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Influence of phonon and electron excitations on the free energy of defect clusters in solids: A first-principles study

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Although many processes of nanostructure evolution in solids occur at elevated temperatures, basic data obtained from ground state energetics are used in the modeling of these phenomena. In order to illustrate the effect of phonon and electron excitations on the free binding energy of defect clusters, first-principles calculations are performed for vacancy-solute pairs as well as vacancy and Cu dimers, trimers, and quadromers in bcc Fe. Based on the equilibrium atomic positions determined by the relaxation of the supercell with the defect in the ground state under constant volume (CV) as well as zero pressure (ZP) conditions, the contribution of phonon excitations to the free binding energy is calculated within the framework of the harmonic approximation. The contribution of electron excitations is obtained using the corresponding ground state data for the electronic density of states. Quasi-harmonic corrections to the ZP-based results do not yield significant changes in the temperature range relevant for applications. At 1000 K the maximum decrease/increase of the ZP-based data for the absolute value of the free binding energy with respect to the corresponding ground state value is found for the vacancy-W (43%)/vacancy-Mn (35%) pair. These results clearly demonstrate that contributions of phonon and electron excitation to the free binding energy of the defect clusters are generally not negligible. The general behavior of the free binding energy of vacancy and Cu dimers, trimers and quadromers is similar to that of the vacancy-solute pairs. The results obtained in this work are of general importance for studies on the thermodynamics and kinetics of defect clusters in solids.

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1. Introduction

The nanostructure of solids has an important influence on their thermal, mechanical, electrical and magnetic properties. Thermodynamics and kinetics of point defects (vacancies, self-interstitials and foreign atoms) and defect clusters determine the evolution of the nanostructure at elevated temperatures. Multiscale modeling can substantially contribute to a better understanding of these processes. For this purpose atomistic rigid-lattice and object kinetic Monte Carlo simulations are employed. The equilibrium state of nanostructures and the phase diagrams of alloys and compounds are often investigated by Metropolis Monte Carlo simulation. The theoretical methods mentioned above require input data which are mainly obtained from first-principle calculations. In most previous studies only ground state properties of point defects and defect clusters determined by Density-Functional-Theory-(DFT)-methods were used to obtain these data. However, at elevated temperatures excitations of phonons, electrons, magnons and other quasi-particles occur so that not the energetics in the ground state but the full thermodynamics, i.e. the free energy of the defects, must be considered. While some authors have pointed out the importance of considering full DFT-based free formation and migration energies of point defects at nonzero temperatures [1–17] only few studies on the free energy of defect clusters have hitherto been published. The work of Yuge et al. [18] is probably the only full DFT-based study which is exclusively related to the free energy of larger embedded defect clusters. These authors found a considerable influence of phonon excitations on the nucleation free energy of Cu clusters in bcc Fe. This quantity is closely related to the free binding energy. In investigations on the solubility of foreign atoms the vibrational contribution to the free formation energy of Cu-Cu dimers in bcc Fe and Fe-Fe dimers in fcc Cu was determined by DFT [2]. Such a method was also applied to calculate the free binding energy of vacancy-solute pairs in studies on the vacancy mechanism of solute diffusion in bcc Fe, fcc Al, and fcc Ni (Refs. [3,5,6,19]). In general

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one can expect that phonon and other excitations may have non-negligible effects on the total free binding energy of embedded defect clusters and on the free binding energy of point defects to these clusters, both of which are crucial input parameters of kinetic and Metropolis Monte Carlo simulations. The replacement of ground state values of the defect binding energy by corresponding free energy data may alter results of the simulations quantitatively and qualitatively. In a fully thermodynamics-based method the migration barriers must be determined by the difference between the free energy at the saddle point and that in the related stable configuration, i.e. the free migration energy must be calculated. However, in state-of-the-art kinetic Monte Carlo simulations migration barriers determined by probing the DFT-energy landscape in the ground state are employed. The corresponding attempt frequencies are mostly set equal to a characteristic vibrational frequency of the solid. In some more detailed DFT-based investigations, in particular on self-diffusion by the vacancy mechanism (cf. Refs. [3,4,15–17,20,21]), contributions of phonon and/or electron excitations to the free migration energy were considered. Also in recent DFT studies on the diffusion of foreign atoms or impurities by the interstitial, the vacancy or the dumbbell mechanism (cf. Refs. [3,5,6,19,22–24]) these contributions were partially taken into account. However, in other recent papers on these diffusion mechanisms the barriers obtained from the DFT-energy landscape in the ground state were used in combination with a constant attempt frequency, i.e. without considering phonon and electron excitations (cf. Refs. [25–29]). It should be also mentioned that several authors clearly demonstrated that the effect of phonon excitations must be considered in first-principles-based calculations of phase diagrams of binary and ternary metallic and non-metallic alloys [30–32]. In these studies DFT methods were applied to supercells containing two or three different atomic species and the free energy of these systems was calculated. From the results temperature-dependent parameters were derived and used in a cluster expansion model for the free energy of larger systems on a rigid lattice. Finally, for a given composition and temperature the equilibrium state of the compound or alloy was determined using rigid-lattice Metropolis Monte Carlo simulations, which yields the phase diagram.

This paper deals with the influence of phonon and electron excitations on the free energy of defect clusters in bcc Fe. The focus is on defect dimers since from their free binding energy temperature-dependent parameters may be derived, which describe the interaction between pairs of foreign atoms or point defects within the framework of a rigid lattice model. So far, these parameters were obtained from ground-state dimer binding energies. Pair interaction parameters are very important input data of rigid-lattice kinetic and Metropolis Monte Carlo simulations since in most previous studies the total energy of a system was modeled by a sum over first and second nearest neighbor pair interaction terms, cf. Refs. [33–38]. Furthermore, the knowledge of the free binding energy of pairs formed by a vacancy and a foreign atom is required in detailed investigations on the vacancy mechanism of impurity diffusion, cf. Refs. [3,5,6,19,24,39]. As already mentioned above, many previous investigations used the ground-state binding energy instead of the free binding energy. In the present work the ground state energetics as well as the vibrational and electronic contributions to the free binding energy of the divacancy, the Cu-Cu dimer in bcc Fe, as well as dimers formed by the vacancy (v) and the foreign atoms C, N, O, Al, Si, Ti, V, Cr, Mn, Co, Ni, Cu, Y, Mo, and W are calculated. Furthermore, the free binding energy of selected trimers (v_3, Cu_3) and quadromers (v_4, Cu_4) in bcc Fe is determined. Besides general thermodynamic and kinetic aspects, present investigations shall contribute to a better understanding and an improved modeling of nanostructure evolution in ferritic Fe and Fe-Cr alloys which are important for practical applications, in particular as basic structural materials for present and future nuclear fission and fusion reactors where the relevant temperatures are between about 600 and 1000 K.

2. Calculation methodology

2.1. Ground state energetics

The DFT calculations were performed with the Vienna ab initio simulation package VASP [40,41] using plane wave basis sets and pseudopotentials generated within the projector-augmented wave (PAW) approach. The exchange and correlation effects were modeled by the Perdew-Burke-Ernzerhof (PBE) parameterization [42] of the generalized gradient approximation (GGA). In all calculations the spin polarized formalism was applied and a plane wave cutoff of 500 eV was used. The Brillouin zone sampling was performed employing the Monkhorst-Pack scheme [43]. For the integration in the reciprocal space the Methfessel-Paxton smearing method [44] was applied with a width of 0.2 eV. The calculations were carried out for bcc-Fe supercells with 54 lattice sites and Brillouin zone sampling of $6 \times 6 \times 6$ k points as well as for supercells with 128 sites and $3 \times 3 \times 3$ k points. For test purposes supercells with 128 sites and $4 \times 4 \times 4$ k points were considered. After introduction of a defect dimer, trimer, or quadromer into the supercell two types of calculations were performed: (i) The positions of atoms were relaxed at constant volume and shape of the supercell (constant volume calculations - CV). The supercell volume corresponds to that of a cell containing perfect bcc Fe. (ii) The positions of atoms as well as the volume and shape of the supercell were relaxed so that the total stress/pressure on the supercell became zero (zero pressure calculations - ZP). The accuracy of the relaxation calculations is determined by two criteria: (i) CV and ZP are stopped if the residual force acting on any atom falls below a given threshold, and (ii) at each step of CV and ZP the energy minimization is performed until the total energy change falls below another threshold. In the present work the threshold values were equal to or lower than 10^{-3} eV/Å and 10^{-5} eV, in first and the second case, respectively. In many cases, especially if the contributions of phonon and electron excitations to the free energy shall be determined, the thresholds 10^{-4} eV/Å and 10^{-7} eV were used. This ensures a high precision of the results.

The binding energy of an embedded defect cluster consisting of n species (point defects or foreign atoms) is defined by

$$E_{bind} = E(X_1 + X_2 + \ldots + X_n) + (n-1)E_0 - \sum_{i=1}^{n} E(X_i) \tag{1}$$

$E(X_1 + X_2 + \ldots + X_n)$ and $E(X_i)$ denote the total energy of supercells with the cluster $X_1 + X_2 + \ldots + X_n$ and the monomer of species X_i, respectively, while E_0 is the total energy of a supercell with perfect bcc Fe. By definition the value of E_{bind} is negative if attraction between the species dominates. In the present work the data for the total energy of supercells with single defect species (v, C, N, O, Al, Si, Ti, V, Cr, Mn, Co, Ni, Cu, Y, Mo, W) obtained in Ref. [17] were used in order to calculate the quantity E_{bind} for the defect clusters.

2.2. Contributions of phonon and electron excitations to the free energy

Vibrational frequencies of supercells with a defect dimer, trimer, or quadromer were calculated using the method implemented in the VASP code. This procedure employs the frozen phonon approach and the harmonic approximation (cf. Refs. [3,45]). In order to calculate the dynamical matrix, finite differences were used, i.e. each atom is displaced along each Cartesian coordinate, and from the forces the matrix is determined. Only

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