Theory, Modeling and Simulation

Multiscale Approach to Theoretical Simulations of Materials for Nuclear Energy Applications: Fe-Cr and Zr-based Alloys

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ABSTRACT

We review basic ideas behind state-of-the-art techniques for first-principles theoretical simulations of the phase stabilities and properties of alloys. We concentrate on methods that allow for an efficient treatment of compositional and thermal disorder effects. In particular, we present novel approach to evaluate free energy for strongly anharmonic systems. Theoretical tools are then employed in studies of two materials systems relevant for nuclear energy applications: Fe-Cr and Zr-based alloys. In particular, we investigate the effect of hydrostatic pressure and multicomponent alloying on the mixing enthalpy of Fe-Cr alloys, and show that in the ferromagnetic state both of them reduce the alloy stability at low Cr concentration. For Zr-Nb alloys, we demonstrate how microscopic parameters calculated from first-principles can be used in higher-level models.

INTRODUCTION

Nuclear energy has become an important part of the energy portfolio for the modern society, contributing, e.g. to reduction of the dependence on the fossil fuels and emission of green-house gases. Advances of the technology would not be possible without tremendous work invested in design of materials, operating for extended periods of time at high temperatures, under irradiation, stress and corrosion. Moreover ongoing development of next generation reactors strengthens demands on materials to be used in fission and future fusion reactors, which include good tensile and creep strength, as high as possible operational temperatures, a control over ductile to brittle transition temperature, resistance to irradiation, high thermal conductivity, low residual activation, compatibility with cooling media, and good weldability [1]. A great challenge is to identify potentially significant materials, to develop efficient technological processes, and to optimize their functionality. Solution to these tasks clearly requires increasing understanding of nuclear materials performance under extreme conditions. In this respect, a new and powerful instrument is now available for researches, computers. Their advances initiated a development of a qualitatively new brunch in science, computer modeling. The major goal of

theory in applications within the materials sciences is to provide fundamental understanding of materials properties and behavior at different external conditions, to accelerate the design of new materials and to discover phenomena with high potential to improve the existing technologies, as well as to create qualitatively new technologies. Therefore, the development of the basic theory, computational algorithms and qualitative models is an important task within the field of materials modeling.

In this work we briefly review recent developments in the field of *ab initio* electronic structure theory and its applications for studies of complex alloy systems. Basic ideas behind state-of-the-art techniques for first-principles theoretical simulations of the phase stabilities and properties of intermetallic compounds and alloys based on multiscale approach are outlined. We concentrate on methods that allow for an efficient treatment of compositional [2] and thermal [3] disorder effects, and illustrate their performance for two systems relevant for nuclear energy applications: Fe-Cr and Zr-based alloys.

In particular, ferritic steels are used to manufacture reactor pressure vessels (RPV). Irradiation-induced accelerated ageing is considered to be a crucial issue that limits the lifetime of nuclear reactors. Fe-Cr steels with 7-18 at.% Cr are considered as promising structural materials for fast neutron reactors due to their relatively low rate of swelling at elevated temperatures [1]. In the binary Fe-Cr alloy a spinodal decomposition can lead to a formation of precipitates of α' phase, but at low chromium concentrations the alloys are anomalously stable [4]. The effect has been a subject of active theoretical investigations [5-7], which significantly improved the understanding of the binary Fe-Cr system. On the other hand, in reality promising steels for RPV contain other elements, including significant amounts of Ni, Mn, and Mo. Their effect on the stability of parent Fe-Cr alloy did not received corresponding attention of the theory. Moreover, the radiation-enhanced formation of defects, like interstitial clusters, dislocations, etc., may lead to the presence of highly compressed areas within the material. How would the local pressure affect the stability of the alloy? Here we investigate the effect of hydrostatic pressure and multicomponent alloying on the mixing enthalpy of Fe-Cr alloys, and show that in the ferromagnetic state both of them reduce the alloy stability at low Cr concentrations. We analyze the effect of pressure in terms of the effective cluster interactions [2], which are *ab initio* parameters for higher level modeling within the multiscale approach.

Hexagonal closed packed (hcp)Zr-based alloys represent another material system widely used in nuclear energy applications, e.g. as fuel cladding materials. Alloying has turned out to provide a significant improvement of materials properties as compared to pure Zr. In particular, Zr-Nb alloys (with about 1 at.% Nb) show strengthening behavior due to polymorphous martensitic α↔β transition. However, an empirical approach is still taken for the selection of alloying additions [1], and improved understanding of Zr-based alloys is clearly required. Here we demonstrate how microscopic parameters calculated from first-principles can be used in higher-level phenomenological models to correlate elastic and plastic behavior of alloys. We argue that the phase transition in Zr-Nb system is associated with pronounced dynamical instabilities of body-centered phase of Zr, and present novel approach to evaluate free energy and describe phase transitions in strongly anharmonic systems [3].

THEORY

In the field of materials modeling a consensus has emerged that a successful theoretical description of materials may be achieved most efficiently in the framework of the so-called

multiscale modeling. By this one understands a solution of the complete simulation problem step-by-step employing theoretical methodologies, which are suitable for the particular length and/or time scale followed by an appropriate coarse graining when proceeding towards the next (larger) scale. For example, one starts with the solution of the quantum mechanical problem within density functional theory (DFT) for a relatively small system (~100 atoms). From these results one determines interactions between different atoms and uses them in simulations (classical molecular dynamics or statistical mechanics, e.g. Monte-Carlo technique), which includes 10^3 to 10^5 particles. In doing so one can study, for example, crack propagations, melting, spinodal decomposition or ordering in metals and alloys. For simulations of mechanical properties and microstructure (i.e. properties on the scale of microns) one often needs to substitute the atomistic description by continuum theories. The latter can be done, for example, in the framework of phenomenological models.

The multiscale modeling experienced certain success. But the fact is that at present its stages are disconnected to a large degree. DFT calculations treat mostly the electronic subsystem, while atomic motions are often neglected. In classical molecular dynamics the lack of input experimental information is often compensated by oversimplified interpolations. Even more this is true for the applications of continuum models at large time and length scales. Unfortunately, a creation of a consistent scheme for the multiscale modeling of materials properties, where all stages are connected to each other, is still a challenge. Below we briefly review recent advances in theoretical treatment of compositional and thermal disorder.

Total energy calculations at zero temperature

Starting with the lowest level description of a simulation system at the DFT level at temperature T=0K, a solution to the quantum mechanical problem for a selected (fixed) atomic configuration $\{R\}$ is provided by the electronic structure theory [2]. Within the DFT one solves the so-called Kohn-Sham (KS) equations for a system of independent "electrons" (characterized by single-particle wave functions). We denote the "electrons" density as $n(r,\{R\})$ and note that it depends on the atomic configuration $\{R\}$ and coordinate r (in contrast to many body wave function, which depends on the coordinates of *all* the electrons in the system). The essence of the KS theory is that it is constructed in such a way that the density of the independent "electrons" obtained from a self-consistent solution of the KS equations is exactly the same as the electron density in the original system of real interacting electrons. The DFT theorems ensure that the converged solution of the KS equations corresponds to the charge density in the (electronic) ground state. The total (potential) energy of a configuration $\{R\}$ can now be calculated as a functional of the one-electron density:

$$E_{\{R\}}^{DFT}[n] = T_s[n] + \int d^3 r V_{ext}(r,\{R\}) n(r,\{R\}) + \iint d^3 r d^3 r' \frac{n(r,\{R\}) n(r',\{R\})}{|r-r'|} + E_{II} + E_{xc}[n] \qquad (1)$$

In Eq. (1) $V_{ext}(r,\{R\})$ is the external potential (e.g. due to nuclei), E_{II} is the classical electrostatic interaction between the nuclei,

$$T_s[n] = \sum_{occ} \varepsilon_{one-el} - \int d^3 r V_{KS}(r,\{R\}) n(r,\{R\}) \qquad (2)$$

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is the kinetic energy of independent electrons with eigenstate energies $\varepsilon_{\text{one-el}}$ moving in the effective potential $V_{KS}(r,\{R\})$. These quantities are obtained by the self-consistent solution of the KS equations, together with the charge density n. The last term in Eq. (1) is the so-called exchange-correlation energy $E_{xc}[n]$, which incorporates the effects of many-body electron-electron interactions, and which must be approximated. For simulations at T=0K presented in this work we used the approximation advocated in Ref. [2], that is we calculated the self-consistent electron densities within the local-density approximation (LDA) [8] and then the total energies in Eq. (1) were calculated in the generalized-gradient approximation (GGA) [9].

A serious problem with the application of the DFT formalism occurs if a configuration $\{R\}$ does not have any translational periodicity, like for a solid solution phase $A_{1-x}B_x$. The point is that in this case group theory, which is the corner stone of the modern electronic structure calculations, cannot be used directly. One obvious way to deal with a disordered system is to consider its fragment(s), to impose periodic boundary conditions, and to solve the DFT problem for such "supercells". In many cases this way of simulating the disorder is acceptable for total energy calculations. However, it is important to remember that this model is based on the use of translational symmetry, which is absent in real random alloys. Moreover, the choice of a supercell is not a trivial task. The problem is that whether a supercell can be considered as (quasi-)random or not in the total energy calculations is exclusively dictated by the nature of the interatomic interactions in this particular system. Careful discussion of the problem can be found in Ref. [2].

As an alternative to the supercell approach one can reconstruct three-dimensional periodicity of the solid solution phase $A_{1-x}B_x$ by mapping it onto an ordered lattice of "effective" atoms, which describe the original system on the average. In terms of the electronic structure problem, one is ultimately interested in processes of electron scattering off the atoms in the system, the so-called multiple-scattering. For completely disordered alloys very successful approximation, the coherent potential approximation (CPA), is constructed by placing effective scatterers at the sites of the original system. Scattering properties of these effective atoms have to be determined self-consistently from the condition that the scattering of electrons off the alloy components, embedded in the effective medium as impurities, vanishes on the average [10]. The CPA is currently one of the most popular techniques to deal with substitutional disorder, and in this work we use its implementation within the exact muffin-tin orbital (EMTO) theory [11]. Details of the calculations for Fe-Cr alloys are the same as in Ref. 7, while for Zr-Nb alloys they are summarized in Ref. [12]

Free energy calculations at finite temperature

In order to describe phase equilibria and to construct phase diagrams within the multiscale approach, we have to move to higher-level theories. One possibility here is offered within the phenomenological thermodynamics approach. For alloy systems one considers most often temperature-composition phase diagrams at ambient pressure. Thus, one deals with a system in thermal and mechanical contact with a constant-temperature constant-pressure heat bath, whose equilibrium is described by the thermodynamic potential

$$G=E+PV-TS=H-TS=F+PV, \tag{3}$$

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where G is the Gibbs free energy, E is the energy of the system, P, V, T represent pressure, volume, and temperature, respectively, S denotes the entropy, $H = E + PV$ is the enthalpy, and $F = E - TS$ is the Helmholtz free energy. If phase α transforms into phase β in a pure material at equilibrium transformation temperature T_c, $G_\alpha = G_\beta$ at T_c.

In a binary system $A_{1-x}B_x$ at constant P and T the G curves as a function of an alloy component fraction x for the phases in equilibrium must share a common tangent. However, this condition defines areas at temperature-composition phase diagram subject to a transformation via nucleation-and-growth mechanism, like the binodal decomposition in Fe-Cr alloys. The alloys within this area are metastable. A condition for the spinodal decomposition, which occurs in systems unstable to any concentration fluctuation, is given by inequality $dG/dx < 0$. The simplest calculations here can be carried out within the mean-filed approximation [2]. One assumes a complete disorder among the alloy components for solution phases and calculates their enthalpies $H_{A_{1-x}B_x}$ from DFT total energies and pressure, obtained e.g. by means of the supercell approach or within the CPA, as described in the previous section. Then one defines the mixing enthalpy ΔH^{mix} and configurational contribution to the mixing entropy ΔS^{mix} as

$$\Delta H_{A_{1-x}B_x}^{mix} = H_{A_{1-x}B_x} - (1-x)H_A - xH_B \qquad \Delta S_{A_{1-x}B_x}^{mix} = -k_B[x \ln x + (1-x)\ln(1-x)], \qquad (4)$$

where $H_{A(B)}$ represents the enthalpy of a standard state, for simplicity taking here as pure alloy components, k_B is the Boltzmann constant. It is now possible to proceed with a construction of the phase diagram. This highly oversimplified approach is supposed to overestimate the order-disorder transition temperature, because of the neglect of the short-range order effects in solid solutions. But in systems with a tendency towards phase separation it may give surprisingly good agreement with more advanced calculations [13], and analysis of the mixing enthalpy often provides important insight into behavior of alloys upon ordering of phase separation. This will be illustrated further in section Discussion.

To go beyond the mean-filed description, one most often uses the so-called canonical ensemble. The thermodynamic potential is the Helmholtz free energy F, which describes a system at constant temperature and volume, and which is calculated as:

$$F(T,V,N) = -k_B T \ln Z(T,V,N) = -k_B T \ln \left[\sum_{\{R\}} \exp\left(-\frac{F_{\{R\}}}{k_B T} \right) \right] \qquad (5)$$

where $Z(T,V,N)$ is the partition function and k_B is the Boltzmann constant. Because for the problem of configurational thermodynamics, which deals with diffusion time scales, the fast degrees of freedom, such as electronic, vibrational and magnetic, can be averaged out, the partition function for the configurational degrees of freedom in Eq. (5) should consist of the free energies $F_{\{R\}}$ of electronic, magnetic and vibrational excitations of alloys with a given configuration $\{R\}$ [2]. In practice DFT calculations are almost always carried out at zero temperature. In principle, vibrational contribution F_{vib} can be included within the so-called quasi-harmonic approximation [2,14] (QHA), where it is calculated from the phonon dispersion relations via the phonon density of states $g(\omega)$ using expression:

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$$F_{vib} = \int_0^\infty g(\omega)\left[k_B T \ln\left(1 - \exp\left(\frac{h\omega}{k_B T}\right)\right) + \frac{h\omega}{2}\right]d\omega \tag{6}$$

However, for large class of alloy systems this will not work. For example, phonon dispersion relations calculated for the body-centered cubic (bcc) phase of Zr at T=0K show imaginary frequencies [3]. This means that free energy cannot be defined within the QHA. On the other hand, bcc Zr is stabilized at high temperature by the anharmonic effects, and bcc (β-phase) precipitates are very important for the improvement of mechanical properties of Zr-Nb alloys, which will be discussed below.

An accurate and easily extendable method to deal with lattice dynamics of solids, the Temperature Dependent Effective Potential Method (TDEP) has been suggested in [3]. It is designed to work even for strongly anharmonic systems where the traditional quasi-harmonic approximation fails. The method is based on *ab initio* molecular dynamics (AIMD) simulations and provides a consistent way to extract the best possible harmonic—or higher order—potential energy surface at finite temperatures. Using a Taylor expansion of the potential energy U in time dependent atomic displacements $u(t)$, truncated after the second-order terms:

$$U = U_0 + \frac{1}{2}\sum_{ij\mu\nu} u_{j\nu}(t)\ D_{\mu\nu}^{ij}\ u_{i\mu}(t), \tag{7}$$

where $D_{\mu\nu}^{ij}$ is the force constant matrix, i and j denote atomic positions, and μ,η are the Cartesian coordinates, TDEP method exploits the potential energy surface at *finite* temperature T by means of AIMD, generating a set of displacements $\boldsymbol{u}_i(t)$ and forces $\boldsymbol{F}_i(t)$, which are consistent with each other. The TDEP force constant matrix can now be determined at the temperature of MD simulation by minimizing the difference between AIMD forces and TDEP forces $\boldsymbol{F}_i(t)= \sum_j \boldsymbol{D}^{ij}\boldsymbol{u_j}(t)$ for the entire MD run. As has been demonstrated in Ref. [3], the procedure is unique, well converged, and at finite temperatures it eliminates the imaginary frequencies obtained in QHA calculations at T=0, bringing the phonon dispersion relations for bcc Zr in very good agreement with available experiment. Consequently, the free energy can now be defined as $F_{TDEP} = U_0 + F_{vib}$, where F_{vib} is given by Eq. (6) and U_0 is determined from AIMD and Eq. (7) as

$$U_0 = \left\langle U_{MD}(t) - \sum_{ij\mu\nu}\frac{1}{2}D_{\mu\nu}^{ij}u_{j\nu}(t)u_{i\mu}(t)\right\rangle \tag{8}$$

It is important to understand that in Eq. (5) the sum runs over all possible states *{R}* of the system. For example, if we need to find F and/or Z for $A_{1-x}B_x$ alloy at fixed composition x and underlying bcc crystal lattice, *{R}* represents all possible occupations of the bcc lattice by *(1-x)N* A and *xN* B atoms. The basic idea of the formalism, which represents a typical first step of the multiscale modeling, is to coarse-grain the problem by eliminating quantum degrees of freedom from the Hamiltonian. This is achieved by mapping DFT total energy functional, Eq. (1), on the configurational energies calculated from classical generalized Ising Hamiltonian:

$$H^{conf} = \frac{1}{2}\sum_s V_s^{(2)}\sum_{i,j\in s}c_i c_j + ... \tag{9}$$

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In Eq. (9) i,j are lattice sites, the occupation numbers c_i in case of a binary alloy take on values 1 or 0 depending on the type of atom occupying site i, and $V_s^{(d)}$ are the effective cluster interactions (ECI), which correspond to clusters of the order d and type s. Different methods have been developed for calculations of ECI from first principles [2]. In this work we employed the so-called screened generalized perturbation method (SGPM) [15].

DISCUSSION

Fe-Cr alloys

A moderate amount of Cr, up to 10%, in ferritic steels has proven to be most beneficial to their ductile to brittle transition temperature as well as to their corrosion resistance and resistance to neutron radiation induced swelling. Though there is a miscibility gap for the alloy concentrations above 10 at. % Cr at room temperature for lower concentrations of Cr the alloy is stable with respect to this decomposition. Moreover, diffuse-neutron-scattering experiments show an anomaly associated with a change of the ordering tendency from the clustering in Cr-rich alloys towards the short-range order for low Cr Fe-Cr alloys, and this effect is now well understood form *ab initio* theory [4-6]. In this work we investigate how this tendency is affected by pressure, which may be present, e.g. locally due to radiation induced defects, as well as by other alloying elements, present in RPV steels.

Figure 1 shows the calculated mixing enthalpy and its second derivative of ferromagnetic Fe-Cr alloys as a function of Cr concentration at ambient pressure and at 20 GPa. The standard states of Fe H_{Fe} in Eq. (4) is the ferromagnetic bcc Fe, while the reference state of bcc Cr is
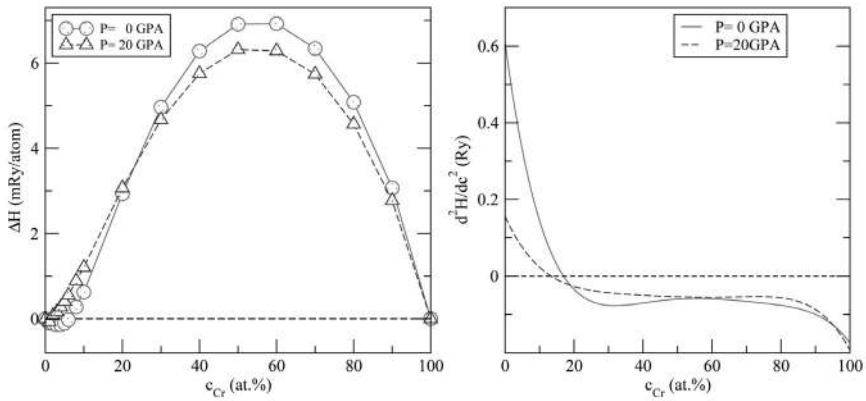

Figure 1. (left) Calculated mixing enthalpy ΔH and (right) its second derivative of ferromagnetic Fe-Cr alloys as a function of Cr concentration at pressures $P = 0$ (full red line, circles) and 20 GPa (dashed blue line, diamonds).
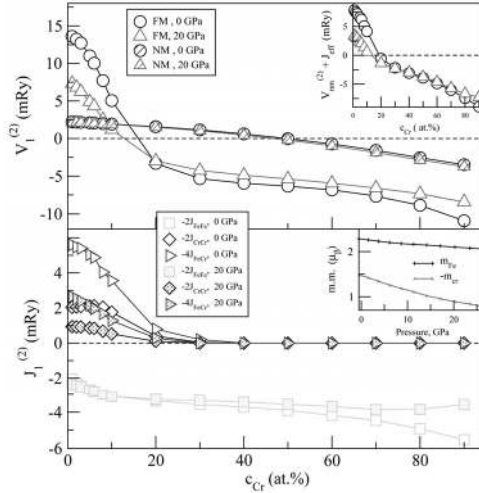
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Figure 2. (top) Calculated pair ECI between nearest neighbors $V_1^{(2)}$, Eq. (9), for ferromagnetic (open symbols) and nonmagnetic (dashed symbols) Fe-Cr alloys as a function of Cr concentration at ambient pressure (black circles) and at P=20 GPa (red trangles); (bottom) Calculated magnetic exchange interaction parameters of the classical Heisenberg Hamiltonian J_{AB} with their respective coefficients as they appear in Eq. (10). Inset in the top panel shows results from model calculations using Eq. (10). Inset in the bottom panel shows the pressure dependence of Fe (m_{Fe}) and Cr (m_{Cr}) magnetic moments in alloy with 3 at.% Cr.

considered to be nonmagnetic. One can see in the left panel that the alloy stabilization is weakened in the case of low-Cr steels. Indeed, with increasing pressure the depth and width of the ΔH minimum decreases. Although the enthalpy is still negative in dilute limit at pressure 20 GPa, the stability of Fe-rich Fe-Cr alloys is greatly reduces. On the other hand, positive values of ΔH for large Cr concentrations decrease, indicating decreasing tendency toward the phase separation in this concentration range with increasing pressure. In the right panel the second derivative of the mixing enthalpy as a function of Cr concentration is plotted at ambient and high pressure. Inspecting the figure, it becomes clear that at high pressure the concentration of Cr corresponding to the onset of spinodal decomposition decreases, i.e., a region of spinodal decomposition becomes wider. Thus, hydrostatic pressure may be detrimental for steels with high Cr composition, close to the border of the spinodal region on the phase diagram.

To understand this behavior, we show in Fig. 2 calculated pair ECI between nearest neighbors $V_1^{(2)}$, Eq. (9), as a function of Cr concentration and pressure. Its negative sign for most of the compositions indicates tendency towards clustering, but in Fe-rich alloys the sign is positive, and the alloys are stable. However, the increase of pressure reduces $V_1^{(2)}$ at low Cr

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concentration, indicating the alloy destabilization, in agreement with conclusion drawn from ΔH calculations. Because in low Cr steels magnetic moments of Cr are antiparallel to magnetic moments of Fe in the (magnetic) ground state [4-7], one can approximate the ECI as a sum of chemical and magnetic terms following a model of Ref. [7] as

$$V_s^{(2,\text{mod})} = V_s^{(2,chem)} + V_s^{(2,magn)} \qquad V_s^{(2,magn)} = -2(J_{FeFe} + 2J_{FeCr} + J_{CrCr}) \qquad (10)$$

where J_{AB} is the magnetic exchange interaction parameter of the classical Heisenberg Hamiltonian. Assuming further that $V_s^{(2,chem)}$ does not depend on the magnetic state, it can be associated with ECI in nonmagnetic alloys. In Fig. 2 it is clearly seen that this term depends weakly on alloy concentration, and it is quite small. Thus, most important contribution into ECI and therefore the stability trends of ferromagnetic Fe-Cr alloys comes explicitly from the magnetic exchange interactions. In Fe-rich alloys at ambient pressure $J_{CrCr} \approx -J_{FeFe}$, and therefore $V_s^{(2,chem)}$ is dominated by J_{FeCr}. However, with increasing pressure magnetic moment at Cr is reduced much stronger than at Fe, as shown in the bottom panel inset in Fig. 3. Thus, J_{CrCr} and J_{FeCr} are reduced much stronger in magnitude than J_{FeFe}, making $V_s^{(2,chem)}$, and consequently $V_1^{(2)}$ less positive. The example above demonstrates how the parameters of higher-level models obtained from first-principles can be used for better understanding of materials behavior. Of course, they can be used directly for modeling of phase diagrams [16].

To investigate the effect of additional alloying elements on the stability of bcc Fe-Cr steels, we calculate the mixing enthalpies and their second derivatives for Fe-Cr-Ni and Fe-Cr-Ni-Mn-Mo systems. The results are shown in Fig. 3. One can see that these elements tend to
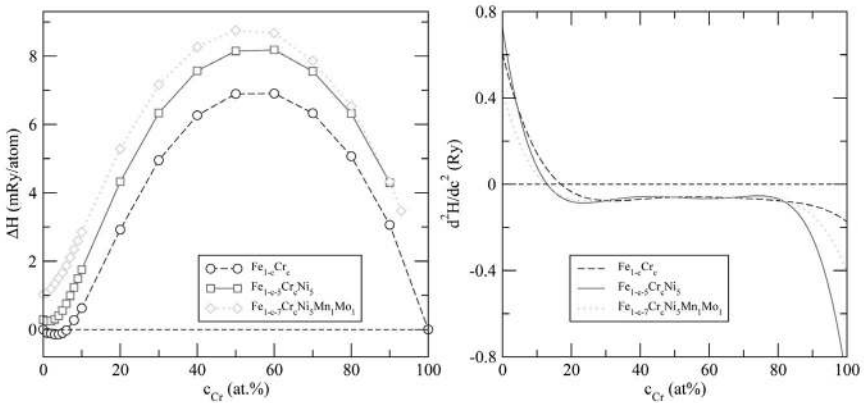

Figure 3. (left) Calculated mixing enthalpy and (right) its second derivative of ferromagnetic binary Fe-Cr alloys (dashed blue line, circles), as well as ternary alloys with 5 at. % Ni (full red line, squares), and multicomponent alloys with 5 at. % Ni, 1 at. % Mn and 1 at.% Mo (dotted green line, diamonds) as a function of Cr concentration

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