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THERMODYNAMIC ASPECTS OF BULK AND SURFACE DEFECTS
- FIRST-PRINCIPLE CALCULATIONS -

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1) Introduction

The first-principle calculation of electronic, magnetic and structural properties of atomic aggregates has evolved into a rapidly growing branch in theoretical solid-state physics. In this paper we discuss recent developments in this theory for perfect crystals, defects and surfaces of covalent semiconductors (e.g. Si and GaAs). For these systems it is now becoming possible to calculate the internal energy and the entropy in a parameter-free way. Experimental investigations are usually performed at non-zero temperature and well defined pressure. The equilibrium structure of the crystal, its surfaces and defects are then determined by the minimum of the Gibbs-enthalpy:

$$G(N,T,P) = U - TS + PV \quad . \quad (1)$$

N , T , P , U , S and V are the particle numbers, temperature, pressure, internal energy, entropy and crystal volume respectively. N , T and P are given by the experimental situation. U , S and V follow from the atomic configuration. The latter must be varied to find the minimum of G among all possibilities.

The formation of intrinsic point defects, as for example vacancies, introduces a significant configurational-entropy gain. As a consequence, these defects may exist at finite temperature in considerable concentration. At a surface the formation of intrinsic defects may be the origin for surface reconstruction. In order to understand bulk and surface defects it is often necessary to take into account that besides the crystal there is also an outer region, which we will call the environment. In a

thermodynamic approach this may be described by the concept of a reservoir of atoms which enters the theory by the atomic chemical potentials (see Section 3).

2) Calculation of the internal energy and entropy at finite temperature

In order to calculate the Gibbs enthalpy one needs to evaluate the internal energy U and the entropy S . They are given by well known equations [1-4]. The internal energy can be written as

$$U = U^{\text{static}} + U^{\text{vib.}} \quad (2)$$

where U^{static} is usually referred to as the static or structural or the total energy (see below). The vibrational contribution to the internal energy is

$$U^{\text{vib.}} = \sum_{i=1}^{3N} \left\{ \frac{\hbar \omega_i}{\exp(\hbar \omega_i / k_B T) - 1} + \frac{1}{2} \hbar \omega_i \right\}, \quad (3)$$

which approaches for high temperatures the form $3Nk_B T$. The energies $\hbar \omega_i$ are the normal vibrational modes. Below we describe a tractable method how they can be calculated from first principles.

The entropy can be written as

$$S = S^{\text{config.}} + S^{\text{vib.}} + S^{\text{e-h}}, \quad (4)$$

where the three terms are the configurational and vibrational contributions and the contribution due to electron-hole pairs. For covalent semiconductors at or below room temperature $S^{\text{e-h}}$ is negligible. The configurational entropy of a defect is given by the number of possible configurations in which the defect can exist (e.g. Ref. 1). The vibrational entropy is

$$S^{\text{vib.}} = k_B \sum_{i=1}^{3N} \left\{ \frac{\hbar \omega_i}{k_B T} \left(\exp\left(\frac{\hbar \omega_i}{k_B T}\right) - 1 \right)^{-1} - \ln \left(1 - \exp\left(-\frac{\hbar \omega_i}{k_B T}\right) \right) \right\} \quad (5)$$

which for high temperatures approaches the form

$$k_B \sum_{i=1}^{3N} (1 - \ln(\hbar\omega_i/k_B T)).$$

From eqs. (2)-(5) it follows that the Gibbs-enthalpy can be easily evaluated if the total energy, U^{static} , and the normal vibrational-mode energies, $\hbar\omega_i$, were known. These quantities can be calculated in a parameter-free way using the density-functional theory /5/. The main approximations of such calculations are the Born-Oppenheimer approximation, the frozen-core approximation and the local-density approximation for the exchange-correlation functional. Using a super-cell approach it is then possible to calculate the total energy (U^{static}) for a perfect crystal or a (periodically repeated) finite number of layers in order to simulate a surface. In other words, the super-cell method is a type of cluster approach where the cluster boundary conditions are chosen as periodic.

Thus, for bulk, near surface and surface defects it is possible to calculate the total energy, U^{static} , of semiconductors with appropriate accuracy. We note in passing, that a Green-function method /6/ may be more accurate. If the Green-function method is viewed as a cluster-type calculation, the cluster is embedded correctly into the macroscopic solid /6/. This approach was recently developed for bulk-defect total energies /7-10/. For surfaces there are still significant technical problems to formulate a feasible theory along this line.

The vibrational frequencies can be calculated from diagonalizing the dynamical matrix. The dynamical-matrix elements may be obtained from the total energies of the equilibrium structure and many distorted geometries. This "direct approach" requires several hundred self-consistent calculations. We believe that this is an unnecessary expense. Instead, Scherz and Scheffler /11/ have adopted a different approach. If the equilibrium geometry is known (e.g. at $T = 0$ from the minimum of the total energy), the change of the total energy for small deviations from the equilibrium geometry is well described by the analytic formula of a valence-force model. We use Keating's valence-force approach, which gives the total-energy change as

$$E(\{\vec{R}_i\}) = \sum_{i=1}^N \left\{ \sum_{\substack{j \\ \text{bonds at} \\ \text{site } i}} \frac{3}{16(\vec{R}_i^0 - \vec{R}_j^0)^2} \alpha_j^i ((\vec{R}_i^0 - \vec{R}_j^0)^2 - (\vec{R}_i - \vec{R}_j)^2) \right. \\ \left. + \sum_{\substack{j \\ \text{bonds} \\ \text{at site } i}} \sum_{\substack{k \\ \text{adjacent} \\ \text{bonds}}} \frac{3}{8 |\vec{R}_i^0 - \vec{R}_j^0| |\vec{R}_i^0 - \vec{R}_k^0|} \beta_{jk}^i ((\vec{R}_i^0 - \vec{R}_j^0)(\vec{R}_i^0 - \vec{R}_k^0) - (\vec{R}_i - \vec{R}_j)(\vec{R}_i - \vec{R}_k)) \right\} \quad (6)$$

Here \vec{R}_i^0 are the positions of the atoms as calculated from the minimum of the total energy. \vec{R}_i are the positions of the displaced atoms. α_j^i and β_{jk}^i are bond-stretching and bond-bending parameters. We note that the Keating approach has been used in the past in semi-empirical calculations for perfect crystals and the parameters α_j^i and β_{jk}^i were fitted to experimental results. In contrast to this empirical approach we [11,12] calculate the parameters from first-principles. To give an example, we consider the calculation for a perfect silicon crystal. The calculated equation of state gives the equilibrium geometry, i.e. the positions \vec{R}_i^0 , and the bulk modulus B^0 . The latter is related to α and β by

$$B^0 = \frac{\sqrt{3}}{4} \frac{1}{\alpha^0} \left(\alpha + \frac{1}{3} \beta \right) \quad (7)$$

We dropped the indices of α and β because in a perfect Si crystal there is only one type of atoms. α^0 is the crystal lattice constant. As we are interested in defect induced changes of the vibrations we consider (theoretically) a situation where the nearest neighbors of one atom distort in a breathing-mode fashion. All other atoms are kept at the equilibrium geometry. The force constant of this distortion is related to α and β by

$$k_b = 16 \alpha + 42 \beta \quad (8)$$

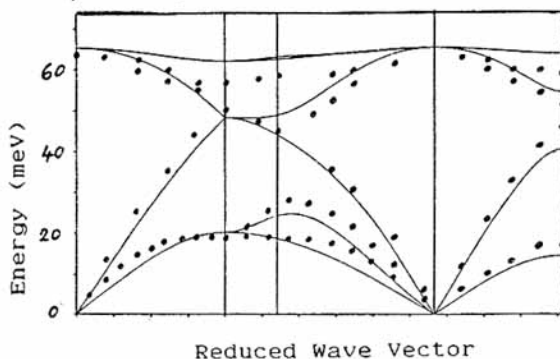
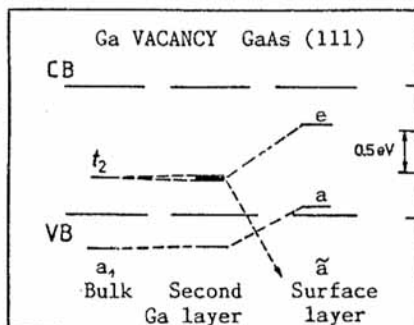


Fig. 1:
Phonon dispersion of Si.
The full lines are obtained using equ.(6) together with values for \vec{R}_i^0 , α and β from self-consistent calculations (see text).

From the theoretical values B^0 and k_b we obtain the values for α and β . Equ. (6) then allows directly and easily to calculate the dynamical matrix and, furthermore, the vibrational frequencies. Fig. 1 shows the results [12] for the phonons of silicon in comparison to experimental data.

In order to describe a crystal with a point defect we follow the same ideas. Because the crystal charge density and the chemical bonding of farther atoms will not be affected significantly by the defect, only few parameters \vec{R}_i^e , α_i and β_{ij} (namely those in the neighborhood of the defect) are changed. As a consequence, only about 10 self-consistent calculations are necessary in order to obtain the defect-induced changes of the Keating parameters and the vibrational frequencies of point defects. This is an enormous saving in the numerical effort, if compared to the "direct method". For a vacancy in the bulk of silicon (using a 16 atom super-cell) we obtained a value for ΔS^{vib} of about $3k_B$ at room temperature. This implies, that the entropy part of the defect induced change of the Gibbs-enthalpy, $T \Delta S^{\text{vib}}$, is indeed negligibly small (~ 0.026 eV at room temperature) if compared to the total-energy part. The latter (i.e. the vacancy formation energy) is about 4 eV. We also mention, that Bachelet et al. [13] have recently calculated the vacancy entropy using an 8-atom super-cell and the direct approach. Their results, as well as an empirical valence-force model calculation of Lannoo and Allan [14] agree well with ours.

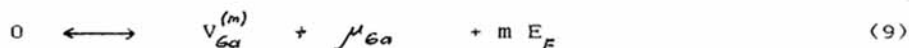
Fig. 2:
The important energy levels of a cation vacancy in GaAs near and at the Ga terminated GaAs(111) surface.



3) The role of electron and atomic chemical potentials

In order to discuss the role of the environment in defect formation we use the Ga vacancy at the GaAs (111) surface as an example. The electronic structure of a bulk Ga vacancy can be qualitatively understood in terms of four dangling bonds which are centered at the four As-atoms around the missing Ga [6]. In an undistorted situation (T_d symmetry) these four dangling bonds give rise to two energy levels: one singlet (a_1) and one triplet (t_2). This picture also holds for the near-surface defect. Only when the Ga-vacancy is directly at the Ga-terminated (111) surface, the situation is changed. Then the Ga vacancy has only three As neighbors. Thus, the symmetry is lowered and one dangling bond is removed, if compared to the bulk situation. As a consequence, the t_2 level splits (see Fig. 2).

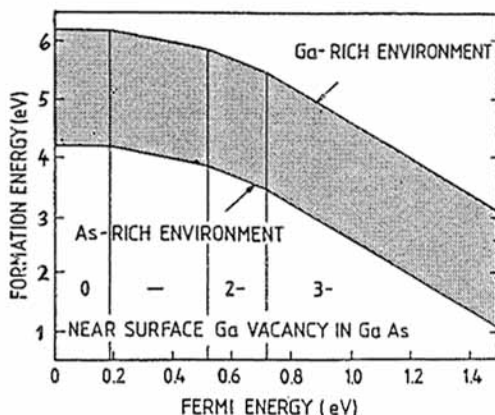
The formation of a near-surface or a surface Ga-vacancy can be described by the following chemical reaction:



The zero on the left stands for the perfect GaAs crystal with surface. μ_{Ga} is the energy of the removed Ga-atom in the Ga reservoir and E_F is the Fermi level. The index (m) means that the vacancy may exist in several charge states, exchanging electrons with the Fermi energy (the reservoir of electrons). Concerning the atomic reservoir we consider three possible, extreme examples:

1) interstitials in bulk GaAs,

Fig. 3:
Formation energy of a Ga
vacancy in GaAs near the
surface.



2) Ga-metal, which may exist in Ga-rich environment as Ga droplets on the surface,

3) As_2 -gas, which together with the removed Ga atom can form a new GaAs unit cell ($\text{Ga} \longleftrightarrow \text{GaAs} - \frac{1}{2}\text{As}_2$).

For surface and near-surface defects the reservoirs 2) and 3) are important. Of course, depending on the partial pressure, the Ga chemical potential may have any value between those of the two limits of 2) and 3). Fig. 3 shows the results of our calculation /15/. The formation energy is displayed as a function of the Ga chemical potential (the dotted region) and of the electron chemical potential (the Fermi energy). Further details of these results are discussed elsewhere.

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