Theoretical Modelling of High Entropy Alloys

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Abstract. High entropy alloys (HEA) containing Co, Fe, Ni have recently enjoyed considerable attention in the physical and material sciences due to their interesting mechanical and magnetic properties that are further enhanced by the additive manufacturing technique often used to process them. HEAs are theoretically difficult to describe as they often form amorphous structures and the Bloch theorem is not applicable. In this article the method of the effective medium is used and the corresponding many body problem is solved self-consistently within the coherent potential approximation. The mixing entropy of HEAs is explained using an optimization approach. The complex micro and multi-phase structures are due to many body effects that are discussed from a calculation of the quasiparticle density of states. It turns out that these many body effects are most significant if the n components of the alloy are present at about equal proportions. Using alternatively a lattice gas model to represent the disordered alloy the existence of a second order phase transition is confirmed; the transition temperature is calculated. Heat capacity and entropy are evaluated as a function of temperature T. It is shown that the results of the two model calculations are in qualitative agreement with one another and must thus be regarded as good and reliable.

1. Introduction

High entropy alloys (HEA) have been studied since 2003 [1] mainly due to their exceptional mechanical properties, i.e. high yield and ultimate strengths, high structural and phase stability, good corrosion resistance, and high hardness. These properties make high entropy alloys suitable for high temperature applications, e.g. gas turbines in the aerospace industry. They are also routinely used in boat structures, racing car bodies, spaceships, and other constructions of a challenging nature. High entropy alloys are novel or composite materials with about equal proportions of several metals. The basic idea is to create a multi-element single phase solid solution alloy. This feature makes HEAs different to conventional alloys which consist of a primary component with small amounts of additional elements added. Examples for such conventional alloys are bronze (88% Cu and 12% Sn) and carbon steel (96% Fe and 4% C). On the other hand, in high entropy alloys additional elements may be added to Fe to form a new material with properties very much different to those of the individual components. As each HEA can be modified by minor variations in the choice of added elements, the possible number of new alloy bases is vast [2]. Elements with different crystal structures are mixed with the possibility to form various new phases. An example is the single phase CoCrFeNi high entropy alloy which forms an f.c.c. crystal lattice even though Ni, Fe, and Co on their own all crystallize in different lattice structures. To form single phase structures a homogeneous distribution of elements is useful but not necessary [3]. Due to their high mixing entropy high entropy alloys often form multi-phase or even amorphous structures. In the CoCrCuFeNi alloy complex microstructures are observed consisting of amorphous regions and magnetic nanoparticles forming a superparamagnetic phase. Other alloys exhibit a gap in the density of states near the Fermi level which makes them interesting due to their electronic and magnetic properties as Kondo insulators [4]. Possible applications as soft magnetic materials are suggested.

High entropy alloys are conveniently produced using the additive manufacturing technology [5]. To prevent component failure a structure and design evaluation known as structural health monitoring SHM [6] can then be performed for a risk based analysis and quality assurance. The aim of the article is to get to a better understanding of the material properties of high entropy alloys. It is organized as follows. In the next section the theory on elementary excitations in disordered alloys is presented and a many body problem is formulated. In Section 3 results are presented for the mixing entropy of an ideal solid solution consisting of n components. The discussion of the quasiparticle density of states reveals that many body effects are most prominent for near equal component concentrations, i.e. $c_\alpha = {}^1/_n$ for all α. These many body effects are ultimately responsible for the microstructure and thus the mechanical properties of high entropy alloys. In Section 4 the lattice gas model is applied to disordered alloys. Conclusions are drawn in Section 5.

2. Theory

The perfectly periodic solid is invariant with respect to translational symmetry operations so that the one particle contribution of the Hamiltonian becomes diagonal in $\boldsymbol{k}$-space. The Bloch theorem may then be applied to reduce the total many body problem to that of a microscopic unit cell determined by the lattice structure. On the other hand, for disordered systems, e.g. alloys, the Bloch theorem is not applicable. For reasons of simplicity we consider a substitutional alloy consisting of several compounds with similar bandstructure. Additionally we restrict the calculation to a one band model to obtain the model Hamiltonian in the formalism of 2nd quantization

$$\boldsymbol{H = H_0 + H_p = \sum_{ij\sigma} T_{ij}\ a^{+}_{i\sigma}\ a_{j\sigma} + \sum_{i\sigma} \eta_{i\sigma}\ a^{+}_{i\sigma}\, a_{i\sigma}}. \tag{1}$$

Here the term $\boldsymbol{H_0}$ denotes a one electron contribution describing the hopping of an electron with spin $\boldsymbol{\sigma}$ from lattice site $\boldsymbol{R_j}$ to lattice site $\boldsymbol{R_i}$. The corresponding hopping integrals are related to the Bloch energies via

$$\boldsymbol{T_{ij} = \frac{1}{N} \sum_{k} \varepsilon\,(k)\ e^{ik\cdot(R_i - R_j)}}. \tag{2}$$

The perturbation $\boldsymbol{H_p}$ arises from different atom types with atomic energy level $\boldsymbol{\eta}$ occupying the lattice site $\boldsymbol{R_i}$. It is this part of the Hamiltonian that is responsible for many body effects. The Hamiltonian of Eq. (1) represents the simplest model to describe electrons in a multicomponent alloy. It contains no electron-electron interaction and only depends on the concentrations of different alloy components. It, however, includes electrons interacting with the local lattice potential via the Bloch energies.

To determine $\boldsymbol{H_p}$ the method of the effective medium [7] may be used. The potential of the fictitious medium is chosen so that the corresponding many body problem can be solved exactly. The perturbation part of the Hamiltonian then describes the deviation of the local potential from that of the effective medium. As this is not known, it is varied until the quasiparticles are not scattered any more at the local potential. This implies that the many body problem becomes an effective one particle problem and the corresponding self-energy

$$\boldsymbol{M_\sigma\,(k, E) = 0}. \tag{3}$$

Alternatively, for the calculation of the one electron Green function $\boldsymbol{G_{k\sigma}\,(E)}$ a configuration average can be performed where for a given set of component concentrations $\boldsymbol{c_\alpha}$ an average over all possible distributions of atoms is calculated. The coherent potential approximation CPA [8] describes a self-consistent calculation where the self-energy $\boldsymbol{M_\sigma\,(k, E)}$ becomes $\boldsymbol{k}$-independent, i.e.

$$\mathbf{M_\sigma\,(k, E) = M_\sigma\,(E)}. \tag{4}$$

The self-energy $\boldsymbol{M_\sigma\,(E)}$ contains the contributions of the perturbation $\boldsymbol{H_p}$, i.e. deviations of the atomic energy levels from the ideal periodic solid. Within the CPA the configuration averaged one particle Green function becomes

$$\langle \boldsymbol{G_{k\sigma}}\,(\boldsymbol{E})\rangle \;=\; \frac{\hbar}{\boldsymbol{E}-\,\boldsymbol{\varepsilon}\,(\boldsymbol{k})+\,\boldsymbol{\mu}-\,\boldsymbol{M_{\sigma}}\,(\boldsymbol{E})}\,. \tag{5}$$

The quasiparticle density of states then follows from the $\boldsymbol{k}$-summation

$$\boldsymbol{\rho_{\sigma}}\,(\boldsymbol{E}) = -\,\frac{\mathbf{1}}{\boldsymbol{N\,\pi}}\;\boldsymbol{Im}\;\sum\nolimits_{\boldsymbol{k}}\frac{\mathbf{1}}{\boldsymbol{E}-\,\boldsymbol{\varepsilon}\,(\boldsymbol{k})-\,\boldsymbol{M_{\sigma}}\,(\boldsymbol{E})} = -\,\frac{\mathbf{1}}{\boldsymbol{\pi}}\;\;\boldsymbol{Im}\;\int_{-\,\infty}^{+\,\infty}\frac{\boldsymbol{\rho_{0}}\,(\boldsymbol{x})}{\boldsymbol{E}-\boldsymbol{x}-\,\boldsymbol{M_{\sigma}}\,(\boldsymbol{E})}\;\;\boldsymbol{dx}. \tag{6}$$

In the second step of Eq. (6) the $\boldsymbol{k}$-summation is replaced by an integral over the free Bloch density of states that can be chosen in such a way to conveniently represent interacting particle systems. Numerical evaluations are presented in the next section.

3. Results

Section 3 contains both analytical and numerical evaluations regarding the mixing entropy and the quasiparticle density of states of high entropy alloys. The corresponding results are presented, discussed, and compared with those of other authors.

3.1 The mixing entropy

The mixing entropy $\boldsymbol{\Delta S}$ for an ideal solid solution consisting of $\boldsymbol{n}$ components is given as

$$\boldsymbol{\Delta S} = \;-\boldsymbol{R}\;\;\sum\nolimits_{\boldsymbol{\alpha}=\mathbf{1}}^{\boldsymbol{n}} \boldsymbol{c_{\alpha}}\;\;\ln \boldsymbol{c_{\alpha}}. \tag{7}$$

Here $\boldsymbol{R}$ denotes the universal gas constant and $\boldsymbol{c_{\alpha}}$ the concentration of components of type $\boldsymbol{\alpha}$. For the case $\boldsymbol{n} = \mathbf{2}$ Eq. (7) simplifies to

$$\boldsymbol{\Delta S} = \;-\boldsymbol{R}\;\,(\boldsymbol{c}\;\;\ln \boldsymbol{c}\;+(\mathbf{1}-\boldsymbol{c})\;\;\ln(\mathbf{1}-\boldsymbol{c})). \tag{8}$$

The mixing entropy $\boldsymbol{\Delta S}$ attains a maximum value if

$$\frac{\boldsymbol{d}\,(\,\boldsymbol{\Delta S})}{\boldsymbol{dc}} \;=\; -\boldsymbol{R}\;\;\ln\!\left(\frac{\boldsymbol{c}}{\mathbf{1}-\boldsymbol{c}}\right) \;=\mathbf{0}. \tag{9}$$

From Eq. (9) follows that $c = \;^{\mathbf{1}}\!/_{\mathbf{2}}$. If the components are present in equal proportions, then $\boldsymbol{\Delta S}$ is maximized with

$$(\boldsymbol{\Delta S})_{\boldsymbol{max}} \;= \boldsymbol{R}\;\;\ln \boldsymbol{n}. \tag{10}$$

The result of Eq. (10) agrees with reference [9] suggesting that with larger values of $\boldsymbol{n}$ the formation of random solid solutions in a multi element alloy system becomes more likely. However, the importance of a high mixing entropy with regard to an energy minimum is reduced with decreasing temperature.

3.2. The Quasiparticle Density of States

Eq. (6) is numerically evaluated for a binary alloy consisting of two components with concentrations c_A and $c_B = 1 -\; c_A$. Corresponding results are depicted in Fig 1 below. The pure crystal is described by the undisturbed density of states with centres of gravity at energies $E\,=\,0.5$ and $E\,=\,1.5$ respectively. Moving away from this trivial situation the densities $\rho(E)$ start overlapping and additionally become more and more deformed. If the centres of gravity are far enough apart, then at intermediate concentrations $c_A \;=\; c_B \;=\; {}^{1}\!/_{2}$ a band splitting is observed. This band splitting is a typical many body effect which becomes more significant when the chemical potential falls into the band gap. In that case the alloy becomes semiconducting with interesting electronic and magnetic phenomena present like hybridization of localized and conduction electrons, mixed valence states, spin glass behavior, and superparamagnetism. Such phenomena are indeed observed in high entropy alloys. Similar results to those presented in Fig 1 below are also reported in reference [10].

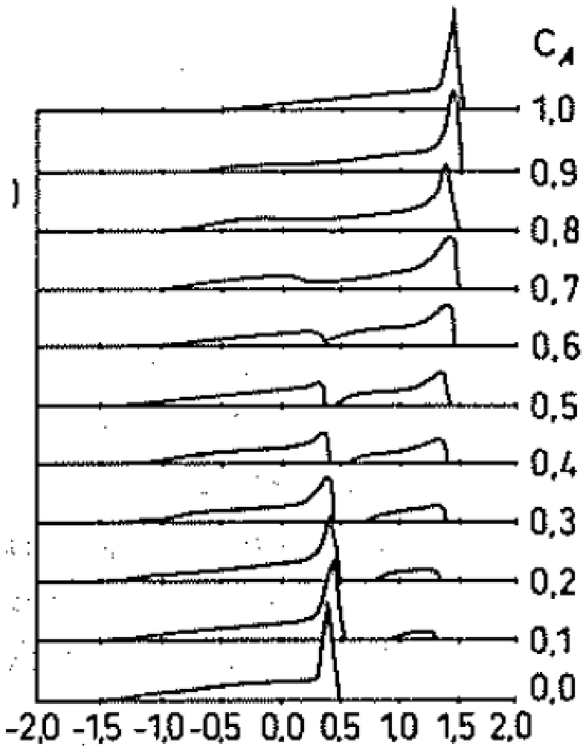

Figure 1. Density of states $\rho(E)$ as a function of energy E for a binary alloy AB plotted for different component concentrations c_A.

4. The Lattice Gas Model

The lattice gas model [11] is applied to describe respectively liquids, disordered alloys, and magnetic systems (Ising model). The total volume V is subdivided into microscopic cells of volume ΔV that are either occupied or unoccupied. One then distinguishes between two situations:

(1) There are large regions that are either completely occupied or unoccupied. Such a phase separation occurs for temperatures $T \leq T_C$.
(2) The occupied cells are statistically distributed over the entire volume V. This vapor phase is realized at temperatures $T > T_C$.

The coexistence line between the phase separated system and the homogeneous system is obtained from the ratio of atoms in the liquid state. This ratio is temperature dependent and described by the implicit equations

$$r\,(T) = \tanh\left(\frac{\alpha\ r(T)}{T}\right),$$
$$T_C = \frac{z\ w}{2\ k_B}. \qquad (11)$$

The transition temperature depends on the number of nearest neighbours z and the interaction energy w between molecules. Similar expressions for T_C are also obtained from other models of phase transitions, e.g. molecular field approximation of Heisenberg model. A numerical evaluation of Eq (11) yields the results of Fig 2 below.

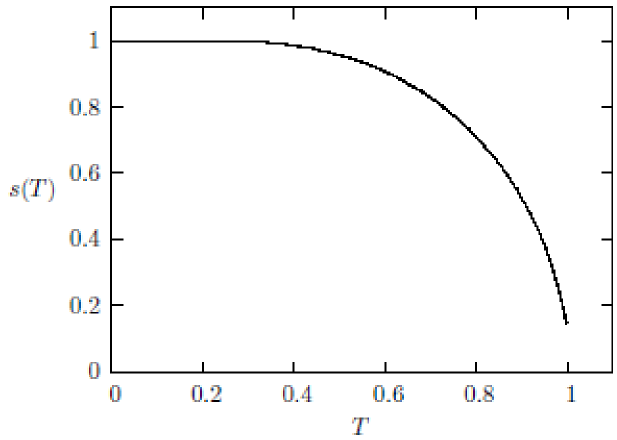

Figure 2. Ratio of atoms $r\ (T)$ $(= s\ (T))$ in the liquid state as a function of temperature T.

At $T = 0$ all atoms are in the liquid state, i.e. $r\ (T = 0) = 1$. With increasing temperature more and more atoms become vaporized and $r\ (T)$ continuously decreases as a function of T. At the transition temperature $r\ (\ T\ =\ T_C\ ) = 0$ as all atoms are vaporized; the corresponding phase transition is of second order. This is further confirmed with the discussion of the heat capacity

$$C_V\ =\ \frac{x^2}{(\cosh x)^2}\ , \tag{12}$$

where $x = \frac{\alpha}{T}$ and the entropy $S\ (T)$ as a function of temperature T . Corresponding results are depicted in Figures 3 and 4 below. As a response function the heat capacity has a peak at the critical temperature T_C ; such peaks are typical for 2nd order phase transitions. The entropy $S\ (T)$ reaches saturation in the high temperature limit where

$$S\ (T)\ \rightarrow N\ k_B\ \ \ln 2. \tag{13}$$

For a binary alloy this is identical to the result of Eq. (10) above. On the other hand, in the low temperature limit

$$S\ (T = 0) = 0. \tag{14}$$

This is in agreement with the 3rd law of thermodynamics. Furthermore, at the critical temperature T_C the entropy function is continuous as expected for a 2nd order phase transition.

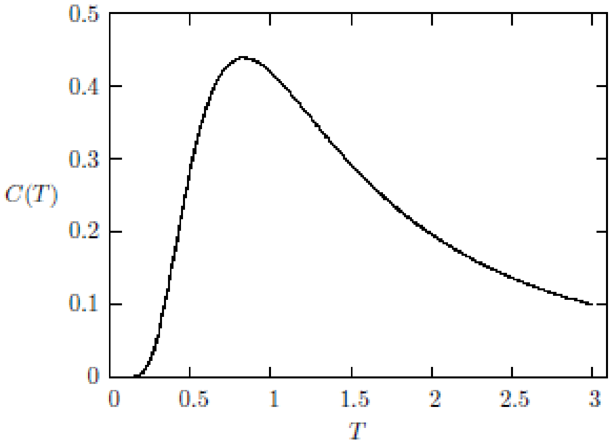

Figure 3. Heat capacity $C_V\ (T)$ as a function of temperature T.

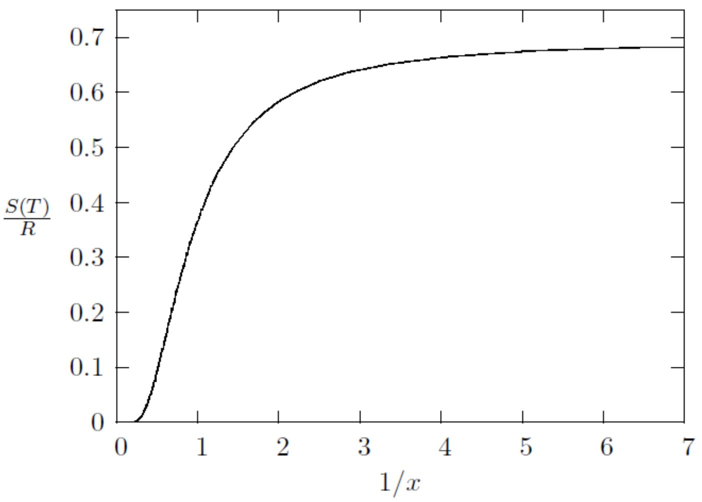

Figure 4. Entropy $S\ (T)$ as a function of temperature T.

5. Conclusions

In this work high entropy alloys are theoretically described using the method of the effective medium; the corresponding many body problem is solved within the coherent potential approximation CPA. The mixing entropy ΔS attains a maximum value for equal distribution of alloy components. The quasiparticle density of states QDOS shows many body effects in exactly the same region of concentrations. From the lattice gas model the critical temperature T_C for phase separation is calculated. The existence of a 2nd order phase transition is confirmed.

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