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Melting of metallic and intermetallic solids: An energetic view from DFT calculated potential wells

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ABSTRACT

Potential wells of metallic and intermetallic phases are constructed by *ab initio* calculation using the density functional theory. The potential wells are presented as a function of a characteristic length scale equivalent to the cubic root of the average atomic volume, to reflect the importance of density on binding. The results show that the characteristics of a potential well dictates the melting temperature of a crystalline solid metal or an intermetallic phase. The energetic requirement for melting is equivalent to an activation state where the slope of the potential well gets close to the positive maximum, or where the well experiences a step change in energetic state. The work offers a way to predict melting points of metallic/intermetallic phases, which is particularly useful to metastable phases, for which it is usually difficult to measure the melting points directly. Such predicted data on melting points are useful for establishing thermodynamic databases for phase diagram calculations.

1. Introduction

There are plenty of evidences that a large variety of properties of condensed matter originate from the fundamental characteristics of cohesion which is dictated by the potential energy as a function of atomic/molecular configurations. An energy landscape can therefore be presented by plotting the *potential energy* against *a collective coordinate* of all atomic configurations [1]. The total energy of a system of atoms/molecules is made of both potential energy and kinetic energy. It has been recognised that the latter is to offer the energetic means to allow the system to visit as many states as possible in the potential energy landscape [1–3]. The thermodynamic properties of a system of atoms at a finite temperature T can be fully presented in terms of the partition function Z:

$$F = U - TS = -k_B T \ln Z \qquad (1)$$

Where F is the free energy, S the entropy, U the potential energy, and k_B the Boltzmann constant. The partition function Z is

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \qquad (2)$$

where E_i represents the energy for the microstate i with respect to the ground state. On the energy landscape of a system of atoms, each specific macroscopic structure or phase of a system is a statistic average of the microstates being visited around an energetic minimum. There can be various potential energy minima to correspond to macroscopic phases such as liquid, relaxed glass, quasicrystalline structures, crystalline states with or without structural defects, etc, with the ground state being the deepest and narrowest valley on the landscape. The dynamic process in a thermally activated system can be simulated by molecular dynamics [4–6], with the potential energy of the system determined by the overall configurations of atomic coordinates.

Molecular dynamic simulation can be carried out using either an *ab initio* approach (AIMD), or using the classic method (CMD) with approximate descriptions for the potential energy. The CMD potential energy for a metallic system should contain both the pair-wise repelling terms and density terms for binding [7,8]. The maximum cohesion or binding of a metallic system corresponds to the equilibrium density where the repelling and attracting forces between atoms are balanced to give minimum potential

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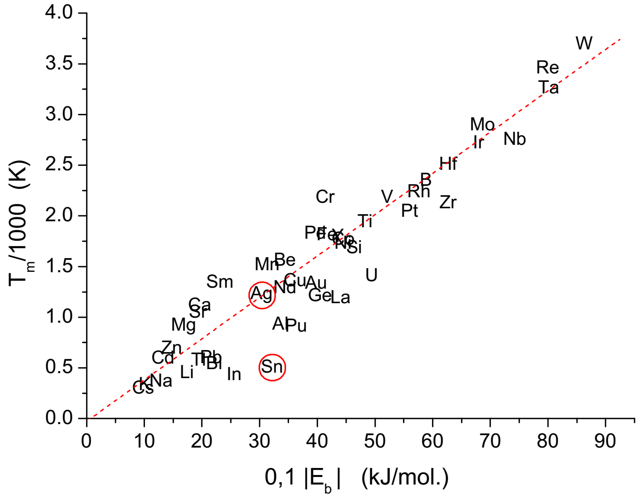

Fig. 1. Experimental melting temperature against 10% of the binding energy, showing a good correlation. The slope of the trend is $3R$. A "normal" metal Ag and an "abnormal" metal Sn are circled.

energy. It has been recognised for a long time that there is good correlation between the cohesion energy and melting point (T_m) in a metallic system [9–12]. Such a correlation is shown in Fig. 1, using experimental data reviewed by Kittel [13]. In this work, we will examine the physical origins of such a correlation, with efforts towards differentiating the "*typical*" metals that follow the general trend closely, from the "*abnormal*" ones that deviate considerably from the general trend.

2. Methodology

Calculations in this work have been performed under the framework of the density functional theory (DFT) [14–16], which states that all ground state properties are functionals of the charge density ρ. Specifically, the total energy E_t is

$$E_t = T[\rho] + U[\rho] + E_{xc}[\rho] \tag{3}$$

where $T[\rho]$ is kinetic energy, $U[\rho]$ the potential field, and $E_{xc}[\rho]$ the exchange-correlation energy. Self-consistent solution of Eq. (3) is equivalent to treating the many-body problem of interacting electrons and nuclei by solving a series of one-electron Kohn–Sham (KS) equations. The final term in Eq. (3), the exchange-correlation energy, requires some approximation for this method to be computationally tractable. The generalised gradient approximated (GGA) functionals have been used throughout this work, as they usually provide a better overall description of the electronic subsystem than the local density approximated (LDA) functionals [17,18]. The calculation was carried out using the well tested CASTEP code [19], which employs plane-wave basis sets to treat valence electrons and pseudopotentials to approximate the potential field of ionic cores (including nuclei and tightly bond core electrons) [19]. The results of DFT calculation using the CASTEP method were compared to those obtained using the all-electron method of DMol3 [20], showing both methods have similar accuracy level on energetic differences between the condense allotropic phases [21]. Therefore, high efficiency and high accuracy for DFT calculations can be achieved using the pseudopotential method of CASTEP, when the results on the ground state elemental structure are calibrated to well-established data.

Geometry optimization was carried out for minimizing the total energy to define the equilibrium state of each structural configuration. Following convention, we define the potential energy as the total energy difference between the condensed configuration and the state of free atoms, i.e. the binding energy. Due to the importance of density on binding in metallic phases, we represent the binding energy with respect to the cubic root of average atomic volumes, to characterize the potential wells of condensed metallic systems. The cubic root of atomic volume is a characteristic crystallographic length scale, which has been successfully used to study the alloying effect on lattice parameters in metallic and intermetallic alloys [22], showing that variation in lattice parameters of a metallic or an intermetallic system due to alloying are dictated by the change in average charge density. Such a length scale is based on the equivalent atomic volume of phases of various structures and is therefore suitable to characterise the density effect in phases of varied crystallographic symmetry.

3. The potential well vs melting temperature

The trend line in Fig. 1 guides one for the correlation between 10% of the binding energy and the melting points (The Pearson's coefficient of regression is 0.88). Interestingly, the slope of the trend line is $3RT$, with R being the gas constant. It is seen in Fig. 1 that there are "typical" metals such as Ag to demonstrate an excellent correlation, while "abnormal" metals such as Sn can deviate significantly from the correlation.

Rose showed that typical metals can be characterized with a universal potential well, which is presented by the binding energy normalised by the absolute equilibrium value, $g = E_b/|E_0|$, as a function of a scaled length a [23].

$$g(a) = E_b/|E_0| = -(1 + a + 0.05a^3)e^{-a} \tag{4}$$

The scaled length a is defined as

$$a = (r_{ws} - r^0_{ws})/L = (r_{ws} - r^0_{ws}) \cdot \left(\frac{|E_0|}{12\pi r^0_{ws} B}\right)^{-1/2} \tag{5}$$

where r_{ws} and r^0_{ws} are Wigner–Seitz radii, with the latter being the equilibrium value. B is bulk modulus, and L is the effective width of the well. The Rose well is shown in Fig. 2 for $a \geqslant 0$. The slope of the well is characteristic of the attractive force between atoms, and according Eq. (4), 90% of the maximum force corresponds to an activated energetic state of $0.9E_0$. In other words, at an energy level that is about 10% higher than the equilibrium binding energy, the attractive force gets fairly close to maximum (90%). It is reasonable to postulate that an atom activated up to such an energetic level may be able to move translationally away from its equilibrium positions without meeting significant resistance from its neighbours. While such translational movements of atoms are common

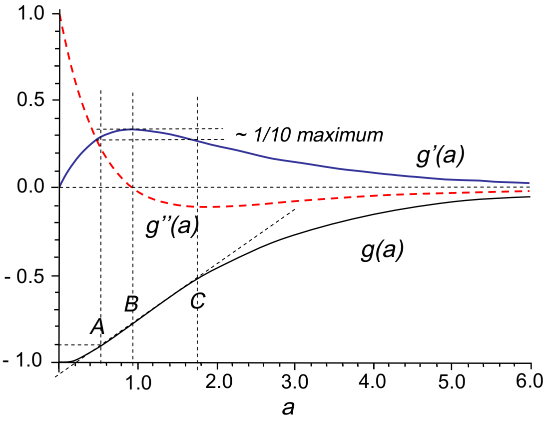

Fig. 2. The Rose well plotted with its first and second derivatives. At activation energy of $0.1E_b$, the slope of the well approaches maximum, since the slope between "A" and "C" is nearly constant.