



Embedded-atom potential for an accurate thermodynamic description of the iron–chromium system



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ABSTRACT

A new potential for the iron–chromium (Fe–Cr) alloy system was optimized for the embedded-atom method (EAM) within the two-band model (TBM) extension. In contrast to previous works, free model parameters are predominantly adapted to available experimental high-temperature data of the mixing enthalpy. As a major improvement, the metastable α/α' miscibility gap is accurately described in agreement with experimental data and a recent CALPHAD parametrization. The potential was also fitted to obtain an enriched solubility for chromium atoms in an iron matrix at 0 K, as it is predicted by several *ab initio* calculations. Furthermore, it was benchmarked against phonon excess entropies at 300 K and 1600 K demonstrating good agreement with respective results of inelastic neutron scattering.

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1. Introduction

The iron–chromium (Fe–Cr) alloy system is of great technological interest since it is the basis of stainless steels [1] and a promising candidate for fusion or fission reactors and spallation neutron sources [2]. It is also one of the rare systems for which particular properties of triple junctions were measured [3]. Thus, it is important to predict its properties by means of theoretical calculations. Density functional theory (DFT) is not capable of calculating extended microstructural features such as grain boundaries, triple junctions, or even impact collision cascades which comprise several thousands to millions of atoms. For these cases, molecular dynamics (MD) or Monte Carlo (MC) simulations are very helpful tools [4]. The main input of such simulations is an appropriate (many-body) interatomic interaction which has to be designed to model the alloy realistically. Prior attempts of deriving an interatomic potential for Fe–Cr alloys concentrated on the reproduction of theoretical DFT data of the mixing enthalpy [5,6]. However, as different approximations for the exchange correlation functional produce already a significant variation of results [7–11], it is not clear which DFT data should be used as a correct reference. In this work, we therefore follow a different approach: instead of using target values from DFT calculations, we predominantly adapt the

potential to high-temperature experimental data of the mixing enthalpy [12–14]. It turns out that in this way, an appropriate description of the important metastable α/α' phase equilibrium with the embedded-atom method (EAM) is obtained. In particular, the critical temperature of the miscibility gap is matched with high accuracy according to experimental data [15–17] and the general shape of the miscibility gap at lower temperatures is predicted in good agreement with experimental phase diagrams and theoretical expectations [11,18].

Our report is organized as follows: In Section 2, we give a description of the EAM formalism and the methods applied here for the calculation of phase diagrams. Then, in Section 3, we briefly discuss the Fe–Cr potentials previously derived in literature and show their respective phase diagrams in comparison with experimental data and CALPHAD evaluations. In Section 4, we optimize the parametrization of our new potential and explicitly demonstrate that fitting the mixing enthalpy to DFT data results in an inappropriate phase diagram, while adapting to experimental data yields a description of the metastable miscibility gap with comparably high accuracy. We also present excess vibrational entropies calculated by our new EAM potential which are found to be in good agreement with experimental data.

We want to emphasize that all calculations, experimental data, and CALPHAD evaluations presented in this work are restricted to the metastable α/α' phases since the formation of the σ phase is very slow [19] and usually kinetically suppressed by the cooling

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rates applied in experiments. For the actual fitting procedure, only direct interaction between iron and chromium was taken into account, while the potentials for pure elements were taken from literature [5,20].

2. Methodology

2.1. Formalism

For a solid consisting of N atoms, the total EAM [21,22] energy is given by

$$U_{\text{tot}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_{t_i t_j}(r_{ij}) + \sum_{i=1}^N F_{t_i}(\bar{\rho}_i), \quad (1)$$

where $V_{t_i t_j}(r_{ij})$ is the pair interaction function between atoms i and j of type t_i and t_j at distance $r_{ij} = |\vec{r}_j - \vec{r}_i|$ and $F_{t_i}(\bar{\rho}_i)$ is the embedding function of type t_i at atomic site i with a local electron density of $\bar{\rho}_i$. The latter is generated by superposition of the electron densities of all surrounding atoms under consideration of their respective type t_j :

$$\bar{\rho}_i = \sum_{j=1, j \neq i}^N \rho_{t_j}(r_{ij}). \quad (2)$$

It has been shown that this EAM formalism is not capable of reproducing a change of sign in the mixing enthalpy [23–25]. Since exactly this feature is important in the Fe–Cr system, the so-called two-band model (TBM) extension has been proposed [26,27] to receive a more realistic description:

$$U_{\text{tot}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N V_{t_i t_j}(r_{ij}) + \sum_{i=1}^N F_{t_i}^d(\bar{\rho}_i^d) + \sum_{i=1}^N F_{t_i}^s(\bar{\rho}_i^s). \quad (3)$$

A second embedding function has been added here. This may be interpreted as the particular impact of a second electron band. However, since the detailed physical justification is difficult, it is better considered as a formal concept to take into account the second order influence of the central atom on the local electron intensity. Nevertheless, we will designate in the following the two terms as contributions of the d- and s-electrons. It should be noted that the single electron contributions of the s-electron density $\bar{\rho}_i^s$ need to be defined in a more general way to allow for the desired change of sign of the mixing enthalpy:

$$\bar{\rho}_i^s = \sum_{j=1, j \neq i}^N \rho_{t_i t_j}^s(r_{ij}), \quad (4)$$

i.e., the single s-electron density depends both on the type of the respective neighbor atom t_j and the type of the central atom t_i . Conventionally, it is assumed that atomic pairs of the same type do not contribute to the total s-electron density:

$$\rho_{t_i t_j}^s(r_{ij}) = 0 \quad \text{for} \quad t_i = t_j, \quad (5)$$

while unlike pairs also fulfill the symmetry relation

$$\rho_{t_i t_j}^s(r_{ij}) = \rho_{t_j t_i}^s(r_{ji}). \quad (6)$$

This convenient choice has the important advantage that previously optimized EAM potentials of pure elements can be further used without any modification when a general potential for an alloy should be constructed. So within the TBM, the only additional functions to model the binary AB alloy are the pair interaction function V_{AB} for unlike atomic species, the two s-embedding functions F_A^s and F_B^s , respectively, and the s-electron density ρ_{AB}^s . All other contributions are already known from the pure components.

2.1.1. Effective pair format

In the standard EAM formalism, an effective pair format was introduced [28] which allows a straight forward comparison of different potentials. The total energy, Eq. (1), is invariant under the transformation

$$\begin{aligned} \tilde{F}(\bar{\rho}) &= F(\bar{\rho}) - k\bar{\rho} \\ \tilde{V}(r) &= V(r) + 2k\rho(r), \quad k \in \mathbb{R}. \end{aligned} \quad (7)$$

Thus, by setting

$$k := \left. \frac{dF(\bar{\rho})}{d\bar{\rho}} \right|_{\bar{\rho}=\bar{\rho}_0} = F'(\bar{\rho}_0), \quad (8)$$

the derivative of the embedding function vanishes for the equilibrium electron density $\bar{\rho}_0$. Furthermore, the equilibrium electron density is usually fixed to unity which is easily achieved by proper inverse scaling of the electron density and the argument of the embedding function.

Owing to the specific formulation of the TBM, we can define a similar effective pair format for the interaction between unlike species as well. For comparison of different potentials, we consider a statically ordered $A_{0.5}B_{0.5}$ alloy (although it may not be energetically favored as in the case of Fe–Cr). Required by Eq. (6), the s-electron density is the same at every atomic equilibrium site of the ordered alloy so that all derivatives of the s-embedding functions vanish after transformation. The entire additional contribution stemming from interaction between unlike species is then simply given by

$$U_{\text{alloy}} = \frac{N}{2} \sum_{i=2}^N V_{AB}(r_i) + \frac{N}{2} (F_A^s(\bar{\rho}^s) + F_B^s(\bar{\rho}^s)), \quad (9)$$

where the prime indicates that only interactions between unlike species are taken into account. It can be easily proven that the following transformation holds for the TBM:

$$\begin{aligned} \tilde{F}_i^s(\bar{\rho}^s) &= F_i^s(\bar{\rho}^s) - k_i \bar{\rho}^s \\ \tilde{V}_{AB}(r) &= V_{AB}(r) + (k_A + k_B) \rho_{AB}^s(r), \quad k_i \in \mathbb{R}. \end{aligned} \quad (10)$$

Again, by defining

$$k_i := \left. \frac{dF_i^s(\bar{\rho}^s)}{d\bar{\rho}^s} \right|_{\bar{\rho}^s=\bar{\rho}_0^s}, \quad (11)$$

the derivatives of the s-embedding functions vanish for the transformed potentials in equilibrium. We also rescale the s-electron density ρ_{AB}^s so that the total s-electron density $\bar{\rho}_0^s$ becomes equal to unity for the given structure.

2.2. Calculation of phase diagrams

In order to calculate binary phase diagrams for a given interatomic potential, MC simulations are carried out in the constant ($\Delta\mu NpT$) semi-grandcanonical ensemble. For a cubic box size with volume V and length L ($dV = 3L^2 dL$) and using scaled particle coordinates within that box ($d\vec{r}_i = L^3 d\vec{s}_i$), the partition function is given by

$$\begin{aligned} Z_{\mu_A, \mu_B, N, p, T}(\{\vec{S}_i\}, c, L) &= \frac{3}{\Lambda_A^{3N}} \exp(\beta\mu_A N) \\ &\times \sum_{\mathcal{P}(\{\vec{S}_i\})} \int_{[0,1]^{3N}} \int_0^\infty \int_0^1 dc dL d^N \vec{s} \\ &\times e^{-\beta(U(\{\vec{S}_i\}) + pL^3 - Nc\mu) + (3N-1) \ln L + \frac{3Nc}{2} \ln \frac{m_B}{m_A}}, \end{aligned} \quad (12)$$

in which the independent variables are the scaled particle positions $\{\vec{S}_i\}$ within the simulation box, the concentration c of component B, and the cubic box length L . The prefactor is extracted for

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