

Calculation of Lindemann's melting Temperature and Eutectic Point of bcc Binary Alloys

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Abstract. Analytical expressions for the ratio of the root mean square fluctuation in atomic positions on the equilibrium lattice positions and the nearest neighbor distance and the mean melting curves of bcc binary alloys have been derived. This melting curve provides information on Lindemann's melting temperatures of binary alloys with respect to any proportion of constituent elements and on their eutectic points. Numerical results for some bcc binary alloys are found to be in agreement with experiment.

Keywords: Lindemann's melting temperature, eutectic point, bcc binary alloys.

1. Introduction

The melting of materials has great scientific and technological interest. The problem is to understand how to determine the temperature at which a solid melts, i.e., its melting temperature. The atomic vibrational theory has been successfully applied by Lindemann and others [1-5]. The Lindemann's criterion [1] is based on the concept that the melting occurs when the ratio of the root mean square fluctuation (RMSF) in atomic positions on the equilibrium lattice positions and the nearest neighbor distance reaches a critical value. Hence, the lattice thermodynamic theory is one of the most important fundamentals for interpreting thermodynamic properties and melting of materials [1-6, 8-15]. The binary alloys have phase diagrams containing the liquidus or melting curve going from the point corresponding the melting temperature of the host element to the one of the doping element. The minimum of this melting curve is called the eutectic point. The melting is studied by experiment [7] and by different theoretical methods. X-ray Absorption Fine Structure (XAFS) procedure in studying melting [8] is focused mainly on the Fourier transform magnitudes and cumulants of XAFS. The melting curve of materials with theory versus experiments [9] is focused mainly on the dependence of melting temperature of single elements on pressure. The phenomenological theory (PT) of the phase diagrams of the binary eutectic systems has been developed [10] to show the temperature-concentration diagrams of eutectic mixtures, but a complete "ab initio" theory for the melting transition is not available [11,16]. Hence, the calculation of melting temperature curve versus proportion of constituent elements of binary alloy and its eutectic point still remains an interesting problem.

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The purpose of this work is to develop a thermodynamic lattice theory for analytical calculation of the mean melting curves and eutectic points of bcc binary alloys. This melting curve provides information on Lindemann's melting temperatures of binary alloys with respect to any proportion of constituent elements and on the eutectic points. Numerical results for some bcc binary alloys are found to be in agreement with experiment [7].

2. Formalism

The binary alloy lattice is always in an atomic thermal vibration so that in the lattice cell n the atomic fluctuation function, denoted by number 1 for the 1st element and by number 2 for the 2nd element composing the binary alloy, is given by

$$U_{1n} = \frac{1}{2} \sum_q (\mathbf{u}_{1q} e^{iq \cdot \mathbf{R}_n} + \mathbf{u}_{1q}^* e^{-iq \cdot \mathbf{R}_n}), \quad U_{2n} = \frac{1}{2} \sum_q (\mathbf{u}_{2q} e^{iq \cdot \mathbf{R}_n} + \mathbf{u}_{2q}^* e^{-iq \cdot \mathbf{R}_n}), \quad (1)$$

$$\mathbf{u}_{1q} = \mathbf{u}_1 e^{i\omega_q t}, \quad \mathbf{u}_{2q} = \mathbf{u}_2 e^{i\omega_q t}, \quad (2)$$

where ω_q is the lattice vibration frequency and q is the wave number.

The atomic oscillating amplitude is characterized by the mean square displacement (MSD) or Debye-Waller factor (DWF) [3, 12-15] which has the form

$$W = \frac{1}{2} \sum_q |\mathbf{K} \cdot \bar{\mathbf{u}}_q|^2, \quad (3)$$

where \mathbf{K} is the scattering vector equaling a reciprocal lattice vector, and $\bar{\mathbf{u}}_q$ is the mean atomic vibration amplitude.

It is apparent that 1/8 atom on the vertex and one atom in the center of the bcc are localized in an elementary cell. Hence, the total number of atoms in an elementary cell is 2. Then if on average s is atomic number of type 1 and $(2 - s)$ is atomic number of type 2, the quantity $\bar{\mathbf{u}}_q$ is given by

$$\bar{\mathbf{u}}_q = \frac{s\mathbf{u}_{1q} + (2-s)\mathbf{u}_{2q}}{2}. \quad (4)$$

The potential energy of an oscillator is equal to its kinetic energy so that the mean energy of atom k vibrating with wave vector q has the form

$$\bar{\varepsilon}_q = M_k |\dot{\bar{\mathbf{u}}}_{kq}|^2. \quad (5)$$

Hence, using Eqs. (2, 5) the mean energy of the crystal consisting of N lattice cells is given by

$$\bar{\varepsilon} = \sum_q \bar{\varepsilon}_q = \sum_q N \left(sM_1 \omega_q^2 |u_{1q}|^2 + (2-s)M_2 \omega_q^2 |u_{2q}|^2 \right), \quad (6)$$

where, M_1, M_2 are the masses of atoms of types 1 and 2, respectively.

Using the relation between u_{2q} and u_{1q} [13], i.e.,

$$u_{2q} = m u_{1q}, \quad m = M_1 / M_2, \quad (7)$$

and Eqs. (5, 6) we obtain the mean energy for the atomic vibration with wave vector q

$$\bar{\varepsilon}_q = N\omega_q^2 |u_{1q}|^2 [sM_1 + M_2(2-s)m^2]. \tag{8}$$

The mean energy for this q th lattice mode calculated using the phonon energy with \bar{n}_q as the mean number of oscillators is given by

$$\bar{\varepsilon}_q = 2\left(\bar{n}_q + \frac{1}{2}\right)\hbar\omega_q. \tag{9}$$

Hence, comparing Eq. (8) to Eq. (9) we obtain

$$|u_{1q}|^2 = \frac{2\hbar\left(\bar{n}_q + \frac{1}{2}\right)}{NM_1\omega_q[s+(2-s)m]}. \tag{10}$$

Using Eq. (4) and Eq. (7) the mean atomic vibration amplitude has the form

$$|\bar{u}_q|^2 = \frac{1}{4}[s+(2-s)m]^2 |u_{1q}|^2. \tag{11}$$

To study the MSD Eq. (3) we use the Debye model, where all three vibrations have the same velocity [3]. Hence, for each polarization with taking Eq. (11) into account we get the mean value

$$|Ku_q|_1^2 = \frac{1}{3}K^2 |u_q|^2 = \frac{1}{12}K^2 [s+(2-s)m]^2 |u_{1q}|^2. \tag{12}$$

When taking all three polarizations the factor 1/3 is omitted, so that using Eq. (10) the MSD or DWF Eq. (3) with all three polarizations is given by

$$W = \frac{1}{2} \sum_q K^2 |u_q|^2 = \frac{1}{4} \sum_q K^2 [s+(2-s)m]^2 \frac{\left(\bar{n}_q + \frac{1}{2}\right)\hbar}{NM_1\omega_q[s+(2-s)m]}. \tag{13}$$

Transforming the sum over q into the corresponding integral [3], Eq. (13) is changed into the following form

$$W = \frac{1}{4}K^2 [s+(2-s)m] \frac{\hbar^2}{M_1} \int_0^{\omega_D} \left\{ \frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2} \right\} \frac{3\omega^3}{\omega_D^3 \hbar\omega} d\omega. \tag{14}$$

Denoting $z = \hbar\omega/k_B T$, $k_B\theta_D = \hbar\omega_D$ with ω_D , θ_D as Debye frequency and temperature, respectively, we obtain

$$W = \frac{3}{4}K^2 [s+(2-s)m] \frac{\hbar^2 T^2}{M_1 k_B \theta_D^3} \int_0^{\theta_D/T} \left\{ \frac{1}{e^z - 1} + \frac{1}{2} \right\} z dz. \tag{15}$$

Since we consider the melting, it is sufficient to take the high temperatures ($T \gg \theta_D$) so that $\frac{z}{e^z - 1} \approx 1$, and $\frac{z}{2} \rightarrow 0$, then the DWF Eq. (15) with using Eq. (7) is given by

$$W = \frac{3}{4} \frac{[M_2 s + (2-s)M_1] \hbar^2 K^2 T}{M_1 M_2 k_B \theta_D^2}, \tag{16}$$

which is linearly proportional to the temperature T as it was shown already [3, 14].

From Eq. (12) with using Eq. (3) for W we obtain

$$\sum_q |u_{1q}|^2 = \frac{24W}{K^2 [s + (2-s)m]^2}. \quad (17)$$

The mean crystal lattice energy has been calculated

$$\bar{\epsilon} = \sum_{k,n} M_k |\dot{U}_{kn}|^2 = \sum_{k,n} \sum_q M_k \omega_q^2 |U_{knq}|^2. \quad (18)$$

Using this expression and Eqs. (6, 7) we obtain the atomic MSF in the form

$$\frac{1}{N} \sum_n |U_{2n}|^2 = m^2 \sum_q |u_{1q}|^2, \quad (19)$$

which by using Eq. (17) is given by

$$\frac{1}{N} \sum_n |U_{2n}|^2 = \frac{24m^2W}{K^2 [s + (2-s)m]^2}. \quad (20)$$

Using W from Eq. (16) this relation is resulted as

$$\frac{1}{N} \sum_n |U_{2n}|^2 = \frac{18m^2 \hbar^2 T}{M_1 [s + (2-s)m] k_B \theta_D^2}. \quad (21)$$

Hence, at $T \gg \theta_D$ the MSF in atomic positions about the equilibrium lattice positions is determined by Eq. (21) which is linearly proportional to the temperature T .

Therefore, at a given temperature T the quantity R defined by the ratio of the RMSF in atomic positions about the equilibrium lattice positions and the nearest neighbor distance d is given by

$$R = \sqrt{\frac{18m^2 \hbar^2 T}{M_1 [s + (2-s)m] k_B \theta_D^2 d^2}}. \quad (22)$$

Based on the Lindemann's criterion the binary alloy will be melted when this value R reaches a threshold value R_m , then the Lindemann's melting temperature T_m for a bcc binary alloy is defined as

$$T_m = \frac{[sM_2 + (2-s)M_1]}{18m} \chi, \quad \chi = \frac{R_m^2 k_B \theta_D^2 d^2}{\hbar^2}, \quad R_m^2 = \frac{1}{Nd^2} \sum_n |U_{2n}|^2. \quad (23)$$

If we denote x as proportion of the mass of the element 1 in the binary alloy, then we have

$$x = \frac{sM_1}{sM_1 + (2-s)M_2}. \quad (24)$$

From this equation we obtain the mean number of atoms in the element 1 for each binary alloy lattice cell

$$s = \frac{2x}{m(1-x) + x}. \quad (25)$$

We consider one element to be the host and another dopant. If the tendency to be the host is equal for both constituent elements, we can take averaging the parameter m with respect to the atomic mass proportion of the constituent elements in alloy as follows

$$\bar{m} = \frac{1}{2} \left[s \frac{M_2}{M_1} + (2-s) \frac{M_1}{M_2} \right]. \tag{26}$$

This equation can be solved using the successive approximation. Substituting the zero-order with s from Eq. (25) in this equation we obtain the one of the 1st order

$$(1-x)\bar{m}^2 + \left[x - (1-x) \frac{M_1}{M_2} \right] \bar{m} - x \frac{M_2}{M_1} = 0, \tag{27}$$

which provides the following solution

$$\bar{m} = \frac{- \left[x - (1-x) \frac{M_1}{M_2} \right] + \sqrt{\Delta}}{2(1-x)}, \quad \Delta = \left[x - (1-x) \frac{M_1}{M_2} \right]^2 + 4x(1-x) \frac{M_2}{M_1}, \tag{28}$$

replacing m in Eq. (23) for the calculation of Lindemann's melting temperatures.

The threshold value R_m of the ratio of RMSF in atomic positions on the equilibrium lattice positions and the nearest neighbor distance at the melting is contained in χ which will be obtained by an averaging procedure. The average of χ can not be directly based on χ_1 and χ_2 because it has the form of Eq. (23) containing R_m^2 , i.e., the second order of R_m , while the other averages have been realized based on the first order of the displacement as Eq. (22). That is why we have to perform average for $\chi^{1/2}$ and then obtain

$$\chi = \left[s\sqrt{\chi_1} + (2-s)\sqrt{\chi_2} \right]^2 / 4, \tag{29}$$

containing χ_1 for the 1st element and χ_2 for the 2nd element, for which we use the following limiting values

$$\chi_2 = 9T_{m(2)} / M_2, \quad s = 0; \quad \chi_1 = 9T_{m(1)} / M_1, \quad s = 2 \tag{30}$$

with $T_{m(1)}$ and $T_{m(2)}$ as melting temperatures of the first or doping and the second or host element, respectively, composing the binary alloy.

Therefore, the melting temperature of bcc binary alloys has been obtained actually from our calculated ratio of RMSF in atomic positions on the equilibrium lattice positions and nearest neighbour distance Eq. (22), which contains contribution of different binary alloys consisted of different pairs of elements with the masses M_1 and M_2 of the same bcc structure.

The eutectic point is calculated using the condition for minimum of the melting curve, i.e.,

$$\frac{dT_m}{dx} = 0. \tag{31}$$

3. Numerical results and comparison to experiment

Now we apply the derived theory to numerical calculations for bcc binary alloys. According to the phenomenological theory (PT) [10] Figure 1 shows the typical possible phase diagrams of a binary alloy formed by the components A and B, i.e., the dependence of temperature T on the proportion x of

element B doped in the host element A. Below isotropic liquid mixture L, the liquidus or melting curve beginning from the melting temperature T_A of the host element A passes through a temperature minimum T_E known as the eutectic point E and ends at the melting temperature T_B of the doping element B. The phase diagrams contain two solid crystalline phases α and β . The eutectic point is varied along the eutectic isotherm $T = T_E$. The eutectic temperature T_E can be a value lower T_A and T_B (Figure 1a) or in the limiting cases equaling T_A (Figure 1b) or T_B (Figure 1c). The mass proportion x characterizes actually the proportion of doping element mixed in the host element to form binary alloy.

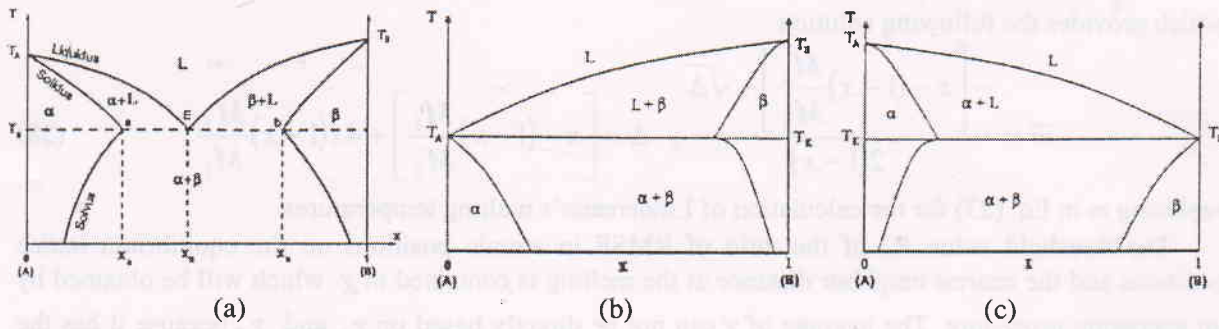


Fig. 1. Possible typical phase diagrams of a binary alloy formed by components A and B.

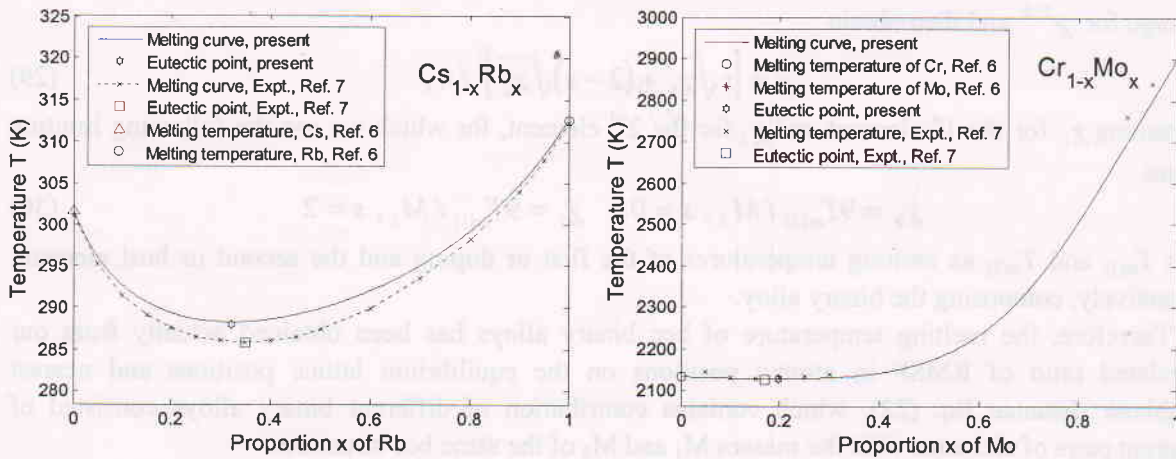


Fig. 2. Calculated melting curves and eutectic points of binary alloys $Cs_{1-x}Rb_x$, $Cr_{1-x}Mo_x$ compared to experimental phase diagrams [7].

Our numerical calculations using the derived theory are focused mainly on the mean melting curves providing information on the Lindemann's melting temperatures and eutectic points of bcc binary alloys. All input data have been taken from Ref. 6. Figure 2 illustrates the calculated melting curves of bcc binary alloys $Cs_{1-x}Rb_x$ and $Cr_{1-x}Mo_x$ compared to experiment [7]. They correspond to the case of Figure 1a of the PT. For $Cs_{1-x}Rb_x$ the calculated eutectic temperature $T_E = 288$ K and the eutectic proportion $x_E = 0.3212$ are in a reasonable agreement with the experimental values $T_E = 285.8$ K and $x_E = 0.35$ [7], respectively. For $Cr_{1-x}Mo_x$ the calculated eutectic temperature $T_E = 2125$ K agrees

well with the experimental value $T_E = 2127$ K [7] and the calculated eutectic proportion $x_E = 0.15$ is in a reasonable agreement with the experimental value $x_E = 0.20$ [7]. Figure 3 shows that our calculated melting curve for $Fe_{1-x}V_x$ corresponds to the phase diagram of Figure 1b and for $Cr_{1-x}Cs_x$ to those of Figure 1c of the PT. Table 1 shows the good agreement of the Lindemann's melting temperatures taken from the calculated melting curve with respect to different proportions of constituent elements of binary alloy $Cs_{1-x}Rb_x$ with experimental values [7].

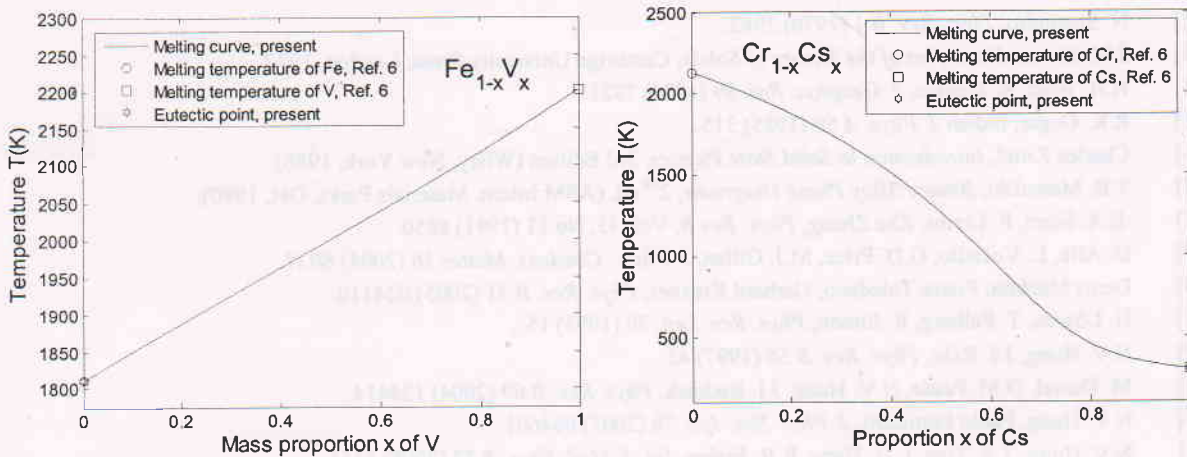


Fig. 3. Calculated melting curve and eutectic point of binary alloys $Fe_{1-x}V_x$ and $Cr_{1-x}Cs_x$.

Table 1. Comparison of calculated Lindemann's melting temperatures $T_m(K)$ of $Cs_{1-x}Rb_x$ to experiment [7] with respect to different proportions x of Rb doped in Cs to form binary alloy

Proportion x of Rb	0.10	0.30	0.50	0.70	0.90
$T_m(K)$, Present	292.6	287.5	290.0	295.0	305.0
$T_m(K)$, Exp. [7]	291.4	286.0	287.4	293.5	304.0

4. Conclusions

In this work a lattice thermodynamic theory on the melting curves, eutectic points and eutectic isotherms of bcc binary alloys has been derived. Our development is derivation of analytical expressions for the melting curves providing information on Lindemann's melting temperatures with respect to different proportions of constituent elements and eutectic points of the binary alloys.

The significance of the derived theory is that the calculated melting curves of binary alloys correspond to the experimental phase diagrams and to those qualitatively shown by the phenomenological theory. The Lindemann's melting temperatures of a considered binary alloy change from the melting temperature of the host element when the whole elementary cell is occupied by the atoms of the host element to those of binary alloy with respect to different increasing proportions of the doping element and end at the one of the pure doping element when the whole elementary cell is occupied by the atoms of the doping element.

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