivatives of state functions are independent of the sequence of differentiation, we obtain the following Maxwell relation

$$\left. \frac{\partial^2 \Phi}{\partial \mu_A \partial a} \right|_{V, T, n_B} = - \left. \frac{\partial n_A}{\partial a} \right|_{V, T, \mu_A, n_B} = \left. \frac{\partial^2 \Phi}{\partial a \partial \mu_A} \right|_{V, T, n_B} = \left. \frac{\partial \gamma}{\partial \mu_A} \right|_{V, T, a, n_B} \quad (5)$$

Inserting in the last equation Wagner's definition of excess given by Eq. (2) leads to

$$\left. \frac{\partial \gamma}{\partial \mu_A} \right|_{V, T, a, n_B} = -\Gamma_A \quad (6)$$

which is equivalent to Gibbs adsorption equation.

The treatment presented so far is valid for liquid/gas and liquid/liquid interfaces. For crystalline solids, complications arise because surface and grain boundary energies depend on crystallographic orientations. The pioneers Gibbs [1], Mullins [3], Cahn [4] and Wagner [5] were well aware of this effect, concluding that Eq. (1) or Eq. (6), respectively, has to be set-up for each individual surface or grain boundary with its individual energy and excess. If this distinction is not made, the grain boundary energy corresponds to an average over all grain boundaries or surfaces, respectively. Besides crystallographic orientation, interfaces of solids have the special feature that they may be strained and, therefore, carry mechanical stresses. In his lattice site model, Mullins [3] discusses this effect and derives the following modified version of the Gibbs adsorption equation for constant temperature

$$d\gamma = -\Gamma_A d\mu_A + \frac{2}{3}(f - \gamma) \frac{dv}{v} \quad (7)$$

where the notation of the present work has been used and  $f$  is the surface stress and  $v$  is the volume of the lattice site or unit cell, respectively. As the second term on the right-hand side of Eq. (7) will be neglected in the following, an additional constraint  $dv = 0$  will be applied. Thus, during a change of interfacial area or defect density in general, the number of lattice sites has to change in order to maintain an unstrained lattice. As an example, the reduction of grain boundary area and the concomitant creation of excess volume by vacancy creation, for instance, lead to a reduction of the number of lattice sites if the excess vacancies are annihilated at the surface.

### 3. General definition of solute excess at a defect and resulting changes of defect formation energies

It is very well known that segregation of solute atoms occurs to other defects besides surfaces, i.e. grain boundaries, stacking faults, dislocations and vacancies may interact attractively with solute atoms. Here the phenomenological approach taken by Wagner [5] proves to be even more helpful when compared with an attempt to define the solute excess by a local surplus of solute concentration. This is especially obvious for dislocations where solute segregation by elastic interaction takes place in the long-ranging strain field of a dislocation. Thus the solute excess is distributed over the whole sample and it becomes difficult at least to define a cut-off radius. However, if we modify the concept shown in Fig. 1 by changing the defect concentration, i.e. grain boundary area or dislocations length, in a solvent crystal with a constant number of B atoms, the cor-

responding change of the number of A atoms is the measure of solute excess. A specific example is depicted in Fig. 2 with palladium as solvent, or B atoms and hydrogen as A atoms.

The modified *Gedankenexperiment* for grain boundaries and solids is exemplified in Fig. 2. There a palladium crystal formed like a dog bone contains either a grain boundary or a dislocation in the wider part of the dog bone. The defected crystal is in a closed vessel containing gaseous hydrogen in equilibrium with the Pd sample. Under these conditions hydrogen is also dissolved in the solid either in normal or defected regions. If the defect is moved by external forces, i.e. a shear stress or a magnetic field from the wider to the narrower region of the crystal, it reduces its area or length, respectively. After attaining a new equilibrium with gaseous hydrogen, the number of hydrogen molecules in the gas phase might have changed. For positive (negative) excess hydrogen at the defect the number of hydrogen molecules increases (decreases). Most of the excess hydrogen corresponding to the annihilated part  $\Delta a$  ( $\Delta l$ ) of the grain boundary area (dislocation length) is then released to the gas phase, giving rise to an increase in  $H_2$  pressure. However, some of the former excess of the annihilated defect remains in the Pd sample, because it has a higher H solubility at the increased  $H_2$  pressure. The sum of the two is the total excess hydrogen  $\Delta n_A$ , which can be determined experimentally as the amount of hydrogen which has to be removed via the valve in order to establish

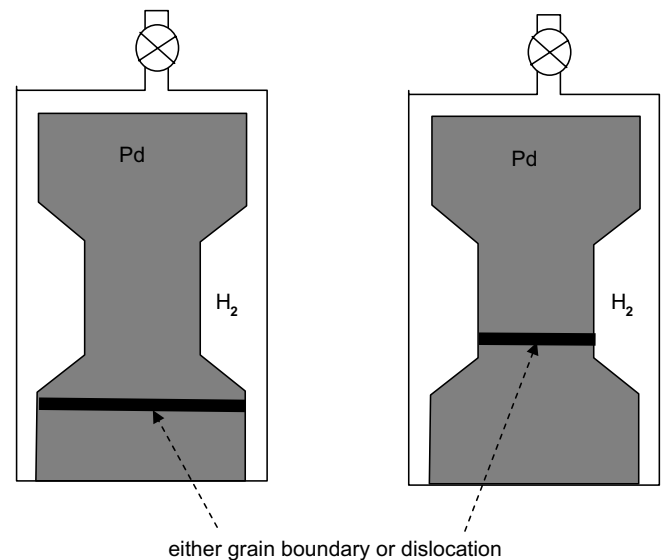


Fig. 2. Wagner's *Gedankenexperiment* modified for grain boundaries and dislocations, respectively. A vessel with a closed valve contains a dog-bone-shaped crystal of palladium and gaseous  $H_2$ . By an external force (e.g. shear stress or magnetic field) the grain boundary (dislocation) is moved from the thick to the thin region. Thus the grain boundary area (dislocation length) is decreased and the excess hydrogen from the annihilated part of the defect is released in the gas phase. Thus the partial pressure of  $H_2$  is increased and the number of moles of H per additional surface area, which have to be removed via the valve in order to establish the initial  $H_2$  pressure, is defined as excess hydrogen.

the initial partial pressure of hydrogen or the initial chemical potential  $\mu_A$ , respectively. Thus an excess has been measured as defined via Eq. (2) for grain boundaries. For dislocations in a sample without grain boundaries this is expressed as

$$\Gamma_A^D = \lim_{\Delta l \rightarrow 0} \frac{\Delta n_A}{\Delta l} \bigg|_{T, V, \mu_A, n_B} = \frac{\partial n_A}{\partial l} \bigg|_{T, V, \mu_A, n_B} \quad (8)$$

In reality, we are dealing with different types of dislocations. Then the definition for solute excess has to be written down for all types of dislocations, i.e. edge, screw or mixed dislocations, in accordance with the statement given at the end of the previous chapter. In the presence of grain boundaries, their area has to be held constant, too.

The decrease in defect area or length, respectively, as presented in Fig. 2 is accompanied by a decrease in the number of lattice sites, because the excess volume of the grain boundary is annihilated. For positive as well as negative grain boundary energies the position in the middle of the dog bone is a metastable one. For positive energies the stable equilibrium is attained by moving the defect out of the crystal and for negative energies (see the discussion in Section 4) a position in the wider parts of the crystal is preferred.

Of course, the procedure described before for palladium and hydrogen being in a system of constant volume can be applied to any solid in equilibrium with the vapour pressure of a solute species. However, with a sample as presented in Fig. 2 the amount of excess solute is very small, and it would be easier to conduct a similar experiment with a polycrystalline (or deformed) Pd sample in a closed vessel as depicted in Fig. 3. For small grain sizes or high dislocation densities the amount of excess hydrogen is larger and easier to determine [11]. A given amount of hydrogen gas, i.e.  $H_2$  molecules, is introduced via a valve and part of it is dissolved as H atoms until equilibrium with gaseous hydrogen at a given partial pressure of hydrogen or given chemical potential  $\mu_H$  is achieved. The number of dissolved H atoms,  $n_A$ , can be determined, for instance, by calculating the difference between the total number of H atoms as introduced and the remaining H atoms in the gas phase, knowing its volume and pressure. In a following step the grain boundary area (total length of dislocation lines) is decreased by an amount  $da$  ( $dl$ ) initiated by grain growth (recovery) during a short excursion to a higher temperature.

Working with non-equilibrium vacancies produced either by radiation or by quenching from elevated temperatures, the same *Gedankenexperiment* as described before can be conducted and the vacancy concentration  $n_V$  can be changed by an infinitesimal amount. Then the solute excess at vacancies is defined as

$$\Gamma_A^V = \frac{\partial n_A}{\partial n_V} \bigg|_{T, V, \mu_A, n_B} \quad (9)$$

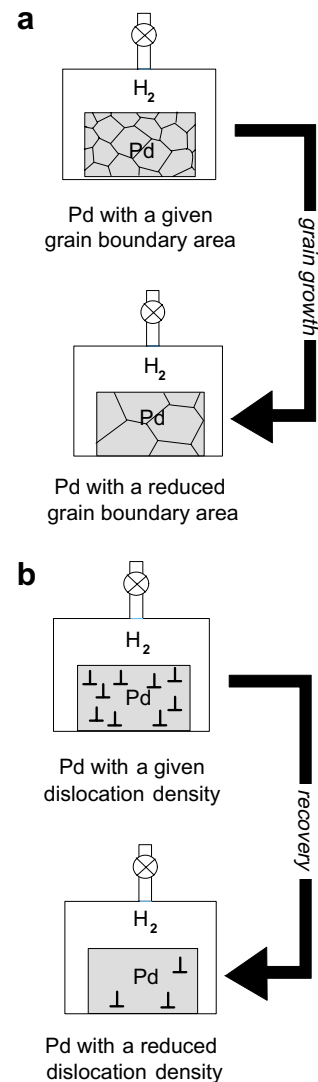


Fig. 3. (a) Wagner's *Gedankenexperiment* (cf. Fig. 1) is applied to grain boundaries in Pd and gaseous  $H_2$ . Hydrogen is also dissolved atomically in the grains and as excess  $H$  in the grain boundaries. By reducing the grain boundary area by an intermediate annealing process some of the excess  $H$  is released into the gas phase. The amount of  $H$  per annihilated grain boundary area, which has to be removed via the valve in order to establish the initial hydrogen partial pressure, is defined as excess  $H$ . (b) Same as (a) but for dislocation in Pd. By reducing the dislocation length during a recovery step the excess  $H$  at these defects is now released into the gas phase. The amount of  $H$  (removed via the valve) per annihilated dislocation length, which is necessary to set up the initial  $H_2$  pressure, is defined as excess  $H$  at dislocations.

and the excess is simply the average number of solute atoms per vacancy.

The major advantage of the generalised definition of excess solute caused by a defect is the use of Eqs. (3)–(6) after slight modifications only. For dislocations, the area,  $a$ , has to be replaced by the dislocation length,  $l$ , and  $\gamma$  becomes the Helmholtz free line energy per unit of length  $F_d$ . For vacancies, area  $a$  has to be replaced by the number of these defects,  $n_V$ , and  $\gamma$  becomes the Helmholtz free energy of formation per vacancy  $F_V$ , i.e.



$$\left. \frac{\partial \gamma_D}{\partial \mu_A} \right|_{V,T,l,n_B} = -\Gamma_A^D \quad \text{and} \quad \left. \frac{\partial F_V}{\partial \mu_A} \right|_{V,T,n_V,n_B} = -\Gamma_A^V \quad (10)$$

As discussed in the introduction, the presence of point defects contributes considerably to the configurational entropy and, therefore, unlike interfaces and line defects, their Helmholtz free energy will become zero at a certain vacancy concentration. At this equilibrium concentration the term  $\gamma da = F_V dn_V$  is zero, whereas for interfaces and line defects it is usually positive (zero or negative values are discussed in Section 4). As a consequence,  $da < 0$  ( $dl < 0$ ) lowers the value of  $\Phi$  in Eq. (4) for extended defects, yielding  $a = 0$  ( $l = 0$ ). Thus the system containing grain boundaries and/or dislocations will be in a metastable state, being in equilibrium with all relevant thermodynamic variables besides  $a$  or  $l$ , respectively. The same is true for non-equilibrium vacancies, where  $F_V$  is positive. It is a crucial assumption for the special Gibbs adsorption isotherm for grain boundaries as well as for the generalized version in this study that the attainment of the stable equilibrium is somehow hindered by kinetic barriers but the equilibrium segregation of solute A to the defects is allowed.

The preceding special treatment for interfaces, dislocations and vacancies can be generalized by introducing a defect density as outlined in Appendix A. Then excess solute of the defect and its change of energy will be covered by one equation for each quantity.

In order to integrate Eq. (6) or (10), one has to know the dependence of  $\Gamma_A$  on  $\mu_A$ . This can be achieved experimentally or in the framework of statistical thermodynamics. For the latter case, one has to know the interaction energies between defect and solute as well as between solute and solute. The latter is becoming important at high levels of segregation when the distance between segregated A atoms is becoming small. However, there are two limiting cases. For very low values of  $\mu_A$  the concentration of A in B is very small and so is the excess solute at the defect. Then Eq. (6) predicts that  $\gamma$  will not change much, as schematically shown in Fig. 4. Although not stated explicitly, this and the following statements are true for Eq. (10) and  $F_D$  or  $F_V$  as well. At high values of  $\mu_A$  the defect may become saturated with A, because of a limited number of segregation sites like sites in the dislocation core or one or two monolayers at the grain boundary. If we denote the corresponding saturated excess by  $\Gamma_A^{\text{sat}}$ , the defect energy decreases linearly with increasing  $\mu_A$  (cf. Fig. 4). The decrease in  $\gamma$  is even more pronounced if  $\Gamma_A$  increases with increasing  $\mu_A$ , i.e. by the formation of a second layer of A atoms at a grain boundary.

Now the intriguing question arises whether we can reach such high values of  $\mu_A$  where the defect energy becomes zero or even negative. The defect energy is the difference of the total energy of the defected and the defect-free material for the same volume, temperature, chemical potential of solute and constant number of solvent atoms. Zero defect energy would imply that the defects, i.e. grain

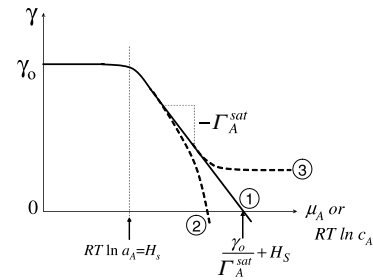


Fig. 4. Schematic dependence of the defect energy,  $\gamma$ , on the chemical potential,  $\mu_A$ , of solute A according to the Gibbs adsorption isotherm (Eq. (1)). At low chemical potentials or activities, the excess A,  $\Gamma_A$ , is negligible and the slope of the curve is zero. If the chemical potential reaches the interaction energy,  $H_s$ , of A with the defect, the excess increases and the slope becomes negative. Saturating the defect with  $\Gamma_A^{\text{sat}}$  leads to a constant slope (line 1) which intercepts the abscissa at the given chemical potential. If the excess does not saturate, line 2 describes the expected dependency. Line 3 describes the behaviour if a new A-rich phase is formed and the logarithm of concentration,  $c_A$ , instead of the chemical potential is used as the variable for the abscissa. In the latter case, the chemical potential and, therefore, the excess and  $\gamma$  remain constant during the phase separation despite increasing concentration.

boundaries and dislocation, become equilibrium defects. Negative formation energies of defects mean that the number or density of defects will increase if, in a partially open system, the necessary excess solute is provided from a reservoir. These predictions will be discussed further below by applying models for the defect solute interaction. In the absence of solute atoms and their segregation, the existence and consequences of negative formation energies have been discussed for triple lines [13–15].

#### 4. Conditions and indications for zero or negative formation energies

The following discussion is mainly restricted to grain boundaries and surfaces, because only three studies referring to negative formation energies of vacancies [12,16] and zero energy for a line defect in a vesicle [17] have been identified by the author. Experimental evidence for decreased formation energies and its consequences are compiled in a subsequent study [11].

##### 4.1. Statistical mechanics

In order to integrate Eq. (6), the relationship between excess  $\Gamma_A$  and  $\mu_A$  has to be known. This relation has been derived for grain boundaries by Weissmüller [6] based on Cahn's definition of excess solute and the Langmuir–McLean equation for segregation, where ideal dilution and constant segregation energy were assumed (cf. Appendix B). In addition, the present author applied Seah's empirical relation between solute segregation to grain boundaries and terminal solubility [18], and predicted [8] that precipitation of an A-rich phase is expected for reasonable values of the grain boundary energy before this quantity becomes zero. Thus high

nucleation barriers for precipitation and/or the failure of Seah's relation are required for zero or negative grain boundary energies.

#### 4.2. Computer simulations

As predicted by Eq. (10), the formation energy of vacancies decreases with the number of solute atoms bound to the vacancy and with increasing chemical potential of hydrogen. This has been proven for hydrogen vacancy complexes in iron by Tateyama and Ohno, applying an ab initio supercell calculation [16]. For an excess of 5 and 6 H atoms per vacancy and a partial  $H_2$  pressure of 2 GPa, negative formation energies of vacancies were calculated.

There are a few studies calculating negative values of surface energies [19–21] and grain boundary energies [22] for solids. Total energies for a restricted number of atoms are calculated in these studies by various techniques. In the case of  $\alpha$ - $Al_2O_3$ , Wang et al. [19] evaluated the energy  $E$  of a thin slab with a constant composition of the two surfaces and the surface energy via the following equation

$$\gamma = E + \Delta G_{\text{vib}} - \sum N_i \mu_i \quad (11)$$

where  $\Delta G_{\text{vib}}$  is the vibrational contribution to Gibbs free energy,  $N_i$  is the number of  $i$ th type of atom and  $\mu_i$  is the chemical potential of  $i$ th type of atom. The results are presented in Fig. 5 for varying chemical potentials of oxygen. However, the following analysis in the framework of the Gibbs adsorption isotherm was not performed in Ref. [19]. For a stoichiometric composition  $N_{i0}$  the sum in Eq.

(11) corresponds to the formation energy of the bulk oxide. Deviations from stoichiometry  $N_i - N_{i0}$  per unit surface area are equivalent to the excess  $\Gamma_i$ . Thus Eq. (11) explicitly contains the integrated form of Eq. (1) for constant excess. The notation in Fig. 5 is such that R represents the bulk, i.e.  $Al_2O_3$ , and the preceding letters describe the composition of the two surfaces of the slab in terms of layers of the corresponding element. Thus  $Al_3O_3$ -R corresponds to  $Al_3O_3-(Al_2O_3)_n-Al_3$ , with the surfaces terminated by Al atoms. Compared with stoichiometry, six O or two (0001) oxygen planes with a coverage of  $1.5 \times 10^{19} \text{ m}^{-2}$  per plane are missing. Then the excess per surface is  $\Gamma_O = -1.5 \times 10^{19} \text{ m}^{-2}$ . This excess is kept constant during the calculation and, according to Eq. (6) and Fig. 5, the slope of the corresponding straight line in Fig. 5 is  $+1.5 \times 10^{19} \text{ m}^{-2}$ . Analogously,  $O_2AlAl$ -R equals  $O_2AlAl-(O_3Al_2)_n-O_2$ , with an excess of one O or one-third of a (0001)-plane. Then the slope in Fig. 5 for this case equals  $-0.25 \times 10^{19} \text{ m}^{-2}$ .  $AlO_3Al$ -R means  $AlO_3Al-(AlO_3Al)_n-AlO_3Al$  and no excess or zero slope, respectively. Within the stability range of  $Al_2O_3$  the surface energies for the various surface compositions and chemical potentials vary considerably but do not reach zero or negative values unless hydrogen is added. Then a hydroxide layer of composition  $H_3O_3Al$ -R gave negative surface energies at high chemical potentials of oxygen, in agreement with Ref. [20]. However, this is not the stable state at the corresponding chemical potentials and a total conversion of the oxide into a hydroxide would lead to the thermodynamic equilibrium state. Contrarily, Łodziana et al. [20] state that reducing the thickness of the simulated slab, i.e. the number of  $AlO_3Al$  layers,  $n$ , leads to an increase in the calculated surface energy from negative to positive values and, therefore, to an equilibrium state of zero energy. These findings are supported by the experimentally observed thermal stability of nanometer-sized alumina particles containing a hydrogen-terminated surface.

Using Lennard-Jones potentials, Millett et al. [22] calculated grain boundary energies for copper as the energy difference between a sample containing one grain boundary and a sample in the single crystalline state. By incorporating Bi atoms into the boundary, they found that the grain boundary energy decreases with increasing excess, reaching negative values of  $\gamma$ . However, they did not show whether at the corresponding chemical potential of Bi thermodynamic equilibrium was attained, i.e. whether Bi atoms remain at the boundary and do not form a precipitate within the grain.

Nielsen et al. [23] applied a coarse-grain model, in order to calculate the surface energy of water in the presence of lipid molecules. For a large excess of lipid molecules, negative surface energies were calculated. Under these conditions, molecular dynamics simulations revealed an instability leading to either an agglomeration (precipitation) of lipid molecules or a wavy surface, i.e. new surface area was created, yielding a lower excess for the closed system.

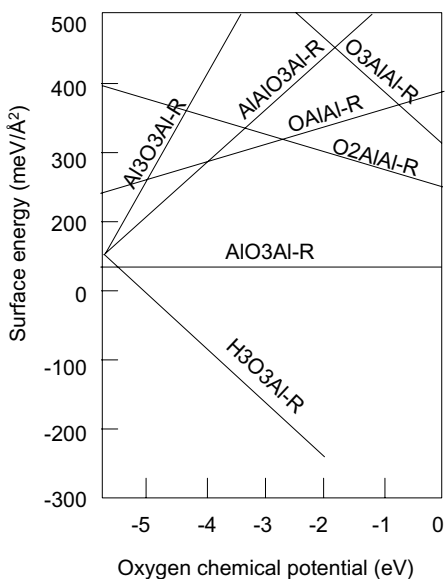


Fig. 5. Surface energy of aluminium oxide obtained from first principle calculations via Eq. (11) for different excesses of aluminium, oxygen and hydrogen plotted vs. the oxygen potential. The notation for the various excesses is explained in the text. Note the negative surface energy for hydrogen-terminated surfaces.

### 4.3. Treatment of wetting by Landau and Lifshitz [24]

Landau and Lifshitz [24] describe in their textbook on theoretical physics the adsorption of molecules from a vapour phase onto the surface of a solid. It is straightforward rendering their treatment into the context of grain boundary segregation by neglecting stress effects. Integration of Eq. (6) is modified to

$$\Delta\gamma = - \int_{-\infty}^{\mu_A} \Gamma_A d\mu_A = - \int_0^{\Gamma_A} \Gamma_A \frac{d\mu_A}{d\Gamma_A} d\Gamma_A \quad (12)$$

where  $\Delta\gamma$  is the change of the surface energy between the two boundaries. If  $\mu_A$  approaches infinity, so does  $\Gamma_A$ , and a liquid film of A forms on the surface if no alloying with the substrate occurs. At this limiting case the interfacial energy is the sum of the surface energy of the liquid  $\gamma_l$  and the energy of the liquid/solid boundary  $\gamma_{sl}$ . For the other limiting case of  $\mu_A \rightarrow -\infty$  the naked surface of the solid has the energy  $\gamma_s$ . Thus we have

$$- \int_0^{\infty} \Gamma_A \frac{d\mu_A}{d\Gamma_A} d\Gamma_A = \gamma_l + \gamma_{sl} - \gamma_s \quad (13)$$

or, with the aid of Eq. (12) and the trivial relation  $\Delta\gamma = \gamma - \gamma_s$ , the following equation was obtained by Landau and Lifshitz [24]:

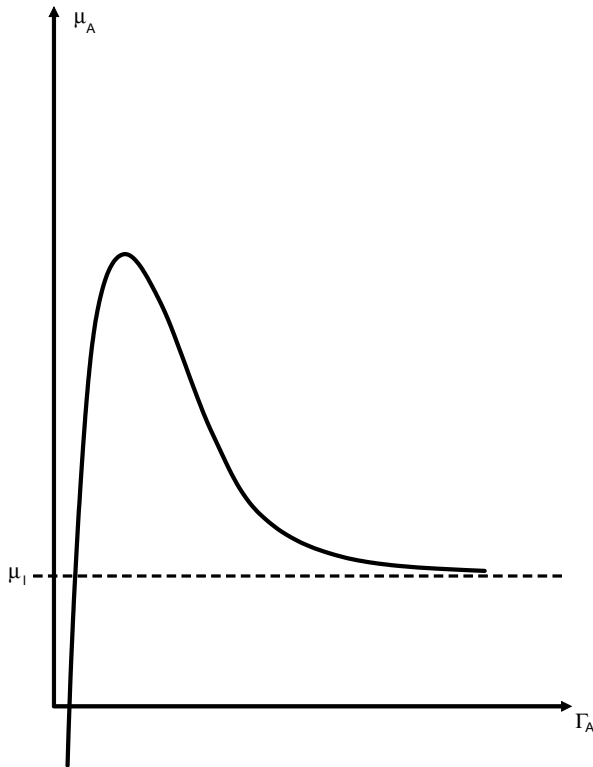


Fig. 6. Possible dependence of the chemical potential of A on excess A on the surface of a solid [24]. The chemical potential  $\mu_l$  is that of A in the liquid form. Equilibrium is attained for  $\mu_A \leq \mu_l$ . Thus, on the left-hand side below the dashed line the surface is in equilibrium with the vapour of A, whereas on the right-hand side a liquid film forms on the surface.

$$\gamma = \int_{\Gamma_A}^{\infty} \Gamma_A \frac{d\mu_A}{d\Gamma_A} d\Gamma_A + \gamma_l + \gamma_{sl} \quad (14)$$

In order to reach a vanishing or even negative value of  $\gamma$  and positive values for both  $\gamma_{sl}$  and  $\gamma_l$ , the derivative  $d\mu_A/d\Gamma_A$  has to become negative. Although this is not possible in equilibrium, it may occur in an interval of  $\Gamma_A$  between an atomically thin adsorption layer of A atoms and a thick layer of the liquid A. A corresponding possible scenario of a  $\mu_A(\Gamma_A)$  dependence as proposed by Landau and Lifshitz [24] is depicted in Fig. 6. The maximum equilibrium coverage of the surface is given by the intercept between the dashed line marking the chemical potential of the liquid phase of A atoms and the  $\mu_A(\Gamma_A)$  curve. For the surface energy  $\gamma$  at this point to become zero or negative requires that the integral in Eq. (14) is negative and that its magnitude is larger than the sum of  $\gamma_{sl}$  and  $\gamma_l$ . In order to prove whether a situation like this may occur,  $\mu_A(\Gamma_A)$  has to be evaluated within the framework of statistical mechanics.

## 5. Consequences of negative formation energies and equilibrium defect concentrations

### 5.1. Conditions for equilibrium

In order to check whether a binary system containing defects will be in equilibrium or at least metastable equilibrium, a derivation given by Landau and Lifshitz [25] will be extended. From a large portion of the binary system with constant pressure  $P_0$ , temperature  $T_0$ , chemical potential of solute atoms  $\mu_A$  and defect energy  $\gamma_0$ , a small part is cut out. Without losing generality, grain boundaries are considered to be the defects. In equilibrium all of the variables mentioned before have the same value in the small system. In order for the remaining large system to be in equilibrium, the free energy  $E_0 - T_0 S + P_0 V + \mu_{A0} n_A + a \gamma_0$  has to be minimal, i.e.

$$\delta E_0 + T_0 \delta S_0 - P_0 \delta V_0 + \mu_{A0} \delta n_{A0} + \gamma_0 \delta a_0 = 0 \quad (15)$$

Next the minimal work  $\delta R_{\min}$  is considered under which the small system changes its variables by  $\delta T$ ,  $\delta P$ ,  $\delta n_A$  and  $\delta a$  (the number of solvent atoms remains unchanged). In order to become minimal the work has to be done reversibly, and it corresponds to the energy change of the whole system. In addition, it has to be positive for a stable or metastable equilibrium state.

$$\delta R_{\min} = \delta E_0 + \delta E > 0 \quad (16)$$

Reversibility requires  $\delta S_0 = -\delta S$ . Conserving total volume, solute content and grain boundary area leads to  $\delta V_0 = -\delta V$ ,  $\delta n_{A0} = -\delta n_A$  and  $\delta a_0 = -\delta a$ . The latter equation requires that defects are either immobile or their creation or annihilation is kinetically hindered. Otherwise for both positive and negative defect formation energies the defect density would change spontaneously (cf. following section). In the present context defects are thought to be

moved virtually across the boundary between the small and the large system only.

Next  $\delta E$  is expanded in a Taylor series around equilibrium values

$$\delta E = \sum_i \frac{\partial E}{\partial i} \delta i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial i \partial j} \delta i \delta j \quad (17)$$

where  $\delta i$  and  $\delta j$  represent the quantities  $\delta S$ ,  $\delta V$ ,  $\delta n_A$  and  $\delta a$ . As usual, derivatives are calculated such that the remaining quantities are kept constant. The first derivatives of  $E$  under equilibrium are

$$\frac{\partial E}{\partial S} = T_0, \quad \frac{\partial E}{\partial V} = -P_0, \quad \frac{\partial E}{\partial n_A} = \mu_{A0}, \quad \frac{\partial E}{\partial a} = \gamma_0 \quad (18)$$

Inserting Eqs. (17) and (18) into Eq. (16) yields

$$2\delta R_{\min} = \sum_{i,j} \frac{\partial^2 E}{\partial i \partial j} \delta i \delta j > 0 \quad (19)$$

The last equation contains a quadratic form, which is positive if the determinant formed by the second derivatives as well as the leading principal subdeterminants (sometimes called the leading principal minors) are positive. As the sequence of terms in the sum of Eq. (19) is arbitrary, the subdeterminant of lowest order is chosen. Thus we obtain

$$\frac{\partial^2 E}{\partial a^2} = \frac{\partial \gamma}{\partial a} > 0 \quad (20)$$

A more rigorous derivation of the last equation including the other subdeterminants as well is provided in [Appendix C](#). Replacing  $a$  in the equations of this section by the dislocation length,  $l$ , or by the number of vacancies,  $n_V$ , leads to equivalent equilibrium conditions

$$\frac{\partial \gamma}{\partial l} > 0 \quad \text{or} \quad \frac{\partial \gamma}{\partial n_V} > 0 \quad (21)$$

Eq. (20) states that the grain boundary energy has to increase for an increasing area or decreasing grain size, respectively. Generally speaking, the defect energy has to increase if the defect density increases, as expressed for dislocations and vacancies in Eq. (21). This was the case for the surface energy of  $\text{Al}_2\text{O}_3$  as calculated in Ref. [20] and as discussed in Section 4.2. For non-interacting defects the defect energy,  $\gamma$ , is independent of the total amount of defects (corresponding to the defect density for a given sample volume), its derivative will be zero and Eqs. (20) and (21) will not be fulfilled. Then equilibrium will not be attained. However, with increasing defect density repulsive interaction among the defects becomes conceivable, giving rise to positive derivatives in Eqs. (20) and (21).

## 5.2. Open and closed systems

In a stable or metastable equilibrium of a partially open ( $d\mu_A = 0$ ) and partially closed ( $dn_B = 0$ ) system of solvent  $B$  and solute  $A$ , Eq. (4) requires the differential of the corresponding state function  $\Phi$  to be zero, i.e.  $d\Phi = 0$ . Under

conditions of constant volume and constant temperature, this is equivalent with the defect energy  $\gamma$  being zero. Negative values of  $\gamma$  give rise to an increasing defect density ( $da > 0$  or  $dl > 0$  or  $dn_V > 0$ ), because  $\Phi$  is lowered this way. This process should lead to a total degradation of the material unless the conditions described by Eqs. (20) and (21) come into play at higher defect densities, leading to  $\gamma = 0$  and a metastable equilibrium defect density.

In a closed system ( $dn_A = 0$ ,  $dn_B = 0$ ) both  $d\mu_A$  and  $da$  (or  $dl$  or  $dn_V$ ) may vary, and the condition  $d\Phi = 0$  yields

$$\gamma da - n_A d\mu_A = 0 \quad \text{or} \quad \left( \frac{\partial \mu_A}{\partial a} \right)_{n_A, n_B, T, V} = \frac{\gamma}{n_A} \quad (22)$$

For  $\gamma < 0$ ,  $\Phi$  is lowered by increasing the defect density, i.e.  $da > 0$ , and Eq. (22) requires that the chemical potential of the solute decreases. Then Eq. (1) predicts an increase in  $\gamma$  for positive excess. Thus the defect density increases until an equilibrium density with  $\gamma = 0$  is attained. This state can be also approached from the other side, starting with a higher defect density than the equilibrium one and  $\gamma > 0$ . Then  $\Phi$  is lowered by decreasing the defect density. Now Eq. (22) requires that the chemical potential of the solute increases and Eq. (1) predicts a decrease in  $\gamma$ , leading again to the equilibrium situation where  $\gamma = 0$ .

In order to provide a less formal insight into the behaviour of the closed system, the reasoning of the last paragraph is repeated for the special case of grain boundaries being the defects. For negative grain boundary energies additional

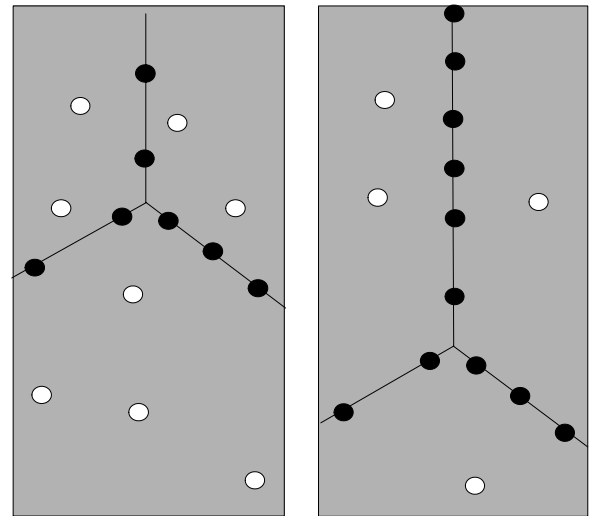


Fig. 7. Solute atoms (circles) partitioning between grains (open circles) and grain boundaries (closed circles) for the case of a positive excess at the boundaries. If the grain boundary energy is negative, free energy could be gained by increasing the grain boundary area of the left-hand tricrystal. This can be achieved by moving the triple point. Then the solute atoms have to be redistributed, as shown schematically for the tricrystal on the right-hand side. Segregation to the newly formed boundary area leads to a decrease in the solute concentration within the grains and a concomitant increase in the chemical potential. The latter causes, via Eq. (1), an increase in the grain boundary energy,  $\gamma$ . The process continues until  $\gamma$  becomes zero. Starting from the right-hand tricrystal and assuming  $\gamma > 0$  leads to the same conclusion of  $\gamma = 0$ .



grain boundary area is generated by the process shown in Fig. 7. Solute atoms from the grain interior segregate at the freshly produced grain boundary area and, therefore, the local concentration within the grains or the chemical potential, respectively, are decreased. Then Eq. (1) predicts a concomitant increase in the boundary energy. This process continues until  $\gamma = 0$ . For  $\gamma > 0$  the free energy is decreased by reducing the grain boundary area,  $a$ , and segregated solute atoms have to be dissolved into the grains. These additional solute atoms increase the chemical potential and reduce via Eq. (1) the grain boundary energy until  $\gamma = 0$ .

## 6. Conclusions

- (a) Due to a new definition of excess solute generated by defects in a solid, the Gibbs adsorption isotherm can be easily extended, including defects like dislocations and vacancies besides surfaces and grain boundaries. Thus experimental findings, such as solute softening and excess vacancies, can be explained in the framework of thermodynamics.
- (b) There is increasing theoretical and experimental evidence that defects (besides point defects) may become stable or metastable equilibrium defects if they give rise to positive excess solute at sufficiently high chemical potential of solute atoms (cf. Ref. [11]). However, no rigorous treatment in the framework of statistical thermodynamics has been done to support the conclusions.
- (c) Simulations show zero and negative defect energies but may not cover the true equilibrium state.
- (d) The common conclusion that negative defect energies leads to an unlimited production of defects is not valid: (i) if the system is closed, because then the chemical potential of solute atoms is decreased and the defect energy approaches zero; and (ii) if the system is open regarding solute atoms and the defect energy increases with increasing defect density.
- (e) By accepting Eq. (4), namely the work term  $\gamma da$  describing the creation and annihilation of defects, Eq. (5) has to be accepted, too. Then  $\Gamma$  is simply an abbreviation of  $\partial n_A / \partial a$  with the corresponding constraints. If this definition is adopted, there is actually no need to compare it with Gibbs' definition of excess as Wagner [5] did. The advantage of this formal treatment lies in its possibility to generalization including other defects as well. Then Gibbs' separation of the solid into regions containing the defect and remaining regions not being affected by the defect has not to be made.

## Appendix A. Generalized equations

In order to derive one expression for all defects, a defect density,  $\rho$ , is introduced as defect area per volume for two-

dimensional defects, defect length per volume for line defects and number of defects per volume for point defects. Thus Eq. (4) is changed to

$$d\Phi = p dV - S dT + \gamma V d\rho + \mu_B dn_B - n_A d\mu_A \quad (A1)$$

where  $\gamma$  now represents the defect energy in general. The formal treatment following Eq. (4) will not change because the total volume,  $V$ , will be kept constant, and a generalized Gibbs adsorption equation is obtained as

$$\left. \frac{\partial \gamma}{\partial \mu_A} \right|_{V, T, \rho, n_B} = -\Gamma_A^\rho \quad (A2)$$

with an excess solute of the defect defined as

$$\Gamma_A^\rho = \frac{1}{V} \left. \frac{\partial n_A}{\partial \rho} \right|_{T, V, \mu_A, n_B} \quad (A3)$$

For dislocations the defect density is equivalent to the dislocation density, for vacancies it corresponds to the vacancy concentration and for grain boundaries it is equal to the grain boundary area per volume. The latter is about three times the reciprocal grain size for nearly spherical grains.

By defining the excess solute via Eq. (A3) in a formal way and by relating it via the Maxwell relations (cf. Eq. (5)) to the defect, formation energy problems are circumvented, which arise by dividing the system into parts which contain the defect and parts which are not affected by the defect.

## Appendix B

Weissmüller [6] derived the following equation for the decrease in grain boundary energy,  $\gamma$ , by combining the Gibbs adsorption equation and the Langmuir–McLean equation for grain boundary segregation and ideal dilute solution:

$$\gamma - \gamma_0 = -\Gamma_A^{\text{sat}} \left[ H_s + RT \ln \frac{n_A}{N_M} \right] \quad (B1)$$

where  $\Gamma_{A, \text{sat}}$  is the excess solute corresponding to a saturation of the boundaries,  $n_A$  is the number of solute atoms in the grains,  $N_M$  is the number of lattice sites and  $H_s$  is the enthalpy of segregation (defined to be positive for solute enrichment at the boundary). Thus the first term in brackets is the energy gain during segregation whereas the second term (always being negative) is the loss of configurational entropy within the grains. For  $\gamma_0 = 1 \text{ J m}^{-2}$ ,  $\Gamma_A^{\text{sat}} = 1.5 \times 10^{-5} \text{ mol m}^{-2}$  (about one monolayer) and  $n_A/N_M = 10^{-3}$ , a rather large value of  $H_s = 84 \text{ kJ mol}^{-1}$  is required at  $T = 300 \text{ K}$  in order to obtain a zero grain boundary energy, i.e.  $\gamma = 0$ . Relation (B1) is contained as a geometrical relation in Fig. 4 for the triangle with the coordinates  $(H_s, \gamma_0)$ ,  $(H_s, 0)$  and  $(H_s + \gamma/\Gamma_A^{\text{sat}}, 0)$ .

## Appendix C

In order to have a non-zero solution of the quadratic form in Eq. (19), the determinant of its coefficients and the corresponding principal minors have to be positive [25], i.e.

$$\begin{vmatrix} \frac{\partial^2 E}{\partial V^2} & \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial n_A \partial V} & \frac{\partial^2 E}{\partial a \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial n_A} & \frac{\partial^2 E}{\partial S \partial a} \\ \frac{\partial^2 E}{\partial n_A \partial V} & \frac{\partial^2 E}{\partial n_A \partial S} & \frac{\partial^2 E}{\partial n_A^2} & \frac{\partial^2 E}{\partial n_A \partial a} \\ \frac{\partial^2 E}{\partial a \partial V} & \frac{\partial^2 E}{\partial a \partial S} & \frac{\partial^2 E}{\partial a \partial n_A} & \frac{\partial^2 E}{\partial a^2} \end{vmatrix} > 0 \quad (C1)$$

$$\begin{vmatrix} \frac{\partial^2 E}{\partial V^2} & \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial n_A \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial n_A} \\ \frac{\partial^2 E}{\partial n_A \partial V} & \frac{\partial^2 E}{\partial n_A \partial S} & \frac{\partial^2 E}{\partial n_A^2} \end{vmatrix} > 0, \quad \begin{vmatrix} \frac{\partial^2 E}{\partial V^2} & \frac{\partial^2 E}{\partial S \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial S^2} \end{vmatrix} > 0 \quad \text{and} \quad \left| \frac{\partial^2 E}{\partial S^2} \right| > 0$$

The second, third and fourth conditions within the last equation are satisfied as shown in Ref. [25]. The first condition is rewritten with the aid of Eq. (18) and expressed as a functional determinant, yielding

$$\frac{\partial(P, T, \mu_A, \gamma)}{\partial(V, S, n_A, a)} = \begin{vmatrix} \frac{\partial P}{\partial V} & \frac{\partial P}{\partial S} & \frac{\partial P}{\partial n_A} & \frac{\partial P}{\partial a} \\ \frac{\partial T}{\partial V} & \frac{\partial T}{\partial S} & \frac{\partial T}{\partial n_A} & \frac{\partial T}{\partial a} \\ \frac{\partial \mu_A}{\partial V} & \frac{\partial \mu_A}{\partial S} & \frac{\partial \mu_A}{\partial n_A} & \frac{\partial \mu_A}{\partial a} \\ \frac{\partial \gamma}{\partial V} & \frac{\partial \gamma}{\partial S} & \frac{\partial \gamma}{\partial n_A} & \frac{\partial \gamma}{\partial a} \end{vmatrix} < 0 \quad (C2)$$

Rearranging this equation leads to

$$\frac{\partial(P, T, \mu_A, \gamma)}{\partial(V, S, n_A, a)} = \frac{\frac{\partial(P, T, \mu_A, \gamma)}{\partial(P, T, \mu_A, a)}}{\frac{\partial(V, S, n_A, a)}{\partial(P, T, \mu_A, a)}} = \frac{\left(\frac{\partial \gamma}{\partial a}\right)_{P, T, \mu_A}}{\left(\frac{\partial(V, S, n_A)}{\partial(P, T, \mu_A)}\right)_a} < 0 \quad (C3)$$

The sign of the denominator in the last equation is obtained from the second condition in Eq. (C1) with the aid of Eq. (18)

$$\begin{vmatrix} \frac{\partial^2 E}{\partial V^2} & \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial n_A \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial n_A} \\ \frac{\partial^2 E}{\partial n_A \partial V} & \frac{\partial^2 E}{\partial n_A \partial S} & \frac{\partial^2 E}{\partial n_A^2} \end{vmatrix} = \begin{vmatrix} -\frac{\partial p}{\partial V} & \frac{\partial T}{\partial V} & \frac{\partial \mu_A}{\partial V} \\ -\frac{\partial p}{\partial S} & \frac{\partial T}{\partial S} & \frac{\partial \mu_A}{\partial S} \\ -\frac{\partial p}{\partial n_A} & \frac{\partial T}{\partial n_A} & \frac{\partial \mu_A}{\partial n_A} \end{vmatrix} = -\frac{\partial(P, T, \mu_A)}{\partial(V, S, n_A)} > 0$$

Thus the denominator in Eq. (C3) is negative, and we finally get from Eq. (C3)

$$\left(\frac{\partial \gamma}{\partial a}\right)_{P, T, \mu_A} > 0 \quad (C4)$$

For vacancies,  $\gamma$  is the same as their Helmholtz free energy of formation,  $F_V$ , and  $a$  has to be replaced by the number

of vacancies,  $n_V$ . Because of the contribution to the configurational entropy, the following relation holds

$$F_V = E_V + RT \ln \frac{n_V}{n_0}$$

where  $E_V$  is the energy of vacancy formation and  $n_0$  is the number of lattice sites. Then the derivative in Eq. (C4) becomes

$$\frac{\partial F_V}{\partial n_V} = \frac{RT}{n_V}$$

which is positive. Thus, for vacancies, the necessary condition in Eq. (C4) for equilibrium always holds and vacancies are equilibrium defects.

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