Local crystal stability evaluation by using average electron-proton binding energy

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Abstract. In this work we introduce a new approach, which clearly takes into account the thermodynamic non-equivalence of structural positions of mobile atoms in the lattice. This approach may be implemented in the framework of the proposed here approach based on analysis of reduced binding energy \( \bar{E}_{bin} \). In this case it is suggested that different positions of crystal lattice atoms located in the centers of coordination polyhedra are characterized by certain values of reduced binding energy. In terms of the assumed approximation, it is suggested that in order to analyze atomic chemical bonding it is necessary to involve positive charges of atom nuclei in the general system with electrons forming a pseudoadiabatic medium Hartree field in this way. As a result, if electrical neutrality of a material retains in the whole, all electrons except the \( i \)-th electron whose interactions are examined will make up for the positive charge of the cluster atom nuclei.

The above mentioned procedure was used for the understanding of nature of high temperature superconductivity and electronic state of metal atoms in the active site of hemoglobin.

1. Introduction

It is suggested in this work that different positions of atoms located in the centers of coordination polyhedra within solid state crystal structures are characterized by certain values of reduced binding energy (RBE) \( \bar{E}_{bin} \). In this approach the calculation procedure of \( \bar{E}_{bin} \) is the main part of problem. According to our proposition, RBE is a parameter, which is numerically equal to average binding energy calculated for one valence electron when it interacts with one proton of the nuclear subsystem of a cluster (if a solid state is concerned), or a molecule (if a molecular form of a substance is analyzed).

The Gibbs energy (\( G \)) is more universal tool for investigations within solid states. The three parts of \( G \) can be calculated: \( E \)- internal energy, \( TS \)- temperature and entropy part, and \( PV \)- pressure and volume part. The objects of investigations in physics, chemistry and biology are the materials with form conservation. The usual methods of investigation of these objects are statistical mechanics and thermodynamics. Physics deals with solids in more rigid form with minimum total energy, chemistry works in the field of normal and high temperatures and pressures, biology - within small deviations of normal temperatures and pressures. According to [1], there are three fields of conditions: 1) low temperature and high pressure for physics, 2) high and usual temperature and pressure for chemistry, 3) usual temperatures and pressures for biology. For solving of physical, chemical and biological problems under usual conditions, only the \( E \) part of Gibbs energy can be used.
2. Methods of calculations

The quantum chemical studies of the effects arising due to mobility of crystal lattice atoms in solid state are currently of great interest. Atom mobility effects are suggested, for example, in structural phase transitions [2], semiconductor-metal [3] and metal-insulator [4] transitions, lattice distortions as a result of iso- [5] and hetero-valent [6] substitutions, spin-Peierls transition [7], ionic conduction of one of sublattices [8], etc. Classical quantum chemical methods describing above processes are restricted by some obligatory assumptions including the adiabatic approximation and the low temperature limit. At nonzero temperatures, the adiabatic approximation in the framework of this approach may be evaded by sequential using of molecular dynamics and quantum chemistry methods at each stage of temperature interval. This approach is called the non-empirical Carr and Parrinello approach [9].

There is, however, an assumption that only the oscillation amplitude of atoms in the vicinity of equilibrium positions determined initially at zero temperatures may increase with temperature. This approach may be used at temperatures far from the lattice softening temperature. In this case theoretical quantum chemistry methods may be applied without additional changes in the calculation scheme.

In quantum chemical description of crystal lattice atom mobility in different structures, a new approach is possible, which clearly takes into account the thermodynamic non-equivalence of structural positions of mobile atoms in the lattice. This approach may be implemented in the framework of the proposed here approach based on analysis of $\bar{E}_{\text{bin}}$ [10]. In this case it is suggested that different positions of crystal lattice atoms located in the centers of coordination polyhedra are characterized by certain values of reduced binding energy. In terms of the assumed approximation, it is suggested that in order to analyze interatomic chemical bonding it is necessary to involve positive charges of atom nuclei into the general system with electrons, which forms a pseudoadiabatic medium Hartree field. As a result, if the electrical neutrality of a material retains in the whole, all electrons except the $i$-th electron whose interactions are examined will make up the positive charge of the cluster atom nuclei, and in the system containing $N_e$ electrons and $N_p$ positively charged atom nuclei protons, provided $N_e = N_p$ confirmed by electrical neutrality of the material, $N_e - 1$ negative electrons will compensate for $N_p - 1$ positive charges of protons. Hence, in order to analyze the stability of a cluster, we need to consider the state and virtually binding energy of only one electron when it interacts with one proton. Diffusion processes within solid states may be analyzed starting from the following reasoning. At certain temperatures, binding energy of valence electrons breaks down, which leads to transition of atoms either to a free neutral state (diffusion of neutral atoms) or to a free charged state (diffusion of charged atoms). When a carrier-deficient structural position is formed, diffusion process takes place if the reduced binding energy value of this structural fragment is smaller (hereafter in absolute values) than before the formation of the defect state, since it is supposed that the appearance of a new position with smaller values of reduced binding energy and consequently a less stable structure is crucial for the process of atomic or ionic diffusion in the structure of solid states.

In this case the emerging crystallographic position is more likely to be occupied by new atoms because a system tends to decrease its energy, i.e. to reach a more stable state. Meanwhile the action of temperature manifests itself in the reverse: reduced binding energy breaks down again under the action of temperature and this leads to the formation of a free, i.e. non-bound ion, which left its localization position. Then the process repeats again after the above scenario.

In this work, the presented Gibbs energy and, consequently, the chemical potential of a cluster were supposed to be proportional to RBE since one of the definitions of the chemical potential relates it to electrical negativity [11], which, according to the Pauling definition, represents the force of attraction of valence electrons in a molecule by a group of atoms [12]. In this case, the dimensionality of a classically defined chemical potential $\mu = dE/dN$, where $E$ is the total energy of a system of electrons and $N$ is the number of particles in the system [11], because the energy of one electron coincides with the dimensionality of the introduced definition $\mu \sim \bar{E}_{\text{bin}} \approx E_{\text{bin}}/N_{ep}$, where $N_{ep} = N_e * N_p$, and $E_{\text{bin}}$ is the binding energy of a system of $N_e$ electrons and $N_p$ protons in a cluster. Consequently, to analyze the
stability of solid structure fragments and estimate the direction of non-equilibrium spontaneous flows in solids, we may use the calculated in this way reduced binding energy \( \bar{E}_{\text{bin}} \). In accordance with the thermodynamic uncertainty principle \[13\], which relates the accuracy of measuring of the Gibbs energy \((\Delta G)^2_{\text{aver}}\) at a certain value of the mean square of inverse temperature \((1/T)^2_{\text{aver}}\) (in K) to the Boltzmann constant \( k_B \)

\[
\frac{1}{k_B} \leq \frac{(\Delta G)^2_{\text{aver}}}{k_B} = \frac{\Delta G}{k_B}^2,
\]

the difference between the \( \bar{E}_{\text{bin}} \) values for clusters (1) and (2) may be employed to estimate the lower boundary of the temperature range for the diffusion motion between system (1) and system (2):

\[
T_m = \frac{|\bar{E}_{\text{bin}}(2) - \bar{E}_{\text{bin}}(1)|}{k_B}.
\]

In this approach, transition between structures may occur if the difference between reduced binding energies characterizing the initial and the final structures is numerically equal to the thermal energy quantum \( |\Delta \bar{E}_{\text{bin}}| = k_B T_m \). Hence it is possible to determine the temperature of transition from the state with the initial RBE value to the state with the final RBE value. Thus, the temperature of structural stability of different crystalline fragments may be evaluated based on quantum chemical calculations only.

In our study, reduced binding energy \((\bar{E}_{\text{bin}})\) is binding energy \((E_{\text{bin}})\) divided by the number of unfrozen cluster electrons and the total cluster nuclear charge. For example, for the \([\text{NaCl}]^{13}\) cluster in NaCl these values are \( E_{\text{bin}} = 0.23 \text{ eV/atom} \), \( N_e = 6 \) and \( N_p = 6 \). Binding energy per one formula unit NaCl is 8.32 eV/f.u. or 4.16 eV/atom. This result agrees well with the experimental value \( \sim 4.00 \text{ eV/atom} \) for NaCl \[14\]. For 3C-SiC, \( E_{\text{bin}} = 0.3235 \text{ eV/atom} \). \[15\], \( N_e = 6 \) and \( N_p = 6 \). In this case, binding energy per a formula unit is 11.65 eV/f.u. or 5.82 eV/atom, which is somewhat smaller than the value 7.39 eV/atom derived from FP-LMTO calculations \[16\].

### 3. Results

The above mentioned procedure was used for the understanding of nature of high-temperature superconductivity (SC). We assume that conducting system in state (1) is a system with the \( n \) number of carriers. When a system loses conductivity, the number of carriers becomes \( n - I \) and the state of this system is (2). In the state with finite conductivity, the system exists within states (1) and (2) with \( n \) and \( n - I \) numbers of carriers simultaneously. When the temperature increases from zero, the SC loss temperature is the \( T_{\text{car}} \) value, if the product \( T_{\text{car}} \times k_B \) is equal to the absolute value of Gibbs energy difference between states (1) and (2). Earlier, the Gibbs energy difference was proposed to be calculated as the difference of reduced binding energy \( \Delta \bar{E}_{\text{bin}} \). \( \chi_r \)-method of discrete variation \[8\] employed in this study for Cu(2) site in YBa\(_2\)Cu\(_3\)O\(_7\) ceramic (I) and Fe site in SrFeO\(_3\) (II) yielded the following results. In model I, \([\text{Cu}(2)\text{O}])^{6}\) (I-I), \([\text{Cu}(2)\text{O}])^{8}\) (I-II), \([\text{Cu}(2)\text{O}])^{10}\) (I-III) clusters were used. Calculated values of reduced binding energy were 0.5661 (I-I cluster), 0.5566 (I-II), 0.6079 (I-III) eV/atom. The difference in \( \bar{E}_{\text{bin}} \) values for I-I and I-II clusters determines the electronic superconductivity loss temperature \( T_{c}^{\text{el}} \). For clusters I-I and I-II, this value is 0.0095 eV/atom and \( T_{c}^{\text{el}} = 110.24 \text{ K} \). The difference in \( \bar{E}_{\text{bin}} \) values for I-I and I-III clusters determines the ionic superconductivity loss temperature \( T_{c}^{\text{lat}} \). In this case the difference in \( \bar{E}_{\text{bin}} \) values for I-I and I-III clusters is 0.0418 eV/atom and \( T_{c}^{\text{lat}} = 485.07 \text{ K} \). Thus, the lattice SC temperature for the Cu(2) site in Y-Ba-Cu-O ceramic was found to be 485.07 K, which is larger than the electronic SC loss temperature 110.24 K. A similar calculation for sites \([\text{FeO}]^{6}\) (II-I), \([\text{FeO}]^{10}\) (II-II), \([\text{FeO}]^{12}\) (II-III) in SrFeO\(_3\) yielded \( T_{c}^{\text{el}} = 649.84 \) K and \( T_{c}^{\text{lat}} = 128.81 \) K. These results indicate that finite oxygen conductivity in SrFeO\(_3\) realizes at smaller temperatures as compared with the electronic SC loss temperature and then extinguishes the electronic SC states in SrFeO\(_3\). Thus, it may be concluded from our research that fulfillment of the condition \( T_{c}^{\text{el}} < T_{c}^{\text{lat}} \) are necessary for the appearance of the electronic SC state.

Another example of quantum-chemical application of RBE is quantum-chemical modeling of possible M \( \rightarrow \) Fe (M = Cr, Mn, Co, Ni, Cu, Zn) substitutions in active sites of \( \alpha \)- and \( \beta \)-subunits of deoxyhemoglobin molecule. The calculations were carried out using the spin-polarized cluster \( \chi_r \)-discrete variation method \[8\]. Parameters of electronic structure, chemical bonding and reduced binding energy values \[10\] were calculated for the \([\text{M}^{2+}\text{N}\])\(^{13}\) (M = Cr, Mn, Fe, Co, Ni, Cu, Zn)
clusters with structures similar to those described in [17], in which other interactions of active sites are replaced by interactions with the Watson sphere charged $+13e$. The temperature $T_m$ of $\alpha <-> \beta$ structure stability loss for active sites of $\alpha$- and $\beta$-subunits of deoxy-hemoglobin molecules with M-$>$Fe substitution effects was estimated as the ratio between the difference of reduced binding energies of active sites of $\alpha$- and $\beta$-subunits and the Boltzmann’s constant $k_B$. It was found for Cr, Mn, Fe atoms that $T_m = 89; 42$ and $41{^\circ}C$, respectively. For Co, Ni, Cu and Zn atoms, the maximum temperatures of structure stability loss were $40; 37; 33$ and $29{^\circ}C$, respectively.

In our opinion, RBE is a sensitive and flexible parameter for the description of local crystal stability within solid states having local order.

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